Particle production in the outflow of a midlatitude storm

C. F. Clement,[1] I. J. Ford,[2] C. H. Twohy,[3] A. Weinheimer,[4] and T. Campos[4]

[1]   The concentrations of atmospheric gases and condensation nuclei (CN) or aerosol in the outflow of a storm were measured aboard a NASA DC-8 aircraft, as described in a companion paper [*Twohy et al.*, 2002]. The data are used here to study the production of the aerosol. Major fluctuations in CN concentration are observed, in correlation with gas-phase species, but these are shown to arise as the result of the mixing of two distinct air masses. It is deduced that the CN originated in a storm outflow air mass and that its concentration before mixing was approximately uniform over a flight distance of about 200 km. The formation of the aerosol by nucleation followed by growth and coagulation is analyzed assuming that it consists of water and sulphuric acid produced locally by the oxidation of SO_2. The analysis uses analytic models, and it is concluded that a 5 min burst of nucleation was followed by growth and coagulation over a period of about 5 hours. Both the mass and number concentrations of the observed aerosol can be reproduced by this analysis within a timescale consistent with that of the storm. The final number concentration is very insensitive to the initial SO_2 concentration.   *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 3314 Meteorology and Atmospheric Dynamics: Convective processes; 3367 Meteorology and Atmospheric Dynamics: Theoretical modeling; *KEYWORDS:* nucleation, burst, aerosol, SUCCESS, storm outflows

1.   Introduction

[2]   Atmospheric aerosol follows a cycle of formation by direct injection from surface sources (for example fires, sea-spray, biological and industrial sources) or gas-to-particle conversion, followed by coagulation and growth by vapor deposition, and finally removal, mainly by rainout. The mass and number concentrations present, particularly those of particles that can act as cloud condensation nuclei, are important in determining the effect of aerosol on the climate. Gas-to-particle conversion, which is mainly responsible for aerosol formation in more remote parts of the atmosphere, particularly the free troposphere [*Clarke et al.*, 1999], is only poorly understood, and even the basic mechanisms that operate are not fully clear [*Kulmala et al.*, 2000; *Yu and Turco*, 2000]. However, there is some evidence that the formation of new particles takes place in transient nucleation events. These events are relatively uncommon, as may be deduced [*Clement and Ford*,

1999a] from observations [*Clarke*, 1992] of an inverse correlation between number concentration and mass. They are also spatially inhomogeneous.

[3]   In a companion paper [*Twohy et al.*, 2002], hereafter designated by paper I, measurements are described of particles in the outflow region of a mesoscale convective system over the midwestern United States. High concentrations of volatile fine particles were measured over huge horizontal distances. The measurements of aerosol characteristics, together with observations of gas concentrations and meteorological variables, were made aboard the NASA DC-8 aircraft as part of the Subsonic Assessment Contrails and Cloud Effects Special Study (SUCCESS) [*Toon and Miake-Lye*, 1998]. The estimates made in paper I show that storms of this type are likely to produce a substantial fraction of the background atmospheric aerosol. It is therefore important to be able to account theoretically for the observed number concentration of the aerosol observed during this particular flight.

[4]   The purpose of this paper is to analyze the data with two particular objectives in mind: First, how can we interpret the aerosol measurements, in the light of what we have recently discovered about the atmospheric mixing processes that occurred during the flight in question [*Clement et al.*, 2000]? This involves considering the correlations between gas concentration data and the particle data. The second objective is to attempt to explain the general characteristics of the observed aerosol, namely the available information on its mass, number concentration and composition. Our

[1]Enviros Ltd., Oxfordshire, UK.
[2]Department of Physics and Astronomy, University College London, London, UK.
[3]College of Oceanography and Atmospheric Sciences, Oregon State University, Corvallis, Oregon, USA.
[4]National Center for Atmospheric Research, Boulder, Colorado, USA.
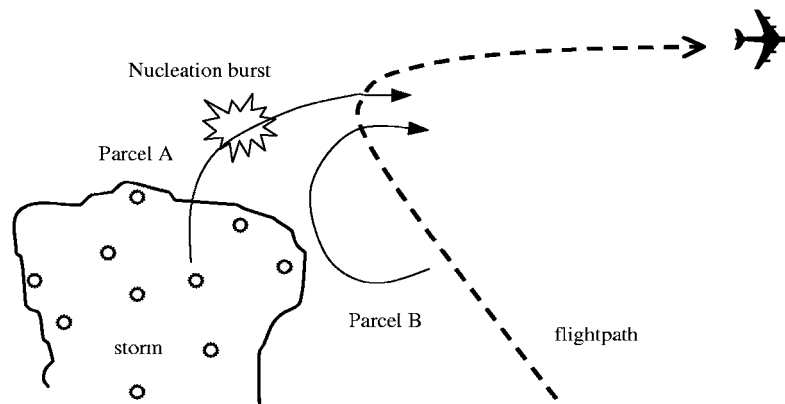
Figure 1. Sketch of the trajectory of an air parcel A emerging from the storm, aerosol production processes occurring within it, and mixing with air mass B before observation by the DC-8.

hypothesis is that the aerosol was formed by the homogeneous nucleation of sulphuric acid-water droplets in the storm outflow followed by growth and coagulation, and we seek to show that the data are consistent with these ideas.

[5] Concentrations of CO and CH_4 measured during the flight have been shown to display remarkable correlations [*Clement et al.*, 2000]. It was deduced that these correlations arose from the mixing of two distinct but internally uniform air masses containing differing concentrations of both species. The high degree of correlation extends to the gas species NO and NO_y, as will be investigated in detail elsewhere. Here, in section 2, we compare the observed concentrations of condensation nuclei (CN) with NO_y concentrations to show that the aerosol originated in one of the air masses, and we deduce its concentration. The comparison with the gas concentrations allows us to understand the major fluctuations in CN concentration, and deduce that the correlation between the CN and NO_y concentrations does not imply an involvement of NO_y in the CN production process.

[6] In section 3 we examine the origin of the aerosol by considering a nucleation event in air parcels emerging from the storm, and then the subsequent growth of the aerosol by vapor deposition with associated coagulation. Sulphuric acid is assumed to be produced from SO_2 by the action of sunlight, and analytic models of the dynamics of nucleation events [*Clement and Ford*, 1999b] are used in conjunction with a model for the rate of homogeneous nucleation of sulphuric acid-water droplets [*Kulmala et al.*, 1998] to predict initial number concentrations. In the conditions of the upper troposphere the nucleation is predicted to be almost barrierless. We estimate the subsequent changes to the aerosol from growth and coagulation using similar simplified analytical models.

[7] Our conclusions, to be supported in detail below, can be summarized in Figure 1, which is a simple sketch showing a vertical view of the trajectory of an air parcel emerging from the storm, and the flight path of the DC-8. For the set of observations that we examine, which cover a limited period of 70500 s to 71500 s during the flight time, the air parcels emerging from the storm, and in which the aerosol is formed, are incorporated into air mass A. The location of the nucleation burst is close to the point of emergence from the storm cloud, and there follows a considerable period of time, which we estimate later, for growth and coagulation of the aerosol. Mixing then takes place with a local air mass B and is particularly strong for the air parcels observed when the plane was climbing through the cirrus anvil, the section between points A and B in Figure 1 of paper I. This figure shows the track of the aircraft viewed from above, indicating the vast extent of the storm and the large horizontal distances involved. We give our conclusions from our analysis in full in section 4.

2. Aerosol Concentration and Mixing

[8] The concentration measurements in paper I were expressed as dimensionless mixing ratios for the gases (volume fractions of gas in air), but as numbers per unit volume at standard temperature and pressure for the aerosol. Here, for convenience, we describe all measurements as concentrations, but in order to describe the formation and behavior of the aerosol, we shall later on adjust the aerosol concentrations to reflect the actual temperature and pressure.

[9] For each atmospheric concentration or variable which was measured in paper I, there are (in most cases) 1001 values measured at 1 second intervals over the range 70500 s to 71500 s (flight time, see paper I) where the highest concentrations of aerosol were observed. Apart from the region $t < 70630$ s, correlations of the appropriate averages of the CO and CH_4 gas concentrations were found to be close to unity during this interval. Short of a very unlikely coincidence, this establishes the fact that their fluctuations in the period 70630 s to 71500 s arise from the mixing of two air masses A and B in which their concentrations were initially uniform [*Clement et al.*, 2000]. We can then apply a similar analysis to the other gases and the aerosol (although there can be no guarantee that their concentrations would also be uniform in the two air masses). We consider air mass A to be the upper air mass, which dominates the mixture in which the plane flies during the later part of the flight, and which consists of the outflow from the large convective storm. Air mass B is from the upper troposphere and contains an aged aerosol at a low concentration. Its initial position underneath the storm outflow A is strongly suggested by the greater mixing between A and B observed by

the DC-8 at the lower altitudes during the climbing portion of the flight.

[10] It was shown by *Clement et al.* [2000] that following the mixing of two uniform air masses A and B, where the initial concentrations of two species, c_1 and c_2, are $c_{1A} > c_{1B}$ and $c_{2A} > c_{2B}$, there is a positive linear relation between c_1 and c_2 if we can neglect the effects of molecular diffusion, i.e.,

$$(c_1 - c_{1B})/(c_{1A} - c_{1B}) = (c_2 - c_{2B})/(c_{2A} - c_{2B}). \qquad (1)$$

We now consider the aerosol (CN) concentrations, which in this section are given, as in paper I, in units of numbers per standard cubic centimeter (st cm^{-3}), i.e., concentrations in air at $p = 1013.26$ mbar, T = 21°C = 294.15 K). If we only had these concentrations and those for NO$_y$, the approximate linear relation found between the two concentrations of the two species, averaged over 10 second intervals and shown in Figure 2, might be thought to implicate the acid oxides of nitrogen in the nucleation process which formed the aerosol. However, such linear relations are also found between pairs of gas concentrations and persuade us that such relations arise according to equation (1) from the mixing of two uniform air masses. The 10 s averaging removes some effects of short time fluctuations in concentrations arising from molecular diffusion, and also problems of possible lack of synchronicity in the two measurements, both topics that will be discussed in a future paper.

[11] The extreme values of data shown in Figure 2 give, according to equation (1), the initial concentrations of the two species in the two air masses A and B, under the assumption that the data sample includes some relatively unmixed samples of the air masses. As illustrated in Figure 1, air mass A probably originated near the ground and was convected up out of the storm, whereas air mass B was located at the top of the troposphere and was not involved in the storm. We deduce that the aerosol concentration in air mass A was about 45000 st cm^{-3}, formed subsequent to the lifting process, and the concentration in B was below 2000 st cm^{-3}. For times after about $t = 70650$ s, where the aerosol from air mass A dominates the mixture, the measured volatility of the aerosol was found to be close to 100% at 250°C. Thus the CN concentration in air mass A was likely to have been close to 100% volatile at this temperature.

[12] Possible origins of the scatter seen in Figure 2 are molecular diffusion, measurement error, and lack of perfect uniformity in the original air masses, but it is clear that at least the larger fluctuations observed in the CN concentration are due to mixing. We can make the following conclusion: the relatively dense aerosol in air mass A was approximately uniform in concentration over a distance of about 200 km. This corresponds to the distance travelled by the plane in the interval 70630 to 71500 s at a mean speed of 227.5 ms^{-1}. At later times, subsequent to mixing, a minimum concentration of about 10000 st cm^{-3} was measured at $t = 70850$ s. The direction of the flight was initially towards the storm, and then, after point B in Figure 1 of paper I, slightly away from its edge so that the age of the observed aerosol was probably increasing in this region. The spread in concentrations for the larger values shown in Figure 2, which mainly come from this later time period,
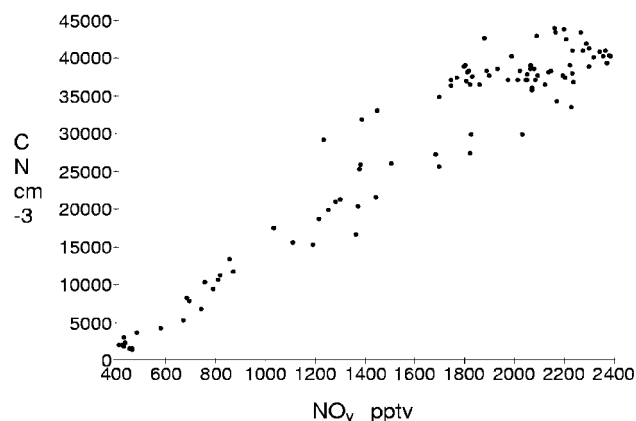
Figure 2. Independent 10 s averages of CN (in standard cm^{-3}) and NO$_y$ concentrations plotted against each other across the whole region $t = 70500-71500$ s.

suggests there could have been fluctuations later in the flight in the more aged aerosol, and a fall-off in concentration was seen in the still more aged aerosol seen for $t > 71500$ s at even later times (after halfway between point B to point C in Figure 1 of paper I).

[13] The aerosol was formed before the mixing took place, so that, considering the distances involved, most of it was likely to be of the order of a few hours old. We estimated the time from the satellite photograph (Figure 1 of paper I) by drawing an arc from the storm center along the cirrus flow direction to a point between points A and B in the figure. This distance was estimated to be 700 km. Dividing this distance by a typical wind speed of 41 ms^{-1} at this altitude, as measured by the DC-8, gives an aerosol age t_p of about 5 hours, and corresponds to an aerosol formation burst at around 10 a.m. local time. This value is well within the lifetime of the storm up to the observation time (13 hours) although there must be a large uncertainty in t_p of perhaps 2.5 hours either way. We shall compare this age of 5 hours with ages required to account for the observed data, in our model of particle formation described in the next section.

[14] The inferred approximate uniformity of the initial aerosol before mixing indicates that the mixing timescale must have been much less than t_p. This is consistent with the very high correlations seen between the gas concentrations, and their likely decay timescale of 100 to 1000 s [*Clement et al.*, 2000]. In the climbing portion of the flight for $t < 71000$ s, the mixing time could not have been more than a few minutes, extending to about 15 min in the subsequent horizontal region where the short timescale correlations were found to have decayed. The aircraft passage time through this region was about 8 min. The formation and growth of the aerosol in air mass A took a much longer time than timescales for its later mixing with B and its observation by the aircraft.

3. Formation of the Aerosol

[15] As stated in paper I, the high observed concentration of the aerosol and its volatile nature indicate that it was

likely to have been freshly formed in the outflow from the storm. The information that we have about the aerosol is that the concentration measured between the diameters of 25 nm (at 50% efficiency) and 60 nm (at 90% efficiency) was about 45000 standard cm^{-3}. We now examine whether models describing the nucleation of sulphuric acid aerosol and its subsequent growth and coagulation are consistent with these observations.

[16] To deal with the physics of the aerosol we need its actual concentration, which scales with temperature T and pressure p in the same way as the molecular concentration in air n:

$$n = p/kT = 10^{25}p(\text{mbar})/1.38T(\text{K}) \quad \text{m}^{-3}, \qquad (2)$$

where k is Boltzmann's constant.

[17] Changing from the standard values of $T = 294$ K and $p = 1013.26$ mbar to the upper tropospheric values of $T = 215$ K and $p = 200$ mbar gives a conversion factor for the aerosol concentration

$$N = 0.27N(\text{st cm}^{-3}) = 12000 \quad \text{cm}^{-3}. \qquad (3)$$

For the formation of the aerosol we first need to estimate P, the production rate of gaseous H_2SO_4:

$$P = 10^{-18}[\text{OH}][\text{SO}_2] \quad \text{m}^{-3}\text{s}^{-1}, \qquad (4)$$

where $[\text{OH}] = n(\text{air})c(\text{OH})$ and $[\text{SO}_2] = n(\text{air})c(\text{SO}_2)$, the concentrations c being the observed mixing ratios. This production rate is a rounded off version of the formulae of *Atkinson et al.* [1992] and *DeMore et al.* [1994], which would introduce multiplicative factors of 0.98 and 0.89, respectively. The rate is very close to values for the lower troposphere because the decrease due to the lower pressure is compensated by an increase caused by the lower temperature.

[18] The concentrations are dimensionless, and the observed value for $c(\text{OH})$ is 2×10^{-12}, or slightly greater [*Brune et al.* 1998]. For the polluted midwestern air convected up by the storm we estimate $c(\text{SO}_2) = 10^{-9}$. This concentration was not directly measured, but is estimated based on an assumed boundary layer concentration of 10 ppb and an extension of the modeling of *Walcek and Taylor* [1986] in which 10% of the SO_2 survives scavenging by cloud droplets in the storm. In section 3.3 we show that our results are relatively insensitive to the actual SO_2 concentration. Taking $p = 200$ mbar and $T = 215$ K then gives $n = 0.674 \times 10^{25}$ m^{-3} and

$$P = 10^{11}\text{m}^{-3}\text{s}^{-1}. \qquad (5)$$

This estimate is used in the following nucleation model, and we then use further simple models to estimate subsequent growth and coagulation.

3.1. Nucleation Burst Model

[19] A number of circumstances make the outflows from major storms likely locations for the production of new particles. The air which is convected upwards through the storm can carry chemical precursors for gas-phase condensable material that originated from lower altitudes. Crucially, pre-existing particles in the air are likely to be scavenged by cloud droplets, so that when the convected air emerges into clear conditions above the storm, the condensable material generated by photo-induced reactions from the precursors cannot easily be removed onto the surfaces of existing aerosol. The density of the condensable vapor then increases, whereas if an aerosol had been present, the density would remain at a relatively low quasi-steady state level. In the absence of existing aerosol, the vapor density can therefore increase until it reaches a level that drives significant nucleation. These newly formed particles then grow at the expense of the remaining vapor; the vapor density decreases, and the rate of nucleation falls as well. Therefore, as long as the growth of the nucleated particles is strong enough to deplete the vapor density significantly, nucleation occurs in a burst in an air parcel travelling along a trajectory out of the storm as shown in Figure 1.

[20] The evolution of the density of vapor in such an air parcel is sketched in Figure 3. The burst occurs around the time that the vapor density reaches a peak. To produce the uniform air mass A, a continuous stream of convected air in which bursts were occurring must have emerged from the storm for a considerable time. At the typical observed horizontal wind speed of 41 ms^{-1} = 148 km h^{-1}, the production of an aerosol over a distance of 200 km would require a time of 81 min. This was the distance flown by the plane during the 1000 s observation period, but the difference in ages within the observed aerosol would certainly be much less than 81 min because the plane changed direction half way through the period (at point B in Figure 1 of paper I) and was not flying along a line corresponding to aerosol emerging from a point source in the storm.

[21] For many nucleation processes, including homogeneous and heterogeneous mechanisms, the dynamics illustrated in Figure 3 can be modeled using relatively simple ideas. Since nucleation takes place at a significant rate only near the time when the vapor density peaks, we can confine our attention to this interval, and make a variety of mathematical approximations in our description of nucleation, growth and vapor depletion.

[22] Models based on these ideas were developed by *Clement and Ford* [1999b]. These models provide formulae for the number of particles nucleated in the air parcel at the end of the burst. The information required to make use of these results are the details of the nucleation and growth rates of the particles. The theory was developed for a particular nucleation rate dependence upon vapor density. The rate was assumed to be proportional to vapor density raised to some power β. When choosing how to represent the growth rate, two versions of the model were developed, applicable to the case where the particles remain submicron in size throughout the burst, and the case where for most of the burst, particles are much larger. Different dependence of the particle growth rate upon radius applies in each case, leading to different formulae for the particle yield. However, results obtained using the two formulae do not differ greatly, as we shall see. The full derivation of the following equations was given by *Clement and Ford* [1999b].
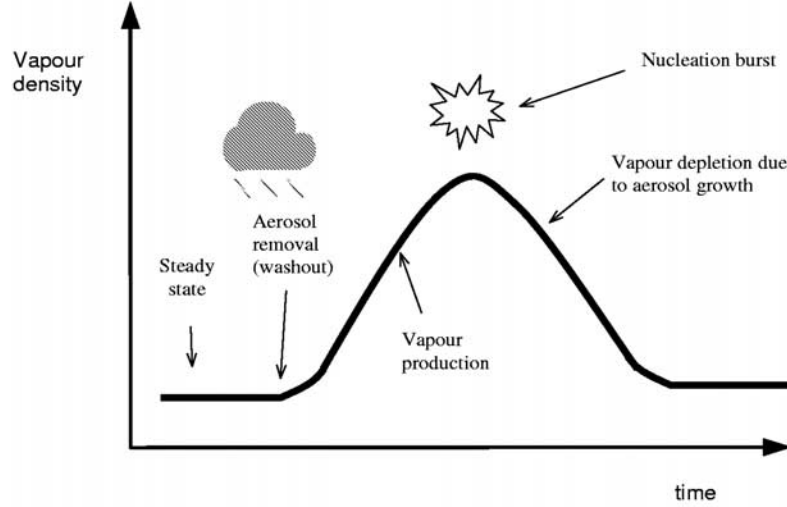
Figure 3. Sketch of the evolution of vapor density during a burst. Vapor production and vapor condensation on existing aerosol maintain an initial steady state, which is disturbed when the existing aerosol is removed. Unrestrained vapor production leads to an increase in density until nucleation can occur at a rate large enough to cut off the increase in density. Nucleation shuts off thereafter.

[23] If the particles grow to micron sizes, the number density of particles nucleated is

$$N_0 = \left(\frac{\pi J_0^3}{2\beta\mu^3\rho_d\eta^2 M_a^2}\right)^{1/4} \left(\frac{8\beta^3 P^4}{\eta^2 M_a^2 \mu^3 \pi^3 J_0\rho_d}\right)^{(3\beta-2)/(4(\beta+6))}, \quad (6)$$

and the result for the case where particles remain small is just

$$N_0 = \left(\frac{J_0}{2\beta\mu\rho_d R_{\min}^2}\right)^{1/(\beta+2)} \left(\frac{P}{2\pi\mu\rho_d R_{\min}^2}\right)^{\beta/(\beta+2)}. \quad (7)$$

The parameters in these expressions refer, as stated above, to the nucleation and growth processes, and are defined as follows. The rate of nucleation is given by

$$J = J_0(T)\rho^\beta, \quad (8)$$

where ρ is the vapor density and J_0 is a prefactor. It was noted previously [*Clement and Ford*, 1999b] that the values of N_0 given by equations (6) and (7) are much less sensitive to the parameter β than is the nucleation rate in equation (8). The rate of change of the radius R of the nucleated particles is modeled as

$$dR/dt = \eta\mu M_a\rho/(1+\alpha R), \quad (9)$$

where $\alpha = (S_p/D)\,(kT/2\pi M_a)^{1/2}$, which involves the vapor diffusivity D, the sticking coefficient S_p, and the mass of the vapor molecule M_a. The parameter μ is given by $S_p(kT/2\pi M_a)^{1/2}/\rho_d$, where ρ_d is the droplet mass density.

[24] The parameter η is an enhancement factor in the mass condensation rate to allow for codeposition of other species along with the principal condensable species of density ρ. For example, if ρ referred to the density of sulphuric acid vapor, then the mass condensation rate on the particles would have to include water deposition as well (at a rate to maintain the activity of acid in the condensed phase). This is taken into account through a factor η equal to $(M_a X_a + M_w X_w)/M_a X_a$, where M_w is the mass of the codepositing molecule, and X_a and X_w are the respective mole fractions in the condensed phase. Finally, $R_{\min}$ is the size of the particles immediately after nucleation.

[25] The yield N_0 of the modeled nucleation burst is now calculable in terms of well defined growth parameters, assuming that we know what species are condensing. It remains to specify the parameters in the nucleation rate. We shall assume that the nucleation is due to binary homogeneous nucleation of water and sulphuric acid, and make use of a correlation for the nucleation rate of droplets based on the classical theory [*Kulmala et al.*, 1998] which is a simplified fit to detailed calculations. We use this correlation at $T = 215$ K, even though this involves some extrapolation of various physical data from higher temperatures.

[26] At this very low ambient temperature, the correlation predicts an approximate proportionality between the nucleation rate and the square of the sulphuric acid vapor density, which would correspond to $\beta = 2$ in equation (8). This is characteristic of barrierless nucleation (where the acid dimer, trimer etc are thermodynamically more stable than the monomer). This dependence is shown in Figure 4. To check that the classical model is realistic in this limit, we have plotted an estimate of the rate of binary collisions between sulphuric acid molecules, for comparison. The temperature was taken to be 215 K, and a water vapor concentration of 50 ppm was chosen. The predicted rate is satisfactorily similar in magnitude to this collision rate.

[27] The expression for J was then used to generate values of J_0 for use in the analytical formulae for N_0. We have used these formulae to predict the N_0 shown in Figure 5, for a realistic range of the sulphuric acid molecular production rate P. For $P = 10^{11}$ m^{-3}s^{-1}, and by inserting properties appropriate to sulphuric acid, the nucleation burst is predicted to last about 5 min and to produce tiny clusters
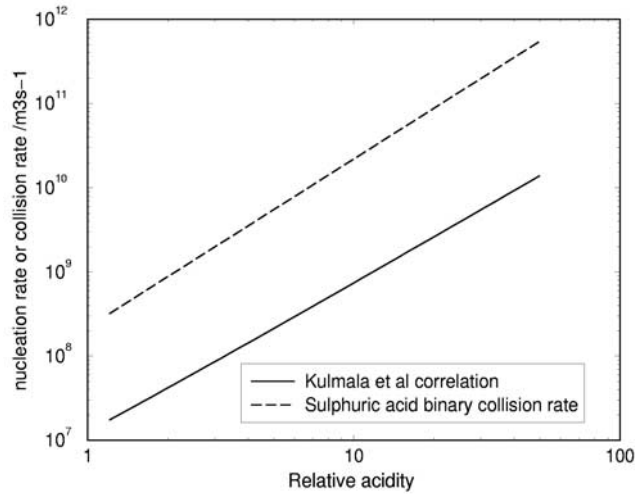
Figure 4. Rate of nucleation of droplets as a function of relative acidity (the ratio of the sulphuric acid vapor density to its equilibrium value over pure sulphuric acid), for a constant water vapor density of 50 ppm and a temperature of 215 K, using the correlation of *Kulmala et al.* [1998], which is based on classical binary nucleation theory. The collision rate of two sulphuric acid molecules (estimated using a molecular radius of 0.4 nm) is shown for comparison.

containing only 3 or 4 acid molecules, together with a number of water molecules. Two predictions of N_0 are given, one suitable for low P (the growth model assuming the particles reach micron sizes, equation (6)), and one for high P (assuming particles remain submicron, equation (7)). The latter is the more appropriate for these conditions, but there is only a small difference between the two predictions.

[28] We can now use Figure 5 as a means of estimating the production of particles in bursts taking place in the outflow from the storm. This of course introduces the assumption that the condensing species are sulphuric acid and water, and that the nucleation mechanism is well modeled by classical theory. On the other hand, the point has been made [*Clement and Ford*, 1999b] that the formulae for N_0 given in equations (6) and (7) are relatively insensitive to the parameters in the nucleation rate. This is a consequence of the nature of the burst as a self-terminated process, and so we can accommodate some uncertainty in the actual nature of the nucleation mechanism. From our estimate in equation (5) for P, and the high P line in Figure 5 from equation (7), we arrive at an initial nucleated concentration of about

$$N_0 = 7 \times 10^{12} \text{m}^{-3} = 7 \times 10^6 \text{cm}^{-3}. \tag{10}$$

The picture we propose of the situation encountered during the SUCCESS flight is given in Figure 1. There is a nucleation burst in the emerging air parcel generated by the mechanism sketched in Figure 3. The products of this burst are then sampled downstream by the aircraft, which climbs into the high level outflow. However, there must be a large time interval, t_p, between the nucleation burst and the aircraft observations to allow for growth and coagulation of

the initial nanometer-sized aerosol, and we now model these processes.

3.2. Aerosol Growth and Coagulation

[29] We would like to account for the final mass of the aerosol, which unfortunately is provided experimentally only within rather wide limits, and also the final number concentration N given by equation (3), which is a factor of about 530 smaller than the nucleated number concentration given by equation (10). Since in the final state practically all the sulphuric acid generated will be condensed on the aerosol, the final mass is given in terms of the acid production rate and the production time, t_p:

$$M_a P t_p = (N/f_{ob})(4\pi/3)R^3\rho_d/\eta, \tag{11}$$

where f_{ob} is the measurement efficiency for particle radius R, $\rho_d = 1.3$ g cm^{-3} is the sulphuric acid density, $\eta^{-1} = 0.36$ is the fractional acid contained in the drops by weight, and $M_a = 1.628 \times 10^{-22}$ g is the mass of a sulphuric acid molecule.

[30] We can estimate the timescale between nucleation and observation in the following way. At the beginning of section 3 we quoted a particle concentration of 45000 st cm^{-3} for particle diameters between 25 and 60 μm. Inserting this concentration and these sizes into equation (11), together with measurement efficiencies appropriate to these diameters and a production rate P of 10^{11} m^{-3}s^{-1}, we obtain an order of magnitude particle age:

(i) $R = 12.5$ nm, $f_{ob} = 0.5$; $t_p = 5644$ s = 94 min
(ii) $R = 30$ nm, $f_{ob} = 0.9$; $t_p = 43,350$ s = 12 hours.

[31] These times, which are likely to be unrealistic limits, bracket the probable lifetime of 5 hours of air mass A emerging from the storm. At the estimated SO$_2$ concentration and H$_2$SO$_4$ production rate, about half the SO$_2$

Particle yield and timescale for nucleation pulse.
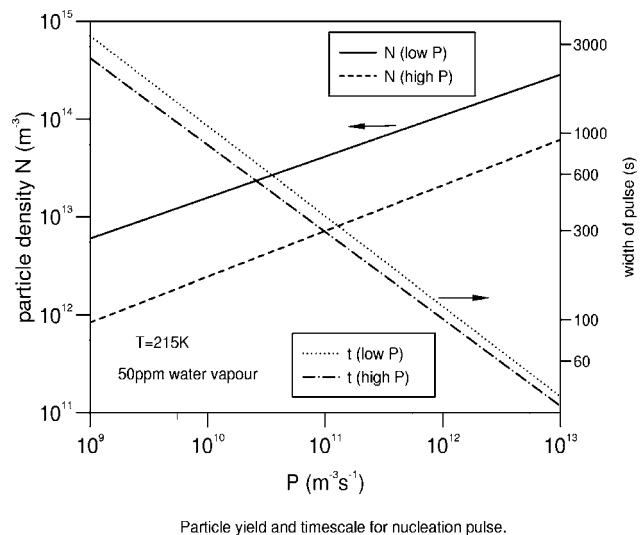
Figure 5. Number density of nucleated particles for a range of assumed vapor molecule production rates P, and for two different growth models, appropriate to high and low molecular production rates. The length of time occupied by the burst is also given.

would be used up in 9 hours, so that the actual production rate would fall off at times over a few hours. However, the simple estimates we have made support the hypothesis that the observed CN aerosol mainly consists of sulphuric acid and water.

[32] For the coagulation of the nanometer sized particles under consideration, we use the free molecule coagulation kernel for same density particles [*Williams and Loyalka*, 1991]:

$$
\begin{aligned}
K(R_1, R_2) &= (6kT/\rho_d)^{1/2}(R_1 + R_2)^2 \left(R_1^{-3} + R_2^{-3}\right)^{1/2} \\
&= 1.168 \times 10^{-16}(R_1 + R_2)^2 \left(R_1^{-3} + R_2^{-3}\right)^{1/2} \mathrm{m^3 s^{-1}}
\end{aligned}
\tag{12}
$$

for $\rho_d = 1.3$ g cm^{-3}, $T = 215$ K and radii measured in nm. It can be verified that this kernel is a very good approximation to more general coagulation kernels [*Oh and Sorensen*, 1997] for sizes up to $R = 30$ nm.

[33] The shortness of the burst means there is little spread in the initial size distribution, so that we consider subsequent growth and coagulation for a monodisperse distribution. For equal $R_1 = R_2 = R$, equation (12) becomes

$$
K(R) = K_0 R^{1/2},
\tag{13}
$$

where $K_0 = 6.607$ m^3 s^{-1}. The corresponding equation for the total number concentration, N, is

$$
dN/dt = -\frac{1}{2} K N^2.
\tag{14}
$$

Since K depends on R, we need another equation relating N and R, and obtain this by assuming a uniform mass transfer rate to the aerosol according to equation (11), omitting the factor f_{ob}, which we write in the form,

$$
N R^3 = N_0 R_0^3 (1 + gt),
\tag{15}
$$

where N_0 is given by equation (10) and R_0 is the radius just after the burst, which we take to be 1 nm (this particular value has little effect on the results), so that $g = 1.186 \times 10^{-3}$ s^{-1}.

[34] We are interested in times much greater than $g^{-1} = 843$ s, for which it is shown in Appendix A that the solution of equations (14) and (15) is

$$
\begin{aligned}
N/N_0 &= \left[1.4g / \left(K_0 R_0^{1/2} N_0 / 2\right)\right]^{6/5} (gt)^{-7/5} \\
&= 0.6722(843/t)^{7/5},
\end{aligned}
\tag{16}
$$

To reproduce the reduction factor of $1/530 = 1.786 \times 10^{-3}$ implied by equations (3) and (10) would require a time of $t = 16.2$ hours. Our estimate of $t = t_p = 5$ hours would give a reduction factor of 9.25×10^{-3}, leaving the particle density 5 times too large, although N_0 is still reduced by a factor of over 100.

[35] Simple dilution by the mixing of air masses A and B could not be responsible for the observed lower value of N, since we have used the maximum unmixed endpoint con-

centration in Figure 2. Some dilution during the 5 hour period between nucleation and observation is a possibility. The storm will not produce a spatially uniform nucleation burst in its outflow, due to fluctuations in precursor concentration, and so some emerging air parcels will remain free of nucleated particles. These will mix with the parcels in which particle production has occurred, reducing the particle concentration, leading to the reasonably uniform aerosol concentration in air mass A. We can reach approximate agreement provided we take into account this and other corrections. Allowing the aerosol to have a spread in size would increase the coagulation rate. This could have a significant effect, particularly at later times, although initially the aerosol growth would keep it fairly monodisperse. Counting efficiency for the condensation particle counter used was only 50% for 12.5 nm radius particles. Increasing N by 2 would reduce the time required to 10 hours. There is also the possibility of some unobserved aerosol below the minimum radius of 12.5 nm which would also improve agreement. Finally, there is removal of the aerosol by coagulation with the background aerosol of a much larger size. This could only be significant when the new aerosol is at very small sizes, since the removal rate limited by diffusion is proportional to R^{-2}. Estimates with an assumed background concentration of about 250 cm^{-3} (about 1000 st cm^{-3}, see paper I), indicate that this effect is not likely to be significant.

[36] The above corrections and the uncertainty in the value of t_p could easily make the observed number concentration consistent with the N_0(equation (10)) predicted by our nucleation model. Thus there is overall consistency between the observed aerosol and the hypothesis that it is a sulphuric acid/water aerosol nucleated in the outflow of the storm.

3.3. Sensitivity to SO$_2$ Concentration

[37] Our model allows us to investigate the dependence of N_0 on the vapor source rate P and hence the initial SO$_2$ concentration. Equation (7) with $\beta = 2$ gives $N_0 \propto P^{1/2}$. The P-dependence of N is obtained by rewriting equation (16) as

$$
N = (2.8/K_0)^{-6/5} t^{-7/5} \left(N_0 R_0^3 g\right)^{-1/5} \propto P^{-1/5},
\tag{17}
$$

since $N_0 R_0^3 g$ is given by the mass transfer rate to the aerosol, which is proportional to P. This very weak, and somewhat surprisingly inverse dependence of N on P, and thus on the SO$_2$ concentration, implies there is little uncertainty in N arising from this cause. For example, a factor of 10 increase in SO$_2$ concentration would reduce N by a factor of 0.63, whereas a decrease by a factor of 10 would increase N by a factor of 1.59. The predicted range of N after $t = 5$ hours would then be only from 102000 cm^{-3} to 41000 cm^{-3} for c(SO$_2$) in the range 10^{-8} to 10^{-10}. The inverse dependence on c arises from increased growth for larger c, and the increase in coagulation rate with size at small R.

[38] However, the dependence of N on P in equation (17) cannot extend to very small values of P where nucleation will be cut off. The insensitivity of aerosol concentrations produced by sulphuric acid nucleation bursts in the upper troposphere to the SO$_2$ concentration probably only applies once a threshold concentration is exceeded. Furthermore,

the insensitivity may not apply if P is greatly increased. It follows from equation (17) that the radius $R \propto P^{2/5}$ and the approximations (12) and (13) for the coagulation kernel cease to be valid at large R. The range of validity of the simple model presented here is an important subject for further study, but is complicated as nucleation can be suppressed by molecular condensation on existing aerosol as well as by subsequent coagulation with the aerosol. We do, however, expect the model to be valid for quite a large range of P because of the weak dependence of N and R on this variable.

[39] An important corollary to the weak dependence of N on the SO_2 concentration is that our observation that the number concentration in air mass A must have been nearly uniform over a 200 km distance does not imply that the precursor SO_2 concentration in the convected air emerging from the storm was so uniform. The observed spread of a factor of about 1.3 in CN concentrations shown in Figure 2 could correspond to a variation of a factor of about 4 in $c(SO_2)$.

4. Conclusions

[40] Analysis of the gas concentrations reported in paper I [*Twohy et al.*, 2002] showed that most of their large fluctuations resulted from mixing of two initially uniform air masses [*Clement et al.*, 2000]. Here we have extended this conclusion to the CN aerosol observed during the flight. Thus there is no reason to conclude that the correlations in concentration between CN and various gas-phase species implies a chemical relationship between them. This aerosol was formed in the air mass A convected up by the storm, which exited the storm largely denuded of aerosol, but which was likely still to contain a considerable concentration of SO_2. Our analysis shows that before the mixing took place with an upper tropospheric air mass B, the aerosol concentration in A was remarkably uniform over a distance of the order of 200 km. Usually, atmospheric aerosol concentrations exhibit considerable fluctuations over much shorter distances, and the mixing of A and B duly produced the observed large fluctuations in concentration.

[41] The main objective of this paper has been to explain the aerosol concentration in A. We have deferred further consideration of the correlations in fluctuations between the aerosol concentrations and those of the gases observed, but such an analysis is likely to be very revealing as to the relative effects of diffusion between aerosol and gases. We intend to return to this topic in a later paper.

[42] We have performed calculations of the formation of the aerosol in air mass A with the basic assumption that it consists of sulphuric acid produced by the oxidation of SO_2 after the air mass emerged from the storm. The calculations involved an analytic model [*Clement and Ford*, 1999b] of a nucleation burst using a correlation [*Kulmala et al.*, 1998] for the rate of sulphuric acid-water nucleation at the temperature and humidity of the upper troposphere. The type of nucleation is almost barrierless (only a factor of 10 smaller than the collision rate of sulphuric acid molecules as shown in Figure 4). The predicted aerosol concentration is 7×10^6 cm^{-3} formed in a burst lasting about 5 min. We have described an analytic model for the subsequent growth

and coagulation of this aerosol. With a timescale of several hours, the best estimate being 5 hours, and within the margin of likely errors, the results are consistent with the observed mass and number concentration of 1.2×10^4 cm^{-3} of the aerosol (concentrations here are actual and not in the standard units used in paper I).

[43] Considering the uncertainties in nucleation theory, which are somewhat reduced in importance in the burst model, this consistency between theory and observation is very uncommon in aerosol science. Although it may be coincidental, and requires confirmation by analysis of other events, it is very supportive of the theories involved and certainly supports the basic premise that the observed CN aerosol consisted primarily of a binary mixture of sulphuric acid and water formed by a nucleation burst. This is in contrast to the suggestion of *Kulmala et al.* [2000] that the limiting factor for the production of global aerosol may be the presence of sufficient condensible vapors to nucleate stable sulphate clusters which contain a third species. Indeed mechanisms other than the homogeneous nucleation process might operate in other circumstances (for example ion-mediated particle production or even ion-ion recombination [*Yu and Turco*, 2000]). These processes might operate for some nucleation events in the lower atmosphere, but events in the upper troposphere could well be dominated by sulphuric acid nucleation bursts in storm outflows. The event analyzed was certainly one of the largest observed to date, and the significance of similar events in forming the upper tropospheric aerosol was pointed out in paper I. The predicted insensitivity of the aerosol number concentration produced by the burst to the initial SO_2 concentration is important for understanding the relationship between SO_2 atmospheric input and climate effects, but would not extend to inputs low enough to give no burst. In the context of the global significance of such events as discussed in paper I, it will be important to investigate further the limits of applicability of the model presented here for a wider range of SO_2 concentrations.

Appendix A

[44] From equations (14) and (15), the equation for N is

$$dN/dt = -(1/2)K_0 R_0^{1/2} N_0^{1/6} N^{11/6} (1 + gt)^{1/6}. \quad (A1)$$

Scaling N to its initial value with $h = N/N_0$, the equation for h is

$$dh/dt = -h^{11/6}(1 + gt)^{1/6}/t_c, \quad (A2)$$

where $t_c = (K_0 R_0^{1/2} N_0/2)^{-1}$ is a timescale. The solution with $h = 1$ at $t = 0$ is

$$h = \left(1 + \frac{5}{7gt_c}\left[(1 + gt)^{7/6} - 1\right]\right)^{-6/5}. \quad (A3)$$

We are interested in the region for which $gt \gg 1$, in which case

$$h \approx (7gt_c/5)^{6/5}(gt)^{-7/5}. \quad (A4)$$

References

Atkinson, R., D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr, and J. Troe, Evaluated kinetic and photochemical data for atmospheric chemistry, supplement IV: IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry, *J. Phys. Chem. Ref. Data*, *21*, 1125–1568, 1992.

Brune, W. H., et al., Airborne in-situ OH and HO_2 observations in the cloud-free troposphere and lower stratosphere during SUCCESS, *Geophys. Res. Lett.*, *25*, 1701–1704, 1998.

Clarke, A. D., Atmospheric nuclei in the remote free troposphere, *J. Atmos. Chem.*, *14*, 479–488, 1992.

Clarke, A. D., V. N. Kapustin, F. L. Eisele, R. J. Weber, and P. H. McMurry, Particle production near marine clouds: Sulfuric acid and predictions from classical binary nucleation, *Geophys. Res. Lett.*, *26*, 2425–2428, 1999.

Clement, C. F., and I. J. Ford, Gas-to-particle conversion in the atmosphere, I, Evidence from empirical atmospheric aerosols, *Atmos. Environ.*, *33*, 475–487, 1999a.

Clement, C. F., and I. J. Ford, Gas-to-particle conversion in the atmosphere, II, Analytical models of nucleation bursts, *Atmos. Environ.*, *33*, 489–499, 1999b.

Clement, C. F., I. J. Ford, and C. H. Twohy, Mixing of atmospheric gas concentrations, *Phys. Rev. Lett.*, *84*, 4010–4013, 2000.

DeMore, W. B., S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina, Chemical kinetics and photochemical data for use in stratospheric modelling, evaluation number 11: NASA panel for data evaluation, *JPL Publ. 94-26*, 1994.

Kulmala, M., A. Laaksonen, and L. Pirjola, Parametrization for sulfuric acid/water nucleation rates, *J. Geophys. Res.*, *103*, 8301–8307, 1998.

Kulmala, M., L. Pirjola, and J. M. Mäkelä, Stable sulphate clusters as a source of new atmospheric particles, *Nature*, *404*, 66–69, 2000.

Oh, C., and C. M. Sorensen, Light scattering study of fractal cluster aggregation near the free molecular limit, *J. Aerosol Sci.*, *28*, 937–957, 1997.

Toon, O. B., and R. C. Miake-Lye, Subsonic aircraft: Contrail and cloud effects special study (SUCCESS), *Geophys. Res. Lett.*, *25*, 1109–1112, 1998.

Twohy, C. H., C. F. Clement, T. Campos, B. G. Gandrud, A. Weinheimer, D. Baumgardner, W. Brune, G. Sachse, and S. Vay, Deep convection as a source of new particles in the midlatitude upper troposphere, *J. Geophys. Res*, *107*, doi:10.1029/2001JD000323, in press, 2002.

Walcek, C. J., and G. R. Taylor, A theoretical method for computing vertical distributions of acidity and sulfate production within cumulus clouds, *J. Atmos. Sci.*, *43*, 339–355, 1986.

Williams, M. M. R., and S. K. Loyalka, *Aerosol Science: Theory and Practice*, Pergamon, New York, 1991.

Yu, F., and R. P. Turco, Ultrafine aerosol formation via ion-mediated nucleation, *Geophys. Res. Lett.*, *27*, 883–886, 2000.

————————————

C. F. Clement, Enviros Ltd., 15 Witan Way, Wantage, Oxfordshire, OX12 9EU, UK. (Charles.F.Clement@btinternet.com)

I. J. Ford, Department of Physics and Astronomy, University College London, Gower Street, London, WC1E 6BT, UK. (i.ford@ucl.ac.uk)

C. H. Twohy, College of Oceanography and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331, USA. (twohy@OCE. ORST.EDU)

A. Weinheimer and T. Campos, National Center for Atmospheric Research, P.O. Box 3000, Boulder, CO 80307, USA. (wein@ucar.edu; campos@ucar.edu)