

The occurrence of sulfuric acid-water nucleation in plumes: urban environment

By VELI-MATTI KERMINEN,* ¹*Finnish Meteorological Institute, Air Quality Department, Sahaajankatu 20E, FIN-00810 Helsinki, Finland*, and ANTHONY S. WEXLER, ²*Department of Mechanical Engineering, University of Delaware, Newark, DE 19716, USA*

(Manuscript received 21 October 1994; in final form 29 June 1995)

ABSTRACT

The production of new sulfuric acid-water particles via homogeneous nucleation was examined in plumes originating from urban point sources. The problem was approached by modeling the time development of the gas phase sulfuric acid concentration during the plume transport, and thereby identifying the meteorological, source-related, and environmental variables governing the behavior of this system. The development of the plume nucleation probability was shown to be dictated by a complicated and nonlinear interaction between the plume dispersion, chemistry, and condensation of sulfuric acid from the gas phase. For all the simulated plumes, those originating from stronger sources and dispersing at slower rates, or having higher SO₂ to fine particulate matter ratios, or higher SO₂ to NO_x concentration ratios, showed greater nucleation probabilities indicative of a higher capability for producing new particles. Nucleation was also favored by cool and humid ambient conditions, greater actinic flux, and higher background hydrocarbon concentrations. The most effective way to decrease the plume nucleation probability was to decrease SO₂ emissions alone. Reducing NO_x or particle emissions may decrease the total particulate mass but leads to higher plume nucleation probabilities, which is likely to increase particle number concentrations farther downwind of the source.

1. Introduction

Anthropogenically derived sulfate in the Earth's atmosphere has stimulated great interest due to its potential influence on visibility degradation, acid rain, human health, and climate. The precursor for the manmade sulfate, SO₂, is emitted predominantly from large, elevated point sources, and a noticeable proportion of it is oxidized in relatively concentrated plumes within a few tens of kilometers of these sources.

The rate at which SO₂ is oxidized to sulfate in plumes has been studied extensively during the last couple of decades (Newman, 1981; Wilson, 1981). In addition to this, substantial effort has been placed on investigating whether the sulfate is formed via homogeneous or heterogeneous path-

ways, and into what particle sizes the main mass of it tends to accumulate (Bassett et al., 1981; Richards et al., 1981; Seigneur, 1982). Much less attention has been given to exploring when sulfate participates in new particle production instead of appearing in pre-existing particles, although a number of field studies has shown that large amounts of nuclei may be produced during plume transport (Whitby et al., 1978; Hegg and Hobbs, 1980; Van Valin and Pueschel, 1981; Meagher et al., 1981) and that these nuclei often modify significantly the plume submicron particle size distribution farther downstream (Hobbs et al., 1979; Wilson and McMurry, 1981).

Total particulate mass and particle number concentration are perhaps the two most important integral properties related to any sulfate aerosol. While phenomena like visibility degradation and aerosol health effects are more closely related to particulate mass, particle number concentration is

* Corresponding author.

extremely important when studying, for example the indirect climate forcing due to sulfate aerosols. In the current work, we concentrate on this latter parameter, with the main objective being to improve our general understanding of the factors governing new particle production in plumes.

Airborne nuclei outnumber frequently any other kind of particles, and have in addition properties completely different from particles emitted directly from sources. Because of their initial small size, nuclei do not participate directly in light scattering or cloud droplet formation near their precursor sources like the majority of accumulation mode particles do. On the other hand, nuclei have a very large diffusion coefficient, so they diffuse easily to the ground and larger particles. This may lead to enhanced acid deposition over a regional scale, since these particles are often extremely acidic. Diffusion of nuclei onto other particles promotes internal mixing of the aerosol. At large or global scale, another effect becomes important: the fraction of nuclei that survive to reach the size of about $0.05\text{--}0.1\text{ }\mu\text{m}$, can themselves act as cloud condensation nuclei. In this way nuclei directly take part in modifying cloud properties and, due to the fact that the smallest activated particles tend to grow very rapidly by heterogeneous sulfate formation in clouds (Hoppel et al., 1994), nuclei further provide a source for new accumulation mode particles. Evidence supporting the important role nucleation mode particles play in clouds can be seen, for example, from the study of Anderson et al. (1994) where they observed that the majority of cloud droplet residual particles were smaller than $0.1\text{ }\mu\text{m}$ in diameter.

Exploring the new particle production in connection with plumes is meaningful only if this environment clearly favors nucleation over that in the background. Using purely theoretical arguments we showed in our recent paper (Kerminen and Wexler, 1995) that this indeed is a case, nucleation probabilities decrease rapidly with aging of the air mass. This result suggests specifically that even at large scales in the lower troposphere, CN counts are likely to be dominated by the nuclei formed in rather concentrated plumes released from strong SO_2 sources.

In this work, we assume that particles are formed via homogeneous nucleation between sulfuric acid and water vapors. The typical composition of airborne nuclei suggests that this is

probably a good assumption, even though the participation of other species, such as organics, cannot be ruled out entirely. The problem will be approached using a two-dimensional, chemically reactive plume model. Though based on Gaussian-like, partially time averaged description of plume dispersion, the model still has a high spatial and temporal resolution, which reveals several features not found in any earlier studies of this subject. The questions we address include (1) when is new particle production via nucleation probable, (2) if nucleation occurs, where is it taking place, and (3) what are the meteorological, environmental, and source related variables that govern the nucleation probability? We will focus our attention on the urban background only, even though the majority of the results can be interpolated also to plumes released in rural areas.

The paper is organized as follows. First, the model and its implementation are described. Next, a few carefully chosen case studies are presented that illuminate the general development of the nucleation probability during the plume transport. After this, we carry out an extensive sensitivity study in order to identify the factors controlling the plume nucleation probability. Finally, the role that emitted species play in this system will be discussed in greater detail to provide insight into the design of emissions control strategies.

2. Model description

In plumes, photochemistry oxidizes SO_2 to sulfate vapor that subsequently condenses on pre-existing particles. Simultaneously, the plume gases and particles mix with the surroundings diluting the plume and mixing background reactive gases and particles with those from the point source. The photochemical production of sulfate vapor increases its concentration and thereby its nucleation probability, whereas dilution with the background and condensation decrease this probability by decreasing the sulfate vapor concentration. In order to accurately predict nucleation in plumes, a mathematical model that accurately represents these processes is developed.

In the current model, plume species are assumed to advect with the mean wind speed downwind from the source, and diffuse vertically and horizontally on planes perpendicular to the wind direction.

In order to provide a sufficient spatial resolution, the plume cross-section is divided into a large number of rectangular shaped cells that expand as the plume grows in size. The model operates at two levels. First, there is a so-called dispersion model that takes care of advection and diffusion. In practice, this includes the transport between different cells, and the interactions between the cells and the background. On the second level, there is a cell model that calculates the changes of the species concentrations within each cell due to chemistry and other significant processes.

The temporal development of the plume is solved using the operator splitting technique:

$$C_i^{j,k}(t + 2\Delta t) = A_y(\Delta t) A_z(\Delta t) A_c(2\Delta t) \times A_z(\Delta t) A_y(\Delta t) C_i^{j,k}(t), \quad (1)$$

where the tensor $C_i^{j,k}(t)$ is the concentration of species i in cell j, k at moment t (McRae et al., 1982). The dispersion operators A_y and A_z describe the horizontal and vertical transport over the time step Δt , respectively. A_c acts in the cell model calculating the effects of various physical and chemical processes on C . In the following the individual components of the model and their implementation will be described.

2.1. The dispersion model

In order to make the transport and diffusion of the plume species more tractable, we assume that the plume is released into, and disperses within, a given stability layer of height h . The plume centerline is assumed to advect with the mean wind speed, U , at height $h/2$, i.e., in the middle of the mixed layer. The mixed layer depth, h , is assumed to be constant with time.

A number of different schemes for simulating the mixing of a reactive plume with the ambient air have been developed (Clark and Cocks, 1988). In this work we apply a model based on a finite difference approximation to the diffusion equation of an expanding grid. The scheme is a two dimensional generalization to that represented by Clark and Cocks (1988), so only its main features are described.

As mentioned earlier, we divide the plume cross-section into a number of rectangular shaped cells. The cells are fixed to expand with time in a way that their height and width at any moment are

equal to σ_z/κ and σ_y/κ , respectively, where κ is an arbitrary constant, and σ_z and σ_y are the vertical and horizontal plume dispersion parameters, respectively. The cells are numbered by index j in horizontal ($j = -N, \dots, N$) and by index k in vertical ($k = -N, \dots, N$), with the total number of cells being $(2N+1)^2$. As the plume vertical extent, $(2N+1)\sigma_z/\kappa$, becomes equal to the mixed layer depth, h , the vertical growth of cells is suppressed, i.e., the plume is confined to disperse inside the given stability layer.

By putting the origin of our coordinate system at the plume centerline, the y and z coordinates of the cell midpoints are given by $y_j = (j-1)\kappa^{-1}\sigma_y$, and $z_k = (k-1)\kappa^{-1}\sigma_z$, respectively. The change of the species concentration, C_i , due to dispersion is obtained from the diffusion equation:

$$\frac{dC_i}{dt} = K_y \frac{\partial^2 C_i}{\partial y^2} + K_z \frac{\partial^2 C_i}{\partial z^2} + \frac{\partial C_i}{\partial y} \frac{\partial y_j}{\partial t} + \frac{\partial C_i}{\partial z} \frac{\partial z_k}{\partial t}, \quad (2)$$

where the "eddy diffusivities", K_i , are related to the dispersion parameters via $K_i = \sigma_i(d\sigma_i/dt)$. The first two terms on the right hand side of eq. (2) describe pure diffusion, whereas the two latter terms are due to the expansion of the cells. Replacing the spatial derivatives in eq. (2) with the corresponding finite differences, a first order partial differential equation for $C_i^{j,k}$ is obtained:

$$\begin{aligned} \frac{dC_i^{j,k}}{dt} = & \tau_{D,y}^{-1} \left[\kappa^2 (C_i^{j+1,k} - 2C_i^{j,k} + C_i^{j-1,k}) \right. \\ & \left. + \frac{1}{2} j (C_i^{j+1,k} - C_i^{j-1,k}) \right] \\ & + \tau_{D,z}^{-1} \left[\kappa^2 (C_i^{j,k+1} - 2C_i^{j,k} + C_i^{j,k-1}) \right. \\ & \left. + \frac{1}{2} k (C_i^{j,k+1} - C_i^{j,k-1}) \right]. \end{aligned} \quad (3)$$

The parameters $\tau_{D,i}^{-1} = \sigma_i^{-1}(d\sigma_i/dt)$ are functions of the plume travel time t , and can be combined together as $\tau_D^{-1} = \tau_{D,y}^{-1} + \tau_{D,z}^{-1}$, which represents the time scale over which the concentrations of emitted species decrease due to the dilution of the plume at a given plume cross-section. After the

plume vertical extent has reached the mixed layer depth, the vertical mixing term of eq. (3) must be modified by replacing κ^2 with $(\sigma_z(2N+1)/h)^2$ and setting $0.5k(C_i^{j,k+1} - C_i^{j,k-1})$ to zero.

In order to determine $\tau_{D,y}$ and $\tau_{D,z}$, an analytical expression for σ_y and σ_z is needed. In state-of-the-art dispersion models, σ_y and σ_z are commonly assumed to be proportional to the lateral and vertical turbulent velocity fluctuations, σ_v and σ_w , respectively (Irwin, 1983; Weil and Brower, 1984; Hanna and Chang, 1992, 1993). In this paper we calculate these parameters according to the procedure proposed by Hanna and Chang (1993), with

$$\sigma_y = \frac{\sigma_v t}{1 + 0.9(t/T_{Ly})^{1/2}}, \quad (4)$$

$$\sigma_z = \frac{\sigma_w t}{\sqrt{1 + t/(2T_{Lz})}}, \quad (5)$$

where T_{Ly} and T_{Lz} represent the lateral and vertical Lagrangian time scales, respectively. The effect of the plume initial buoyancy on dispersion will be neglected, which is justified as long as we are not too close to the source. Information needed for specifying the parameters in eqs. (4) and (5) are the friction velocity, u_* , the convective velocity scale, w_* , and the Monin-Obukhov length, L . In the current work L and u_* are prescribed, after which w_* is obtained from the relation $(u_*/w_*)^3 = 0.4h^{-1}L$ (Hanna and Chang, 1993). This procedure, though incomplete for coupling all the meteorological variables involved, can be considered adequate for elucidating the influence of different stability conditions on the behavior of our system.

The model introduced above should produce a Gaussian concentration distribution for inert species as long as the plume vertical extent is much less than the mixed layer depth. The accuracy of the model can be influenced by altering three parameters, the time step Δt , N or κ . We tested the dispersion model using a number of different values for these three variables. A combination that was numerically efficient yet maintained the Gaussian distribution within a few per cent accuracy over most of the spatial and temporal range of our interest was $\Delta t = 0.01\tau_D$, $\kappa = 3.0$, and $N = 12$. This set of parameters will be used in all the simulations performed here.

2.2. The cell model

A major component of the cell model is the air chemistry module. The gas phase operator applied here is based on the SAPRC mechanism developed especially for the atmospheric transport modelling. The history of this mechanism originates from the work of Atkinson et al. (1982), and more updated versions of it has been described, for example, by Lurmann et al. (1986) and by Carter (1990). The SAPRC mechanism has several options regarding to what extent the hydrocarbons are lumped. A detailed description of these options, as well as examples of the testing of the mechanism, can be found from the reports of Carter et al. (1986, 1988). The version of SAPRC used in the current study contains a total of 128 reactions between 49 species, of which 8 represents lumped hydrocarbon groups (ALK1, ALK2, OLE1, OLE2, OLE3, ARO1, ARO2, RCHO). The only reaction producing gas phase sulfuric acid is assumed to be the oxidation of SO_2 by the hydroxyl radical, which is probably a good assumption in case we are not at the immediate neighborhood of the stack (Cocks and Fletcher, 1982). Heterogeneous chemistry that may play an important role in particulate sulfate production at high relative humidities, is not incorporated. The justification and limitations of this assumption will be discussed a little later.

Although a number of processes, in addition to chemical reactions, may influence the species cell concentrations, in this work we are interested in those that may significantly change the gas phase sulfuric acid concentration, a key quantity for evaluating the nucleation probability. Sulfuric acid vapor is formed via chemical pathways and depleted via condensation onto pre-existing aerosol particles. Assuming that the partial pressure of H_2SO_4 over the particle surface is negligible, which is justified for the accumulation mode range particles considered in the current work (Bolsaitis and Elliott, 1990), the rate at which $\text{H}_2\text{SO}_4(\text{g})$ is transported into the particulate phase (s^{-1}) can be evaluated from

$$\tau_\infty^{-1} = 2\pi D_i \int_0^\infty \frac{D_p n(D_p) dD_p}{1 + (2\lambda/\alpha D_p)}, \quad (6)$$

where D_i is the diffusion coefficient for H_2SO_4 molecules in air, D_p is the particle diameter, $n(D_p)$ the particle size distribution function, λ is the mean

free path of air, and α is the accommodation coefficient for sulfuric acid molecules on the particle surface (Wexler and Seinfeld, 1992). The quantity τ_∞ , termed the condensation time scale, plays an essential role when evaluating the nucleation probability, as we will see later.

In order to determine the condensation rate, the aerosol size distribution function, $n(D_p)$, must be known. In our previous studies we discussed how different sized particles absorb condensing vapors, and showed that both in background and in plumes, the condensate appears dominantly in the accumulation mode particles (Kerminen and Wexler, 1994, 1995). In the current study we therefore approximate the dry particle size distribution, $n_d(D_p)$, by two log-normal modes in the accumulation size range (0.1–1 μm). One of these modes represents background particles, the other represents those originating from the source. Both modes are divided into 10 size sections, which gives a sufficient accuracy when calculating the condensation rate, τ_∞^{-1} . The model can be easily extended to handle more generalized size distributions when necessary.

Processes that may modify $n_d(D_p)$ during the plume transport will influence the condensation rate. The primary mechanism affecting n_d is the plume dilution, which is already included in the dispersion model. Heterogeneous sulfate production, condensation, evaporation, coagulation, gravitational settling, nucleation, and deposition or emissions may influence $n_d(D_p)$. If nucleation is strong enough, newly borne nuclei may become an important sink for sulfuric acid. However, since we are primarily interested in when and where nucleation most probably occurs, the question of whether nucleation itself modifies n_d becomes less relevant. In earlier work (Kerminen and Wexler, 1995) we showed that in most point source plumes, neither coagulation nor gravitational settling significantly modifies the accumulation mode particle size distribution. The same does not necessarily apply to condensation or heterogeneous sulfate production. After flue gases have been released and cooled, primary constituents condensing onto the particulate phase are sulfates and nitrates together with ammonia. Plume particles may also absorb SO_2 to form sulfate heterogeneously, especially at higher ambient relative humidities. Hegg et al. (1985) conducted elemental particulate concentration measurements for several plumes and various

downwind distances. The change in plume particulate sulfate and nitrate volume fraction was in most cases relatively small within the first few kilometers from the source, and was normally much smaller than the change in the total particulate concentration due to the plume dilution. Results similar to this have been reported by several other investigators: normally individual particles do not grow significantly during the first few tens of minutes of the plume transport, at least not in the accumulation mode size range (Richards et al., 1981).

Typically, the simulations we will represent later concern a time period of less than a half an hour after the plume release. Since condensation, as well as emissions or deposition, affect commonly the dry particle size distribution over much longer time scales, it is thus justified that we neglect their influence on n_d . But how about heterogeneous sulfate production? On rare occasions this process may cause SO_2 to be oxidised as fast as $5\% \text{ h}^{-1}$ (Newman, 1981; Wilson, 1981), in which case the plume $\text{SO}_2(\text{g})$ concentration would become significantly perturbed after about 2–3 h of the travel time (with respect to the concentration modified by plume dilution). More than $\text{SO}_2(\text{g})$, heterogeneous sulfate production may influence the fine particulate mass and hence $n_d(D_p)$: if $[\text{SO}_2(\text{g})]$ to fine particulate mass ratios in emissions are unusually high (on the order of 5–10), n_d might be affected significantly within an hour under conditions of extremely rapid SO_2 oxidation. The above discussion demonstrates that even when the heterogeneous sulfate production dominates over the gas-phase derived one, it does not commonly perturb significantly the $\text{H}_2\text{SO}_4(\text{g})$ concentrations essential for nucleation calculations during relative short plume travel times. An exception for this is a plume with unusually high SO_2 to sulfate conversion rate combined with large $\text{SO}_2(\text{g})$ to fine particulate mass ratio, in which case the size of individual particles may be affected enough to increase the condensational sink for $\text{H}_2\text{SO}_4(\text{g})$. The effects that these rare occasions may have on the plume nucleation probability will be discussed in a qualitative sense later when analyzing the simulations.

Although we have shown that the dry size distribution, $n_d(D_p)$, can be assumed fixed, the amount of water vapor absorbed by particles must be evaluated to obtain $n(D_p)$ at different relative

humidities. This issue is far from trivial, since it requires information on the hygroscopic properties of the particles concerned. A common observation for atmospheric particles is that they exhibit two distinctly different hygroscopic characteristics: strongly hygroscopic particles, and less hygroscopic or almost hydrophobic ones (Covert and Heintzenberg, 1984; Svenningsson et al., 1992; Zhang et al., 1993). In this work we assume that the aerosol consists of exactly two types of particles, more and less hygroscopic ones, and calculate their equilibrium size according to the curves proposed by Zhang et al. (1993, their Fig. 8) for the Grand Canyon aerosol. The free parameter to be explored later is the partitioning of particles between these two hygroscopy classes. The assumption that particles are in equilibrium with water vapor inevitably fails at relative humidities close to 100 %. Later we see, however, that nucleation is very unlikely at those high humidities.

2.3. Evaluating the nucleation probability

A crucial point is how the significance of nucleation during the plume transport is estimated. In principle, this can be carried out by either modeling new particle formation explicitly, or simply by evaluating whether nucleation is likely to take place in the prevailing conditions. In current work the latter approach is chosen for the following reasons. First, the nucleation rates predicted by the current theories, as well as the experimental values, differ from each other so tremendously that predicting the number of new nuclei is virtually impossible (Wyslouzil et al., 1991; Raes et al., 1992). Second, the latter method provides us practically all the information needed for estimating the significance of different variables affecting the nucleation probability, which is the primary goal of this study.

When the ambient temperature and relative humidity are known, we can fairly reliably estimate how much sulfuric acid is needed to generate any significant particle formation, as discussed more thoroughly by Kerminen and Wexler (1994). This so-called critical sulfuric acid gas phase concentration, C_{crit} , is obtained from the following formula:

$$C_{\text{crit}} = 0.16 \exp(0.1T - 3.5rh - 27.7), \quad (7)$$

where the temperature, T , is in Kelvin, the relative humidity, rh , is on a scale 0–1, and C_{crit} is in $\mu\text{g m}^{-3}$ (Jaecker-Voirol and Mirabel, 1989; Wexler et al., 1994). It is clear that uncertainties in the nucleation rate also generate inaccuracies for C_{crit} , changing this rate by 2–3 orders of magnitude changes C_{crit} up to 50 %, as one can see by looking at the nucleation rate curves (Jaecker-Voirol and Mirabel, 1989; Kulmala and Laaksonen, 1990). For the purposes of this work, the dependence of C_{crit} on T and rh is more important than its exact magnitude. In this respect, eq. (7) can be considered relatively accurate, since the behavior of the nucleation rate curves as a function of T and rh is much better established than the actual nucleation rate.

Keeping in mind the above restrictions, how should local plume nucleation be identified? An insightful way to do it is to introduce the ratio $C_{\text{sa}}/C_{\text{crit}}$, where C_{sa} refers to the concentration of sulfuric acid in the gas phase. Values of $C_{\text{sa}}/C_{\text{crit}}$ close to or greater than unity identify situations where nucleation between sulfuric acid and water is likely to take place. Henceforth the quantity $C_{\text{sa}}/C_{\text{crit}}$ will be termed the “nucleation probability”, keeping in mind that because this ratio may be greater than unity, it does not represent an actual mathematical probability.

2.4. Initial conditions

The model is initialized by adding the concentrations of source derived species (according to their Gaussian distribution) to the respective background concentrations at a certain moment t_0 of the plume travel time. This procedure may cause error in the concentrations of reactive species soon after the initialization. All of the analyses used here are taken sufficiently downwind from the source, so that specifics in the initial conditions play a insignificant rôle in predictions. Tests of the model confirmed the validity of this procedure. Before the model can be run, a number of quantities must be specified, including meteorological parameters, the background concentrations and emission rates of different species, and the variables associated with condensation and actinic flux. A list of the values chosen for later simulations is summarized in Table 1, and will be discussed next.

All the meteorological variables needed by the model are assumed to be constant in both time and space. Stability conditions are explored in the

Table 1. Initial values of the model variables used in the base case simulations

Species	Background concentrations (ppb)	Source rates (kg h ⁻¹)		Other parameters
		moderate	strong	
NO	10	50	500	<i>meteorological</i>
NO ₂	10	—	—	<i>T</i> : 20°C
SO ₂	5	100	1000	<i>rh</i> : 60%
CO	5000	—	—	<i>U</i> : 5 m s ⁻¹
CH ₄	1700	—	—	<i>h</i> : 1000 m
CH ₂ =CH ₂	50	—	—	<i>u</i> _* : 0.3 m s ⁻¹
ALK1	75	—	—	<i>condensational</i>
ALK2	75	—	—	
OLE1	25	—	—	
OLE2	25	—	—	
ARO1	50	—	—	<i>D</i> _{p, s} : 0.2 μm
ARO2	50	—	—	<i>D</i> _{p, B} : 0.2 μm
HCHO	30	—	—	<i>α</i> _S : 0.03
CH ₃ -CHO	10	—	—	<i>α</i> _B : 0.03
RCHO	10	—	—	<i>actinic flux</i>
MEK	10	—	—	
<i>M</i> _f	50 μg m ⁻³	—	—	plume release time: 12.00
<i>Q</i> _{par, f}	—	20	200	latitude: 40°
				season: summer

range from extremely unstable to nearly neutral. A stable stratification will not be considered, since it does not commonly exist during insolation necessary for the new particle formation. In the base cases, we assume a mean wind speed of 5 m s⁻¹, an ambient temperature of 20°C, and a relative humidity of 60%. The Monin-Obukhov length has one-to-one correspondence to the atmospheric stability and is left as a free parameter. The values of $L = -10^5$ m and $L = -10$ m are used when referring to neutral or very unstable conditions, respectively. The friction velocity is set constant, $u_* = 0.3$ m s⁻¹, and a mixed layer depth of 1000 m is assumed.

The concentrations of background species are assumed to remain constant during the simulations, and are chosen to reflect typical urban, daytime values. Hydrocarbon, aldehyde and ketone (MEK) concentrations are selected mainly according to the data provided by Isidorov (1990). For simplicity, we have split the lumped alkanes (ALK), alkenes (OLE) and aromatics (ARO) evenly between the two reactivity groups (1 and 2) specified by the chemistry module. The background concentrations of alcohols and biogenic hydrocarbons are set to be zero, whereas the amount of ozone and free radicals are determined by running the chemistry module for a sufficient

time in the background. The gas phase sulfuric acid concentration in background is assumed to correspond to its steady state value C_{ss} , a quantity explained later.

The emission rates of various species form perhaps the most diverse set of possible combinations. For our base case we have selected three emitted species: SO₂, fine particulate matter, and NO_x, the latter of which is assumed to be entirely as NO. The ratio between these species is assumed to be 10:2:5 (in kg h⁻¹), a realistic value for flue gas from coal-fired power plants (Hegg and Hobbs, 1980). Two source types of different strength will be used: a so-called moderate source with $Q_{SO_2} = 100$ kg h⁻¹, and a strong source with $Q_{SO_2} = 1000$ kg h⁻¹. The heat and moisture associated with emissions are assumed to be dissipated by the time we start our analysis, so that the plume temperature and relative humidity can be considered the same as those in the ambient air. For heat, this assumption is valid after flue gases have diluted by a factor of about 10 to 100 (Kerminen and Wexler, 1995). The effect that emitted water vapor may have on the nucleation probability will be studied later.

The condensation rate of sulfuric acid, τ_∞^{-1} , depends on several particulate properties. In the base case we assume that all the emitted fine par-

ticles (described by the source rate $Q_{\text{par},f}$) belong to the less hygroscopic category, whereas all the fine background particles (described by M_f) are more hygroscopic. The mass mean (dry) particle diameter and the geometric standard deviation of the accumulation mode are assumed to be $0.2\ \mu\text{m}$ and 1.5, respectively, for both the background and the source related particles. An accommodation coefficient of 0.03 for sulfuric acid is chosen.

Finally, parameters associated with the actinic flux are needed for determining the photochemical reaction rates. In our base cases, we will examine plumes released at 12.00 on a clear day in the midlatitudes during the summer.

3. Case studies

3.1. Qualitative behavior of the nucleation probability in plumes

To illustrate how the nucleation probability develops in plumes, we have chosen four cases that represent rather different plume dispersion characteristics. The first and second cases describe plumes released from moderate ($Q_{\text{SO}_2} = 100\ \text{kg h}^{-1}$) and strong ($Q_{\text{SO}_2} = 1000\ \text{kg h}^{-1}$) sources, respectively, under very unstable conditions. The third and fourth cases correspond to the same sources, but the stratification is assumed to be neutral. The horizontal distribution of the nucleation probability at the plume cross section is depicted in Fig. 1 as a function of time.

There are a number of similarities between the 4 simulations. First, the nucleation probability is initially very low near the plume centerline, as can be seen most clearly in cases (b) and (d). This is due to low $\text{O}_3(\text{g})$ concentration (primary source for OH) caused by the high $[\text{NO}(\text{g})]$ to $[\text{NO}_2(\text{g})]$ ratio in the very concentrated plume, as well as due to the relatively high $\text{NO}_2(\text{g})$ concentration (primary sink for OH), which by reducing the plume OH concentration slows the $\text{H}_2\text{SO}_4(\text{g})$ production rate. Second, the local maximum in the nucleation probability is found initially near the plume edge, and it moves toward the plume centerline where it reaches its absolute maximum. Then it decreases gradually toward the background value. In zones exhibiting the highest nucleation probabilities at a given plume cross section, the concentration of SO_2 is about 20–80 times and NO_x about 10–20 times that in the back-

ground, regardless of the case and the plume travel time. These values correspond to very diluted regions of the plume, the respective concentrations in the flue gas range typically from 10^4 to 10^6 times those in the background.

The features described above depend crucially on the plume OH concentration development, which in turn is strongly dependent on the plume ozone chemistry. In our simulations, predicted O_3 concentrations were low (~ 1 ppb) in very concentrated stages of the plume, between 10 and 30 ppb in zones of the highest nucleation probabilities, and on the order of 50 ppb in the background. This is in qualitative agreement with both observations and earlier model studies, according to which ozone is almost totally depleted near the source region but builds up gradually toward the background value that it normally exceeds after a few hours of plume transport time (Meagher et al., 1981; Cocks and Fletcher, 1989; Janssen et al., 1990; Joos et al., 1990). The evolution of the plume OH concentration was even more dramatic; compared to the background value, $[\text{OH}]$ was 2–3 orders of magnitudes lower in concentrated plume stages, and about the same or slightly greater in zones of the highest nucleation probabilities. Similar OH profiles have been predicted earlier using reactive plume models (How and Isaksen, 1981; Cocks and Fletcher, 1989).

Under the conditions applied here, plume OH concentrations reach values of $1\text{--}2 \cdot 10^8\ \text{cm}^{-3}$, which corresponds to $\text{SO}_2(\text{g})$ oxidation rate of about $0.5\text{--}1\ \% \text{ h}^{-1}$. This rate would be smaller during morning or evening hours and at higher latitudes, and is possibly lower than the rate at which SO_2 is oxidized heterogeneously in the aerosol phase not accounted for in the model. As mentioned earlier, however, heterogeneously formed sulfate cannot take part in new particle production, and neither gas- nor aerosol-phase SO_2 oxidation can perturb the in-plume $\text{SO}_2(\text{g})$ concentrations significantly during the relatively short plume travel times considered here. In plumes with uncommonly high ratio of SO_2 to fine particulate matter and at large transport times, heterogeneously derived sulfate might modify the plume particulate size distribution enough to accelerate the uptake of $\text{H}_2\text{SO}_4(\text{g})$, in which case the curves describing the nucleation probability would lie somewhat lower than the ones predicted here.

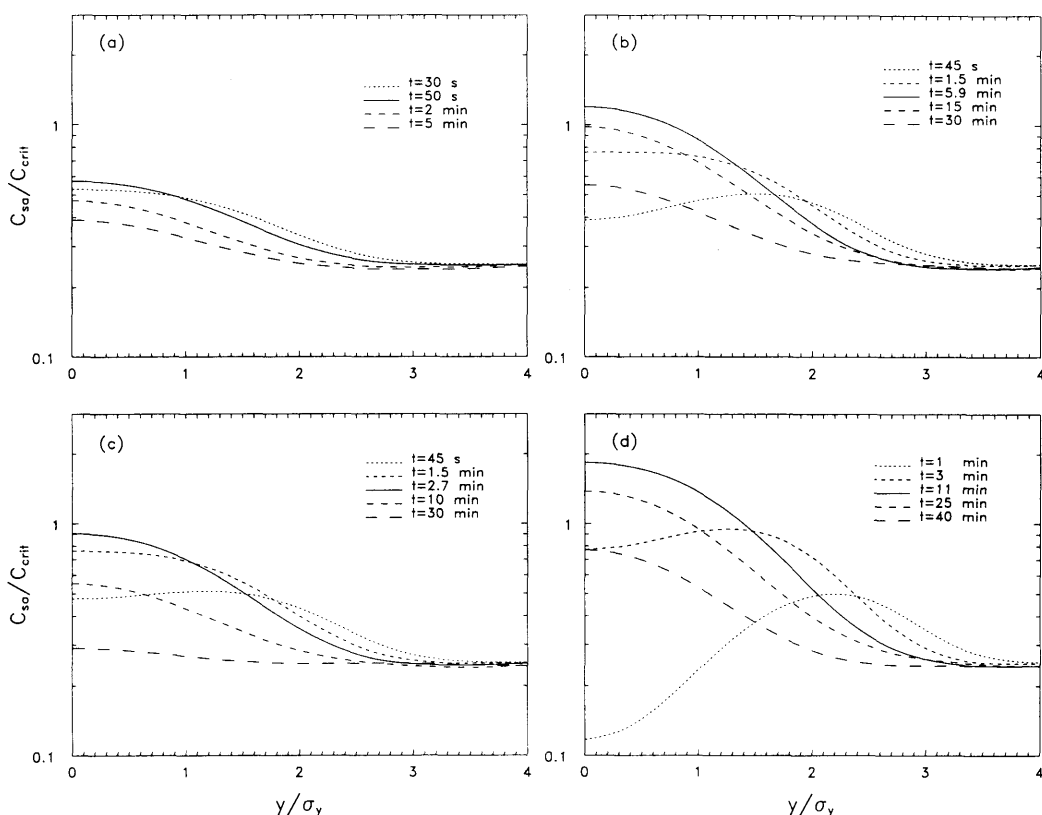


Fig. 1. The nucleation probability, C_{sa}/C_{crit} , along the line $z = 0$ in the plume cross section at different plume travel times. The cases correspond to (a) moderate and (b) strong source under unstable conditions, and (c) moderate and (d) strong sources under neutral conditions. Solid lines represent the situation when the nucleation probability achieves its absolute maximum.

The behavior of the plume nucleation probability provides an explanation for another phenomenon sometimes but not commonly reported, high CN counts in plume edges (Wilson, 1978; Hobbs et al., 1979; Meagher et al., 1981). For example, if we performed a CN measurement over the cross section of the case (d) plume after a few minutes of its travel time, we would be likely to observe elevated CN counts in regions far from the plume centerline due to nucleation there. Our simulations suggest, however, that even when nucleation first takes place in the edge regions, stronger particle formation is expected near the plume centerline at later times.

Despite the fact that both the background concentrations and emission ratios are identical for the four cases, the plumes show distinctly different

nucleation probabilities. This unexpected behavior is due to nonlinear interactions between the plume dispersion, chemistry and condensation of sulfuric acid, and will be discussed in more detail in the following subsection. Anyway, both atmospheric stability and source strength seem to play a crucial role in determining whether nucleation is likely to take place in a certain plume.

3.2. The maximum in the plume nucleation probability

The absolute maximum in the nucleation probability, $(C_{sa}/C_{crit})_{max}$, is almost always located near the plume centerline, and provides a practical measure for the nucleation capacity of the plume in question. To get a better idea of the behavior of this quantity, we performed simulations using

both moderate and strong sources while continuously varying the stability conditions from extremely unstable to neutral. The values of $(C_{sa}/C_{crit})_{max}$ and their time of occurrence, t_{max} , are plotted in Table 2. From the table, we can see that the plumes associated with the stronger source generate nucleation probabilities greater than those originating from moderate sources. In addition to this, $(C_{sa}/C_{crit})_{max}$ is the greater, the later in plume development it is achieved.

To shed some light on why the nucleation probabilities behave like this, we decompose C_{sa} as follows:

$$C_{sa} = k\phi\Gamma[\text{OH}], \quad (8)$$

where k is the reaction rate between SO_2 and OH radical, $\phi = C_{sa}/C_{ss}$, $\Gamma = [\text{SO}_2]/\tau_\infty$, and C_{ss} is the steady state sulfuric acid concentration (Kerminen and Wexler, 1994). Of these quantities, k is approximately constant throughout the plume (excluding the hot gas immediately after the stack), while $[\text{OH}]$ varies substantially and depends on how the plume chemistry develops. The factor Γ is proportional to the ratio of $[\text{SO}_2]$ to the fine particulate matter, is practically independent of the chemistry, and decreases from the high flue gas value, Γ_s , toward the commonly smaller background value, Γ_b . The value of Γ is a key determinant of whether the examined region of the plume is more source or background like with respect to SO_2 and fine particulate matter. The parameter ϕ describes how much the $\text{H}_2\text{SO}_4(g)$ concentration differs from its steady state value $C_{ss} = P\tau_\infty$, where $P = k[\text{OH}][\text{SO}_2]$ is the production rate of sulfuric acid in the gas phase.

An investigation concerning the above cases revealed that at the $(C_{sa}/C_{crit})_{max}$ points, Γ varied less than 50 % between the different cases, and cannot thus explain the differences in the nucleation probabilities achieved. Contrary to this, both ϕ and $[\text{OH}]$ are larger for greater stability or source strength, with ϕ varying between about 0.2 and 0.7, and $[\text{OH}]$ between 0.8 and 1.4 times the value in the background. A reason for the variance of ϕ is obvious. In cases with lower ϕ , the ratio τ_D/τ_∞ was clearly below unity, indicating that plume dilutes too rapidly for the steady state approximation to hold. For the cases with $\phi \approx 0.7$, τ_D/τ_∞ was slightly over unity — $\phi \approx 1$ would require that $\tau_D \gg \tau_\infty$.

Analogous to the quantity τ_D/τ_∞ describing the interaction between plume diffusion and condensation, the ratio τ_D/τ_K known generally as the Damköhler number (τ_K is the time scale over which the $\text{NO}-\text{NO}_2-\text{O}_3$ system evolves toward its local chemical equilibrium) can be used when comparing diffusion to the plume chemistry. A Damköhler number smaller than unity indicates that diffusion is faster than chemical reactions in the plume, whereas with $\tau_D/\tau_K \gg 1$ the opposite is true (Janssen et al., 1990). Knowing the sensitivity of the plume OH concentration to the relative amounts of O_3 and NO_2 , it is clear that the magnitude of the Damköhler number may affect the local sulfuric acid production and thereby the plume nucleation probability.

Following the arguments of Janssen et al. (1990), the time scale τ_K can be estimated to be on the order of a few minutes for the plumes we are considering. Since τ_D is proportional to the plume time t , the Damköhler number becomes greater than unity (allowing the local chemical equi-

Table 2. *The moment and the value of the maximum nucleation probability, $(C_{sa}/C_{crit})_{max}$, in plumes from moderate and strong sources under different atmospheric stabilities*

Monin-Obukhov length, L (m)	Moderate source		Strong source	
	t_{max} (min)	$(C_{sa}/C_{crit})_{max}$	t_{max} (min)	$(C_{sa}/C_{crit})_{max}$
−5	0.67	0.54	5.0	1.08
−10	0.82	0.58	6.0	1.20
−25	1.2	0.64	7.0	1.35
−100	1.6	0.73	8.5	1.55
−1000	2.2	0.85	10.1	1.74
−10 ⁴	2.6	0.90	10.7	1.82
−10 ⁵	2.7	0.92	11.0	1.84

librium to be achieved) after some 5–10 min of the plume travel time. The influence of the small value of the Damköhler number can be seen particularly for plumes originating from the moderate source: those with smaller $t_{\max}$ show consistently somewhat higher O_3 to NO_2 ratios and lower OH concentrations at regions of about an equal dilution state. Similar phenomenon cannot be identified for plumes exhibiting their maximum nucleation probability after several minutes of their travel time.

The analysis performed above forms a qualitative picture of the development of the plume nucleation probability. Initially when the plume still is rather concentrated, high NO to NO_2 ratio and the concomitant low O_3 concentration reduce the plume OH concentration inhibiting sulfuric acid production and nucleation. When the plume dilutes the OH concentration rises rapidly, finally exceeding that in the background. Concurrent to this [OH] rise, the factor Γ decreases from the somewhat higher flue gas value toward the smaller value in the background, such that the product [OH] Γ first goes up, reaches a maximum at a rather diluted stage of the plume, and then starts to decrease gradually. If the plume dilution were slow enough ($\tau_D \gg \tau_\infty, \tau_K$), the product [OH] Γ would be a function of the plume dilution state only, ϕ would be about unity, and the quantity $(C_{sa}/C_{crit})_{\max}$ could be predicted from the background concentrations and emission rates of various species together with the actinic flux. This is not, however, normally the case, since both chemistry and condensation interact in complicated ways with the plume diffusion. It is worthwhile noting that without this nonlinear interaction, we should in principle detect the same nucleation probabilities at the plume edge as the maximum observed later at the centerline. Similarly, atmospheric stability would not have considerable effect on the nucleation probabilities achieved.

4. Sensitivity studies

For the present, we have studied the general behavior of the plume nucleation probability, and its dependence on the atmospheric stability and source strength. In this section dependence on the other variables is explored. The investigation is

carried out by individually varying each variable, and examining how these changes alter the development of C_{sa}/C_{crit} , and especially the value of $(C_{sa}/C_{crit})_{\max}$. To see how these variations are linked with the plume dispersion characteristics, all four cases depicted in Fig. 1 are covered. A summary of the results is given in Table 3.

4.1. Meteorological variables

Temperature and relative humidity affect the plume nucleation probability via both C_{sa} and C_{crit} . To isolate these two effects, we performed sensitivity studies where both C_{sa} and C_{crit} vary with T or rh , and then studies where C_{crit} was artificially held constant. The former studies reflect changes in the ratio C_{sa}/C_{crit} , whereas the latter ones tell us when the $H_2SO_4(g)$ concentration alone is changed. From Table 3 we can see that higher temperatures generate more sulfuric acid in the gas phase, which is expected due to faster chemistry. The increase in C_{sa} is, however, overcome by the decrease in C_{crit} , so that cooler temperatures favor nucleation.

Features similar to temperature variations can be seen when investigating relative humidity. Though higher rh means greater absorption of water into the particulate phase and larger aerosol surface area, which causes $H_2SO_4(g)$ to be depleted more rapidly from the gas phase, the stronger dependence of C_{crit} on rh dictates the maximum nucleation probabilities achieved. An interesting situation occurs when the ambient relative humidity is above 90%, since at high humidities particles absorb so much water that the increased sink for $H_2SO_4(g)$ cannot be balanced by the decrease in C_{crit} . For our cases this phenomenon takes place between 90 and 95% rh , causing $(C_{sa}/C_{crit})_{\max}$ to be smaller under higher relative humidity conditions. Near 100% relative humidity, nucleation becomes very unlikely.

Changing the mixed layer depth, h , has a minor influence on the nucleation probability, except for plumes from strong sources under very unstable conditions. For this case, the plume vertical extent reaches h well before the $(C_{sa}/C_{crit})_{\max}$ is achieved. It is clear that the significance of h may be much greater during the early morning hours when the mixed layer depth still is rather small.

Other meteorological variables influencing $(C_{sa}/C_{crit})_{\max}$ are the mean wind speed, U , and the friction velocity, u_* . From the Gaussian concen-

Table 3. The sensitivity of the maximum nucleation probability, $(C_{sa}/C_{crit})_{max}$, to different environmental, source-derived and aerosol variables for moderate and strong sources under very unstable ($L = -10$ m) and neutral ($L = -10^5$ m) conditions

Quantity	Test case	Moderate source		Strong source	
		unstable (%)	neutral (%)	unstable (%)	neutral (%)
T	0°C, C_{crit} const.	-23	-25	-30	-25
	0°C	+470	+460	+420	+460
	30°C, C_{crit} const.	+20	+7	+5	+3
	30°C	-56	-70	-61	-62
rh	30%, C_{crit} const.	+9	+7	+9	+11
	30%	-62	-62	-62	-61
	90%, C_{crit} const.	-25	-25	-32	-37
	90%	+114	+115	+95	+80
h	+50%	-4	-1	-17	-6
	-50%	+9	+2	+40	+18
Q_{SO_2}	+50%	+31	+40	+42	+45
	-50%	-31	-40	-42	-45
$[SO_2]_B$	+50%	+19	+10	+8	+5
	-50%	-19	-10	-8	-5
Q_{NO_x}	+50%	-12	-13	-9	-11
	-50%	+29	+28	+16	+21
$[NO_x]_B$	+50%	-9	-9	-7	-7
	-50%	+15	+12	+9	+7
$[HC]_B$	+50%	+21	+24	+18	+20
	-50%	-30	-34	-27	-30
ε_S	+50%	-4	-7	-8	-12
	-50%	+5	+9	+9	+17
ε_B	+50%	-15	-13	-17	-20
	-50%	+41	+28	+38	+38

tration distribution we can see that U and Q are tied via the ratio Q_i/U , which means that U scales the source strength. In reality the situation is more complicated, since U also affects atmospheric stability. The friction velocity, u_* , only affects the stability conditions, and will not be studied here.

4.2. Source rates and background concentrations

Numerous variations concerning the background concentrations and source rates were tested, the most important of which are summarized in Table 3. The major species affecting the nucleation probability is sulfur dioxide. From the table we can see that $(C_{sa}/C_{crit})_{max}$ is almost linear in Q_{SO_2} , which is obvious when looking at the relation (8), according to which $C_{sa} \propto \Gamma \propto [SO_2]$.

The nonlinearity in the nucleation probability is caused by the SO_2 in the background, such that if both Q_{SO_2} and $[SO_2]_B$ are changed by the same amount, the response becomes completely linear. This behavior indicates that (1) sulfur dioxide has little affect on the overall plume chemistry as modelled, and (2) the plume $H_2SO_4(g)$ concentration is directly proportional to production rate P , implying that any nonlinearities in C_{sa} are caused by the condensation term, τ_{∞} , or mixing.

Unlike sulfur dioxide, NO_x affects the nucleation probability via the plume chemistry. If the NO_x concentration (either via Q_{NO_x} or $[NO_x]_B$) is increased, the NO to NO_2 ratio favorable for ozone formation, and hence higher OH concentration, is achieved at later stages in the plume

development. This reduces $(C_{sa}/C_{crit})_{max}$, since the factor Γ is smaller at more diluted regions of the plume. A change in Q_{NO_x} generates a somewhat greater effect than a change in $[NO_x]_B$, which is expected since $[NO_x]/[NO_x]_B$ is on the order of 3–6 at t_{max} .

Another factor worth studying is the flue gas $[NO]$ to $[NO_2]$ ratio, since this influences $[O_3]$ and thereby $[OH]$. In power plant emissions, more than 95% of NO_x is typically in the form of NO (Bultjes and Talmon, 1987). Performing model runs where 5% of Q_{NO_x} were assumed to be present as NO_2 had little effect on the plume C_{sa}/C_{crit} development, and practically no effect on the maximum nucleation probability achieved. Equally, changing the background NO to NO_2 ratio by $\pm 50\%$ had less than a 5% influence on $(C_{sa}/C_{crit})_{max}$ in all four cases studied. Regarding new particle formation in plumes, the overall NO_x concentration seems to be more important than its distribution between NO and NO_2 .

Hydrocarbons speed up the plume chemistry, and have the net effect of converting NO to NO_2 without depleting ozone. For our cases a $\pm 50\%$ change in the background hydrocarbon and carbonyl concentrations changed $(C_{sa}/C_{crit})_{max}$ by ± 20 –30%, which reflects the important role these species play in the urban environment. Even more than the nucleation probability, the change in $[HC]_B$ affected t_{max} . This suggests that in areas with lower HC concentrations, the plume chemistry is much slower, and the development of the nucleation probability becomes more a long-range transport phenomenon. The effects of emitted hydrocarbons was not examined, since HC concentration is normally rather low in emissions from large combustion sources (Georgopoulos and Seinfeld, 1986).

Considering finally the strong dependence of C_{crit} on the relative humidity, it is possible that the water emitted from the source affects the plume nucleation probability. Though emission rates of water vapor are not commonly reported, we can estimate that with a typical flue gas SO_2 concentration of 500 ppm and a high water concentration of 20% (200000 ppm), the rate Q_{H_2O} is about a hundred times Q_{SO_2} (in terms of mass). Using the ratio $Q_{H_2O}/Q_{SO_2} = 100$, we repeated the four basic model runs. The simulations revealed that C_{crit} was increased significantly only during the first couple of minutes of the plume development, and

even then only near the plume centerline where C_{sa} was too low to allow any nucleation. The value of $(C_{sa}/C_{crit})_{max}$ was changed less than 1% in all the 4 cases. We conclude that the water associated with emission may assist the new particle formation in rather specific conditions only, i.e., an extremely high ratio of Q_{H_2O} to both Q_{SO_2} and Q_{NO_x} , and very low ambient humidity.

In conclusion, major species affecting the plume nucleation probability are SO_2 , NO_x , particulate matter and hydrocarbons. Nucleation is favored by (1) a high ratio of Q_{SO_2} to Q_{NO_x} , which generates a certain plume OH concentration earlier when Γ is greater, and (2) a high ratio of Q_{SO_2} to $Q_{par, f}$, which increases the factor Γ throughout the plume development. From background concentrations, increase in $[SO_2]$ and $[HC]$, and decrease in $[NO_x]$ generate higher nucleation probabilities in the plume.

4.3. Condensational parameters

Pre-existing particles absorb sulfuric acid from the gas phase, and control how the nucleation probability develops in the plume. The influence that particles have on C_{sa} can in principle be described using a single parameter, the condensation time scale τ_∞ . In plumes, τ_∞ depends on the fine particulate emission rate, $Q_{par, f}$, the background fine particulate concentration, M_f , the accommodation coefficient of sulfuric acid for both these particle categories, α_s and α_B , the hygroscopic properties of these particles, and the aerosol size distribution, $n(D_p)$. Since the concentration of the emitted particles changes as the plume dilutes, τ_∞ is a function of the plume travel time, t .

Instead of studying the effects of all of the above mentioned variables, insight can be obtained by introducing the following two parameters:

$$\varepsilon_s = \frac{Q_{par, f}}{\alpha_s \bar{D}_{p, s} [1 + (\alpha_s \bar{D}_{p, s} / 2\lambda)]}, \quad (9)$$

$$\varepsilon_B = \frac{M_f}{\alpha_B \bar{D}_{p, B} [1 + (\alpha_B \bar{D}_{p, B} / 2\lambda)]}, \quad (10)$$

where $\bar{D}_{p, s}$ and $\bar{D}_{p, B}$ are the mass mean diameter of the fine dry particulate mode representing the source derived and the background particles, respectively. The quantity ε can be simplified if the accommodation coefficient of the condensing

species is smaller than about 0.1, which probably holds for sulfuric acid (Van Dingenen and Raes, 1991), and if the mass mean diameter and geometric standard deviation of the fine mode are in the range typical for the atmospheric aerosol. In this case condensation is surface accommodation limited ($\alpha \bar{D}_p / 2\lambda \ll 1$), and the denominator in both (9) and (10) reduce to the product $\alpha \bar{D}_p$. Whether this simplification is justified or not, τ_∞ for sulfuric acid can be assumed to be a function of four independent variables only: ε_s , ε_B , the relative humidity, and the plume travel time.

According to Table 3, the maximum nucleation probability is more sensitive to particles in the background than those originated from the source. A reason for this is that $(C_{sa}/C_{crit})_{max}$ occurs in a region where the total plume particulate concentration is diluted to near the background level. In plumes with smaller Q_{SO_2} to $Q_{par, f}$ and larger Q_{SO_2} to Q_{NO_x} ratios, the role of source derived particles becomes more important. Unlike SO_2 , the plume nucleation probability is not linear with the total particulate concentration, because of the nonlinear interaction between condensation and plume dilution revealed by the fact that ϕ differs from unity.

As mentioned earlier, $(C_{sa}/C_{crit})_{max}$ increases with increasing relative humidity until rh reaches the point, rh_{max} , where the condensational sink for $H_2SO_4(g)$ becomes large enough to overcome the decrease in C_{crit} . The location of rh_{max} depends almost entirely on the hygroscopic properties of the particles involved. While in our base cases rh_{max} was around 90–95%, it may be situated above 99% if all the particles are only weakly hygroscopic. Equally, if all the particles could be considered more hygroscopic, rh_{max} may drop below 90%.

The major uncertainty in estimating the plume nucleation probability comes from the error associated with the parameters ε_s and ε_B , which in turn can be ascribed to our poor knowledge of the accommodation coefficient, α . In the urban environment, particles often contain a considerable fraction of organic matter, which probably reduces α compared to that for pure salt-water solution particles (Gill et al., 1983, Däumer et al., 1992). Thus, it is quite possible that α is smaller than the value of 0.03 adopted in the base case. In addition, there is no guarantee that accommodation coefficient of the source related particles, α_s ,

would be the same as that for particles in background, α_B .

4.4. Actinic flux

The concentration of hydroxyl radicals, and hence the nucleation probability, are strongly dependent on the actinic flux. For example, if our plumes are released at 9.00 or 15.00, or we assume a latitude of 60–70° instead of 40°, the value of $(C_{sa}/C_{crit})_{max}$ will be reduced by 15 to 30%. When actinic fluxes typical during Winter time are used, our base case plumes show about 50–60% lower nucleation probabilities. At higher latitudes the differences between the Summer and Winter actinic fluxes is even more pronounced, causing, for instance, the difference of around 90% in $(C_{sa}/C_{crit})_{max}$ at the latitude of 60°.

Before drawing any firm conclusions with regard to actinic flux, it should be kept in mind that the evolution of many meteorological parameters are somehow tied with insolation. At the latitude of 40°, for example, a temperature drop of 10 K would compensate for the weaker actinic flux in Winter as compared to Summer. Similar to seasonal variations, diurnal cycles of temperature and relative humidity may be as significant as the corresponding changes in the actinic flux. For example, we might expect that the cool and humid conditions, which favor nucleation, are found during the morning hours rather than at noon when the actinic flux is greatest.

5. Source rates and the nucleation probability

The only practical way particle number (and mass) concentrations in plumes can be affected is via emissions control. According to the sensitivity studies performed earlier, the source related species having the greatest influence on the in-plume particle production are SO_2 , NO_x , and fine particulate matter. From Q_{SO_2} , Q_{NO_x} and $Q_{par, f}$, three independent variables can be formed. In this work we choose the ratios $Q_{SO_2}/Q_{par, f}$ and Q_{SO_2}/Q_{NO_x} to represent the first two of them, with the third one being the overall source strength. In order to provide a better graphical presentation, we non-dimensionalize these variables as follows:

$$\gamma_1 = \frac{\Gamma_s}{10\Gamma_B} \approx \frac{\varepsilon_B Q_{SO_2}}{10\varepsilon_s [SO_2]}, \quad (11)$$

$$\gamma_2 = Q_{\text{SO}_2}/Q_{\text{NO}_x}, \quad (12)$$

$$\gamma_3 = \frac{5 \text{ m s}^{-1} Q_{\text{SO}_2}}{1000 \text{ kg h}^{-1} U}. \quad (13)$$

A physical understanding of γ 's can be obtained by changing each one alone. For example, γ_1 characterizes the nucleation potential of the source compared to the background when chemical and meteorological effects are excluded. Changing γ_2 shifts the peak in the nucleation probability temporally, illustrating the rôle of the plume chemistry. Different values of γ_3 refer to sources with similar chemical composition but different effective source strength, Q/U . In the base cases simulated earlier, values of $\gamma_1 \approx 2$, $\gamma_2 = 2$ and $\gamma_3 = 0.1$ and 1 were used.

Fig. 2 depicts how a change in any γ_i influences $(C_{\text{sa}}/C_{\text{crit}})_{\text{max}}$ while keeping the other two γ 's constant. Parameters other than source rates are assumed to be the same as earlier. For this particular set of ambient conditions, plume nucleation is possible for points above the horizontal line. Changing the ambient temperature, relative humidity, actinic flux or other background variables causes this line to move up or down changing the range of γ where new particles may form. The curves for γ 's are not very sensitive to these changes (excluding major modifications in the

background hydrocarbon concentrations), so they can be considered to be representative for a wide range of ambient conditions. Physically, increasing the value of γ_1 with constant γ_2 and γ_3 corresponds to a decrease in fine particulate emission rate, $Q_{\text{par}, f}$. Increasing γ_2 means decreasing NO_x emissions alone, while reduction in γ_3 is equivalent to decreasing all the three emission rates by the same amount.

A feature worth mentioning again is the significance of the atmospheric stability. For most cases, a change from unstable to neutral conditions increases $(C_{\text{sa}}/C_{\text{crit}})_{\text{max}}$ by a similar amount as a 5–10 fold increase in the γ 's. The role of the stability conditions is smaller when the plume becomes vertically mixed, a hint of which can be obtained by looking at the starting points of the γ_1 curves or the end points of the γ_3 curves. In each of those cases $(C_{\text{sa}}/C_{\text{crit}})_{\text{max}}$ corresponds to a plume travel time of about half an hour, which is well beyond the time it takes for the plume vertical extent to reach the mixed layer depth.

Besides its qualitative nature, Fig. 2 provides some useful insight on how to design control strategies when trying to decrease particle number concentrations downwind of a source located in a typical urban background. First, although an equal cut in all emission rates (smaller γ_3) reduces effectively particulate mass from the resulting plume, it commonly is not the best possible way to decrease the plume nucleation probability, especially not under relatively neutral conditions. Second, decreasing either Q_{NO_x} or $Q_{\text{par}, f}$ is equal to going up along γ_1 or γ_2 curves, the effect of which is actually to provide better conditions for new particle production. Especially, removing fine particles from emissions in hope of lowering the downwind particle number concentrations may in some conditions have a totally opposite effect, many more new particles may be formed during the plume dispersion. Inevitably, the most effective way to inhibit nucleation in plumes is to decrease SO_2 emissions alone.

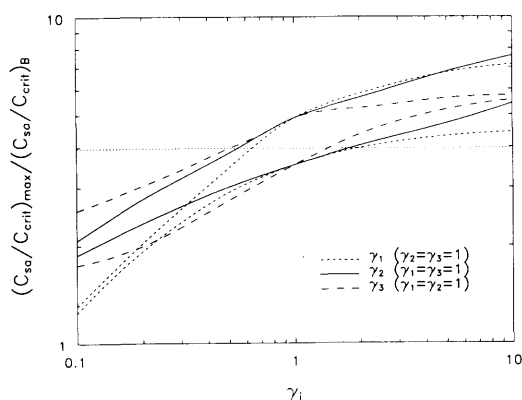


Fig. 2. The maximum plume nucleation probability, $(C_{\text{sa}}/C_{\text{crit}})_{\text{max}}$, scaled with the corresponding background value, $(C_{\text{sa}}/C_{\text{crit}})_{\text{B}}$, as a function of the quantities γ_i , $i = 1, 2, 3$ (see text for discussion). The lower curves represent very unstable conditions ($L = -10 \text{ m}$), while for upper curves a neutral stratification is assumed ($L = -10^5 \text{ m}$).

6. Summary and conclusions

In addition to total particulate mass, particle number concentration is an important parameter in many regional and global scale atmospheric problems like the aerosol climatic forcing. In this

work, factors governing the production of new particle via nucleation of sulfuric acid and water in point source plumes released in an urban environment was studied. The problem was approached by determining the gas phase sulfuric acid concentration, C_{sa} , during the plume development using a detailed, chemically reactive, plume-aerosol model, and comparing this quantity to the so called critical concentration, C_{crit} , required for nucleation. The ratio C_{sa}/C_{crit} was called the nucleation probability. By this procedure, we were able to estimate when and where new particle formation is likely to occur, and determine what factors govern this phenomenon. The plume was simulated using a two-dimensional model based on a finite difference approximation to the diffusion equation in an expanding grid. Processes taken into account were advection and diffusion of the species involved, the gas phase chemistry, and condensation of sulfuric acid into the particulate phase.

The qualitative behavior of the plume nucleation probability can be summarized as follows. Initially in very concentrated regions of the plume, high NO to NO₂ ratios decrease the OH concentration suppressing the formation of sulfuric acid, inhibiting nucleation. Dilution and the concomitant diffusion of reactive hydrocarbons into the plume allows NO to be converted gradually to NO₂, which causes the hydroxyl radical concentration to rise rapidly. Concurrent with the [OH] increase, the ratio of [SO₂] to the fine particulate matter tends to decrease from a normally higher flue gas value toward the lower value in the background, which increases the condensational depletion of H₂SO₄(g) with respect to its production. A competition between these two processes, the [OH] rise and the [SO₂] to fine particulate matter decrease, causes a maximum in the plume nucleation probability, C_{sa}/C_{crit} , at rather diluted regions of the plume, where SO₂ and NO_x concentrations are roughly 5 to 100 times those in the background. The local maximum in the nucleation probability appears first at plume edges, explaining the high CN counts reported sometimes far from the plume centerline. When the plume ages, the maximum in C_{sa}/C_{crit} moves toward the plume interior and increases, such that the highest nucleation probabilities (and thus stronger new particle production) are expected near the plume centerline. The behavior of this system is qualitatively

the same when the role of heterogeneous sulfate production not modeled here is significant, only the decline of C_{sa}/C_{crit} as a function of plume time would become more pronounced.

The development of the ratio C_{sa}/C_{crit} depends not only on the plume dilution state, but also on a rather complex interaction between the plume dispersion, chemistry and condensation of H₂SO₄(g). In effect, plumes originating from weaker sources under very unstable conditions seem to have much lower nucleation probabilities than plumes released from stronger sources into more stable stratification, because in plumes diluting more rapidly, both NO_x-O₃ chemistry and condensation of sulfuric acid proceed over longer times scales compared to mixing, which finally results in lower OH and H₂SO₄(g) concentrations at a given plume dilution state.

The rôle of different meteorological, source related and environmental variables was studied by examining how changes in them alter the maximum plume nucleation probability, $(C_{sa}/C_{crit})_{max}$. Major factors turned out to be the ambient temperature and relative humidity, both of which modified mainly the quantity C_{crit} . Nucleation was favored by lower temperatures and higher relative humidities, except when *rh* rose beyond 90–95 %. In this case the plume particulate phase absorbed so much water that the increased condensational sink for sulfuric acid decreased C_{sa} more than it decreased C_{crit} . The seasonal and diurnal variations of both temperature and relative humidity are tied with variations of another important quantity, the actinic flux. Greater actinic flux generates higher OH concentrations leading to greater nucleation probabilities. Diurnally, conditions most favorable for nucleation occur most probably during the first few hours after the sun rise.

Among the species concentrations, those affecting $(C_{sa}/C_{crit})_{max}$ most are the concentrations of SO₂, fine particulate matter, NO_x, and hydrocarbons. Higher background hydrocarbon concentrations accelerate the plume chemistry, which finally generates greater plume nucleation probabilities. Higher SO₂ to fine particulate matter ratios in either emissions or in the background generate higher sulfuric acid concentrations throughout the plume development, thus giving greater $(C_{sa}/C_{crit})_{max}$. Higher plume nucleation probabilities are also observed with higher SO₂ to

NO_x emission ratios. Lower NO_x concentrations in the background elevate $(C_{\text{sa}}/C_{\text{crit}})_{\text{max}}$ slightly.

According to our study, the most efficient way for decreasing particle number concentrations downwind of a typical urban source is to cut SO_2 emissions alone. Without exception cutting NO_x or particulate emissions generates higher plume nucleation probabilities, which may actually cause an increase in the number of particles farther downwind of the source. Removing SO_2 , NO_x and particulates together, which in general reduces most efficiently total particulate mass from the

plume, does not decrease the plume nucleation probability as efficiently as pure SO_2 control.

7. Acknowledgements

This work was supported by the Academy of Finland and the Foundation of Jenny and Antti Wihuri. Fred Lurmann is gratefully acknowledged for providing us the SAPRC code. Computer resources were provided by a grant from the IBM Environmental Research Program.

REFERENCES

- Anderson, T. L., Covert, D. S. and Charlson, R. J. 1994. Cloud droplet number studies with a counterflow virtual impactor. *J. Geophys. Res.* **99**, 8249–8256.
- Atkinson, R., Lloyd, A. C. and Wines, L. 1982. An updated chemical mechanism for hydrocarbon/ NO_x / SO_2 photo-oxidations suitable for inclusion in atmospheric simulation models. *Atmos. Environ.* **16**, 1341–1355.
- Basset, M., Gelbard, F. and Seinfeld, J. H. 1981. Mathematical model for multicomponent aerosol formation and growth in plumes. *Atmos. Environ.* **15**, 2395–2406.
- Bolsaitis, P. and Elliott, J. F. 1990. Thermodynamic activities and equilibrium partial pressures for aqueous sulfuric-acid-solutions. *J. Chem. Engng. Data* **35**, 69–85.
- Buitjes, P. J. H. and Talmon, A. M. 1987. Macro- and micro-scale mixing in chemical reactive plumes. *Bound.-Layer Meteor.* **41**, 417–426.
- Carter, W. P. L. 1988. *Documentation of a gas-phase photochemical mechanism for use in airshed modelling*. Report, California ARB Contract No. A5-122-32, October.
- Carter, W. P. 1990. A detailed mechanism for the gas-phase atmospheric reactions of organic compounds. *Atmos. Environ.* **24A**, 481–518.
- Carter, W. P. L. and Atkinson, R. 1988. *Development and implementation of an up-to-date photochemical mechanism for use in air shed modeling*. Report, California ARB Contract No. A5-122-32, October.
- Carter, W. P. L., Lurmann, F. W., Atkinson, R. and Lloyd, A. C. 1986. *Development and testing of surrogate species chemical reaction mechanism*, EPA-600/3-86-031, August.
- Clark, P. A. and Cocks, A. T. 1988. Mixing models for the simulation of plume interaction with ambient air. *Atmos. Environ.* **22**, 1097–1106.
- Cocks, A. T. and Fletcher, I. S. 1982. Possible effects of dispersion on the gas phase chemistry of power plant effluents. *Atmos. Environ.* **16**, 667–678.
- Cocks, A. T. and Fletcher, I. S. 1989. Major factors influencing gas-phase chemistry in power plant plumes during long range transport (II). Release time and dispersion rate for dispersion into an “urban” ambient atmosphere. *Atmos. Environ.* **23**, 2801–2812.
- Covert, D. S. and Heintzenberg, J. 1984. Measurement of the degree of internal/external mixing of hygroscopic compounds and soot in atmospheric aerosols. *Sci. Total Envir.* **36**, 347–352.
- Däumer, B., Niessner, R. and Klockow, D. 1992. Laboratory studies of the influence of thin organic films on the neutralization reaction of H_2SO_4 aerosol with ammonia. *J. Aerosol Sci.* **23**, 315–325.
- Georgopoulos, P. G. and Seinfeld, J. H. 1986. Mathematical modeling of turbulent reacting plumes (II). Application to the NO – NO_2 – O_3 system. *Atmos. Environ.* **20**, 1809–1818.
- Gill, P. S., Graedel, T. E. and Weschler, C. J. 1983. Organic films on atmospheric aerosol particles, fog droplets, cloud droplets, raindrops, and snowflakes. *Rev. Geophys. Space Phys.* **21**, 903–920.
- Hanna, S. R. and Chang, J. C. 1992. Boundary-layer parameterizations for applied dispersion modeling over urban sites. *Bound.-Layer Meteor.* **58**, 229–259.
- Hanna, S. R. and Chang, J. C. 1993. Hybrid plume dispersion model (HPDM) improvements and testing at three field studies. *Atmos. Environ.* **27A**, 1491–1508.
- Hegg, D. A. and Hobbs, P. V. 1980. Measurements of gas-to-particle conversion in the plumes from five coal-fired electric power plants. *Atmos. Environ.* **14**, 99–116.
- Hegg, D. A., Hobbs, P. V. and Lyons, J. H. 1985. Field studies of a power plant plume in the arid southwestern United States. *Atmos. Environ.* **19**, 1147–1167.
- Hobbs, P. V., Hegg, D. A., Eltgroth, M. W. and Radke, L. F. 1979. Evolution of particles in the plumes of coal-fired power plants (I). Deductions from field measurements. *Atmos. Environ.* **13**, 935–951.
- Hoppel, W. A., Frick, G. M., Fitzgerald, J. W. and Wattle, B. J. 1994. A cloud chamber study on the effect that nonprecipitating water clouds have on the aerosol size distribution. *Aerosol Sci. Technol.* **20**, 1–30.

- Hov, O. and Isaksen, S. A. 1981. Generation of secondary pollutants in a power plant plume: a model study. *Atmos. Environ.* **15**, 2367–2376.
- Irwin, J. S. 1983. Estimating plume dispersion. A comparison of several sigma schemes. *J. Clim. Appl. Meteor.* **22**, 92–114.
- Isidorov, V. A. 1990. *Organic chemistry of the Earth's atmosphere*. Springer-Verlag, Berlin.
- Jaecker-Voirol, A. and Mirabel, P. 1989. Heteromolecular nucleation in the sulfuric acid-water system. *Atmos. Environ.* **23**, 2053–2057.
- Janssen, L. H. J. M., Nieuwstadt, F. T. M. and Donze, M. 1990. Time scales of physical and chemical processes in chemically reactive plumes. *Atmos. Environ.* **24A**, 2861–2874.
- Joos, E., Millancourt, B., Van Duuren, H. and Römer, F. G. 1990. Physico-chemical study by two aircraft of a plume from a coal-fired power plant. *Atmos. Environ.* **24A**, 703–710.
- Kerminen, V.-M. and Wexler, A. S. 1994. Post-fog nucleation of H_2SO_4 - H_2O particles in smog. *Atmos. Environ.* **28**, 2399–2406.
- Kerminen, V.-M. and Wexler, A. S. 1995. The interdependence of aerosol processes and mixing in point source plumes. *Atmos. Environ.* **29**, 361–375.
- Kulmala, M. and Laaksonen, A. 1990. Binary nucleation of water-sulfuric acid system: comparison of classical theories with different H_2SO_4 saturation vapor pressures. *J. Chem. Phys.* **93**, 696–701.
- Lurmann, F. W., Lloyd, A. C. and Atkinson, R. 1986. A chemical mechanism for use in long-range transport/acid deposition computer modeling. *J. Geophys. Res.* **91**, 10905–10936.
- McRae, G. J., Goodin, W. R. and Seinfeld, J. H. 1982. Numerical solution of the atmospheric diffusion equation for chemically reacting flows. *J. Comput. Phys.* **45**, 1–42.
- Meagher, J. F., Stockburger, L. III, Bonanno, R. J. and Luria, M. 1981. Cross-sectional studies of plumes from a partially SO_2 -scrubbed power plant. *Atmos. Environ.* **15**, 2263–2272.
- Newman, L. 1981. Atmospheric oxidation of sulfur dioxide: a review as viewed from power plant and smelter plume studies. *Atmos. Environ.* **15**, 2231–2239.
- Raes, F., Saltelli, A. and Van Dingenen, R. 1992. Modelling formation and growth of H_2SO_4 - H_2O aerosol: uncertainty analysis and experimental evaluation. *J. Aerosol Sci.* **23**, 759–771.
- Richards, L. W., Anderson, J. A., Blumenthal, D. L., Brandt, A. A., McDonald, J. A., Waters, N., Macias, E. S. and Bhardwaja, P. S. 1981. The chemistry, aerosol physics, and optical properties of a western coal-fired power plant plume. *Atmos. Environ.* **15**, 2111–2134.
- Seigneur, C. 1982. A model of sulfate aerosol dynamics in atmospheric plumes. *Atmos. Environ.* **16**, 2207–2228.
- Svenningsson, I. B., Hansson, H.-C., Wiedensohler, A., Ogren, J. A., Noone, K. J. and Hallberg, A. 1992. Hygroscopic growth of aerosol particles in the Po Valley. *Tellus* **44B**, 556–569.
- Van Dingenen, R. and Raes, F. 1991. Determination of the condensation accommodation coefficient of sulfuric acid on water-sulfuric acid aerosol. *Aerosol Sci. Technol.* **15**, 93–106.
- Van Valin, C. C. and Pueschel, R. F. 1981. Fine particle formation and transport in the Colstrip, Montana, powerplant plume. *Atmos. Environ.* **15**, 177–189.
- Weil, J. C. and Brower, R. P. 1984. An updated Gaussian plume model for tall stacks. *J. Air Poll. Control. Assoc.* **34**, 818–827.
- Wexler, A. S. and Seinfeld, J. H. 1992. Analysis of aerosol ammonium nitrate: departures from equilibrium during SCAQS. *Atmos. Environ.* **26A**, 579–591.
- Wexler, A. S., Lurmann, F. W. and Seinfeld, J. H. 1994. Modelling urban and regional aerosols (I). Model development. *Atmos. Environ.* **28**, 531–546.
- Whitby, K. T., Cantrell, B. K. and Kittelson, D. B. 1978. Nuclei formation rates in a coal-fired power plant plume. *Atmos. Environ.* **12**, 313–321.
- Wilson, W. E. 1978. Sulfates in the atmosphere: a progress report on project MISTT. *Atmos. Environ.* **12**, 537–547.
- Wilson, W. E., Jr. 1981. Sulfate formation in point source plumes: a review of recent field studies. *Atmos. Environ.* **15**, 2573–2581.
- Wilson, J. C. and McMurry, P. H. 1981. Studies of aerosol formation in power plant plumes (II). Secondary aerosol formation in the Navajo generating station plume. *Atmos. Environ.* **15**, 2329–2339.
- Wyslouzil, B. E., Seinfeld, J. H., Flagan, R. C. and Okuyama, K. 1991. Binary nucleation in acid-water systems. II. Sulfuric acid-water and comparison with methanesulfonic acid-water. *J. Chem. Phys.* **94**, 6842–6850.
- Zhang, X. Q., McMurry, P. H., Hering, S. V. and Casuccio, G. S. 1993. Mixing characteristics and water content of submicron aerosols measured in Los Angeles and at the Grand Canyon. *Atmos. Environ.* **27A**, 1593–1607.