The possible role of organics in the formation and evolution of ultrafine aircraft particles

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Abstract. We investigate the potential contribution of organic species emitted by aircraft engines to the formation of ultrafine volatile particles detected in jet wakes. The model employed here includes both acidic and organic aerosols—in their "pure" states and mixed with soot—as well as small ion clusters and electrically charged particles. The microphysical treatment accounts for the effects of charge, within the framework of a multicomponent size-resolved kinetically controlled vapor-aerosol system. Owing to their high proton affinities, water/acid solubility, and/or reactivities with liquid sulfuric acid and other inorganic compounds, certain organic constituents known to be generated by aircraft engines are likely to condense onto ions and charged particles and/or to be taken up by liquid sulfuric acid particles, where these particles are expected to act as efficient reaction sites. The present simulations, which are constrained by in situ measurements, indicate that in the case of very low sulfur emissions, organic species in the exhaust stream can dominate the mass of volatile particles detected at very early times. In the case of fuels with medium to high sulfur contents, the organic emissions may still contribute a significant fraction of the total aerosol mass and alter the composition of the exhaust particles.

1. Introduction

Particles emitted by aircraft may enhance the background aerosol concentrations in the upper troposphere and lower stratosphere [e.g., *Hofmann*, 1991; *Hofmann et al.*, 1998]. In view of increasing commercial traffic and plans for a large fleet of high-speed civil transport (HSCT) aircraft, the environmental effects of aircraft particulate emissions have been the focus of intense investigation [e.g., *Turco et al*, 1980; *Schumann*, 1994; *World Meteorological Organization*, 1995; *NASA*, 1993, 1995, 1997; *Fabian and Kärcher*, 1997; *Brasseur et al.*, 1998].

As part of the effort to assess the impacts of aviation, major field campaigns have been carried out, providing unique firsthand data concerning gas and particle emissions. Among these campaigns are, Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA), Subsonic Assessment: Near-field Interactions Flight (SNIF), Subsonic Assessment: Cloud and Contrail Effects Special Study (SUCCESS), the SULFUR missions, and Pollution from aircraft emissions in the North Atlantic fight corridor (POLINAT). It is now clear that large quantities of ultrafine volatile particles (whose emission indices can range up to 2 orders of magnitude above those of soot particles) are formed in both supersonic [*Hofmann and Rosen*, 1978; *Fahey et al*, 1995] and subsonic aircraft plumes [e.g., *Schumann et al.*, 1996; *Petzold et al.*, 1997; *Anderson et al.*, 1998; *Miake-Lye et al.*, 1998; *Pueschel et al.*, 1998; *Schröder*

et al., 1998]. Sulfuric acid has been identified as the main component of these observed ultrafine particles because of the apparent dependence of the measured condensation nuclei (CN) concentrations on fuel sulfur content (FSC) and their volatility.

In order to assess properly the role of aircraft particulates, their formation mechanisms and properties (number concentration, size distribution, and composition) must be better understood. Earlier simulations based on the standard classical theory of binary homogeneous nucleation of H_2SO_4 and H_2O suggested that large numbers of ultrafine volatile particles are generated in fresh aircraft plumes [e.g., *Zhao and Turco*, 1995; *Kärcher et al.*, 1995; *Brown et al.*, 1996a; *Taleb et al.*, 1997; *Danilin et al.*, 1997; *Andronache and Chameides*, 1997]. However, more detailed comparisons of specific in situ particle properties between simulations and measurements have only recently been carried out [*Yu and Turco*, 1997, 1998a, b; *Kärcher et al.*, 1998a, b; *Yu et al.*, 1998]. For example, in an analysis of CN data obtained during the SULFUR-5 mission in April, 1997 (as described by *Schröder et al.* [1998]), *Yu et al.* [1998] concluded that the observations behind the Deutsche Forschungsanstalt für Luftund Raumfahrt (DLR) research aircraft ATTAS could not be reproduced unless the microphysical effects of chemiionization were considered. In the case of high-sulfur fuel (HS, with an FSC of 2700 ppmm), the fraction of the sulfur oxidized to $SO_3 + H_2SO_4$ (S_c)—assuming that H_2SO_4 and H_2O are the only condensing species—was estimated to be ~2%, the expected fractional conversion determined from concomitant in situ measurements [*Curtius et al.*, 1998]. However, in the case of low-sulfur fuel (LS, FSC=20 ppmm), the value of S_c required to explain the CN measurements was as high as 55%. This value is more than 5 times greater than the value predicted for an ATTAS-type aircraft

[Brown et al., 1996b] and is inconsistent with the total sulfuric acid measurements [Curtius et al., 1998]. This led Kärcher et al. [1998b] to suggest that species other than H_2SO_4—most likely exhaust hydrocarbons—may contribute to or control initial particle growth with low-sulfur fuels.

It is well known that organic compounds may contribute significantly to the aerosols in the troposphere. For example, atmospheric cloud condensation nuclei (CCN) measurements have indicated that organic species may make up a significant portion of CCN mass at marine sites [Novakov and Penner, 1993; Rivera-Carpio et al., 1996; Novakov et al., 1997]. Observations by Novakov and Penner [1993] also found that organic aerosols dominate the total mass (and number) of nucleation mode particles (diameter $d < 60$ nm), providing strong evidence of gas-to-particle conversion of organic species through nucleation and condensation. Recently, electron microscope analysis of residual particles ($d > 100$ nm) from aircraft contrails during the SUCCESS campaign also found the presence of volatile organic substances in these particles [Twohy and Gandrud, 1998]. While there exists observational evidence of gas-to-particle conversion for organic species, the composition of organic particles (hence the corresponding aerosol precursors) are not well characterized.

In this study, we investigate the potential role of condensable organic compounds (i.e., those organics that can be involved in the aerosol phase)—designated here as particulate organic matter (POM)—in the formation and growth of aircraft plume ultrafine particles. For this purpose, we employ a detailed aerosol microphysics model that includes chemiion effects [Yu and Turco, 1997, 1998b]. The present simulations are constrained by data obtained during the SULFUR-5 mission, as described by Schröder et al. [1998] and analyzed by Kärcher et al. [1998a, b] and Yu et al. [1998].

2. Plume Organics: Measurements and Potential POM

Aircraft engines are known to emit organic compounds as a result of incomplete fuel combustion [e.g., Lazano et al., 1968; Katzman and Libby, 1975; Conkle et al., 1980; Spicer et al., 1992, 1994; Slemr et al., 1998]. Among the organic compounds directly detected in jet exhaust are alkenes (mostly ethene), aldehydes (mostly formaldehyde, CH_2O), alkynes (mostly ethyne), and some aromatics. The emission indices (EI) of organic species depend strongly on the power setting and type of engine [Spicer et al., 1994]. Ground measurements by Spicer et al. [1994] showed that EI of total organics decreased from ~ 18 g/kg fuel (alkenes, ~ 9 g/kg fuel; aldehydes, ~ 3 g/kg fuel) at idle to ~ 0.71 g/kg fuel (alkenes, ~ 0.28 g/kg fuel; aldehydes, ~ 0.15 g/kg fuel) at 30% and ~ 0.04 g/kg fuel (alkenes, ~ 1.6 mg/kg fuel; aldehydes, ~ 9 mg/kg fuel) at 80% power setting on a TF-39 engine, and from ~ 9 g/kg fuel (alkenes, ~ 4 g/kg fuel; aldehydes, ~ 2 g/kg fuel) at idle to ~ 0.1 g/kg fuel (alkenes, ~ 30 mg/kg fuel; aldehydes, ~ 16 mg/kg fuel) at 30% and ~ 0.2 g/kg fuel (alkenes, ~ 22 mg/kg fuel; aldehydes, ~ 54 mg/kg fuel) at 80% power setting on a CFM-56 engine. For various power settings and types of engine, the weight percentage of aldehydes changes slightly (from 16 to 27%), while it changes significantly for alkenes (from 3 to 52%) [Spicer et al., 1994].

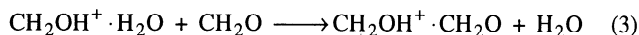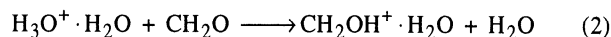In-flight measurements of nonmethane hydrocarbons (NMHCs) in ATTAS exhaust plumes during the SULFUR-5 mission showed an NMHC EI of 50-180 mg/kg fuel (alkenes, 30-125 mg/kg fuel; alkynes, 14-42 mg/kg fuel) [Slemr et al., 1998]. Because of the technical limitations of Slemr et al.'s [1998] measurements, emissions of NMHCs with more than 9 C atoms, of carbonyl compounds, and of polycyclic aromatic hydrocarbons such as reported by Spicer et al. [1994] could not be detected. However, on the basis of Slemr et al.'s [1998] comparisons of in-flight measurements with those of Spicer et al. [1994], it may be inferred that the EI for aldehydes is about one third of that for alkenes, which yields an estimated aldehyde (mostly formaldehyde and acetaldehyde) EI of ~ 10-42 mg/kg fuel.

Many organic compounds, especially short-chained, unsaturated hydrocarbons such as alkenes and alkynes, are known to dissolve in and/or react with cold aqueous sulfuric acid solutions [Solomons, 1996]. For example, when alkenes are added to cold concentrated sulfuric acid, they dissolve owing to protonation and formation of alkyl hydrogen sulfates. Thus alkenes and alkynes, which have been quantified in aircraft plumes, may be taken up by liquid sulfuric acid and therefore contribute to the overall mass of the volatile plume particles. Since the total mass of the sulfuric acid particles is closely related to the H_2SO_4 vapor emission ($\propto$ FSCx S_c), we expect that the absolute quantities of alkenes and alkynes taken up by particles increase with increasing FSC. While the uptake of alkenes and alkynes by acid may be significant for high FSC cases, it is unlikely to be important for very low FSC cases because of the limited amount of acid solution available.

Another candidate organic family that may be involved in forming a particulate phase is that of the aldehydes. The oxygen atom in the carbonyl group allows the aldehydes to form strong hydrogen bonds with water. As a result, low molecular weight aldehydes (such as CH_2O and CH_3CHO) are very soluble in water [Solomons, 1996]. Laboratory studies also indicate that CH_2O is readily taken up by acid solutions [Tolbert et al., 1993; Jayne et al., 1996]. Further, CH_2O can react with HNO_3 to form HCOOH and HONO in the presence of ternary $H_2SO_4 + H_2O + HNO_3$ mixtures [Iraci and Tolbert, 1997]. Moreover, aldehydes detected in aircraft exhaust (mostly CH_2O and CH_3CHO) have larger proton affinities than H_2O (the proton affinities of CH_2O, CH_3CHO, and H_2O are 718, 781, and 697 kJ/mol, respectively [Lias et al., 1984]). Hence the aldehydes readily react with hydronium to form protonated core ions. For example, laboratory studies at room temperature [Fehsenfeld et al., 1978] found that, as is typical for exothermic proton transfer, the reaction

$$H_3O^+ + CH_2O \xrightarrow{K_1} CH_2OH^+ + H_2O \qquad (1)$$

is fast with $K_1 = 2.2 \times 10^{-9}$ cm^3/s. The following reactions involving CH_2O have also been identified to be exothermic [Fehsenfeld et al., 1978]:

$$H_3O^+ \cdot H_2O + CH_2O \longrightarrow CH_2OH^+ \cdot H_2O + H_2O \qquad (2)$$

$$CH_2OH^+ \cdot H_2O + CH_2O \longrightarrow CH_2OH^+ \cdot CH_2O + H_2O \qquad (3)$$

Fehsenfeld et al. [1978] also noted that all exothermic proton transfer reactions that had been investigated have very large rate constants. Since significant amounts of aldehydes (mostly CH_2O and CH_3CHO) are expected in the ATTAS plume (see above) and large concentrations of chemiions are suggested in fresh aircraft plumes [Yu and Turco, 1997, 1998b; also see section 3], the emitted aldehydes are likely to be involved in

forming ultrafine volatile particles because of their large proton affinity and high water/acid solubility.

3. Plume Microphysics Including Chemi ion Effects and Organics

It is known that chemiionization reactions in hydrocarbon flames generate copious positive ions (CHO^+) and electrons, with charge concentrations as large as $10^8 - 10^{11} / cm^3$ [*Calcote* 1962; *Keil et al.*, 1984]. Large concentrations of negative ions in jet engine exhaust plumes have also been detected in recent ground-based measurements [*Arnold et al.*, 1998a]. The primary positive ions (CHO^+) quickly undergo proton exchange with water to form H_3O^+. The resulting hydronium core ion then rapidly clusters with water vapor and reacts with other polar molecules (such as CH_2O and CH_3CHO; see section 2). By contrast, the electrons produced via chemiionization rapidly attach to O_2, forming O_2^-, which subsequently reacts with nitrogen and sulfur species to form the stable terminal negative ions NO_3^- and HSO_4^-. These latter ions efficiently combine with water, H_2SO_4, and HNO_3 to create cluster ions such as $HSO_4^-(H_2SO_4)_n(H_2O)_m$. Because of electrostatic effects, charged nascent plume aerosols formed upon these ions grow much faster than neutral aggregates. Indeed, the resulting "ion mode" aerosols, to a major extent, appear to comprise the ultrafine particles detected in aircraft plumes, as demonstrated by *Yu and Turco* [1997, 1998a, b], *Kärcher et al.* [1998b], and *Yu et al.* [1998]. In these previous simulations, owing to the lack of information concerning positive ions and clusters, H_2SO_4 (associated with H_2O) was considered to condense both on positive and negative ions at roughly the same rates (considering the high supersaturations encountered in the early plume).

As noted in section 2, however, CH_2O and CH_3CHO have large proton affinities and readily react with hydronium to form protonated core ions. Polar organic molecules are also likely to attach rapidly to positive core ions, forming charged clusters such as $CH_2OH^+(CH_2O)_n(H_2O)_m$. Sulfuric acid molecules, on the other hand, are less likely to attach to positive ions, but could still react heterogeneously with organic compounds clustered onto those positive ions, most likely at a kinetically limited rate. Because sulfuric acid condenses rapidly on negative ions, the bisulfate ion comprises the majority of the core species. Nitric acid is likewise highly electronegative and prone to condensation on negative ions. When positive and negative ions such as those just described recombine, mixed acid/organic microparticles result in which the components may react internally. Because of the high water/acid solubility of aldehydes and reactions of alkenes and alkynes with liquid sulfuric acid, these organic species can also be taken up—likely at a kinetically limited rate—by sulfuric acid particles formed in an aircraft plume.

Recent measurements of ion mass spectra in aircraft engine exhaust reveal the expected sulfuric acid-based clustered negative ions, as well as nitrate ions at low sulfur levels [*Frenzel and Arnold*, 1994; *Arnold et al.*, 1998b]. However, no data concerning the composition of the positive ion clusters in aircraft exhaust have yet been reported, although work is underway to identify the positive ion constituency (F. Arnold, personal communication, 1998).

Organic-based aerosols may also be stabilized and grow as a result of reactions with gas phase species. For example, sulfu-
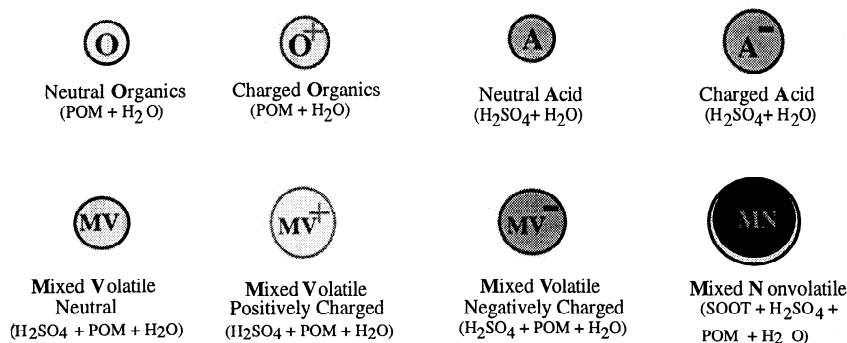
ric acid, sulfur trioxide, and nitric acid all react vigorously with a variety of organic compounds to form sulfates, sulfones, nitrates, and other organic compounds that are highly polar with high boiling points (such as alkenes, alkynes, and aldehydes). Thus while some of the primary organic species of interest have relatively high vapor pressures at the ambient temperatures of interest ($\sim$-50°C), their reaction products (e.g., alkyl hydrogen sulfate) and binary mixtures (e.g., CH_2O-H_2O) are much more likely to remain in the condensed phase as particulate organic matter. This material will, of course, contribute to the overall mass of the volatile particles formed on chemiions. Owing to the lack of detailed information on the organic species present in the plume and their thermodynamic properties, we treat all of the potential particle-forming hydrocarbons generically as POM.

In this study, we evaluate the potential role of condensable organic species (i.e., POM) in the formation and growth of plume aerosols. Toward this end, we distinguish between the initial tendency for organic species to collect on positive ions and particles and for sulfuric acid to condense on negative ions and particles. We assume that the POM precursors are stabilized after they "condense" onto positive charged particles or are taken up by acid aerosols (i.e., evaporation is neglected). The evolution of the aerosol size distribution, beginning with simple molecular clusters, is carried out using the kinetic approach developed by *Yu and Turco* [1997, 1998a, b]. Our microphysical code treats an interactive, size-resolved aerosol system including any number of types of particles and any number of compositions for each type of particles [*Yu*, 1998].
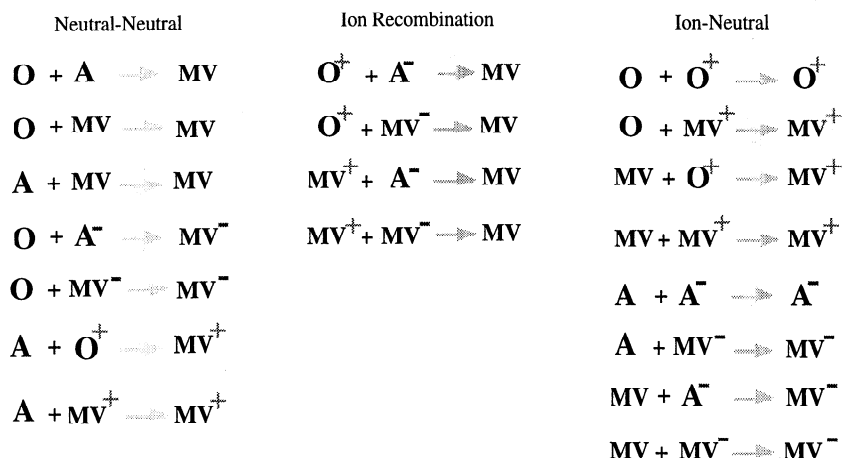
The various types of aerosols and some of the important particle–particle interactions treated here are identified in Figure 1. Eight distinct types of aerosols, in addition to pure soot, are tracked as they interact and evolve in the near-field wake. The primary interactions (i.e., coagulation rates) among these particles can be divided into three categories: neutral-neutral coagulation, ion-neutral coalescence, and ion-ion recombination. The coagulation sticking coefficient and enhancement factor due to electrical charge effects are different in each of these three categories [*Yu and Turco*, 1998b]. The size-dependent coagulation kernels at molecular scales are consistent with laboratory measurements of these processes (i.e., ion-ion recombination coefficients, ion-neutral molecule reaction rates, and high-pressure third-body stabilized molecular association reaction rates; for details, see *Yu and Turco* [1998b]).

As discussed in section 2, POM may include various organic species such as CH_2O, CH_3CHO, C_2H_4, and C_2H_2. Note that C_2H_4 and C_2H_2 can be taken up by liquid sulfuric acid particles, but are less likely to cluster onto positive ions. For low FSC cases, the dominant component of POM is likely to consist of aldehydes (CH_2O and CH_3CHO). As a first-order approximation, we treat all POM aldehydes equivalent to CH_2O; that is, we determine the initial concentration of "condensable" neutral organic vapors corresponding to an assumed mass emission index for aldehyde-based POM (EI_{POM}) that is consistent with measurements using the molecular weight of CH_2O. The amount of water associated with CH_2O is based on equilibrium calculations similar to those for H_2SO_4. Since this approximation does not consider the uptake by acid droplets of alkenes and alkynes, it may underestimate the contribution of organic species to the volatile aerosols in cases with relatively high FSCs.

Aerosol System in Aircraft Plumes

Neutral Organics
(POM + H$_2$O)

Charged Organics
(POM + H$_2$O)

Neutral Acid
(H$_2$SO$_4$+ H$_2$O)

Charged Acid
(H$_2$SO$_4$+ H$_2$O)

Mixed Volatile
Neutral
(H$_2$SO$_4$ + POM + H$_2$O)

Mixed Volatile
Positively Charged
(H$_2$SO$_4$ + POM + H$_2$O)

Mixed Volatile
Negatively Charged
(H$_2$SO$_4$ + POM + H$_2$O)

Mixed Nonvolatile
(SOOT + H$_2$SO$_4$ +
POM + H$_2$ O)

Interactions Between Aerosols

Neutral-Neutral	Ion Recombination	Ion-Neutral
O + A → MV	O$^+$ + A$^-$ → MV	O + O$^+$ → O$^+$
O + MV → MV	O$^+$ + MV$^-$ → MV	O + MV$^+$ → MV$^+$
A + MV → MV	MV$^+$ + A$^-$ → MV	MV + O$^+$ → MV$^+$
O + A$^-$ → MV$^-$	MV$^+$ + MV$^-$ → MV	MV + MV$^+$ → MV$^+$
O + MV$^-$ → MV$^-$		A + A$^-$ → A$^-$
A + O$^+$ → MV$^+$		A + MV$^-$ → MV$^-$
A + MV$^+$ → MV$^+$		MV + A$^-$ → MV$^-$
		MV + MV$^-$ → MV$^-$

Figure 1. (top) Schematic illustrating the eight principal types of aerosols, with their general composition indicated in parenthesis, and (bottom) some of the key particle–particle interactions, treated in our model. For the simulations presented in this paper, POM is taken to be equivalent to the simplest aldehyde, CH$_2$O. Therefore, O and O$^+$ may be considered to have compositions equivalent to (CH$_2$O)$_n$(H$_2$O)$_m$ and CH$_2$OH$^+$(CH$_2$O)$_n$(H$_2$O)$_m$, respectively.

Since sulfuric acid will not tend to condense on positive ions until a sufficient solvating shell has accumulated, by which time the positively charged clusters would have grown to relatively large sizes, the interaction of acid molecules with these clusters is calculated assuming a neutral-neutral interaction. That is, the electrostatic charge effect, which diminishes rapidly with increasing particle size, is expected to have only a relatively small influence on acid uptake by positive species. Hence acid condensation at an early stage of positive ion growth should be negligible compared to the uptake of water and organic species. The same situation applies to the collection of organic material on negatively charged ions and microparticles.

To illustrate some of the possible interactions between the various species in the plume, consider the fate of the organics emissions. Initially, the abundance of gas phase condensable organic molecules, which is equivalent to O at time zero, is equated with the concentration of CH$_2$O inferred from EI$_{POM}$, while the initial concentration of molecular organic ions, O$^+$,

is equated with the positive chemiions. As the plume evolves, O clusters onto or reacts with O$^+$, as well as with MV$^+$, which is formed as O$^+$ interacts with acid molecules and clusters, A. The uptake of O by O$^+$ and MV$^+$ is rapid in part because of the high proton affinity and polarizability of O (at a rate controlled by ion-neutral coagulation). Additional O is taken up by A, A$^-$, MV, MV$^-$, and MN because of its high water/acid solubility (with this interaction being kinetically limited). Of course, O may cluster with itself to form larger neutral organic clusters—effectively equivalent to the homogeneous nucleation and growth of pure organic aerosols—although these particles will be smaller than the ion mode aerosols generated simultaneously in the plume. Evaporation of the condensed O is not considered in this study.

It should be noted that the coagulation of particles carrying the same sign of electrical charge is unlikely at the sizes of interest here, and thus can be neglected. The scavenging of volatile particles (neutral and charged) by the considerably larger pure and mixed soot particles can be treated as neutral-neutral

coagulation (not indicated in Figure 1), given that the charge effect is again relatively small for larger particles. The self-coagulation of each of the neutral particle types (also omitted from Figure 1) is included in all of the simulations discussed below.

4. Simulations and Analysis

Figure 2 shows the evolution of the "apparent" emission indices (AEIs) corresponding to the total number of particles larger than a specific threshold size in the LS SULFUR-5 experiment. This emission index is comparable to the readings that would be obtained using a CN counter with the same lower cutoff, or threshold, particle diameter. Note that the AEIs vary with time, as expected, for the reasons discussed below, and approach a maximum or plateau value of roughly $\sim 10^{17}$/kg fuel. One can also distinguish between the AEI for the total number of particles, the AEI for those particles that are volatile (i.e., that can be evaporated at reasonable temperatures within the inlet system), and—by taking the difference between the former two—the AEI for particles with nonvolatile cores. Ultrafine particles with diameters below ~ 10 nm are essentially all volatile for the cases of interest, while the particles larger than ~ 15 nm are mainly nonvolatile.

In Figure 2, predicted AEIs can be contrasted with measurements for the total number of particles with $d > 5$ nm taken during the SULFUR-5 mission [Schröder et al., 1998]. In the simulations, initial positive and negative chemiion concentrations of 10^9/cm^3 are assumed (see below). Moreover, S_c is assigned a value of 10%—consistent with chemical simulations [Brown et al., 1996b]—yielding an overall H_2SO_4

emission index of 6 mg/kg fuel. With these constraints, it is necessary to assume a POM emission index of 23 mg/kg fuel to bring simulated and observed variations in $AEI_{d>5\,nm}$ into agreement (Figure 2). A smaller value of S_c changes the results only slightly because CH_2O (with H_2O) is the dominant component of the detectable volatile particles in the low FSC case when $S_c \leq 10\%$. For example, if we had chosen S_c to be 5% (i.e., $EI_{H_2SO_4} = 3$ mg/kg fuel), then an EI_{POM} of ~ 24 mg/kg fuel would be required to obtain similar agreement between simulated and observed $AEI_{d>5\,nm}$ values. The EI_{POM} inferred from Figure 2 is well within the range of measured organic emissions during the experiments of interest, accounting for <25% of the total organic material in the plume [Slemr et al., 1998]. Since we treat all POM as an equivalent quantity of CH_2O in this study, a value of 23 mg/kg fuel is also within the range of estimated aldehyde emissions in ATTAS exhaust (10-42 mg/kg fuel; see section 2). Note that in the LS case, particles with diameters larger than 14 nm are dominated by soot (or mixed nonvolatile particles, MN, since soot is readily coated by volatile materials). Accordingly, $AEI_{d>14\,nm}$ values—both predicted and observed—corresponding to the total particulate depend primarily on the soot emission parameters and are decoupled from the evolution of the ultrafine volatile particle AEIs.

Measured AEIs are expected to be sensitive to the detection efficiency of the CN counter near its lower cutoff size (~ 5 nm in Figure 2). The potential sensitivity is emphasized in Figure 2 by the fairly wide range between the predicted AEIs corresponding to 4 nm and 6 nm. Indeed, as argued by Yu et al. [1998], the orderly progression of the calculated AEIs with increasing cutoff sizes (between 2 nm and ~ 9 nm in Figure 2) can be explained by the growth of an aerosol mode with a mean size below 5 nm during the period illustrated. Figure 3 shows this situation in terms of the corresponding simulated evolution of the ultrafine particle size distribution. The distinct modal structure, which is dominated by ion mode particles [Yu and Turco, 1997], explains, for example, why $AEI_{d>2\,nm}$ stabilizes by ~ 0.1 s: because the ion mode particles have grown larger than 2 nm by this time, while the neutral-mode particles have been suppressed and remain smaller than 2 nm. At the
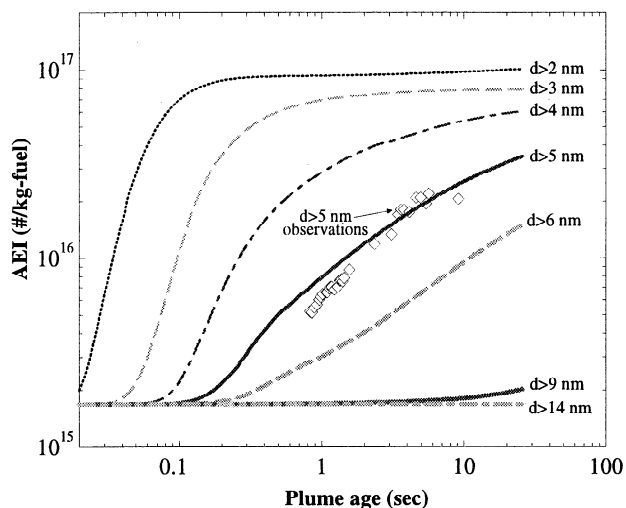
Figure 2. Computed evolution of the AEI for the total number of particles larger than certain assumed cutoff sizes for conditions that apply to the LS SULFUR-5 case (each line represents the variation over time of the AEI corresponding to a specific cutoff diameter). Key model parameters are the sulfuric acid emission index, $EI_{H2SO4} = 6$ mg/kg fuel (i.e., $S_c = 10\%$ and FSC=20 ppmm), the emission index of condensable organic compounds, $EI_{POM} = 23$ mg/kg fuel, and the initial chemiion concentration, $n_{io} = 2 \times 10^9$/cm^3 (with half of the ions being positive and half negative). Shown for comparison are measured AEI values (diamonds) corresponding to particles with $d > 5$ nm taken from Schröder et al. [1998].
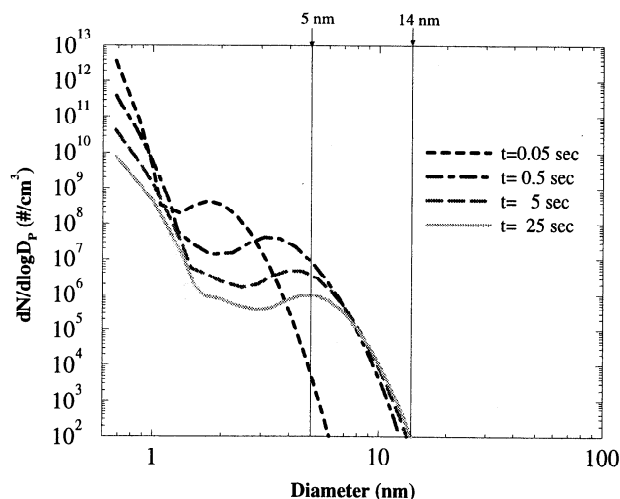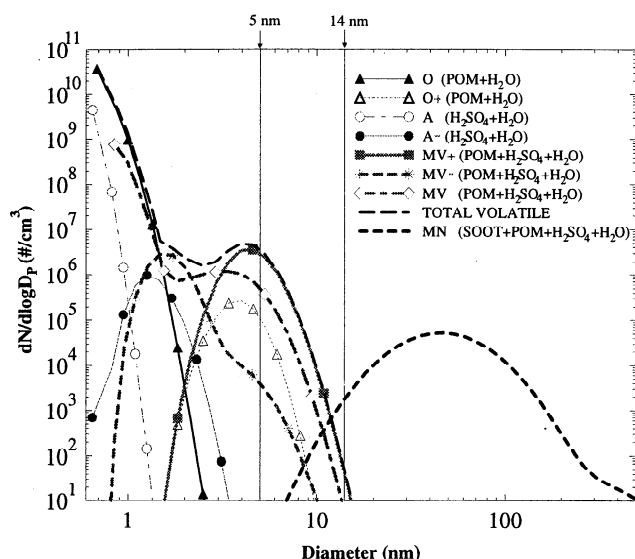

Figure 3. Number size distributions of total volatile particles (i.e., all of the particle types in Figure 1 except for the mixed nonvolatile MN particles) at four different plume ages for the same case described in Figure 2.

plume ages corresponding to the SULFUR-5 measurements, however, $AEI_{d>5\,nm}$ has not yet stabilized, since the mean size of ion mode particles is just approaching 5 nm [*Kärcher et al.*, 1998b]. Hence the measured emission index will be highly sensitive to the detection efficiency near the threshold of the CN counter. This uncertainty, in turn, is propagated into the value of the POM emission index inferred by matching simulations with observations.

Remarkably, a variety of measurements indicate that the number of ion-mode aerosols formed on chemiions, as expressed by the AEI, reaches a distinct plateau that is relatively invariant between experiments. For example, similar maximum AEIs are found in the HS SULFUR-5 measurements under discussion here, as well as in data taken during SNIF and other field programs (B. Anderson, personal communication, 1998). We suggest that this result may be understood in terms of the principle of invariance in a coagulating, expanding plume expressed by *Turco and Yu* [1997, 1998]. In the present circumstances, chemiions initially ejected from engine combustors at high concentrations represent the interacting microparticle system in which ion-ion recombination is the dominant "coagulation" process. Indeed, the ion-ion recombination coefficient (with typical values of $\sim 3 \times 10^{-7}\,cm^3/s$, determined primarily by Coulombic attraction) represents the effective coagulation kernel for this system. Hence the ion-ion recombination coefficient and plume volume unambiguously define a dimensionless "invariant" number, N_T, for this system [*Turco and Yu*, 1997]. At the timescales of interest (~1 ms), the invariant number is equivalent to $\sim 10^9$ ions/cm³, which we have taken as the initial chemiion concentrations for the present simulations.

Figure 4 decomposes the total particle size distribution into the different types of aerosols defined in Figure 1. Owing to the relatively higher emission index of condensable organic species (23 mg/kg fuel) and relatively lower emission index of H_2SO_4 (6 mg/kg fuel), and because of the preferred condensation of organic species on positive ions, the majority of the volatile aerosols in the prominent ion mode near 5 nm con-
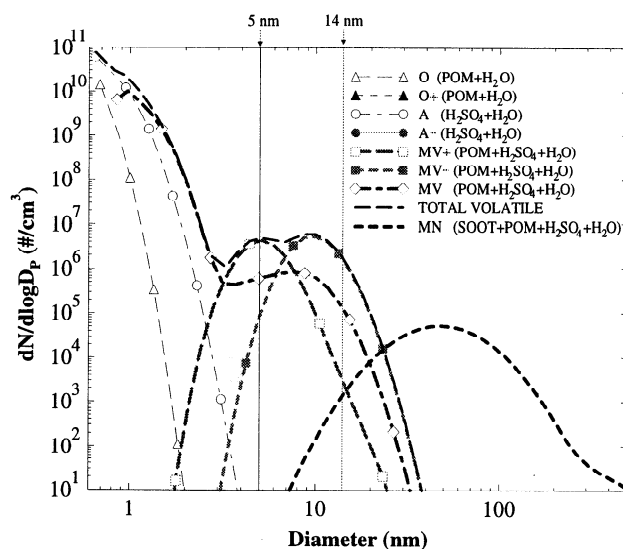
Figure 5. Same as Figure 4, except for the HS SULFUR-5 case with $EI_{H_2SO_4}$=248 mg/kg fuel (i.e., S_c=3% and FSC=2700 ppmm). Other parameters are similar to those used for the simulations shown in Figure 2.
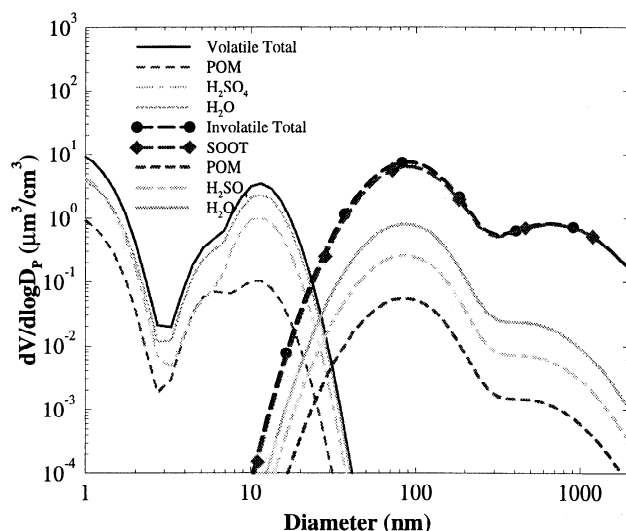
sists of positively charged and neutral mixed volatile particles (MV^+ and MV). The neutral mixed particles are produced mainly by the neutralization of MV^+ by MV^- and A^- (with a smaller contribution from the neutralization of O^+). In this case, the mean sizes of the negatively charged particles (both MV^- and A^-) are considerably smaller than those of the positively charged particles.

As $EI_{H_2SO_4}$ increases (with increasing FSC and/or S_c), the negatively charged particles increase in size and eventually grow larger than the positively charged aerosols. This is seen in the decomposed size distributions for the high-sulfur fuel (case HS) in Figure 5. Under these circumstances, the single ion mode predicted by *Yu and Turco* [1997] bifurcates into two distinct submodes, with the separation between them determined by the relative abundances of emitted POM and sulfuric acid. It follows that, as EI_{POM} decreases relative to $EI_{H_2SO_4}$, the subion mode associated with MV^+ shifts toward smaller sizes and eventually "merges" with the neutral mode, leaving behind a distinct negative ion mode consisting mainly of MV^- (analogous to the positive ion mode composed of MV^+ and MV in Figure 4). Note that in the HS case, O^+ and A^- have been completely converted to MV^+ and MV^- as a result of the ample abundances of sulfuric acid and organic vapors.

Figure 6 shows component-resolved volume size distributions for the plume aerosols corresponding to the simulations in Figure 5. To simplify the presentation, material held by the different types of volatile particles has been aggregated. The total sulfuric acid and POM in the aerosols are partitioned between three dominant modes, that is, the neutral, ion, and soot modes. Within the ion mode, two submodes are seen, associated primarily with MV^+ and MV^- (refer to Figure 5). While acid is the dominant component (aside from water) in the larger MV^- mode (recall that this is the HS case), POM also contributes a noticeable fraction to the volume of these particles. The volume fractions of acid and POM in the smaller MV^+ mode are similar. POM also contributes a significant fraction to the total volatile material coating soot particles (the nonvolatile particles dominating the largest sizes in Figure 6).

Figure 4. Number size distributions of individual aerosol types (as defined in Figure 1) at a plume age of 5 s for the same case shown in Figures 2 and 3.

In Figure 6, only 23 mg/kg fuel of CH_2O is considered as POM. There is more than an adequate amount of sulfuric acid available in this case to absorb the CH_2O. However, since C_2H_4 and C_2H_2 may also be taken up by liquid acid particles and their EIs are generally comparable to those of the aldehydes (see section 2), the contribution of organics to volatile particles may be understated in the high FSC case. The uptake of organic species that is found to occur at all particle sizes in the present simulations—and its likely reaction with sulfuric acid—may significantly alter the overall chemical properties of plume aerosols, leading to further consequences, such as modified activity as cloud condensation nuclei. There is currently little information, if any, available to evaluate these potential effects quantitatively.

Figure 7 depicts the evolving AEIs for the total aerosol population in the HS case (the same case illustrated in Figures 5 and 6). The measured AEI's for $d>5$ nm and $d>14$ nm [Schröder et al., 1998] are plotted for comparison. The chemiion mechanism developed for aircraft plume modeling, modified to include organic species—with preferential condensation of sulfuric acid and organic compounds on negative and positive ions/particles, respectively—provides an excellent replication of the observations. Even the gradual increase apparent in $AEI_{d>5 \text{ nm}}$ at $t>1$ s can be explained in terms of the continuing growth of the smaller MV^+ ion mode particles in this instance (refer to Figure 5). In these simulations, a value of $S_c=3\%$ reproduces both the measured $AEI_{d>5 \text{ nm}}$ and $AEI_{d>14 \text{ nm}}$. The predicted $AEI_{d>5 \text{ nm}}$ (for $t>1$ s) is not very sensitive to S_c (as long as $S_c>1\%$) since, in the HS case, the MV^- subion mode particles, which are dominated by sulfuric acid, have already grown beyond 5 nm in size. However, $AEI_{d>14 \text{ nm}}$ is very sensitive to S_c, providing a strong constraint on this parameter. The inferred value of $S_c=3\%$ is in excellent accord with other values quoted in the literature. On the other hand, uncertainties in the CN counting efficiency near the detection threshold of 14 nm implies an uncertainty in the inferred S_c. Also note that if we include the uptake of
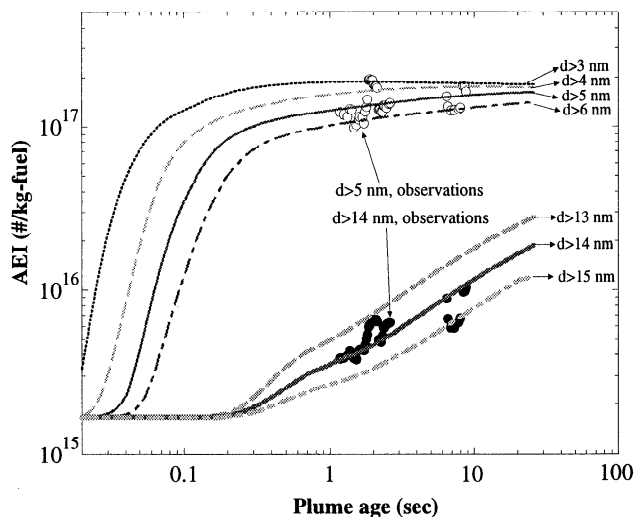
Figure 7. Calculated evolution of the apparent emission index (AEI) for the total number of particles exceeding certain cutoff sizes for conditions that apply to the HS case (Figures 5 and 6). The model parameters are as follows: $EI_{H_2SO_4}=248$ mg/kg fuel, $EI_{POM}=23$ mg/kg fuel, with $n_{io}=2\times10^9/cm^3$. Measured values of AEI corresponding to particles with $d>5$ nm (open circles) and $d>14$ nm (solid circles) are shown for comparison [Schröder et al., 1998].

alkenes and alkynes by sulfuric acid particles in this case, a smaller value of S_c would reproduce the measurements.

5. Summary and Discussion

We have developed a comprehensive microphysics code that tracks different types of aerosols, including ions, and neutral and charged particles having a range of compositions. The model treats a multitype, multicomponent size-resolved interactive particulate system. In the present work, we have introduced condensable organic species (which in the condensed state are identified as "particulate organic matter," or POM) as a separate aerosol component to investigate its potential role in the formation and growth of ultrafine particles in aircraft plumes. We have also extended an earlier treatment of chemiions by allowing preferential initial condensation of sulfuric acid on negatively charged ions and organic compounds on positively charged ions. The simulations performed with this model have been constrained using continuous CN measurements (at two threshold sizes of $d>5$ nm and $d>14$ nm) obtained in ATTAS wakes during the SULFUR-5 field experiment, in which both low and high sulfur-containing fuels were burned [Schröder et al., 1998].

Our major findings are based on a series of simulations and sensitivity tests described in the text. The chemiion-induced volatile aerosol mode previously identified by Yu and Turco [1997] is found to become bifurcated into two submodes, particularly when exhaust sulfur emissions are low and organic emissions are more prominent. Both of the resulting ultrafine modes consist of volatile particles of mixed composition (sulfuric acid and various organic compounds and their reaction products). One of the bifurcated modes is associated with positive ions (designated by the abbreviation MV^+, for mixed-composition volatile positively charged particles), while the other is associated with negative ions (MV^-). The mean size

Figure 6. Volume size distributions associated with the total volatile and nonvolatile particles at 5 s for the HS simulation described in Figure 5. The relative composition of the particles as a function of size is also given in terms of the aggregated volumes of POM, sulfuric acid, water, and soot.

of the MV^+ particles is sensitive mainly to the emission index of POM, when sulfur emissions are minimal, while the size of the MV^- particles is more sensitive to the emission index of sulfuric acid. The separation between the ion modes depends on the relative abundances of emitted sulfuric acid and condensable organic compounds and on the physical/chemical properties of the latter.

In the low-sulfur fuel (LS) case (with FSC=20 ppmm), the exhaust sulfuric acid fraction, S_c, was taken to be 10%, a value determined earlier by *Brown et al.* [1996b] using a chemistry model designed to calculate the composition of aircraft engine emissions. This reasonable acid fraction in our plume microphysics model requires a POM emission index, $EI_{POM} \sim 23$ mg/kg fuel, to explain the observed variation in the "apparent" emission index for particles larger than 5 nm ($AEI_{d>5\,nm}$). In the LS simulation, the MV^- mode is too small to contribute to the measured CN concentrations, and the MV^+ mode dominates the particles with $d>5$ nm. Using the same POM emission index in the high-sulfur (HS) case, an S_c value of 3% accurately reproduces the measured ultrafine particle emission indices, $AEI_{d>5\,nm}$ and $AEI_{d>14\,nm}$. In this case, the mean size of MV^- particles is larger than that of the MV^+ particles, because of the higher emissions of H_2SO_4, and the MV^- mode dominates the volatile particles having $d>14$ nm. The MV^+ mode contributes only marginally to the measured number of particles with $d>5$ nm.

We note that the magnitude of $AEI_{d>5\,nm}$ in the LS ATTAS case appears to be substantially larger than that measured in a 757 wake during SUCCESS [e.g., *Miake-Lye et al.*, 1998] or behind an F-16 during SNIF (B. Anderson, personal communication, 1998), pointing to a significant, but perhaps not unexpected, engine-dependent variation in organic emissions.

The present study, based on detailed microphysical simulations, has been constrained using in situ measurements where possible. The results, summarized above, suggest that when LS fuel is burned in aircraft engines, organic compounds in the exhaust can dominate the mass of the volatile ultrafine particles initially formed in the wake. Even when fuels with medium to high sulfur contents are used, we find that organic species may still significantly modify the composition and chemistry of the plume aerosols. The overall contribution of organic species depends on the emission index and the speciation of the "condensable" organic vapors, which are not well characterized. The fraction of emitted organic material that enters the particulate phase may be related to the proton affinity, water/acid solubility, and/or acid reactivity of the specific organic compounds in the exhaust. On the basis of the available limited observational data, we identify aldehydes (mainly CH_2O and CH_3CHO) as potential POM, regardless of FSC, and small chained alkenes (primarily C_2H_4) and alkynes (mostly C_2H_2) as potential POM for moderate to high FSCs.

To ascertain whether or not organic compounds are a significant component of the aircraft-generated particulate or if they contribute to the creation of viable atmospheric condensation nuclei, further laboratory studies and in situ measurements are required. For example, we need to characterize comprehensively the composition and variability of the organic emissions and determine the propensity of the dominant species to condense on or react with ions and charged sulfuric acid aerosols in the exhaust stream. Further information concerning the composition of the positively charged chemiion clusters detected behind aircraft engines, as well as the charged and neutral ultrafine particles sampled in wakes, is essential to the validation of any theory in this regard.

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