SECTION VI

CONCLUSIONS

In this section, conclusions of the results (presented in **Section V)** from the air monitoring for six-months at the Pamlico River airshed are made.

This section includes conclusions derived from:

- Meteorology and observer network data
- Nephelometer, ADS and TEOM fine particulate matter data
- ADS associated sample analyses chemical data

6.1 METEOROLOGY AND OBSERVER NETWORK DATA

The following conclusions from meteorology and observer network data are made:

- Evaluation of cumulative wind roses, generated for each site, indicates the predominant wind direction pattern of southwest, south-southwest. This wind direction has potential to transport PCS emissions primarily to the Hardison and Kilby Island sampling sites.
- Wind roses generated for June 1-3, 2000, at a time of ozone Code Red levels in central NC indicated eastward transport of this central North Carolina air mass into the study area.
- Only 35 valid observations from the citizen odor observer network were received during this six-month study and 30 of these have occurred when wind directions were from PCS to the observer.
- Observations of odor were described by observers as similar to rotten egg/sulfur-like, acid like, acrid, pungent, chemical in nature and smelling like a waste treatment plant odor.
- Odors were experienced, both inside and outside of the observer's residences, lasting between 10 minutes to 2 hours.
- The average wind speed during 30 observations was 8.2 miles per hour indicating that none of the observations may due to regional temperature inversion or the fumigating plume.
- Evaluation of nephelometer data from four monitoring sites, during the 30 odor observation periods, does not indicate relative increases in $PM_{2.5}$ mass concentrations. This may imply that the responsible pollutant(s) for the odor observations are likely to be present in the gaseous form and not in the fine particulate matter form.
- Further, it may be hypothesized that these odorous gaseous pollutants (not quantified in the present study through ADS sample chemical analyses) may be associated with a transient coning plume to which regional citizens were exposed.

6.2 NEPHELOMETER, ADS AND TEOM DATA

Integrated nephelometers provided continuous readings in the units of $Beta_{scat}$, 24-hour a day at four sites. Additionally, regional airborne $PM_{2.5}$ concentrations, as $\mu g/m^3$, were monitored using ADS and TEOM. The ADS gravimetrically provided 24-hour averages of $PM_{2.5}$ concentrations at each site. The TEOM gave hourly averages (that were converted to 24-hour averages) of $PM_{2.5}$ mass on a real time basis, at the Bath site. The following conclusions are drawn from the nephelometer, ADS, and TEOM data that were part of **Section V**:

- The regression analysis of nephelometer $Beta_{scat}$ values and 24-hour averages of ADS $PM_{2.5}$ concentrations for four sites show a good correlation with $r^2=0.8042$. This r^2 value implies that these two monitoring techniques are nearly equivalent to one another and further, the nephelometer readings can be reliably converted to $PM_{2.5}$ concentrations relative to a specific site.
- The nephelometer data from the Bath site also correlated well ($r^2=0.8995$) with the collocated TEOM, 24-hour averages of $PM_{2.5}$ concentrations, implying the two method's, near equivalency. However, at this stage, it is difficult for the DAQ-ATAST to assess the effects of modifications to the TEOM (for details see **Sections III, IV and V**) and thus more work on this subject matter may be warranted.
- Further, the above conclusions suggest that the nephelometer data can be utilized both for regional visibility studies as well as for the fine particulate matter airborne concentration evaluations.
- A good correlation with $r^2=0.9230$ was obtained when 24-hour averages of $PM_{2.5}$ concentrations from ADS and TEOM were treated to regression analysis indicating that these two monitoring methods are nearly equivalent and give similar data.
- The averages of $PM_{2.5}$ concentrations measured for the study period at all sites by the nephelometer, ADS and TEOM (only at the Bath site) were found to be 12.95, 12.95 and 11.90 $\mu g/m^3$, respectively. A good agreement among the three monitoring methods may be regarded as another indication of near method equivalency.
- The ratio of $Beta_{scat}$ readings over $PM_{2.5}$ concentrations from ADS and TEOM for four sites gave essentially the same value with the average being 0.31 with 5.90% RSD. The similarity of the ratio at all sites indicates that the physical properties e.g. size distribution, shape, density, refractive index, etc of the fine particulate matter mass 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 to produce much of the fine particulate matter mass could also be responsible for this similarity.
- During the study period there were a total of 14 episodic events triggered because of nephelometer values attaining the set $PM_{2.5}$ concentrations (65 $\mu g/m^3$), resulting in the collection of 14 short-term ADS samples. However, chemical analyses of these samples did not provide expected elevated concentrations of chemical pollutants because of the data logger programming errors. Consequently, very little air passed through the designated ADS episodic denuder, during the 4-hour sampling period. As a result the 14 recorded episodes are based only on the nephelometer readings of

relatively higher $PM_{2.5}$ concentrations (>65 $\mu g/m^3$) and the chemical data from ADS sample analyses do not support any of the episodic events.

Therefore, establishing (based on the above presented data) the potential promise for the near method equivalency between nephelometer and ADS, nephelometer and TEOM, and ADS and TEOM may be considered as a significant contribution of this six-month study. However, it may be cautioned that this conclusion i.e. near method equivalency, is related only to a specific monitoring area, i.e. Pamlico River airshed, and study duration of six-month. Hence, this conclusion should **not** be used for other monitoring locations without at least some preliminary work that should include evaluation of a stable relationship between regional $PM_{2.5}$ concentrations and nephelometer $Beta_{scat}$ values.

The light scattering ($Beta_{scat}$) coefficient of ambient air can be monitored very conveniently and reliably using an integrated nephelometer. The information thus obtained has applications to studies of both visibility degradation and the concentrations of airborne $PM_{2.5}$. The nephelometer is a simple device both in electronic and optical senses and its cost (< $6000) is very reasonable in comparison with other optical instruments performing similar functions. Operational experiences over the six-month study (continuous 24-hour, 7 day per week basis) indicate that the unit is simple, reliable, easy to install and operate in the field and the zero drift is negligible.

Evaluations of environmental pollution by necessity require timely assessment of the degree of pollution to develop a control strategy approach and more importantly determine human health effects. Based on our six-month experience with the denuder technology, the "Weekly Air Particulate Sampler" may be an ideal sampling device for collection of data used to evaluate and assess the human health effects of air pollution. Air samples for organic volatile and semi-volatile compounds, acidic and basic gaseous pollutants and fine particulate matter [61] can be quantitatively and concurrently collected and subsequently analyzed for a variety of pollutants. Furthermore, the $PM_{2.5}$ mass collected on the Teflon™ filters can be also analyzed for particle morphology, organic carbon, elemental carbon, water-soluble anions, cations, and toxic metals. Importantly, real time ADS measurements with an on-line IC are possible (still in the developmental stages) for acidic and basic gaseous pollutants, aerosols and fine particulate matter [61].

Therefore, it is concluded that the air monitoring approach that involves a combination of nephelometer and ADS may be ideal to investigate and characterize air quality, particularly when the sources of environmental pollution are due to a diverse array of pollutants such as organic volatile and semi-volatile compounds, acidic and basic gases and fine particulate matter (including particulate metals).

6.3 ADS ASSOCIATED SAMPLE ANALYSES CHEMICAL DATA

The ADS operated at four monitoring sites continuously, collecting 24-hour samples for acidic and basic gases and fine particulate matter from midnight to midnight. The related details of ADS operations are part of **Sections III** and **IV**. The following conclusions are derived from the ADS sample analyses chemical data:

- Only 18% of the total sample collected/analyzed had nitrite concentrations above the LQL (0.40 $\mu g/m^3$) in the denuder extracts with average concentrations being near the LQL.
- Concentrations of gaseous nitric acid and particulate nitrate were quantified in about 50% of the ADS samples collected during 31 cycles. However, the concentrations averaged close to the LQL (i.e. 0.40 $\mu g/m^3$). Specifically, the concentrations for gaseous nitric acid averaged 0.59 $\mu g/m^3$, particulate nitrate 0.37 $\mu g/m^3$ and nitric acid on Nylon filters 0.33 $\mu g/m^3$ respectively.
- Gaseous sulfur dioxide and ammonia, and particulate sulfate and ammonium were quantitatively determined in more than 90% of the samples. The concentrations on average for sulfur dioxide and sulfate being 10X the LQL (0.23 $\mu g/m^3$ and 0.35 $\mu g/m^3$, respectively) and for ammonia and ammonium 5X the LQLs (0.23 $\mu g/m^3$)
- The $PM_{2.5}$ concentrations were determined in all samples collected during 31 cycles.
- The average ADS concentrations at four sites for $PM_{2.5}$ were 12.95 $\mu g/m^3$ with 52% RSD, sulfur dioxide 2.35 $\mu g/m^3$ with 97% RSD, ammonia 1.54 $\mu g/m^3$ with 103% RSD, sulfate 3.82 $\mu g/m^3$ with 73% RSD and ammonium 1.34 $\mu g/m^3$ with 71% RSD. The assessment/implications of these pollutant airborne concentrations in terms of risk analysis and/or human health effects is beyond the scope of the present study. Therefore, the task is left to the appropriate authorities within the Department of Environment and Natural Resources (DENR).
- A regression analysis of micromole ammonium against sulfate concentrations of four sites indicate good correlations of r^2= 0.8454 for St. Hooker, r^2= 0.8548 for Bath, r^2= 0.8688 for Hardison, r^2= 0.8584 for Kilby Island with a composite r^2= 0.8569. The good correlation for each site implies that the primary water soluble $PM_{2.5}$ mass in the Pamlico River airshed, most likely is ammonium sulfate. Additionally, the molar ratio between ammonium and sulfate was calculated and found to be 1.01. The value further supports that the ammonium and sulfate ions found in the Teflon™ filter extracts were derived from the fine ammonium sulfate particulate mass.
- Evaluation of the 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 are consistently from the N and

NE at all of the sites and the rise at the St. Hooker site is quite sharp, the indication is that the episode at the St. Hooker site is 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.

- Collectively, the various data sets (meteorology, nephelometry, ADS collection /analysis results) support the following:
  - SO_2 concentrations in the area are primary-source driven, i.e. PCS related but are not at levels of eminent concern (see **Section 5.5.2.2 page V-26**).
  - NH_3 concentrations are related to a variety of potential sources ranging from site-specific to local to area sources.
  - $PM_{2.5}$, $SO_4^{=}$, and NH_4^{+} concentrations are regionally controlled with the potential to be impacted by emissions from PCS as secondary contributors.

- 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,
  - Experienced no major process malfunction or non-routine maintenance issues.

- 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.