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On the mechanisms controlling the formation and properties of volatile particles in aircraft wakes

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Abstract. New observations taken in aircraft wakes, including the DLR ATTAS, provide strong constraints on models of aircraft plume aerosols. Using a comprehensive microphysics code, we have performed sensitivity studies to identify the key microphysical mechanisms acting in such plumes. Analysis of these simulations reveals that the largest volatile plume particles—those most likely to contribute to the background abundance of condensation nuclei—are dominated by ion-mode particles when chemiions are included. Moreover, such modeling demonstrates that standard treatments of plume microphysics—in the absence of chemiions—fails to explain field measurements. The principal factor controlling the population of ultrafine plume particles is the number of chemiions emitted by the aircraft engines. Since the ions are a byproduct of the combustion itself, and their abundance in the exhaust stream is controlled by ion-ion recombination, the initial ion concentrations—and so the eventual emission indices for ion-mode particles—are expected to be relatively invariant. Our results indicate that reductions in fuel sulfur content, while not likely to lower the total number of volatile particles emitted, would decrease the size of the ion-mode particles in fresh aircraft wakes, reducing their atmospheric lifetimes and potential environmental effects.

Introduction

In view of increasing commercial airline traffic, and a planned fleet of supersonic passenger jets, the environmental effects of the associated particulate emissions are of national and international concern. A reliable assessment of the impacts of aircraft emissions requires a through understanding of the mechanisms that control the production and physical properties of the particles deposited in the atmosphere.

During a SULFUR-5 mission in April, 1997, measurements of condensation nuclei (CN) having diameters $d>5$ *nm* and $d>14$ *nm* were carried out simultaneously and continuously at distances equivalent to plume ages of 0.5–20 *s*, at two altitudes (with and without contrail formation), and for two sulfur content fuels (high sulfur fuel, "H," at 2700 *ppmm*; and low sulfur fuel, "L," at 20 *ppmm*) (Schröder et al., 1998). Constrained by these observations, detailed numerical simulations of the plume encounters have been conducted using the model of Yu and Turco (1997, 1998a), which explicitly resolves the interactions of charged and neutral, volatile and nonvolatile, and pure and mixed particles. Some of the initial results, confirming the critical role of chemiions in volatile aerosol formation, were reported by Kärcher et al. (1998). Here, a series of sensitivity studies are described that aim to identify the mechanisms controlling the evolution of ultrafine particles in such plumes. The implications for strategies to modify the physical properties of the emitted aerosols are discussed. To limit the scope of the analysis, we focus on cases where contrails were absent.

Plume Parameters and Microphysics

It is well established that the properties of the ultrafine aircraft particles are influenced by the concentration of H_2SO_4 vapor in the exhaust (designated as $[H_2SO_4]_0$, where SO_3 is taken to be equivalent to H_2SO_4 since it is rapidly converted to H_2SO_4). $[H_2SO_4]_0$ is a function of the fuel sulfur content (FSC) and fraction of fuel sulfur (η) oxidized to SO_3+H_2SO_4. The parameters FSC and η can be combined to yield the H_2SO_4 mass emission index (i.e., EI_{H2SO4}=FSCx η x98/32, in *ppmm* or *mg-H_2SO_4/kg-fuel*). Other key parameters in wake simulations are the soot emission index and plume dilution ratio, as well as ambient environmental conditions. We introduce another important factor into these calculations: the total initial chemiion (CI) concentration (n_{io}) at a plume age of 1 *ms*. In aircraft exhaust, the CI's quickly form charged clusters by attracting a variety of molecular species, including sulfuric acid and water (Frenzel and Arnold, 1994). The initial growth rate of these charged clusters is greatly enhanced due to the electrostatic forces exerted by the ionic charge (Yu and Turco, 1997).

The soot emission index for the ATTAS engines is well characterized (Petzold et al., 1998). Moreover, for the field experiments of interest (i.e., SULFUR-5), the ambient environmental state and plume dilution rate are also defined observationally (Schröder et al., 1998). That leaves η (or EI_{H2SO4}) and n_{io} as the two least constrained parameters affecting ultrafine particle properties (in cases without contrail formation).

To simulate the early phases of aerosol formation under the extremely variable dynamical conditions encountered in a jet wake, we have applied a "kinetic" microphysical approach, in which coagulation—extrapolated to molecular scales—is the key process driving aerosol evolution. The kinetic approach is appropriate for simulating collision-controlled interactions at high H_2SO_4 and water vapor supersaturations during the early entrainment phase of the plume. In this approach, charged and neutral aerosols are precisely tracked by explicitly accounting for all of the corresponding particle-particle interactions. The effects of chemiions in enhancing the aerosol growth rate (via coagulation and condensation) are introduced through size-dependent coagulation kernels corresponding to each type of interaction (charged-charged, charged-neutral, and neutral-neutral); thus, condensation is equivalent to the limiting case of coagulation between a molecule (or small molecular cluster) and a particle. In this study, for purposes of comparison, we also employ a standard microphysical modeling approach

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without CI effects. A detailed description of these numerical models, and the microphysics of ionized aerosols, can be found in previous work (Turco et al., 1979; Yu and Turco, 1997, 1998a,b; Yu, 1998).

Sensitivity Studies

Sensitivity to Microphysical Treatment: It has previously been shown (Kärcher et al., 1998) that simulations based on the kinetic approach, including CI's, reproduce quite well the observed evolution of the "apparent" ultrafine volatile particle emission indices (EI's) [these "apparent" indices are in general a function both of time and the minimum CN cutoff size used in counting the aerosols, and thus do not represent the total number of particles in the plume]. By matching simulations with measurements, and assuming that the volatile particles are composed exclusively of H_2SO_4 and H_2O, the following parameters were deduced by Kärcher et al. (1998): $n_{io}=2x10^9/cm^3$, and $\eta=1.8\%$ for high sulfur (H) fuel (corresponding to an effective sulfuric acid vapor emission index, $EI_{H2SO4}=149$ *ppmm*); and $n_{io}=2x10^9/cm^3$, and $\eta=55\%$ for low sulfur (L) fuel (corresponding to $EI_{H2SO4}=34$ *ppmm*).

Simulations with the standard microphysical model are much less successful in explaining these observations. For example, Figure 1 shows the predicted evolution of aerosol properties for case H (as otherwise defined in the work of Kärcher et al., 1998, but with optimum—and likely, unrealistic—growth

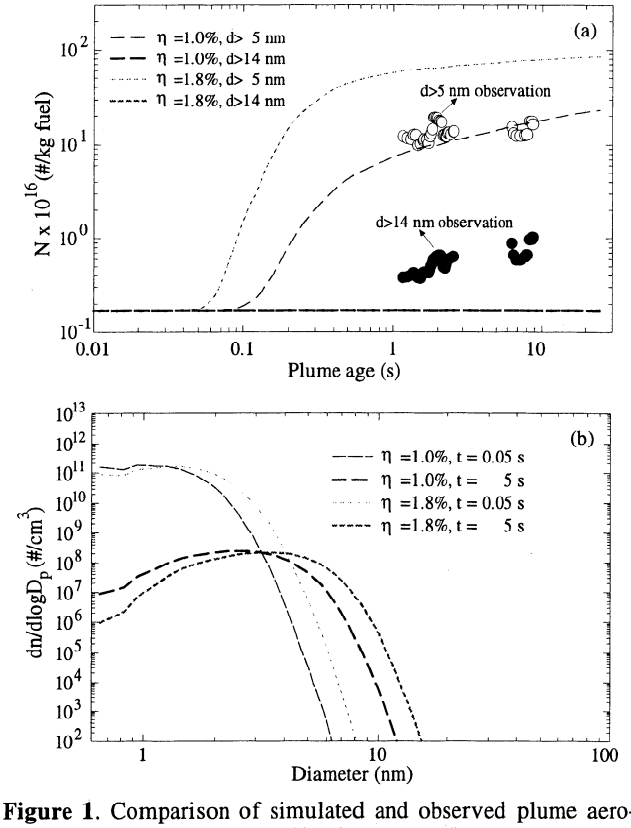

Figure 1. Comparison of simulated and observed plume aerosol properties for the high sulfur fuel case, H. The simulations are based on the standard treatment of microphysics, in which optimum aerosol growth parameters are assumed, and CI effects are neglected; η has been assigned values of 1.0% and 1.8%. Panel (a) shows computed values of the "apparent" particle EI's for $d>5$ *nm* and $d>14$ *nm*, along with measurements taken in an ATTAS wake. Panel (b) gives the corresponding predicted size distributions of the volatile particles at $t=0.05$ and 5 *s*.

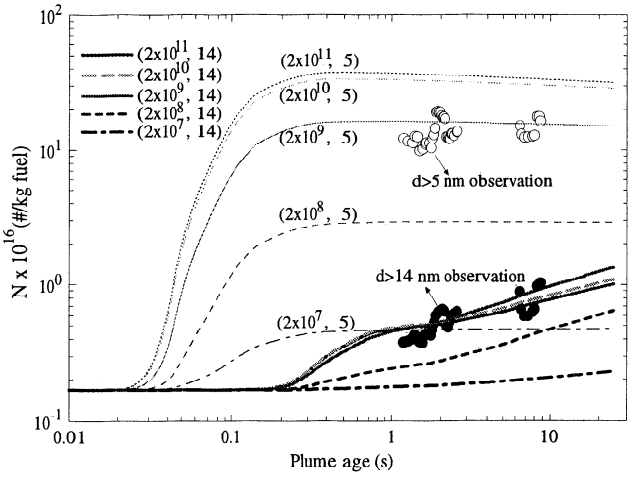

Figure 2. Predicted evolution of particle "apparent" EI's (for $d>5$ *nm* and $d>14$ *nm*) assuming different initial CI concentrations, n_{io}. Compared are measured emission indices for particles with $d>5$ *nm* and $d>14$ *nm*. In the legend, the first number gives the value of n_{io} *(#/cm³)*, while the second number is the particle cutoff diameter (5 or 14 *nm*) used to determine the equivalent CN sampling rate for the predicted volatile particle size distributions.

assumptions incorporated to compensate for the absence of CI effects, in the manner described by Yu and Turco, 1997, 1998a). In Figure 1a, calculated particle emission indices for $d>5$ *nm* and $d>14$ *nm* (corresponding to the cutoff sizes sampled) are illustrated for two values of η (1.0% and 1.8%), along with measured EI values. By choosing $\eta=1.0\%$, the simulated $EI_{d>5\text{-}nm}$ lies close to the data (Figure 1a); however, the corresponding $EI_{d>14\text{-}nm}$ is much too low. To increase this latter value, a higher η ($\geq 6\%$) could be used; however, $EI_{d>5\text{-}nm}$ would then be too large ($\geq 2x10^{18}$*/kg-fuel*). Thus, no single value of η simultaneously satisfies the observed $EI_{d>5\text{-}nm}$ and $EI_{d>14\text{-}nm}$. Moreover, a closer inspection of the temporal variation in $EI_{d>5\text{-}nm}$ for this model shows a distinct upward slope that is not obvious in the measurements (where, the observed "apparent" $EI_{d>5\text{-}nm}$ has, by one second, stabilized at ~$1.5x10^{17}$*/kg-fuel*).

In Figure 1b, the volatile particle size distributions in the standard model are seen to be unimodal, as opposed to bimodal when chemiions are present (as illustrated in Fig. 2 of Kärcher et al., 1998, for the kinetic model). The fact that measured EI's—corresponding to specific lower cut-off sizes—tend to stabilize beyond a certain plume age provides strong inferential evidence that the size distribution is in fact bimodal, with the larger (ion) mode growing at the expense of the smaller (neutral) mode. Simulations carried out for the SULFUR-5 experiment suggest that, after one second, the lower CN cutoff diameter lay below the peak in the ion-mode particle size spectrum, while the upper cutoff diameter lay somewhat above the peak. Hence, as the ion-mode particles continued to grow, the total number of particles below the lower cutoff remained fairly constant, while the number above the upper cutoff appeared to increase. The failure of the standard model to explain such observations is related to the predicted unimodality, as well as the slower growth rate, of the neutral mode. In Figure 1a, for example, with $\eta=1.8\%$, the simulated $EI_{d>5\text{-}nm}$ is already much higher than the measured values, while $EI_{d>14\text{-}nm}$ is much lower. It follows that, in the high-sulfur simulations, chemiion ef-

fects seem to be necessary to reproduce the observed behavior of the ultrafine particle emissions.

Sensitivity to Initial Chemiion Concentrations: The influence of the initial CI concentration, n_{io}, on the apparent emission indices for particles with d>5 *nm* and d>14 *nm* are shown in Figure 2, along with the SULFUR-5 field data. Here, η=1.8% is assumed, since this value is consistent with other independent estimates of this parameter (also see below). Simulations using the reference value of $n_{io}=2x10^9/cm^3$ accurately reproduce the observed behavior of both $EI_{d>5\text{-}nm}$ and $EI_{d>14\text{-}nm}$. However, while calculations with $n_{io}>2x10^9/cm^3$ also closely match observed $EI_{d>14\text{-}nm}$, the number of particles with d>5 *nm* is too large by a factor of ~2 (notwithstanding a possible adjustment in the value of η owing to uncertainties in its magnitude). For values of $n_{io}\leq 10^9/cm^3$, the predicted EI's are very sensitive to the CI emissions, indicating that an initial chemiion concentration of $10^9/cm^3$ or larger is required to reproduce the ultrafine particle measurements taken during the SULFUR-5 mission. These results also lead to the conclusion that the number of larger volatile aerosols injected into the atmosphere is limited by the chemiion abundance. Because the CI's are the product of fuel combustion itself, and are controlled by ion-ion recombination, it is less likely that their concentrations are highly variable, or subject to modification.

Arnold et al. (1998) measured the total concentration of negative chemiions having masses below ~220 *amu* of ~$3x10^7/cm^3$ at ~10 *ms* in the exhaust of a jet engine in a ground test. These numbers are roughly consistent with CI concentrations of ~$10^9/cm^3$ at ~1 *ms* for an ion-ion recombination coefficient of ~10^{-7}-10^{-6} cm^3/s, taking into account plume aging, dilution, and reduced sampling efficiency of growing cluster ions and charged particles (Yu and Turco, 1998a).

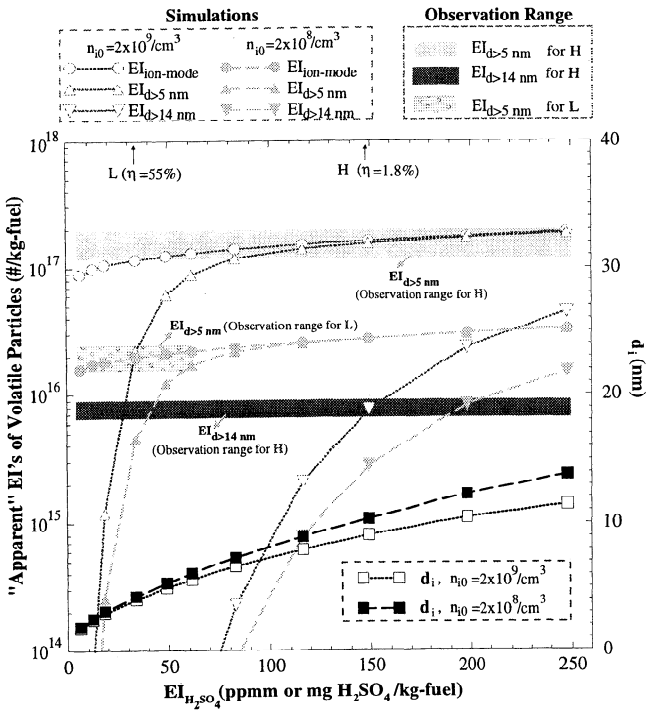

Figure 3. Simulated "apparent" volatile particle emission indices are shown for the total ion-mode, and for threshold CN sizes, d>5 *nm* and d>14 *nm*, at a plume age of 9 *s*, as a function of the H_2SO_4 mass emission index, EI_{H2SO4}. Also illustrated is the computed mean diameter of the ion-mode particles, d_i. Model results are given for two initial CI concentrations, n_{io}: $2x10^9/cm^3$ (open symbols); and $2x10^8/cm^3$ (filled symbols). For comparison, shaded areas define the measured range of EI values (total CN minus nonvolatile CN) corresponding to the two cutoff sizes, at t≈9 *s*, during SULFUR-5; in case H, data are provided for 5 *nm* and 14 *nm*, and in case L, for 5 *nm* (Schröder et al., 1998).

Sensitivity to Sulfuric Acid Emission Indices: Figure 3 illustrates predicted volatile particle emission indices (for the two cutoff sizes employed in SULFUR-5) at a plume age of ~9 *s*, as a function of EI_{H2SO4}. For comparison, measured ranges of volatile particle EI's (at t~9 *s* in the SULFUR-5 H and L experiments) are indicated by shading in the figure (noting that no significant concentrations of volatile particles with d>14 *nm* were measured in case L) (Schröder et al., 1998).

When $n_{io}=2x10^9/cm^3$, a wide range of EI_{H2SO4} (>80 *ppmm*) produce results that match the observed $EI_{d>5\text{-}nm}$ at 9 *s* for case H. By contrast, with $n_{io}=2x10^8/cm^3$, the measured $EI_{d>5\text{-}nm}$ cannot be attained with any value of EI_{H2SO4} in the range considered. On the other hand, both $n_{io}=2x10^9/cm^3$, with $EI_{H2SO4}\cong 150$ *ppmm*, and $n_{io}=2x10^8/cm^3$, with $EI_{H2SO4}\cong 200$ *ppmm*, reproduce the measured $EI_{d>14\text{-}nm}$ in case H. However, there is a unique solution that matches *both* the observed $EI_{d>5\text{-}nm}$ and $EI_{d>14\text{-}nm}$, when n_{io}~$2x10^9/cm^3$ with EI_{H2SO4}~150 *ppmm*. Thus, measurements of the ultrafine particle emission index at two different cut-off sizes provides a strong constraint on the model simulations, allowing the mechanism of aerosol formation to be inferred with greater certainty. For case L, with $n_{io}=2x10^9/cm^3$, a value of EI_{H2SO4}~32 *ppmm* (i.e., η~55%) is necessary to reproduce the observations. Further, with $n_{io}=2x10^8/cm^3$, EI_{H2SO4}~60 *ppmm* (i.e., η~100%) is required. Note that such high sulfuric acid fractions are unlikely, and the observed growth of the CN during SULFUR-5 may have been associated with organic compounds in the exhaust stream (Kärcher et al., 1998). If other condensing species come into play, the aerosol composition at low EI_{H2SO4} will deviate significantly from pure H_2SO_4/H_2O. Accordingly, the analysis in Figure 3 becomes invalid below an EI_{H2SO4} value that is determined by the emission indices of the co-condensates.

If we apply the standard microphysical modeling approach without consideration of electrical charge effects (as in Figure 1), the simulated "apparent" volatile particle emission indices—$EI_{d>5\text{-}nm}$ and $EI_{d>14\text{-}nm}$—at 9 *s* continue to increase as EI_{H2SO4} increases (these results are not shown in Figure 3). In case H, an EI_{H2SO4} of ~496 *ppmm* would be needed to match the observed $EI_{d>14\text{-}nm}$ (resulting in a predicted mean diameter of the unimodal size distribution, d_i, of ~5.9 *nm* at 9 *s*). However, to match the observed $EI_{d>5\text{-}nm}$, an EI_{H2SO4} of ~83 *ppmm* would be required (corresponding to d_i~2.6 *nm* at 9 *s*). In other words, as noted earlier (and referring to Figure 1), the standard microphysics cannot consistently reproduce the observed $EI_{d>5\text{-}nm}$ and $EI_{d>14\text{-}nm}$ simultaneously in case H.

When the effects of chemiionization are included in the simulations, the size distributions of the volatile particles are found to be bimodal (Yu and Turco, 1997). Under these conditions, the ion-mode particles are much larger than the neutral-mode particles and, in the near-field wake, only the former are likely to be detected by CN counters having threshold sizes ≥4 *nm*. Moreover, the ion-mode particles, which grow at the expense of neutral-mode aerosols, effectively continue to absorb sulfuric acid formed in the aging plume, and thus are more apt to have significant chemical and climatic impacts. In Figure 3, it can be seen that, within the range of EI_{H2SO4} tested (≤250 *ppmm*), only a fraction of the total ion-mode particles are actually measured by CN counters with cut-off sizes of 14 *nm* (at a plume age of 9 *s*). On the other hand, essentially all of the

ion-mode particles are detected by CN counters with lower cut-off sizes of 5 *nm*, when $EI_{H2SO4} \geq 100$ *ppmm* (indicating an ion-mode diameter $d_i >> 5$ *nm*; also compare $EI_{ion\text{-}mode}$ and $EI_{d>5\text{-}nm}$ in Fig. 3). When $EI_{H2SO4} < 80$ *ppmm* (and so, $d_i \leq 5$ *nm*), $EI_{d>5\text{-}nm}$ is very sensitive to the sulfuric acid emission index. However, as EI_{H2SO4} varies over a wide range, both $EI_{ion\text{-}mode}$ (Fig. 3) and the standard geometric deviation of the ion-mode particles (~1.3, not shown) change only slightly. In other words, reductions in EI_{H2SO4} (corresponding to reductions in FSC or η) are not expected to be effective in reducing the total number of volatile ion-mode particles. However, reducing EI_{H2SO4} does reduce the size of the these particles, which influences their atmospheric lifetimes and impacts.

When $EI_{H2SO4} \geq 80$ *ppmm*, then $d_i > 5$ *nm*, and $EI_{d>5\text{-}nm}$ stabilizes for larger EI_{H2SO4}. Hence, there is an apparent upper limit to $EI_{d>5\text{-}nm}$ that is clearly associated with the ion-mode aerosols. Note that, although very high concentrations of neutral-mode particles are also present, their sizes in the near-field lie below the threshold for detection; moreover, these particles are subsequently scavenged by the larger aerosols as the plume evolves. The emission index for total ion-mode aerosols (in practice, the upper limit to the detectable number) depends on the initial chemiion concentration and, hence, on ion-ion recombination rates (also see Figure 2). Considering the expected high abundances of CI's in the engine combustors, n_{io} is most likely limited by rapid ion-ion recombination in the vicinity of the exit plane. Moreover, the total number of ions that survive the first few milliseconds of plume expansion following emission also depends on the charge recombination coefficient (Yu and Turco, 1998a), and on the dilution rate (Turco and Yu, 1997). Other sensitivity tests, in which these physical parameters were varied over reasonable ranges, suggest that the absolute upper-limit to the "apparent" emission index for volatile particles is $\sim 4 \times 10^{17}$/*kg-fuel*, consistent with existing measurements (e.g., Anderson et al., 1998).

Summary

We have used a comprehensive aerosol microphysics model to analyze ultrafine particle measurements taken in ATTAS wakes during the SULFUR-5 field mission. The most striking result of this comparative study is the confirmation that chemiions (CI's) emitted by the aircraft engines seem to play a critical role in determining the properties of the measured volatile ultrafine particles, which were previously identified as "ion-mode" aerosols (Yu and Turco, 1997). Sensitivity studies indicate that CI abundances are relatively invariant, and thus their evolution places a limit on the total number of larger volatile particles emitted by aircraft. Since the production of CI's has not been directly linked to the quantity of sulfur in the fuel, reductions in fuel sulfur content are not likely to be effective in reducing the total number of volatile ion-mode particles formed. Nevertheless, these particles are predicted, and observed, to increase in size with increasing availability of sulfuric acid vapor in the exhaust.

The present simulations demonstrate that a "kinetic" microphysical treatment, including chemiionization effects, can successfully explain aerosol measurements taken during the SULFUR-5 campaign, for those cases with substantial fuel sulfur. By contrast, the standard approach to plume modeling—based on "classical" nucleation theory, and neglecting ion effects—fails to reproduce observations. Purely physical arguments have also been forwarded to show that the standard model is inappropriate for simulating aerosol formation and evolution in rapidly expanding aircraft wakes (Yu and Turco, 1998a). It follows that previous computational studies of aircraft particulates may have missed or misinterpreted the basic mechanisms controlling aerosol formation in jet plumes.

The sensitivity studies carried out here indicate that initial CI concentrations in the exhaust stream should be ~$10^9/cm^3$ to reproduce the SULFUR-5 field data. It is speculated that concentrations in the engine combustors are much greater than $10^9/cm^3$, but are reduced to a relatively uniform number via ion-ion recombination within milliseconds of emission (Yu and Turco, 1997). CI abundances estimated in this way appear to be consistent with currently available plume ion measurements.

Although the present study focuses on plumes formed by the ATTAS, the ultrafine particle properties and behavior are expected to be similar in plumes generated by other aircraft. Accordingly, the results given here represent a general description of the prompt aerosol emissions of operating aircraft. Future work should focus on the longer-term evolution of the ion-mode aerosols in the far-field wake so that the impact of these particles on upper atmospheric composition can be properly assessed. In addition, more precise measurements of chemiions and charged particles in aircraft plumes are needed to verify the importance of electrical charge in the generation of volatile plume particles.

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