ASSISTANCE AGREEMENT QUARTERLY REPORT
for the reporting period April 13, 2002 through July 12, 2002

September 30, 2002

St. Louis - Midwest Particulate Matter (PM) Supersite Monitoring Program
EPA Assistance ID No. R-82805901-0

Work Progress and Status

Tenth quarter activities included routine data collection, validation and analysis. Efforts were continued towards securing funding for a second year of data collection at the East St. Louis (IL) core site and a deployment of the movable platform at Reserve (KS) to support regional haze studies.

1. *Routine Data Collection*.
   - **Core Site Operations**. The St. Louis – Midwest Supersite commenced field monitoring at the East St. Louis core site in April 2001. Particle size distribution measurements started on April 1, 2001 and most other semicontinuous and integrated samplers were operational by April 16, 2001. Some samplers (e.g., HSPH toxicological sampler, HSPH medium-volume dichotomous sampler) required additional development and were not deployed until May or June 2001. Based on this startup sequence, the St. Louis – Midwest Supersite core site measurements under this cooperative agreement shall include the period April 1, 2001 through May 31, 2002 and thus the core site measurements have been completed.
   - **Satellite Site Operations**. The St. Louis – Midwest Supersite program also includes measurements at two satellite sites periodically over a one-year period. Relatively modest sampling was conducted towards this objective during the period April 1, 2001 through May 31, 2002 because numerous instruments deployed in this measurement program are prototypes and it was deemed important to keep the movable platform at the core site to ensure high data completeness and to provide a robust data set for determining measurement precision and other performance indices. The satellite site measurements will be completed by mid-2003. This does not sacrifice any of the data collection objectives, however, as additional funding is being programmed to continue the core site operations through May 31, 2003 (see item #2 below) and thus there still will be simultaneous core site and satellite site measurements to provide an assessment of spatial differences in the high time resolution PM measurements as set forth in our original Supersites proposal.

2. *Second Year Measurement Program*. A Request for Assistance Agreement has been submitted to USEPA Region VII to support: a second year of measurements at the East St. Louis (IL) core site; and two six-week deployments of the movable platform at Reserve (KS). The sustained core site operations will include most of the Year 1 matrix. This will

provide a significantly larger data set to support our investigations of aerosol dynamics and climatology, and will provide added power to the various exposure and health effects studies drawing upon the St. Louis – Midwest Supersite data. In addition to these objectives, the second year of measurements are designed to also address questions concerning regional haze. To this end, in collaboration with the Sac & Fox Nation of Missouri, the movable platform will be deployed for two six-week periods in rural Reserve (KS). While the second year measurement program will be funded through a separate cooperative agreement, forthcoming quarterly reports will draw upon the data which, in light of the aforementioned reasons, complements the Year 1 measurements conducted on behalf of this cooperative agreement. Details concerning the Year 2 measurement program will presented in the next quarterly report.

3. *Coordination with the St. Louis Community Air Project (CAP) Air Toxics Measurement Program.* In May 2002, Mr. James Hirtz commenced a three-month IPA assignment with Dr. Jay Turner at Washington University. Mr. Hirtz is the USEPA Region VII Technical Lead for the CAP project which features air toxics monitoring in the Benton Park neighborhood of the City of St. Louis. In collaboration with Dr. Turner, he has been integrating the St. Louis – Midwest Supersite's detailed meteorology and aerosol data set with the CAP data. Additional details will be presented in the next quarterly report. One preliminary finding, however, is that the East St. Louis (IL) Supersite core site and the Benton Park (St. Louis City, MO) CAP core site show excellent agreement for 24-hour average elemental carbon; this suggests that – at least for elemental carbon - microscale and middle influences at the two sites are either similar in behavior or small compared to the regional background. This issue is further discussed under item #4 below.

4. *Middle Scale Contributions to PM-2.5 Black Carbon at the East St. Louis (IL) Core Site*. One of the several data analysis tasks currently underway includes an estimation of middle scale contributions to PM-2.5 black carbon. This is an important assessment as the site because the East St. Louis core site is relatively close to a major interstate. A qualitative assessment prior to site selection provided confidence that the site would be largely representative of urban/regional scale behavior, but quantitative analysis is desired to support this hypothesis. Using the methodology set forth by Watson and Chow (2001)[1], middle scale contributions (approximately 0.1 – 1 km from the receptor) to the five-minute average aethalometer black carbon data were estimated for the period November 8, 2001 through December 11, 2001. The mean hourly-average middle scale contribution was 14% at the East St. Louis (IL) core site and 11% at the Park Hills (MO) rural satellite site. Figure 1 shows the total black carbon and middle scale contributions at the East St. Louis core site for a one-week period. Middle scale contributions to the total black carbon concentration are relatively small with the exception of a few morning spikes (note especially the mornings of December 6-7). The same time series is shown in Figure 2 with the y-axis expanded to show only the range 0-1500 ng/m^3 for the black carbon concentration and the morning rush hour period denoted by rectangular boxes; the seven-day time series is Monday through

[1] J.G. Watson and J.C., Chow (2001) *J. Air Waste Manage. Assoc., 51*, 1522-1538.

Sunday. There appears to be a middle scale contribution peak each weekday morning which coincides with the rush hour period; this peak is not present on the weekends. In most cases, however, the middle scale contribution even during the weekday morning rush hour period is relatively small compared to the total black carbon concentration. There are few hourly periods when the middle scale contribution accounts for virtually all of the hourly-average black carbon concentration; furthermore, these cases do not exclusively correspond to the rush hour periods. These results are preliminary and the analysis is currently being expanded to include a fully year of data segregated by season, weekdays/weekends, and wind direction.

Figures 3 and 4 are time series analogous to Figures 1 and 2, respectively, for the Park Hills (MO) rural satellite site. In this case, the total black carbon concentrations are much lower and there is no structure to the middle scale contributions (which must be qualified because we have not yet determined the robustness of the Watson and Chow method at such low black carbon concentrations).

5. *Wintertime PILS Nitrate Measurements.* An issue of significant interest is the performance of semicontinuous nitrate monitors during cold weather, notably when the ambient temperature is much lower than the shelter temperature housing the unit. A Georgia Tech/Brookhaven National Laboratory (GT/BNL) Particle-into-Liquid Sampler (PILS) unit has been operating at the East St. Louis core site since Summer 2001 and the system was modified in early December 2001 in an attempt to suppress nitrate volatilization from particulate matter upon entering the shelter. The approach was to introduce a sheath flow of ambient air around the sample line along the entire sample path inside the shelter – including the denuders - prior to the zone for mixing the ambient sample with superheated steam. The premise – as with similar designs for nitrate units such as the R&P 8400N – is to keep the sample as close to ambient temperature as possible to suppress nitrate volatilization in the warmer shelter environment. The scatter plot shown in Figure 5 demonstrates the success of this modification to the PILS unit. A comparison of daily-average PILS nitrate to daily-average HEADS nitrate (a substrate-based method) shows excellent agreement for the period December 8, 2001 through January 8, 2002. The success of this approach is reinforced by Figure 6 which is a time series for the same period with the daily-average surface temperature superposed. There is a relatively large dynamic range for both the daily-average temperature (-7°C to +9°C) and the daily-average PILS nitrate concentration (1 $\mu g/m^3$ to 7 $\mu g/m^3$) with good agreement between PILS nitrate and the substrate-based HEADS nitrate over the entire period.

Personnel

The Principal Investigator has been participating in two programs which provide opportunities for undergraduate students to work with the Air Quality Laboratory at Washington University on Supersite-based projects. These programs include a recently-awarded NSF REU (Research Experience for Undergraduates) program based in the Environmental Engineering Program at Washington University and also this program's ongoing Summer Undergraduate Internship Program. This summer four undergraduate students – two from Washington University and two

from other institutions – are working full-time on Supersite-related sampling and data analysis activities. An explicit effort was made to recruit students from underrepresented groups in engineering and science, and towards this end the four students include three females. Together with the two students who worked full-time with our Supersite under the Summer 2001 Undergraduate Internship Program and two undergraduate students who worked part-time during the academic year 2001-2002, to date eight undergraduate students have substantively contributed to the field sampling operations including five females and one African American male. One student from last year's program – Ms. Elizabeth Simon – graduated with a bachelor's degree in Environmental Studies and has subsequently been hired by Sonoma Technology, Inc., and thus will continue to work in the air quality field.

Expenditures

There are no adjustments to the project budget.

Quality Assurance

Data validation will be a major activity in the eleventh quarter, including populating the St. Louis – Midwest Supersite relational database. This database was developed by Desert Research Institute and draws extensively upon the database designed and implemented for the CRPAQS/Fresno Supersite.

Results

Selected results were presented as items #4 and #5 under the Section "Work Progress and Status".

Planned Activities for the Forthcoming Quarter

Eleventh quarter activities will focus on: data validation for the full first year of semicontinuous and integrated sampling; retrospective analysis of SEAS slurry samples for hourly-average metals (University of Maryland) and high-volume filter samples for 14-hour average organics speciation (University of Wisconsin) for an initial set of three one-week periods each encompassing a different type of signature in the governing meteorology and aerosol bulk-species behavior (these three one-week periods have already been identified); integrating the Supersite particulate matter and CAP air toxics data sets; and other data analyses to investigate aerosol climatology in St. Louis.

There will be four presentations at the AAAR Annual Meeting (October 2002) which draw upon the St. Louis – Midwest Supersite data, and two manuscripts are currently being prepared for submission in October to peer-reviewed journals: an overview of the St. Louis – Midwest Supersite program (Dr. Turner, lead author); and a field evaluation of the Sunset Labs Semicontinuous ECOC analyzer (Dr. Schauer, lead author).

The St. Louis – Midwest Supersite team will hold its third data analysis workshop on October 23, 2002. A major objective of this workshop is to identify a suite a topics warranting papers and to assign data analysis and writing tasks to team members.

Publications and Presentations

Project overview briefings were presented at: (1) Washington University Chemical Engineering Department Seminar Series, St. Louis, MO, April 22, 2002; (2) Gateway Society of Hazardous Materials Managers Environmental Compliance Seminar, St. Louis, MO, April 25, 2002; (3) USEPA Region VII Regional Air Meeting, Kansas City, MO, May 14-15, 2002; and (4) Sonoma Technology, Inc., Petaluma, CA, June 12, 2002.

Quarterly Report Summary

See Attached

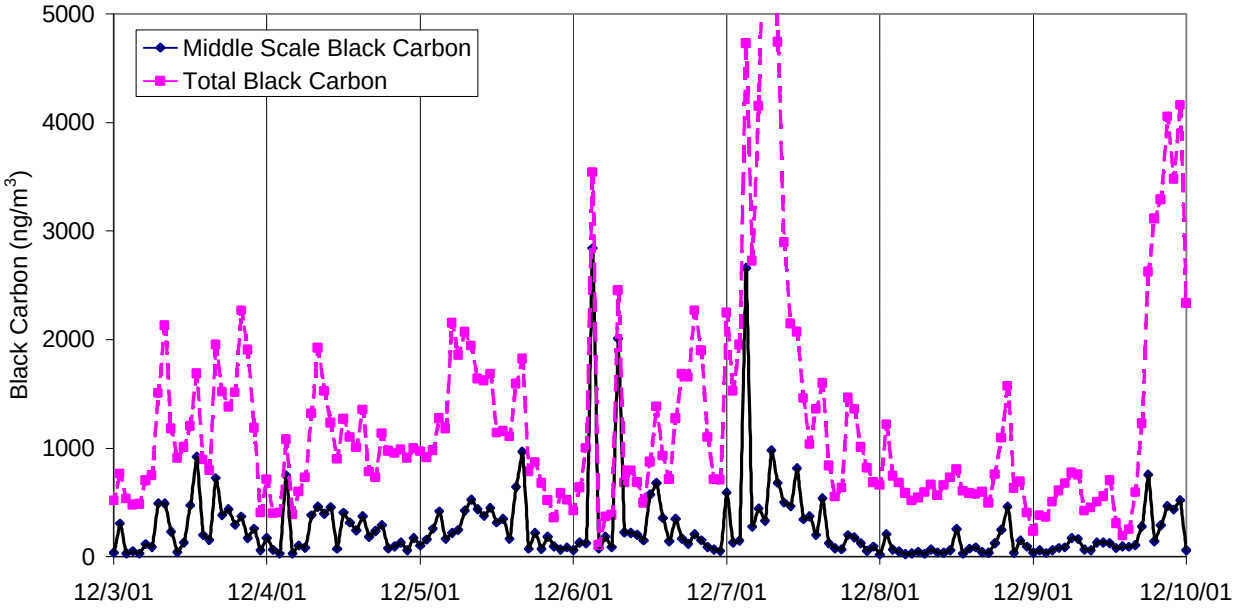

Figure 1. Time series for the hourly-average of 5-minute middle scale contributions to the aethalometer black carbon measured at the East St. Louis (IL) core site, December 3-9, 2001.

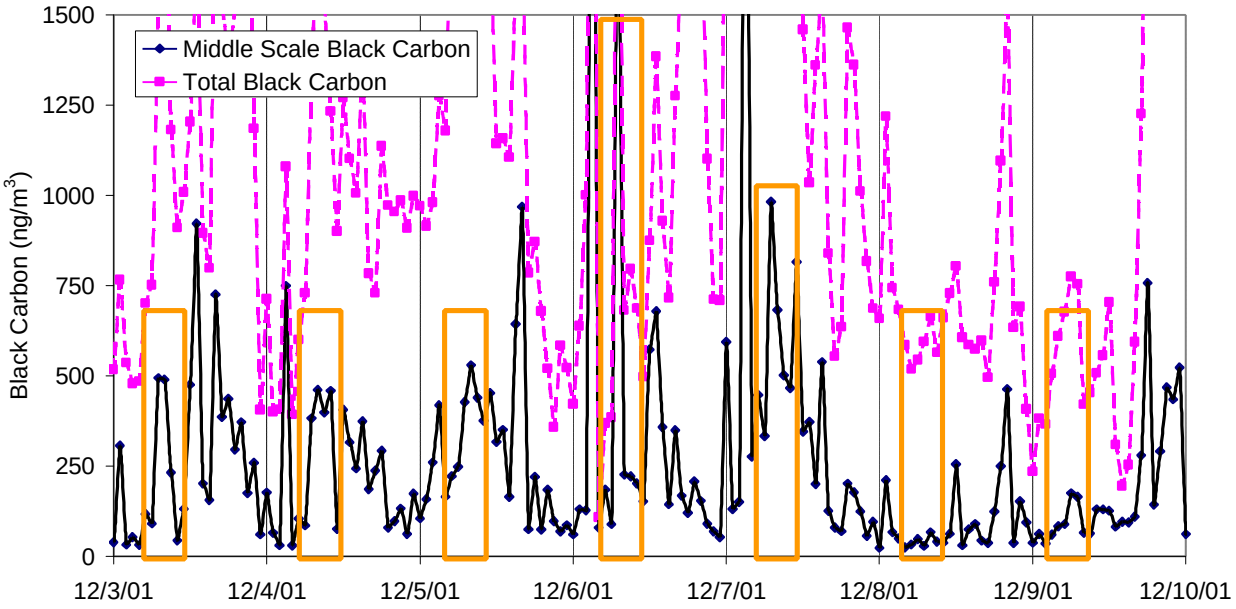

Figure 2. Time series of Figure 1 with expanded scale for the aethalometer black carbon concentration and the morning rush hour periods highlighted by the rectangular boxes.

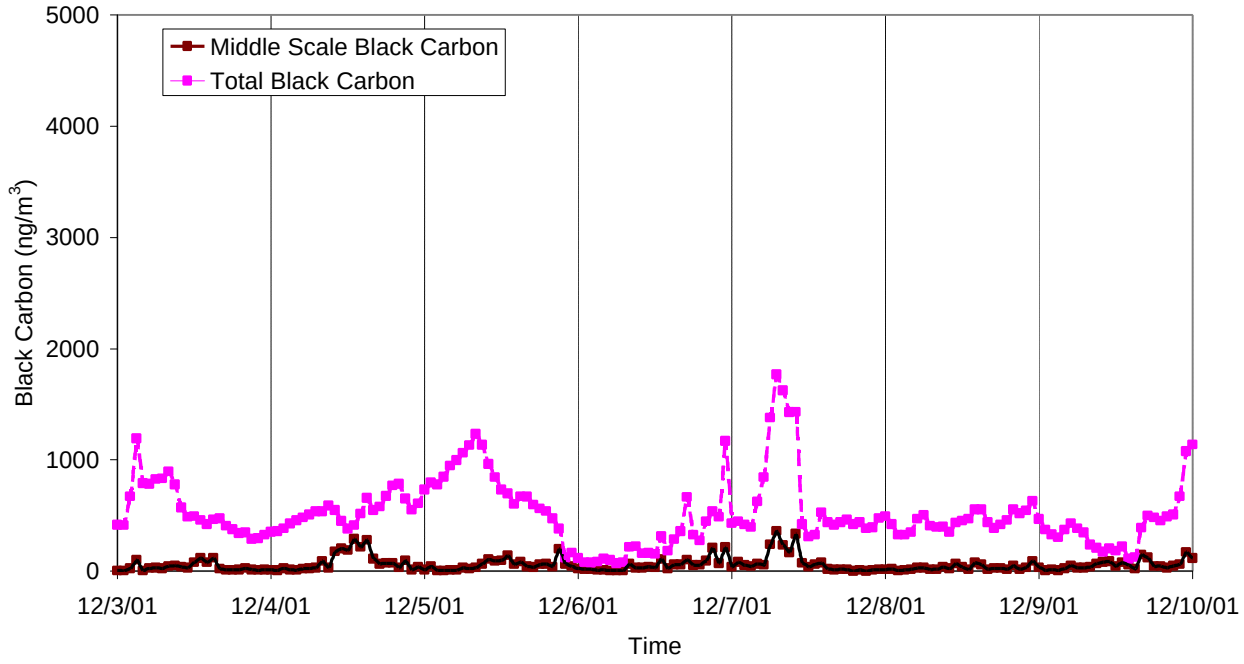

Figure 3. Time series for the hourly-average of 5-minute middle scale contributions to the aethalometer black carbon measured at the Park Hills (MO) rural satellite site, December 3-9, 2001.

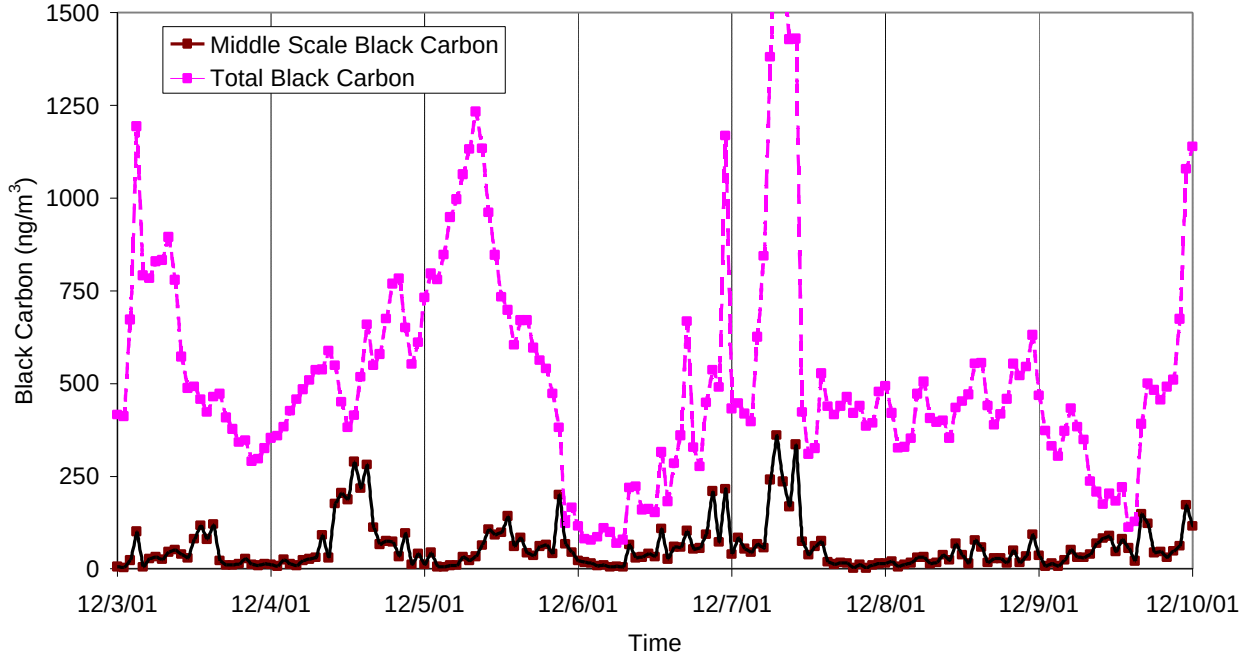

Figure 4. Time series of Figure 3 with expanded scale for the aethalometer black carbon concentration.

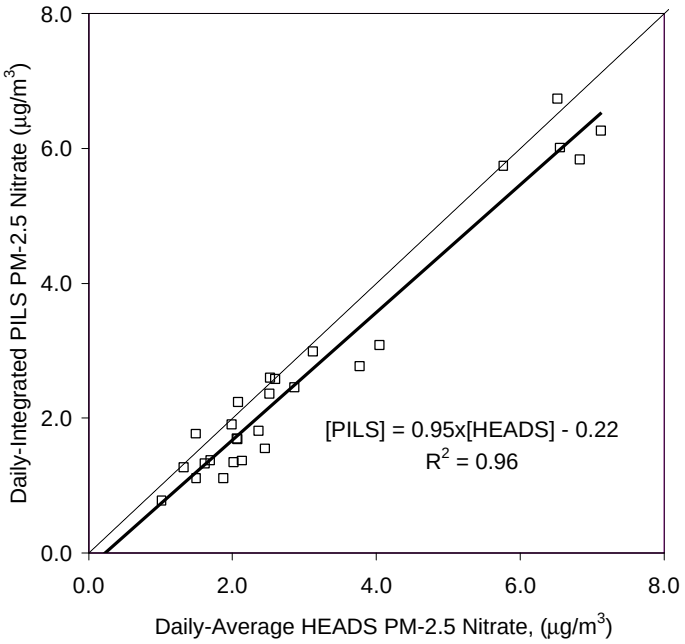

Figure 5. Scatter plot for daily-average PM-2.5 nitrate measured by the Particle-into-Liquid Sampler (PILS) versus the Harvard-EPA Annual Denuder System (HEADS), December 8, 2001 through January 8, 2002.

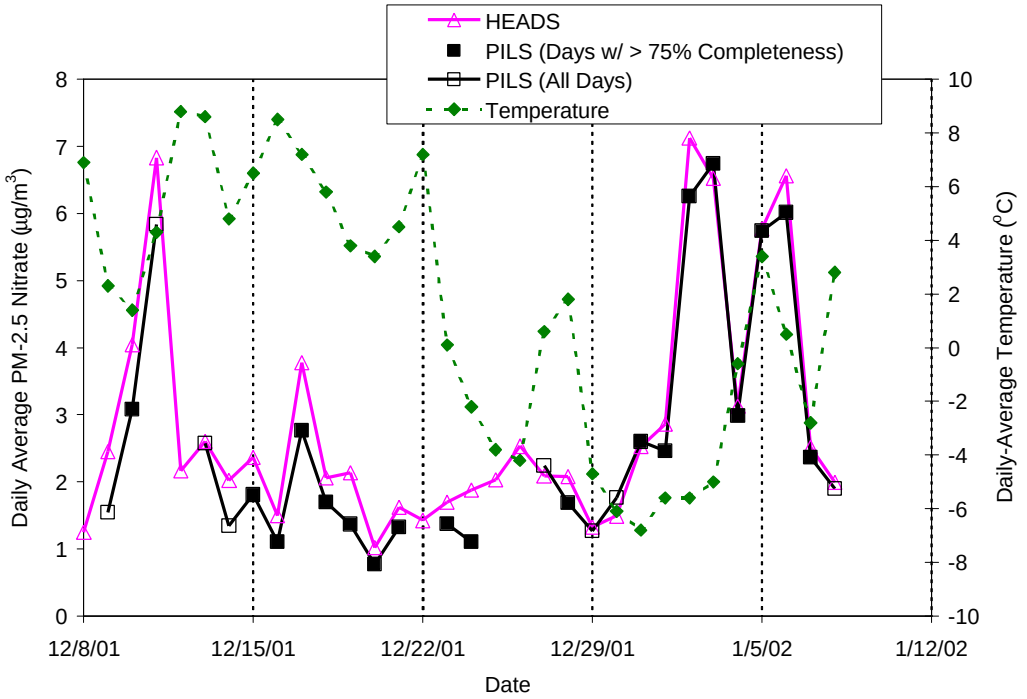

Figure 6. Time series for daily-average PM-2.5 nitrate measured by the Particle-into-Liquid Sampler (PILS) versus the Harvard-EPA Annual Denuder System (HEADS), December 8, 2001 through January 8, 2002.