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Influence of Ohio River valley emissions on fine particle sulfate measured from aircraft over large regions of the eastern United States and Canada during INTEX-NA

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[1] Aircraft measurements of fine inorganic aerosol composition were made with a particle-into-liquid sampler coupled to dual ion chromatographs (PILS-IC) as part of the NASA INTEX-NA study. The sampling campaign, which lasted from 1 July to 14 August 2004, centered over the eastern United States and Canada and showed that sulfate was the dominant inorganic species measured. The highest sulfate concentrations were observed at altitudes below 2 km, and back trajectory analyses showed a distinct difference between air masses that had or had not intercepted the Ohio River valley (ORV) region. Air masses encountered below 2 km with a history over the ORV had sulfate concentrations that were higher by a factor of 3.2 and total sulfur (S) concentrations higher by 2.5. The study's highest sulfate concentrations were found in these air masses. The sulfur of the ORV air masses was also more processed with a mean sulfate to total sulfur molar ratio of 0.5 compared to 0.3 in non-ORV measurements. Results from a second, independent trajectory model agreed well with those from the primary analysis. These ORV-influenced air masses were encountered on multiple days and were widely spread across the eastern United States and western Atlantic region.

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1. Introduction

[2] Sulfate (SO_4^{2-}) is a major component of the eastern United States aerosol. It is formed from various reactions of sulfur dioxide (SO_2) in the aqueous phase [Lovejoy *et al.*, 1996] and from the hydroxyl radical (OH) initiated gas-phase oxidation of SO_2 [Wine *et al.*, 1984]. Fossil fuel electric power generation accounted for 65.6% of 2002 SO_2 emissions in the United States (U.S. Environmental Protection Agency, National Emissions Trends Summary 1970–2002: Average annual emissions, all criteria pollutants, <http://www.epa.gov/ttn/chief/trends/index.html>). The tall emission stacks possessed by many of the electricity generating units are beneficial in mitigating local pollution and fumigation events but they can enhance long-range pollution transport [Fisher, 1986]. The long-range transport of sulfate has been observed in many studies [Altshuller, 1980; Anderson *et al.*, 2002; McCurdy *et al.*, 1999; Dutkiewicz *et al.*, 2000; Wolff *et al.*, 1985]. Transport events can occur

over significant distances and often impact the ground-level air quality of affected areas.

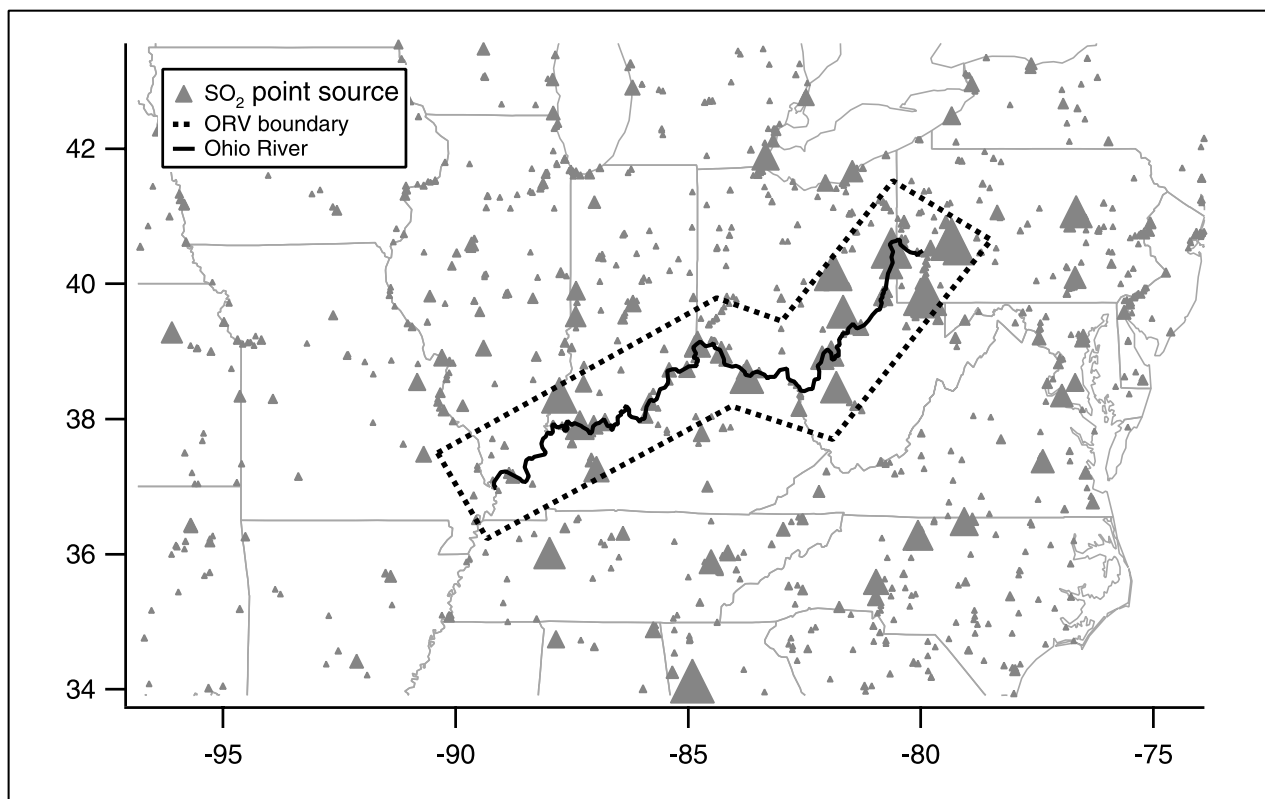
[3] The region bordering the Ohio River contains a large number of power plants that consume fossil fuels, primarily coal, making it a highly concentrated SO_2 emission source. This region was heavily targeted by the 1990 Clean Air Act Amendments (CAAA) for reductions in SO_2 emissions [Lynch *et al.*, 2000]. Phase I of the CAAA mandated SO_2 emissions reductions in 21 states [U.S. Congress, 1990]. These states included the seven states bordering the Ohio River, which contained 63% of targeted plants [U.S. Congress, 1990]. The mandated reductions in SO_2 began in 1995 and have produced significant reductions in SO_2 and SO_4^{2-} concentrations however, SO_4^{2-} remains a major component of the eastern U.S. aerosol [Malm *et al.*, 2002; Holland *et al.*, 2004]. According to the EPA 2002 National Emissions Inventory, the area outlined in Figure 1 accounted for roughly 25% of U.S. point source SO_2 emissions (U.S. Environmental Protection Agency, Final 2002 National Emissions Inventory, <http://www.epa.gov/ttn/chief/net/2002inventory.html>), despite the area's small land coverage (approximately two percent of U.S. land coverage). In this paper, we refer to the area outlined in Figure 1 as the Ohio River valley (ORV).

[4] Several ground-based studies have observed higher $\text{PM}_{2.5}$ sulfate concentrations associated with air masses from the ORV. In the six warmest months of a 1-year period,

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Source: U.S. EPA National Emissions Inventory

Figure 1. Operationally defined Ohio River valley (ORV) region (area inside the dotted line). Also shown are the Ohio River (thick solid line) and SO₂ point sources (shaded triangles) with annual SO₂ emissions greater than 100 tons yr⁻¹, scaled according to 2002 emissions (U.S. EPA 2002 National Emissions Inventory).

sulfate concentrations in Queens, New York were a factor of 2.1 higher when the air mass origin was the Industrial Midwest (which includes the ORV) as compared to all other source regions [Dutkiewicz *et al.*, 2004]. Measurements made in Pittsburgh in the summer of 2000 showed that air masses with ORV influence had PM_{2.5} sulfate concentrations that were higher by a factor of 3.5 over air masses with no ORV influence [Anderson *et al.*, 2002].

[5] In the summer of 2004 measurements of fine inorganic aerosol species were measured with a particle-into-liquid sampler coupled to dual ion chromatographs (PILS-IC) [Orsini *et al.*, 2003] aboard the National Aeronautical and Atmospheric Administration (NASA) DC-8 research aircraft as part of the NASA-sponsored Intercontinental Chemical Transport Experiment–North America (INTEX-NA) field campaign. The INTEX-NA study sought to characterize and investigate the transport and transformation of both aerosol and gas-phase species over large spatial scales. Of particular interest was the processing and outflow of pollution from the North American continent. To sample an expansive domain the study included flights based out of California, Illinois, and New Hampshire. Although the sampling domain included much of the United States, parts of Canada, and areas off the eastern and western coasts of North America, sampling was concentrated east of the Mississippi River. In addition to aerosol composition, a host of other aerosol and gas-phase measurements were made on the

DC-8. For a complete description of the measurements made and a more detailed description of the INTEX-NA study, see H. B. Singh *et al.* (Overview of the Summer 2004 Intercontinental Chemical Transport Experiment–North America (INTEX-A), submitted to *Journal of Geophysical Research*, 2006). Each of the 18 flights made by the DC-8 sampled over a large altitude range (~300 m to ~11000 m) and included multiple 10 to 60-min periods of sampling at constant altitude. Many of these level sampling legs were conducted near the surface, with altitudes below 2 km. Accounting for almost 20% of flight time for the entire study, there were 80 low-level constant altitude sampling passes in which fine aerosol chemical composition was measured. These low-level runs were carried out on every flight, over the entire sampling domain. The purpose of this paper is to investigate the influence of the ORV emissions on all low-altitude observations made throughout the large geographical region sampled during this study. This analysis was conducted using SO₄²⁻ and SO₂ measurements as well as multiple back trajectory models.

2. Instrumentation/Sampling

2.1. Sulfate Measurements

[6] Particles were sampled with a standard shrouded diffuser inlet [Huebert *et al.*, 2004] that operated near isokinetically. The inlet was shared by a number of inves-

tigators. We extracted a flow of 15 L min^{-1} from the inlet and conducted the sample through a micro orifice impactor (MOI) [Marple *et al.*, 1991] to selectively sample particles with aerodynamic diameters less than $1 \mu\text{m}$. Potential gaseous interferences (e.g., NH_3 , HNO_3 , SO_2) were removed with acidic and basic denuders, along with a monolith activated carbon denuder (MAST Carbon Ltd, Surrey, UK), all placed immediately upstream of the composition analysis. Following the denuders the aerosol chemical composition was measured online with a PILS-IC. Sample integration time was 1.5 min, and sample frequency was every 2.45 min. For the cation system, a Cation 1–2 column (Metrohm, Herisau, Switzerland) with 8.5 mM L-tartaric acid/4.1 mM dipicolinic acid eluent was used at a flow rate of 1.5 mL/min. For the anion system, a Metrosep A Supp 5–100 column (Metrohm, Herisau, Switzerland) with 11 mM sodium carbonate/6 mM sodium bicarbonate eluent was used at a flow rate of 1.05 mL/min. All separations were isocratic and column heaters were employed to maintain a constant column temperature of 30°C . Measured species, with limit of detection (LOD) in $\mu\text{g}/\text{m}^3$ given in parenthesis, included Na^+ (0.2), Ca^{2+} (0.2), NH_4^+ (0.2), K^+ (0.5), Mg^{2+} (0.1), Cl^- (0.02), NO_3^- (0.04), and SO_4^{2-} (0.03). Traceable standards were analyzed at several points throughout the study to ensure calibration of ICs remained valid. Over the course of the study, the calibrations for each species remained, on average, within 7.6% of initial calibrations. To quantify any instrumental background, several measurements were made during each flight in which the sample airflow was directed through a high-efficiency filter for complete particle removal. The relative measurement uncertainty for SO_4^{2-} is estimated to be 20% on the basis of uncertainties in sample airflow rate, liquid flow rate, and instrument precision. All aerosol mass concentrations are reported at standard conditions (20°C , 1 atmosphere).

2.2. Sulfur Dioxide Measurements

[7] SO_2 mixing ratios were measured with a chemical ionization mass spectrometer (CIMS). The system utilized SF_6^- as a reagent ion to simultaneously detect SO_2 and pernitric acid (HO_2NO_2) [Slusher *et al.*, 2001; Huey *et al.*, 1995]. The basic configuration of the CIMS was nearly identical to that described by Huey *et al.* [2004]. The sensitivity of the instrument for SO_2 was measured every 4 min for 1 min by the standard addition of isotopically labeled sulfur dioxide ($^{34}\text{SO}_2$). The background noise of the instrument was measured every 10 min for 1 min by passing the sampled air through an activated carbon scrubber. Typical detection limits during INTEX were less than 10 pptv for a 1 min integration defined at a signal-to-noise ratio of three. Measurement uncertainty for SO_2 was 15%. A more detailed description of the CIMS instrument is given by S. L. Kim *et al.* (Measurement of HO_2NO_2 in the upper troposphere during ICARRT-INTEX-NA 2004, submitted to *Journal of Geophysical Research*, 2006).

3. Results

[8] For each of the measured aerosol species, statistical results for measurements at all altitudes for the entire study are presented in Table 1. With a $1.38 \mu\text{g}/\text{m}^3$ mean, SO_4^{2-}

was the dominant inorganic species measured throughout the study. It was found in the highest concentrations among all inorganic species and was rarely below the LOD ($0.03 \mu\text{g}/\text{m}^3$). The vertical distribution of SO_4^{2-} (Figure 2a) showed a distinct profile in which the highest concentrations were observed in the lowest two kilometers. Although sulfur dioxide had a similar vertical profile to sulfate (Figure 2b), there was very little correlation between the two species ($r^2 = 0.15$) because of different reactivities and atmospheric lifetimes.

[9] In the following analysis we focus on low-level sampling passes, where a low-level pass is defined as a period of time in which the aircraft was sampling at a near-constant altitude below 2 km (above the surface) for a minimum of 9.4 min, allowing at least four PILS-IC measurements to be made. Over the course of the study, aerosol chemical composition was measured during 80 such sampling legs, 75 of which were included in the analysis. The data along each pass were averaged and treated as a single observation. For the 75 low-level legs the mean sampling interval was 19.2 min long, allowing for an average of 7.7 individual aerosol composition measurements to be made per leg. The mean altitude for these constant altitude legs was 667 m (in relation to the surface), while the mean horizontal distance covered was 161 km. For all 75 passes, the mean and median SO_4^{2-} concentrations were $2.44 \mu\text{g}/\text{m}^3$ and $1.20 \mu\text{g}/\text{m}^3$, respectively. On average, SO_4^{2-} accounted for 36.2% of total sulfur ($\text{SO}_4^{2-} + \text{SO}_2$) on a molar basis. The mean and median total sulfur (S) concentrations were $2.69 \mu\text{gS}/\text{m}^3$ and $2.09 \mu\text{gS}/\text{m}^3$, respectively. The SO_4^{2-} concentration relative standard deviation (RSD) within each pass provides an indication of the concentration variability encountered along that leg of the flight track. The mean RSD for the 75 passes analyzed was 39.1%.

4. Comparisons of Ohio River Passes to Non-Ohio River Passes

[10] To assess the ORV influence on boundary layer SO_4^{2-} observations, back trajectories for several points along every pass were analyzed. Trajectories were obtained using the NOAA Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model with FNL meteorological data [Draxler and Hess, 1998]. Typically, trajectories for the first, last, and midpoint samples were run for every leg to ensure consistency along the pass. The trajectories for each leg were qualitatively analyzed to determine if the sampled air mass had passed over the ORV, defined by the region outlined in Figure 1. Trajectories were run up to 7 days back, although 3 days was often sufficient to make the determination.

[11] Of the 80 low-altitude legs conducted over the course of the study, five were excluded from the trajectory analysis. Four of the excluded passes were conducted within the designated ORV region and were thus not included. Another was excluded because of the inconsistent nature of the back trajectories along the pass making the air mass' history somewhat ambiguous. Thus 75 out of 80 BL passes were included in the analysis.

[12] According to the HYSPLIT model, 16 of the passes appear to have ORV influence while 59 appear to have no

Table 1. Overall Results for Each Species Measured Throughout the Study^a

Species	Mean, $\mu\text{g}/\text{m}^3$	Standard Deviation, $\mu\text{g}/\text{m}^3$	Minimum (LOD/2), $\mu\text{g}/\text{m}^3$	Maximum, $\mu\text{g}/\text{m}^3$	Percentage of Measurements > LOD	LOD, $\mu\text{g}/\text{m}^3$
Na^+	0.1	0.15	0.1	4.4	0.7	0.2
NH_4^+	0.9	1.33	0.1	8.3	44.6 ^b	0.2
Ca^{2+}	0.1	0.14	0.1	4.2	<0.2	0.2
K^+	0.3	0.18	0.25	7.7	<0.2	0.5
Mg^{2+}	0.1	0.05	0.05	1.9	<0.2	0.1
Cl^-	0.02	0.11	0.01	4.34	3.1	0.02
SO_4^{2-}	1.38	2.39	0.02	19.35	87.5	0.03
NO_3^-	0.09	0.26	0.02	2.90	18.6	0.04

^aHalf the LOD value was used in calculating the mean for data points below the LOD. Values at 20°C and 1 atm.

^b NH_4^+ measurements on 9 of 18 flights.

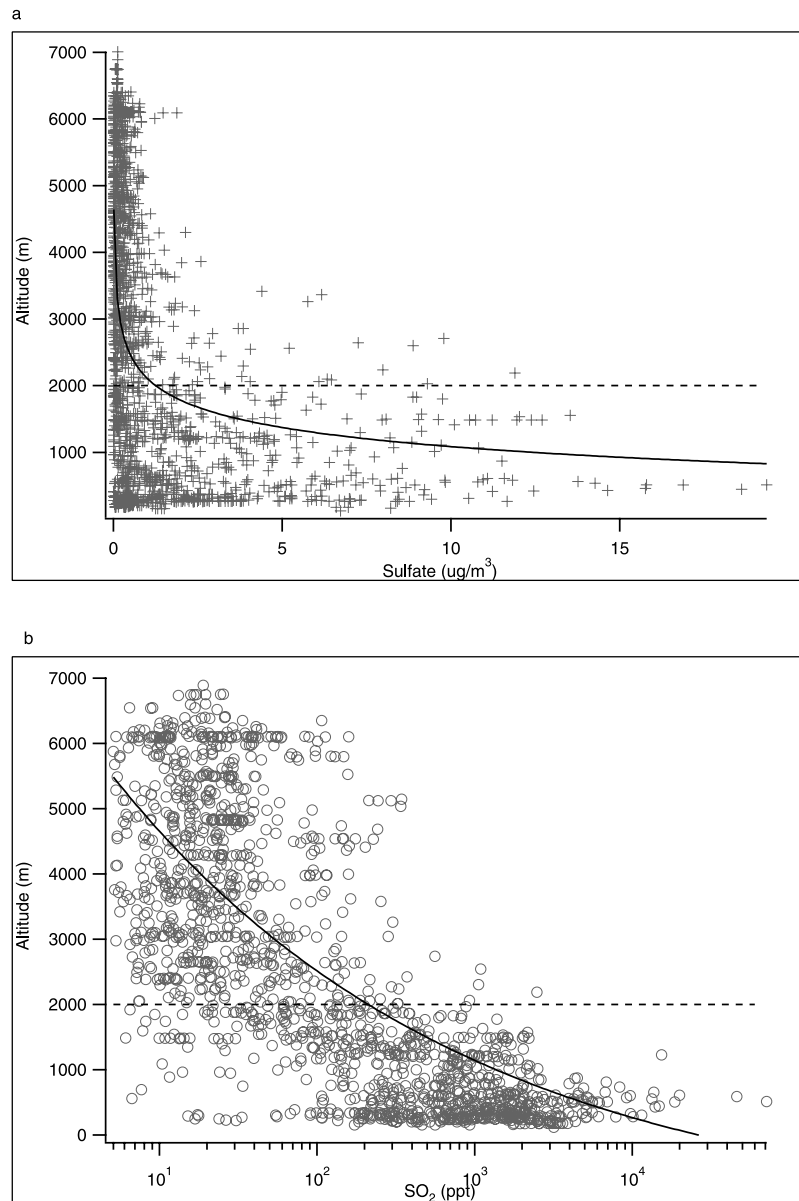


Figure 2. Altitude profile of (a) sulfate and (b) sulfur dioxide (SO_2) over the entire study. Our analysis is focused on the lowest two km where highest sulfate concentrations were observed. (Note that the SO_2 concentration is plotted on a log scale.) Fit lines in both figures are included to show general trends. The 1-min SO_2 results were merged to 1.5-min SO_4^{2-} measurement times for comparison. Despite qualitatively similar altitude profiles, $\text{SO}_4^{2-} - \text{SO}_2$ r^2 between the two species was 0.15.

Table 2. Comparison of Ohio River Valley Passes to Non-Ohio River Valley Passes With Both Trajectory Models

	All Passes	HYSPLIT		FLEXPART	
		ORV	Non-ORV	ORV	Non-ORV
Number of passes	75	16	59	23	52
Mean total S, $\mu\text{g S/m}^3$	2.69	5.10	2.05	4.87	1.74
Median total S, $\mu\text{g S/m}^3$	2.09	3.44	1.57	3.69	1.20
SO_4^{2-} mean, $\mu\text{g/m}^3$	2.44	5.30	1.68	5.54	1.08
SO_4^{2-} median, $\mu\text{g/m}^3$	1.26	4.03	0.72	4.53	0.59
SO_4^{2-} pass % RSD	39.1%	28.9%	41.9%	26.3%	44.8%
$\text{SO}_4^{2-}/(\text{SO}_4^{2-} + \text{SO}_2)$, molar ratio	0.362	0.492	0.330	0.486	0.308

influence from the ORV. Although a simplistic analysis, the measurements show a distinct difference between these two air mass types (Table 2). The back trajectory results indicate that air masses with ORV influence have higher SO_4^{2-} and total S concentrations than air masses with no ORV influence. The mean SO_4^{2-} concentration was a factor of 3.2 higher in ORV passes ($5.30 \mu\text{g/m}^3$) than in non-ORV passes ($1.68 \mu\text{g/m}^3$). Likewise, the mean total S concentration was a factor of 2.5 higher in ORV passes ($5.10 \mu\text{g S/m}^3$) than in non-ORV passes ($2.05 \mu\text{g S/m}^3$). The highest mean SO_4^{2-} concentration observed throughout the study ($14.18 \mu\text{g/m}^3$ on 20 July 2004) was in an air mass with ORV influence observed over North Carolina that had advected from the ORV to the measurement site in about 1.5 days. Median values, also presented in Table 2, show that the observed results were representative and were not merely driven by several extreme measurements. Another distinct difference between the air mass types was the fractional conversion of SO_2 to SO_4^{2-} . In ORV air masses, SO_4^{2-} accounted for 49.2% of total S ($\text{SO}_4^{2-} + \text{SO}_2$) on a molar basis while in non-ORV air masses SO_4^{2-} accounted for 33.0% of total S.

[13] The ORV air masses were similar in character to the four passes conducted directly within the ORV region. These four passes, which were excluded from the trajectory analysis because of sampling location, were conducted on separate days and were consistent in length (21.1 min) and altitude (650 m mean) with all of the low-altitude passes. The mean SO_4^{2-} concentration within the ORV region was $4.80 \mu\text{g/m}^3$, slightly lower than the ORV passes, however the total S concentration was about 50% higher ($7.82 \mu\text{g S/m}^3$) than that of the ORV passes.

[14] Despite the relatively low SO_4^{2-} concentrations observed in the non-ORV air masses, most of the non-ORV air masses had SO_4^{2-} concentrations well above a continental background. A modeling study carried out by Park *et al.* [2004] reported a continental SO_4^{2-} background over the United States, which included both natural and transboundary pollution from Mexico, Canada, and Asia, of roughly $0.3 \mu\text{g/m}^3$. Less than 20% (10 of 52) of non-ORV passes had mean SO_4^{2-} concentrations lower than this background value. It is thus likely that anthropogenic emissions from other unidentified sources influenced the majority of low-altitude measurements made throughout the study.

[15] The low-altitude air masses with ORV influence were encountered over seven flights with dates ranging from 8 July to 13 August 2004. Not only were the observations frequent, but they were geographically widespread as well. Air masses with ORV influence were sampled from southern Louisiana to the eastern coast of Newfoundland,

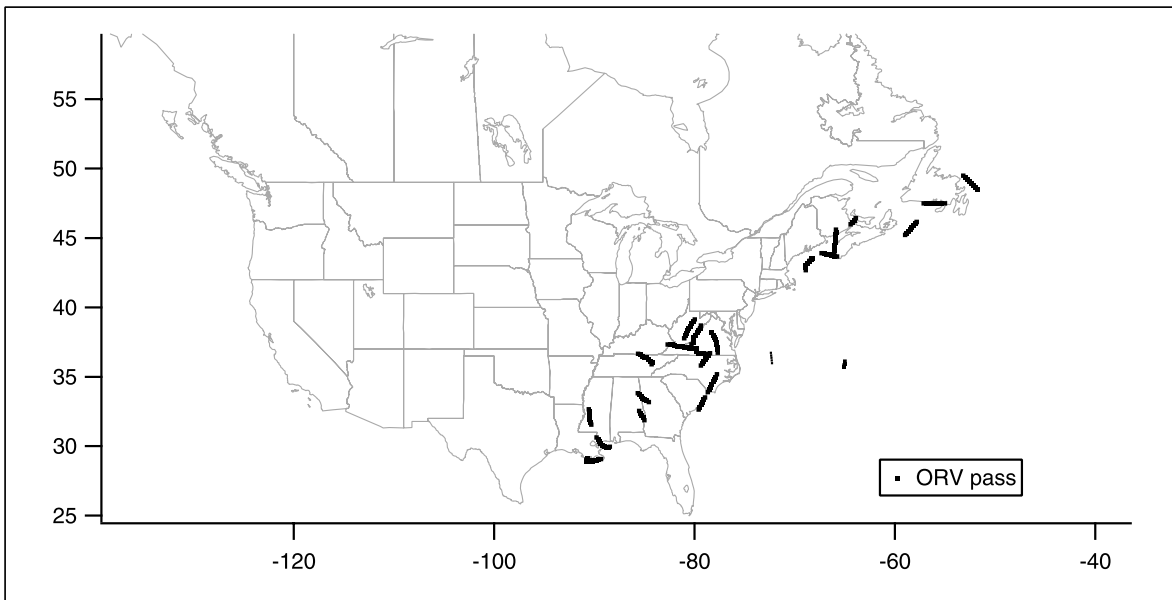
Canada. In many cases, the air masses were hundreds of kilometers from the ORV source region.

[16] Back trajectory models have uncertainty that is difficult to quantify [Fuelberg *et al.*, 1996]. To increase the confidence of the present analysis an alternate model, independent of HYSPLIT, was used to conduct the same analysis. FLEXPART is a widely used particle dispersion model [Stohl *et al.*, 1998]. The FLEXPART model was used with ECMWF meteorological data to generate quantitative dispersion model runs for each platform of the ICARTT campaign. Extending beyond classical backward trajectories, the FLEXPART model also accounts for turbulence and convection by calculating 40,000 trajectories incorporating stochastic wind components. The model output consists of a sensitivity function to emission input that was also folded with fluxes taken from an inventory of anthropogenic emissions, yielding potential source contributions for SO_2 and other species. Results from the FLEXPART model (Table 2) are consistent with those from the HYSPLIT model. According to FLEXPART, 23 of the 75 passes appear to have ORV influence while 52 appear to have no influence from the ORV. Although FLEXPART diagnosed a greater number of passes (it identified three additional flights) with ORV influence than HYSPLIT, the discrepancies between the air mass types are consistent between the two models. The mean SO_4^{2-} concentration is higher by a factor of 5.1 in ORV-influenced passes than in non-ORV passes. The ORV and non-ORV mean total S concentrations for the FLEXPART results also agree well with the HYSPLIT results.

[17] Air masses identified by FLEXPART as having ORV influence were geographically widespread as well. The ORV air masses were sampled in two general locations (Figure 3). Fourteen of the air masses were encountered across the southeastern United States. Although this area was quite broad, it represented cases of transport from northerly and northwesterly winds with transport times from the ORV to measurement point of 1.2 ± 0.7 (mean \pm standard deviation) days. The other general region where ORV-influenced air masses were sampled was off the northeastern coast of the United States and Canada. Seven ORV-influenced air masses were sampled in this region and these represented an outflow of pollution from the North American continent with typical transport time of 3.0 ± 1.2 days. It should be noted that 27 low-altitude sampling passes were conducted in these two regions in which there was no apparent ORV influence.

[18] The possible influence of sources outside of the ORV region on the identified ORV passes needs to be considered.

a



b

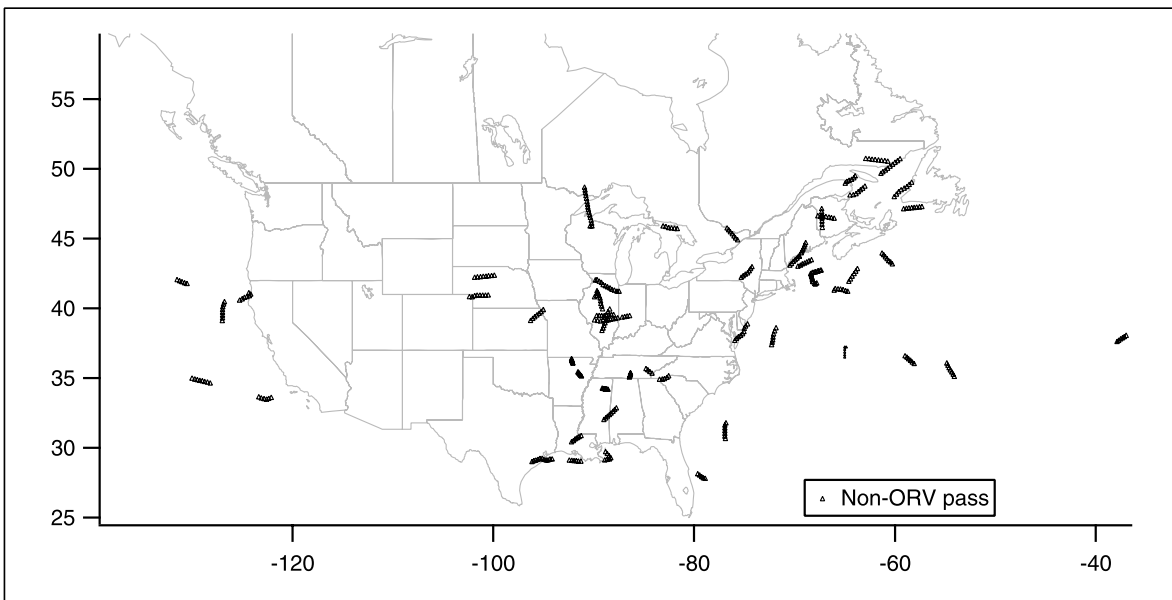


Figure 3. (a) Geographic distribution of level flight legs below 2 km altitude with evidence of Ohio River valley influence and (b) passes without ORV influence.

It is probable that local sources had at least a modest influence on most of the low-altitude measurements made throughout the study. However, local source contributions appear to be much greater in the non-ORV passes than in the ORV passes, as evidenced by the sulfate relative standard deviation within each pass. As the mean pass length was 19.3 min long, the RSD for each pass was calculated from an average of about 8 measurements. The RSD for ORV passes was 28.9% while the RSD for non-ORV passes was 41.9%. The higher RSD for non-ORV passes indicates less homogeneity within these air masses

than the ORV passes. It is likely that anthropogenic emissions from local sources present in the ORV passes were dampened by the presence of a high background from long-range pollution transport. Thus the strong SO_4^{2-} background produced more of a uniform regional signature with greater SO_4^{2-} concentration homogeneity within each ORV air mass.

[19] Though there was a significant difference in SO_4^{2-} concentrations between the two defined air mass types, not all elevated SO_4^{2-} concentrations observed throughout the study were attributed to the ORV. Using the FLEXPART results, the highest mean SO_4^{2-} concentration in a non-ORV

air mass was $6.46 \mu\text{g}/\text{m}^3$ (20 July 2004). Approximately ten percent (5 of 52) of non-ORV air masses had mean SO_4^{2-} concentrations greater than $2.44 \mu\text{g}/\text{m}^3$, the mean for all low-altitude passes. The mean SO_4^{2-} percentage of total S in these five air masses was 46%, while the mean SO_4^{2-} RSD was 31.2%. These results are very similar to the overall results for all of the ORV passes, an indication that long-range pollution transport from regions other than the ORV was observed. Likewise, not every air mass with ORV influence had elevated SO_4^{2-} concentrations. The lowest mean SO_4^{2-} concentration in an ORV air mass was $1.57 \mu\text{g}/\text{m}^3$ (6 August 2004). Approximately 17% (4 of 23) of the ORV passes had mean SO_4^{2-} concentrations below $2.44 \mu\text{g}/\text{m}^3$. The mean SO_4^{2-} percentage of total S in these four air masses was 42%, while the mean SO_4^{2-} RSD was 32.9%. These results are also similar to the overall results for all of the ORV passes. Many factors could explain the lower observed SO_4^{2-} concentrations in these air masses. Among the most likely are cloud processing and wet deposition, and the altitude of an air parcel in relation to the mixing height as it passed over the source region.

[20] Overall, we observed low-altitude air masses with a history over the ORV to contain substantially higher SO_4^{2-} and total S concentrations. These ORV-influenced air masses showed strong evidence for long-range pollution transport. The results might seem intuitive and somewhat expected, given the high density of SO_2 emissions coming from the region of interest. However, the magnitude of the disparity in SO_4^{2-} concentration (greater than a factor of three) between the two defined air mass types is notable. Also surprising was the prevalence (ORV influence detected on at least seven different flights) and the widespread geographic distribution of sampled air masses with ORV influence.

[21] **Acknowledgments.** The authors gratefully acknowledge the financial support of NASA through contracts NNG04GB42G and NNG06GA78G and thank the DC-8 crew and support team.

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