

Air Quality Study in the Vicinity of Harrisburg, NC

ATAST Investigation Number: 06020

August 3, 2006 - August 23, 2007

NC Division of Air Quality

Toxics Protection Branch

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ACRONYMS

AQL - Air Quality Laboratory of the Toxics Protection Branch
ATAST - Air Toxics Analytical Support Team
COC - Chain of Custody
DAQ - Division of Air Quality
EPA-Environmental Protection Agency
ICP-MS – Inductively Coupled Plasma Mass Spectrometry
LDL – Lower Detection Limit
LQL - Lower Quantitation Limit
m³ - Cubic meter
mL - Milliliter (10⁻³ Liters)
µg - Microgram (10⁻⁶ grams)
mg - Milligram (10⁻³ grams)
MRO – Mooresville Regional Office
NCAAQS - North Carolina Ambient Air Quality Standard
ng - Nanogram (10⁻⁹ grams)
NIST - National Institute of Standards and Technology
ppm - Parts per million
QA/QC - Quality Assurance/Quality Control
QAM - Quality Assurance Manager
QAPP – Quality Assurance Project Plan
SEM-EDS – Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy
SOP - Standard Operating Procedures
TPB - Toxics Protection Branch

1.0 INTRODUCTION

The Mooresville Regional Office (MRO) received numerous complaints from businesses near a galvanizing facility, Galvan Industries, in the town of Harrisburg, NC. These complaints describe odors, “acidic” gases, hazy smoke, and particulate deposition, which are believed to be emanating from the nearby galvanizing operation and are thought to be causing damage to buildings and motor vehicles. Assistance from the Toxics Protection Branch (TPB) was requested by the MRO to characterize chemical composition of the odors, hazy smoke and particulate deposits. After discussions with MRO staff and owners of property adjoining the facility, the study was carried out from August 2006 to August 2007, the results of which are presented in this report.

1.1 Background

Galvan Industries, Inc., in operation since the 1960’s, performs hot zinc galvanizing of steel and iron materials used for a wide range of products in order to provide protection to the metal against corrosion. As described by the MRO, the galvanizing process involves processes that include shot blasting, cleaning and degreasing with sodium hydroxide and sulfuric acid, pre-fluxing with a mixture of zinc chloride and ammonium chloride, and applying a zinc coating of iron and steel products in a kettle. The facility has typically operated sixteen hours per day (two shifts per day), six days per week, fifty-two weeks per year.

The main part of the facility is located in Cabarrus County, although the western part of the contiguous facility property, including the shot-blasting building, is located in Mecklenburg County. This area is reported as mixed zoning; a combination of commercial, light industrial, office, and residential land use. Many complaints have originated from owners of property adjacent to Galvan’s northern fence line. These properties consist of a commercial storage facility and an office complex. Highway 49 runs in an east to west direction to the north of these properties. A railroad line marks the southern border of the Galvan Industries location. A concrete mixing facility is located about a quarter mile to the southeast of Galvan Industries.

1.2 Study Design

The complaints received by the MRO consisted of unpleasant odors, hazy smoke, a rust-colored precipitate and experiences with burning sensations of the eyes, nose, throat and skin that some complainants associated with “acidic” vapors. Other observations noted damaged or dead

vegetation at the northern facility fence line.

Acid gases and aerosols were selected for monitoring due to effects on property and people near the facility fence line. Some of those effects observed by DAQ staff included damage to trees along the fence line and physical sensations of burning eyes and nose.

A Zellweger Analytics chemical tape sampler was initially set up at the ADS Monitoring Site, for the purposes of performing “screening” monitoring for acid gases. On September 9, 2006, a Weekly Air Particulate Sampler designed for simultaneous particle and gas collection using Annular Denuder technology (or Annular Denuder System as they are referred to in this report (ADS))¹ was installed to provide the more precise sampling of gas and aerosol composition. The sites were also equipped with meteorological sensors.

In addition to acid gas and aerosol sampling, total suspended particulate (TSP) was selected for monitoring due, in part, to the presence of deposits of a rust colored material observed on nearby property, and reports of smoke or a “cloudy haze” compel the use of filter sampling. Staff observed that the rust colored deposits adhered to surfaces so thoroughly that obtaining appropriate samples of that material from deposits without contamination from the underlying material could be difficult to accomplish. Filter TSP concentrations are compared with the North Carolina Ambient Air Quality Standard (NCAAQS) for TSP². If necessary, particulate matter composition could be determined by using other analytical methods.

The purpose of this study was to characterize the chemical composition of the air quality immediate to the complainants’ properties through the identification and measurement of acidic gases, aerosols and particulates in their vicinity.

1.2.1 Monitoring Activities

The Quality Assurance Project Plan (QAPP) (See Appendix A) was developed based on discussions with MRO, TPB field observations, and research on air emissions from galvanizing processes. TPB monitoring practices for urbanized areas and the capacity and capabilities of TPB were also considered.

¹ The technology was designed to meet USEPA Compendium Method IP-9 and Compendium Method IO-4.2, *Determination of Atmospheric Fine Particles and Gases in Ambient Air Using Annular Denuder Technology*.

² North Carolina Administrative Code 15A 2D.0403

The sampling plan was devised to collect samples as either a composite 24-hr sample or collect samples on a fixed-time interval continuous basis depending on the compound being sampled and the sampling method used. The following table outlines groups of monitored compounds, the sampling media used, the sample collection time interval and the collection location(s). Meteorological data were collected during sampling periods using 4 and 7-meter towers.

General Sampling Information			
Type of sample	Monitor type	Time Interval	Site(s)
Sulfuric Acid (H ₂ SO ₄)	Chemical tape meter	2 min	ADS Monitoring Site
Annular Denuder System (ADS)	Coated denuders; Teflon and nylon filters	24 hr	ADS & Off-Axis Monitoring Sites
Total Suspended Particulates (TSP)	Hi-Vol samplers with glass filters	24 hr	TSP & Off-Axis Monitoring Sites
Meteorology	Climatronics Tacmet II sensors	5 min 15 min	ADS & Off-Axis Monitoring Sites

Table 1

1.2.2 Sampling Sites

An ambient air-monitoring site was installed near the Galvan Industries’ northern fence line, in the parking lot directly north of the facility. This site contained the tape meter and ADS system. Meteorological equipment to measure wind speed, wind direction, temperature, relative humidity, and barometric pressure was also installed. This site is indicated as “**ADS Monitoring Site**” in Figure 1. A monitoring site for TSP was established at a commercial storage facility with property contiguous to Galvan Industries’. This is shown as “**TSP Monitoring Site**” in Figure 1. This site was equipped with two TSP monitors that alternated sample collection every third day beginning on December 22, 2006.

A site located out of the prevailing wind direction and further away from the galvanizing process was established about a quarter mile west of the study area. The purpose of this monitoring site was to provide TSP and ADS samples believed to be minimally, or uninfluenced by any activities from the galvanizing process. It was located directly west of the study area so as to be minimally influenced by advection of emissions from the galvanizing process by prevailing winds, which were observed to be most often from the southwest and the northeast. By virtue of

this location it is presumed to be “off-axis” of the prevailing wind direction and therefore, of any particulate or gas plume emitted by the galvanizing facility. This site is designated as the “**Off-Axis Site**” and its location is shown in Figure 1. TSP samples were collected at this site beginning January 24, 2007.



Figure 1. Site Locations

The details of sampling systems and periods of operation are listed in Table 2.

ADS Monitoring Site			
<i>System</i>	<i>Sampling period</i>	<i>Sampling parameters</i>	<i>Sampling duration</i>
Tape meter	August 3, 2006 to August 23, 2006	Mineral acids	Continuous
Meteorological Systems (Sonic)	August 3, 2006 to August 23, 2007	Wind speed, direction temperature, relative humidity and barometric pressure	Continuous
ADS-Weekly Air Particulate Sampler	September 9, 2006 to April 4, 2007	Acid gases and fine particulates (PM 2.5)	24-hr samples 6 days per week
TSP Monitoring Site			
<i>System</i>	<i>Sampling period</i>	<i>Sampling parameters</i>	<i>Sampling duration</i>
Total Suspended Particulate matter (TSP) Samplers	December 22, 2006 to August 22, 2007	Total suspended particulate matter	24-hour samples every third day
Meteorological Systems (Crossarm)	August 23, 2007 & continuous	Wind speed, direction temperature, relative humidity and barometric pressure	Continuous
Off-Axis Monitoring Site			
<i>System</i>	<i>Sampling period</i>	<i>Sampling parameters</i>	<i>Sampling duration</i>
ADS-Weekly Air Particulate Sampler	January 19, 2007 to April 4, 2007	Acid gases and fine particulates (PM 2.5)	24-hr samples 6 days per week
Total Suspended Particulate matter (TSP) Samplers	January 24, 2007 to August 22, 2007	Total suspended particulate matter	24-hour samples every third day
Meteorological Systems	January 19, 2007	Wind speed, direction temperature, relative humidity and barometric pressure	Continuous

Table 2. Site Configurations

1.2.3 Sampling Study Chronology

The air monitoring study began on August 3, 2006 with the installation of the Zellweger tape meter for detecting mineral acids and meteorological sensors at the initial site, identified as the ADS Monitoring Site. Sampling for acid gases and fine particulates using a Weekly Air Particulate Sampler with Annular Denuders (ADS) commenced on September 9, 2006. ADS collected 24-hour samples from September 9, 2006 to April 4, 2007 on a six-day per week sample schedule.

Samplers for Sampling for Total Suspended Particulate matter (TSP) began on December 22, 2006 at the location identified as the TSP Monitoring Site and collected 24-hour samples on an every- third-day schedule through August 2007.

Sampling at the Off-Axis Site began January 19, 2007. The site was equipped with Weekly Air Particulate Sampler with Annular Denuders (ADS) for acid gases and fine particulates and meteorological sensors. Samplers for Total Suspended Particulate matter (TSP) were installed on January 24, 2007.

Tape meter sampling rapidly concluded on August 23, 2006. Although ADS sampling operated for different time periods, all ADS sampling was concluded on April 4, 2007. TSP sampling by TPB was concluded at all sites on August 22, 2007. On August 23, 2007, the TPB decommissioned the TSP samplers used in this study. The meteorological systems at the ADS Monitoring Site were decommissioned. On the same date, meteorological monitoring was added to the TSP Monitoring Site. The meteorological system at the Off-Axis Site remains operational while additional monitoring by the DAQ continues with oversight by the MRO.

1.2.4 Quality Assurance/Quality Control

The QAPP developed for TSP monitoring by the DAQ Ambient Monitoring Section was followed for all 24-hour integrated TSP samples, with some modifications of calibration and audit method that are believed to increase both accuracy and precision of the method. Standard operating procedures (SOPs) were followed for ADS sampling. These SOPs include QA/QC activities. The TPB QAPP procedures for meteorological data were followed. The calibration of the Zellweger Single Point Monitor was checked in accordance with the manufacturer.

2.0 Meteorological Data

Each site was equipped with meteorological sensors that recorded data at 5 or 15-minute intervals at a height of 4 meters at the ADS Monitoring Site and seven meters for the Off-Axis Site. Data were collected for wind speed, wind direction, wind direction standard deviation, temperature, barometric pressure and relative humidity. Wind speed and direction varied significantly at the two sites due to micrometeorological differences, therefore in the event that one sensor malfunctioned, data from the other site was not substituted in the meteorological data analysis.

Meteorological data collected for this study served two purposes. First, the temperature and barometric pressure data was used to calculate correction factors for TSP flow measurements to correct the sample volumes to a standard temperature and pressure. Second, the wind speed and wind direction data were used to construct wind roses for each 24-hour sample period to causally relate sources in the event of high TSP or ADS readings. For convenience, the daily wind roses for the ADS sampling period are included in Appendix B. The wind roses for the TSP sample days are presented in Appendix C. Section 5 also displays the wind roses for days in which the TSP was above the 24 hour NCAAAQS of 150 ug/m^3 .

The wind roses describe the direction *from* which the wind was blowing, and present the wind speeds from those directions as rays of varying lengths and color representing the percentage of time the wind originated from that direction and the range of speeds observed. To illustrate how to interpret a wind rose, Figure 2. is used as an example. In this figure, the value of 0% in the center represents the percentage of the data below the lowest wind speed (see the key at bottom of the graph), in this case one mile per hour. The three rays in the figure show the direction from which the wind was blowing during the 24-hour period. In this case, the wind was almost exclusively from the southwest, with the wind speed between 1 and 15 miles per hour. The wind rose also shows that the winds were from the southwest approximately 62% of the time, from the west-southwest approximately 33% of the time, and from the south-southwest approximately 5% of the time. Because interest is in a specific site location, and its proximity to the galvanizing facility, light and variable winds were included in all datasets. Each wind rose consists of data for the 24-hour sample day. The wind rose does not give information about the temporal wind direction variations, and only indicates the percentage of time during the sampling period that the winds originated from a particular direction.

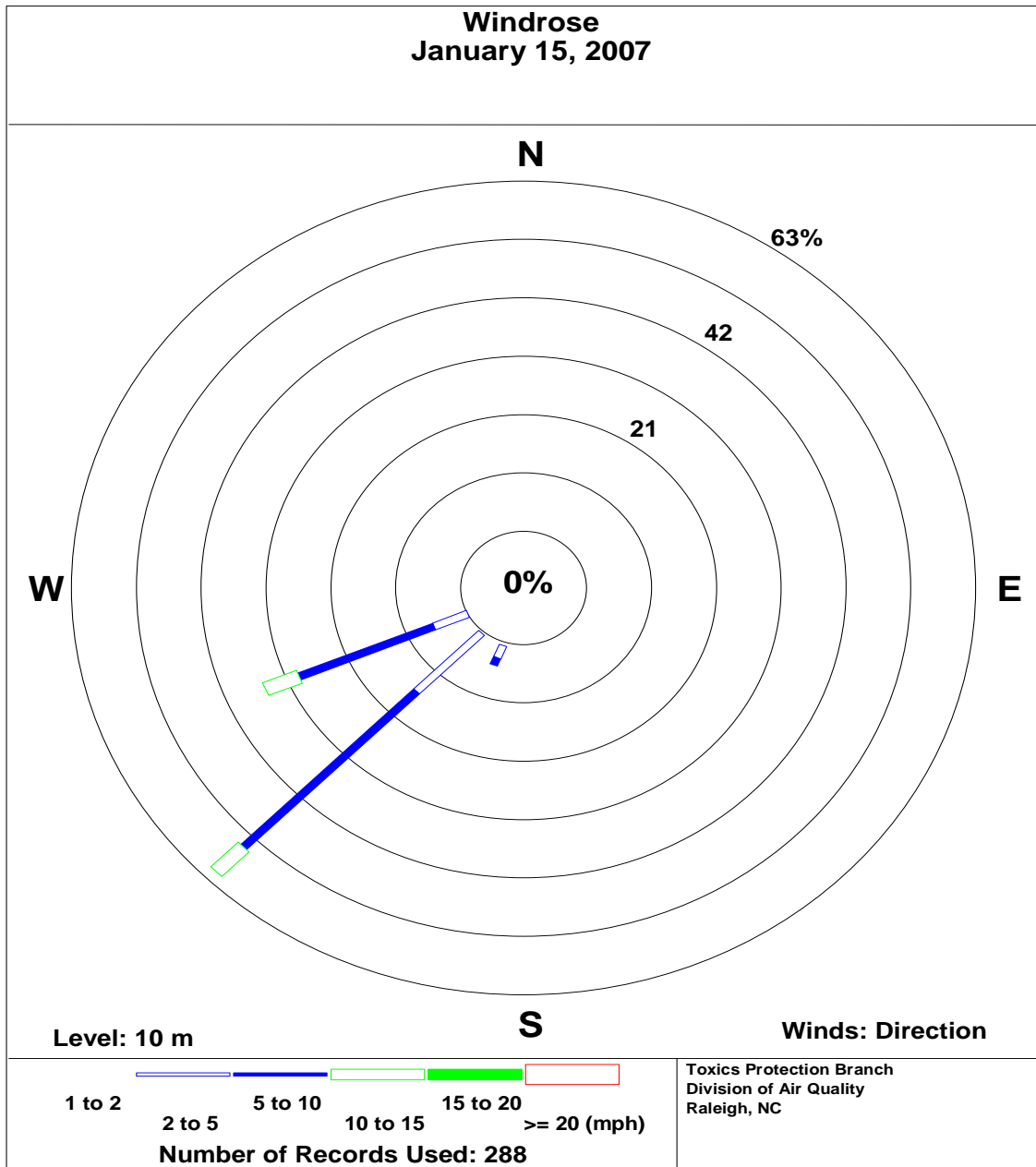


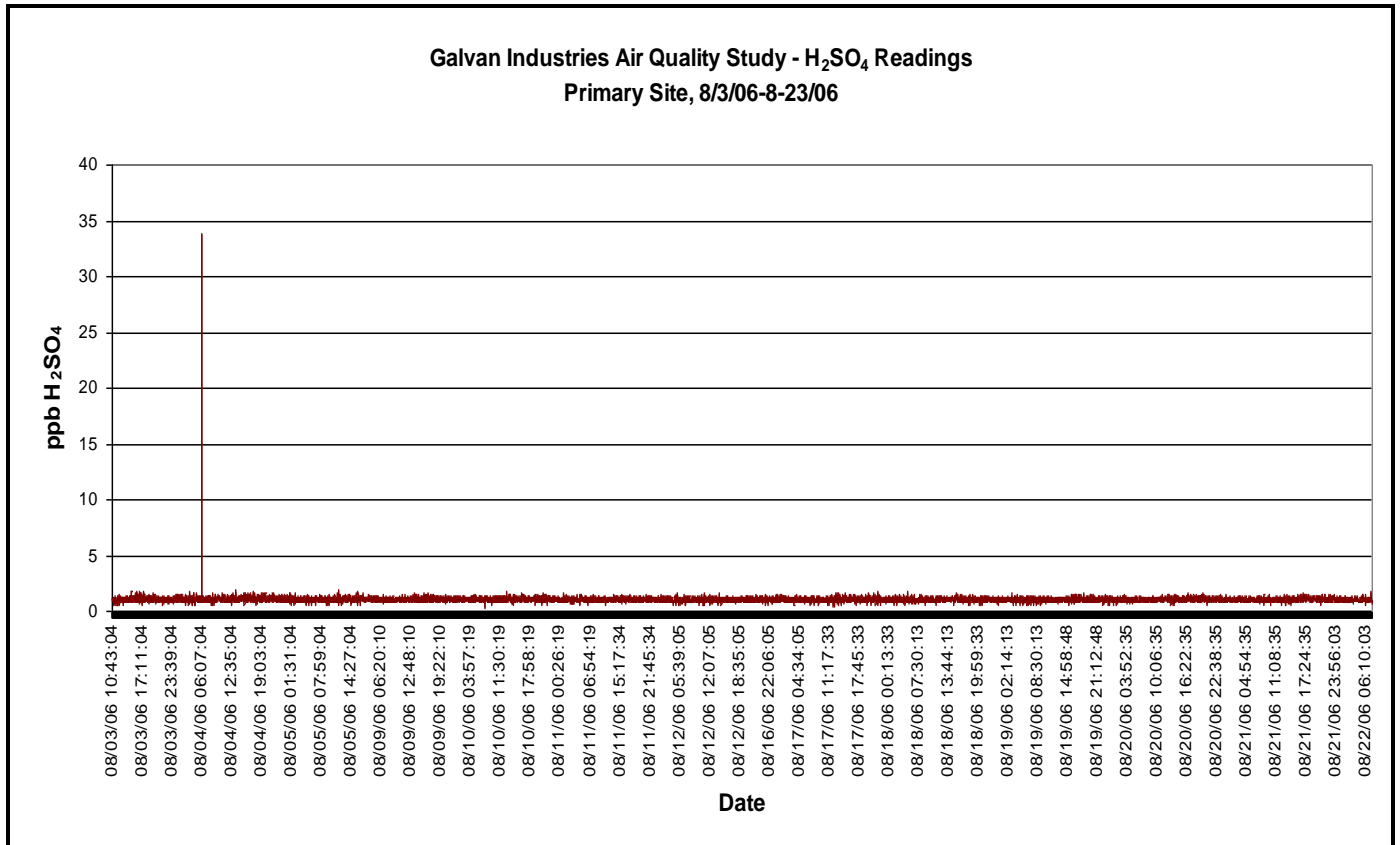
Figure 2. Example of Wind Rose

3.0 CHEMICAL TAPE MONITORING

Sulfuric acid monitoring was conducted using a Honeywell (Zellweger) MDA Single Point Monitor (SPM) equipped with a chemically treated paper tape specific for mineral acids and an LED optical sensor that monitors color development. Quantitation is based on the degree of color change. The manufacturer has determined its Lower Detection Limit (LDL) for sulfuric acid to be 26 parts per billion (ppb).

Measurements from the ADS Monitoring Site were continuously data logged and downloaded weekly for data analysis using a Logic Beach Data Logger. Data were collected every two minutes, from August 2 to August 23, 2006 for a total of 8,100 data points. Of these values, all but one were below the LDL of 26 ppb (see Figure 3). Although the SPM data showed a low or negative response to mineral acids, TPB staff experienced irritating effects such as burning of skin, eyes and nose from the area surrounding the SPM and at other times observed a cloudy haze. ADS systems were installed shortly thereafter. Use of the ADS is generally a more accurate and sensitive method for sampling of acidic gases and aerosols in ambient air.

**Figure 3. Mineral Acids measured as sulfuric acid at ADS Monitoring Site
August 3-August 23, 2006.**

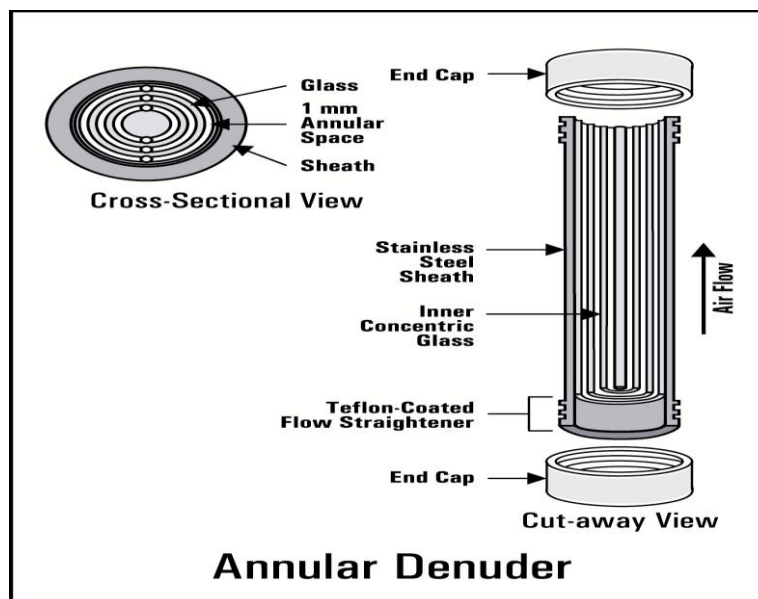


4.0 ANNULAR DENUDER SYSTEM MONITORING

4.1 Method

Annular Denuder System (ADS) monitoring was done using EPA Compendium Method IO-4.2, “*Determination of Reactive Acidic and Basic Gases and Strong Acidity of Atmospheric Fine Particles (<math> <2.5\mu\text{m}</math>)*” (Appendix D). Weekly Air Particulate Sampler (URG Corporation’s³), Model URG-2000-01J, was used in this study. The sample collection occurs via two annular denuders and a filter pack connected in series. The annular denuders consist of concentric cylinders of chemical-coated glass that react with acidic or basic gases in the sample, see Figure 4.1. The denuders take advantage of the difference in diffusion and chemical properties of gases and particles. For example, gases such as SO_2 and HNO_3 have diffusion coefficients of about 0.15 cm/second while particles of aerodynamic size between 0.1 and 2.5 micrometer have diffusion coefficients less than 0.05 cm/second. Therefore, with laminar airflow, acidic gases passing through an annular denuder space can be selectively removed from the air stream, if the walls of the denuder are coated with an alkaline material such as sodium carbonate. The URG multi-channel denuders, used in the present study, are composed of two concentric glass tubes with a closed cylinder in the center, all of which are enclosed in a Teflon™ coated stainless steel sheath. This sheath not only prevents glass denuder breakage but also serves as a flow straightening section. The inner surfaces of these tubes are etched to provide greater surface area for coating.

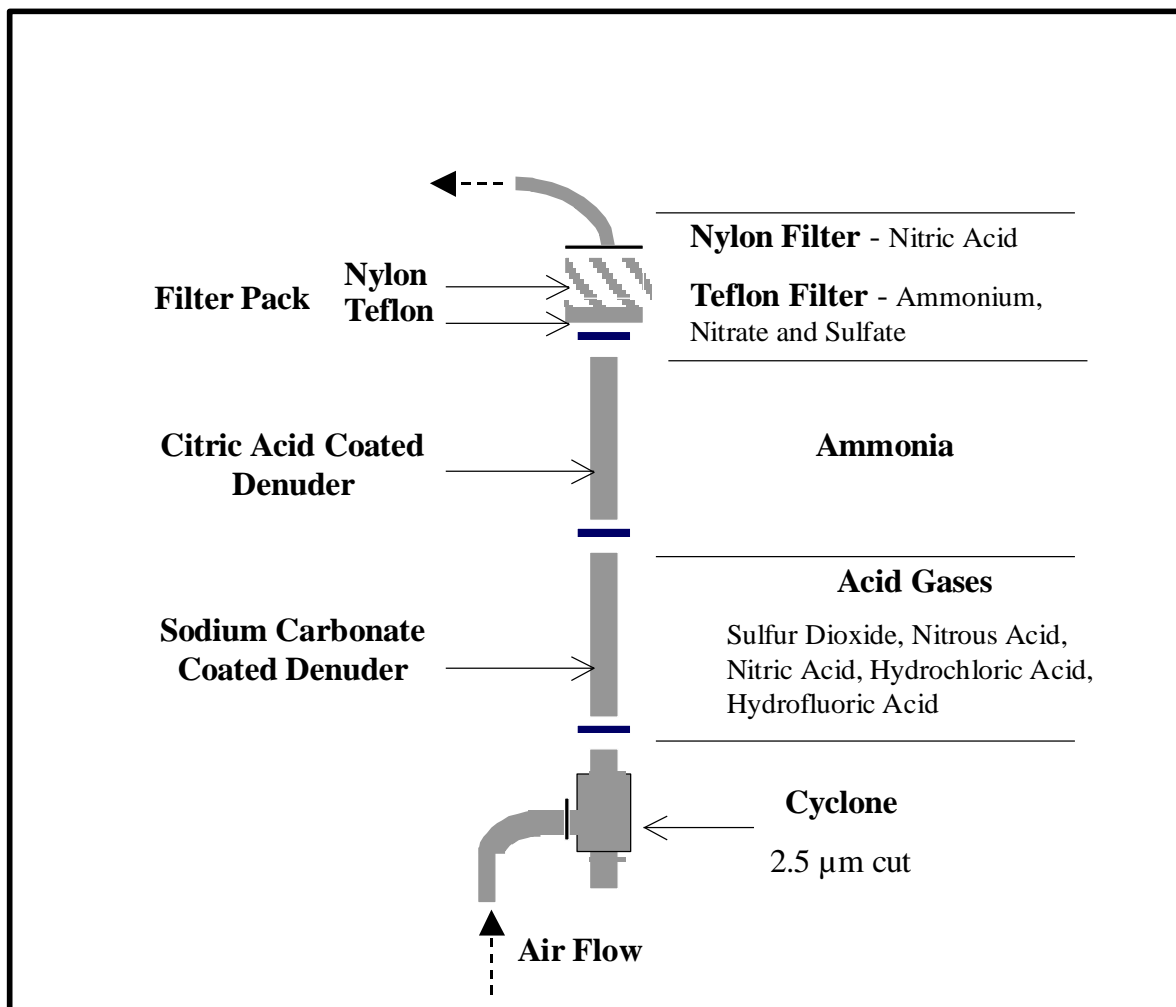
Figure 4.1 Annular Denuder Internal Schematic with Cross Sectional View



³ URG, Chapel Hill, NC, www.urgcorp.com

The schematic of a typical ADS field assembly is given in Figure 4.2. Air is drawn through the ADS by a pump. The airflow initially enters a Teflon™ coated cyclone that effectively removes coarse particles of >2.5 micrometers in aerodynamic diameter. The airflow then leaves the cyclone and enters the first of the two denuders that are connected in series. From this point, the air stream passes only through coated glass annular space until it reaches the filter pack. The first denuder is coated with sodium carbonate, Na₂CO₃ (A 50% [v/v] solution of methanol in de-ionized water containing 1% [w/v] glycerol and 1% [w/v] Na₂CO₃) to collect acidic gases and the second with citric acid, C₆H₈O₇ (A 50% [v/v] solution of methanol in de-ionized water containing 1% [w/v] C₆H₈O₇) to collect basic gases.

Figure 4.2 Typical ADS Field Assembly

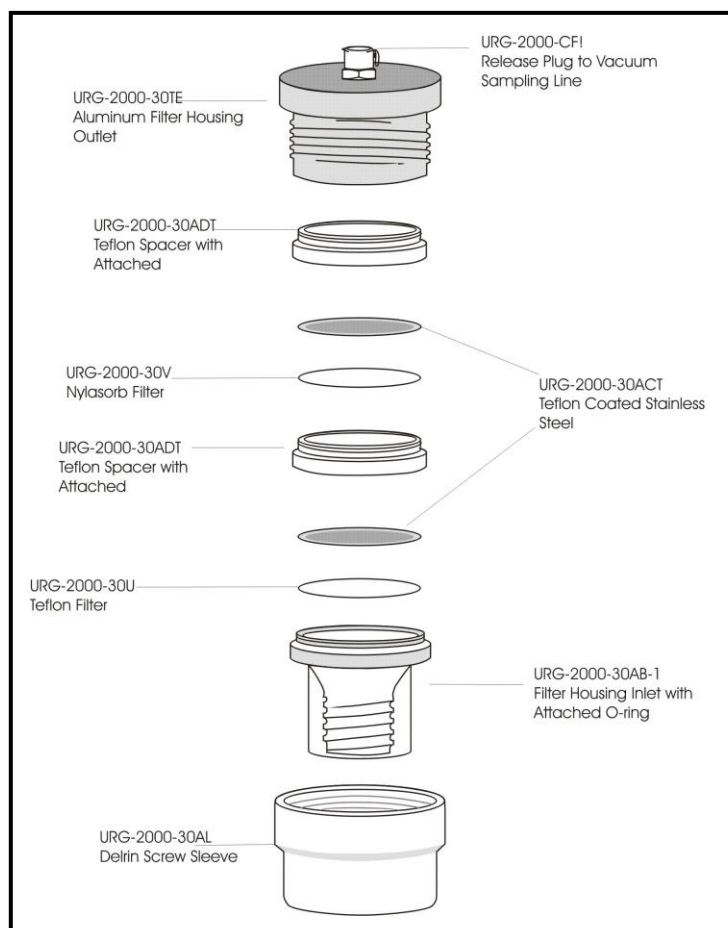


Since the airflow through the annular denuders must be laminar in order to ensure that the gases separate from the fine particles, the concentric tubes are inset approximately 25 mm from the flow entry end of the annular denuder (see Figure 4.1) to allow the air stream to become laminar

before entering the reactive section. Once the air stream leaves the reactive denuder section, fine particles ($PM_{2.5}$) are collected in the filter pack.

The filter pack consists of two filters, connected in series (see Figure 4.3). Ammonium, nitrate and sulfate are collected first by a 2- μ m, Teflon™ membrane filter⁴. The second filter, 1- μ m nylon filter⁵, collects any nitric acid that may result due to particulate decomposition from ammonium nitrate particles collected on the Teflon™ filter.

Figure 4.3 Filter Pack Internals



4.2 Sampling Period

Sampling for acid gases and fine particulates at the ADS Monitoring Site began on September 9, 2006 and continued until April 4, 2007. A total of 197 samples including blanks were collected over this sampling period. Sampling for acid gases and fine particulates at the Off-Axis

⁴ Whatman, North America PM_{2.5} membrane PTFE

⁵ Pall Corporation Nylasorb membrane disc filters

Monitoring Site began on January 19, 2007 and continued until April 4, 2007. A total of 88 samples including blanks were collected.

4.3 Sample Preparation and Collection

All denuders and filters for the ADS were prepared at the TPB Laboratory for field sampling following EPA Compendium Method IO-4.2 and procedures. As previously discussed, Weekly Air Particulate samplers were installed at the ADS Monitoring and Off-Axis Monitoring sites. The samplers operated continuously, collecting 24-hour samples for acidic and basic gases and fine particulate matter from midnight to midnight, for six consecutive days. On the seventh day, all samples were collected and a new set of denuders (8 assemblies) was installed at each sampling site. Sample collection resumed at midnight on the seventh day to initiate the next six consecutive day period of continuous 24-hour sampling. This schedule continued for the duration of the study resulting in a total of 22 cycles for the ADS Monitoring Site and 11 cycles for the Off-Axis Monitoring Site. Each sample assembly consisted of a filter pack (one each, Teflon™ and nylon filters) for fine particulate matter and acidity, and two denuders, one for acidic gases and the other for basic gases. Eight denuder assemblies were required because the first six assemblies were used for collecting samples for consecutive 24-hour periods, the seventh assembly was used for the field blank, and the eighth assembly was used as a trip blank. Chemical analysis of the field blank was considered an indication of passive adsorption of analytes under study during assembly and storage at the TPB Laboratory, transportation to the field and/or during installation in the ADS. A trip blank, sealed at the TPB Laboratory was included with the denuder assemblies from the lab to the field and back to assess if any analytes could be attributed to denuder preparation at the lab and/or during transportation. One trip blank was assigned per sampling site for each sample period.

The annular denuder sampling system collects gaseous nitric acid (HNO₃), nitrous acid (HNO₂), hydrochloric acid (HCL), hydrofluoric acid (HF), sulfur dioxide (SO₂), ammonia (NH₃), particulate sulfate (SO₄⁻), particulate nitrate (NO₃⁻), particulate ammonium (NH₄⁺) and other acidic particles. The acidic gases together with sulfur dioxide were collected on the sodium carbonate (Na₂CO₃) coated denuder and ammonia was collected on the citric acid denuder. Particulate sulfate, nitrate and ammonium were collected on the Teflon™ filter. Some of the particulate nitrate from the Teflon™ filter decomposes/evaporates over the collection period and is therefore collected on the nylon filter. Particulate nitrate from the Teflon™ filter is quantified

as nitric acid. Also collected on the Teflon™ filter are fine particles that contain hydrogen (H⁺) ions. The concentration of these H⁺ ions indicates the level of acid aerosols present in the ambient atmosphere.

4.4 ADS Sample Handling and Custody Requirements

At the DAQ-TPB laboratory, denuder and filter pack assemblies sufficient for one sampling cycle for each of the two sites, were prepared, labeled and assembled. As previously discussed, a denuder assembly consisted of a sodium carbonate coated denuder connected in series with a citric acid coated denuder followed by a filter pack that comprised of a Teflon™ and a nylon filter.

All prepared denuder assemblies were placed in shipping cases and transported to the sites together with the official Chain-of-Custody (COC) form and Field Data Sheets to record sample collection details. At the sampling site, denuder assemblies (8 assemblies) were installed in the ADS enclosure and the data logger was programmed to initiate ADS sampling at midnight.

All sampled denuders and filter packs, including field and trip blanks, were collected every seven days for the duration of the ADS sampling period. The procedure included placing the sampled denuders and filter packs in site-specific shipping cases for transportation, under COC, to the TPB laboratory for extraction and chemical analysis. Field Data Sheets were completed with required information at the respective sites, after sample retrieval, and these were sent along with the denuder samples to the TPB laboratory.

4.5 Sample Extraction and Analysis

A Dionex Model DX-500⁶ Ion Chromatograph (IC) coupled to a conductivity detection system was used to analyze denuder and filter extracts of the ADS field samples. The DX-50 pump was configured with 25- μ l pump heads to provide the low volume flows required by the 2-mm micro bore columns. Calibrations were performed (IC) calibrated using certified standards from Spex CertiPrep, Inc.⁷

All denuders and filters were prepared and extracted in accordance with standard operating

⁶ Dionex Corporation, Sunnyvale, CA www.dionex.com

⁷ Spex CertiPrep, Inc. Metuchen, NJ www.spexcsp.com

procedures and the recommended analytical procedures. The pH of the Teflon™ filter extracts were determined immediately after extraction with a pH meter coupled to an “internal” automatic temperature compensator. The meter was calibrated using a minimum of two standard buffer solutions prior to determinations.

The IC analytical method for determining inorganic acidic and basic constituents of the denuder and filter extracts was the EPA recommended method “*Determination of Reactive Acidic and Basic Gases and Strong Acidity of Atmospheric Fine Particle (<2.5 um)*”, *Method IO-4.2*.

Table 4.1 summarizes the IC instrument parameters used in the analysis of all field samples. The instrument was calibrated prior to each batch analysis with a reagent blank and seven calibration standards covering the typical range of field sample concentrations. The Reagent Blanks (RG), a mid-range Calibration Verification Standards (CVS), and the Laboratory Control Samples (LCS) were routinely interspersed in each batch of field samples and analyzed. The LCS vendor source(s) is different from calibration standards. A LCS for various analytes were analyzed and recoveries calculated to 1) verify accuracies of the instrument calibration standards and 2) further document that the IC was operating within the acceptable limits during sample analyses. Both the LCS and calibration standards were purchased from outside commercial sources and are traceable to the National Institute of Standards and Technology (NIST)⁸.

⁸ NIST is a non-regulatory agency within the U.S. Department of Commerce and provides standard reference materials

Table 4.1 Ion Chromatograph Instrument Parameters

Parameter	Anion Analysis	Cation Analysis
Analytical Column:	AS9-HC, 2-mm x 250-mm (Dionex Corporation)	CS12A, 2-mm x 250-mm (Dionex Corporation)
Guard Column:	AG9-HC, 2-mm x 50-mm (Dionex Corporation)	CG 12A, 2-mm x 50-mm (Dionex Corporation)
Eluent:	10 mM Sodium Carbonate	15 mM H ₂ SO ₄
Flow Rate:	0.25 mL/min	0.25 mL/min
Back Pressure:	<1600 psi	<1600 psi
Injection Volume:	5 µL (Loop)	5 µL (Loop)
Suppressor:	ASRS-Ultra, (2-mm) Auto Suppression Recycle Mode (Dionex Corporation)	CSRS-Ultra, (2-mm) Auto Suppression Recycle Mode (Dionex Corporation)
Background Temperature	<25 µS Ambient	< 2 µS Ambient

Table 4.2 lists the quality control (QC) limits for the IC analysis of the denuder and filter extract samples. Included in this table are definitions of acronyms commonly associated with chemical analysis of samples.

Table 4.2 Quality Control Limits For Ion Chromatography

QA Parameter	Control Limits	Frequency	Comments
Laboratory Reagent Blank (LRB)	<2X LQL	Daily	
Laboratory Control Sample (LCS)	75 – 125% Recovery	Daily	
Fortified Matrix Sample (FMS)	75 – 125% Recovery	1 per batch of 8 samples	<i>Fortified Field Sample (Spiked 1 –5 times the measured value)</i>
Field or Lab Duplicates	Less than ±20% Relative Percent Difference	1 per batch of 8 samples	<i>Fortified Field Sample or Split Field Sample</i>
Calibration Check Standard	85 – 115% Recovery (mid range)	Every 10 Samples	<i>75 – 125% Recovery if less than the mid range of the Standard Curve</i>
Initial Calibration Least Squares Regression	> .99 Correlation Coefficient (r ²)	Each Curve	<i>At least 5 std levels (not forced through 0)</i>
LOWER QUANTATION LEVEL (LQL) – The lowest standard used in determining the standard curve.			
CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.			
CALIBRATION CHECK STANDARD -- An individual Calibration solution that verifies previously established calibration curves.			
DUPLICATE -- Two sample aliquots, taken in the laboratory from a single sample bottle, and analyzed separately with identical procedures. The analyses indicate precision associated specifically with the laboratory procedures, removing any associated variables attributed to sample injection, preservation, or storage procedures.			
LABORATORY CONTROL SAMPLE (LCS) -- An aliquot of reagent water or other blank matrices to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.			
LABORATORY FORTIFIED MATRIX SAMPLE (FMS) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The FMS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the FMS corrected for background concentrations.			

4.6 Results and Discussion

During the study, 150 24-hour integrated samples were collected at the ADS Site, and 66 24-hour samples were collected at the Off-Axis Site using the ADS samplers. Chemical pollutants monitored and quantified using ADS sampling included gaseous nitrous (HNO_2) and nitric (HNO_3) acids, sulfur dioxide (SO_2) and ammonia (NH_3). The particulate fraction of the sample was analyzed for nitrate (NO_3^-), sulfate (SO_4^{2-}), and ammonium (NH_4^+). The average, minimum, and maximum measurements for each analyte at both sites for the study period are summarized in Table 4.3. Analytical results of individual samples are presented in Appendix E.

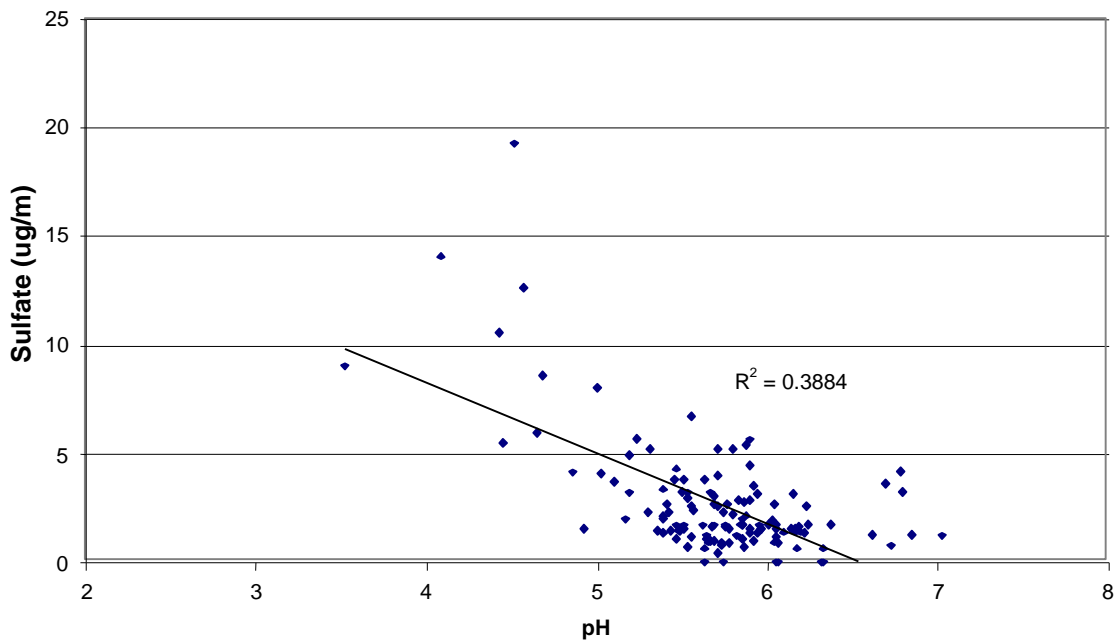
Table 4.3 Analytical results for ADS samples

	Analyte	Minimum		Maximum		Average		Standard Deviation	
		ADS Site	Off-Axis	ADS Site	Off-Axis	ADS Site	Off-Axis	ADS Site	Off-Axis
Acidic/Basic Gases	HF (ug/m3)	0.00	0.00	3.93	1.09	0.78	0.30	0.62	0.23
	HCl (ug/m3)	0.00	0.00	17.57	2.05	0.66	0.29	1.92	0.39
	HNO3 (ug/m3)	0.00	0.00	37.97	12.14	2.01	1.58	3.26	2.48
	H3PO4 (ug/m3)	0.00	0.00	29.51	10.73	0.83	0.29	2.78	1.49
	SO2 (ug/m3)	0.00	0.00	22.96	19.45	5.49	5.77	4.30	4.09
	NH3 (ug/m3)	0.00	0.00	3.80	1.60	0.41	0.17	0.79	0.41
Particulates (Teflon Filter)	Acidity (pH)	3.53	4.96	7.03	7.05	5.71	5.65	0.53	0.47
	Fluoride (ug/m3)	0.00	0.00	1.08	0.29	0.01	0.01	0.10	0.05
	Chloride (ug/m3)	0.00	0.00	4.13	1.28	0.53	0.12	0.64	0.21
	Nitrate (ug/m3)	0.00	0.00	1.16	1.72	0.13	0.21	0.28	0.41
	Phosphate (ug/m3)	0.00	0.00	5.92	0.00	0.04	0.00	0.48	0.00
	Sulfate (ug/m3)	0.00	0.00	19.63	9.49	3.42	2.21	3.50	2.10
	NH4+ (ug/m3)	0.00	0.00	4.26	3.90	0.51	0.71	0.87	0.95
(Nylon Filter)	HNO3 (ug/m3)	0.00	0.00	4.90	4.06	0.43	0.66	0.77	0.75

One of the analytes targeted was sulfuric acid on the presumption that it would be emitted from the sulfuric acid baths, and would be collected on the Teflon™ filter of the ADS filter pack. Sulfuric acid aerosols captured by the Teflon™ filter would be detected by a low pH and the presence of sulfate in the filter extract. Sulfate may also be present in the form of other aerosols, such as ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$. However, due to the proximity of the ADS Site to the sulfuric acid baths, and the acrid smell noted in the area, it would be expected that sulfuric acid aerosol would dominate the sulfate fraction of the aerosols collected in the ADS samples. Figure 4.4 is a plot of the pH of the Teflon™ filter extracts with the measured sulfate in the extracts, showing the correlation between low pH (high acidity) and high sulfate concentration.

Figure 4.4 Sulfate vs. pH at ADS Site

**Sulfate correlated with pH in Teflon filter extracts from ADS Site,
9/9/07 - 3/7/07**

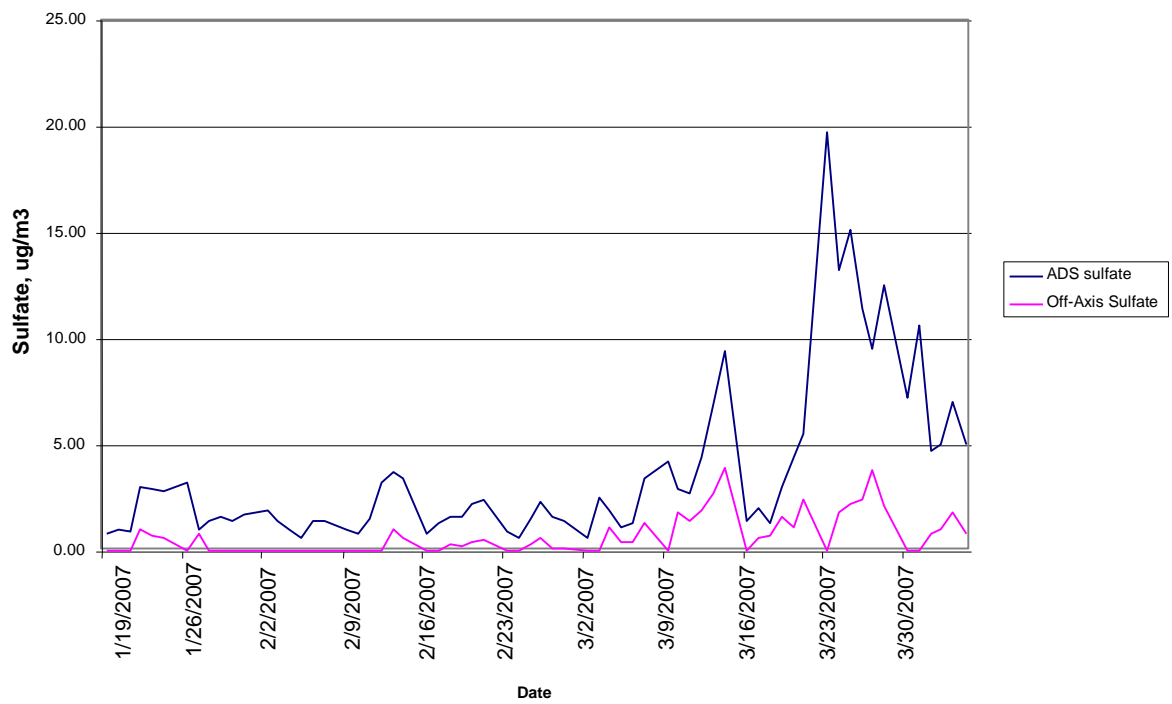


It is also possible to compare the aerosol sulfate concentrations of the two sites. The sulfate measurements at the ADS Site are plotted with those at the Off-Axis site in Figure 4.5, showing consistently greater sulfate concentrations at the ADS Site.

It should be noted that the ADS samplers are designed to sample only fine particulate matter, with particles of greater than 2.5 microns being removed by a cyclone prior to entering the denuder assemblies. Any particle with a diameter greater than this would not be sampled using this method.

Figure 4.5 Sulfate Particulate at ADS and Off-Axis Sites

Sulfate particulate at ADS and Off-Axis Sites, January 17 to April 4, 2007



5.0 TOTAL SUSPENDED PARTICULATE MONITORING

5.1 Method

Samples for TSP were collected using high volume Graseby-Anderson⁹ samplers. Each particulate sample was collected on a single 8 x10 inch, 0.3 µm pore size Whatman[®] EPM 2000 high purity glass microfiber filter. The filters were equilibrated to a constant relative humidity and weighed prior to sampling by the Ambient Monitoring Section of DAQ. The pre-weighed filters were installed in the TSP samplers and scheduled to begin sampling at midnight on the appointed day and to sample for a 24-hour period. The filters were collected at the time of the next filter installation, typically within a 3 to 6 day period, and transported under COC to the Ambient Monitoring Section to be equilibrated and re-weighed to obtain a total particulate weight in accordance with their Total Suspended Particulate Quality Assurance (QA) Plan Section 2.4 (see Appendix F). After obtaining the post-sampling weight, the filters were returned under COC to the Ambient Monitoring Particulate Laboratory for storage. The results were reported to the TPB project manager via the Ambient Monitoring Section's AQ-41 particulate monitoring data sheet. The TPB project manager then calculated the flow rate and TSP concentration for each 24-hour sample period using the calibration curve that was determined for each sampler at the beginning of the study, pre- and post-sample differential pressures, and the 24-hour average temperature and barometric pressure.

5.2 Quality Assurance and Quality Control Procedures

The TSP Samplers were calibrated prior to the start of the study in accordance with TPB Standard Operating Procedures and audited during the course of the study. Sampler pressure readings, which correspond to sample flow rate, were checked at the beginning and end of each sampling event. TPB performed quality assurance calculations for TSP. All audits of Off-Axis Site samplers were well within the accuracy limits established by EPA. Initial audits of TSP site samplers were well within the accuracy limits established by EPA, but final audits were 1% above the EPA limit and samplers were coated with brown residue.

5.3 Data Management

The Project Manager transferred total particulate weights for each sample manually from the AQ-41 data sheet to spreadsheet software. Final TSP values were calculated with electronic

⁹ Grasby Anderson, Atlanta, Georgia

software using the total particulate weight and the total sample volume. A final sample volume was calculated using 24-hour average temperature and pressure data collected by TPB meteorological instrumentation. The QA Manager verified all spreadsheet calculations.

5.4 Results

Beginning on December 22, 2006 and through August 22, 2007, 78 TSP samples were collected at the TSP Monitoring Site, not including collocated duplicate samples. Of these 78 sample events, the results of 10 were above the North Carolina Ambient Air Quality Standard (NCAAQS) of 150 ug/m^3 . There are corresponding samples from the Off-Axis Site for seven of these events, each of which shows a reduced particulate loading when compared to the TSP Site samples. These results are shown in Table 5.1 below. The table shows the results from each of the four TSP samplers at both sites. 'N/A' indicates that the sampler did not run on that day.

It should be noted that the samples collected on March 28 are all above 150 ug/m^3 on all four TSP samplers. The DAQ Ambient Monitoring Section, which provided the weights of the filters, observed that the filter characteristics were consistent with an increased amount of pollen typically seen during peak pollen season, and that might account for the increased particulate loading on all the filters. However, it should again be noted that the TSP Site concentrations are higher than the Off-Axis Site concentrations.

A failure of the meteorological sensor at the ADS Site prevented collection of wind direction data for the TSP Monitoring Site for a period from February 15 through March 20, 2007. Other meteorological parameters were unaffected. On all other days in which the TSP concentration

Table 5.1 Dates TSP Exceeded NCAAQs (150 µg/m³)

Date	TSP Monitoring Site		Off-Axis Site	
	Sampler 1	Sampler 2	Sampler 3	Sampler 4
1/15/07	N/A	201	N/A	N/A
2/20/07	N/A	211	N/A	N/A
3/7/07	191	N/A	62	N/A
3/13/07	169	N/A	91	N/A
3/28/07	225	229	180	167
4/3/07	N/A	168	N/A	93.
4/24/07	154	N/A	43	N/A
5/15/07	161	146	45	44
7/11/07	156	N/A	35	N/A
8/16/07	183	N/A	60	N/A

was determined to exceed 150 µg/m³, the wind direction is shown to be in large part from the southwest, suggesting a source of the particulates from that direction.

A table of all TSP results and wind roses from available meteorology for the TSP sample events are included in Appendix C.

6.0 METALS ANALYSIS OF TSP FILTER SAMPLES

6.1 Analysis by ICP/MS

To further characterize the particulate matter collected by TSP sampling, certain filters were selected for metals analysis by ICP-MS, in particular any metals such as zinc that might be produced by the galvanizing process. The filters were weighed in accordance with the Total Suspended Particulate QA Plan Section 2.4 as described in Section 4. After obtaining the post-sampling weight, the filters were then transported under COC to Eastern Research Group (ERG)¹⁰ for analysis in accordance with EPA Compendium Method IO-3.5, *Determination of Metals in Ambient Particulate Matter Using Inductively Coupled Plasma/Mass Spectrometry (ICP/MS)*.

Two sets of four TSP filter samples were taken to ERG for metals analysis, and were selected so as to characterize certain conditions at the TSP and Off-Axis Sites. The first batch of four samples consisted of paired filters from the two sites on two days, one day when there was a higher level of particulate loading at the TSP Site relative to the Off-Axis Site (2/17/07), and one day when the particulate loading was about the same at both sites (2/14/07). The goal was to determine if the additional particulate loading at the TSP Site would show any unusual amounts of metals that could suggest a source of particulates. The results of the metals analysis are shown in Table 6.1. These data show elevated levels of zinc at the TSP Site compared to the Off-Axis Site on both the ‘high’ and the ‘low’ days. The zinc content is remarkable; especially on the ‘high’ day given it is 9.4% of the total particulate loading by weight. The metals content of the samples are illustrated in graphical form in Figures 6.1, and the zinc content is shown in Figure 6.2.

¹⁰ Eastern Research Group, Research Triangle Park, NC

Table 6.1 Results of Metals Analysis for TSP samples collected on 2/14/07 and 2/17/07 at the TSP and Off-Axis Sites

RESULTS				
Sample Date	2/17/2007	2/14/2007	2/17/2007	2/14/2007
TSP sampler	#1	#2	#3	#3
Filter ID	Q401821	Q401822	Q401819	Q401823
ANALYTE	TSP-high	TSP-low	Off-Axis high	Off-Axis Low
TSP ($\mu\text{g}/\text{m}^3$)	81.82	24.18	28.51	15.79
Antimony (ng/m^3)	1.26	0.59	1.27	0.448
Arsenic (ng/m^3)	1.61	0.78	1.13	0.502
Beryllium (ng/m^3)	0.03	0.01	0.01	0.01
Cadmium (ng/m^3)	0.53	0.24	0.19	0.235
Chromium (ng/m^3)	31.20	6.16	3.56	2.92
Cobalt (ng/m^3)	0.72	0.28	0.23	0.168
Lead (ng/m^3)	67.20	9.07	5.82	5.45
Manganese (ng/m^3)	47.40	19.80	11.90	7.39
Mercury (ng/m^3)	ND	0.01	0.02	0.029
Nickel (ng/m^3)	12.80	5.37	2.48	3.31
Selenium (ng/m^3)	1.51	3.15	1.50	3
Copper (ng/m^3)	65.35	106.14	49.49	61.39
Zinc (ng/m^3)	7720.85	1112.73	168.07	76.15
% Zinc	9.44	4.60	0.59	0.48

Figure 6.1 Comparison of Metals Analysis for TSP Filters Collected on 2/14/07 and 2/17/07 at TSP and Off-Axis Sites

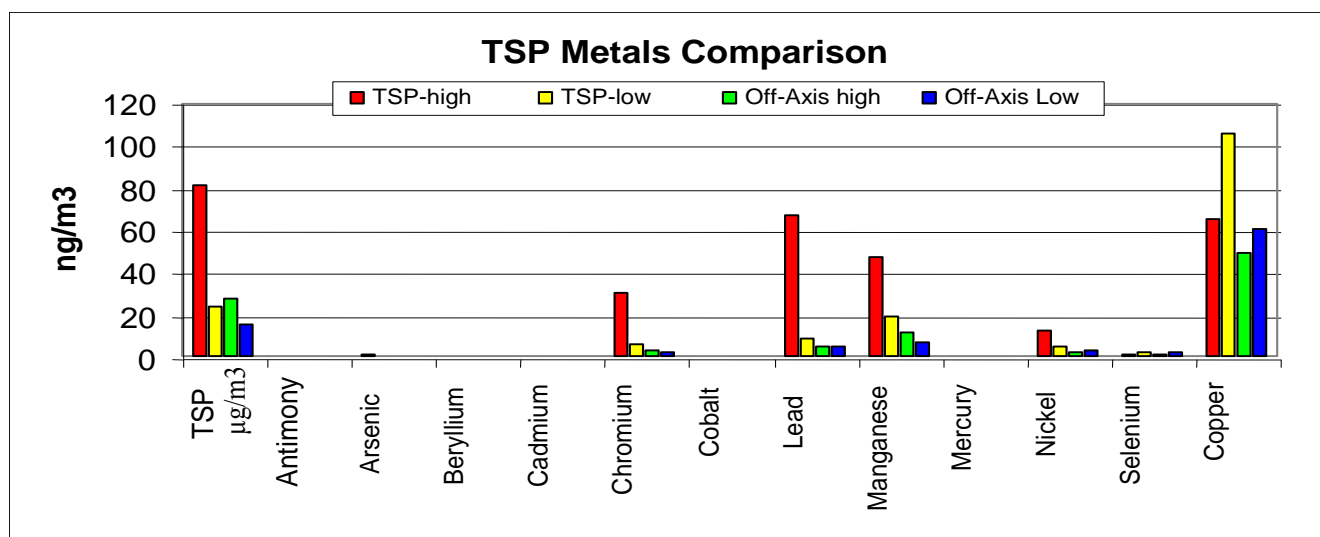
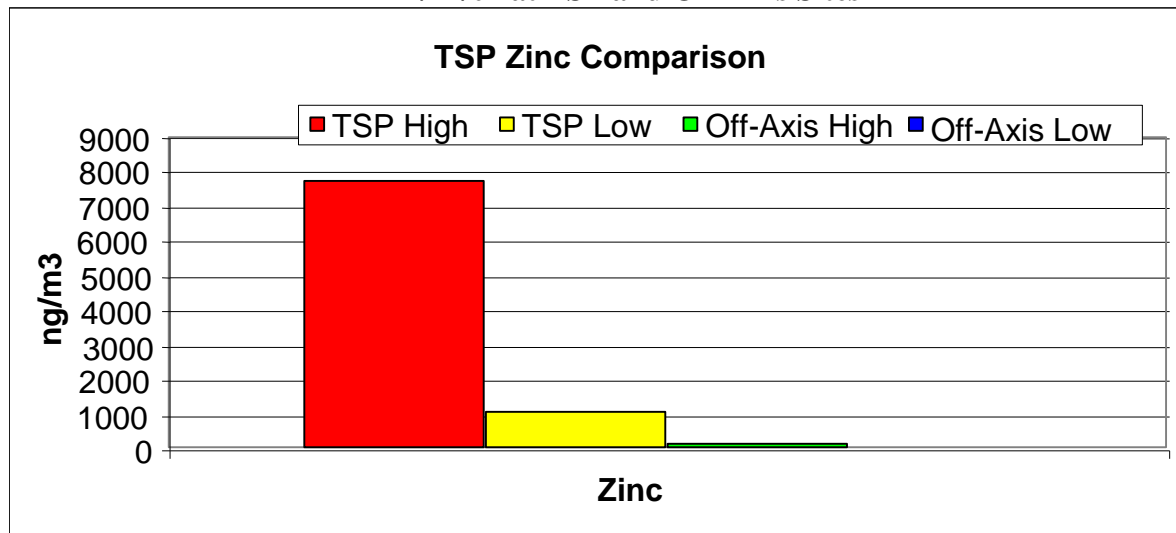


Figure 6.2 Comparison of Zinc Concentration for TSP Filters Collected on 2/14/07 and 2/17/07 at TSP and Off-Axis Sites



The second batch of samples selected for metals analysis were four samples collected on May 15, 2007. On this day, all four TSP samplers ran, providing collocated samples at both the TSP and the Off-Axis Sites. A sample collected this day produced data above of the TSP NAAQS from one of the TSP Site samplers. These four samples provide a measure of metals content of samples on a day that was believed to be source influenced and also provided collocated samples to compare for precision. The results of this analysis are shown in Table 6.3 below. The results again show high levels of zinc at the TSP Site for both samples compared to the Off-Axis Site, and zinc content of the particulate matter more than 13% at the TSP site in comparison with less than 0.5% found at the Off-Axis Site. The metals content of the May 15 samples are illustrated in graphical form in Figures 6.3, and the zinc and iron content for the four samples are shown in Figure 6.4.

The ERG laboratory reports for metals analysis are included in Appendix G.

Table 6.2 Results of Metals Analysis for TSP samples collected on 5/15/07 at the TSP and Off-Axis Sites

Sample Date	5/15/2007	5/15/2007	5/15/2007	5/15/2007
TSP sampler	#1	#2	#3	#4
Filter ID	G7027465	G7027466	G7027463	G7027464
ANALYTE	TSP	TSP (coloc.)	Off-Axis	Off-Axis (coloc.)
TSP ($\mu\text{g}/\text{m}^3$)	161.15	146.21	45.38	44.15
Antimony (ng/m^3)	0.94	0.90	0.59	0.56
Arsenic (ng/m^3)	3.34	2.98	0.54	0.53

Beryllium (ng/m ³)	0.04	0.03	0.01	0.01
Cadmium (ng/m ³)	0.65	0.68	0.16	0.17
Chromium (ng/m ³)	36.80	30.30	2.77	2.63
Cobalt (ng/m ³)	1.10	0.96	0.22	0.21
Lead (ng/m ³)	81.20	70.80	4.02	3.75
Manganese (ng/m ³)	95.80	79.70	12.80	12.40
Mercury (ng/m ³)	ND	0.03	0.01	0.01
Nickel (ng/m ³)	20.60	19.50	1.77	1.98
Selenium (ng/m ³)	1.15	1.10	0.66	0.61
Iron (ng/m ³)	4420	3720	392	366
Copper (ng/m ³)	66.8	171.0	35.1	42.6
Zinc (ng/m ³)	21200	17100	80	105
% Zinc	13.16	11.70	0.18	0.24

Figure 6.3 Comparison of Metals Analysis for TSP Filters Collected on 5/15/07 at TSP and Off-Axis Sites

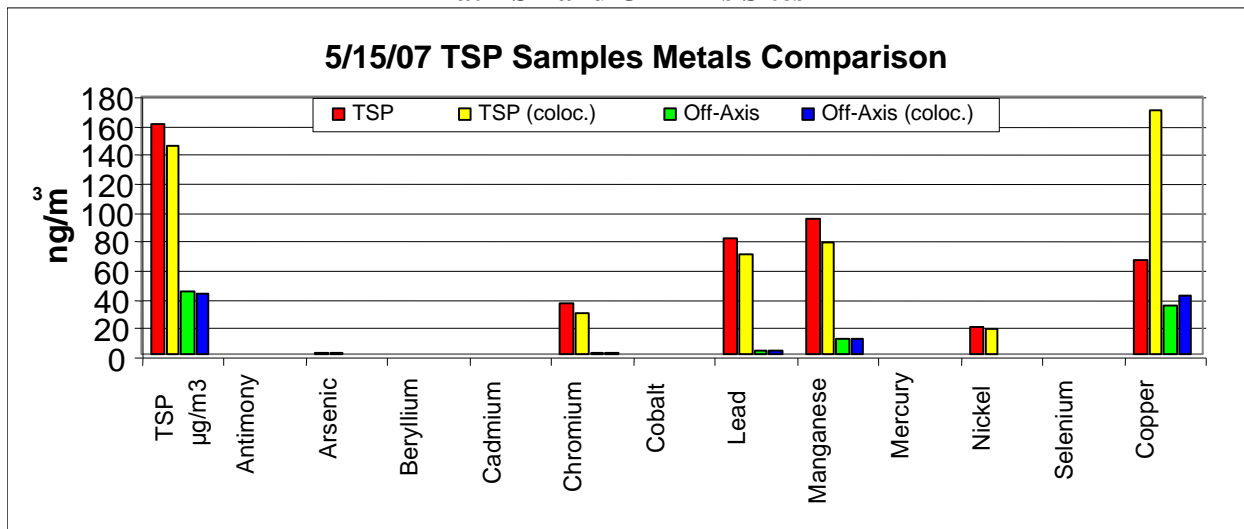
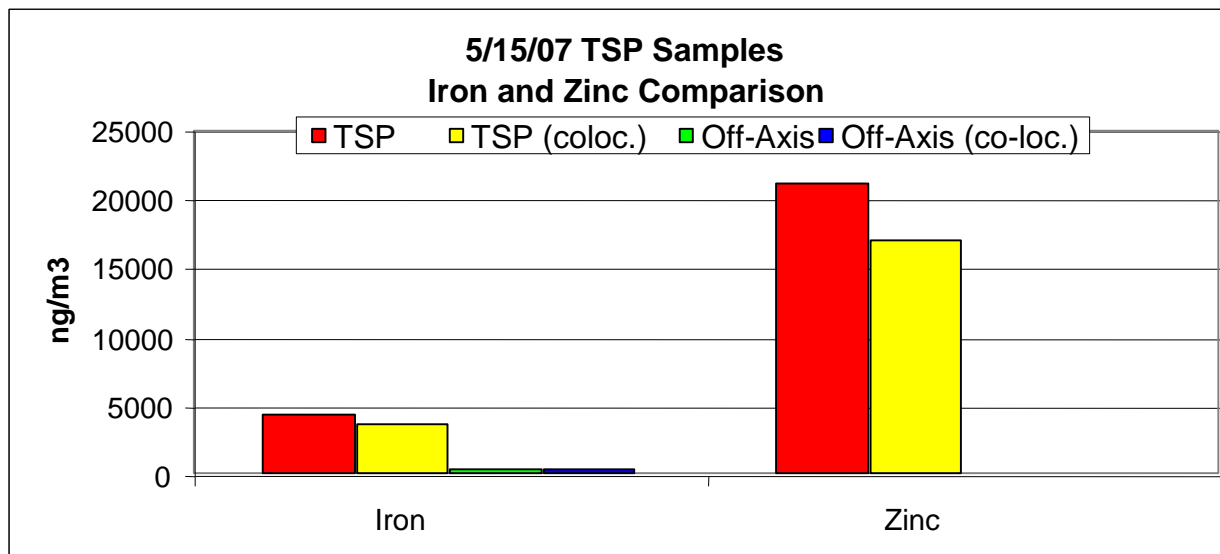


Figure 6.4 Comparison of Zinc and Iron Concentration for TSP Filters Collected on 5/15/07 at TSP and Off-Axis Sites



6.2 Analysis by SEM-EDS

Two of the TSP filter samples collected on 5/15/07 were selected for analysis by Scanning Electron Microscopy with Energy Dispersive X-Ray Spectrometry (SEM-EDS) at Research Triangle Institute (RTI)¹¹. SEM-EDS is a qualitative technique that gives information on particle morphology and elemental composition. One filter from each monitoring site was analyzed using this technique for comparison. The RTI report summarizes the findings as follows:

For the Off-Axis Site sample,

“Sample G702463: The sample had a variety of particle types, predominated by pollen and alumina-silica particles (typical for earth crustal particles). One zinc containing particle was located, as well as particles containing amounts of iron and calcium. Zinc containing particles were very uncommon in this sample.”

And for the TSP Site sample,

“Sample G702465: This sample was dominated by zinc, zinc/chlorine, and silica particles. Particles were also noted with sulfur and alumina. There were very few organic particles found. The zinc-containing particles represented approximately 30%-50% of the particle population.”

The SEM-EDS analysis offers further confirmation that zinc-containing particles exist in the TSP samples collected at the TSP Site. The full RTI report, including micrographs, elemental spectra, and elemental maps, is included in Appendix H.

¹¹ Research Triangle Institute, Research Triangle Park, NC.

APPENDIX A: QUALITY ASSURANCE PROJECT PLAN

APPENDIX B: WIND ROSES FOR ANNULAR DENUDER SAMPLE PERIOD

APPENDIX C: WIND ROSES FOR TOTAL SUSPENDED PARTICULATE SAMPLE PERIOD

APPENDIX D: EPA COMPENDIUM METHOD IO-4.2, “DETERMINATION OF REACTIVE ACIDIC AND BASIC GASES AND STRONG ACIDITY OF ATMOSPHERIC FINE PARTICLES (<2.5 μ M)”

APPENDIX E: ANALYTICAL RESULTS OF ADS SAMPLES

APPENDIX F: DAQ TOTAL SUSPENDED PARTICULATE QUALITY ASSURANCE PLAN

APPENDIX G: METALS ANALYSIS REPORTS

APPENDIX H: SEM-EDS ANALYSIS REPORT