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Electron microscope analysis of residual particles from aircraft contrails

Cynthia H. Twohy and Bruce W. Gandrud

National Center for Atmospheric Research, Boulder, Colorado

Abstract. Ice crystals larger than about 5 μm diameter were separated from interstitial particles in aircraft contrails and evaporated. Residual particles larger than 0.1 μm were analyzed by electron microscopy. Soot, metals, and volatile organic substances, apparently from the aircraft exhaust, were found. However, the residual particles also contained high percentages of minerals, thought to be crustal in origin, that were often mixed with sulfur. The percentage of particles in our samples (representing the larger residual particles from relatively large ice crystals) identified as exhaust-derived and the percentage apparently derived from the ambient aerosol were roughly equal, suggesting that ambient particles may be important in contrail formation. Possible explanations for this are presented.

Introduction

The potential importance of particles in aircraft exhaust to atmospheric chemistry and climate has recently been explored in a series of modeling studies and experiments focussed on plume and contrail formation and evolution. Still, a number of questions remain. One of these is the identification of the nuclei for contrail ice. Nuclei composition has been surmised based on model predictions, but has not yet been verified with experimental evidence.

Modeling studies suggest that the primary nuclei of condensation for contrails are soot (black carbon) aggregates, possibly coated with sulfuric acid (Kärcher et al., 1996). Smaller sulfuric acid particles are ubiquitous in aircraft exhaust (Pueschel et al., 1997). However, they are predicted to be too small to effectively nucleate ice crystals unless the fuel sulfur levels are quite high (Kärcher et al., 1996), or saturation with respect to liquid water is achieved in the plume (Jensen et al., 1997a). Ambient aerosol particles have generally been considered to be present in too low abundances to be important in contrail formation.

A great deal of information has been learned recently about the size and number concentration of exhaust and contrail particles, including changes in microphysics with fuel sulfur content (Schumann et al., 1996, Brown et al., 1997). However, differences between plume measurements and models, for example in the amount of sulfur gases oxidized to sulfur (VI) species in the aircraft plume, persist (Fahey et al., 1995). Chemical measurements of the composition of contrail ice have just recently been attempted. This paper presents single-particle chemical analysis of the actual material incorporated into ice crystals in two different aircraft contrails.

Experiment

A counterflow virtual impactor (CVI) was installed on the NASA DC-8 aircraft for the SUCCESS (Subsonic Assessment: Contrail and Cloud Effects Special Study) experiment held in April and May of 1996. The CVI sampled the contrail of a 757 aircraft deployed for this purpose, as well as the DC-8's own contrail, under different environmental conditions and at varying distances downstream of the engine exits.

The principle of operation of the CVI is described in Noone et al. (1988). The CVI sampled particles larger than about 5 μm aerodynamic diameter, so it sampled the larger ice crystals in these contrails. Once collected, the ice crystals were evaporated and the resulting water vapor (measured with a Lyman-alpha hygrometer) was used to derive the ice water content of the sampled crystals (Twohy et al., 1997). After evaporation of the components volatile at 10°C, the residual particles larger than about 20 nm diameter were measured with a TSI 3760 condensation nucleus counter. The number of residual particles is assumed to equal the number of ice crystals originally sampled by the CVI. Another TSI 3760 condensation nucleus counter measured the non-volatile residual particles, those remaining of detectable size after the sample was heated to 250°C. Since the counterflow air out the CVI tip efficiently rejects particles smaller than 5 μm, we know that the sampled residual particles were originally embedded in the ice crystals, and not simply exhaust particles from the aircraft plume. Particle concentrations are originally enhanced inside the CVI, but all data presented here have been corrected back to equivalent concentrations at ambient conditions.

Residual particles were also impacted onto electron microscope grids for later chemical analysis, on which this paper focusses. Particles collected were measured with a JEOL 200-CX analytical electron microscope (AEM) at the National Institute of Standards and Technology in Boulder, Colorado. Two impactor stages collected particles of different sizes: those larger than 0.54 μm aerodynamic diameter, and those remaining that were larger than 0.14 μm aerodynamic diameter. For more realistic particle densities of 1.5 g cm^{-3}, spherical particles larger than 0.42 μm diameter would be collected on the first stage and ones larger than 0.10 μm on the second stage. Thus, both the impaction process and the minimum size detectable by the AEM limited the size of residual particles presented here to those larger than about 0.1 μm diameter. A two-stage sample was collected for each of the two contrail cases described below and a number of particles on each grid were sized and analyzed chemically via X-ray spectrometry. Elements with atomic numbers larger than 4 are detectable by this technique, excluding nickel (the grid base material), and silicon and oxygen (the grid coating).

Two contrail cases are presented here: one contrail generated by the 757 aircraft on 7 May 1996 (20:34 to 20:45 UTC) and one generated by the DC-8 itself on 12 May (23:34:35 to 23:36 UTC and 23:40 to 23:41 UTC). Both contrails were visible to the human eye. The 757 contrail was sampled about 22 km behind the aircraft, and no natural cirrus was present in the immediate environment. The DC-8 intercepted its own contrail after performing a twenty-minute racetrack pattern; assuming the contrail was generated just behind the aircraft and using the average aircraft speed of 232 m s^{-1}, we estimate the length of the DC-8 contrail to be about 280 km. The DC-8 contrail was generated in an environment highly supersaturated with respect to ice that also contained patchy cirrus (Jensen et al., 1997a; Heymsfield and Lawson, 1997). Based on NO measurements (Weinheimer et al., 1997), we estimate that during about half of this

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sample period, we sampled cirrus crystals, rather than solely contrail ice. Average ambient temperatures and pressures were 216K and 223 mb for the 757 contrail, and 222K and 237 mb for the DC-8 contrail. Also, while the 757 contrail was sampled over the southwestern United States, the DC-8 contrail was produced over the Pacific Ocean near the California/Oregon border.

Results

The number of total and non-volatile residual particles sampled by the CVI throughout the 757 contrail penetrations are shown in the first two panels of Figure 1. (The two CN measurements agreed within 1% when both were measuring an unheated aerosol sample, so differences upon heating are expected to be due solely to the particle volatility.) The two traces are similar in magnitude and structure, with an average ratio of non-volatile to total particles of 0.90. Based on laboratory calibrations, the particles volatile at 250°C are expected to be either sulfuric acid (as a pure substance or with a non-volatile core smaller than about 20 nm diameter, the lower detection limit of the condensation nucleus counter) or volatile organic species. Slightly higher volatile fractions were measured in the 757 contrails sampled on 4 May (not shown), especially when high-sulfur fuel was used. Peak ice water contents (last panel of Figure 1) were a few mg m^{-3}, and together with the total number concentrations in the first half of the sampling period indicate mass-weighted crystal sizes of about 11 μm diameter. (Number-mean diameters would be smaller). The "cut size", or minimum particle size collected by the CVI, was increased to about 14 μm diameter between 20:39:20 and 20:41:40; this is reflected in a substantial decrease in number concentration, a slight decrease in ice water content (IWC), and an increase in mass-weighted size to about 17 μm diameter. (Note that both cut size samples were collected on only one set of electron microscope grids, to ensure adequate particle numbers). Particle number concentrations and IWCs were about a factor of two higher in the DC-8 contrail on 12 May (not shown), and mass-weighted crystal diameters were about 15 μm. Volatility measurements were not available on this day.

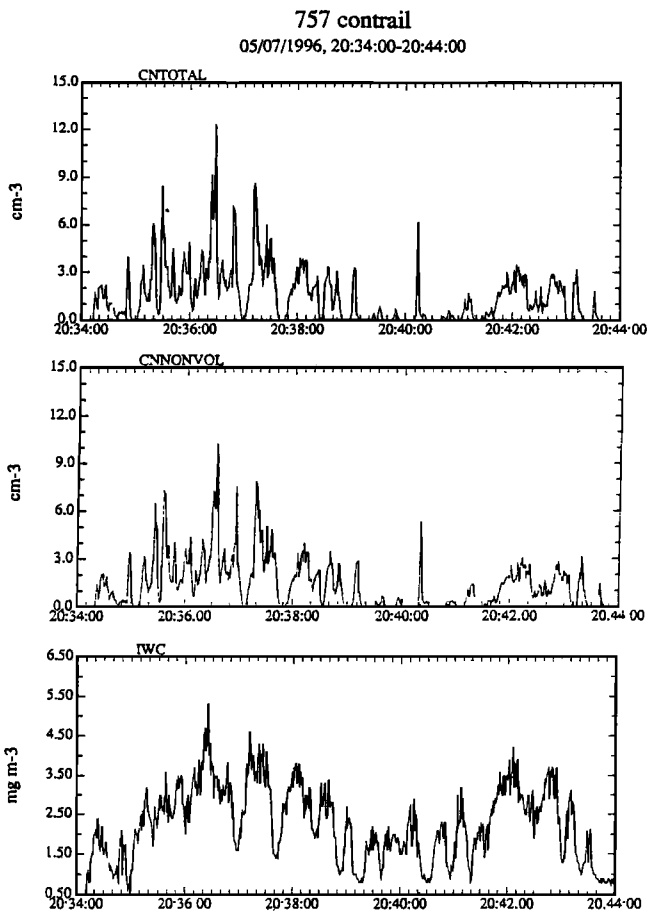

Figure 1. UTC time series of total and non-volatile residual particle number concentration (first and second panels, respectively) and ice water content (third panel) measured by the CVI in the 7 May 757 contrail. The CVI minimum cut size was about 5 μm diameter, except during 20:39:20 to 20:41:40, when it was increased to 14 μm.

The compositions measured for the residual particles from the contrail ice are summarized in Figure 2. One of the largest class of particles found in both cases were minerals, often internally mixed with sulfur. Minerals were primarily calcium-containing compounds, but also contained sodium and aluminum, probably derived from crustal materials. Iron-containing particles were also included in the mineral category, unless the composition indicated large amounts of chromium, in which case it was classified as a metal (apparently a steel alloy), as was titanium. The elements in the mineral category could also be classified as metals, following the classification scheme of Sheridan (1989), but our metal category was used to distinguish materials apparently derived from the aircraft itself. Metal particles were also occasionally mixed with sulfur.

Soot (black carbon) was primarily identified on the basis of its chain-aggregate morphology, as well as the lack of X-ray signals substantially above background levels. Soot chains often collapsed under the electron beam. Unidentified non-volatile particles often had small amorphous shapes, which could be soot, or large angular planar shapes, which could be silicates (which could not be positively identified since the grids were SiO coated). Crustal particles, including silicates, were found to be one of the most frequent types of ice nuclei, as measured with a continuous flow diffusion chamber (Chen et al., 1997), in the background aerosol during SUCCESS. Many of the unidentified volatile particles contained carbon peaks with areas at least 2-3 times above the background noise level, suggesting that these were organic compounds. Low but measurable levels of hydrocarbons have been measured in engine exhaust, even at cruise, by Spicer et al. (1994). No pure sulfuric acid particles (identified by their characteristic liquid morphology with satellite rings) were found in our contrail samples, although they were observed in ambient upper tropospheric samples in the same particle size range.

The sample from 12 May probably contained some cirrus as well as DC-8 contrail particles; thus we cannot absolutely say that all the mineral particles contained in this sample were derived from contrail ice, rather than natural cirrus. However, the 757 contrail sample from 7 May was cirrus-free, and actually contained higher percentages of minerals (and lower percentages of soot) than the 12 May sample. This would indicate that the mineral aerosols are important in nucleating contrail ice, and not just cirrus crystals.

Unfortunately there is a large uncertainty in the percentages calculated for different particle types and we cannot be assured that all particle types were detected, since only 76 particles for the 757 contrail and 36 particles for the DC-8 contrail were analyzed. Information on particles from both the large and small impactor stages was combined, since one of the two stages of each sample (the large particle one for the 757 contrail and the small one for the DC-8 contrail) yielded less than ten particles. For many areas of the grid, the thin coating of SiO did not survive the impaction process (particularly for the large particle stages of the impactor), and the effective grid area was greatly reduced. This means that the percentage of particles larger than 0.1 μm (relative to the total measured by the CNC) cannot be accurately determined. An attempt was made to analyze all particles present on intact grid material, except for the small stage of the 757 contrail sample, where numerous particles were found. Some particles that were initially sized detached from the grid surface due to static repulsion forces under the

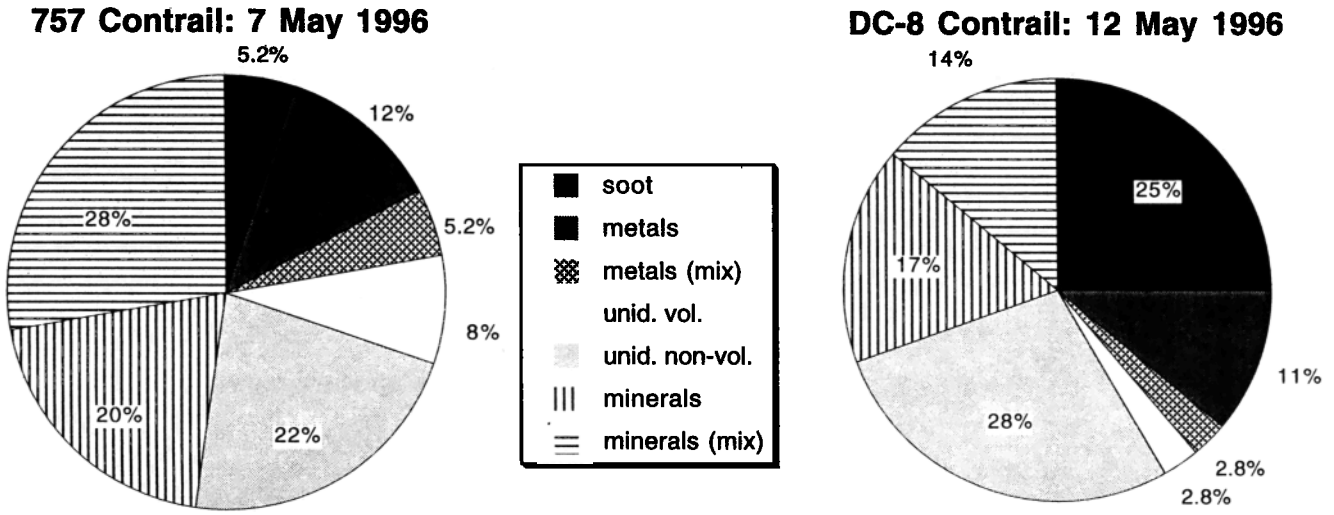

Figure 2. Pie chart showing percentages of various residual particle types observed in the 757 and DC-8 contrails. Soot was identified by its morphology, metals were Fe/Cr or Ti, and minerals were predominately Ca, but also Na, Al, K, and/or Fe. "Mix" means sulfur was also present in substantial abundance. Non-volatiles could be silicates or soot, while at least some volatiles contained carbon.

focussed electron beam; many of these appeared to be minerals by their morphology, but they were not included in our final statistics. Although our sample size is small, we are confident that the compositions we present are correct, since X-ray analysis was performed on every particle actually used in our results.

The mean sizes of the different particle types (based on the average of their length and width as they appeared on the grid) for both samples are summarized in Table 1. The particles that contained both Ca and S (probably $CaSO_4$) were apparently partly liquid when they hit the grid, since they were often present as groups of small droplets on the grid. The volatile particles also appeared to spread out on the grid. These particle types were difficult to size accurately, and are not included in the table. The relatively large size of all the particles is probably a result of the minimum detection limit of 0.1 μm. While the soot, metals, and unidentified non-volatiles were similar in size, the mean size of the mineral particles was significantly larger.

Discussion

At first it seems surprising that no pure sulfuric acid or soot coated with sulfuric acid, the particle types thought to be most common in the exhaust, were found in the residual particles from the contrail ice. There are possible several explanations for this and the prevalence of other particle types.

First, our 0.1 μm detection limit means that particles smaller than this were not included in this analysis. The mean diameter of soot particles in the exhaust of an ATTAS aircraft was estimated to be 0.06 μm (Schumann et al., 1996), and in fact, the majority of contrail nuclei have in other experiments been observed to be smaller than 0.1 μm (J. Ström, personal communication, 1996). Also, the monolayer of sulfate predicted to increase the nucleating abilities of soot (Brown et al., 1997) is probably too thin to be detected by the X-ray analysis. CVI volatility measurements extending to sizes smaller than 0.1 μm suggest that pure sulfuric acid particles may act as contrail nuclei in some cases, especially if high-sulfur fuel is used (Cynthia Twohy and Bruce Gandrud, unpublished data).

Table 1. Typical Sizes of Residual Particles

TYPE	DIAMETER (μm)
Soot	0.42
Metals	0.36
Minerals	0.88
Unidentified Non-volatile	0.38

Sized as (length + width) / 2.

$CaSO_4$ and volatile particles not included due to large sizing uncertainty.

Nuclei that are large initially not only have a better chance of forming ice (e.g., Kärcher et al., 1996), but may form the largest crystals as they grow by water vapor diffusion (e.g., Hudson and Rogers, 1986; Twohy et al., 1989). The mineral particles were relatively large, and are known to be good ice nuclei (Chen et al., 1997). Also, larger than expected amounts of calcium were observed in bulk aerosol samples taken in the upper troposphere over the southwestern U. S. during SUCCESS (Talbot et al., 1997); these particles were apparently transported by convection from the earth's surface. For these reasons, we might expect high concentrations of mineral particles to be present in the larger crystals sampled by the CVI in the contrails. The large crystals are the ones with the most radiative importance, and the ones most likely to survive longer in a subsaturated environment, or to grow if the contrail spreads to form a cirrus cloud. It is not known how representative these samples are of contrails in different locations or seasons. Heintzenberg et al. (1996) found high concentrations of crustal minerals in residual particles from cirrus clouds, but this was shortly after the eruption of Mt. Pinatubo.

Most mineral particles are alkaline, and therefore an acidic gas like SO_2 will tend to condense preferentially on these particles and be oxidized to sulfate, especially if the humidity is high (Dentener et al., 1996). This probably explains the large numbers of Ca-containing residual particles that were observed to be mixed with sulfur. The addition of soluble sulfate ions to the particles would increase the probability of their acting as nuclei for heterogeneous freezing (Kärcher et al., 1996) or as cloud condensation nuclei (CCN). It seems unlikely that the number of mineral particles would be sufficient to have a substantial effect on gas-phase sulfur and nitrogen chemistry in the plume, but it would be interesting to explore this further.

Irregularly shaped metal particles, apparently stainless steel alloys and occasionally titanium, were found in the contrail ice as well. In a simple experiment with an aircraft auxiliary power unit, metals were

found to be significantly enhanced in exhaust relative to their fuel abundance (Grobecker, 1975). Whether the source of the metal particles in this experiment was the engine itself or the fuel (with metals perhaps leeched in during storage) is not known, but metals from contrails do act as ice nuclei (Chen et al., 1997).

If we assume that the soot and metals were derived from the aircraft exhaust and the mineral particles originated from the ambient air, then we can use Fig. 2 to estimate that at least 22% to 39% (depending on the sample) of the residual particles sampled originated from the exhaust, while at least 31% to 48% originated from the ambient (background) aerosol. The ambient particles could be either ingested at the engine inlet or entrained into the plume downstream of the engine. As discussed earlier, the particles included in this analysis are biased toward larger sizes, due to the collection characteristics of the CVI and the detection limit of the analysis. Still, these results suggest that ambient aerosol particles may be more important than previously thought in contrail formation. Modeling efforts (Jensen et al., 1997b) also suggest this is the case.

Conclusions

Measurements of the composition of contrail ice revealed that particles other than soot and sulfuric acid are involved in contrail formation. Mineral particles, apparently of crustal origin, were the most prevalent particle type larger than 0.1 μm present in contrail ice larger than 5 μm. These mineral particles could be important either as heterogeneous freezing nuclei, or as cloud condensation nuclei, especially if coated with sulfate (which was observed on many of the calcium-containing particles). Sulfur dioxide vapor from the exhaust plume is expected to efficiently condense and be converted to sulfate on the alkaline mineral particles. Metal particles, as well as soot and volatile compounds apparently emitted from the aircraft, also played a role in contrail formation.

The importance of pure sulfuric acid or soot coated with it could not be positively determined since particles smaller than 0.1 μm were not measured in this analysis; it is expected that these particles may play a role in nucleating some of the crystals in the contrail. However, the larger minerals, metals, and soot observed with the CVI samples may produce the largest ice crystals, which are the most likely to survive to form cirrus clouds and be radiatively important.

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C.H. Twohy, B.W. Gandrud, National Center for Atmospheric Research, P.O. Box 3000, Boulder, CO 80307-3000. (e-mail:twohy@ucar.edu; gandrud @ucar.edu)

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