

**DIVISION OF AIR QUALITY
TOXICS PROTECTION BRANCH
AIR TOXICS ANALYTICAL SUPPORT TEAM (ATAST)**

**CHEMICAL CHARACTERIZATION OF AEROSOLS
AND FINE PARTICULATE MATTER IN
THE AIRSHED AT THE PAMLICO RIVER**

ATAST Investigation Number 99013

FINAL STUDY REPORT

March 22, 2001

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TERMS

ADS	Annular Denuder System
ATAST	Air Toxics Analytical Support Team
Beta_(scat)	Beta Scatter Units for Nephelometer Output
COC	Chain of Custody
IC	Ion Chromatography
ug (mg)	Micrograms
mg	Milligrams
m³	Cubic Meters
NAAQS	National Ambient Air Quality Standard
NCDAQ	North Carolina Division of Air Quality
NC DOT	North Carolina Department of Transportation
NIST	National Institute of Standards and Technology
PCS	Corporate Entity in Aurora, NC
PM_{2.5}	Particulate Matter (Size range =2.5 micron)
PM₁₀	Particulate Matter (Size range =10 micron)
QAPP	Quality Assurance Project Plan
r²	Statistical Parameter that Defines the Correlation Between Two Variables
SOP	Standard Operating Procedure
TEOM	Tapered Element Oscillating Micro-balance
US-EPA	United States Environmental Protection Agency
WaRO	Washington Regional Office

NOTICE

This study report entitled “Chemical Characterization of Aerosols and Fine Particulate Matter in the Airshed at the Pamlico River” was a collaborative effort to characterize air quality in the Pamlico River region. The collaborators included the North Carolina Division of Air Quality’s (NCDAQ) Air Toxics Analytical Support Team (ATAST), the Washington Regional Air Quality Office (WaRO) and PCS Phosphate, Inc., (PCS). A variety of instruments, equipment and other related commercial products were used during this intensive six-month study.

Mention of any trade names or company names, or use of commercial products in this report, does not constitute an endorsement by the NCDAQ or any of the collaborators.

PREFACE

This study report entitled “Chemical Characterization of Aerosols and Fine Particulate Matter in the Airshed at the Pamlico River” was a collaborative effort to characterize air quality of the Pamlico River region. The collaborators were the North Carolina Division of Air Quality’s (NCDAQ) Air Toxics Analytical Support Team (ATAST), the Washington Regional Air Quality Office (WaRO) and PCS Phosphate, Inc., (PCS).

The ATAST was the lead entity for the study. This included program initiation, study design, planning, protocol implementation, supervision and operation of three of the four field sites and chemical analysis of all field-collected samples. Staff from PCS Phosphate, Inc. operated the fourth site, deployed/retrieved the samples and shipped field samples to the DAQ laboratory for analysis. The Washington Regional Air Quality Office requested this study and was also involved in sampling site selection and field operations.

The ATAST deeply appreciates technical and study related operational assistance provided by WaRO and PCS Phosphate, Inc. The cooperation from all stakeholders, for various facets of the study, has been excellent during this six-month period.

The following staff members with their affiliation were involved in the study:

- | | |
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- ATAST expresses appreciation to John Hardison, Steve Kiess, and Beth Modlin, Mayor, Town of Bath, for approving monitoring site locations on private property and Town of Bath property during this study.
- ATAST also expresses appreciation to Jeff Credle, Manager, DOT Bayview Ferry Landing, and other Bayview Ferry Landing staff for use of the NC Department of Transportation (DOT) communications tower as a platform for meteorology measurements and use of DOT property during the ADS collocation exercise.

EXECUTIVE SUMMARY

INTRODUCTION

A collaborative study involving the North Carolina Division of Air Quality (NCDAQ) and PCS Phosphate, Inc., (PCS) was carried out to quantify concentrations of acidic and basic gaseous pollutants, aerosols and particulate matter in Pamlico River airshed from May 1, 2000 to October 31, 2000. The designed study also collected regional episodic air quality events triggered by the nephelometer that was used as a surrogate indicator for $PM_{2.5}$ concentrations. This six-month monitoring program was carried out with the deployment of meteorological sensors, nephelometers, a Tapered Element Oscillating Microbalance (TEOM) monitor and Annular Denuder Systems (ADS). Additionally, a network of local citizens was formed to report unusual occurrences of fog, haze, and odors.

Five monitoring sites were established based on the regional wind rose data, land use, topography and other related considerations. The sites included:

1. **St. Hooker Site** located upwind (SSW) of the PCS facility.
2. **Hardison Site** was downwind (NE) of PCS, along the north shore of the Pamlico River.
3. **Kilby Island Site** was also located downwind (N) of PCS, on the Pamlico River north shore and is in the general direction of the regional wind patterns.
4. **Bath Site** was further north (N) from the Kilby Island site.
5. **Ferry Landing Meteorology Site** located at the Bayview Ferry Landing, on a 30-meter radio tower of the Department of Transportation (DOT), NNE of PCS.

MONITORING SYSTEMS

At each site, continuous meteorological data were collected at 2 and 10-meters for wind speed, wind directions, temperature, humidity, solar radiation and barometric pressure. Additionally, at the 30-meter elevation, meteorological data were acquired for the evaluation of regional upper level atmospheric conditions. The meteorological data were recorded at all sites every 10 seconds and averages for 15 minutes, 1-hour, and 24-hour, stored in the data loggers and downloaded every sixth day.

Visibility monitoring using nephelometers was carried out 24-hours per day at each of the four sampling sites. Further, nephelometer's readings ($Beta_{scat}$) permitted verification of a relationship between scattering coefficient and $PM_{2.5}$ concentrations for the region and also to establish a trigger point to initiate an episodic or short-term sampling. The light scattering data were averaged every hour and 24-hours with an additional averaging period of every 15 minutes initiated for the second half of the study period. All data were downloaded to a laptop computer, every sixth day.

The TEOM was used only at the Bath site to monitor regional airborne $PM_{2.5}$ concentrations. *This instrument was originally a continuous PM_{10} model, and was modified to a $PM_{2.5}$ sampler via installation of a cyclone that would remove particulate matter larger than*

2.5 microns from the air stream. Data from this sampler was used to establish a relationship between the light scattering coefficients from the nephelometer and fine particulate concentrations. The data averaging for the TEOM was every 30-minutes, 1-hour and 24-hour and the data were downloaded every sixth day.

Each site had a “Weekly Air Particulate Sampler” for collection of ADS samples. The samplers operated continuously, collecting 24-hour samples from midnight to midnight, for five consecutive days. On the sixth day, five samples were collected and a new set of denuders (8 assemblies) installed. Each ADS sample assembly consisted of a filter pack (Teflon™ and nylon filters) for collecting fine particulate matter and acidity, and two denuders in series, one to collect acidic gases and the other to collect basic gases. The configuration for the study was such that the first five assemblies were collecting samples for consecutive 24-hour periods. The 6th assembly was used for the field blank, the 7th assembly was for collecting episodic/short-term samples. The 8th assembly was used for a trip blank, a quality assurance measure to account for potential contamination during shipping.

For the short-term and/or episodic event sample collection, the data loggers were programmed to switch the ADS from its current (primary) sampling assembly to 7th assembly, when nephelometer Beta_{scat} values averaged at or above a trigger point ($65 \mu\text{g}/\text{m}^3$) for one 15-minute averaging period. After triggering episodic sampling, the ADS was to collect a sample for a 4-hour sampling period. At the end of this 4-hour sampling period, the data loggers were also programmed to return to the previous sampling channel and continue sampling.

SAMPLE CHEMICAL ANALYSIS

The ADS collected 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 acidic particles. The acidic gases were collected on a sodium carbonate (Na₂CO₃) coated denuder and ammonia was collected on a phosphorus acid denuder. Particulate sulfate, nitrate and ammonium were collected on the Teflon™ filter. Some of the particulate nitrate from the Teflon™ filter decomposes/ evaporates and was subsequently collected on the Nylon filter and quantified as nitric acid. Also collected on the Teflon™ filter were fine particles that contain hydrogen (H⁺) ions.

An Ion Chromatograph (IC), equipped with anion and cation exchange columns, a membrane suppressor, and a conductivity detector was used for quantifying concentrations of acidic and basic ions in sample solutions of denuder and filter extracts. The IC analysis of the sodium carbonate denuder extracts determined ambient air sulfur dioxide (SO₂) concentrations as total sulfate (SO₄⁻) and the phosphorus acid denuder extracts determined the ambient air ammonia (NH₃) concentrations as ammonium (NH₄⁺) ion. Consequently, all data in the report were reduced to gaseous sulfur dioxide and ammonia based on these measurements.

DATA QUALITY MEASURES

The Quality Assurance Manager performed meteorological sensor field audits at the beginning, midpoint and conclusion of the study. Meteorological data recovery for all sites has averaged

96%, over the course of the study. The calibration of nephelometers was checked on a monthly basis and the data recovery was 93% for the entire six-month study. As a part of quality assurance protocols, a ten day collocation exercise of three nephelometers was carried out. The inter-correlation between the three instruments produced r^2 of 0.9833, 0.9874, 0.9943, and the percent difference ranged from 0.42 to 4.41%. Initial and final calibrations of the TEOM were performed in the field and no deviations were noted. The TEOM data recovery from August 11 through October 31, 2000 was 96%. (*Note: the TEOM was placed in the field on August 11, 2000.*) The ADS PM₁₀ head and PM_{2.5} cyclones were routinely cleaned and its flow rates, at all sites were checked during the study period. The average flow rates during the study period through the ADS unit at each site were found to be within $\pm 10\%$ of the manufacturer suggested rate of 10 liter/min. The overall ADS sample collection efficiency for the study duration at all sites was 95%. The precision of ADS samplers was evaluated by collocation monitoring and the data obtained indicates satisfactory collection efficiency for analytes of interest (see Table 4.5 for more detailed information.)

The IC analytical method for determining acidic and basic constituents of the denuder and filter extracts was the US-EPA Method IO-4.2 "Determination of Reactive Acidic and Basic Gases and Strong Acidity of Atmospheric Fine Particle (<2.5 μm)". The instrument was calibrated, before each analytical batch or cycle run with a reagent blank and calibration standards, covering the typical range of field sample concentrations. Additionally, several types of quality assurance samples were incorporated and analyzed concurrently with groups of field samples for data quality control.

STUDY RESULTS AND DISCUSSION

Evaluation of cumulative wind roses, generated for each site, indicates dominant wind directions of southwest, south-southwest and north-northeast during the study period. The former wind patterns have the potential to transport PCS emissions to the Hardison and Kilby Island sites while north- northeast winds could transport PCS emissions to the St. Hooker site. Ozone Code Red levels were attained from June 1-3, 2000 in the Raleigh-Durham area and wind roses for this period at the PCS Study sites indicated the potential for eastward transport of the air mass from central to eastern North Carolina.

Thirty-five valid (46-total) observations from citizen odor observer network were documented. Thirty of 35 observations occurred when wind direction was from PCS to the observer and odors were described as similar to rotten egg/sulfur-like, acid-like, acrid, pungent, chemical in nature and smelling like a waste treatment plant odor. These odors were encountered both inside and outside of the observer's residences, lasting between 10 minutes to 2 hours with average wind speed of 8.2 miles per hour. Evaluation of the nephelometer data during the citizen observations time period indicates no elevation of airborne PM_{2.5} concentrations. There were also no odor observations during 14 episodic events triggered by the nephelometers. Therefore, it was concluded that the responsible pollutant(s) for the 30 odor observations are likely to be present in the gaseous form. Further, it is hypothesized that these odorous gaseous pollutants may be associated with a passing coning plume to which regional citizens were exposed.

Integrated nephelometers provided continuous readings ($\text{Beta}_{\text{scat}}$) 24-hours a day at four sites for six-months. The average nephelometer reading of all sites for the study duration was $4.01\text{E-}05$ and this translates into $\text{PM}_{2.5}$ concentration of $12.95 \mu\text{g}/\text{m}^3$. Additionally, regional airborne $\text{PM}_{2.5}$ concentrations, as $\mu\text{g}/\text{m}^3$, were monitored using ADS and TEOM. The former gravimetrically provided 24-hour averages of $\text{PM}_{2.5}$ concentrations at each of the sites and the later gave hourly averages of $\text{PM}_{2.5}$ mass on a real time basis, only at the Bath site. The average $\text{PM}_{2.5}$ concentrations of all sites for the six-month study duration for ADS and TEOM were 13.15 and $11.90 \mu\text{g}/\text{m}^3$ respectively. The developed relationship between $\text{Beta}_{\text{scat}}$ and the ADS $\text{PM}_{2.5}$ concentrations, 24-hour averages for four sites show good correlation with $r^2 = 0.8042$. This indicates that these two monitoring techniques are equivalent to one another and that the nephelometer readings for this geographic location can be reliably converted to $\text{PM}_{2.5}$ concentrations. The nephelometer at the Bath site also correlated well with the collocated TEOM $\text{PM}_{2.5}$ concentrations with $r^2 = 0.8995$, again indicating that these two are equivalent sampling techniques and $\text{Beta}_{\text{scat}}$ readings can be converted to $\text{PM}_{2.5}$ concentrations. It may be noted that $\text{Beta}_{\text{scat}}$ values can be utilized both for regional visibility studies and fine particulate matter concentrations. Similarly a good correlation ($r^2 = 0.923$) was obtained when 24-hour averages of $\text{PM}_{2.5}$ concentrations from ADS and TEOM were plotted. Further, the usefulness of $\text{Beta}_{\text{scat}}$ data, as a surrogate for $\text{PM}_{2.5}$ concentration was determined through a simple ratio analysis ($\text{Beta}_{\text{scat}}/\text{PM}_{2.5}$).

The ratios between the monitoring methods (e. g. nephelometer, ADS, TEOM) at all sites produced similar results with the average being 0.31 ± 0.02 . The similarity of the ratio implies that the physical properties e.g. size distribution, shape, density, refractive index, etc., of the fine particulate matter collected at each of the four sites were essentially similar. Further, the physical and chemical processes such as coagulation and condensation that may be responsible for producing much of the fine particulate matter mass could be responsible for this similarity.

Chemical pollutants monitored and quantified via ADS sampling during the six-month study (31 sampling cycles) included gaseous nitrous (HNO_2) and nitric acids (HNO_3), sulfur dioxide (SO_2), ammonia (NH_3) and fine particulate $\text{PM}_{2.5}$ mass, nitrate (NO_3^-), sulfate (SO_4^{2-}) and ammonium (NH_4^+). Nitrite (NO_2^- indicator of nitrous acid) was found in only 18% of the samples analyzed with the average of these being near the Lower Quantification Limit (LQL) ($0.40 \mu\text{g}/\text{m}^3$). Gaseous nitric acid and particulate nitrate each were determined in about 50% of the ADS samples, with the average concentrations being closer to the LQL ($0.40 \mu\text{g}/\text{m}^3$). Specifically, the concentrations for gaseous nitric acid averaged $0.59 \mu\text{g}/\text{m}^3$, particulate nitrate $0.37 \mu\text{g}/\text{m}^3$ and nitric acid on Nylon filters $0.33 \mu\text{g}/\text{m}^3$. Consequently, given the relatively low number of samples with levels above the LQL and the averages being very close to the LQL, no further discussion for these pollutants is included in the report.

In comparison, gaseous sulfur dioxide and ammonia and particulate sulfate and ammonium were quantified in more than 90% of the analyzed samples with concentrations being 10 times the LQL for sulfur dioxide and sulfate and 5 times LQL for ammonia and particulate ammonium. The concentrations of $\text{PM}_{2.5}$ were determined in all (100%) collected samples.

The study average concentrations of these five pollutants for four sampling sites were found to be:

- Sulfur dioxide = $2.35 \mu\text{g}/\text{m}^3 \pm 2.28$ (RSD 97%)
- Ammonia = $1.54 \mu\text{g}/\text{m}^3 \pm 1.58$ (RSD 103%)
- PM_{2.5} = $12.95 \mu\text{g}/\text{m}^3 \pm 6.73$ (RSD 52%)
- Sulfate = $3.92 \mu\text{g}/\text{m}^3 \pm 2.80$ (RSD 73%)
- Ammonium = $1.34 \mu\text{g}/\text{m}^3 \pm 0.95$ (RSD 71%)

The higher percent Relative Standard Difference (RSD) is attributed to a wide range of these pollutant concentrations monitored at four sites and the number of samples analyzed.

A regression analysis of micromole ammonium against sulfate indicates a good $r^2 = 0.8454$ for St. Hooker, $r^2 = 0.8548$ for Bath, $r^2 = 0.8688$ for Hardison and $r^2 = 0.8584$ for Kilby Island. The good correlation for each of the four sites implies that the primary water-soluble particles in the Pamlico River airshed may be ammonium sulfate. Additionally, the molar ratio between ammonium and sulfate was found to be 1.01 and this value further supports that the ammonium and sulfate ions found in the Teflon™ filter extracts were derived from the fine ammonium sulfate particulate mass.

One of the objectives of the study was to collect and chemically analyze individual “episodic event” samples as defined by the nephelometers’ readings. These “episode” samples were to be collected over a 4-hour period by having a data logger program instruct the ADS to switch the airflow from the primary denuder (the one running for that day) to a dedicated episode denuder for 4-hours and then returning the airflow to the primary denuder. However due to data logger programming errors, this sequence did not occur. Subsequent ADS operation experiments after the close of the study and review of raw data showed that there was minimal diversion of the air stream to the episode denuder. Therefore it was concluded that the air volume diverted from the primary denuder was minimal and the values reported for the primary denuders would be representative of containing a collected “episode” as part of the 24-hour period. These values were therefore reported as “estimated” values.

There were fourteen nephelometer-triggered-episodes referred to as “triggered episodes”, which could have been collected by the ADS. From these fourteen triggered episodes, twelve were collected. Two triggered-episodes were not collected because one episode occurred during a scheduled sampler change out day when the ADS samplers are not running and the other occurred when sampler did not run due to an equipment malfunction. Additionally, of these twelve, six triggered-episode collection periods were found to have been collected when the nephelometer triggered the collection ADS based on exceeding a 10-second-average, $65 \mu\text{g}/\text{m}^3$ level rather than the study-defined 15-minute-average of $65 \mu\text{g}/\text{m}^3$ level. The remaining six triggered-episodes did meet these criteria for an “episode event”. These six episode-events occurred on four dates in October 2000.

Evaluation of these six “episodes” meteorological, nephelometry, and chemistry data indicated that they were due to the following:

October 14, 2000: Although the wind directions at all of the sites were consistent with transport of air masses from the direction of PCS to the sites, the event was observed at only the Hardison site without a corresponding increase in PM_{2.5} levels being recorded at the other sites. Therefore,

this event is surmised to be due to a localized, potentially site-specific, increase in the $PM_{2.5}$ level such as river traffic or residential activities.

October 16, 2000: Evaluation of the meteorological and the nephelometry data indicated that the increase in $PM_{2.5}$ at the Hardison and Bath sites and to a lesser extent at the Kilby Island and St. Hooker sites was due to the dispersion of a localized source of $PM_{2.5}$ other than PCS such as burning or farming activities.

October 17, 2000: An episode was triggered by the nephelometer at the St. Hooker site. Because the wind directions were consistently from the N and NE at all of the sites and the rise at the St. Hooker site was quite sharp, the indication is that the episode at the St. Hooker site was a local effect such as some operation at PCS (which is NNE to NE of the site). A potential connection to operations at PCS is supported by the SO_2 and NH_3 concentrations. Both of these concentrations are elevated compared to the values for the other three sites, although these concentrations are not especially high and are for a 24-hour period.

October 22, 2000: Episodes were triggered by the nephelometer at the Kilby Island and St. Hooker sites. Evaluation of the relevant data sets indicated that this event was due to a regional effect and potentially due to the intrusion of a $PM_{2.5}$ laden air mass from the NW or W over a calm surface layer because of a typical morning boundary layer separation. The event was then observed as the boundary layer began breaking up thus allowing material in this upper layer to mix toward the surface and increasing the $PM_{2.5}$ concentrations. However, this scenario does not preclude the possibility that the air mass from the NW and/or W contained sufficient concentrations of precursors to the formation of $PM_{2.5}$ and that the mixing with the constituents already in place in the stagnate surface layer such as SO_2 caused the regional “in-place” formation of the observed $PM_{2.5}$ concentrations. This scenario may be supported by the fact that the SO_2 concentrations in the area during this time were elevated.

Evaluation of chemistry and meteorological data during and subsequent to Code Red ozone days in the Raleigh-Durham area of May 31 and June 1, 2, 3 and 4, 2000 was performed. This evaluation indicated that various regional conditions were present which support the supposition of an observed increase in $PM_{2.5}$ across the four sites was affected by the regional transport of ozone, its precursors, and other fine particulate matter from central North Carolina to eastern North Carolina during June 1-3, 2000. However, it is not possible to determine whether the $PM_{2.5}$ observed in this event was 1) delivered to the area, 2) formed in the area as a result of secondary reactions with ammonia and sulfur dioxide already present in the area or 3) a combination of the two.

An objective engineering review and evaluation of PCS facility operations data during the six-month period of this study showed that the PCS daily production and emission levels were consistently within the permitted levels in all instances. Furthermore, in most cases there was a favorably wide margin between the production/emission levels and the corresponding permit limits. This data also indicates that PCS operated in a normal and representative mode throughout the study period. In terms of their annual emission inventory records, the data reflects that PCS has maintained or reduced its annual emission levels for nearly all of the primary emissive pollutants of interest to this study.

In addition, based on a thorough review of the hourly operating logs and maintenance records from three pertinent plant areas for the seven episode days, ATAST concluded that PCS was:

- Operating clearly within the permitted limits,
- Using good industrial operating and record keeping practices,
- Applying a systematic approach to diagnose and prevent equipment problems, and
- Experienced no major process malfunction or non-routine maintenance issues.

And finally, the evidence suggests no direct linkage between the episodic events as defined in this study and any peculiarities or irregularities with PCS production or emission levels.