

## SEARCHing for Answers

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### Introduction

Many studies have demonstrated associations between atmospheric particulate matter (PM) with aerodynamic diameter less than 2.5  $\mu\text{m}$  ( $\text{PM}_{2.5}$ ) and health effects (1, 2). In particular, evidence has arisen that hourly increases in  $\text{PM}_{2.5}$  levels may lead to the onset of myocardial infarctions within a few hours after exposure (3). As a result of these health concerns, the U.S. Environmental Protection Agency promulgated regulations on the maximum  $\text{PM}_{2.5}$  concentrations to which the general public should be exposed. More recently, studies have suggested that not only the total concentration is important, but knowledge of the abundance of the individual chemical constituents of  $\text{PM}_{2.5}$  may be linked with particular health endpoints (4-6). Furthermore, in the past decade, the study of atmospheric PM has intensified due to the identification of its potential impacts on climate change (7, 8).

In response to these concerns, the Southeastern Aerosol Research and Characterization Study (SEARCH) was implemented in 1998-1999 in an effort to provide extensive long-term data on the sources and chemical characteristics of atmospheric particulate matter (PM), in particular for the southeastern United States with its distinctive meteorological and demographical characteristics. The SEARCH study's objectives include: (i) development of a long-term chemical climatology of PM; (ii) advancement of the understanding of PM composition, variability and sources; (iii) establishment of a platform for the development and testing of new measurement methods related to PM; and, (iv) collaboration with states, federal agencies and others in carrying out special studies at selected network sites.

SEARCH is unique in the breadth, high time resolution and longevity of trace atmospheric measurements that have been made at eight sites across the southeastern U. S. At four pairs of urban/rural or urban/suburban monitoring sites located in Atlanta, GA (JST and YRK), Birmingham, AL (BHM and CTR), Gulfport, MS (GFP and OAK), and Pensacola, FL (PNS and OLF), (see Figure 1) meteorological (temperature, pressure, wind speed and direction, humidity, solar insolation), trace gas ( $\text{O}_3$ ,  $\text{SO}_2$ ,  $\text{CO}$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{NO}_y$ ,  $\text{HNO}_3$ ,  $\text{NH}_3$ ), fine PM ( $\text{PM}_{2.5}$  mass and composition), and coarse PM data ( $\text{PM}_{10-2.5}$  mass and composition) have been routinely collected since the network's inception. The SEARCH dataset provides a rich repository for the investigation of many scientific questions concerning the sources, formation and behavior of atmospheric PM. This paper presents a broad overview of selected results from investigations that have been undertaken to date with SEARCH data. Details of the network including descriptions of measurement methods, data adjustment techniques, and quality control procedures can be found in various published articles (9-13) and on the Atmospheric Research & Analysis, Inc., website (<http://www.atmospheric-research.com>).

## Results and Discussion

SEARCH PM measurements include both integrated 24-hr filter-based  $PM_{2.5}$  and  $PM_{10-2.5}$  mass and composition as well as semi-continuous (5 min resolution)  $PM_{2.5}$  mass and composition. Figure 2 presents typical composition data for filter-based  $PM_{2.5}$  from the JST site in midtown Atlanta and Figure 3 presents monthly variation of this data at all sites in the network. “Best Estimate” data is a reconstruction of  $PM_{2.5}$  mass and composition taking into account nitrate, ammonium and organics that volatilize from the primary filter after initial collection. Organic matter comprises the largest fraction of  $PM_{2.5}$  Best Estimate (BE) mass at each site ( $4 - 7 \mu\text{g}/\text{m}^3$ ), accounting for 30–36% of the total. In combination with black carbon, which by itself is a fairly small contributor to total mass (4-10%), carbonaceous matter as a whole makes up 35-45% of total  $PM_{2.5}$  BE mass across SEARCH. Sulfate accounts for 25-30% of total BE mass, with concentrations falling within a fairly narrow range ( $3.5 - 4.8 \mu\text{g}/\text{m}^3$ ). Ammonium concentrations account for 9-12% of total  $PM_{2.5}$  BE mass ( $1 - 2 \mu\text{g}/\text{m}^3$ ). Ratios of

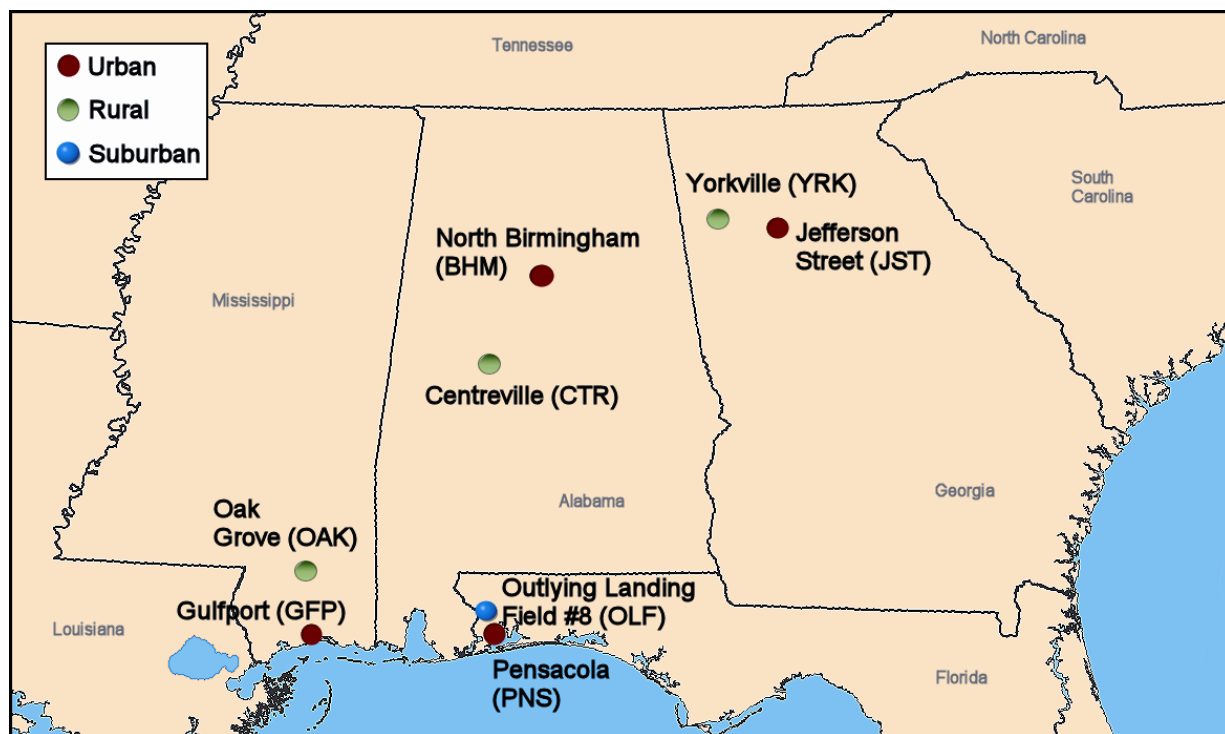
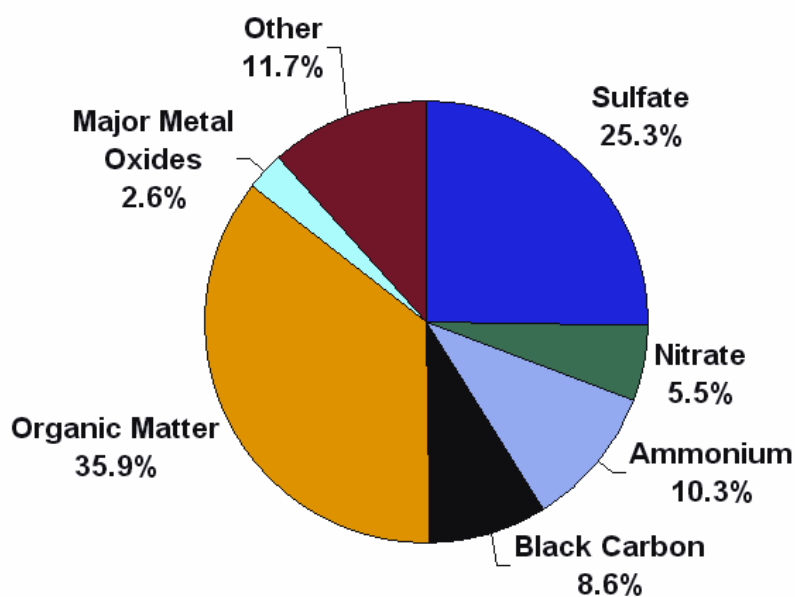


Figure 1. Location of SEARCH monitoring sites in the southeastern U. S.

$([\text{SO}_4^{2-}] + [\text{NO}_3^-])/[\text{NH}_4^+]$  (as equivalents) increase from 1.1 to 1.3 from north to south across the network and the degree of neutralization as defined by the ratio  $([\text{NH}_4^+] - [\text{NO}_3^-])/[\text{SO}_4^{2-}]$  (as equivalents) decreases from 0.92 to 0.73-0.78, possibly indicating a reduction in available ammonia as one goes from the continental interior towards the Gulf of Mexico. Nitrate concentrations are low ( $0.4 - 1.0 \mu\text{g}/\text{m}^3$ ) and account for less than 6% of total  $PM_{2.5}$  BE mass. Major metal oxides (MMOs) contribute less than 5% to total  $PM_{2.5}$  BE mass at all sites. “Other” is a derived quantity considered to be a combination of species not measured, particle-bound water, analytical error, and uncertainty in the assumed form of PM components. Aside from

particle-bound water perhaps the most important of this latter group is the molecular form of organic carbon which comprises OM, where a constant factor of 1.4 is used. The “Other” category accounts for 10-19% of the total PM<sub>2.5</sub> BE mass (2.0 – 2.5 µg/m<sup>3</sup>), which is a lesser but not inconsequential portion of the total mass.

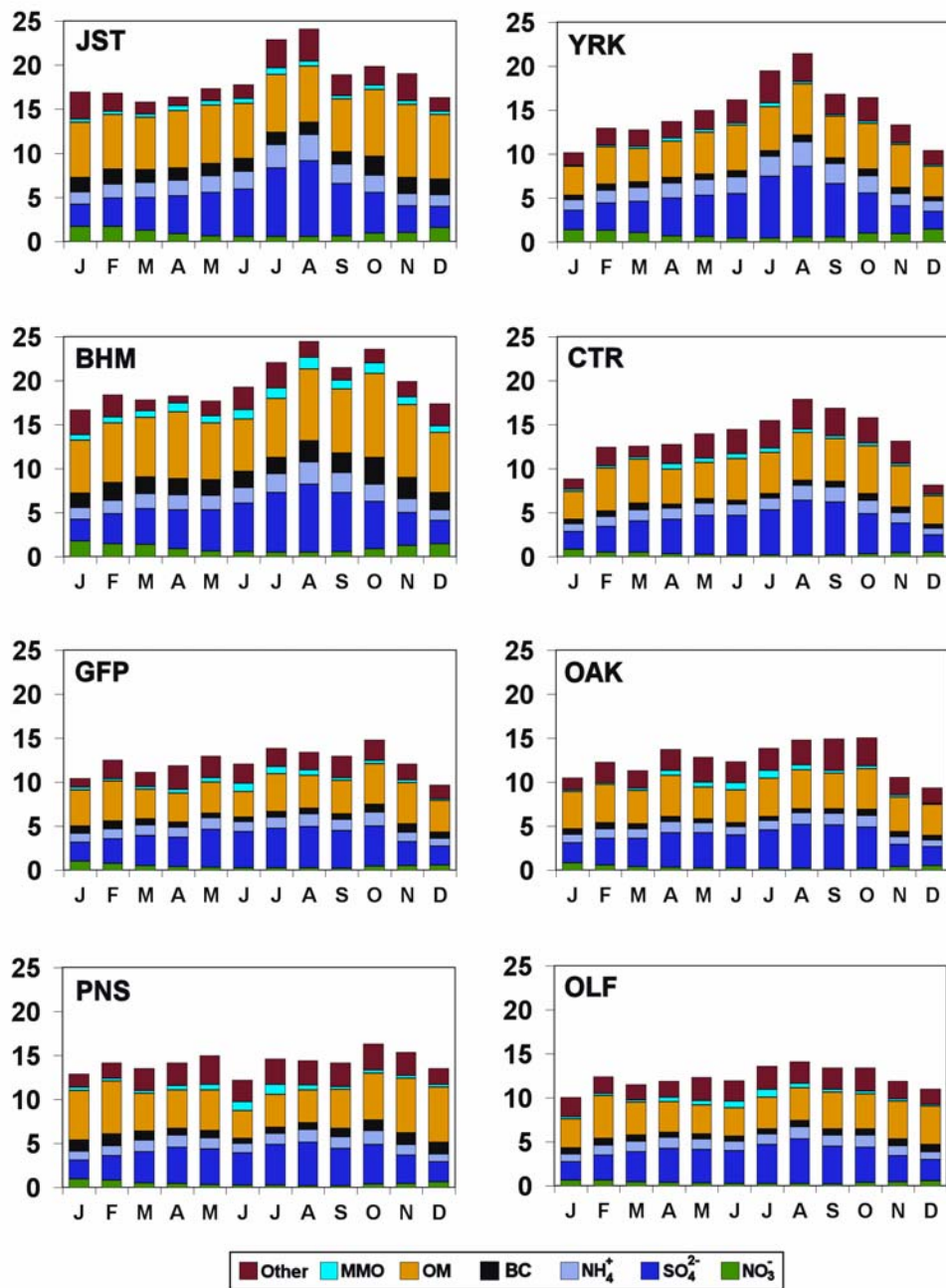
Figure 3 presents monthly average PM<sub>2.5</sub> Best Estimate mass and composition for all SEARCH sites. Monthly-averaged Best Estimate mass concentrations exhibit a distinct seasonality with higher concentrations during the warmer months, generally peaking in July-August. This seasonality is more pronounced at the more northerly sites JST, YRK, BHM, and CTR than at more southerly locations. In fact, data for the southern sites show virtually no summertime enhancement of PM<sub>2.5</sub> compared to other seasons. Sulfate is a primary driver of the observed seasonality, with values 2.2-3.9 times larger in July-August than in December-January. The larger sulfate concentrations during warm months are likely due to increased photochemical activity and/or increased precursor emissions during summer as a result of peak electricity generation during this time. OM, in contrast, shows a relatively flat pattern,



**Figure 2. Best Estimate PM<sub>2.5</sub> mass and composition from SEARCH site JST in midtown Atlanta, GA.**

possibly reflecting substitution of secondary production during the warm (growing) season with primary production (e.g., wood smoke) during the cold season. Nitrate concentrations peak during the cool months of December-January and reach minima during July-August, consistent with the thermodynamics of gas/particle partitioning of ammonium nitrate. At all sites, MMO concentrations peak during April-August and reach their lowest values during December-January. Reasons for this pattern are unclear, but could be related to rainfall and/or soil moisture and/or long-range transport of African or Asian dust.

Deployment of continuous PM analyzers in the SEARCH network began in 1998 and continues today as new technologies are developed. Measurement of PM<sub>2.5</sub> mass is performed using a dried, 30°C tapered element oscillating microbalance (TEOM). Light scattering by nephelometry complements the TEOM. Measurements of major constituents include: (a) SO<sub>4</sub><sup>2-</sup> via reduction to SO<sub>2</sub>; (b) NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> via respective catalytic oxidation and

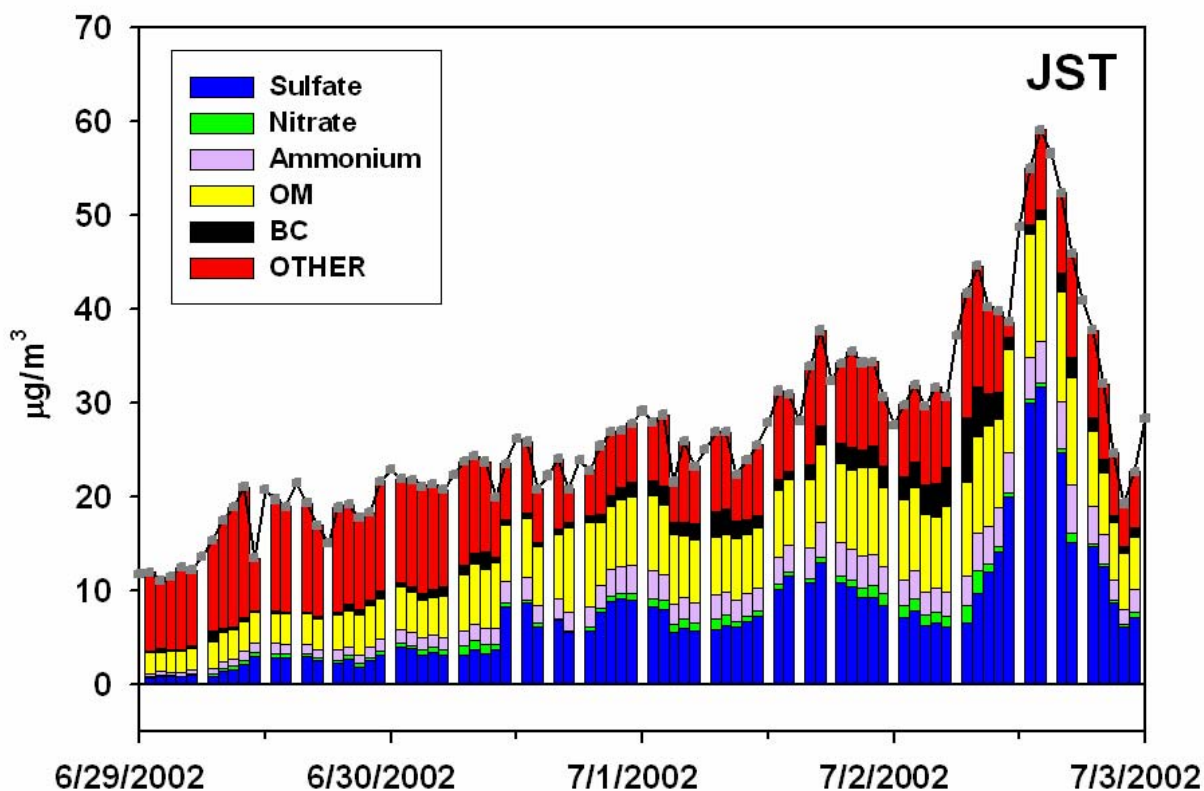


**Figure 3. Best Estimate  $PM_{2.5}$  mass and composition from filter-based measurements at SEARCH sites.**

reduction to  $NO$ , (c) black carbon (BC) by optical absorption, (d) total carbon (TC) by combustion to  $CO_2$ , and (e) organic carbon by difference between the latter two measurements. These continuous measurements are intended to be long-term, and in conjunction with co-measured meteorological and trace gas data, offer opportunities for: (1) investigating sources and chemical and physical dynamics of  $PM_{2.5}$ ; (2) evaluating chemical

transport and transformation models; and; (3) assessing the effectiveness of emissions reduction programs.

Figure 4 presents hourly mass and composition data from a high-PM<sub>2.5</sub> episode that occurred in the southeast during June-July, 2002. At the Atlanta site (JST), a multi-day buildup of PM<sub>2.5</sub> mass began on June 29 and culminated in a peak near 60 µg/m<sup>3</sup> during the afternoon of July 2. Sulfate concentrations are seen to be the driving influence in this mass increase, rising from a value near 1 µg/m<sup>3</sup> on June 29 to > 30 µg/m<sup>3</sup> during the mass concentration maximum on July 2. Other components, most notably OM and BC, also contributed to the total mass increase, but sulfate dominated the change, going from < 10% of the total mass on June 29 to over 50% on July 2. Using high-temporal resolution mass and composition data such as this allows detailed analysis of the factors contributing to high pollution episodes such as the one presented here.

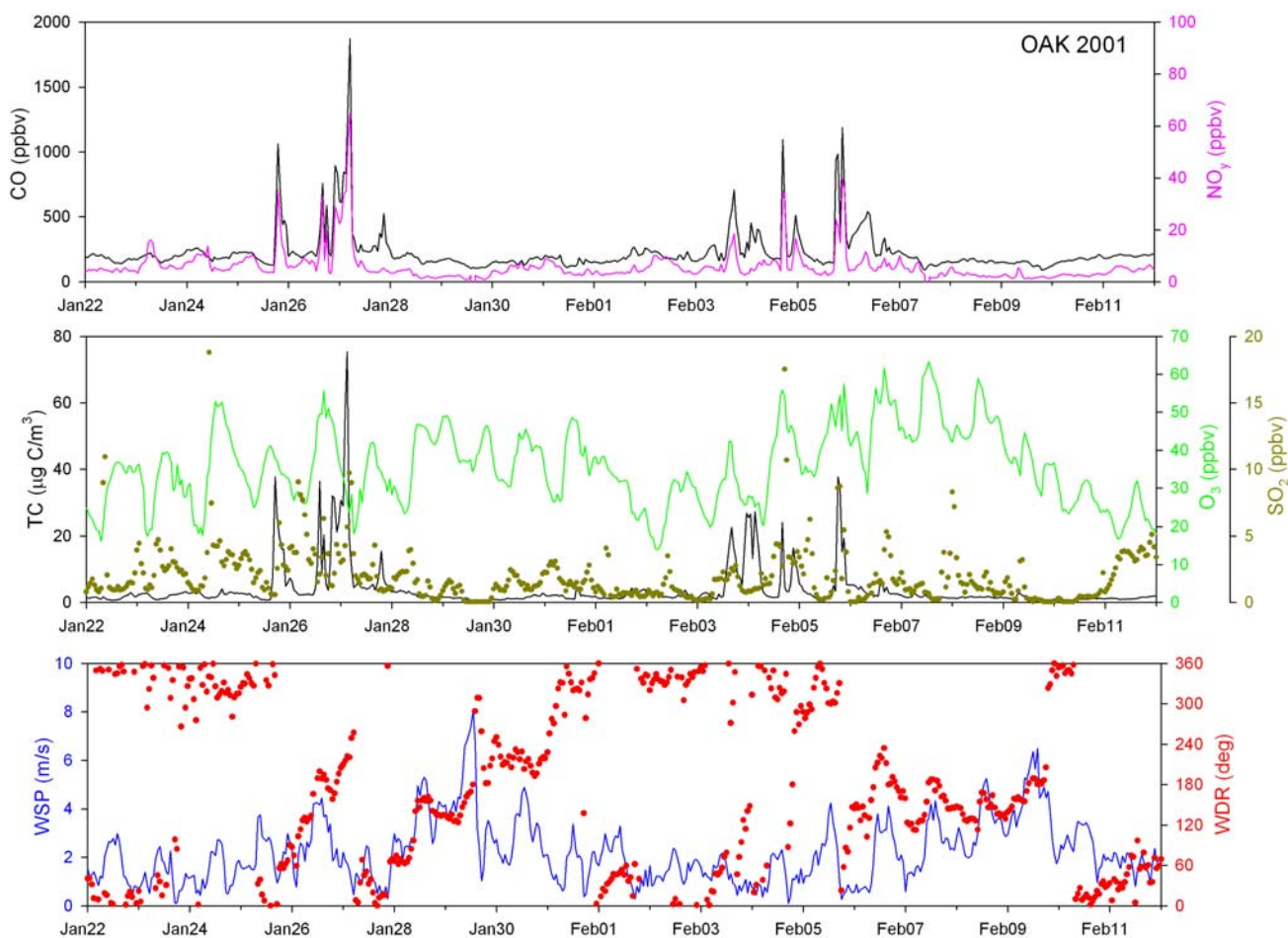


**Figure 4. Hourly PM<sub>2.5</sub> mass and composition at SEARCH site JST during June-July 2002.**

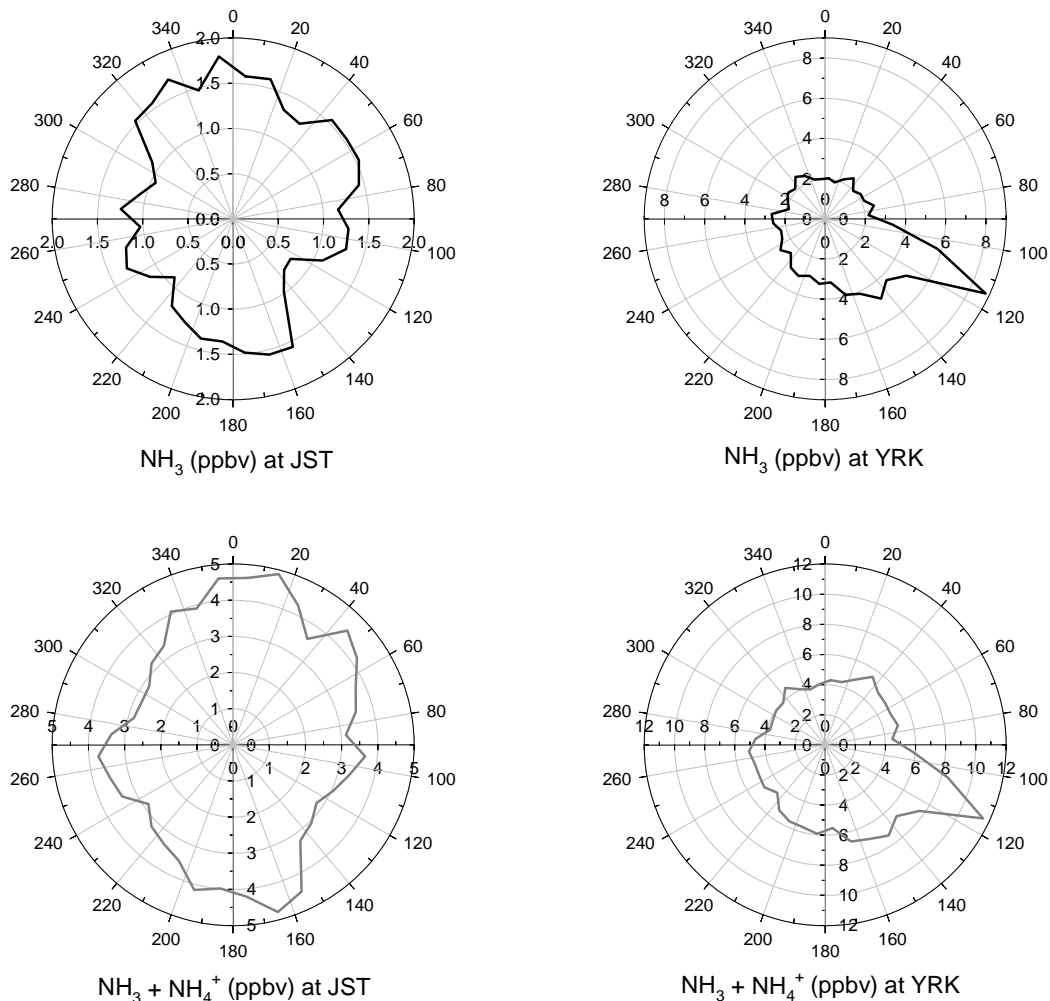
Controlled burning activities are prevalent in the southeastern U. S. during winter months and are used by various government agencies to control vegetation accumulation, mitigate disease and insect infestations, and manage habitat for endangered species. Smoke plumes from these fires are regularly observed at SEARCH sites during these times. The measurements made at the sites present a unique opportunity to characterize the chemical nature of these plumes and provide an initial gauge of the overall effect that these activities have on the air quality of the southeastern region. An example of a smoke plume interception



at OAK (Oak Grove, MS) in 2001 is shown in Figure 5. CO, NO<sub>y</sub>, and PM<sub>2.5</sub> total carbon (TC) concentrations all increased sharply on two separate occasions during late January and early February. The first episode, January 25-27, occurred as the wind direction swung from west-northwest to east to south over January 25 and 26. CO and TC values are seen to follow each other closely over the episode and CO:NO<sub>y</sub> molar ratios in the plume are 25-35, quite different from typical urban plume ratios < 10. O<sub>3</sub> mixing ratios through the episode were not substantially higher than before or after the passage of the plume and SO<sub>2</sub> values were slightly elevated. The second episode occurred February 3-6, again as wind direction shifted from west-northwest through the east to the south on February 3, and again on February 4. Once again, CO and PM<sub>2.5</sub> TC tracked each other closely, CO:NO<sub>y</sub> molar ratios obtained similar values as in the first episode, and O<sub>3</sub> increased somewhat as the episode continued. In both of these plumes, PM<sub>2.5</sub> TC concentrations reached very high values ranging from 15 μg/m<sup>3</sup> to nearly 80 μg/m<sup>3</sup>. As additional evidence that these plumes represent fires, satellite fire detection data for this time period was obtained from the U. S. Forest Service Remote Sensing Applications Center website. Several fires were detected in southern Mississippi, western Alabama and eastern Louisiana during this time period with the closest occurring 53 km west of the OAK site, 64 km southwest of the site, and 54 km north-northwest of the site.



**Figure 5. Biomass burning event observed at SEARCH site OAK in 2001.**



**Figure 6. Measurements of gaseous and total ammonia as a function of wind direction at SEARCH sites JST and YRK.**

In an effort to better characterize the dynamics of  $\text{NH}_3$  in the atmosphere of the southeastern U. S., continuous  $\text{NH}_3$  measurements were implemented at three SEARCH sites in 2007, an industrial-residential site located at Jefferson Street in midtown Atlanta, Georgia (JST), a rural-agricultural site located near Yorkville, Georgia (YRK), approximately 55 km west-northwest of the Jefferson Street, Atlanta site, and a rural-forested site near Oak Grove, Mississippi (not reported here). Figure 6 presents  $\text{NH}_3$  and total ammonia ( $\text{NH}_x = \text{NH}_3 + \text{NH}_4^+$ ) as a function of wind direction. The mixing ratio averages presented in these plots are the means of all hourly-average values falling into  $10^\circ$  wind direction bins, and are plotted at the midpoint of each bin. At JST there is a slight tendency for larger  $\text{NH}_3$  and  $\text{NH}_x$  values when winds are generally from the  $350^\circ$ - $20^\circ$  and  $150^\circ$ - $170^\circ$  sectors, which may be related to motor vehicle exhaust. A trucking facility is located  $< 100$  m due north of the JST site, while a parking lot and a moderately-traveled urban two-lane road lies within 150 m to the south.

In contrast, the wind direction plots for YRK exhibit a markedly different tendency. In the 110-150° sector, two large peaks occur for both NH<sub>3</sub> and NH<sub>x</sub> and are substantially larger than the means for all other wind sectors. In fact, excluding the quadrant 90-180°, the mixing ratio values for NH<sub>3</sub> and NH<sub>x</sub> are only slightly larger at YRK than at JST. YRK is located in a mixed agricultural and forested landscape and is situated in a pasture with nearby poultry-rearing houses, the two closest of which are about 1.3 km from the YRK site. Two more distant facilities are 2.6-3.0 km away. All of these poultry houses lay within the directional sector of 100°-160° with respect to the YRK site, and the two major peaks in the NH<sub>3</sub> and NH<sub>x</sub> plots of Figure 6 (at 115° and 145°) correspond very closely to the direction of the two closest broiler facilities. Of the 40 hourly-average NH<sub>3</sub> values > 20 ppbv measured at YRK during July through December 2007, 27 (67.5%) have hourly-average wind directions from within the 110-150° sector and 39 (97.5%) fall within the 90-180° sector. Similarly, for the 167 hourly-average NH<sub>3</sub> values > 10 ppbv, 90 (53.9%) have wind directions within the 110-150° sector and 146 (87.4%) fall within the 90-180° sector. It therefore seems very likely that the high average values and large variability of NH<sub>3</sub> and NH<sub>x</sub> observed at YRK are due directly to emissions from the nearby poultry facilities. Back-trajectory analyses of selected episodes of high NH<sub>3</sub> further confirm this hypothesis.

## Summary

By the end of 2008, more than ten years of data will have been collected at eight continuously operating sites in SEARCH. The comprehensive nature and rigorous quality assurance of the data collected at each SEARCH location provides a rich repository for scientific investigations of atmospheric chemistry and air quality processes, for both gaseous species and PM. SEARCH is slated to continue operation through 2011, with possible further extension beyond that time. All data collected as part of SEARCH is freely available from Atmospheric Research & Analysis, Inc.'s website (<http://www.atmospheric-research.com>). Special data requests can be sent to Eric Edgerton ([eedgerton@atmospheric-research.com](mailto:eedgerton@atmospheric-research.com)).

## References

1. Laden, F., Neas, L. M., Dockery, D. W., Schwartz, J. (2000) Association of fine particulate matter from different sources with daily mortality in six U. S. Cities. *Environ. Health Perspectives*, 108, 941-947.
2. Somers, C. M., McCarry, B. E., Malek, F., Quinn, J. S. (2004) Reduction of particulate air pollution lowers the risk of heritable mutations in mice. *Science*, 304, 1008-1010.
3. Peters, A., Dockery, D. W., Muller, J. E., Mittleman, M. A. (2001) Increased particulate air pollution and the triggering of myocardial infarction. *Circulation*, 103, 2810-2815.
4. Peel, J. L., Tolbert, P. E., Klein, M., Metzger, K. B., Flanders, W. D., Todd, K., Mulholland, J. A., Knox, T., Ryan, P. B., Frumkin, H. (2005) Ambient air pollution and respiratory emergency department visits. *Epidemiology*, 16, 164-174.
5. Metzger, K. B., Tolbert, P. E., Klein, M., Peel, J. L., Flanders, W. D., Todd, K., Mulholland, J. A., Ryan, P. B., Frumkin, H. (2004) Ambient air pollution and cardiovascular emergency Department Visits. *Epidemiology*, 15, 46-56.
6. Klemm, R. J., Lipfert, F. W., Wyzga, R. E., Gust, C. (2004) Daily mortality and air pollution in Atlanta: Two years of data from ARIES. *Inhalation Toxicology*, 16, Supplement 1, 131-141.



7. Charlson, R. J., Lovelock, J. E., Andreae, M. O., Warren, S. G. (1987) Oceanic phytoplankton, atmospheric sulfur, cloud albedo and climate. *Nature*, 326, 655-661.
8. Intergovernmental Panel on Climate Change (2001) *Climate Change 2001: The Scientific Basis*, Cambridge University Press, Cambridge, UK.
9. Hansen, D. A., Edgerton, E. S., Hartsell, B. E., Jansen, J. J., Kandasamy, N., Hidy, G. M., Blanchard, C. L. (2003) The Southeastern Aerosol Research and Characterization Study: Part 1 – Overview. *J. Air & Waste Manage. Assoc.*, 53, 1460-1471.
10. Edgerton, E. S., B. E. Hartsell, R. D. Saylor, J. J. Jansen, D. A. Hansen, and G. M. Hidy (2005) The Southeastern Aerosol Research and Characterization Study: Part II. Filter-based measurements of fine and coarse particulate matter mass and composition. *J. Air & Waste Manage. Assoc.*, 55, 1527-1542.
11. Edgerton, E. S., B. E. Hartsell, R. D. Saylor, J. J. Jansen, D. A. Hansen, and G. M. Hidy (2006) The Southeastern Aerosol Research and Characterization Study: Part III. Continuous measurements of PM<sub>2.5</sub> mass and composition. *J. Air & Waste Manage. Assoc.*, 56, 1325-1341.
12. Edgerton, E. S., R. D. Saylor, B. E. Hartsell, J. J. Jansen, and D. A. Hansen (2007) Ammonia and ammonium measurements from the southeastern United States. *Atmos. Environ.*, 41, 3339-3351.
13. Edgerton, E. S., G. S. Casuccio, R. D. Saylor, T. L. Lersch, B. E. Hartsell, and J. J. Jansen (2008) Measurements of PM<sub>10-2.5</sub> organic, elemental and carbonate carbon in the southeastern U. S. *J. Air & Waste Manage. Assoc.*, in press.

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