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**MEASUREMENT OF SULFUR DIOXIDE, NITRIC ACID, AND AMMONIA  
WITH ANNULAR DENUDER SYSTEMS AND INTERCOMPARISON WITH  
COLLOCATED TECHNIQUES**

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## List of Abbreviations and Acronyms

ADS	Annular Denuder System(s)
ANOVA	Analysis of Variance
ARL	Air Resources Laboratory
ATDD	Atmospheric Turbulence and Diffusion Division
BARC	Beltsville Agricultural Research Center
CASTNET	Clean Air Status and Trends Network
EDT	Eastern Daylight Time
IC	Ion Chromatography
MARGA	Monitoring Instruments for Aerosols and Gases
NADP	National Atmospheric Deposition Program
NIST	National Institute of Standards and Technology
NOAA	National Oceanic & Atmospheric Administration
PTFE	polytetrafluoroethylene
URG	University Research Glassware
USDA	U.S. Department of Agriculture
U.S. EPA	U.S. Environmental Protection Agency

**MEASUREMENT OF SULFUR DIOXIDE, NITRIC ACID, AND  
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L. Myles

ABSTRACT. Trace gases, such as sulfur dioxide (SO<sub>2</sub>), nitric acid (HNO<sub>3</sub>), and ammonia (NH<sub>3</sub>), play important roles in atmospheric chemistry and, in sufficient concentrations, may negatively affect local or regional air quality. These compounds are also major components of atmospheric aerosols, which influence Earth's energy budget by reflecting solar radiation. Annular denuder systems were deployed at a suburban field site near Beltsville, MD, to quantify these trace gases during a collaborative experiment in August and September 2005. Two fast-response devices, Monitoring Instruments for Aerosols and Gases (MARGA), were collocated at the site for comparison to the integrated annular denuder technique. Diurnal variations in SO<sub>2</sub> and HNO<sub>3</sub> were observed with maximum concentrations measured during the day. Good agreement between the techniques was found for SO<sub>2</sub> ( $R^2 \geq 0.77$ ) and HNO<sub>3</sub> ( $R^2 \geq 0.69$ ). However, divergent NH<sub>3</sub> concentration data from the ADS and MARGA were most likely the result of low ambient levels observed during the experiment. The MARGA systems measured slight diurnal variations in NH<sub>3</sub> concentration that were not apparent in ADS measurements.



## 1. INTRODUCTION

Atmospheric trace gases have nearly negligible mixing ratios that can belie their significant influence on chemical cycles in the atmosphere and on biogeochemical cycles on land and in the oceans. Trace gases are products of natural processes and/or anthropogenic activity. Several trace gases have been documented as major contributors to air pollution on urban, regional, and even global scales (Seinfeld and Pandis, 1998). Therefore, much effort has been focused on quantifying trace gases in different ecosystems.

Sulfur dioxide, nitric acid, and ammonia are trace gases which are anthropogenically emitted by large-scale processes (e.g. electric utilities, intensive agriculture) and, at sufficient levels, impact ecosystem health in their gas phase as well as when incorporated into particulate matter (Wright and Schindler, 1995). Sulfur dioxide ( $\text{SO}_2$ ), which is emitted primarily from fossil fuel combustion and electricity generation, has long been identified as a contributor to acid precipitation (Likens and Bormann, 1974; National Acid Precipitation Assessment Program, 1990). Both wet and dry deposition mechanisms transfer  $\text{SO}_2$  from the atmosphere to vegetation and soils (Hicks and Matt, 1988; Warneck, 1989). Emissions of  $\text{SO}_2$  in the U.S. have decreased considerably (~40% by some estimates) since the promulgation of The Clean Air Act of 1970 and subsequent amendments. Despite this reduction, atmospheric levels of  $\text{SO}_2$  still exceed national standards in many locations and continue to raise environmental and economic concerns (Rico, 1995).

Like  $\text{SO}_2$ , nitric acid ( $\text{HNO}_3$ ) is a component of acid precipitation (Galloway and Likens, 1981). However,  $\text{HNO}_3$  is not directly emitted into the atmosphere. Rather it is an oxidation product of  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ), whose major anthropogenic sources are electric utilities and gasoline/diesel vehicles. Deposition of  $\text{HNO}_3$  and other reactive nitrogen species to terrestrial and aquatic ecosystems has been shown to alter nutrient cycling and promote eutrophication (Matson *et al.*, 2002).

Ammonia ( $\text{NH}_3$ ) is the predominant basic gas in the atmosphere and is emitted directly from animal waste and fertilizer applications. Deposited  $\text{NH}_3$  may cause physiological changes in plants (Pearson and Soares, 1998), eutrophication (Paerl, 1997), and soil nutrient loss (Galloway, 2000). While  $\text{SO}_2$  and  $\text{NO}_x$  emissions are regulated in the U.S., there are currently no policies to mitigate  $\text{NH}_3$  emissions. Since  $\text{NH}_3$  emissions emanate from large non-point sources, like agricultural operations, they are often difficult to quantify and regulate.

Atmospheric concentrations of trace gases are usually in the parts per billion or parts per trillion range, especially distant from emissions sources. Physical and chemical properties, such as adsorptivity and reactivity, also complicate quantitative measurement of trace gases (Pang *et al.*, 2002). This report details the results of an intensive field operation period to measure  $\text{SO}_2$ ,  $\text{HNO}_3$ , and  $\text{NH}_3$  with annular denuder systems near Beltsville, MD, in late summer/early fall over natural vegetation. The annular denuder technique is well-documented and analytically precise for field measurement of several trace gases. Initial comparisons to data from collocated instruments, Monitoring Instruments for Aerosols and Gases (MARGA) systems, are also reported.

## 2. ANNULAR DENUDER SYSTEMS

Annular denuder systems (URG Corp., Chapel Hill, NC) were used to measure SO<sub>2</sub>, HNO<sub>3</sub>, and NH<sub>3</sub> during the intensive period. The preparation and deployment of annular denuder systems (ADS) was derived from *U.S. EPA Compendium Method IO-4.2: Determination of reactive acidic and basic gases and strong acidity of atmospheric fine particles (< 2.5 μm)* by Winberry et al. (1999). The arrangement of each ADS allowed the sample air stream to enter a Teflon<sup>®</sup>-coated glass elutriator inlet before proceeding through tandem annular denuders and a single-stage filter pack (Fig. 1). A single elutriator inlet, fitted with a porous ceramic frit, eliminated particles with a diameter of 2.5 μm or greater ( $D_p > 2.5 \mu\text{m}$ ) from the sample air stream. The elutriator inlet was coupled to a Teflon<sup>®</sup>-coated aluminum manifold (URG Corp., Chapel Hill, NC) with five ports. Four ports were used for sample ADS with one port reserved for blank ADS deployment.

Coupled to each manifold port were short (30 mm o.d. x 150 mm length) and long (30 mm o.d. x 242 mm length) annular denuders followed by a filter pack. Annular denuders are stainless steel tubes that house two inner concentric tubes of etched glass and one center tube of solid glass (Winberry *et al.*, 1999). The inner tubes are flush with the outer stainless steel tube on one end of an annular denuder. The other ‘non-flush’ or flow straightener end is always positioned to face the sample air stream (Fig. 2). The inner glass tubes are etched to provide a sufficient surface for coating solutions to adsorb gases from the sample air stream. Finally, a single-stage filter pack (47 mm o.d.) was coupled to each long denuder. Filter packs consist of Teflon<sup>®</sup>-coated aluminum housing units which encase Teflon<sup>®</sup>-coated stainless steel support screens and are covered by polyoxymethylene sleeves (URG, 2008).

The use of ADS to accurately sample trace gases is widely cited in the literature (e.g. Bai and Wen, 2000; Lee *et al.*, 1993; Myles *et al.*, 2007). Several researchers, including Pang et al. (2002) and Dasch et al. (1989), have evaluated the analytical performance of ADS. High collection efficiencies and reduced sampling artifacts, when compared to other more-established sampling methodologies, are advantages of ADS sampling. Previous work by NOAA/ARL/ATDD, which has utilized ADS for several years to sample trace gases and particles, has found ADS to offer good analytical precision (Meyers *et al.*, 2006; Myles *et al.*, 2007) and sufficient robustness for field deployment (Myles, 2004).



Fig. 1. ADS sampling arrangement.

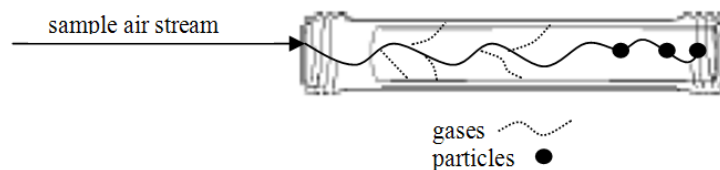
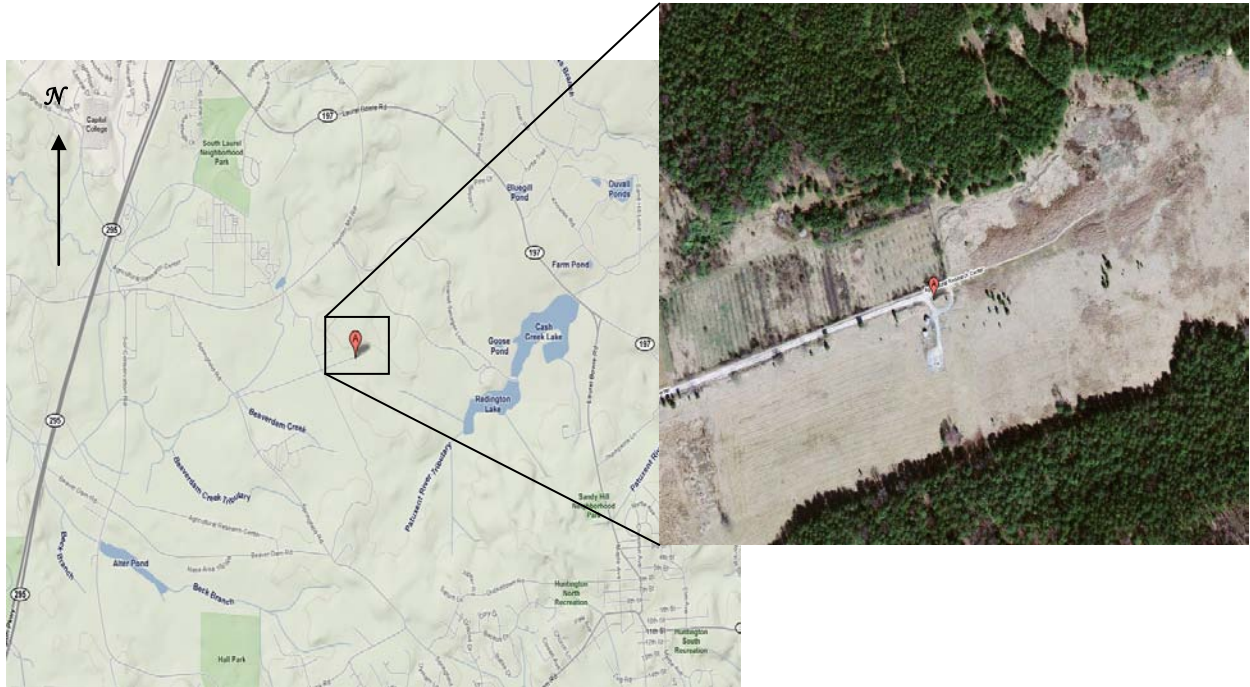


Fig. 2. Cross-sectional view of an annular denuder. After the sample air stream enters the flow-straightener end, trace gases adsorb to etched glass surfaces while particles continue through the denuder for collection on a filter pack (Adapted from URG, 2008).

### 3. EXPERIMENTAL PROTOCOL

All instrumentation for the intensive operation period was installed at an established site at the U.S. Department of Agriculture (USDA) Henry A. Wallace Beltsville Agricultural Research Center (BARC) in Prince George's County, MD. The site ( $39.0284^{\circ}$  N,  $-76.8171^{\circ}$  W; 46 m elevation; Fig. 3) was collocated with existing U.S. EPA Clean Air Status and Trends Network (CASTNET) and National Atmospheric Deposition Program (NADP) instrumentation. The area is located in suburban Maryland ~9.5 km northeast of Washington, DC, and ~3 km west of the Baltimore-Washington Parkway, a major artery into the Nation's Capital. The area is adjacent to the South Tract of the Patuxent Research Refuge, a 5,197 ha tract operated by the U.S. Fish and Wildlife Service for wildlife research and management. Small lakes and tributaries of the Patuxent River are interspersed along the landscape ~1.5 km to the east and southeast of the site. The terrain at the site was relatively flat with small fir trees scattered across the immediate landscape leading to stands of various hardwood trees. Grass at the site was ~38-40 cm tall. A single-lane gravel road, stretching ~2 km from the closest paved road, led to four instrument shelters (three mobile and one permanent) at the site. Vehicular traffic near the site was restricted during the operation period.



**Fig. 3. Terrain map and aerial photo of Beltsville sampling site (from Google Maps™).**

NOAA/ARL/ATDD's instrumentation was affixed to the eastern corner of a scaffold on the roof of a mobile shelter (Fig. 4). The single ADS inlet was placed at a height ~5 m above ground. The sample air stream flowed through the ADS at  $20.4 \text{ L min}^{-1}$ , which was facilitated by an oil-less vacuum pump (Gast<sup>®</sup>, Benton Harbor, MI) that was placed in a weather-proof container on the roof. The sample flow rate was maintained by a mass-flow controller (Aalborg<sup>®</sup>, Orangeburg, NY). Norprene<sup>®</sup> tubing (Cole Parmer, Vernon Hills, IL) was used to connect the vacuum pump, mass-flow controller, and ADS.

Integrated ADS samples were collected from August 12 - September 9, 2005. Four 6-h samples were collected per 24-h period with start times of 0300, 0900, 1500, and 2100 EDT. Field blank ADS were deployed five times during the operation period. The field blank ADS was prepared in similar fashion to the sample ADS; however, it was not connected to the vacuum pump.



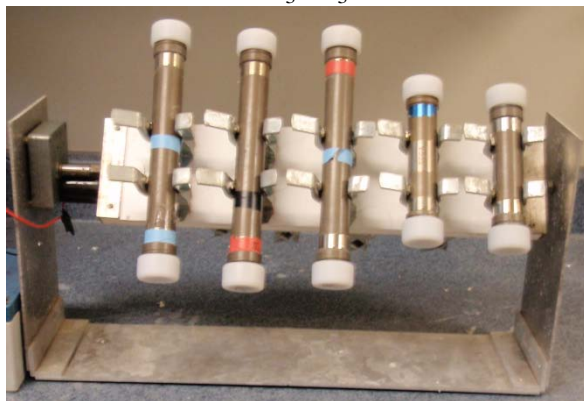
**Fig. 4. Instrument shelters at the Beltsville sampling site. ADS are shown (red circle) attached to roof scaffolding in the first image.**

As mentioned in the previous section, annular denuders must be coated with chemical solutions to adsorb trace gases from the sample air stream. Large aliquots (500 mL) of coating solutions were prepared in the NOAA/ARL/ATDD laboratory, stored in amber bottles, and shipped overnight to the Beltsville intensive location. The coating solution for short annular denuders was 1% phosphorus acid ( $\text{H}_3\text{PO}_3$ ). Perrino and Gherardi (1999) found that  $\text{H}_3\text{PO}_3$  is an optimal coating solution to capture  $\text{NH}_3$  because it has >99% collection efficiency; is sufficiently selective for  $\text{NH}_3$ ; retains  $\text{NH}_3$  in a stable medium; has a high operative capacity; and tolerates high relative humidity. The solution was prepared by dissolving 1%  $\text{H}_3\text{PO}_3$  in a 90:10 methanol-water solution. The coating solution for long annular denuders was 1% sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) in 1% glycerol in a 1:1 water-methanol solution. The collection efficiency of this coating solution for acidic gases ( $\text{SO}_2$  and  $\text{HNO}_3$ ) was found to be >99% for a range of relative humidities (Brauer *et al.*, 1989). Water for solution preparation and ADS extraction was provided by a Milli-Q Ultrapure Water Production Unit (Millipore<sup>™</sup>, Billerica, MA). The resistivity of water from the unit was at least  $18.2 \text{ M}\Omega \text{ cm}^{-1}$ .

All annular denuder preparation and extraction was completed on site. To avoid contamination during preparation, ADS components were only handled with gloved-hands. All components of



the ADS (annular denuders, end caps, couplers, and filter pack parts) were thoroughly cleaned by soaking in an ultrapure water bath. Both short and long annular denuders were then attached to a glass drying manifold (URG Corp., Chapel Hill, NC). Ultra-high purity zero air was blown through the manifold to remove any water from the annular spacing inside the denuders. Annular denuders were dried for ~ 2.5 min on each end. After the drying process, the flush end of each annular denuder was capped. Coating solutions were decanted into the flow straightener end of each annular denuder from Dispensette<sup>®</sup> bottle-top dispensers (BrandTech Scientific, Essex, CT). Short annular denuders were coated with 10 mL of 1% H<sub>3</sub>PO<sub>3</sub> solution to collect NH<sub>3</sub>. Long annular denuders were coated with 10 mL of 1% Na<sub>2</sub>CO<sub>3</sub> solution to collect SO<sub>2</sub> and HNO<sub>3</sub>. With both ends capped, annular denuders were placed for ~ 7 min on a battery-powered rotating device that was designed and built at NOAA/ARL/ATDD (Fig. 5). The device rotated annular denuders 360° around a center axis, which facilitated the movement of coating solution across the inner etched glass surfaces. Afterward, the coating solutions were decanted into a labeled waste container, and the annular denuders were dried again for ~ 2.5 min on each end. Capped annular denuders were then stored in an air-tight container until assembled for deployment.

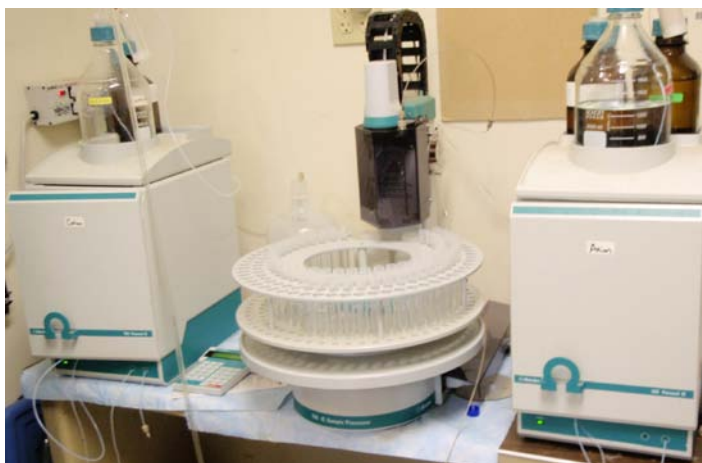


**Fig. 5. Battery-powered rotating device for annular denuders.**

ADS were deployed with daily sampling start times of 0300 (morning), 0900 (day), 1500 (evening), and 2100 (night) EDT. After deployment, ADS components were decoupled, and samples from annular denuders were extracted. Both short and long annular denuders were extracted with ~10 mL of ultrapure water. To ensure the accuracy of extraction volumes, Dispensette<sup>®</sup> bottle-top dispensers were used to decant ultrapure water into pre-weighed, sterile 15 mL Nunc<sup>™</sup> polypropylene sample tubes with high density polyethylene caps (Thermo Fisher Scientific, Rochester, NY). Volumes of extracting solution (i.e., ultrapure water) were then weighed on a portable top-loader balance (A&D Company, San Jose, CA) to obtain a mass (g) and subsequently, a better approximation of volume (1 mL of water weighs ~1 g). Extracting solutions were decanted into the flow-straightener ends of annular denuders, and both ends were covered with clean end caps. Annular denuders were rotated for ~ 7 min to facilitate complete removal of samples from inner etched glass. The sample was decanted from each annular denuder back into the sample tube, which was then capped and refrigerated until shipment for analysis.

Prior to analysis, samples were allowed to return to room temperature. National Institute of Standards and Technology (NIST)-traceable Dionex<sup>®</sup> Combined Seven Anion Standards and Six Cation Standards were run pre-analysis, after every 12 samples, and post-analysis. Anion standards contained certified concentrations of 100 mg L<sup>-1</sup> NO<sub>3</sub><sup>-</sup> and 150 mg L<sup>-1</sup> SO<sub>4</sub><sup>2-</sup> while cation standards contained 400 mg L<sup>-1</sup> ammonium (NH<sub>4</sub><sup>+</sup>). Analysis of standards yielded results within ±1 mg L<sup>-1</sup>. A Metrohm 790 Personal Ion Chromatography System (Fig. 6) with a

Metrosep A Supp 5 anion column (4.0 x 100 mm) and a Metrosep C2 cation column (4.0 x 100 mm) was used to analyze the samples. The anion eluent solution was composed of 3.2 mM  $\text{Na}_2\text{CO}_3$  and 1.0 mM sodium bicarbonate ( $\text{NaHCO}_3$ ). The cation eluent solution was composed of 4.0 mM tartaric acid ( $\text{C}_4\text{H}_6\text{O}_6$ ) and 0.75 mM dipicolinic acid ( $(\text{C}_5\text{H}_3\text{N})(\text{COOH})_2$ ). The flow rate was  $0.71 \text{ mL min}^{-1}$  through a  $20 \mu\text{L}$  sample loop. The IC lower limit of detection for each species was  $0.1 \text{ mg L}^{-1}$ , and all blank samples were below this value. Sample concentrations below the IC limit were not reported; all reportable concentrations have units of  $\mu\text{g m}^{-3}$ .



**Fig. 6. NOAA/ARL/ATDD's Metrohm 790 Personal Ion Chromatography System.**

#### 4. SULFUR DIOXIDE (SO<sub>2</sub>)

For SO<sub>2</sub>, a small number of samples (<2%) had concentrations below the IC lower limit of detection. Each SO<sub>2</sub> concentration measured with ADS during the experimental period is listed in Appendix A. The minimum and maximum concentrations were 0.11 µg m<sup>-3</sup> and 36.95 µg m<sup>-3</sup>, respectively. Atmospheric concentrations of trace gases (including SO<sub>2</sub>) not in proximity to point sources are usually lognormally distributed, where  $Y = \ln(X)$  (Csanady, 1973). The histogram of SO<sub>2</sub> concentrations in Fig. 7 appears to support this assumption, as does an Anderson-Darling test. Therefore, the geometric mean, 2.49 µg m<sup>-3</sup>, and geometric standard deviation, 1.44 µg m<sup>-3</sup>, are the statistical parameters that best describe the measured SO<sub>2</sub> concentration.

Further examination of the data set revealed differences in SO<sub>2</sub> concentration based on the time when the samples were collected. As mentioned previously, ADS samples were collected for 6-h intervals at 0300, 0900, 1500, and 2100, which are correspondingly labeled morning, day, evening, and night in this paper. The highest geometric mean (with geometric standard deviation) SO<sub>2</sub> concentration, 8.20(1.08) µg m<sup>-3</sup>, was found in day samples. The next highest geometric mean SO<sub>2</sub> concentration was measured during evening hours and is less than half of the day value at 3.86(1.03) µg m<sup>-3</sup>. Similar geometric mean SO<sub>2</sub> concentrations were measured in the morning and at night, 1.21(1.33) and 1.08(1.27) µg m<sup>-3</sup> respectively. Seemingly, SO<sub>2</sub> day concentrations were higher than concentrations measured during the other three periods, as illustrated by the box plots in Fig. 8. The means of natural logarithms of SO<sub>2</sub> concentration are shown as red diamonds while the medians are represented as white lines dividing the second and third quartiles (shaded boxes). Box plot upper and lower whiskers indicate 75<sup>th</sup> and 25<sup>th</sup> percentiles, respectively.

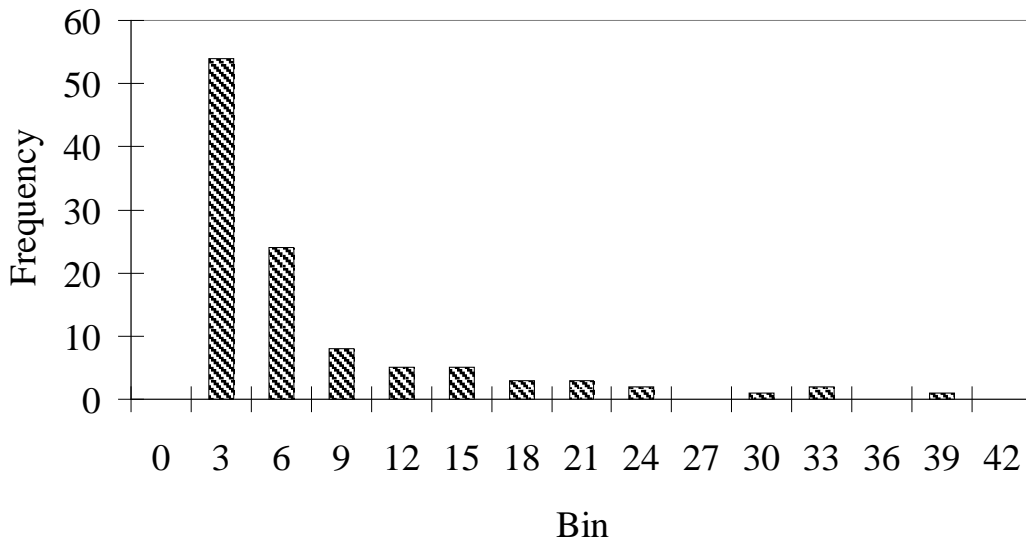
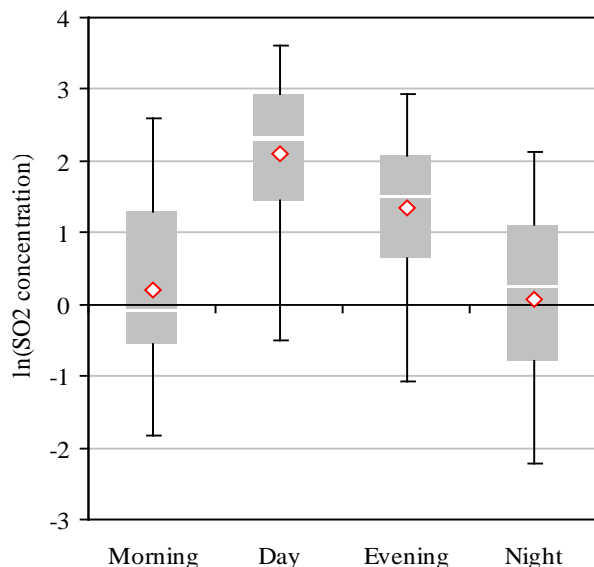


Fig. 7. Histogram of SO<sub>2</sub> concentrations from ADS.

To determine if the differences were statistically significant, logarithms of SO<sub>2</sub> concentration were investigated using a one-way analysis of variance (ANOVA). For  $\alpha = 0.05$  (95% confidence), the null hypothesis was rejected. The observed  $F$  statistic was 17.82 while the critical value was 2.69, implying a significant difference between SO<sub>2</sub> concentrations in samples collected at the four times.

It has long been known that SO<sub>2</sub> concentration may exhibit diurnal variations, especially away from point sources (Garland and Derwent, 1979; Martin and Barber, 1981). Recent studies by Meng *et al.* (2009) found that SO<sub>2</sub> concentration peaks around noon or in early afternoon with a somewhat steady decline to very low concentrations during early morning hours. The SO<sub>2</sub> concentration results from this study seem to show comparable diurnal patterns. One possible explanation for the observed SO<sub>2</sub> concentration variation is that SO<sub>2</sub> emissions are trapped above a nocturnal inversion layer and only reach lower altitudes when the temperature at ground level increases and vertical mixing ensues (Meng *et al.*, 2009). Preliminary results by White and Morris (2008) from Beltsville studies during the same time period also point to meteorological influences on SO<sub>2</sub> concentration patterns.

At the Beltsville site, the ADS was collocated with two MARGA systems (ECN, The Netherlands; Applikon, Switzerland). The matching MARGA systems continuously measured sulfur and nitrogen-based gases and aerosols with a steam-jet aerosol collector and a rotating wet denuder with on-line ion chromatography analysis. MARGA instrument description and supporting information concerning CASTNET deployment are detailed elsewhere (Lear, 2005; Otjes *et al.*, 2006; White and Morris, 2008). During the Beltsville experiment, MARGA generated hourly average concentrations of HNO<sub>3</sub>, HNO<sub>2</sub>, NH<sub>3</sub>, SO<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, and base cations. The MARGA inlets were placed at a height of 4 m.



**Fig. 8. Box plots of the natural logarithms of ADS SO<sub>2</sub> concentrations by sample time. Red diamonds represent means of SO<sub>2</sub> concentration natural logarithms. White lines divide the second and third quartiles (shaded boxes). Upper and lower whiskers indicate 75<sup>th</sup> and 25<sup>th</sup> percentiles, respectively.**



Hourly SO<sub>2</sub> concentrations from both MARGA systems (M-116 and M-216) were averaged over a 6-h period to compare with ADS SO<sub>2</sub> values (Appendix A). Averages from the MARGA data were only included in this analysis if at least 50% (3 of 6) of the individual values were available. Histograms of SO<sub>2</sub> concentrations from M-116 and M-216 appear to follow lognormal distributions (Fig. 9). Therefore, geometric means and standard deviations were calculated for each dataset.

Overall, the SO<sub>2</sub> concentration geometric means from both MARGA systems were higher than the ADS value, 2.49(1.44) µg m<sup>-3</sup>. The geometric mean SO<sub>2</sub> concentrations for M-116 and M-216 were 3.21(1.24) and 3.72(1.20) µg m<sup>-3</sup>, respectively. The average maximum difference between ADS and MARGA SO<sub>2</sub> concentrations was 2.85 µg m<sup>-3</sup>. It is noted that MARGA data were not available until August 16, four days after ADS measurement began, and that M-216 also had missing data on September 6-9.

As shown in Fig. 10, SO<sub>2</sub> concentrations from both MARGA systems seem to exhibit diurnal variations. Although the paired MARGA systems sampled from adjacent inlets, the magnitude of change shown by the box plots is somewhat less pronounced for M-216 (Fig. 10b). The box plots of SO<sub>2</sub> concentration logarithms from M-116 and M-216 (Fig. 10) and from the ADS (Fig. 8) appear similar and display overall consistent patterns of maximum values during the day.

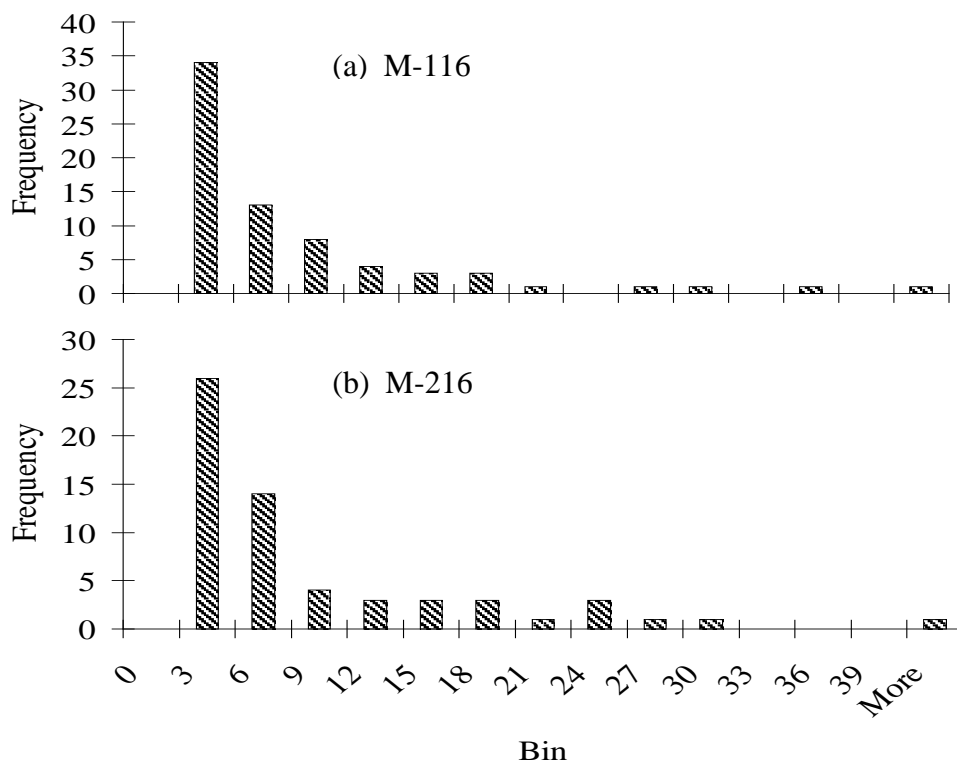
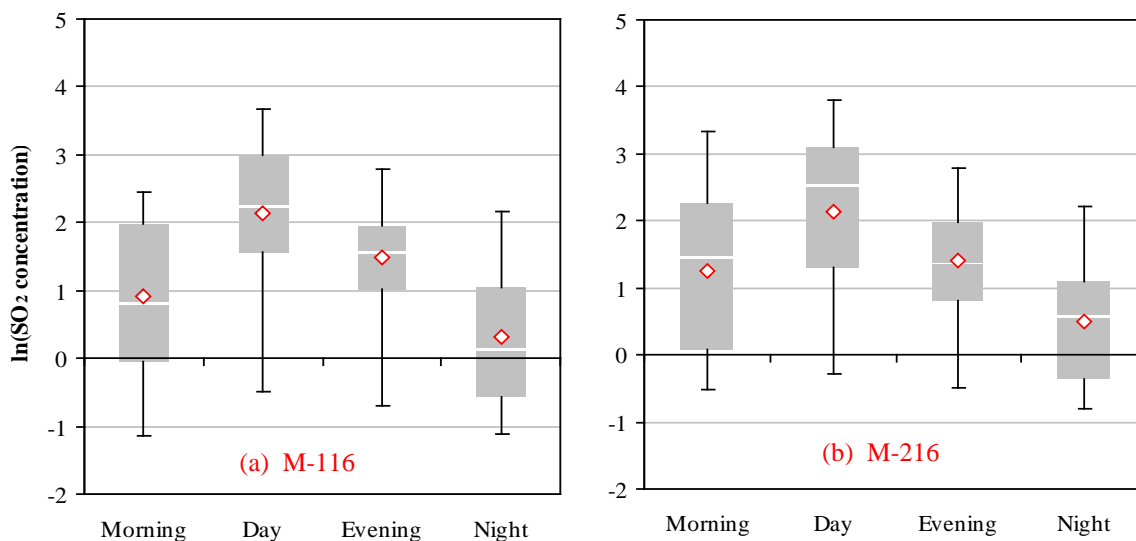


Fig. 9. Histograms of SO<sub>2</sub> concentration from MARGA systems M-116 and M-216.



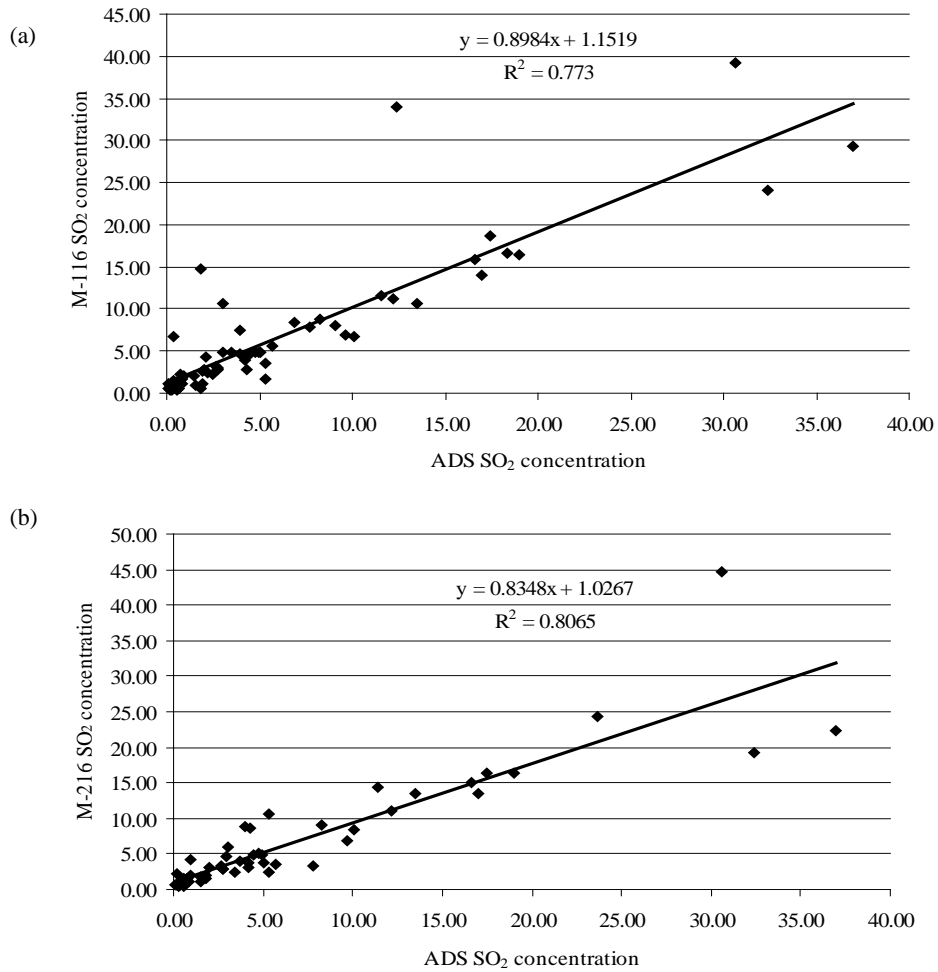
**Fig. 10.** Box plots of the natural logarithms of  $\text{SO}_2$  concentration from both MARGA systems (M-116 and M-216) by sample time. Symbols as noted in Fig. 8.

In Table 1, geometric means of  $\text{SO}_2$  concentration from both MARGA systems were compared to ADS values by time of day. The highest geometric means were found during the day regardless of measurement technique.  $\text{SO}_2$  concentration from the ADS measured only ~3% lower than the MARGA systems. There is an intriguing contrast between morning samples measured by both techniques. Morning  $\text{SO}_2$  concentrations from the ADS had a geometric mean of  $1.21(1.33) \mu\text{g m}^{-3}$  less than half of the geometric means from M-116 and M-216,  $2.50(1.12)$  and  $3.54(1.30) \mu\text{g m}^{-3}$ , respectively. This disparity may partially be explained by differences in sample number during the morning ( $N_{\text{ADS}} = 28$ ;  $N_{\text{M-116}} = 18$ ;  $N_{\text{M-216}} = 11$ ). Lower  $\text{SO}_2$  concentrations may have been below the MARGA lower limit of detection for some of the morning samples resulting in missing data or insufficient values to formulate an average for comparison.

During the Beltsville experiment,  $\text{SO}_2$  concentration was relatively low, as expected, given that the sampling site is distant from large point emissions sources. Diurnal variations with maximum concentrations during the day were observed in the ADS data set.  $\text{SO}_2$  concentrations from both MARGA systems followed this pattern also. Generally, the correlation between  $\text{SO}_2$  concentration measured with the ADS and both MARGA systems was quite good as illustrated by Fig.11.

**Table 1. Geometric means ( $X_{geo}$ ) and geometric standard deviations ( $\sigma_{geo}$ ) of SO<sub>2</sub> concentration by time of day for the ADS and both MARGA systems.**

Time of Day	ADS $X_{geo}$ ( $\sigma_{geo}$ ) ( $\mu\text{g m}^{-3}$ )	M-116 $X_{geo}$ ( $\sigma_{geo}$ ) ( $\mu\text{g m}^{-3}$ )	M-216 $X_{geo}$ ( $\sigma_{geo}$ ) ( $\mu\text{g m}^{-3}$ )
Morning	1.21(1.33)	2.50(1.12)	3.54(1.30)
Day	8.20(1.08)	8.40(1.16)	8.43(1.16)
Evening	3.86(1.03)	4.37(0.98)	4.04(0.91)
Night	1.08(1.27)	1.37(1.01)	1.65(0.92)



**Fig. 11. Relationship between ADS SO<sub>2</sub> concentration versus (a) M-116 and (b) M-216 SO<sub>2</sub> concentration.**

## 5. NITRIC ACID (HNO<sub>3</sub>)

All HNO<sub>3</sub> concentrations measured with the ADS are listed in Appendix B. The minimum HNO<sub>3</sub> concentration was 0.16 µg m<sup>-3</sup>, and the maximum was 8.87 µg m<sup>-3</sup>. An Anderson-Darling test and the histogram of HNO<sub>3</sub> concentration shown in Fig. 12 affirmed that the underlying distribution of these samples was lognormal. The geometric mean and geometric standard deviation, preferred parameters for lognormal distributions, are 1.08 and 1.15 µg m<sup>-3</sup>, respectively.

When HNO<sub>3</sub> concentrations were segregated by time of sample collection, a diurnal variation became apparent. The highest geometric mean, 2.95(0.72) µg m<sup>-3</sup>, was observed during the day. Evening samples had a geometric mean of 1.87(0.79) µg m<sup>-3</sup>. Morning and night samples had similar geometric means, 0.42(0.53) and 0.37(0.74) µg m<sup>-3</sup>, respectively. A box plot of HNO<sub>3</sub> concentration natural logarithms (Fig. 13) graphically illustrates these shifts. There appears to be a sharp increase in HNO<sub>3</sub> concentration from samples collected during the morning to those from the daytime period. An one-way ANOVA was used to test the significance of these differences. The null hypothesis was rejected at  $\alpha = 0.05$  (95% confidence) with an observed  $F$  statistic of 52.74 and a  $F$  critical value of 2.70. The results of the ANOVA suggest that the differences between HNO<sub>3</sub> concentrations at the four collection times were significant.

Considering the box plots in Fig. 13, it seems that similarities exist between morning and night HNO<sub>3</sub> samples. The Student's  $t$ -test (unequal variances; two-tailed) was applied to these HNO<sub>3</sub> concentration natural logarithm data sets. At  $\alpha = 0.05$ , the null hypothesis was accepted implying that morning and night values did not differ significantly ( $p = 0.58$ ). Therefore, HNO<sub>3</sub> concentrations measured during these times may represent the same underlying population.

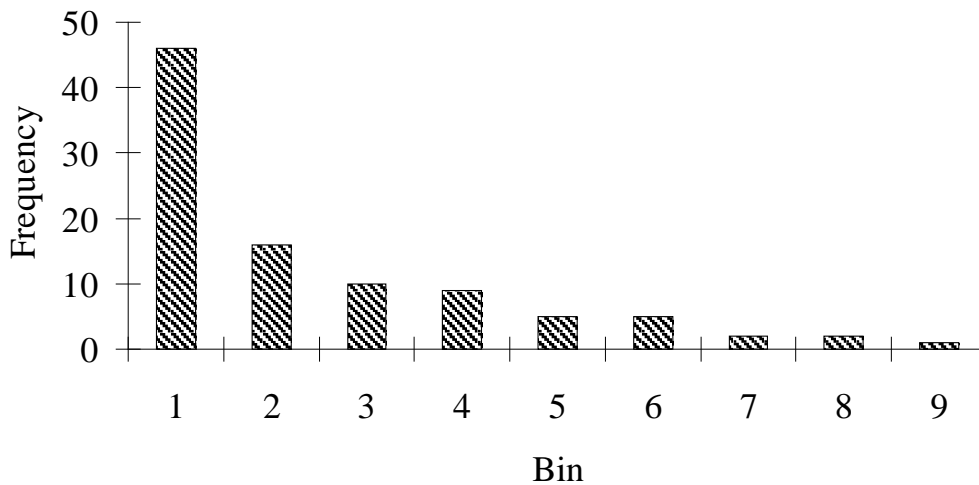
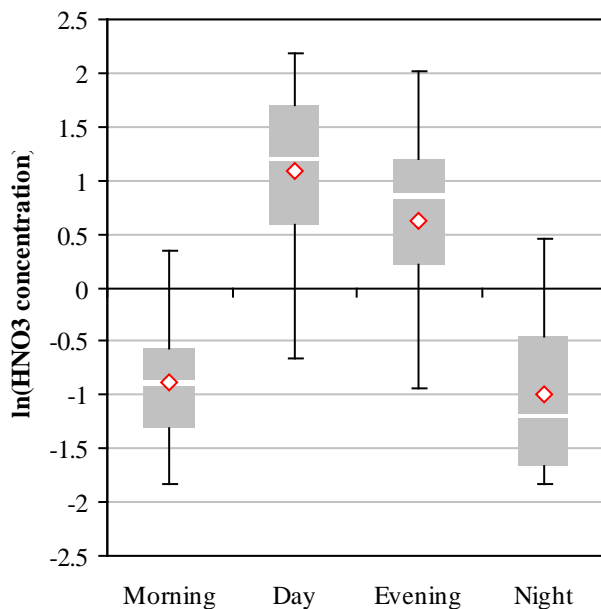


Fig. 12. Histogram of HNO<sub>3</sub> concentrations from the ADS.



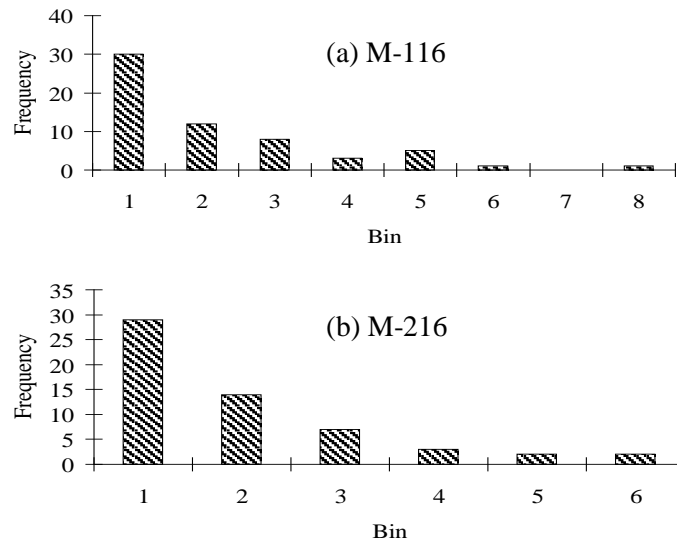
**Fig. 13. Box plots of the natural logarithms of ADS HNO<sub>3</sub> concentrations by sample time. Symbols as noted in Fig. 8.**

The diurnal variation of HNO<sub>3</sub> concentration measured in this study is expected given its photochemical formation via the reaction of nitrogen dioxide (NO<sub>2</sub>) with the hydroxyl radical (OH). The photolysis of ozone (O<sub>3</sub>) produces OH radicals during the day. Hence, HNO<sub>3</sub> concentration is dependent upon temperature and solar radiation (Aneja *et al.*, 1994). Midday maximum HNO<sub>3</sub> concentrations have been reported for similar experiments (Harrison and Allen, 1990; Kitto and Harrison, 1992). The rather low night and morning HNO<sub>3</sub> concentrations measured during this study are similar to findings by Danalatos and Glavas (1999) and support the strong influence of photochemistry and meteorology on the diurnal variation of HNO<sub>3</sub>.

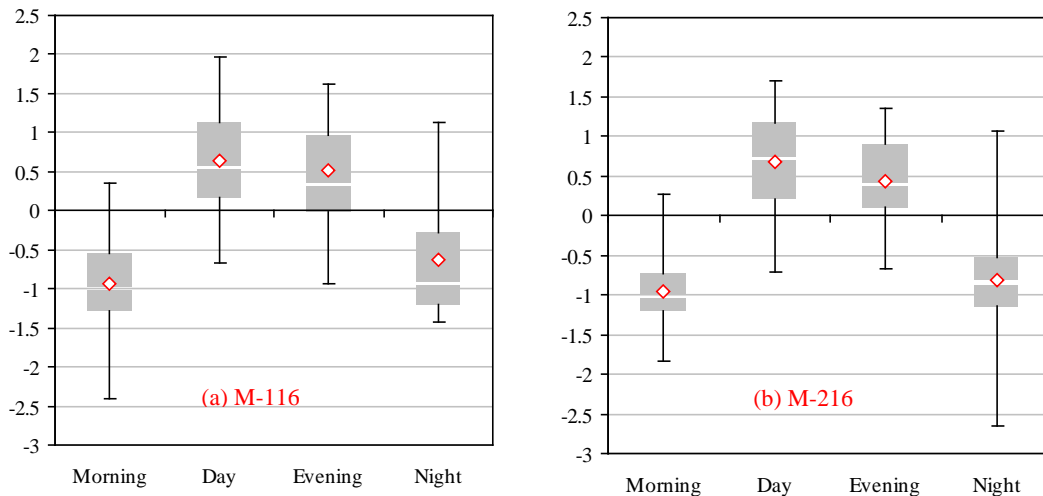
Hourly HNO<sub>3</sub> concentrations from the two MARGA systems (M-116 and M-216) were averaged over 6-h. If less than 3 of 6 individual concentrations were not measured by the MARGAs, then averages were not reported. As shown in Fig. 14, the HNO<sub>3</sub> concentrations measured by M-116 and M-216 appear lognormally distributed. The overall geometric mean HNO<sub>3</sub> concentrations from M-116 and M-216 were 1.04(1.00) and 0.91(1.00) µg m<sup>-3</sup>, respectively. The average maximum difference between ADS and MARGA HNO<sub>3</sub> concentrations was only 0.85 µg m<sup>-3</sup>, indicating that both techniques reported similar values during the study.

Box plots of MARGA HNO<sub>3</sub> concentrations by sample time (Fig. 15) seem to show a diurnal variation comparable to that measured with ADS. Table 2 displays the geometric means of HNO<sub>3</sub> concentration by time of day for both MARGA systems and the ADS. The ADS technique presented the highest HNO<sub>3</sub> concentrations for most sample times. The exception was at night when both MARGA systems reported slightly higher values than the ADS. However, morning and night HNO<sub>3</sub> concentrations, regardless of measurement technique, were lower than day and evening concentrations.

Nitric acid concentrations measured with the ADS during the study were low with most values under  $5 \mu\text{g m}^{-3}$ . It is proposed that these levels were typical of background concentrations given the absence of strong sources. Maximum day concentrations are consistent with other studies reported in the literature and are indicative of photochemical and meteorological influences on  $\text{HNO}_3$  concentration. Even with very low concentrations, data from the two techniques (ADS and MARGA) agreed fairly well with  $R^2$  values of 0.69 and 0.77 as shown in Fig. 16.



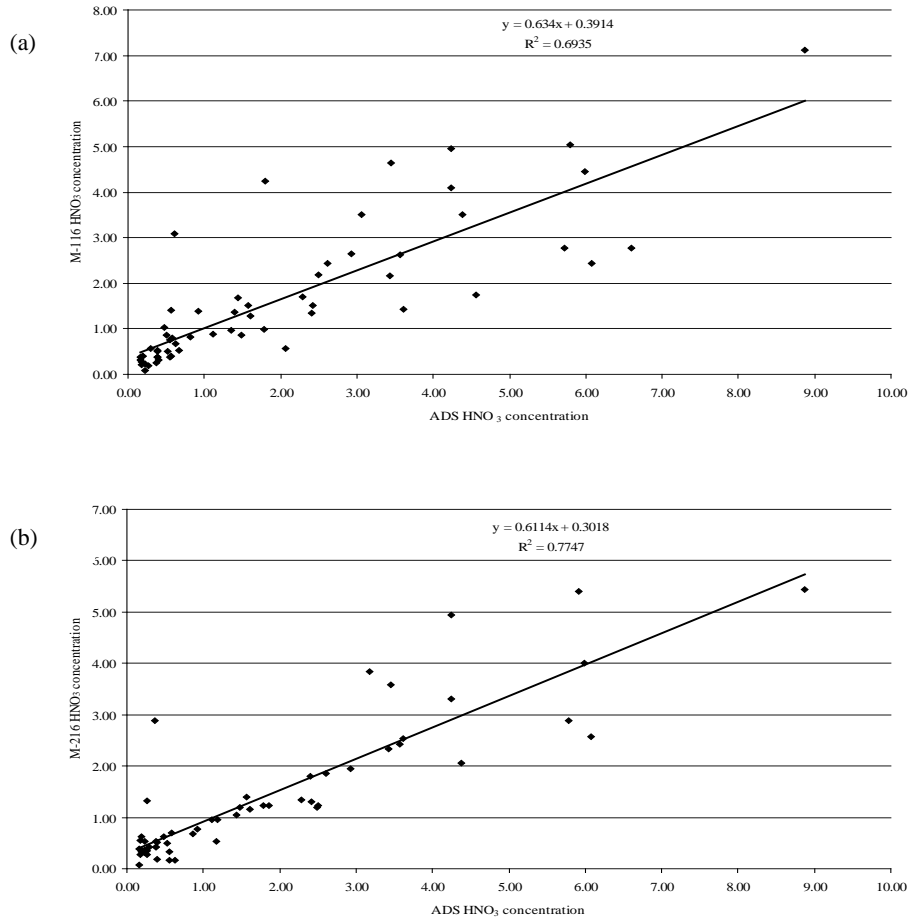
**Fig. 14. Histograms of  $\text{HNO}_3$  concentration from MARGA systems M-116 and M-216.**



**Fig. 15. Box plots of the natural logarithms of  $\text{HNO}_3$  concentration from both MARGA systems (M-116 and M-216) by sample time. Symbols as noted in Fig. 8.**

**Table 2. Geometric means ( $X_{geo}$ ) and geometric standard deviations ( $\sigma_{geo}$ ) of  $\text{HNO}_3$  concentration by time of day for the ADS and both MARGA systems.**

Time of Day	ADS $X_{geo}$ ( $\mu\text{g m}^{-3}$ )	M-116 $X_{geo}$ ( $\mu\text{g m}^{-3}$ )	M-216 $X_{geo}$ ( $\mu\text{g m}^{-3}$ )
Morning	0.42(0.53)	0.39(0.73)	0.38(0.58)
Day	2.95(0.72)	1.91(0.73)	1.96(0.72)
Evening	1.87(0.79)	1.67(0.76)	1.55(0.61)
Night	0.37(0.74)	0.54(0.79)	0.44(0.85)



**Fig. 16. Relationship between ADS  $\text{HNO}_3$  concentrations versus (a) M-116 and (b) M-216  $\text{HNO}_3$  concentration.**

## 6. AMMONIA (NH<sub>3</sub>)

The lack of large NH<sub>3</sub> emissions sources in proximity to the Beltsville site inhibited concentrations during the experimental period. Approximately 25% of all ADS samples had NH<sub>3</sub> concentrations below the IC limit of detection. Measurement techniques with low detection limits are needed to accurately measure ammonia concentrations in the atmosphere. Ammonia's ability to exist in three phases (gas, liquid, and particulate) has complicated measurement and hampered instrument development (Norman *et al.*, 2009). In addition, NH<sub>3</sub>'s own chemical properties, including its preferred reactions to form NH<sub>4</sub><sup>+</sup> particulates, make accurate measurement difficult (Hicks *et al.*, 1991; Myles, 2004; Phillips *et al.*, 2004). However, several studies have successfully utilized annular denuders to measure NH<sub>3</sub> under a variety of meteorological conditions (Bari *et al.*, 2003; Edgerton *et al.*, 2007; Myles *et al.*, 2007). NH<sub>3</sub> concentrations measured with the ADS are shown in Appendix C.

The range of NH<sub>3</sub> concentrations measured with the ADS was only 2.21 µg m<sup>-3</sup>. The histogram of NH<sub>3</sub> concentration in Fig. 17 appears to follow a lognormal distribution. An Anderson-Darling test also found that ADS NH<sub>3</sub> concentrations were characteristic of a lognormal distribution. Thus, the geometric mean (geometric standard deviation) was 0.56(0.69) µg m<sup>-3</sup>. Unlike the acidic gases mentioned previously, NH<sub>3</sub> data from the ADS did not follow a diurnal pattern (Fig. 18). The geometric means of morning, day, evening, and night were 0.58(0.67), 0.60(0.65), 0.59(0.73) and 0.44(0.72) µg m<sup>-3</sup>, respectively. This similarity is unexpected since other workers (Allen *et al.*, 1988; Phillips *et al.*, 2004) have reported diurnal variations in NH<sub>3</sub> concentration. Danalatos and Glavas (1999), however, noted that higher mixing heights offset increases in daytime NH<sub>3</sub> emissions and may dampen NH<sub>3</sub>'s diurnal variation. In this study, very low NH<sub>3</sub> concentrations may also have precluded the ADS measurement of diurnal variation. An one-way ANOVA of the ADS NH<sub>3</sub> concentrations resulted in acceptance of the null hypothesis that samples from morning, day, evening, and night were similar. For  $\alpha = 0.05$  (95% confidence), the observed  $F$  statistic was 0.94, and the critical  $F$  value was 2.72 ( $p = 0.42$ ).

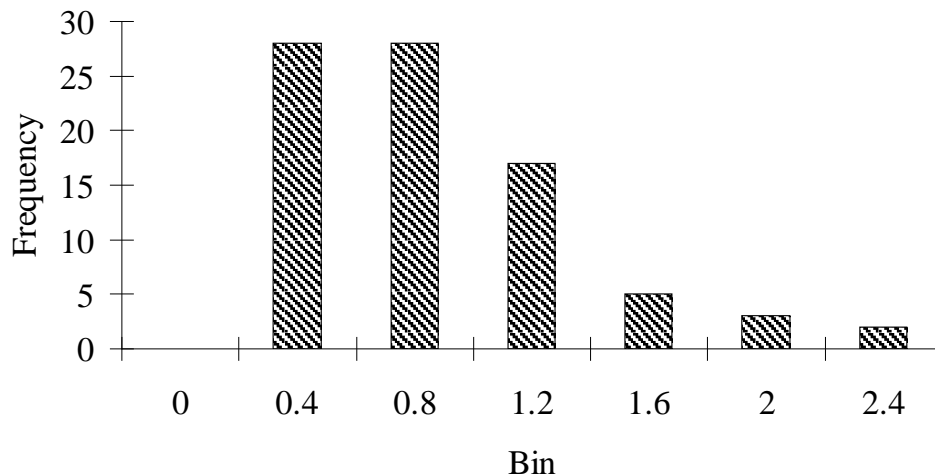


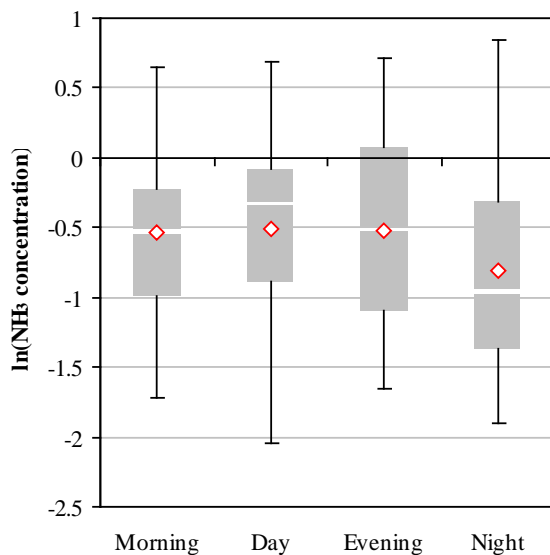
Fig. 17. Histogram of NH<sub>3</sub> concentrations from ADS.



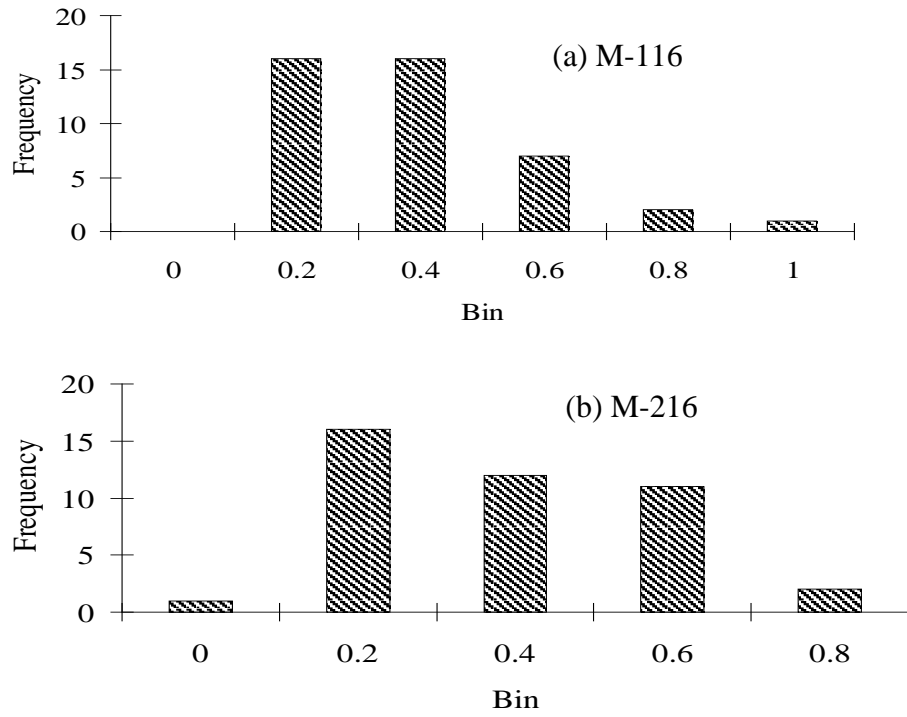
Six-hour average  $\text{NH}_3$  concentrations from the MARGA systems, M-116 and M-216, are listed in Appendix C. Histograms of these values appear to follow lognormal distributions (Fig. 19). The geometric means (geometric standard deviations) of  $\text{NH}_3$  concentration from M-116 and M-216 were 0.25(0.63) and 0.26(0.63)  $\mu\text{g m}^{-3}$ , respectively. These values were approximately half of the geometric mean  $\text{NH}_3$  concentration from ADS. Another inconsistency between the  $\text{NH}_3$  concentration measured by the two techniques was the apparent diurnal variation seen in the datasets from both MARGA systems (Fig. 20). As shown in Table 3, the highest  $\text{NH}_3$  concentrations were measured by the MARGA systems during the day. Morning and night samples had very low geometric mean  $\text{NH}_3$  concentrations.

One-way ANOVA of the two MARGA datasets showed a statistically significant difference between  $\text{NH}_3$  concentrations measured at various times. For M-116, the observed  $F$  statistic was 8.28 and the  $F$  critical value was 2.85 ( $p = 0.00023$ ). For M-216, the observed  $F$  statistic was 4.04 and the  $F$  critical value was 2.85 ( $p = 0.014$ ). The ANOVA statistics suggest that both MARGA systems measured diurnal variations of  $\text{NH}_3$  concentration even at the very low concentrations observed in this study. The ADS, however, was unable to measure any variation and reported similar  $\text{NH}_3$  concentrations for all sampling times. As a consequence, there is no correlation between  $\text{NH}_3$  concentration measured by ADS and the MARGA systems (Fig. 21).

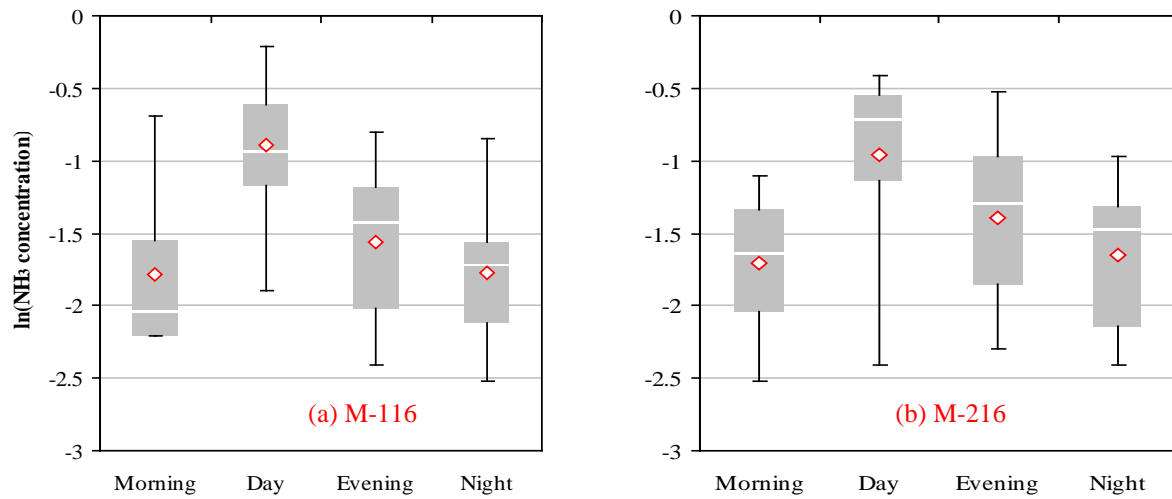
Diurnal variation of  $\text{NH}_3$  concentration is difficult to quantify, even in proximity to emissions sources (Phillips *et al.*, 2004). Meteorological parameters, such as mixing height and air temperature, as well as  $\text{NH}_3$ 's own affinity for deposition often hinder accurate measurement (Allen *et al.*, 1988). MARGA systems analyze samples in near-real time and likely provide better resolution than the integrated ADS technique, especially at low concentrations.



**Fig. 18.** Box plots of the natural logarithms of ADS  $\text{NH}_3$  concentrations by sample time. Symbols as noted in Fig. 8.



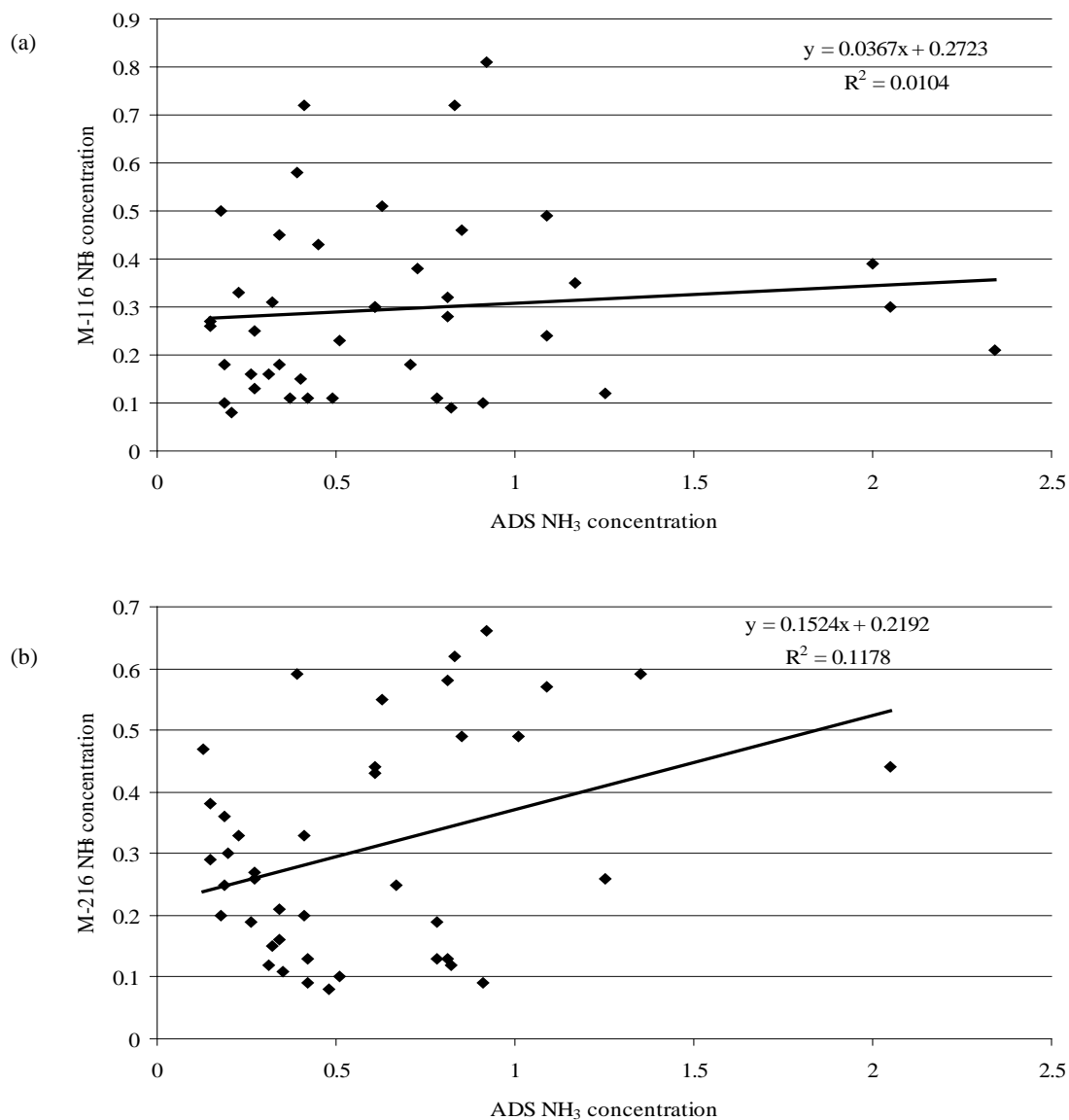
**Fig. 19. Histograms of  $\text{NH}_3$  concentration from MARGA systems M-116 and M-216.**



**Fig. 20. Box plots of the natural logarithms of  $\text{NH}_3$  concentration from both MARGA systems (M-116 and M-216) by sample time. Symbols as noted in Fig. 8.**

**Table 3. Geometric means ( $X_{geo}$ ) and geometric standard deviations ( $\sigma_{geo}$ ) of  $NH_3$  concentration by time of day for the ADS and both MARGA systems.**

Time of Day	ADS $X_{geo}$ ( $\mu g\ m^{-3}$ )	M-116 $X_{geo}$ ( $\mu g\ m^{-3}$ )	M-216 $X_{geo}$ ( $\mu g\ m^{-3}$ )
Morning	0.58(0.67)	0.17(0.57)	0.18(0.47)
Day	0.60(0.65)	0.41(0.45)	0.38(0.63)
Evening	0.59(0.73)	0.21(0.55)	0.25(0.57)
Night	0.44(0.72)	0.17(0.51)	0.19(0.53)



**Fig. 21. Relationship between ADS  $NH_3$  concentration versus (a) M-116 and (b) M-216  $NH_3$  concentration.**

## 7. SUMMARY

Annular denuder systems were utilized to measure three trace gases ( $\text{SO}_2$ ,  $\text{HNO}_3$ , and  $\text{NH}_3$ ) at the U.S. EPA CASTNET site near Beltsville, MD. Two Monitoring Instruments for Aerosols and Gases (MARGA) systems were collocated with the ADS during this study. Trace gas concentrations were relatively low and reflected the absence of local emissions sources for all species. Data from both the ADS and MARGA techniques showed diurnal concentration variations for  $\text{SO}_2$  and  $\text{HNO}_3$ . Highest values were seen during the day with similar minimum concentrations measured at night and in the morning. In general, good agreement between the techniques was found for  $\text{SO}_2$  ( $R^2 \geq 0.77$ ) and  $\text{HNO}_3$  ( $R^2 \geq 0.69$ ). Comparable trends in concentration have been reported in the literature for both species (Danalatos and Glavas, 1999; Meng *et al.*, 2009).

Ammonia concentrations were very low during this study, and the ADS technique measured relatively stable concentrations regardless of time of day. Conversely, diurnal variations of  $\text{NH}_3$  concentration were apparent in data from both MARGA systems. As a result,  $\text{NH}_3$  concentrations from the ADS and MARGA systems showed no correlation. The inability of the ADS to measure diurnal variations of  $\text{NH}_3$  concentration contributed to the disparity.

Overall, the ADS performed well, but several issues with measurement of  $\text{NH}_3$  must be addressed in future work. In environments distant from  $\text{NH}_3$  emissions sources, longer sampling times may promote better sample resolution. Better extraction methods (i.e., longer rotation times) may facilitate more efficient removal of  $\text{NH}_3$  from denuders and optimize the sample for IC analysis. If diurnal variations of  $\text{NH}_3$  are sought, then fast-response techniques, such as the MARGA, may be preferable.

## 8. ACKNOWLEDGEMENTS

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## Appendix A: Measurements of SO<sub>2</sub> Concentration

Concentrations ( $\mu\text{g m}^{-3}$ ) of SO<sub>2</sub> from annular denuder systems (ADS SO<sub>2</sub>) and 6-h mean SO<sub>2</sub> concentrations from both MARGA systems (M-116 and M-216).

Date/ Time (EDT)	ADS SO <sub>2</sub> ( $\mu\text{g m}^{-3}$ )	M-116 ( $\mu\text{g m}^{-3}$ )	M-216 ( $\mu\text{g m}^{-3}$ )	Date/ Time (EDT)	ADS SO <sub>2</sub> ( $\mu\text{g m}^{-3}$ )	M-116 ( $\mu\text{g m}^{-3}$ )	M-216 ( $\mu\text{g m}^{-3}$ )
8/12/2005 1500	1.19	-	-	8/26/2005 1500	17.01	14.02	13.56
8/12/2005 2100	-	-	-	8/26/2005 2100	0.80	1.85	1.17
8/13/2005 0300	3.53	-	-	8/27/2005 0300	0.21	-	0.60
8/13/2005 0900	4.97	-	-	8/27/2005 0900	2.21	2.48	-
8/13/2005 1500	13.38	-	-	8/27/2005 1500	0.80	1.60	1.54
8/13/2005 2100	4.09	-	-	8/27/2005 2100	1.83	0.61	2.08
8/14/2005 0300	4.41	-	-	8/28/2005 0300	0.91	2.02	4.27
8/14/2005 0900	13.28	-	-	8/28/2005 0900	2.99	4.87	4.71
8/14/2005 1500	8.24	-	-	8/28/2005 1500	4.22	3.83	3.82
8/14/2005 2100	3.35	-	-	8/28/2005 2100	0.55	0.81	1.47
8/15/2005 0300	1.75	-	-	8/29/2005 0300	0.16	-	0.77
8/15/2005 0900	4.18	-	-	8/29/2005 0900	6.49	-	-
8/15/2005 1500	0.77	-	-	8/29/2005 1500	1.97	1.15	-
8/15/2005 2100	1.28	-	-	8/29/2005 2100	0.14	0.55	0.69
8/16/2005 0300	0.93	-	-	8/30/2005 0300	0.17	0.80	-
8/16/2005 0900	1.63	-	-	8/30/2005 0900	18.34	16.61	-
8/16/2005 1500	4.50	-	-	8/30/2005 1500	-	-	-
8/16/2005 2100	1.76	-	1.79	8/30/2005 2100	4.32	2.88	8.63
8/17/2005 0300	4.24	-	-	8/31/2005 0300	13.50	10.60	13.43
8/17/2005 0900	21.83	-	23.64	8/31/2005 0900	4.48	4.59	4.89
8/17/2005 1500	1.31	-	1.62	8/31/2005 1500	4.78	4.79	5.13
8/17/2005 2100	0.24	-	-	8/31/2005 2100	8.28	8.70	9.07
8/18/2005 0300	0.78	-	27.90	9/1/2005 0300	3.05	10.60	5.91
8/18/2005 0900	36.95	29.35	22.38	9/1/2005 0900	12.17	11.18	11.17
8/18/2005 1500	19.00	16.42	16.43	9/1/2005 1500	4.98	4.93	4.95
8/18/2005 2100	2.79	2.74	2.77	9/1/2005 2100	0.27	0.96	-
8/19/2005 0300	0.85	1.08	1.14	9/2/2005 0300	0.82	-	-
8/19/2005 0900	0.61	0.62	0.75	9/2/2005 0900	29.34	-	-
8/19/2005 1500	0.34	0.50	0.62	9/2/2005 1500	7.86	-	-
8/19/2005 2100	0.25	0.33	0.48	9/2/2005 2100	3.93	-	-
8/20/2005 0300	0.65	1.58	-	9/3/2005 0300	2.48	2.25	-
8/20/2005 0900	5.06	4.90	3.78	9/3/2005 0900	1.51	2.00	1.84
8/20/2005 1500	5.68	5.64	3.50	9/3/2005 1500	1.76	-	1.65
8/20/2005 2100	6.84	8.34	-	9/3/2005 2100	0.40	1.56	1.03
8/21/2005 0300	2.12	4.23	-	9/4/2005 0300	7.74	7.90	-
8/21/2005 0900	9.12	7.99	-	9/4/2005 0900	7.78	-	3.37
8/21/2005 1500	3.93	4.67	-	9/4/2005 1500	3.71	-	4.07
8/21/2005 2100	0.55	0.51	0.59	9/4/2005 2100	1.95	2.67	3.03
8/22/2005 0300	1.55	0.89	1.06	9/5/2005 0300	5.28	3.50	10.67
8/22/2005 0900	32.41	24.10	19.24	9/5/2005 0900	23.65	-	24.27
8/22/2005 1500	10.06	6.77	8.42	9/5/2005 1500	5.28	1.72	2.49
8/22/2005 2100	2.62	3.09	3.40	9/5/2005 2100	0.61	0.53	0.63
8/23/2005 0300	3.98	7.51	8.89	9/6/2005 0300	0.74	2.21	-
8/23/2005 0900	-	14.63	22.62	9/6/2005 0900	12.41	33.94	-
8/23/2005 1500	16.61	15.87	15.13	9/6/2005 1500	1.81	14.79	-
8/23/2005 2100	4.15	4.39	3.15	9/6/2005 2100	0.13	1.15	-
8/24/2005 0300	11.53	11.65	-	9/7/2005 0300	0.41	6.79	-
8/24/2005 0900	3.46	4.79	2.45	9/7/2005 0900	-	-	-
8/24/2005 1500	2.71	2.92	2.98	9/7/2005 1500	1.98	2.77	-
8/24/2005 2100	0.53	0.40	0.45	9/7/2005 2100	0.11	0.59	-
8/25/2005 0300	0.19	0.92	2.16	9/8/2005 0300	0.22	0.32	-
8/25/2005 0900	30.60	39.28	44.63	9/8/2005 0900	19.19	-	-
8/25/2005 1500	9.67	7.00	6.82	9/8/2005 1500	7.04	-	-

Date/ Time (EDT)	ADS SO <sub>2</sub> (μg m <sup>-3</sup> )	M-116 (μg m <sup>-3</sup> )	M-216 (μg m <sup>-3</sup> )	Date/ Time (EDT)	ADS SO <sub>2</sub> (μg m <sup>-3</sup> )	M-116 (μg m <sup>-3</sup> )	M-216 (μg m <sup>-3</sup> )
8/25/2005 2100	0.97	-	2.00	9/8/2005 2100	2.43	-	-
8/26/2005 0300	0.19	0.51	-	9/9/2005 0300	0.73	-	-
8/26/2005 0900	11.39	-	14.32	9/9/2005 0900	17.44	18.69	16.47

### Appendix B: Measurements of HNO<sub>3</sub> Concentration

Concentrations ( $\mu\text{g m}^{-3}$ ) of HNO<sub>3</sub> from annular denuder systems (ADS HNO<sub>3</sub>) and 6-h mean HNO<sub>3</sub> concentrations from both MARGA systems (M-116 and M-216).

Date/ Time (EDT)	ADS HNO <sub>3</sub> ( $\mu\text{g m}^{-3}$ )	M-116 ( $\mu\text{g m}^{-3}$ )	M-216 ( $\mu\text{g m}^{-3}$ )	Date/ Time (EDT)	ADS HNO <sub>3</sub> ( $\mu\text{g m}^{-3}$ )	M-116 ( $\mu\text{g m}^{-3}$ )	M-216 ( $\mu\text{g m}^{-3}$ )
8/13/2005 0300	0.70	-	-	8/25/2005 0900	4.24	4.96	4.94
8/13/2005 0900	4.96	-	-	8/25/2005 1500	5.79	5.03	2.88
8/13/2005 1500	3.06	-	-	8/25/2005 2100	0.19	-	0.63
8/13/2005 2100	0.88	-	-	8/26/2005 0900	4.38	3.50	2.05
8/14/2005 0300	0.57	-	-	8/26/2005 1500	2.93	2.64	1.95
8/14/2005 0900	7.21	-	-	8/26/2005 2100	0.48	1.03	0.62
8/14/2005 1500	3.40	-	-	8/27/2005 0300	0.27	-	0.27
8/14/2005 2100	0.85	-	-	8/27/2005 0900	0.81	0.81	-
8/15/2005 0300	0.41	-	-	8/27/2005 2100	0.37	0.26	2.89
8/15/2005 0900	2.89	-	-	8/28/2005 0900	2.42	1.52	1.31
8/15/2005 1500	2.30	-	-	8/28/2005 1500	2.49	2.19	1.20
8/15/2005 2100	0.25	-	-	8/29/2005 0900	1.63	-	-
8/16/2005 0300	0.52	-	-	8/29/2005 1500	0.56	0.39	-
8/16/2005 0900	1.35	-	-	8/30/2005 0900	1.35	0.97	-
8/16/2005 1500	0.43	-	-	8/30/2005 1500	0.50	0.87	-
8/16/2005 2100	1.17	-	0.54	8/30/2005 2100	0.16	0.31	0.07
8/17/2005 0300	1.42	-	-	8/31/2005 0300	0.55	0.76	0.16
8/17/2005 0900	5.92	-	5.40	8/31/2005 0900	1.44	1.67	1.05
8/17/2005 1500	3.17	-	3.84	8/31/2005 1500	0.92	1.39	0.78
8/18/2005 0300	0.27	-	1.32	8/31/2005 2100	0.63	0.68	0.16
8/18/2005 0900	8.87	7.11	5.44	9/1/2005 0300	0.40	0.31	0.19
8/18/2005 1500	3.45	4.63	3.59	9/1/2005 0900	2.29	1.70	1.34
8/18/2005 2100	1.57	1.51	1.39	9/1/2005 1500	1.61	1.29	1.16
8/19/2005 0300	0.58	0.79	0.69	9/2/2005 0300	0.25	-	-
8/19/2005 0900	0.52	0.51	0.49	9/2/2005 0900	5.41	-	-
8/19/2005 1500	0.39	0.52	0.51	9/2/2005 1500	3.36	-	-
8/19/2005 2100	0.23	0.24	0.31	9/2/2005 2100	1.08	-	-
8/20/2005 0300	0.23	0.09	0.36	9/3/2005 0300	0.67	0.53	-
8/20/2005 0900	6.08	2.44	2.58	9/3/2005 0900	1.11	0.89	0.95
8/20/2005 1500	4.24	4.10	3.31	9/3/2005 1500	0.87	-	0.68
8/20/2005 2100	0.61	3.09	-	9/3/2005 2100	0.19	0.39	0.33
8/21/2005 0300	0.56	1.41	-	9/4/2005 0300	0.55	0.37	0.33
8/21/2005 0900	3.06	3.51	-	9/4/2005 0900	1.86	-	1.24
8/21/2005 1500	1.80	4.25	-	9/4/2005 1500	1.19	-	0.96
8/21/2005 2100	0.17	-	0.56	9/4/2005 2100	0.38	0.38	0.43
8/22/2005 0300	0.27	0.19	0.35	9/5/2005 0300	0.38	0.37	0.43
8/22/2005 0900	3.57	2.62	2.42	9/5/2005 0900	2.51	-	1.23
8/22/2005 1500	2.40	1.35	1.80	9/5/2005 1500	1.48	0.87	1.19
8/22/2005 2100	0.30	0.56	0.43	9/5/2005 2100	0.18	0.28	0.27
8/23/2005 0300	0.38	0.50	0.54	9/6/2005 0300	0.18	0.20	-
8/23/2005 0900	5.99	4.46	4.01	9/6/2005 0900	2.07	0.57	-
8/23/2005 1500	3.43	2.16	2.33	9/6/2005 1500	1.78	0.99	1.24
8/23/2005 2100	0.24	-	0.53	9/7/2005 0900	4.56	1.75	-
8/24/2005 0300	0.66	-	-	9/7/2005 1500	1.40	1.36	-
8/24/2005 0900	3.61	1.43	2.54	9/8/2005 0900	6.60	2.78	-
8/24/2005 1500	2.61	2.43	1.86	9/8/2005 1500	7.48	-	-
8/24/2005 2100	0.19	0.39	0.37	9/8/2005 2100	0.18	-	-
8/25/2005 0300	0.16	0.37	0.38	9/9/2005 0900	5.72	2.78	-

### Appendix C: Measurements of NH<sub>3</sub> Concentration

Concentrations ( $\mu\text{g m}^{-3}$ ) of NH<sub>3</sub> from annular denuder systems (ADS NH<sub>3</sub>) and 6-h mean NH<sub>3</sub> concentrations from both MARGA systems (M-116 and M-216).

Date/ Time (EDT)	ADS NH <sub>3</sub> ( $\mu\text{g m}^{-3}$ )	M-116 ( $\mu\text{g m}^{-3}$ )	M-216 ( $\mu\text{g m}^{-3}$ )	Date/ Time (EDT)	ADS NH <sub>3</sub> ( $\mu\text{g m}^{-3}$ )	M-116 ( $\mu\text{g m}^{-3}$ )	M-216 ( $\mu\text{g m}^{-3}$ )
8/12/2005 1500	0.94	-	-	8/27/2005 0900	0.73	0.38	-
8/13/2005 0300	1.63	-	-	8/27/2005 1500	0.32	0.31	0.15
8/13/2005 0900	0.72	-	-	8/27/2005 2100	0.15	0.26	0.38
8/13/2005 1500	0.59	-	-	8/28/2005 0900	0.41	0.72	0.20
8/13/2005 2100	0.53	-	-	8/28/2005 1500	0.34	0.45	0.16
8/14/2005 0900	1.10	-	-	8/28/2005 2100	1.25	0.12	0.26
8/14/2005 1500	1.50	-	-	8/29/2005 0300	1.02	-	-
8/14/2005 2100	0.73	-	-	8/29/2005 0900	0.22	-	-
8/15/2005 0900	0.64	-	-	8/29/2005 2100	2.34	0.21	-
8/15/2005 1500	1.58	-	-	8/30/2005 0300	0.78	0.11	0.19
8/15/2005 2100	0.18	-	-	8/30/2005 0900	2.00	0.39	-
8/16/2005 0300	1.91	-	-	8/30/2005 1500	1.09	0.24	-
8/16/2005 0900	0.46	-	-	8/30/2005 2100	0.71	-	-
8/16/2005 1500	0.34	-	-	8/31/2005 0900	0.81	0.28	0.13
8/16/2005 2100	0.35	-	0.11	8/31/2005 1500	0.51	0.23	0.10
8/17/2005 0300	0.59	-	-	9/1/2005 0300	0.37	0.11	-
8/17/2005 0900	1.01	-	0.49	9/1/2005 2100	0.33	-	-
8/17/2005 1500	1.35	-	0.59	9/2/2005 2100	0.72	-	-
8/17/2005 2100	0.24	-	-	9/3/2005 1500	0.20	-	0.30
8/18/2005 0300	0.41	-	0.33	9/3/2005 2100	0.31	0.16	0.12
8/18/2005 0900	0.83	0.72	0.62	9/4/2005 0900	0.31	-	-
8/18/2005 2100	0.19	0.18	0.25	9/4/2005 1500	0.67	-	0.25
8/19/2005 0300	0.42	0.11	0.13	9/4/2005 2100	0.91	0.10	0.09
8/19/2005 0900	0.42	-	0.09	9/5/2005 0300	0.27	0.13	0.27
8/19/2005 2100	1.11	-	-	9/5/2005 0900	0.13	-	0.47
8/20/2005 0300	0.78	-	0.13	9/5/2005 1500	0.26	0.16	0.19
8/20/2005 0900	0.63	0.51	0.55	9/5/2005 2100	0.21	0.08	-
8/20/2005 1500	0.61	0.30	0.44	9/6/2005 0300	0.71	0.18	-
8/20/2005 2100	0.32	-	-	9/6/2005 0900	1.17	0.35	-
8/21/2005 0900	0.40	0.15	-	9/6/2005 2100	0.45	0.43	-
8/21/2005 1500	0.49	0.11	-	9/7/2005 0300	0.27	0.25	0.26
8/22/2005 0300	0.48	-	0.08	9/7/2005 0900	0.15	0.27	0.29
8/22/2005 0900	0.81	0.32	0.58	9/7/2005 1500	0.82	0.09	0.12
8/22/2005 1500	0.19	0.10	0.36	9/7/2005 2100	0.78	-	-
8/23/2005 0300	0.18	0.50	0.20	9/8/2005 0300	1.34	-	-
8/23/2005 0900	0.61	0.30	0.43	9/8/2005 0900	1.02	-	-
8/24/2005 0300	0.31	-	-	9/8/2005 1500	1.07	-	-
8/24/2005 0900	1.09	0.49	0.57	9/8/2005 2100	0.42	-	-
8/24/2005 1500	2.05	0.30	0.44	9/9/2005 0300	0.80	-	-
8/25/2005 0900	0.39	0.58	0.59	9/9/2005 0900	0.92	0.81	0.66
8/25/2005 1500	0.23	0.33	0.33	9/8/2005 2100	0.42	-	-
8/25/2005 2100	0.34	0.18	0.21	9/9/2005 0300	0.80	-	-
8/26/2005 0900	0.85	0.46	0.49	9/9/2005 0900	0.92	0.81	0.66