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Tropospheric sulfate distribution during SUCCESS: Contributions from jet exhaust and surface sources

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Abstract. The distribution of SO_4^\ominus aerosol over the central US during SUCCESS indicates that surface sources of SO_4^\ominus and SO_2 in the western US caused SO_4^\ominus enhancements up to 10 km altitude. The mean (median) SO_4^\ominus mixing ratio in the mid- and upper-troposphere increased from 24 (16) pptv over the Pacific ocean to 58 (29) pptv over the central plains. Above 10 km the SO_4^\ominus mixing ratio was essentially the same in both regions, and also when the geographic classifications were further partitioned into upper tropospheric and lower stratospheric categories (mean near 40 pptv). No obvious enhancements of SO_4^\ominus could be detected in jet exhaust plumes, but this may reflect the difficulty of keeping a large airborne sampling platform within a turbulent wake for time periods longer than a few seconds. Expected SO_4^\ominus enhancements (based on observed CO_2 enhancements and emission factors for these two species) were generally much smaller than the variability of ambient SO_4^\ominus mixing ratios, so our null result does not mean that aircraft do not emit H_2SO_4 .

Introduction

Increasing emissions from jet aircraft into the upper troposphere and lower stratosphere are cause for concern, as they may modify atmospheric chemistry and the Earth's climate. The NASA Subsonic Aircraft: Contrail and Cloud Effects Special Study (SUCCESS) project was a multiple aircraft sampling campaign conducted to examine several aspects of potential impacts jet exhaust may have on the atmosphere. Two primary objectives were to: 1) establish how particles, gases and contrails from jet aircraft interact with natural cirrus clouds, and 2) to sample within very young exhaust plumes in order to confirm model predictions of the "near-field" chemical and dynamical evolution of such plumes.

Sulfuric acid is expected to be one of the products of combustion in jet engines. In the upper troposphere and lower stratosphere, aircraft-derived H_2SO_4 may form new aerosol particles, or condense on pre-existing particles (those in the ambient air as well as the abundant small particles emitted in jet exhaust) [e.g., Karcher, 1995; Anderson et al., 1996; Hagen et al., 1996]. In either case, adding to the mass or number of SO_4^\ominus aerosols in this region of the atmosphere could have wide ranging impacts on the radiative properties of high clouds and the cycling of reactive atmospheric species. More generally, the global distribution and budget of tropospheric SO_4^\ominus aerosol is of great interest due to the possibility that the radiative impact of these particles is counteracting greenhouse warming [e.g., Charlson et al., 1992].

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In this paper we present the first direct measurements of SO_4^\ominus aerosol in jet exhaust plumes. However, most of the samples collected during SUCCESS were not impacted by jet exhaust, so we also have a unique data set on the distribution of SO_4^\ominus in the troposphere and lower stratosphere above the central US during spring. This data set provides evidence that continental surface sources played an important role in the SO_4^\ominus budget throughout most of the troposphere.

Methods

The dual-inlet aerosol sampling system we fly on the DC-8 has been described previously [Dibb et al., 1996]. We used one probe to collect samples for soluble ionic species and the second for the natural radionuclide tracers ^7Be and ^{210}Pb during SUCCESS. Talbot et al. [in press] describe the sampling, analytical strategy and protocols used to characterize the composition and abundance of soluble ionic species in aerosol during SUCCESS. We collected 207 pairs of filters during flights 2 - 19 on the NASA Ames DC-8 airborne laboratory. Aerosol sampling was restricted to flight legs at constant altitude. The SUCCESS focus on contrails, cirrus, and jet exhaust resulted in a strong bias toward the upper troposphere and lower stratosphere, with 80% of our samples collected above 8 km and > 59% above 10 km. Most of the flights (3 - 16) originated and returned to Salina, Kansas, so a large majority of our samples were collected in air above the central US, particularly the region surrounding the Department of Energy CART site in northern Oklahoma. During the first several hours of the Ames to Salina transit (Flt. 2), the last segments of the return transit (Flt. 17) and the final 2 flights over the Pacific ocean, the DC-8 encountered oceanic air masses.

Results and Discussion

Mixing ratios of SO_4^\ominus varied widely at any given altitude when all SUCCESS samples are considered together (Figure 1). As noted, the sample vertical distribution was strongly skewed to higher altitudes, but the mean mixing ratios (standard deviation) of 199 (142), 78 (77), and 36 (44) pptv in < 4, 4 - 8, and 8 - 10 km altitude bins, respectively, steadily decreased with height. Above 10 km the mean mixing ratio increased to 44 ± 53 pptv. The decrease over the 4 - 10 km range is accentuated if one considers median mixing ratios rather than means (238, 48, 22 and 37 pptv in the same 4 bins). This aggregated view of the data suggests a strong surface source of SO_4^\ominus , and/or the precursor SO_2 , with decreasing influence up to 10 km. It is not evident, *a priori*, from this overview whether continental (largely anthropogenic) or marine (biogenic) sources are responsible for the enhanced SO_4^\ominus mixing ratios at lower altitudes. Similarly, the increased SO_4^\ominus mixing ratio above 10 km might be due to stratospheric aerosol, deep convective pumping of SO_4^\ominus and SO_2 from the

boundary layer, or emissions from one or more of the jet aircraft involved in the experiment. A primary objective of SUCCESS was to position the DC-8 so that it could sample directly in jet exhaust plumes (from itself as well as T-39 and B-757 aircraft). We will first examine the impact of jet exhaust on SO_4^\ominus mixing ratios to determine whether "in plume" samples should be removed from the data set before other questions are addressed on the distribution of SO_4^\ominus over the US in spring 1996.

Encounters with Aircraft Exhaust Plumes

Despite carefully planned and executed flights targeting exhaust plumes, it proved difficult to keep the DC-8 within any aircraft wake for longer than a few seconds. As a result, our "plume" samples, which integrated for intervals of 5 - 15 minutes, always included a large component of ambient air surrounding the plume. Fortunately, several fast response sensors on board the DC-8 allow us to determine the length of time spent in exhaust plumes for each plume-impacted sample. We use CO_2 data for this purpose here, but similar results are found if CO , water vapor [Vay *et al.*, in press], NO or NO_y [Campos *et al.*, in press] are used as the plume tracer.

Vay *et al.* [in press] used somewhat restrictive criteria to identify plume encounters suitable for calculation of emission factors. Obvious enhancements in the mixing ratios of plume indicators were rejected if it was not possible to determine which aircraft created the plume (at times the DC-8 followed the B-757 at several km range, with the T-39 in between at 10s to 100s of m behind the B-757) or if mixing ratios in ambient air varied widely before and after the plume encounter. Thus the list of plume encounters based on CO_2 spikes is not complete, but the SO_4^\ominus data in this subset of plume encounters indicates that a more exhaustive compilation is not warranted.

Clear CO_2 spikes, meeting the requirements noted above, indicate that the DC-8 had 227 encounters with jet exhaust during SUCCESS. The length of individual encounters ranged from 4 to 139 seconds. These episodes correspond to 23 aerosol sampling intervals, with most of our plume-impacted samples including multiple encounters. The length of time spent in plume during our collection intervals ranged from 9 to 585 seconds (mean 185, median 16 seconds). On average, the plume-impacted filters were only "in plume" 18% of the time (median 11%). More than 1/2 of the CO_2 plume encounters (121/227) and our plume-impacted samples (12/23) occurred on the three flights (13 - 15) when the DC-8 followed the B-757. Time spent in plume on these flights increased slightly (mean (median) 231 (19) seconds), and our sample integration times were intentionally shortened, so the fraction of time spent in plume during impacted samples increased to 23%, on average (median 24%). We thus expect that any SO_4^\ominus signal in exhaust plumes should be most apparent in this series of flights.

During flights 13 - 15 we collected 35 samples above 9 km. Mixing ratios of SO_4^\ominus averaged 32 ± 35 pptv (median 24 pptv). These concentrations are comparable to all measurements in the 8 - 10 km bin and lower than the SUCCESS mean and median above 10 km (Figure 1). The 12 plume-impacted samples did tend to have higher mixing ratios than the others collected on these 3 flights, but the mean (40 ± 45 pptv) and median (31 pptv) were still at least 10% below the overall mission values in the > 10 km bin.

Mixing ratios of SO_4^\ominus and CO_2 (averaged to the aerosol integration times) show a weak increasing trend with fraction

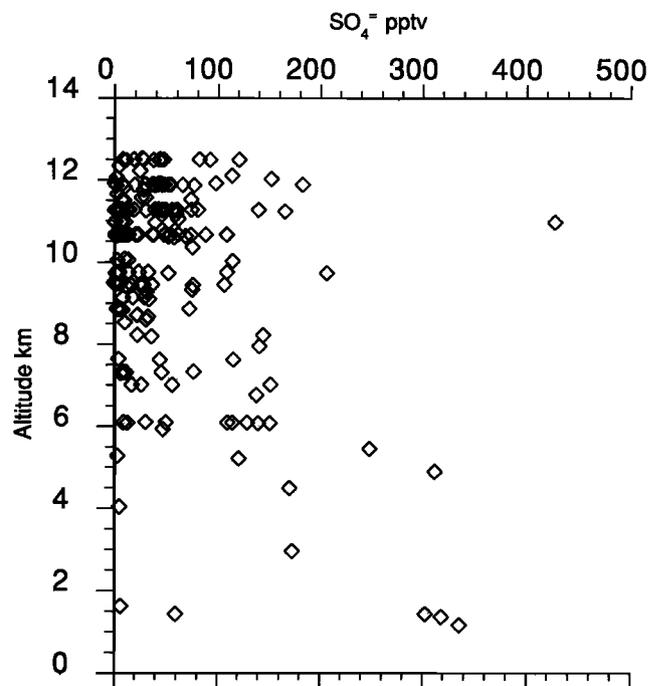


Figure 1. Scatter plot of SO_4^\ominus mixing ratio versus altitude during SUCCESS. All samples from flights 2 - 19 are plotted.

of time in plume (Figure 2a). Much of the scatter presumably reflects real differences in the character of the plume (due to age, operating parameters of the emitting combustor(s), fuel type, etc. (see discussions by Miake-Lye *et al.*, in press; Anderson *et al.*, in press a, b; Vay *et al.*, in press; Campos *et al.*, in press), plus variations in the composition of surrounding ambient air, but the small magnitude of any SO_4^\ominus signal is largely due to dilution. Enhancements of CO_2 rarely exceeded 3 ppmv and never reached 10 ppmv (taking 365 ppmv as an estimate of ambient CO_2 concentration), compared to enhancements on the order of 30 ppmv CO_2 that were commonly observed for individual plume encounters. Emissions factors of approximately 72 moles CO_2 (kg fuel) $^{-1}$ and 10^{16} volatile ultrafine particles (kg fuel) $^{-1}$ were determined for B-757 exhaust during SUCCESS [Anderson *et al.*, in press a]. Following the lead of these authors, we assume that the volatile particles were a 70/30% mixture of H_2SO_4 and H_2O with a mass median diameter (mmd) of 15 nm, yielding a predicted enhancement of ~ 3.5 pptv SO_4^\ominus per ppmv enhancement of CO_2 . The dotted line in Figure 2b reflects this slope and indicates expected SO_4^\ominus contributions from exhaust if all $\text{CO}_2 > 365$ ppmv is entirely from the B-757.

The relationship between SO_4^\ominus and CO_2 in Figure 2b is not a very strong test of the validity of the estimated emission factors for these species, since the 3.5 pptv ppmv $^{-1}$ slope is dependent on the particle radius 3 , which is not very well constrained for this data set. Further, the variability of ambient SO_4^\ominus mixing ratio is larger than the expected exhaust signal in most cases (see samples on flts 13 - 15 with CO_2 mixing ratios near 365 ppmv (Figure 2b)). However, the data from these 3 flights with most frequent and persistent plume encounters, and the calculations based on emission factors, suggest that aircraft exhaust never contributed more than 30 pptv SO_4^\ominus to any SUCCESS filter sample and in most cases the contribution was more likely on the order of a few pptv or less. We thus retain all plume impacted samples in the data set for the discussion that follows.

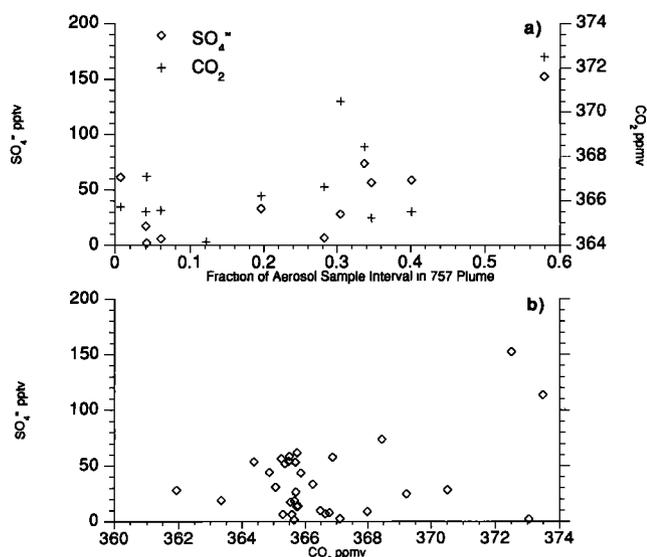


Figure 2. Comparison of $\text{SO}_4^=$ and CO_2 mixing ratios during SUCCESS flights 13 - 15 when the DC-8 followed the B-757. A) Mixing ratios plotted as a function of aerosol sample integration time actually in exhaust plumes for the 12 plume-impacted sample intervals on flights 13 - 15. B) Scatter plot of $\text{SO}_4^=$ against CO_2 for all 35 samples collected above 9 km during these 3 flights. The dotted line reflects a slope of $3.5 \text{ pptv } \text{SO}_4^= (1 \text{ ppmv } \text{CO}_2)^{-1}$, as discussed in the text.

Sulfate Distribution in the Continental Troposphere

We focus now on the series of flights departing from, and returning to, Salina (3 - 16) to eliminate samples with strong marine influence. This filter retains 178 of the samples collected during SUCCESS, but includes quite a few samples from the lower stratosphere as well as upper tropospheric air with strong stratospheric inputs. Since stratospheric intrusions may play an important role in determining upper tropospheric composition at mid-latitudes during spring [e.g., Staley, 1982; Dutkiewicz and Husain, 1985], we would like to further filter the data set to exclude truly stratospheric samples but retain upper tropospheric samples impacted by stratospheric influx. We use ^7Be concentrations $> 1000 \text{ fCi } \text{scm}^{-1}$ to identify stratospheric air. Selecting a single threshold value of ^7Be (or any other tracer) to make such discrimination is problematic, particularly near the tropopause where 2-way exchange between the stratosphere and troposphere is active. Our choice of $1000 \text{ fCi } ^7\text{Be } \text{scm}^{-1}$ reflects a break point in a scatter plot of ^7Be against N_2O , with nearly constant mixing ratios of N_2O (312 - 315 ppbv) in the ^7Be -defined tropospheric samples and decreasing N_2O at higher ^7Be concentrations. Mixing ratios of N_2O in stratospheric air defined this way range 279 - 313 ppbv, with the 312 - 313 ppbv overlap between troposphere and stratosphere confirming the difficulty of making a sharp division on the basis of a single tracer. Similarly, using $1000 \text{ fCi } ^7\text{Be } \text{scm}^{-1}$ as the threshold yields tropospheric O_3 values between 29 and 109 ppbv compared to a stratospheric range of 61 - 638 ppbv. Obviously, our division between stratospheric and tropospheric air masses is artificial, but still useful.

We identified 37 of the samples collected over the central US as stratospheric on the basis of ^7Be concentrations > 1000 (and up to 11,000) $\text{fCi } \text{scm}^{-1}$. Mixing ratios of $\text{SO}_4^=$ in these

samples ranged from below detection limits (of a few pptv) to 183 pptv, with a mean of 44 ± 47 and median of 42 pptv (see also Table 1 in Talbot *et al.* [in press]). The mean is identical to, and the median slightly higher than, those for the $> 10 \text{ km}$ bin for the entire mission (Figure 1 and discussion thereof). The altitude distribution of $\text{SO}_4^=$ in the continental troposphere (Figure 3a) thus retains the decreasing trend from the surface to 10 km, with a smaller increase above 10 km than seen in the overview (Figure 1). Comparison of the mean \pm std. dev. (median) $\text{SO}_4^=$ mixing ratios above 10 km over the continent (39 ± 62 (30) pptv) and for the three flights over the Pacific (36 ± 40 (20) pptv) reveals only a small increase in $\text{SO}_4^=$ during passage over more than 1/2 of the US at high altitudes. However, in the 4 - 10 km range $\text{SO}_4^=$ mixing ratios roughly double between the west coast and the central plains (24 ± 23 (16) versus (58 ± 70 (29) pptv).

We hypothesize that the enhancement of $\text{SO}_4^=$ in the mid- and upper-troposphere over the central US is due to convective pumping of boundary layer air, impacted by natural and anthropogenic surface sources, to higher levels. Talbot *et al.* [in press] point out similar enhancement of soil-derived Ca^{2+} throughout the troposphere during SUCCESS, and we note that comparing the vertical distribution of CH_4 over the continent (Figure 3b) and in marine air (not shown) also indicates significant pumping of boundary layer air well up into the free

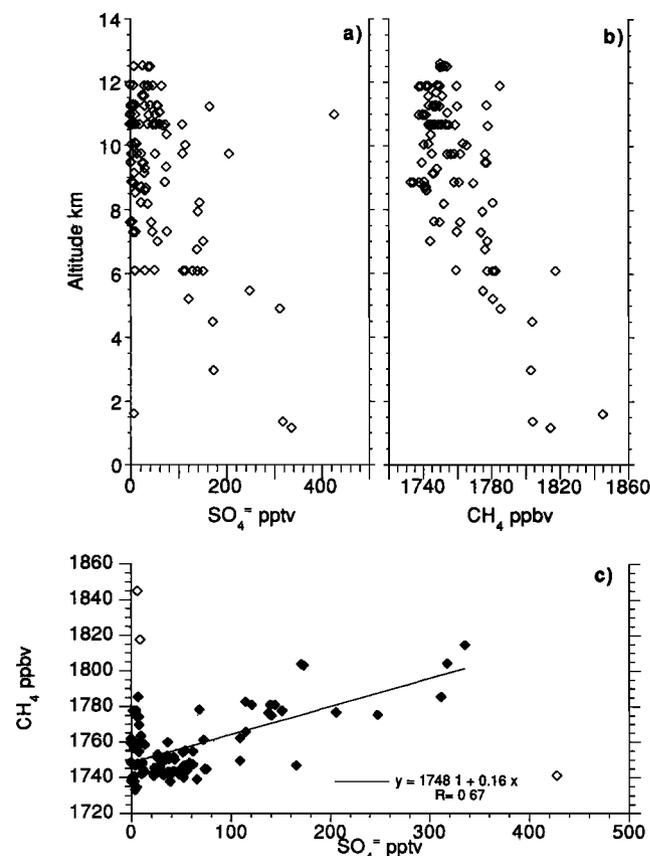


Figure 3. Free tropospheric samples over the central US during SUCCESS. Altitude profiles of $\text{SO}_4^=$ (A), CH_4 (B) and a scatter plot of CH_4 against $\text{SO}_4^=$ (C) are presented. The linear best fit in (C) does not consider the 3 open symbols. The similar decreasing trends in mixing ratio with height and the relationship between $\text{SO}_4^=$ and CH_4 indicate that surface sources in the US made important contributions to the free tropospheric burden of both species during spring, 1996.

troposphere. During the flights over the Pacific ocean, 65% of CH₄ measurements (averaged to aerosol integration intervals) were < 1740 ppbv and none exceeded 1750 ppbv. Over the continent nearly all samples exceeded 1740 ppbv (Figure 3b), with mean \pm std dev (median) concentrations of 1762 \pm 19 (1760) and 1750 \pm 10 (1748) ppbv in the 4 - 10 and > 10 km altitude bins, respectively. Since the enhancement of CH₄ in the mid- and upper-troposphere must reflect emissions from surface sources in the US, the relationship between CH₄ and SO₄⁼ (Figure 3c) indicates that continental surface sources of SO₂ and SO₄⁼ (largely anthropogenic) also made a major contribution to the SO₄⁼ burden in the free troposphere up to 10 km during the SUCCESS experimental period in spring 1996.

Conclusions

Sulfate mixing ratios in aerosol collected in jet exhaust plumes sampled by the DC-8 during SUCCESS did not convincingly demonstrate SO₄⁼ enhancements in the plumes. The small enhancements expected on the basis of emission factors calculated from measurements of volatile ultrafine particles and CO₂ [Anderson *et al.*, in press] were comparable to, or smaller than, the variability in ambient SO₄⁼ mixing ratio we measured at cruise altitudes throughout SUCCESS. The difficulty experienced by the pilots as they attempted to keep the DC-8 within the turbulent wake of several jet aircraft resulted in large dilutions of plume air by ambient, even though we used sample integration times as short as 4 minutes. Verification of expected SO₄⁼ enhancements in jet exhaust plumes will require a different sampling platform if filter sampling is used, or instrumentation that can quantify SO₄⁼ mixing ratios on the time-scales of seconds characterizing the duration of plume encounters at the km-scale separation ranges of interest during SUCCESS.

The SUCCESS SO₄⁼ data set provides important insight into the sources of tropospheric SO₄⁼ over the central US in spring. At altitudes > 10 km there was little difference in SO₄⁼ mixing ratio between the lower stratosphere and upper troposphere over the continent or the Pacific ocean. The source of SO₄⁼ in this altitude range is therefore poorly constrained given the longer lifetime of aerosols and greater potential for very long-range transport in the jet stream, but it does not seem that surface sources of SO₂ and SO₄⁼ within the US play a major role. Between 4 and 10 km, US surface sources must be significant, since SO₄⁼ mixing ratios double between the west coast and the central plains. Similar enhancements in CH₄, dust and other tracers of boundary layer air in the mid- to upper-troposphere suggest that deep convection, without efficient precipitation scavenging, must have been frequent over the western half of the continent in

spring of 1996. Whether such vigorous vertical lifting of soluble boundary layer tracers into the free troposphere is the norm during spring, or a result of the drought in 1996, is unclear from the SUCCESS data set, but should be investigated further.

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