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September 28, 2011

EPA-CASAC-11-010

The Honorable Lisa P. Jackson
Administrator
U.S. Environmental Protection Agency
1200 Pennsylvania Avenue, NW
Washington, DC 20460

Subject: Review of EPA's Photochemical Assessment Monitoring Stations (PAMS) Network Re-engineering Project

Dear Administrator Jackson:

The Clean Air Scientific Advisory Committee (CASAC) Air Monitoring and Methods Subcommittee (AMMS) held three public teleconference calls on May 16, May 17, and July 18, 2011 to review EPA's Photochemical Assessment Monitoring Stations (PAMS) Network Re-engineering project. The chartered CASAC reviewed the AMMS PAMS Review Report during the August 29, 2011 public teleconference, and approved the Report after the teleconference. EPA's Office of Air Quality Planning and Standards requested the CASAC AMMS Subcommittee to review its White Paper entitled "White Paper on EPA's PAMS Network Re-engineering project" (April 2011), respond to charge questions, and provide advice and ideas on how to improve the PAMS program. This letter provides CASAC's response to this advisory request and summarizes CASAC's views on monitoring issues pertaining to EPA's PAMS Network Re-engineering project. The CASAC and Panel membership is listed in Enclosure A. CASAC's responses to EPA's charge questions are presented in Enclosure B. References that support the response to Charge Question 17 are provided in Enclosure C. Finally, Enclosure D is a compilation of individual panel member comments.

The 1990 Clean Air Act (CAA) Amendments required that EPA revise ambient air quality surveillance regulations to include provisions for enhanced monitoring of ozone (O_3), oxides of nitrogen (NO_x), volatile organic compounds (VOCs), selected carbonyl compounds, and meteorological parameters. Under the CAA, states were required to adopt and implement a program to improve ambient monitoring activities and the monitoring of emissions of NO_x and VOC. Each State Implementation Plan (SIP) for the affected areas must contain measures to implement the ambient monitoring of such air pollutants. EPA subsequently required states to establish PAMS as part of their SIP monitoring networks in ozone nonattainment areas classified as serious, severe, or extreme. In 2006, EPA revised the PAMS requirements to allow PAMS monitoring to be more customized to local data needs, and to provide states with flexibility to reduce the overall size of their PAMS programs and to use the associated resources for other types of monitoring they consider more useful. The chief objective of the PAMS requirements is to provide an air quality database that will assist air pollution control agencies in evaluating, tracking the progress of, and, if necessary, refining control strategies for attaining the ozone National Ambient Air Quality Standards (NAAQS). In addition, data from the PAMS will aid in preparation of air quality trends, assist in evaluating photochemical model performance, and help states implement the most cost-effective regulatory controls.

In its White Paper, EPA identified several issues associated with the current PAMS Network Design, including poor spatial coverage (with PAMS sites mostly in coastal areas), limited value for model development/testing, limited seasonal monitoring of PAMS, and limited network design for assessing extremes in variables associated with PAMS monitoring. EPA identified various options to address these issues, including lengthening the PAMS monitoring season, providing for mobile PAMS sites, and adding PAMS measurements to the existing urban “NCore” multi-pollutant network that integrates several advanced measurement systems for particles, pollutant gases and meteorology.

Overall, CASAC concludes that EPA’s proposed approaches for monitoring methods and network design pertaining to EPA's PAMS Network Re-engineering project are appropriate, and that the network will continue to assist in developing a better understanding of ozone chemistry, transport, modeling, and attainment demonstration. CASAC provides the following priority recommendations to strengthen and improve the PAMS program. Additional details on these and other recommendations are discussed within the enclosed report.

First, EPA should revise PAMS network objectives to reflect a balanced approach that would enable state and local agencies to more effectively support their local attainment efforts and allow EPA to continue to evaluate national trends of ozone precursors. CASAC finds that the existing uniform national network design model for PAMS is outdated and too resource intensive, and recommends that greater flexibility for network design and implementation of the PAMs program be transferred to state and local monitoring agencies to allow monitoring, research and data analysis to be better tailored to the specific needs of each ozone problem area. The PAMS monitoring season should not be mandated and rigid; it should be flexible, adopted on a region-by-region basis, and based on rational guidance utilizing location specific ozone observations. This flexibility should not conflict with national goals for the PAMS program.

Second, PAMS data analysis at the national and regional levels should focus on trending, accountability analyses for emission reduction programs, and evaluation of air quality models. Trending must be carefully conducted given the range of objectives that are used to site monitors. For example, accountability analyses on the ozone precursors profile, ozone itself, and on other pollutants should examine the impact of increased ethanol use in motor vehicle fuels. As data analyses are carried out, there should be interaction with data users to assure that the analyses will address issues associated with air quality modeling. CASAC also recommends that PAMS data be used to conduct national or regional analyses to investigate ozone formation potential. Such analyses should support model development for secondary organic aerosol formation. Furthermore, since the lack of easy access to PAMS data is often cited as a major obstacle to its use, CASAC strongly recommends that PAMS data be made available through a user-friendly portal to promote more widespread use. Also, in the re-design of the overall PAMS network, EPA should break away from the 1990’s instrumentation and sampling methods and consider newer, less expensive and more suitable monitoring packages.

Third, EPA should reduce the minimum national requirements for reporting of specific organic species under the PAMS network, and provide various criteria for such reporting. CASAC recommends that EPA should add more biogenic VOC species to the required species monitoring list given the current trends of lower anthropogenic VOCs and the implications for rural areas. In addition, CASAC recommends adding additional compounds that may help track emissions from additional non-mobile sources or more recent fuel formulations from mobile sources.

In closing, CASAC appreciates the opportunity to provide input to EPA at this stage in the process, and trusts that our comments will be useful to EPA as it revises the PAMS program. We look forward to receiving the Agency's response.

Sincerely,

/Signed/ ***/Signed/***

Mr. George A. Allen, Chair CASAC Air Monitoring and Methods Subcommittee	Dr. Jonathan M. Samet, Chair Clean Air Scientific Advisory Committee

Enclosures

NOTICE

Enclosure A – Roster

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Abbreviations and Acronyms

ACARS	Aircraft Communications Addressing and Reporting System
AMDAR	Aircraft Meteorological Data Relay
AMMS	Air Monitoring and Methods Subcommittee
AOD	Aerosol Optical Depth
CAA	Clean Air Act
CASAC	Clean Air Scientific Advisory Committee
CMAQ	Community Multiscale Air Quality Model
CRD	Cavity Ringdown
CO	Carbon Monoxide
DOAS	Differential Optical Absorption Spectroscopy
EPA	U.S. Environmental Protection Agency
FID	Flame Ionization Detector
GC	Gas Chromatograph
LOD	Limit of Detection
MS	Mass Spectrometer
NAAQS	National Ambient Air Quality Standards
NATTS	National Air Toxics Trends Sites
NEI	National Emission Inventory
NOAA	National Oceanic and Atmospheric Administration
NO_x	Oxides of Nitrogen
OAQPS	EPA Office of Air Quality Planning and Standards
ORD	EPA Office of Research and Development
O_3	Ozone
PAMS	Photochemical Assessment Monitoring Stations
PM	Particulate Matter
QA/QC	Quality Assurance/Quality Control
RPO	Regional Planning Organization
SAB	EPA Science Advisory Board
SIP	State Implementation Plan
SOA	Secondary Organic Aerosol
SOx	Sulfur Oxides
TNMH	Total Non-Methane Hydrocarbon
VOCs	Volatile Organic Compounds

Enclosure B
CASAC Air Monitoring and Methods Subcommittee (AMMS)
Consensus Responses to Charge Questions

Background:

Section 182 (c)(1) of the 1990 Clean Air Act (CAA) Amendments required the EPA to promulgate rules for enhanced monitoring to obtain more comprehensive and representative data on ozone air pollution:

> *"In order to obtain more comprehensive and representative data on ozone air pollution, not later than 18 months after November 15, 1990, the Administrator shall promulgate rules, after notice and public comment, for enhanced monitoring of ozone, oxides of nitrogen, and volatile organic compounds. The rules shall, among other things, cover the location and maintenance of monitors. …"*

Section 185(b) of the CAA required EPA to work with the National Academy of Sciences (NAS) to conduct a study on the role of ozone precursors in tropospheric ozone formation and control.

> *"The Administrator, in conjunction with the National Academy of Sciences, shall conduct a study on the role of ozone precursors in tropospheric ozone formation and control. The study shall examine the roles of* NO_x *and VOC emission reductions, the extent to which* NO_x *reductions may contribute (or be counterproductive) to achievement of attainment in different nonattainment areas, the sensitivity of ozone to the control of* NO_x*, the availability and extent of controls for* NO_x*, the role of biogenic VOC emissions, and the basic information required for air quality models."*

In 1992, the NAS finalized the report entitled "Rethinking the Ozone Problem in Urban and Regional Air Pollution" (National Academy of Sciences, 1992). The report found that "Ambient air quality measurements now being performed are inadequate to elucidate the chemistry of atmospheric VOCs or to assess the contributions of different sources to individual concentrations of these compounds." which made several recommendations for improving monitoring for precursors of ozone:

> *"New measurement strategies that incorporate more accurate and precise measurements of the individual trace compounds involved in ozone chemistry should be developed to advance understanding of the formation of high concentrations of ozone in the United States and to verify estimates of VOC and* NO_x *emissions."*

In response to these requirements and the recommendations of the NAS report, on February 12, 1993, EPA revised the ambient air quality surveillance regulations in Title 40 Part 58 of the Code of Federal Regulations (40 CFR Part 58) to include provisions for enhanced monitoring of ozone (O_3), oxides of nitrogen (NO_x), volatile organic compounds (VOCs), selected carbonyl compounds, and meteorological parameters. The revisions required states and local monitoring agencies ("monitoring agencies") to establish Photochemical Assessment Monitoring Stations (PAMS) in ozone nonattainment areas classified as serious, severe, or extreme. The chief objective of the enhanced ozone monitoring revisions is to provide an air quality database that will assist air pollution control agencies in evaluating, tracking the progress of, and, if necessary, refining control strategies for attaining the ozone National Ambient Air Quality Standards (NAAQS). Ambient concentrations of ozone and ozone precursors will be used to make attainment/nonattainment decisions, aid in tracking VOC and NO_x emission inventory reductions, better characterize the nature and extent of the ozone problem, and prepare air quality trends. In addition, data from the PAMS provide an improved database for evaluating photochemical model performance, especially for future control strategy mid-course corrections as part of the continuing air quality management process. The data will be particularly useful to states in ensuring the implementation of the most cost-effective regulatory controls.

Twenty two areas were identified as being subject to PAMS at the time the rules were promulgated. Since then the number of areas subject to PAMS has grown to 25. Each PAMS area was required to install between 2 and 5 PAMS sites depending on the population of the area.[1] Four types of PAMS sites were identified: a) upwind (Type 1); b) maximum precursor emission rate (Type 2); c) maximum ozone (Type 3); and d) extreme downwind (Type 4) sites. The number and type of sites required was contingent on the population of the PAMS area.

In 2006, the PAMS requirements were revised to lower the minimum requirements for PAMS. The following changes were made to the PAMS requirements:

- The number of required PAMS sites was reduced; only one Type 2 site is required per area regardless of population, Type 4 sites are not required, and only one Type 1 or one Type 3 site is required per area.
- The requirements for speciated VOC measurements were reduced. Speciated VOC measurements are only required at Type 2 sites and one other site (either Type 1 or Type 3) per PAMS area. Carbonyl sampling is only required in areas classified as serious or above for the 8-hour O_3 standard.
- Conventional NO_2/ NO_x monitors are only required at Type 2 sites.
- High sensitivity NO_y monitors are required at one site per PAMS area (either Type 1 or Type 3).
- High sensitivity carbon monoxide (CO) monitors are required at Type 2 sites.

The intent of these revisions were to “allow PAMS monitoring to be more customized to local data needs rather than meeting so many specific requirements common to all subject O_3 nonattainment areas; the PAMS changes would also give states the flexibility to reduce the overall size of their PAMS programs—within limits—and to use the associated resources for other types of monitoring they consider more useful” (71 FR 2714).

EPA’s Office of Air Quality Planning and Standards (OAQPS) sought CASAC advice and ideas on how EPA can improve the PAMS program. CASAC focused on the following charge questions as part of its review, and provides the following responses to these charge questions.

Charge Question 1: *How should EPA prioritize the current PAMS objectives? What current objectives, if any, should be deemphasized or eliminated?*

As noted in EPA’s *Technical Assistance Document for Sampling and Analysis of Ozone Precursors* (USEPA, 1998), the current PAMS objectives are:

- Provide a speciated ambient air database which is both representative and useful for ascertaining ambient profiles and distinguishing among various individual VOC. These data

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[1] Flexibility was allowed such that some sites were able to serve as more than one PAMS area. For example a site could serve as an extreme downwind site (Type 4) for one area and an upwind site (Type 1) for another.

can later be used as evaluation tools for control strategies, cost-effectiveness, and for understanding the mechanisms of pollutant transport.

- Provide local, current meteorological and ambient data to serve as initial and boundary condition information for photochemical grid models. These data can later be used as a baseline for model evaluation and to minimize model adjustments and reliance on default settings.
- Provide a representative, speciated ambient air database which is characteristic of source emission impacts. These data can be particularly useful in analyzing emissions inventory issues and corroborating progress toward attainment.
- Provide ambient data measurements which would allow later preparation of unadjusted and adjusted pollutant trends reports.
- Provide additional measurements of selected criteria pollutants. Such measurements can later be used for attainment/nonattainment decisions and to construct NAAQS maintenance plans.
- Provide additional measurements of selected criteria and non-criteria pollutants from properly-sited locations. Such measurements can later be used for evaluating population exposure to air toxics as well as criteria pollutants.

In general, all of these objectives for the network remain valid and important, and will continue to assist in developing a better understanding of ozone chemistry, transport, modeling, and attainment demonstration. Additional objectives are emerging, including characterizing precursors of secondary organic aerosols, and characterizing long range transport of pollutants.

CASAC suggests that the objectives could be expressed in more concise language, and that objectives may need to be revised to include both a national and regional focus because national objectives may be different from regional objectives.

In prioritizing objectives for the network, CASAC notes that the network has been addressing some of these objectives (such as establishing baselines for VOC concentrations) for more than 15 years. In contrast, some objectives require the collection of new data. For example, changes in the composition of fuel and exhaust emissions as fuels evolve under Renewable Fuel Standards will require the collection of new datasets over the next decade. In addition, CASAC recommends that prioritization of objectives be region or air shed specific. Different non-attainment areas will have different outstanding questions to be answered, whether it is more VOC data and trends, or inventory uncertainties, or background conditions, or upper air meteorology. Prioritizing objectives should include both national and regional objectives.

Regarding the role of PAMS in terms of air toxics and climate relevant gases, EPA should consider these as secondary objectives.

Charge Question 2: *What additional objectives should EPA consider for the PAMS program at this time?*

CASAC concludes that EPA should consider the following additional objectives for the PAMS program:

1) Provide compound-specific diurnal patterns to evaluate emission profiles (as specified in emissions models by source) and for evaluation of the air quality modeling system overall (e.g., see Doraiswamy et al., 2009; Ren et al., 2003; and Ren et al., 2006).

2) Measurement of secondary organic aerosol (SOA) precursors with an emphasis on gathering data to support development of effective strategies for the reduction of SOA.

Charge Question 3: *What are the advantages and disadvantages of the current design with multiple sites per PAMS area? What changes, if any, should be made in the number and spatial distribution of required sites?*

The current PAMS network design calls for an array of sites around each PAMS area. Four different types of PAMS sites are identified in the current network design:

- *Type 1 Sites: Upwind and background characterization site.* These sites are established to characterize upwind background and transported ozone and its precursor concentrations entering the area and will identify those areas which are subjected to overwhelming incoming transport of ozone. The #1 sites are located in the predominant morning upwind direction from the local area of maximum precursor emissions and at a distance sufficient to obtain urban scale[2] measurements.
- *Type 2 Sites: Maximum ozone precursor emissions impact site.* These sites are established to monitor the magnitude and type of precursor emissions in the area where maximum precursor emissions representative of the MSA/CMSA are expected to impact and are suited for the monitoring of urban air toxic pollutants. The #2 Sites are located immediately downwind (using the same morning wind direction as for locating Site #1) of the area of maximum precursor emissions and are typically placed near the downwind boundary of the central business district (CBD) or primary area of precursor emissions mix to obtain neighborhood scale measurements. Additionally, a second #2 Site may be required depending on the size of the area.
- *Type 3 Sites: Maximum ozone concentration site.* These sites are intended to monitor maximum ozone concentrations occurring downwind from the area of maximum precursor emissions. Locations for #3 Sites should be chosen so that urban scale measurements are obtained. Typically, these sites are located 10 to 30 miles from the fringe of the urban area.
- *Type 4 Sites: Extreme downwind monitoring site.* These sites are established to characterize the extreme downwind transported ozone and its precursor concentrations exiting the area and will identify those areas which are potentially contributing to overwhelming ozone transport into other areas. The #4 Sites are located in the predominant afternoon downwind direction from the local area of maximum precursor emissions at a distance sufficient to obtain urban scale measurements.

The PAMS network was designed to capture upwind, urban core and downwind concentrations of ozone and ozone precursors and to use these data to support control strategy development and atmospheric modeling, with respect to the 1-hour ozone standard. However, given the current 8-hour standard with potentially very different (broader) areas of non-attainment than with the 1-hour standard, CASAC concludes that EPA should reassess and perhaps redefine the current meaning of upwind and downwind.

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[2] Urban scale defines concentrations within an area of city-like dimensions, on the order of 4 to 50 kilometers. Within a city, the geographic placement of sources may result in there being no single site that can be said to represent air quality on an urban scale. Neighborhood scale defines concentrations within some extended area of the city that has relatively uniform land use with dimensions in the 0.5 to 4.0 kilometers range. The neighborhood and urban scales have the potential to overlap in applications that concern secondarily formed or homogeneously distributed air pollutants.

CASAC concludes that temporal changes in the character and intensity of precursor emissions need to be captured by the network. In some Type 1 areas, the currently placed upwind ozone monitors are or could become non-attainment, depending on the level of the NAAQS. Long-range and medium-range transport are likely to be more important in the context of an 8-hour standard than a 1-hour standard. At the same time, the mix of VOC emissions is changing due to changes in fuel composition, among other factors, and NO_x emissions are declining, due to control of stationary and mobile sources.

The process of locating PAMS sites should seek to minimize redundancy, but provide robust information for defining ozone gradients and fluxes. Network design should rely on a combination of observations and model projections to define ozone production regions and modes of transport. Flexibility on the number and types of sites should still be available to the local and regional air quality agencies to meet their specific needs.

Charge Question 4: *Should EPA consider requiring PAMS measurements in areas other than areas classified as serious and above for the ozone NAAQS to improve spatial coverage?*

CASAC concludes that EPA should consider requiring PAMS measurements in areas other than areas classified as serious and above for the ozone NAAQS to improve spatial coverage. EPA could require such measurements to better characterize regional-scale ozone problems.

Since PAMS requirements originated, long-range transport of ozone has been recognized as more important than previously considered. Thus, there is a need to establish boundary conditions for the models and to provide tests for biogenic VOC emissions models. In addition, there are now areas in both the eastern and western US where natural gas development is rapidly expanding. These areas are sources of NO_x and VOC that contribute to downwind ozone concentrations. CASAC requests that EPA consider adding PAMS measurements to a set of sites that are part of existing air monitoring networks. This addition might involve only a slight change to current measurements at these sites, and could therefore be done at minimal cost.

Charge Question 5: *Should EPA consider requiring PAMS measurements at a new subset of ozone sites in addition to the traditional PAMS (e.g., maximum concentration sites in all non-attainment areas, all urban NCore sites)?*

CASAC recommends extending the existing PAMS network by adding regional PAMS monitoring sites. This would improve spatial characterization, identify undocumented sources and contribute to better understanding of ozone precursor chemistry. Regional PAMS sites should be located at existing regional ozone sites with due consideration of NCORE and other infrastructures. The site selection criteria should be flexible and adapted to the needs of each region. It is understood that given the limited resources, the regional PAMS sites would be added at the expense of some of the current urban sites. At regional sites, the sampling methods can be simpler than the urban PAMS sites.

In the re-design of the overall PAMS network, EPA should break away from the 1990’s instrumentation and sampling methods and consider newer, less expensive and more suitable monitoring packages.

Charge Question 6: *What role, if any, should mobile or temporary sites play in the PAMS program?*

CASAC concludes that mobile or temporary sites can provide useful measurement approaches for targeted purposes. Although mobile and temporary sites can be very useful, CASAC does not recommend that EPA make them mandatory across the country. They should be deployed at the discretion of state and local monitoring agencies based on specific local needs. Temporary sites can be constructed on a transportable platform (e.g., a trailer that can be moved from one location to another). A transportable monitoring platform can be deployed to a location for a period of time (e.g., a week to a year depending on the purpose of the deployment) during which some or all PAMS parameters can be monitored. Although this type of temporary site does not provide data for trending over a long period of time, it may provide a good indication on levels of ozone and its precursors. Deployment at a location for a month or multiple months would be most useful. Unless the purpose of monitoring is for long-term trending or NAAQS compliance determination, the information that can be extracted from any monitoring site gradually diminishes as the monitoring period is extended. By utilizing mobile or temporary sites, a monitoring agency can explore more locations and therefore achieve a better understanding about the spatial distribution of ozone and its precursors. Compared to fixed monitoring sites, mobile or temporary sites provide the needed flexibility and enable monitoring agencies to strike a balance between the temporal and spatial domains in the budget constrained environment.

Flexibility is desired because it will allow monitoring, research and data analysis to be tailored to the specific needs of each ozone problem area. Flexible approaches will also likely provide the information needed to select regionally specific workable control strategies, and meet the broad needs of diverse groups of stakeholders who use PAMS data.

Mobile and temporary sites could replace some Type 2 sites (i.e., source-oriented sites). A deployment of multiple months aimed at a particular source area would generate a considerable amount of data that is consistent with the purpose of Type 2 sites. Two transportable units are desirable because they can be deployed as a pair, one for upwind and the other for downwind from suspected major precursor sources. Using mobile or temporary sites to replace fixed Type 2 sites provides more flexibility and is more cost effective.

If monitoring agencies already have mobile or temporary monitoring platforms, they can also use them for other purposes, such as for screening candidate sites for permanent monitoring sites. CASAC concludes that intensive ozone study campaigns are valuable to understand ozone issues and help develop ozone mitigation strategies, and mobile (including aircraft) and temporary sites can play an important role in these campaigns. There have been some discussions on highly-equipped mobile/transportable monitoring platforms for near road monitoring. There may be some synergy to combine this type of near road monitoring with a mobile/transportable PAMS platform that could be used for studies on air toxics hot spots, suspected transport issues, model validation, etc.

CASAC emphasizes the importance of proper documentation associated with mobile and temporary PAMS monitoring activities. The documentation should cover not only the typical monitoring information (e.g., location, date, time, etc.), but also the context within which the mobile or temporary sites are deployed (e.g., the reasons, surrounding sources, historic information at this location, etc.).

Charge Question 7: *EPA has received feedback that the PAMS program needs to be as flexible as possible to help states meet specific needs. In consideration of this potential objective, what are the committee's views on the relative merits of revising PAMS to be a very flexible program with relatively*

few requirements versus a program that is highly specified? If the more flexible model were adopted, what minimum requirements, if any, should be included?
CASAC agrees that flexibility is desired because it will allow monitoring, research and data analysis to be tailored to the specific needs of each ozone problem area. This approach is also likely to provide the information needed to select regionally specific workable control strategies. In addition, a diverse group of stakeholders use PAMS data and thus the PAMS network should meet broad needs.

A national PAMS program is too rigid a structure to be able to adequately characterize the ozone problem in each area of the country. The parameter list would have to include monitoring for precursors and meteorological conditions that are not relevant in one area even though they are in another. This nationally uniform network design model is outdated and too resource intensive.

The responsibility for implementation of the PAMS program should remain with the state and local monitoring agencies. These agencies are the most knowledgeable about the sources and meteorological conditions in their regions and they have the ability and authority to implement control strategies. In some regions such as the northeast where multiple state and local monitoring agencies are within one ozone region, the research and data analysis aspects of the PAMS program should be coordinated. In the past, the Regional Planning Organization (RPO) model was an effective way to coordinate these activities.

CASAC has further recommendations regarding how a more flexible PAMS program could be implemented. Data collection and quality assurance methods should be uniform to the extent possible to assist with data comparisons from one ozone region to another. This will also assist the varied stakeholders who use this data for other purposes. CASAC emphasizes that the flexible approach to PAMS should be implemented as a part of a specific strategy for each ozone area. The implementation should include documentation of the goal, the data analysis needed to address the goal and the network design and data collection required for the data analysis. This approach should eliminate the lack of attention to data, inefficient network design and the slow progress of model development.

Charge Question 8: *Should the current PAMS monitoring season framework be retained or should the period for required measurements be revised (e.g., lengthened or determined on a case-by-case basis) based on analyses of ambient data, meteorology, climatology, or other factors?*

EPA's current PAMS precursor monitoring requires that monitoring must be conducted throughout the months of June, July and August (as a minimum) when peak O_3 values are expected in each area. Alternate precursor monitoring periods may be submitted for approval to the EPA Administrator as a part of the annual monitoring network plan. EPA has noted that limiting the PAMS season to these three months saves resources by not requiring sampling during the off season. EPA has recognized that the usefulness of the data for model development and evaluation may be limited due to only measuring when conditions favor high ozone formation.

It would be desirable to extend the PAMS monitoring season beyond the current June, July, August sampling period. However, establishing the monitoring season should not be mandated and rigid; it should be flexible and adopted and coordinated on a regional airshed basis (i.e., within the same ozone region). This flexibility should not conflict with national goals for the PAMS program. A longer monitoring season would have many advantages. In some areas, such as Baton Rouge, there are more exceedances in May than in July or August. Thus extended PAMS monitoring would benefit the regulatory process. There is a springtime ozone bulge over most regions but the causes may differ by region. Extending the monitoring period of Type 2 PAMS into winter-time may provide better characterization of precursor emissions because the composition of emissions are generally unchanged and the composition is better preserved in winter-time than in summer-time. The extended monitoring would provide the opportunity to validate and to improve the performance of the Community Multiscale Air Quality Model (CMAQ) model. It is recognized that expanding the sampling season would require adjustment to other aspects of the monitoring program, such as fewer stations or different sampling frequencies. If an auto-GC is used (see responses to Charge Questions 11-12) at a PAMS site, the adjustment will be smaller. In general, it may be better to run auto-GC instruments year round at some sites, even if only a subset of the data are needed.

Charge Question 9: *What criteria should EPA consider when re-evaluating the PAMS target VOC list?*

As noted in EPA's *PAMSGram Volume 18* guidance document (2000), available at the following web address: http://www.epa.gov/ttn/amtic/files/ambient/pams/pamsgrm18.pdf, a large number of target Volatile Organic Chemical (VOC) compounds are being measured at PAMS sites. EPA has collected over fifteen years of data for these PAMS target VOC compounds. EPA wishes to revisit this list of compounds and hopes to identify a smaller list of compounds for analysis. EPA has noted that a smaller list may be desirable because there would be a decrease in analysis and reporting costs due to the lower number of compounds, and it may be possible to reduce the complexity and the cost of the use of a dual Gas Chromatograph (GC) detector that is required to analyze the complete list of target compounds if a shorter list of priority compounds is identified. In addition to removing compounds, EPA is also considering adding PAMS target VOC compounds such as biogenic compounds and compounds important for the understanding of SOA formation. Further, EPA is considering whether to add carbonyls to the PAMS target list for all sites.

Regarding the elimination of some target compounds, CASAC suggests that EPA consider cases where such compounds are important for certain airsheds. In such situations, CASAC recommends that measurements be retained.

EPA should consider the following general guidance in identifying targeted PAMS VOC species in order of importance. The ranking is not absolute and may vary depending on the location of the site:

1. VOC species that are markers of emission sources such as biogenic (isoprene); gasoline vehicles (acetylene, benzene, isopentane); diesel vehicles (dodecane); solvents (n-decane); natural gas (ethane); and industry-specific markers;
2. VOC ozone forming potential;
3. VOC with measured concentrations above the lower limit of detection (LOD) for more than a certain percentage of the time and sites (to be determined by EPA); and
4. VOC species that are representative of urban, regional and rural environments;

Recognizing the importance of secondary objectives, the following should be considered depending on the characteristics of the site:

1. VOC contribution to secondary organic aerosol (SOA) forming potential; and
2. VOC identified as air toxics or likely air toxics precursor.

In addition, EPA should reduce the minimum national requirements for reporting of specific organic species required to be measured under the PAMS network, and provide criteria for such reporting.

<u>Charge Question 10:</u> *Are there specific compounds that EPA should consider adding or subtracting from the target list?*

The AMMS Subcommittee did not have many specific suggestions for compounds to be added or subtracted from the current PAMS target list.

The Subcommittee agreed that each current species and potential additional species should be carefully and systematically considered using the criteria suggested in response to Charge Question 9. Although quantification of many compounds is relatively low-effort since they can be quantified as part of the same analytical run, there are still resources required in the quality assurance/quality control (QA/QC) and reporting of these compounds. In general, there is a high degree of co-linearity among compounds on the current PAMS VOC list. If a relatively large subset of the current target list is determined to be minimally useful based on established criteria, then there is potential for some resource savings and they should be considered for removal. At the same time, it is important to note that any eliminated compounds still need to be analytically resolved from target compounds to avoid confounding effects and over-estimation of the latter.

There was strong agreement that the addition of more biogenic species such as terpenes or sesquiterpenes would be helpful given the current trends of lower anthropogenic VOCs and the implications for rural areas. CASAC suggests adding additional compounds that may help to track emissions from additional non-mobile sources or more recent fuel formulations from mobile sources. Addition of several isoprene daughter products, such as glyoxal, methylglyoxal, and methacrolein might be useful for elucidating photochemical production of both ozone and SOA.

CASAC further suggests an effort to identify the major unidentified peaks that are often observed in the TO-15 analysis and consider these compounds for addition if deemed important based on established criteria. Even if they remain unidentified, provisions for reporting them might allow a national assessment of their abundance. Similarly, CASAC suggests an examination of the late-eluting, unresolved carbon "slug," whether those species could be further resolved using different methods, and whether those species may be important to ozone formation.

Regarding which VOCs would be very important for rural air chemistry, biogenic VOCs are considered most important for ozone and SOA formation. However, another important reason to measure VOCs is because of their utility as tracers of sources or chemistry. With these considerations in mind, a prioritized list of eight VOCs that would be most important for rural air chemistry are as follows, with brief justifications.

<u>Isoprene.</u> Isoprene is the most important VOC for ozone and SOA formation in non-urban air. Emissions and their variability are very uncertain. Although the short lifetime of isoprene makes quantitative interpretation of observations difficult, even qualitative interpretation is very useful in terms of determining the presence of isoprene and its variability.

<u>Acetylene.</u> Acetylene is emitted solely by combustion and has an atmospheric lifetime of about 10 days. It is more sensitive than CO as a tracer of combustion, because of its shorter lifetime and because it doesn't have non-combustion sources. A positive correlation with acetylene provides irrefutable evidence of a combustion source.

Benzene. Benzene has a similar atmospheric lifetime to acetylene. Its principal source is combustion but evaporation is also significant. Benzene/acetylene ratios can be used to distinguish fossil fuel from biomass combustion. Benzene can also be used as a tracer of aromatics (e.g., Parrish et al., 2005).

Ethane. The source of ethane is almost exclusively from fugitive natural gas releases during production, transport, and storage, unlike other VOCs. EPA's National Emission Inventory (NEI) database inventories considerably underestimate observations of ethane (e.g., Xiao et al., 2008) suggesting that natural gas emissions of methane in the U.S. are similarly underestimated. Ethane observations provide a great tracer for natural gas emissions.

n-butane, n-pentane. These come mainly from mobile sources. Butane has an atmospheric lifetime of about 1 day, pentane is much shorter. The pentane/butane ratio thus provides a tracer for the age of air since it was exposed to combustion sources, i.e., a photochemical clock.

Propene. It would be helpful to include an alkene such as propene in the list. Propene has the advantage that it is an important ozone precursor, it is often simulated explicitly in models (and hence can be used for model evaluation), and has both anthropogenic and biogenic sources (e.g., Goldstein et al., 1995).

Ethanol (or other markers for use in tracking long-term trends of biofuel emissions). Biofuel usage is expected to significantly increase, which will impact emissions from vehicles, distribution systems, and production. The committee recommends monitoring for biofuel marker because biofuels are becoming more widely used in the market.

Charge Question 11: *What are the advantages and disadvantages of manual canister sampling versus field deployed auto-GCs?*

Three options are currently allowed under PAMS for measuring the target VOC species during the PAMS monitoring period.

- Hourly measurements using an automatic gas chromatograph (auto-GC),
- Eight 3-hour canister samples every third day,
- One 3-hour canister sample in the morning and in the evening and continuous Total Non-Methane Hydrocarbons (TNMH).

As EPA has noted, while these options provide flexibility, they also add complexity to the data set which may hamper data analysis.
The deployment and attributes of auto-GC versus canister based sampling systems is very much based on the PAMS monitoring objective(s) to be addressed.

Auto-GC Advantages: Field deployed auto-GCs provide (hourly average) diurnal concentrations (not possible with 24-hr avg. canister) that are particularly useful in evaluating air quality models and performing diagnostic emission attribution studies. These data can be provided on a near real-time basis and presented along with other precursor species (e.g., oxides of nitrogen and carbon monoxide) collected over similar averaging times. These data can be collected year round and may be aggregated to 3-hr, 12-hr and 24-hr averages.

Auto-GC Disadvantages: Operation and maintenance and data validation requires significant resources (highly skilled personnel and equipment/supplies) typically much greater than costs associated with the manual canisters. Not all VOCs are efficiently collected and resolved by auto GCs.

Manual Canister Advantages: Canister sampling systems are generally less resource intensive than the auto-GC systems, and utilize central GC laboratories with well established, reproducible cryo-focusing techniques. The canister systems will likely provide a lower cost solution (relative to auto-GCs) for annual trend analyses of VOCs and characterizing VOC composition by season.

Manual Canister Disadvantages: Canisters are not practical for high temporal resolution sampling (i.e., hourly average) and can have artifact species loss and transformation issues related to canister residence time.

Charge Question 12: *Are the new commercially available auto-GCs appropriate for use at PAMS sites? What additional evaluations are necessary to determine the suitability of auto-GC's for use in the PAMS network?*

Auto-GCs for routine, semi-continuous measurement of PAMS compounds include a sample pre-concentrator coupled to a gas chromatograph (GC) with a Flame Ionization Detector (FID) (Mass Spectrometer, MS, detectors have been used in special studies). Conventional systems are based on instruments developed for laboratory applications that have been modified for field use. Commonly used pre-concentrators for PAMS deployments include the Perkin Elmer ATD400 Automatic Thermal Desorption and the XonTech Model 930. Broadway and Tipler (2009) describe the latest version of the Perkin Elmer ATD400. Markes, an Agilent channel partner, makes a commercial pre-concentrator at least comparable to the Perkin Elmer ATD400, and has been deployed for field operations. The XonTech Model 930 (Oliver et al., 1996) appears to have also been used at some locations, especially in California. Typically two GC columns are needed to measure the full suite of PAMS target compounds. A promising development in the auto-GC technology has been the design and integration of system components into packages specifically designed for ambient air measurements. One example is the Synspec Spectras Ozone Precursor Analyzer (Model 955 POCP, Synspec BV) that is a dual GC/detector system with one analyzer for C2-C5 compounds (Model 611) and another analyzer for C6-C10 compounds (Model 811).

While the available technology appears promising, comprehensive evaluations are needed to assess suitability for national monitoring. There are many factors to be considered when evaluating available technology. For example, data quality, field robustness, required level of expertise to operate and maintain the analyzers, and cost should be assessed. A description of each available unit should be developed that includes compounds measured, minimum detection limits, reproducibility, recovery rate, accuracy, known interference, moisture management, power and space requirements, purchase costs, operating supply requirements, and standard operating procedures. The available units should be obtained and compared using the methods used in prior VOC comparison studies as a guide for methods and performance (see Dr. Chow's individual comments for references). It is also necessary to update the field auto-GC requirements originally described in U.S. EPA (1998).

Public comments provided by Dr. Babich (Connecticut Department of Environmental Protection) summarize one state's efforts to evaluate one of the new generation analyzers (in this case, the Synspec 955 PCOP) including comparisons to collocated conventional systems. Such evaluations should be encouraged and ideally coordinated with EPA to ensure a comprehensive evaluation emerges. AMMs recommends that the capabilities of new Auto-GCs for measuring oxygenated VOCs be assessed. During the transition to new technologies, collocation of canisters with new auto-GCs is recommended.

Charge Question 13: *What role, if any, should TNMH monitors play in the PAMS program?*

TNMH monitors provide an indication on the levels of VOC present in the atmosphere. They are the only practical method to gauge general, aggregated VOC levels with time resolutions comparable to the measurement of the other ozone precursor, NO_y. These TNMH monitors have similar field operation characteristics and capital cost as other gaseous ambient air monitoring instruments. Having monitors for both ozone precursors (VOC and NO_y) and ozone at similar time resolution provides a more complete picture on the atmospheric ozone formation process.

CASAC recognizes the limitations of the TNMH monitors. They have different response factors for different VOC species. Therefore, different compounds present at the same volumetric concentrations may lead to very different TNMH readings. CASAC also recognizes that it is impossible to measure the exact total VOC concentrations by any other single monitor. To measure the exact total VOC concentrations, a monitoring system would have to capture, separate, detect, and quantify hundreds of VOC species in a timeframe preferably less than an hour. Between the choices of having no information on total atmospheric VOC levels and having an indicator of total atmospheric VOC levels from TNMH monitors, the latter is much more desirable because the end users of the PAMS data will have some idea about both VOC and NO_y.

The sum of all VOC species analyzed by GC can be used as another measure of aggregated VOC. It is common to see some unresolved peaks at the end of GC analysis of PAMS samples when temperature is raised to purge the column. There may also be some unidentified VOC peaks even before the high temperature purge. The TNMH monitors can provide an indicator for the unidentified VOC, which can be calculated as the difference between the TNMH value and the sum of the speciated VOC by GC.

In an area where the VOC composition is reasonably understood (e.g., near a major VOC source), the data generated by a relatively inexpensive TNMH monitor at very high time resolution can be used as a surrogate for some specific VOC species either as ozone precursors or air toxics.

Some samples collected for PAMS analysis are taken when an elevated VOC level is suspected, i.e., the VOC exceeded a pre-determined trigger level. For these “triggered” samples (either for canister sampling or Auto-GC sampling), TNMH monitors provide the trigger signal to activate the samplers. This role of TNMH should not be ignored. Even for TNMH monitors, a development that can lower the detection limit would be very important because the detection limit of current commercially available TNMH monitors may not be low enough for monitoring locations away from urban centers.

Charge Question 14: *Should carbonyls be required at all VOC speciation sites?*

Carbonyls were identified as an important precursor to ozone and were added to the original PAMS VOC target list.

Due to concerns regarding the quality and cost of carbonyl sampling, in 2006 EPA removed the requirement to measure carbonyls (formaldehyde, acetaldehyde, and acetone) at all PAMS areas except those classified as severe or extreme for the 8-hour ozone standard. EPA asked CASAC to consider if advances have been made in carbonyl sampling that would warrant adding carbonyl sampling back to the required sampling at all VOC speciation sites.

There are many compelling scientific reasons to measure carbonyls. They are a very important part of ozone chemistry almost everywhere; for example, aldehydes such as formaldehyde and acetaldehyde are ubiquitous and have relatively high maximum incremental reactivity (MIR) values. Some carbonyls, formaldehyde in particular, are important air toxics.

CASAC recommends that carbonyl measurements not be required at *all* VOC speciation sites. However, it is important to measure carbonyls at select sites including those with high emissions (Type 2) and regional sites (Types 1 and 4). The choice of which compounds should be measured should be part of an overall strategy for a region. For example, carbonyl measurements at high emission sites are important because the incorporation of higher levels of ethanol into the nation's gasoline supply is predicted to increase emissions of carbonyls such as acetaldehyde. The potential effects of these changes on ambient concentrations in high emission areas need to be monitored. Carbonyls also need to be monitored at more regional sites because, as important secondary species, they provide insight into the extent of oxidation. At these sites, carbonyls and other oxygenated organics likely contribute the bulk of the reactivity. Carbonyl data also provides an important constraint for oxidation mechanisms.

Carbonyls comprise a very broad class of atmospheric organics. Therefore it is important to identify a list of high priority carbonyls. EPA should evaluate the relative importance of carbonyls to their general ozone reactivity based on existing ambient and kinetic data. CASAC concludes that formaldehyde, acetaldehyde, methyl-glyoxal, glyoxal, and acrolein are higher priority carbonyls that should be considered for measurement under the PAMS program. These are all important oxidation products. The recent NATA analysis indicates that formaldehyde is one of the most important air toxics. CASAC concludes that acetone is a less important carbonyl for the PAMS program. Identifying a target list of carbonyls will help focus method development efforts.

Although it is important to measure carbonyls, CASAC has concerns about existing measurement methods, especially whether such methods are robust enough for routine monitoring in the PAMS network. To the extent that the methods can be shown to be accurate, then carbonyl measurements should be part of the routine PAMS program. If they are not reliable, CASAC concludes that it is important for EPA to support continued methods development and to incorporate carbonyls into PAMS as special studies.

Charge Question 15: *What issues have been addressed, and what issues still need to be addressed with the current TO-11A method for carbonyl sampling?*

The TO-11A method includes collection of carbonyls onto dinitrophenylhydrazine (DNPH) coated substrates, *in situ* derivitization of hydrazine to hydrazone, and desorption of the hydrazone in the laboratory with analysis by high-performance liquid chromatography (MS could also be used). Potential issues include positive and negative artifacts from contamination, reaction with ambient oxidants (especially ozone), incomplete collection efficiency, and carbonyl generation on the substrate. Steps have been taken to address some of these issues. For example, an ozone scrubber must be used with the DNPH cartridge. Improved preparation, handling, and storage presumably have improved the reproducibility (with additional room for improvement as noted below) but there remain concerns about accuracy. Collection efficiency depends on ambient conditions with relatively high humidity needed to promote the derivitization reaction. Comparisons to continuous analyzers often show the TO-11A method is biased low by up to 25% at low humidity. CASAC recommends that EPA conduct a more detailed review of the literature to assess the state of the science associated with the current TO-11A method for carbonyl sampling. Several research groups and analytical laboratories have extensive experience with carbonyl sampling and analysis; their perspectives would be valuable as part of the review. In addition, CASAC recommends a formal field evaluation of carbonyl methods.

Quality assurance protocols for both field sampling and laboratory analysis operations should be reviewed and strengthened as warranted. Network-wide data quality assessments are not routinely conducted for PAMS. National Air Toxics Trends Sites (NATTS) also measure carbonyls by TO-11A. The most-recent NATTS QA Annual Summary, conducted for calendar year 2008, demonstrates network-wide overall precision of ~20% for formaldehyde which is similar to many of the canister-based VOC precisions. However, five of the 15 stations reported data that exceeded the 15% precision Measurement Quality Objective (MQO) at one station was nearly 50%. Many states perform the analysis in house. Proficiency testing of a single sample across fourteen laboratories was within the 25% bias MQO. Overall, these results are promising but do not reflect actual data quality since they are "ideal" laboratory generated samples. Thus these MQOs are a best-case scenario and still point out the need for refined QA/QC protocols and periodic QA assessments for PAMS.

Several carbonyls are often detected and reported by the analytical laboratories but only three - formaldehyde, acetaldehyde, and acetone **-** are typically reported for NATTS. The NATTS carbonyls target analyte list should be evaluated with consideration of additional carbonyl compounds that may be of interest to PAMS.

Charge Question 16: *What other methods should be considered as an alternative to the manual TO-11A method for carbonyl sampling?*

There are a number of time-integrated, substrate based and continuous methods for measuring carbonyls. The substrate based methods are largely modest variations on the DNPH type methods. These should be pursued following some of the recommendations in the response to charge question 15.

CASAC agrees there may be promise in the emerging continuous methods. These include wet chemistry based approaches, differential optical absorption spectroscopy (DOAS), proton-transfer reaction mass spectrometry (chemical ionization) and tunable laser IR absorption spectroscopy. There are multiple vendors for several of these approaches. There have been some formal evaluations of these methods with mixed results. In one study an atmospheric simulation chamber was used to evaluate five formaldehyde analyzers/samplers representing four different measurement principles (Wisthaler et al., 2008). Numerous analytical issues were encountered and the degree of agreement between instruments varied depending on the chamber conditions. Overall, the agreement between methods was deemed "fair" and the authors also called for development of a validated reference standard. Continuous methods often measure individual or small numbers of carbonyls. Therefore development of continuous methods will need to be coordinated with the selection of high priority, target carbonyls.

Although none of the alternative carbonyl methods are ready for deployment in PAMS, carbonyls are important enough that there needs to be a focused development effort. Methods which can accurately and precisely measure a subset of high priority carbonyls such as acrolein, acetaldehyde and formaldehyde would be more useful than methods that produce poor quality data for a larger set of carbonyls. CASAC concludes that it is important for EPA to enable continued development of carbonyl measurement methods.

Charge Question 17: *Are direct measurement NO_2 or photolytic NO_2 analyzers suitable for deployment in the PAMS network? What additional evaluations are necessary to determine the suitability for use in the PAMS network??*

CASAC concludes that direct measurement NO_2 or photolytic NO_2 analyzers are suitable for deployment in the PAMS network. Currently, NO_2 is required at Type 2 (maximum emission) PAMS sites, and NO_y has been measured at Type 1 (upwind) and Type 3 (maximum O_3) sites since 2006. There is ample evidence (e.g., Dunlea et al., 2007; Steinbacher et al., 2007; and Winer et al., 1974) that NO_2 is overestimated by FRM monitors that use a catalyst to convert NO_2 and other compounds (e.g., PAN, HNO_3, nitrate) to NO, especially in rural and remote locations where NO_x may not be the dominant species in NO_y. In addition, ammonium nitrate collected on a pre-filter at cooler temperatures can volatilize to HNO_3 during warmer parts of the day, thereby increasing the apparent NO_2 (Chow et al., 2002; and Chow et al., 2005). Another problem with conventional NO_x analyzers stems from use of a single detector (time-sharing) to measure NO and NO_2. This synchronization effect occurs when atmospheric NO_x is changing rapidly. Under these conditions, the difference between the NO_x channel and the NO channel can have an unreasonably large absolute values (positive or negative). Care needs to be exercised to flag unreasonably high or low NO_2 concentrations during data processing and/or validation.

Several photolytic and cavity ringdown systems are commercially available, and all of these require further evaluation before they can be considered viable for PAMS. Photolytic converters (e.g., Castellanos et al., 2009; Nakamura et al., 2003; and Thornton et al., 2003) use ultraviolet to violet light to photolyze NO_2 to NO plus an oxygen radical. Reported converter efficiencies range from 30% to 90%. Conversion stability depends on the stability of the light source, ambient ozone concentrations and the cleanliness of the photolysis chamber. Intense light sources that heat the sample should be avoided, as they may cause positive artifacts due to shifts in thermal equilibrium (e.g., peroxyacetyl nitrate (PAN) and PAN homologues to NO_2). Residence time downstream of the photolytic converter should be minimized in order to prevent significant back reaction with ambient ozone. In principle, a single analyzer equipped with a photolytic converter for NO_2 and a catalytic converter for NO_y could be used to measure NO, NO_2, NO_x, NO_y and NO_z (i.e., NO_y-NO_x). This 3-channel approach may be highly successful in rural/remote areas, but could aggravate synchronization effects in urban areas, because the detector would be time-shared among three channels instead of two.

Cavity ringdown (CRD) instruments (e.g., Fuchs et al., 2009; and Osthoff et al., 2006) are specific to NO_2 and appear to have required sensitivity for measurements in rural areas (0.1 ppb or better); however, very little information is available on the long-term (i.e., 6 months or more) operation of such analyzers. CRD analyzers offer the promise of artifact-free NO_2 measurements, but they are stand-alone instruments that do not (at present) provide any information on NO, NO_x or NO_y. Luminol detectors (e.g., Gaffney et al., 1999; and Kelly et al., 1990) separate PAN from NO_2, but they tend to be operationally messy and unreliable.

As with the field auto-GCs, available NO_2 monitors need to be field compared in different environments during different seasons and over extended periods of time. Standard operating procedures and data validation criteria need to be developed and vetted. Cleaning, calibration, and zeroing intervals need to be specified. Minimum detection limits, reproducibility, power and space requirements, purchase costs, and operating supplies also need to be defined. Previous comparison studies (e.g., Dunlea et al., 2007; Vaughan et al., 1997; and Zenker et al., 1998) can be used as a guide for methodology and expected tolerances.

Citations and additional references that support the above response to Charge Question 17 are provided in Enclosure C.

Charge Question 18: *What observational approaches (surface based sondes and optical remote sensing, aircraft platforms, satellites) are best suited to assist such assessments? What routinely collected surface measurements and in what locations would complement vertical profile and total column observations?*

It is important to characterize background ozone concentrations, and delineating contributions from local and regional sources and long range transport. Such contributions have evolved into important assessment needs to support both the standards setting risk assessment process and subsequent implementation. A number of options exist to obtain ozone and nitrogen oxide vertical profile information, including surface based sondes, optical remote sensing, aircraft platforms, and satellites.

Satellite remote sensing offers promise to improve understanding of the spatial distribution of ozone precursor emissions, ozone formation, and transport. The daily coverage of satellites along with ~10km spatial resolution constitutes a consistent global-scale dataset for several atmospheric chemical constituents (Hoff and Christopher, 2009). For the PAMs program, this information is more suited to analysis of regional area-wide biogenic precursor concentrations and is not as useful for small scale sources or for analysis of ozone episodes (Millet et al., 2008).

Satellite sensors have numerous limitations in accuracy, precision and spatio-temporal coverage. The column-concentrations measurements are difficult to calibrate and have interferences from clouds, other chemicals and surface reflectance. Satellite observations are best used in conjunction with other observations and/or chemical transport models. Surface-based column observations e.g. for ozone (Dobson instruments) and aerosol optical thickness (Sun-photometers) provide suitable, high-grade comparison data for the satellite sensors. These should be utilized in conjunction with the satellite data.

A variety of innovative monitoring approaches may be necessary in different areas of the country. Various approaches and technologies should be considered and funded under the PAMS program if a state or local agency can justify the need for this data. For instance, satellite data have recently been used to determine land use factors to estimate biogenic emissions. Land based remote sensing techniques can be useful for source characterization for area wide sources such as marine and airports, railyards, and large industrial facilities.

Observations from commercial aircraft would provide a very useful source of data for vertical profiling relevant to long-range transport of ozone. The value of these data has been demonstrated with the MOZAIC program in Europe. Although it is resource intensive, EPA should consider support for such a program for the US. IAGOS would be an excellent opportunity to develop this as an interagency initiative.

Ozonesondes are similarly useful as long as they offer a sufficiently high-density record to generate statistics. Weekly ozonesonde measurements are not very useful because it is difficult to interpret the snapshot data measured by the sonde. Daily measurements at a few selected sites would be of considerable value, as has been demonstrated by the use made of the Trinidad Head daily ozonesonde data.

Direct satellite observations of tropospheric ozone have too much noise to detect individual events, and this situation is unlikely to change until the GEO-CAPE geostationary satellite gets launched in the early 2020s. Satellite observations of CO and aerosol optical depth (AOD) are more useful for detecting events such as fire or dust plumes. The value of these satellite data could be augmented by high-quality surface CO and AOD data at the PAMS sites.

A relatively inexpensive addition to PAMS sites would be a ground-based sun photometer measurement of AOD, as is done in the AERONET network. This would provide a link between the satellite observations of AOD and the conditions measured at the site. In addition, the concurrent measurements of AOD and PM2.5 at the site would assist in relating the satellite AOD data to surface air quality.

One would expect ground-based lidar to provide the best source of vertical information over the PAMS sites, but cost is prohibitive except perhaps for aerosol lidars (ceilometers). Even then, CASAC finds that states and other air quality organizations do not regularly use routine ground-based aerosol lidar data because interpretation is complicated by cloud cover. Therefore, CASAC does not recommend the addition of lidars at the PAMS sites.

Wind, temperature, and humidity observations from radiosonde and aircraft are the main sources of upper air information for meteorology. For mesoscale meteorology, the horizontal coverage of radiosondes is too sparse. Aircraft observations through Aircraft Meteorological Data Relay (AMDAR) sample an atmospheric profile in the vicinity of airports (see Charge Question 19). However, not all aircraft are equipped with AMDAR or have the system activated. Observations inferred from an enhanced tracking and ranging (TAR) air traffic control radar can fill this gap. See S. de Haan (2011).

Charge Question 19: *Is it necessary to collect upper air wind speed and wind direction data at PAMS sites?*

State and local monitoring agencies are required to make both surface and upper-air meteorological measurements as part of the PAMS rulemaking. The PAMS regulation does not require a specific list of the meteorological variables to be monitored. Current PAMS guidance recommends a list of parameters to be monitored, including wind direction, wind speed, temperature, humidity, atmospheric pressure, precipitation, solar radiation, UV radiation, and mixing height. EPA is interested in alternatives to collecting mixing height data and upper air wind speed data. EPA is also interested in exploring if and how NOAA upper air data can be used to meet the PAMS upper air data needs.

CASAC concludes it would be useful to collect upper air data at or near PAMS sites, but the utility of upper air wind speed and wind direction data greatly depends on local or regional needs. In some areas of the country, data from a single upper air wind monitor can represent a wide region. In other areas with more complex topography and recirculation patterns, several monitors may be needed. Therefore, such measurements should not be required as necessary components at all or most PAMS sites or areas, but instead should be supported as needed based on regional modeling needs and uncertainties.

Upper air wind data taken at multiple sites is important in areas with complex terrain, strong upper-level recirculations, upslope/downslope flow, marine boundary layers, and strong sea breezes. The measurements are useful in developing and testing conceptual frameworks of upper air transport and mixing at finer scales to evaluate modeling efforts. While finer scale resolution may not be needed for national applications of CMAQ and MM5, local or regional models with 2-5 km grid scale resolution need to account for these meteorological phenomena. Upper air wind measurements may not need to be routine or long-term given that these conceptual frameworks are not likely to change over time, although some continuous measures are being used for forecasting purposes.

If other sources of upper air wind data are deemed sufficient for modeling needs, then PAMS requirements to collect such data should be considered met. The current network of PAMS upper air wind profilers are expensive to maintain and the hardware is nearing the end of its expected lifespan. Furthermore, some PAMS upper air wind data are used infrequently and costs of the data may not be justified; EPA should consider ending the requirement for collecting such data. Disinvestment in these measurements may be appropriate in some areas of the country.

CASAC concludes that EPA should consider alternatives to the classic, expensive and noisy RASS/Profiler upper air instruments for PAMS (also see response to Charge Question 20). NOAA collects upper air data through the ACARS (Aircraft Communications Addressing and Reporting System) and AMDAR (Aircraft Meteorological Data Relay) observational systems which provide reports from commercial aircraft during flight. Such data may be useful for the PAMS program. See http://www.nco.ncep.noaa.gov/sib/restricted_data/restricted_data_pmb/acars+amdar/. EPA should work with NOAA to help ensure that this data are accessible to states and state organizations.

Charge Question 20: *How should NOAA data be incorporated into the PAMS program?*

The PAMS rule requires meteorological monitoring but is not specific about which meteorological parameters must be measured. When the PAMS network was established, most areas opted to install RADAR profilers. These profilers provide measurements of wind speed and direction with relatively high vertical resolution (60-160 m, up to maximum altitudes of 1.5 or 4 km). These PAMS profilers are now old and will require expensive upgrades if they are to continue to operate in the PAMS network. EPA seeks guidance regarding other options for obtaining the required meteorological information. One possibility is to use wind profile data from other agencies, such as NOAA, which generally provide wind speeds and directions with lower vertical resolution (250 m) at altitudes up to 16.25 km. Another possibility would be to use ceilometers to measure mixing heights. See Emeis et al., 2008; Eresmaa et al., 2006; and Tsaknakis et al (2011).

The Subcommittee's discussion focused on two points: (i) is good use routinely made of data from the PAMS RADAR profilers?, and (ii) where available, could the lower resolution data from profilers operated by other agencies be used in place of the PAMS RADAR profilers? While there are examples of limited use of the data (e.g. to obtain supporting data for special studies such as identifying flow patterns associated with elevated ozone and PM layers measured by aircraft) overall the data are underutilized and its collection does not justify the cost.

Data for meteorological fields from other sources, such as NOAA and NWS networks, are already being used for modeling ozone concentrations. Discontinuing the use of the PAMS RADAR profilers would not seriously impair ozone modeling capabilities, since other sources of data are generally adequate for most forecasting or SIP modeling purposes. Some committee members suggested that ceilometers could provide data that might be useful by local or regional modeling in targeted areas, such as near coasts.

Upper air data (temperature and wind) are collected by NOAA from commercial aircraft under the ACARS and AMDAR observing systems as noted in the previous charge question response.

These data could be very useful, especially near coastal areas. EPA should work with NOAA to help ensure that this data are accessible to states and state organizations. It would be helpful if existing meteorological data storage systems like MADIS or “FED” (the new VIEWS) could be used. There has been much discussion regarding inter-agency cooperation; this is a good example of where that approach has value.

Charge Question 21: *How can PAMS data best be used? What specific data analyses should be conducted?*

As part of the grant guidance EPA provides for how the PAMS grant money should be utilized, the EPA states that 25% of the PAMS funds should be spent on data analysis. However, over the years, states and EPA have been criticized for not effectively making use of PAMS data. This may be due in part to the relatively limited flexibility provided for the design of the network. Flexibility in PAMS requirements would enhance the potential for data analysis.

As part of the effort to prioritize, refine and identify new objectives for PAMS, EPA should identify specific data analysis goals for each objective. A component of this would be to determine progress towards achieving that objective and be facilitated by defining more specific objectives. As part of creating a more flexible set of requirements, state and local agencies performing PAMS monitoring need to identify analyses necessary to support specific objectives.

Although PAMS data have not been widely used in academic analyses, PAMS data are valuable to local and state agencies because they provide substantial insight into the character in a particular air shed. A significant portion of this analysis has been somewhat informal and not documented in traditional reports.

CASAC suggests there are national or regional analyses that could be done to investigate ozone formation potential, secondary organic aerosol formation model development and performance, and effectiveness of emission control strategies. The conduct of these analyses could benefit from incentivized partnerships between state and academic institutions.

Standard temporal analyses should be performed for all PAMS sits, including: Secular trends, seasonal, weekly and when possible diurnal pattern. These would help inferring sources contributions, as well as transformation and removal processes. Episodocity analyses derived from concentration distribution functions would indicate which PAMS species have persistent sources and which compounds originate from episodic sources.

Combining the PAMS concentration data with temperature, humidity and other weather parameters are indicative of meteorological influences on ozone and its precursors. Combining concentration data with back-trajectories yields information about the general direction of sources. Back-trajectory analysis for multiple sites can be used to triangulate the location of source areas.

Data analysis at the national and regional levels should focus on trending, accountability analyses for emission reduction programs, and evaluation of air quality models. Trending must be carefully conducted given the range of objectives that are used to site monitors. For example, accountability analyses on the ozone precursors profile, ozone itself, and on other pollutants should examine the impacts of increased ethanol use in motor vehicle fuels. As data analyses are carried out, there should be interaction with data users to assure that the analyses will address issues associated with air quality modeling (e.g., CMAQ and NATA). PAMS data could also be used to conduct national or regional analyses to investigate ozone formation potential and secondary organic aerosol formation model development. Not conducting these sorts of analyses seems like a significant missed opportunity that could benefit from incentivized partnerships between state and other institutions.

Charge Question 22: *How should any recommended data analyses be implemented? Should these analyses be conducted at the state, regional, or national level?*

A detailed response to this charge question needs to be tethered to the monitoring objectives and implementation strategy for PAMS. These aspects might well change through the PAMS re-engineering process. That said, the Subcommittee offers the following perspectives on data analyses. Unlike monitoring programs to determine NAAQS compliance, the main purpose of PAMS is to support air quality management by providing insights into the nature of the ozone air quality problem. Thus, PAMS data must be effectively used to justify the investment in the PAMS program.

Analyses should likely be implemented at state, regional and national levels. As part of EPA's PAMS grant guidance, EPA states that currently 25% of PAMS funds should be set aside for data analysis. These funds are included in the state/local agency allocations and the general feeling is that these funds are in many cases being used for broader needs within the monitoring program. A re-engineered PAMS program should include a mechanism to link the PAMS funding to accountability of the monitoring agencies' use of their PAMS data. While the need for a data analysis funding set aside (25% or some other level) is not clear, approval of PAMS allocations should be contingent upon the receiving agency providing a detailed data analysis plan with follow-up that the analysis has been conducted. This approach acknowledges that the state/local agencies should have flexibility to design their PAMS program to address airshed-specific needs and plans for data analysis should be considered an integral part of the program.

Consistent with the above philosophy, the Subcommittee envisions a significant role for regional planning organizations (RPO) in planning both PAMS measurement strategies and data analysis when coordination between states is needed to holistically address ozone air quality issues. Several RPOs have already been serving this role including the contracting of data analyses.

A re-engineered PAMS program should have mechanisms in place that would promote a closer coordination and collaboration with the air quality modeling community. EPA may consider sponsoring an annual or bi-annual workshop or symposium to promote data analysis and collaboration with other related programs and communities.

In support of the above considerations, CASAC strongly urges that EPA consider ways to update PAMS data analysis tools, including the development of new tools as warranted, with attention given to the spectrum of analysis objectives at the state, regional, and national level. The lack of easy access to PAMS data is often cited as a major obstacle to its use. Therefore, the data must be available through a user-friendly portal to promote more widespread use. EPA should leverage the infrastructure and success of other programs such as VIEWS (now FED) did for IMPROVE. Some funds should be set aside to develop national scale web-based data analysis tools similar to those available on the FED website, but tailored to PAMS data analysis. FED provides a successful and existing infrastructure for this purpose.

Charge Question 23: *Should more or less of the PAMS funding be allocated to data analysis?*

As part of EPA's PAMS grant guidance, EPA states that currently 25% of PAMS funds should be set aside for targeted data analysis (e.g., trend analysis, control strategy analysis, or model validation) beyond routine reporting. However, it appears that these monies are not being spent entirely on data analysis but are also used to implement the monitoring network. In these times of limited resources, it may be difficult for state and local agencies to give up 25% of the money dedicated to PAMS.

There is also a need for more information from EPA on what their data analysis expectations are? It would be very helpful to identify or develop case studies on data analyses (include how and why specific analysis were conducted) that can be circulated so that people can learn from what others did.

EPA should consider multiple mechanisms for conducting data analysis, including a more periodic focused effort using a competitive grant process to produce more useful results. CASAC concludes it would be helpful if EPA funded a competitive grants program every few years specifically focused on the analysis of PAMS data; this has been done in the air toxics program. For example, four or five separate PAMS data analysis projects could be funded with each round of grants. The competitive process would give EPA an idea of what can be done with the data and what the research needs are with respect to such data. This data analysis should be done on a regional or airshed basis. Some of the PAMS data analysis funds should be spent on making the data more accessible as noted in Question 22.

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Enclosure D
Compilation of Comments from Individual Members of the CASAC Air Monitoring and Methods Subcommittee (AMMS)

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DR. LINDA BONANNO D-4
DR. DOUG BURNS D-8
DR. JUDITH CHOW D-9
DR. KENNETH DEMERJIAN D-33
MR. DIRK FELTON D-39
DR. PHIL FINE D-46
DR. PHIL HOPKE D-51
DR. RUDOLF HUSAR D-56
DR. PETER H. MCMURRY D-60
DR. ALLEN ROBINSON D-62
DR. ARMISTEAD (TED) RUSSELL D-68
DR. JAMIE SCHAUER D-71
DR. JAY TURNER D-75
DR. YOUSHENG ZENG D-77

Comments from Mr. George Allen

Charge Question 12: Are the new commercially available auto-GCs appropriate for use at PAMS sites? What additional evaluations are necessary to determine the suitability of auto-GC's for use in the PAMS network?

Dr. Babich's public comments on new PAMS GC technologies are posted with other comments for this meeting. His experience with new GC methods is encouraging, and is important to consider for this charge question. It is time to move from older and fragile "lab" GC PAMS technologies and toward robust field instruments that can measure key biogenic species. ORD should be supporting this effort.

Charge Question 13: Role, if any, of TNMH Monitors in PAMS program.

Existing TNMH (or TNMOC) analyzers may be suitable for urban areas where TNMH levels are elevated, but method sensitivity is not sufficient for non-urban sites. While it would be useful to have a TNMH measurement to compare to total "PAMS HC", existing TNMH analyzers have a varying response to different VOC compounds, reducing the value of the measurement.

Charge Questions 14, 15, and 16: Need for and issues with Carbonyl Sampling at PAMS sites.

Carbonyl measurements (primarily formaldehyde and acetaldehyde) are critical for the PAMS and air toxic programs, but have not been measured with consistent or known data quality. The existing DNPH sorbent tube method is not sufficiently robust to fill this need, but other methods suitable for routine and widely deployed network use are not yet available. ORD should support development and evaluation of new methods.

Charge Question 17: Suitability of Direct Measurement NO2 or Photolytic NO2 Analyzers For Deployment in PAMS Network

"True" photolytic NO2 and robust NOy measurements in a single analyzer are highly desirable at all PAMS sites, including urban sites; this is the only practical way to get a good measurement of NOz. Commercial instruments meeting this need are presently in development.

Charge Questions 21 and 22: PAMS data analysis.

Last year NESCAUM initiated review of PAMS data needs and analysis covering the NE corridor. The following two documents summarize the results:
http://www.nescaum.org/documents/mac/mac-committee-meeting-3/allen-pams-wg-review.pdf/

and

http://www.marama.org/presentations/2011_DataAnalysis/Underhill_NESCAUM_PAMSWorkgroup_jan2011pdf.pdf

Tom Downs from Maine-DEP analyzed all available data from all the PAMS sites in the OTC domain; the results for each site are at:
http://www.maine.gov/dep/ftp/DEP_PAMS/NESCAUM_PAMS_ANALYSES/

A template used for this analysis is at:
http://www.maine.gov/dep/ftp/DEP_PAMS/NESCAUM_PAMS_ANALYSES/TEMPLATE%20hour%20or%203-hr%20site%20PAMS%20ANALYSIS.zip

The PAMS community (both data generators and users) would benefit from user-friendly access to PAMS data along with web-based tools to assist in data analysis; a major obstacle to routine use of the data is the lack of such access and tools. In the IMPROVE / RPO-regional haze community, the VIEWS web site has been a valuable source of data and analysis tools over the last decade. Recently, VIEWS has been moved to a new funding structure and web site: http://views.cira.colostate.edu/fed/
This is a continuation and expansion of VIEWS, funded by FLMs. It is intended to include water data also.

It would be very useful if PAMS data were included in the FED database, along with some PAMS- specific screening, validation, and analytical tools. This concept is not new; in 2002, EPA funded a project that added air toxics data to VIEWS:
http://views.cira.colostate.edu/web/Projects/ATDA.aspx
but that has not been updated for many years. A substantial amount of other relevant AQS data are already in FED, including ozone. For screening tools, FED could incorporate existing screening functions used in VOCDat or similar tools into the system. For analysis tools, FED could implement the concepts behind the analytical template that Tom Downs (Maine DEP) put together for the Nescaum PAMS analysis last year.

Finally, EPA-OAQPS might be able to fund this effort with the $150k/year taken off the top of PAMS STAG program funds for national scale data analysis every year.

Comments from Dr. Linda Bonanno

Charge Question 1: How should EPA prioritize the current PAMS objectives? What current objectives, if any should be deemphasized or eliminated?

Charge Question 2: What additional objectives should EPA consider for the PAMS program at this time?
Charge questions 1 and 2 can be combined as stated below.

Objectives may need to be revised on regional basis because national objectives may be different from regional objectives

Original objectives can be reworded as suggested below.

1) Track and verify trends, transport, background concentrations and atmospheric chemistry of ozone and its precursors. This will assist in assessing key constituents in ozone formation and VOC and NOx mitigation emission strategies and target controls [e.g. to assess VOC trends in response to: a) to phase 1& 2 RFG (with specific look at catalytic converter performance in response to Tier 2 gasoline sulfur control and mobile source air toxic MSAT controls; b) introduction of low sulfur diesel fuel; c) 2007 diesel emission emissions standard; d) the economic recession; and e) introduction of renewable fuels].

2) Provide local, current meteorological and ambient data to serve as initial and boundary conditions for photochemical grid models, for baseline information for model evaluation and to improve forecasting. This can be enhanced by special studies that allow wider spatial measurements. This could be accomplished with “mobile” sites that would be moved periodically.

3) Provide a representative, speciated ambient air database which is characteristic of source emission impacts to improve emission inventories, corroborate progress towards attainment, and enhance air toxics monitoring network and exposure modeling.

Additional objectives include:

1) Separate natural biogenic precursors from anthropogenic biogenic precursors because anthropogenic precursors may be subject to mitigation strategies, e.g., CAFOs and eutrified water bodies.

2) Provide compound specific diurnal patterns to evaluate emission profiles (as specified in emissions models by source) and for evaluation of the air quality modeling system overall (e.g., see Doraiswamy et al., 2009 and Ren et al.,2003, Ren et al., 2006).

3) Measurement of SOA precursors with an emphasis on developing effective strategies for reduction of SOA

Charge Question 3: What are the advantages and disadvantages of the current design with multiple sites per PAMS area? What changes, if any, should be made in the number and spatial distribution of required sites?

Disadvantages include that multi state control over a PAMS network, probably better to have those PAMs sites

Charge Question 4: Should EPA consider requiring PAMS measurements in areas other than areas classified as serious and above for the ozone NAAQS to improve spatial coverage?

Yes potentially in areas where extensive fracking is occurring.

Charge Question 5: Should EPA consider requiring PAMS measurements at a new subset of ozone sites in addition to the traditional PAMS (e.g., maximum concentration sites in all non attainment areas, all urban NCore sites) ?

It would depend on available resources and regional needs. I don't think it should be required but can be worked into the 'flexibility' of the PAMS network.

Charge Question 6: What role, if any, should mobile or temporary sites play in the PAMS program?

Mobile/temporary sites can be a cost effective way to capture better spatial coverage for modeling, forecasting and emission inventory purposes. They may also serve as a way to reduce the total # of permanent sites and therefore resources expended

Charge Question 7: EPA has received feedback that the PAMS program needs to be as flexible as possible to help states meet specific needs. In consideration of this potential objective, what are the committee's views on the relative merits of revising PAMS to be a very flexible program with relatively few requirements versus a program that is highly specified? If the more flexible model were adopted, what minimum requirements, if any, should be included?

Flexibility region to region (airshed to airshed) will allow each region to best capture the compounds related to ozone formation. That being said, it is important to have consistent QA procedures in place. Some special studies could be done to compare different methods, sampling periods etc so that region to region comparisons can be done.

Charge Question 8: Should the current PAMS monitoring season framework be retained or should the period for required measurements be revised (e.g., lengthened or determined on a case-by-case basis) based on analyses of ambient data, meteorology, climatology, or other factors?

Should be determined on a case by case basis (regionally).

Charge Question 9: What criteria should EPA consider when re-evaluating the PAMS target VOC list?

Compounds that are rarely detected should be deleted from the list.

Charge Question 10: Are there specific compounds that EPA should consider adding or subtracting from the target list?

For carbonyls, most important are acrolein, acetaldehyde and formaldehyde

Charge Question 11: What are the advantages and disadvantages of manual canister sampling versus field deployed auto-GCs?

Charge Question 12: Are the new commercially available auto-GCs appropriate for use at PAMS sites? What additional evaluations are necessary to determine the suitability of auto-GC's for use in the PAMS network?

Charge Question 13: What role, if any, should TNMH monitors play in the PAMS program?

Charge Question 14: Should carbonyls be required at all VOC speciation sites?

Yes

Charge Question 15: What issues have been addressed, and what issues still need to be addressed with the current TO-11A method for carbonyl sampling?

Precision and accuracy.

Charge Question 16: What other methods should be considered as an alternative to the manual TO-11A method for carbonyl sampling?

There are some methods based on TO-11A (DNPH) that appear promising (Uchiyama, S., et al., 2010). More work needs to be done to determine precision and accuracy before deploying in the field.
Uchiyama, S., Inaba Y., Kunugita, N., Determination of acrolein and other carbonyls in cigarette smoke using coupled silica cartridges impregnated with hydroquinone and 2,4-dinitrophenylhydrazine. J Chrom A 1217 (2010) 4383-4388.
Charge Question 17: Are direct measurement NO2 or photolytic analyzers suitable for deployment in the PAMS network? What additional evaluations are necessary to determine their suitability for use in the PAMS network?

Charge Question 18: What observational approaches (surface based sondes and optical remote sensing, aircraft platforms, satellites) are best suited to assist such assessments? What routinely collected surface measurements and in what locations would complement vertical profile and total column observations?

Charge Question 19: Is it necessary to collect upper air wind speed and wind direction data at PAMS sites?

Not at all sites, best to choose regionally representative locations

Charge Question 20: How should NOAA data be incorporated into the PAMS program?

Charge Question 21: How can PAMS data best be used? What specific data analyses should be conducted?

Data analyses should focus on objectives of network and also include ideas from independent researchers which may or may not be in line with PAMS objectives.

Charge Question 22: How should any recommended data analyses be implemented? Should these analyses be conducted at the state, regional, or national level?

Implementation of PAMS data analysis should be on a regional (air shed) basis and also on a national level. Competitive bids or subcontractor, competitive preferred to getting independent researchers to show EPA what can be done with the data and what their data analysis needs are. The RFP could emphasize the objectives of the PAMS network.

Charge Question 23: Should more or less of the PAMS funding be allocated to data analysis?

Although 25% is informally set aside for data analysis, it appears that these monies are not being spent on data analysis but on implementing the monitoring network. In these times of limited resources, it may be difficult for states to give up 25% of the money dedicated to PAMS. It may be a more reasonable approach for EPA to set aside 3-5% of the 14 million every 3 years for competitive grants for data analysis of PAMS data. The competitive process will give USEPA an idea of what can be done with the data and what the research needs are in respect to such data.

Comments from Dr. Doug Burns

Charge Question 2: What additional objectives should EPA consider for the PAMS program at this time?

- Current network design does not allow flexibility in choosing monitoring locations. Might consider allowing states the flexibility to ascertain whether Type 2 sites are located appropriately.
- Consider strategies that allow wider spatial measurements that might better support model evaluation. This could be accomplished with “mobile” sites that would be moved periodically.
- Consider requiring some measurements outside of the June-August period. Wouldn’t concentrations be expected to be about as high or higher in September than June? For example, Bloomer et al., 2010 show that the > 40 ppb ozone contour for eastern rural sites (based on data from 5 eastern CASTNET sites) extends from May through October.

Charge Question 4: Should EPA consider requiring PAMS measurements in areas other than areas classified as serious and above for the ozone NAAQS to improve spatial coverage?

It seems that there are two potential elements to this question:

a. To what extent are we certain that the areas currently classified as serious or above are accurate today? There have been major increases in population in many urban areas since the 1990s such as Orlando, Charlotte, Las Vegas, etc. Is it possible that these and other urban areas should be classified as “serious” ozone areas given current conditions?
b. Is the importance of models sufficient in a regulatory context to consider modeling needs as part of PAMS? And would appropriate models benefit from the availability of more spatially widespread ozone and precursor measurements? If the answer is yes to these questions, then more widespread measurements should be encouraged.

Charge Question 20: How should NOAA data be incorporated into the PAMS program?

Consideration should be given to incorporating NOAA upper air wind data into the PAMS program. The PROFILER site locations are clearly not adequate to address PAMS needs. However, it appears that upper air wind data available through the CAP PROFILER web site includes sites near to several of the severe and non-attainment areas such as NYC, Boston, Baltimore/Washington DC, LA, Houston, etc. However, data do not appear to be available for all ozone non-attainment areas. Some key questions need to be addressed such as whether data available through NOAA are of sufficient spatial and temporal resolution to meet the needs of PAMS, and the expected long-term viability of the currently available sites considering various funding sources.

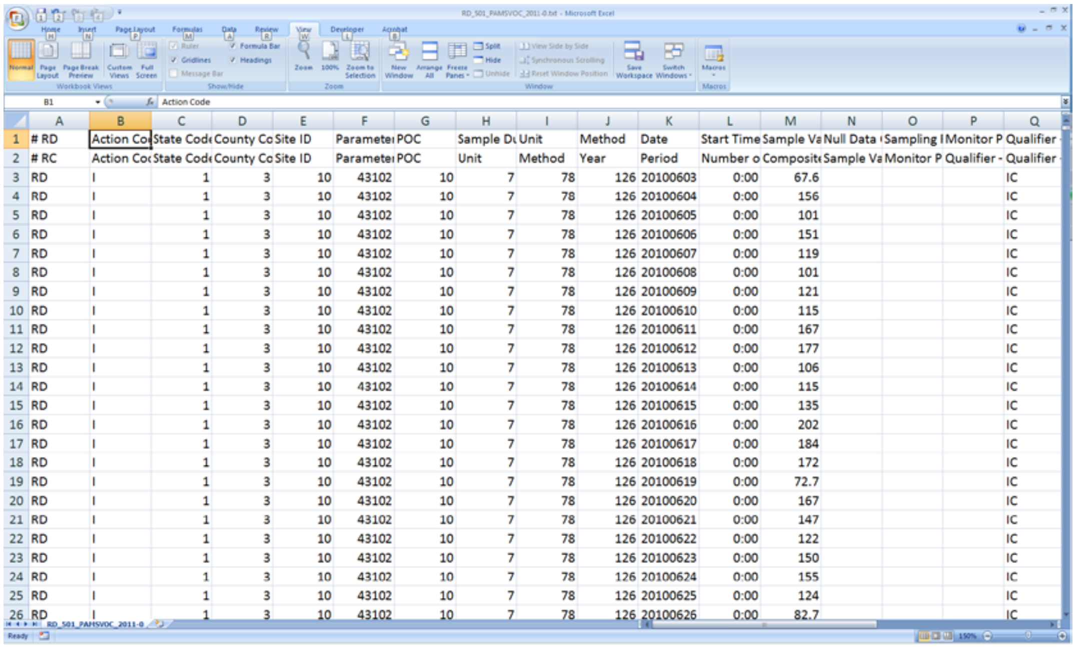
Comments from Dr. Judith Chow

Charge Question 1: How should EPA prioritize the current PAMS objectives?

The six PAMS objectives could be shortened and made less redundant. They have been re-ordered below with some comments on how well they are being met as follows:

i. *Provide a speciated ambient air database which is both representative and useful for ascertaining ambient profiles and distinguishing among various individual VOC. These data can later be used as evaluation tools for control strategies, cost-effectiveness, and for understanding the mechanisms of pollutant transport.*

> This has been, and still should be, the primary objective for PAMS, to provide a reliable data set that can be used for a wide range of purposes. Unfortunately, the data documentation and access is deficient. The PAMS description websites (U.S.EPA, 2011a; 2011b) haven't been updated since the late 1990s, so it is difficult to figure out what is measured and at which location(s). For example: 1) "AQS Discoverer" requires jumping through a lot of hoops, and it is not clear that PAMS data can be found there; 2) "Query AQS Data" states "Notice: This data is not being updated. Last update on March 4, 2010"; and 3) the "Download AQS data" seems to have all the data in flat files that look like Figure 1, but there is a lot of searching needed to find site codes and parameter codes to assemble a useful data base. This may be part of the reason that PAMS data are minimally exploited. EPA should consider updating the PAMS websites to make them more user-friendly, including better data documentation. VIEWS (2010) provides a better example of a query structure and data extraction method that is useful to investigators.



	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
1	# RD	Action Co	State Code	County Co	Site ID	Parameter	POC	Sample Du	Unit	Method	Date	Start Time	Sample Va	Null Data	Sampling I	Monitor P	Qualifier -
2	# RC	Action Co	State Code	County Co	Site ID	Parameter	POC	Unit	Method	Year	Period	Number o	Composite	Sample Va	Monitor P	Qualifier -	Qualifier -
3	RD	I	1	3	10	43102	10	7	78	126	20100603	0:00	67.6				IC
4	RD	I	1	3	10	43102	10	7	78	126	20100604	0:00	156				IC
5	RD	I	1	3	10	43102	10	7	78	126	20100605	0:00	101				IC
6	RD	I	1	3	10	43102	10	7	78	126	20100606	0:00	151				IC
7	RD	I	1	3	10	43102	10	7	78	126	20100607	0:00	119				IC
8	RD	I	1	3	10	43102	10	7	78	126	20100608	0:00	101				IC
9	RD	I	1	3	10	43102	10	7	78	126	20100609	0:00	121				IC
10	RD	I	1	3	10	43102	10	7	78	126	20100610	0:00	115				IC
11	RD	I	1	3	10	43102	10	7	78	126	20100611	0:00	167				IC
12	RD	I	1	3	10	43102	10	7	78	126	20100612	0:00	177				IC
13	RD	I	1	3	10	43102	10	7	78	126	20100613	0:00	106				IC
14	RD	I	1	3	10	43102	10	7	78	126	20100614	0:00	115				IC
15	RD	I	1	3	10	43102	10	7	78	126	20100615	0:00	135				IC
16	RD	I	1	3	10	43102	10	7	78	126	20100616	0:00	202				IC
17	RD	I	1	3	10	43102	10	7	78	126	20100617	0:00	184				IC
18	RD	I	1	3	10	43102	10	7	78	126	20100618	0:00	172				IC
19	RD	I	1	3	10	43102	10	7	78	126	20100619	0:00	72.7				IC
20	RD	I	1	3	10	43102	10	7	78	126	20100620	0:00	167				IC
21	RD	I	1	3	10	43102	10	7	78	126	20100621	0:00	147				IC
22	RD	I	1	3	10	43102	10	7	78	126	20100622	0:00	122				IC
23	RD	I	1	3	10	43102	10	7	78	126	20100623	0:00	150				IC
24	RD	I	1	3	10	43102	10	7	78	126	20100624	0:00	155				IC
25	RD	I	1	3	10	43102	10	7	78	126	20100625	0:00	124				IC
26	RD	I	1	3	10	43102	10	7	78	126	20100626	0:00	82.7				IC

Figure 1. Example of PAMS data read into an Excel Spreadsheet using 2011 VOC data downloaded from U.S. EPA (2011c)

ii. *Provide ambient data measurements which would allow later preparation of unadjusted and adjusted pollutant trends reports.*

A consistently-acquired data set is needed to determine the effectiveness of control strategies. The data base has been only minimally exploited for this purpose (Blanchard et al., 2010; Fortin et al., 2005; McCarthy et al., 2007), but the results show that some of the control strategies have been effective. This is important for the purposes of accountability in multipollutant air quality management (Hidy and Pennell, 2010; van Erp et al., 2008).

iii. *Provide a representative, speciated ambient air database which is characteristic of source emission impacts. These data can be particularly useful in analyzing emissions inventory issues and corroborating progress toward attainment.*

This objective is also important for accountability. Again, the PAMS data have been minimally exploited for this purpose (Brown et al., 2007; Cardelino and Chameides, 2000; Choi and Ehrman, 2004; Fujita, 2001; Gan and Hopke, 2003; Henry et al., 2002; Leuchner and Rappengluck, 2010; Mukerjee et al., 2004; Scheff and Yu, 1997; Xie and Berkowitz, 2006), and state/local agencies are encouraged to evaluate PAMS measurements and apply them to air quality modeling.

iv. *Provide additional measurements of selected criteria pollutants. Such measurements can later be used for attainment/nonattainment decisions and to construct NAAQS maintenance plans.*

This depends on the specific needs of each region. It appears that most of the PAMS measurements are located at existing sites that already acquire compliance measurements. This objective is probably not essential.

v. *Provide additional measurements of selected criteria and non-criteria pollutants from properly-sited locations. Such measurements can later be used for evaluating population exposure to air toxics as well as criteria pollutants.*

The PAMS VOC data has aided in the interpretation of other measurements and provided a basis for human exposure estimates (Blanchard and Tanenbaum, 2006; Chinkin et al., 2003; Chung et al., 2003; Lewis et al., 1998; 1998a; Main et al., 1998b; Reiss, 2006; Reissell et al., 2003; Seila et al., 2001; 2002a; Sistla et al., 2002b; Sistla and Aleksic, 2007; U.S.EPA, 1996; Vukovich, 2000; Xie and Berkowitz, 2007). If air toxics are to be included as part of the PAMS objectives, the current list of 56 PAMS target VOCs needs to be evaluated or modified to include more air toxic species.

vi. *Provide local, current meteorological and ambient data to serve as initial and boundary condition information for photochemical grid models. These data can later be used as a baseline for model evaluation and to minimize model adjustments and reliance on default settings.*

Although meteorological data are useful at any monitoring site, and can be acquired cost-effectively with other measurements, the surface measurements represent more middle- to neighborhood-scales than the larger urban- to regional-scales that are appropriate for photochemical assessments. Surface meteorological data and much of the vertical meteorological information is available from the regional climate centers (DRI, 2011). More information on the vertical structure, e.g., through profilers and acoustic sounders (Berman et al., 1997; Berman et al., 1999; Beyrich, 1997; Crescenti et al., 2000; Gunter, 2007; Hanna et al., 2006; Michelson and Seaman, 2000; Prabha et al., 2002; Reitebuch et al., 2000) would be useful, especially for O_3 reservoirs aloft, recirculation via sea breezes, upslope/downslope flow, convergence zones and eddies, and low-level jets.

Charge Question 2: What additional objectives should EPA consider for the PAMS program at this time? What current objectives, if any, should be deemphasized or eliminated?

The suggestions for improving forecasting, understanding secondary organic aerosols, air toxics, and climate forcing substances are all good objectives. In order to make the best use of the existing resources, U.S. EPA should consider objectives consistent with the multi-pollutant/multi-effect directions for air quality management (Brook et al., 2009; Chow et al., 2010; Dominici et al., 2010; ECOS, 2010; Greenbaum and Shaikh, 2010; Hart et al., 2011; Hidy and Pennell, 2010; Mauderly and Samet, 2009).

Charge Question 3: What are the advantages and disadvantages of the current design with multiple sites per PAMS area? What changes, if any, should be made in the number and spatial distribution of required sites?

The four site types seem logical and comprehensive. However, the terms “upwind” and “downwind” are not very descriptive, as many of the O_3 clouds are regional in nature (e.g., southeastern, northeastern, and midwestern U.S.). Less complex “satellite sites” that are portable, and possibly temporary (e.g., less than a year) would be useful for better defining the spatial extent of the attainment area (Clark County Department of Air Quality and Environmental Management, 2004; Seitz, 2000). Inexpensive measurement technologies are available for this (e.g., 2B Technologies, 2010a; 2B Technologies, 2010b; Betts, 2009; Martin et al., 2010; Mason et al., 2011). Flexibility on the number and types of sites should still be available to the local and regional air quality management districts to meet their specific needs.

Charge Question 4: Should EPA consider requiring PAMS measurements in areas other than areas classified as serious and above for the ozone NAAQS to improve spatial coverage?

> This need not be a requirement, but some network resources should be available to local and regional air quality management entities that make a case for greater spatial coverage. For example, the fast-expanding extraction of natural gas in Wyoming and Pennsylvania is accompanied by increasing NO_x and VOC emissions that may increase the O_3 levels. It would be good to begin the measurement of these emissions before NAAQS are exceeded.

Charge Question 5: Should EPA consider requiring PAMS measurements at a new subset of ozone sites in addition to the traditional PAMS (e.g., maximum concentration sites in all non-attainment areas, all urban NCore sites)?

These sites should be based on specific needs, as specified by the local or regional air quality managers. It is probably a good idea to consider PAMS measurements at maximum concentration sites in all non-attainment areas as well as those of urban NCore sites to provide better insights into elevated O_3 phenomena.

Charge Question 6: What role, if any, should mobile or temporary sites play in the PAMS program?

As noted above, this type of mobile or temporary site should be expanded. Satellite sites should be used to exchange some accuracy and precision for denser spatial coverage to identify hot spots, boundaries, and carryover phenomena. They would be inexpensive and portable with wireless communications. A mobile site could be configured with more complex instrumentation, such as the auto-GC that obtains higher time resolution continuously with greater number of atmospheric components for shorter monitor periods at a specific location.

Charge Question 7: EPA has received feedback that the PAMS program needs to be as flexible as possible to help states meet specific needs. In consideration of this potential objective, what are the committee's views on the relative merits of revising PAMS to be a very flexible program with relatively few requirements versus a program that is highly specified? If the more flexible model were adopted, what minimum requirements, if any, should be included?

The program must remain flexible. It should require well-reasoned plans from the air quality management entities for each region that propose a conceptual model for elevated concentrations, then justify the measurements needed to enhance or disprove that model.

Charge Question 8: Should the current PAMS monitoring season framework be retained or should the period for required measurements be revised (e.g., lengthened or determined on a case-by-case basis) based on analyses of ambient data, meteorology, climatology, or other factors?

Analysis of the existing data from PAMS and other networks should be used to justify monitoring periods appropriate to each domain. Flexibility of monitoring periods/seasons should be given to the local agency to justify the needs for the region. Special studies at different regions during different seasons can be used to refine specific monitoring periods for each domain.

Charge Question 9: What criteria should EPA consider when re-evaluating the PAMS target VOC list?

It is probably a good idea for EPA to document the rationale for the selection of the current 56 target PAMS VOCs. The following criteria need to be considered when re-evaluating the PAMS target list:

Compounds in VOC profiles from existing sources in the domain: needed for tracking trends when emissions are reduced, to identify marker species from major pollution sources and for secondary aerosol formation, to apportion ambient VOC to different sources for top-down inventory verification, and for evaluating models through comparison with ambient measurements (Watson et al., 2001). Carbonyls are directly emitted as well as being formed in the atmosphere (Ban-Weiss et al., 2008; Di et al., 2009; Guarieiro et al., 2009; Ho et al., 2006; Kundu et al., 2010; Muller et al., 2006) and should be included as part of the PAMS target list. The basic 56 PAMS species should be retained as a minimum. These VOC compounds are evolved from the analysis of dual-GC detector, so removing some of the target compounds from the current list is unlikely to achieve much cost savings on analyses, although additional resources may be required for data validation. Also, the sum of these species has been adopted in many places (not just the U.S.) to represent total hydrocarbons (Watson et al., 2001).

Reactive O_3 precursors: most of these are a subset of the emission profile compounds.

Potentially toxic substances: ideally, these should be a subset of emission profile compounds, since the majority of hazardous air pollutants (HAPs; http://www.epa.gov/oar/oaq-caa) selected for the U.S. EPA 1999 National-Scale Air Toxics Assessment (U.S. EPA, 2006) were organic compounds, classes, or mixtures. The Urban Air Toxics list is shown below (U.S. EPA 1999, 2006; Table from Mauderly and Chow, 2008). Most of the 21 VOCs for the Urban Air Toxics do not overlap with the PAMS target VOC list. For multipollutant air quality management, the PAMS target list should be expanded to include air toxic VOCs

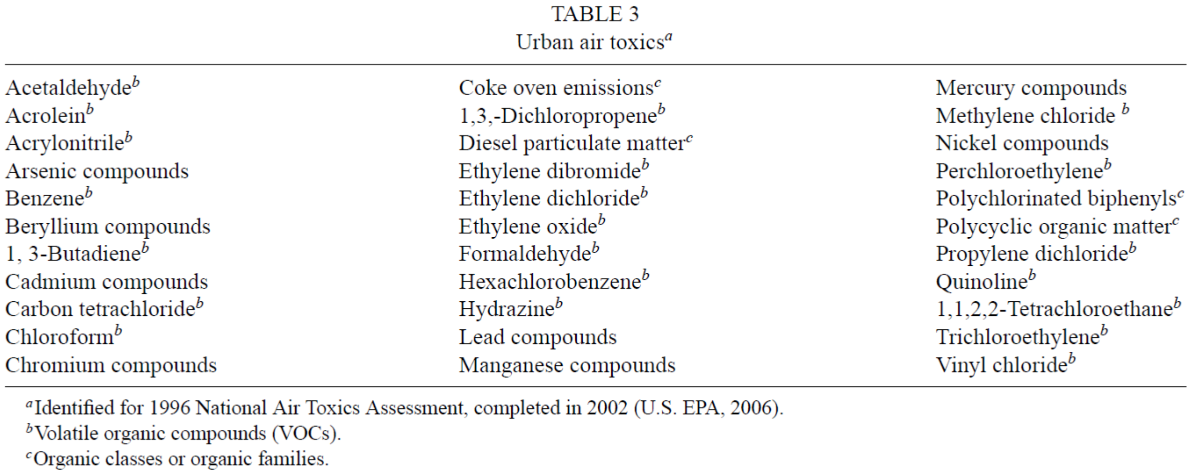


TABLE 3
Urban air toxics[a]

Acetaldehyde[b]
Acrolein[b]
Acrylonitrile[b]
Arsenic compounds
Benzene[b]
Beryllium compounds
1, 3-Butadiene[b]
Cadmium compounds
Carbon tetrachloride[b]
Chloroform[b]
Chromium compounds
Coke oven emissions[c]
1,3,-Dichloropropene[b]
Diesel particulate matter[c]
Ethylene dibromide[b]
Ethylene dichloride[b]
Ethylene oxide[b]
Formaldehyde[b]
Hexachlorobenzene[b]
Hydrazine[b]
Lead compounds
Manganese compounds
Mercury compounds
Methylene chloride [b]
Nickel compounds
Perchloroethylene[b]
Polychlorinated biphenyls[c]
Polycyclic organic matter[c]
Propylene dichloride[b]
Quinoline[b]
1,1,2,2-Tetrachloroethane[b]
Trichloroethylene[b]
Vinyl chloride[b]

[a] Identified for 1996 National Air Toxics Assessment, completed in 2002 (U.S. EPA, 2006).
[b] Volatile organic compounds (VOCs).
[c] Organic classes or organic families.

(From Mauderly and Chow, 2008)

End-products: usually more oxygenated species with lower vapor pressures that also might result in secondary organic aerosol formation (Miracolo et al., 2010; Presto et al., 2010; Robinson et al., 2007)

Compounds from the above that can be cost-effectively quantified.

Charge Question 10: Are there specific compounds that EPA should consider adding or subtracting from the target list?

Full advantage should be taken of the acquired samples to obtain as many of the compounds as possible that meet the criteria stated in Question 9. Even unidentified peaks have value (Gan and Hopke, 2003).

Charge Question 11: What are the advantages and disadvantages of manual canister sampling versus field deployed auto-GCs?

The canisters (Batterman et al., 1998; Castellnou et al., 1998; Doezema et al., 2010; Eklund et al., 2004; Evans et al., 1998; Gholson et al., 1989; Heo et al., 2001; McClenny et al., 1991; Merrifield, 1987; Oliver et al., 1986; Plass-Dulmer et al., 2006; Schmidbauer and Oehme, 1988; Sin et al., 2001; Sulyok et al., 2001) are considered to be the standard method, with well-established procedures for quality assurance (QA) and quality control (QC). VOC canisters contain enough air to be submitted to many different analyses and re-analyses. Even without adequate temporal or spatial resolution, canister data are useful for trend analysis that meet the criteria listed in the response to Question 9 with low capital investment. The disadvantage of canisters are: 1) they are labor intensive; 2) some VOCs deteriorate with storage time; 3) reliable results are not available for heavier hydrocarbons above C_{12} – these are not so important for O_3, but are very important for photochemical secondary organic aerosol formation (Pandis et al., 1992); and 4) low time resolution, which is limited by the number of canisters that can be filled and changed.

The field auto-GCs (Altshuller et al., 1966; Bartenbach et al., 2007; Chang et al., 2010; Chung et al., 2003; Cisper et al., 1995; Crutzen et al., 2000; Daughtrey et al., 1998; Derwent et al., 1999; Farmer et al., 1994; Fujita et al., 1996; Kabir and Kim, 2010; Lu, 1996; Maris et al., 2003; Oliver et al., 1996; Rappenglück et al., 1998; Rappenglück and Fabian, 1999; Seila et al., 2001; Wang et al., 1999; Yamamoto et al., 1998; Yamamoto et al., 2000) provide hourly data (high time resolution) by absorbing the VOCs on a chilled substrate, then thermally releasing them into the GC. As compared to the infrequent sampling by canister, the auto-GC has the advantage of real-time continuous measurement to allow a better understanding of atmospheric processes and pollution formation, and can be used for source identification by receptor modeling. The auto-GC can be operated year-round, which minimizes the controversy created by the limitations of canisters to specific time periods or seasons. The disadvantages of the auto-GC include: 1) not all of the VOCs are efficiently collected on the substrate by auto-GC; 2) a high capital investment is required, including trained field technicians to operate and maintain the instrument and a trained chemist to validate the hourly data (QA/QC; i.e., standards calibration), which can be labor intensive; and 3) the compounds measured are less comprehensive than those obtained from the canisters through laboratory analysis. More collocated comparisons between canister and field auto-GC should be conducted at different types of PAMS sites during different seasons to establish the equivalence and comparability between the two approaches.

Charge Question 12: Are the new commercially available auto-GCs appropriate for use at PAMS sites? What additional evaluations are necessary to determine the suitability of auto-GC's for use in the PAMS network?

Several commercial pre-concentration and GC analysis units are available (AMA Instruments, 2011; Broadway and Tipler, 2009; Ecotech, 2011; SRI Instruments, 2011; Synspec, 2011a; Synspec, 2011b; Synspec, 2011c), but they are poorly documented for the most part. Several of them require two collocated instruments to obtain the low and high C-number compounds. Broadway and Tipler (2009) describe the latest incarnation of the Perkin Elmer ATD400 Automatic Thermal Desorption unit that was used as several of the PAMS sites. The XonTech Model 930 (Oliver et al., 1996) appears to have also been used at some locations, especially in California. Comprehensive descriptions of each available unit, better than that on the manufacturer's websites, need to be assembled that would include an instrument description, compounds measured, minimum detection limits, reproducibility, power and space requirements, purchase costs, operating supplies (i.e., gases, absorbents, spare parts), and standard operating procedures. A subset of available units should be obtained and compared, using prior VOC comparison studies (Apel et al., 1994; Apel et al., 1998; Apel et al., 2003; Apel and Calvert, 1994; Chang et al., 2010; Durana et al., 2002; Fujita et al., 1994; Fujita et al., 2003; Gurka, 1984; Kuster et al., 2004; Liikala et al., 1996; Lonneman et al., 1989; Maris et al., 2003; McClenny et al., 1985; Rappengluck et al., 2006; Schmidbauer and Oehme, 1988; Shreffler, 1993; Sistla and Aleksic, 2007; Tang et al., 2006) as a guide for methods and performance. This information can then serve as a basis to evaluate the appropriateness of commercially available auto-GCs for use at PAMS sites.

It would be worthwhile to update the field auto-GC requirements in U.S. EPA (1998).

Charge Question 13: What role, if any, should TNMH monitors play in the PAMS program?

The definition of total non-methane hydrocarbons (TNMH) and how it should be measured needs to be clarified. TNMH is useful to bound the hydrocarbon content, provide better time resolution, and for certain observational models (Cardelino and Chameides, 2000).

Charge Question 14: Should carbonyls be required at all VOC speciation sites?

Carbonyls are important primary emittants and photochemical end-products. As more renewable fuels are added to gasoline and diesel (Correa and Arbilla, 2008; Di et al., 2009; Guarieiro et al., 2009; Lin et al., 2009; Liu et al., 2009b; Pang et al., 2006; Pang et al., 2008; Peng et al., 2008; Tanner et al., 1988; Yuan et al., 2009), there may be changes in their ambient concentrations that should be tracked.

Charge Question 15: What issues have been addressed, and what issues still need to be addressed with the current TO-11A method for carbonyl sampling?

The major issues with DNPH sampling and analysis for carbonyls are: incomplete collection, losses due to chemical reactions (e.g. with O_3), creation of new carbonyls as additional pollutants are pulled through the DNPH cartridge, and contamination. These biases can be minimized through appropriate precautions, established standard operating procedures, and enhanced QA/QC measures (Dillon and Gao, 1994; Ho et al., 2011; Kleindienst et al., 1998; Lee et al., 2006; Lee and Zhou, 1993).

Charge Question 16: What other methods should be considered as an alternative to the manual TO-11A method for carbonyl sampling?

Batterman et al. (1998) didn't have much success obtaining accurate concentrations of butanal, pentanal, hexanal, heptanal, octanal, nonanal and benzaldehyde from stainless steel canisters. They found ~18 day half-lives for aldehydes in humidified air-filled canisters; half –lives were ~6 days for dry air. Better results have been found for certain carbonyls collected on Tenax and analyzed by thermal desorption (Ho and Yu, 2004; Kim and Pal, 2010; Lee et al., 2006). To consider alternate methods to the manual TO-11A method, a comparison study should be conducted to evaluate the pros and cons of the different methods for carbonyl speciation.

Charge Question 17: Are direct measurement NO2 or photolytic NO2 analyzers suitable for deployment in the PAMS network? What additional evaluations are necessary to determine the suitability for use in the PAMS network?

Currently, NO_2 is required at Type 2 (maximum emission) sites, where NO_y has been measured at Type 1 (upwind) and Type 3 (maximum O_3) sites since 2006.

Several photolytic and cavity ringdown systems are commercially available (Aerodyne Research Inc., 2011; Air Quality Design, 2011; EcoPhysics, 2011; Los Gatos Research, 2011) that require further evaluation. There is ample evidence (Dunlea et al., 2007; Steinbacher et al., 2007; Winer et al., 1974) that NO_2 is overestimated by FRM monitors that use a catalyst to convert NO_2 and other compounds (e.g., PAN, HNO_3, PM nitrate) to NO, especially in rural and remote locations where NO_x may not be the dominant species in NO_y. Ammonium nitrate collected on a pre-filter at cooler temperatures can convert to HNO_3 during warmer parts of the day, thereby increasing the apparent NO_2 (Chow et al., 1994; Chow et al., 2002; Chow et al., 2005). Photolytic converters (Castellanos et al., 2009; Gao et al., 1994; Kley and McFarland, 1980; Nakamura et al., 2003; Ryerson et al., 2000; Thornton et al., 2003) use ultraviolet light to transform NO_2 to NO. Reported converter efficiencies range from 40% to 90%, and the conversion stability is not reported. Some researchers use intense light sources that heat the sample, which may cause some changes in equilibrium (e.g., PAN to NO_2). The cavity ringdown instruments (Castellanos et al., 2009; Fuchs et al., 2009; Osthoff et al., 2006) appear to be most specific to NO_2. Luminol detectors (Gaffney et al., 1999; Kelly et al., 1990) separate PAN from NO_2, but they tend to be messy and unreliable.

As with the field auto-GCs, available NO_2 monitors need to be field compared at different environments during different seasons. They should be described with minimum detection limits, reproducibility, power and space requirements, purchase costs, operating supplies, and standard operating procedures. Previous comparison studies (Dunlea et al., 2007; Fehsenfeld et al., 1990; Goyal and Gavane, 2005; Gregory et al., 1990; Mackay et al., 1988; Nakamura et al., 2003; Osthoff et al., 2006; Steinbacher et al., 2007; Thornton et al., 2003; Vaughan et al., 1997; Zenker et al., 1998) can be used as a guide for methodology and expected tolerances.

Charge Question 18: What observational approaches (surface based sondes and optical remote sensing, aircraft platforms, satellites) are best suited to assist such assessments? What routinely collected surface measurements and in what locations would complement vertical profile and total column observations?

Satellite detection is a useful adjunct, but the spatial scale (~10 km) and temporal resolution (often once or twice per day) is insufficient for many photochemical episodes and spatial scales (Fishman et al., 2002; Hidy et al., 2009; Hoff and Christopher, 2009; Liu et al., 2009a; Martin, 2008). Unmanned aerial vehicles with microsensors (Char et al., 2010; Ogren and Winstrand, 2008; Pereira et al., 2009; Sitnikov et al., 2005; Spiess et al., 2007) represent an emerging technology that has yet to be exploited. Tethered balloon-borne sondes (Schnitzhofer et al., 2009; Thompson et al., 2007a; Thompson et al., 2007b; Wohrnschimmel et al., 2006; Worden et al., 2007) have also proven useful.

Charge Question 19: Is it necessary to collect upper air wind speed and wind direction data a PAMS sites?

Yes. Vertical structures of wind data provide additional information about atmospheric transport phenomena. Note comment related to Question 1. These measurements should be based on a conceptual framework of upper air transport, carryover, and recirculation.

Charge Question 20: How should NOAA data be incorporated into the PAMS program?

It is a good idea to include NOAA meteorological data into the PAMS program, and use it as much as possible. As noted in the response to Question 1, NOAA’s climate centers are an efficient source of meteorological data.

Charge Question 21: How can PAMS data best be used? What specific data analyses should be conducted?

Analysis for PAMS data should include: trend analyses, source apportionment to verify emission inventories and target emission reductions, observational models to determine NOx/VOC inflections, model input for initial and boundary conditions, and model ground-truthing.

Charge Question 22: How should any recommended data analyses be implemented? Should these analyses be conducted at the state, regional, or national level?

Some of the resources should be reserved for specific data analysis projects. As noted in the response to Question 1, a better data base is needed to make the data easier to obtain and use. It should be used by anyone who wants to use it. The number of published articles and reports for the PAMS network are only about 10–15% of those using data from the IMPROVE network.

Charge Question 23: Should more or less of the PAMS funding be allocated to data analysis?

A greater number of quality reports and peer reviewed publications should be expected if 25% of the PAMS fund is to be used for data analysis. It doesn't seem that any resources are allocated to method characterization and data analyses. The PAMS websites aren't even kept up to date, as noted in the response to Question 1.

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Comments from Dr. Kenneth Demerjian

The CASAC AMMS Panel is requested to respond to the following charge questions in regard to monitoring topics related to PAMS Network Re-engineering.

Charge Question 1: How should EPA prioritize the current PAMS objectives? What current objectives, if any should be deemphasized or eliminated?

The program objectives identified in the current whitepaper over lap and are not concise. PAMS design objectives must be identified along with specified analyses to be performed to meet those objectives, for example;

The PAMS VOC measurements should be applied to:

1) Track and verify that trends in species specific VOCs are consistent with VOC mitigation emission strategies and target controls (e.g. assess VOC trends in response to: 1) to phase 1& 2 RFG (with specific look at catalytic convertor performance in response to Tier 2 gasoline sulfur control and mobile source air toxic MSAT controls; 2) introduction of low sulfur diesel fuel; 3) 2007 diesel emission emissions standard; 4) the economic recession; and 5)introduction of renewable fuels.
2) Provide compound specific diurnal patterns to evaluate emission profiles (as specified in emissions models by source) and for evaluation of the air quality modeling system overall (e.g., see Doraiswamy et al., 2009 and Ren et al.,2003, Ren et al., 2006).

Charge Question 2: What additional objectives should EPA consider for the PAMS program at this time?

See above.

Charge Question 3: What are the advantages and disadvantages of the current design with multiple sites per PAMS area? What changes, if any, should be made in the number and spatial distribution of required sites?

The spatial distribution of the current PAMS design was envisioned to capture the upwind, urban central and downwind concentrations of VOCs. These data were intended to support model evaluations and improve diagnostic evaluation of ozone’s response to VOC concentration perturbations from high density urban emissions. Continuous (hourly measurements) at central urban sites should remain as the foundation for the network. Upwind inflow sites should be restricted to regions with specific interstate transport issues (e.g. NE corridor or enhanced biogenic influence such as Atlanta).

Charge Question 4: Should EPA consider requiring PAMS measurements in areas other than areas classified as serious and above for the ozone NAAQS to improve spatial coverage?

Yes – measurements at some NCore sites (see next question) and at some rural sites to help assess background VOC's contribution to policy relevant background O3.

Charge Question 5: Should EPA consider requiring PAMS measurements at a new subset of ozone sites in addition to the traditional PAMS (e.g., maximum concentration sites in all non-attainment areas, all urban NCore sites) ?

EPA should consider PAMS measurements at a subset of regional oriented NCORE sites to characterize the composition of aged anthropogenic VOCs and biogenic VOC content to assess their contribution to regional ozone production and secondary organic aerosol production.

Charge Question 6: What role, if any, should mobile or temporary sites play in the PAMS program?

Mobile or temporary sites can be deployed to characterize spatial distribution of VOCs in the vicinity of unique industrial sources (chemical or refinery operations) or where intrastate transport is occurring between major metropolitan areas.

Charge Question 7: EPA has received feedback that the PAMS program needs to be as flexible as possible to help states meet specific needs. In consideration of this potential objective, what are the committee's views on the relative merits of revising PAMS to be a very flexible program with relatively few requirements versus a program that is highly specified? If the more flexible model were adopted, what minimum requirements, if any, should be included?

Without knowing the specifics of the "very flexible program" it is impossible to make informed comments. But, it would seem that providing a framework for States to consider when addressing their targeted issues would be appropriate. The framework would, for example, identify operational flexibilities with respect to the needs for national data sets as well as methodological measurement options and the utility of special study deployments. That being said, my experience has been that states typically are quite knowledgeable when it comes to their measurement needs.

Charge Question 8: Should the current PAMS monitoring season framework be retained or should the period for required measurements be revised (e.g., lengthened or determined on a case-by-case basis) based on analyses of ambient data, meteorology, climatology, or other factors?

The current PAMS monitoring season framework should be determined on a case-by case basis with the intent to shorten the measurement period (and reduce cost). A variety of analysis techniques using ambient air quality and meteorological data are available.

PAMS measurements during the non-photochemical season should be considered on a special studies basis. Previous studies suggest possible flaws in our understanding of winter-time chemistry (Ren et al, 2006) and may also have implications on secondary aerosol production.

Charge Question 9: What criteria should EPA consider when re-evaluating the PAMS target VOC list?

In developing the target VOC list, consideration should be given to site characterization (i.e., urban or regional) and the following overall compound specific criteria:
The VOC is good marker for specific emission sources;
The VOC is a precursor of or is urban air toxic;
The VOC's reactivity (high ozone forming potential)
The VOC's secondary organic forming potential
The VOC is above LOD 30% or more of the time

Charge Question 10: Are there specific compounds that EPA should consider adding or subtracting from the target list?

Consider adding one or more biogenic VOCs that are representative of the "terpene class of compounds" This is easier said than done.

Charge Question 11: What are the advantages and disadvantages of manual canister sampling versus field deployed auto-GCs?

Field deployed auto-GCs provide diurnal concentrations (not possible with 24-hr avg. canister) that are particularly useful in evaluating air quality models and performing diagnostic emission attribution studies.

Manual canisters can play a role in supporting annual trend analyses of VOCs and tracking the effectiveness of specific emission control programs.
A cost analysis should be performed comparing the autoGC and canister approaches, given the PAMS measurement objectives to be addressed. Consideration might be given to a hybrid approach.

Charge Question 12: Are the new commercially available auto-GCs appropriate for use at PAMS sites? What additional evaluations are necessary to determine the suitability of auto-GC's for use in the PAMS network?

There is limited state experience with new commercially available dual column dual detector auto-GCs provide. These systems need to be evaluated against traditional canister analyses and standard 1st generation auto-GCs via side-by-side comparisons would be useful.

Charge Question 13: What role, if any, should TNMH monitors play in the PAMS program?

There are important reasons to quantify the magnitude of unidentified hydrocarbons in the atmosphere. The PAMS unidentified compounds which appear as an unresolved peak on the auto- GC column as a result of the temperature purge at the end of the 40-min temperature program representative of high molecular weight compounds (i.e. $>C_{10}$) which likely contribute to local/regional ozone production and to local secondary organic aerosol production. TNMH serves to quantify an additional increment of unidentified hydrocarbon in the atmosphere which is determined from the difference between TNMH-PAMSTotalHC.

Charge Question 14: Should carbonyls be required at all VOC speciation sites?

Carbonyl measurements should be considered on a special studies basis with specific objectives and advanced measurement technologies. (e.g., traffic related formaldehyde concentration exposure; gasoline and diesel on-road direct emission measurements of formaldehyde; and photochemical production of secondary formaldehyde in urban and regional environments. These applications would deploy advanced fast response measurement technologies to monitor atmospheric formaldehyde (e.g. tunable laser IR absorption spectroscopy or differential optical absorption spectroscopy).

Charge Question 15: What issues have been addressed, and what issues still need to be addressed with the current TO-11A method for carbonyl sampling?

Charge Question 16: What other methods should be considered as an alternative to the manual TO-11A method for carbonyl sampling?

Under strategic special study deployment consider differential optical absorption spectroscopy, DOAS; tunable laser IR absorption spectroscopy.

Charge Question 17: Are direct measurement NO2 or photolytic analyzers suitable for deployment in the PAMS network? What additional evaluations are necessary to determine their suitability for use in the PAMS network?

Yes - direct measurement NO2 or photolytic analyzers are suitable for deployment in the PAMS network. These measurements can be phased in and inter-compared with traditional NOx boxes prior to phasing out the NOx boxes.

Charge Question 18: What observational approaches (surface based sondes and optical remote sensing, aircraft platforms, satellites) are best suited to assist such assessments? What routinely collected surface measurements and in what locations would complement vertical profile and total column observations?

Charge Question 19: Is it necessary to collect upper air wind speed and wind direction data at PAMS sites?

If these data are available from a NWS surface met observation site that is regionally representative, these data should be acquired and made part of the data set.

Charge Question 20: How should NOAA data be incorporated into the PAMS program?

NOAA/NWS met data should be incorporated into the PAMS data base on an hourly average basis similar to that for the current PAMS met measurement parameters.

Charge Question 21: How can PAMS data best be used? What specific data analyses should be conducted?

Diurnal patterns of specific marker VOCs; see figure 1 below
Annual trends of specific marker VOCs; see figure 2 below
Estimate of SOA production potential; see figure 3 below
Estimate VOC reactivity index and O3 production potential.

Charge Question 22: How should any recommended data analyses be implemented? Should these analyses be conducted at the state, regional, or national level?

Each organization has a role to play and vested interest in the analyses and interpretation of results. Independent funding should be considered for competitive solicitations to explore diagnostic analyses approaches to address process science and policy relevant objectives.

Charge Question 23: Should more or less of the PAMS funding be allocated to data analysis?

The PAMS analysis budget of 25% of total expenditures is reasonable, if properly allocated. EPA might consider setting aside a portion (15% of the PAMS analyses funds) to support independent scientists to develop diagnostic approaches, as mentioned above, to address process science and policy relevant objectives.

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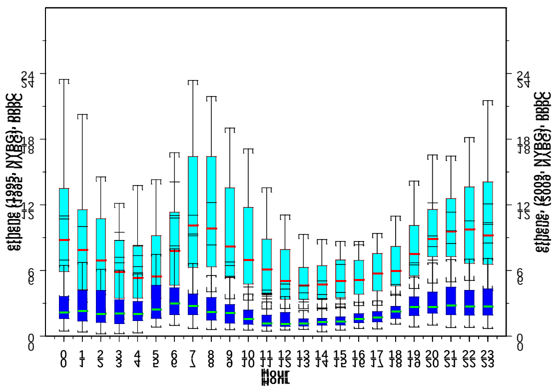
Figures:

ethene diurnal NYBG 1995 vs. 2009



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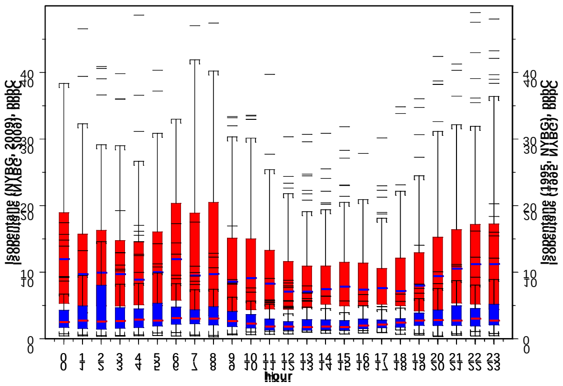

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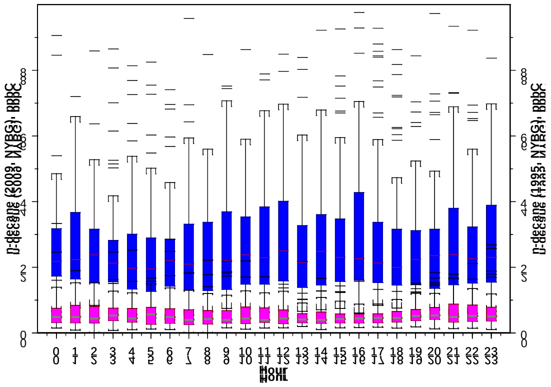

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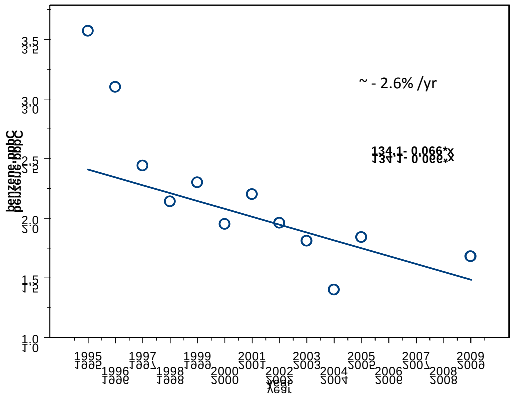

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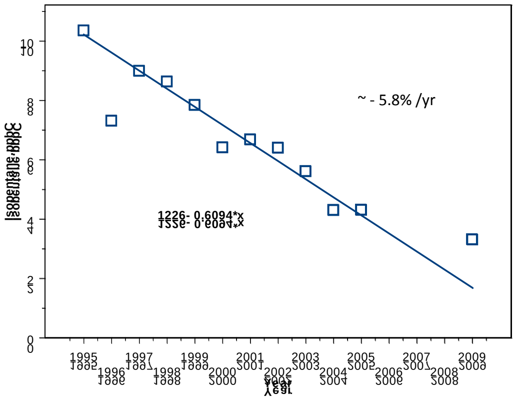

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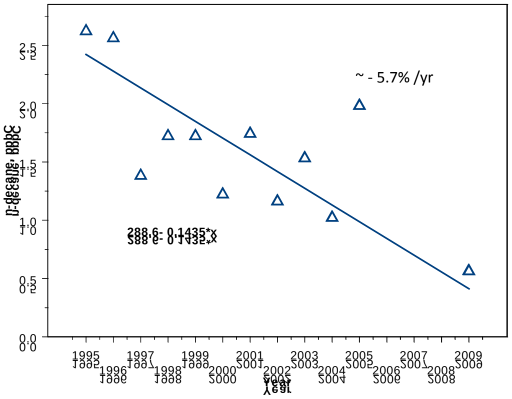

Comments from Mr. Dirk Felton

Charge Question 1: How should EPA prioritize the current PAMS objectives? What current objectives, if any, should be deemphasized or eliminated?

The most important priorities in the current program are to provide a speciated VOC database for photochemical modeling and for evaluation of the emissions inventory. Neither of these objectives is currently being met. The photochemical grid models utilize VOCs by functional group which are not provided by the PAMs program and the source emissions impact cannot be evaluated because the emissions inventory is not VOC specific. The EPA should move towards a harmonization of the overall approach from emission inventory through ambient data collection and atmospheric model demonstration. All of these elements need to be consistent with each other for the system to work cohesively.

Charge Question 2: What additional objectives should EPA consider for the PAMS program at this time?

The existing PAMs network design favors urban areas which had been designated as severe for the 1-Hr Ozone standard. The PAMs objectives should be expanded to include data collection in support of research to determine the significance of regional background Ozone in relation to locally produced and transported anthropogenic Ozone. This research should include an identification of natural biogenic precursors that are not subject to mitigation strategies as well as biogenic precursors resulting from anthropogenic activities such as agricultural and livestock operations.

Charge Question 3: What are the advantages and disadvantages of the current design with multiple sites per PAMS area? What changes, if any, should be made in the number and spatial distribution of required sites?

The concept of a PAMs area has to be reconsidered. The implementation of targeted control strategies that were designed to reduce the local 1-Hr exceedences has been effective. This, in combination with the longer 8-Hr average form of the standard has resulted in monitors that exceed the standard by a smaller margin but these exceedences are now occurring over much larger areas. This means that the criteria that defines a Type 1 and Type 2 site are becoming less distinct. In some areas, the upwind Ozone monitors are non-attainment. It would be better to define Ozone production regions based on the source categories that are prevalent in each of these areas.

Once an Ozone production region is defined, the monitoring needs for that region can be determined and a monitoring and data analysis plan can be implemented. The plan must be tailored to the specific source categories including mobile sources, industrial, agricultural, power sector, biogenic and meteorology that contribute to the Ozone problem in that region. Special studies and analysis projects can then be designed as gaps are discovered in the knowledge base for each area. This should be more effective than the current design which emphasizes Type 1 sites which often are not really background, redundant type 2 monitors and Type 3 and 4 sites which are less helpful for control strategy development.

All of the sites must be designed to be neighborhood scale or larger. Ozone is a regional problem and solutions that are designed to control a micro-scale problem will not be effective. The exception to this is a special purpose monitor installed to perform source characterization that can be utilized to determine the influence of multiple similar sources over a wide area.

Charge Question 4: Should EPA consider requiring PAMS measurements in areas other than areas classified as serious and above for the ozone NAAQS to improve spatial coverage?

Yes, there are areas of the country where the moderate classification could be more or less intractable depending on where the level of the standard is set. These areas are often geographically distinct from the existing PAMs areas which at one time had been classified as serious. PAMs measurements may be needed in order to determine the precursor mix as well as potential control strategies for these geographically distinct moderate areas.
It may not be necessary to add PAMs measurements to areas classified as moderate if they are adjacent to areas where PAMs measurements are already implemented. These moderate areas will likely respond to whatever control strategies are implemented for the adjacent area where the Ozone problem is more significant.

Charge Question 5: Should EPA consider requiring PAMS measurements at a new subset of ozone sites in addition to the traditional PAMS (e.g., maximum concentration sites in all non-attainment areas, all urban NCore sites)?

The PAMs program needs to be flexible enough to permit new sites and specific monitoring parameters where they are needed. In some areas, NOx monitoring might be more effective than VOC or Carbonyl measurements.

Requiring monitoring for specific parameters where it will not be helpful should not be part of the program.

Charge Question 6: What role, if any, should mobile or temporary sites play in the PAMS program?

The PAMs program should be flexible enough to permit short-term monitoring to help define the aerial extent of the impact of source categories. This is the kind of information necessary to develop viable control strategies. One thing that has been demonstrated by the existing PAMs VOC dataset is that the VOC fingerprint for a particular region tends to remain consistent even as the overall concentrations rise and fall. It may be possible to reduce the number of Type 2 sites and use short-term, mobile or other unconventional monitoring to help expand the geographic representativeness of the PAMs measurements.

Charge Question 7: EPA has received feedback that the PAMS program needs to be as flexible as possible to help states meet specific needs. In consideration of this potential objective, what are the committee's views on the relative merits of revising PAMS to be a very flexible program with relatively few requirements versus a program that is highly specified? If the more flexible model were adopted, what minimum requirements, if any, should be included?

The PAMs program needs the ability to support research needs for Ozone problems that vary regionally due to precursor composition, meteorology and available, viable control strategies. Biogenic precursors for instance, don't lend themselves to viable control strategies so a PAMs program targeting a region heavily impacted by biogenic VOCs may need to obtain detailed information on NOx, upper air meteorology or another parameter that will help in the formulation of a successful control strategy.

The PAMs program should not be classified as a monitoring program. This is too rigid a structure to be effective in dealing with the Nation's Ozone problem. The PAMs program needs to become a resource with a number of monitoring and data collection options with a significant portion of resources set aside for special studies and data analysis. Program requirements should be reduced to the extent possible while recognizing the value of keeping enough of the traditional Type 2 sites for trends analysis. The EPA should, however, make the methods used for monitoring as uniform as possible so the data can be useful for comparisons from one Ozone research area to another. Some of the PAMs program categories should include:

Category 1: Monitoring and Data Collection

- Trend: 1-Hr VOC using Field GC, auto-system or newer alternative
- Trend: 3-Hr or 24-Hr Carbonyl
- NOx, NOy, TNMOC and Trace CO
- Additional Ozone monitoring (upwind, high altitude, off-shore)
- Upper air Meteorology: (Profiler, Ceilometer, Vertical temperature)
- Solar radiation (Visible/UV/multiband)

Category 2: Special Studies:

- Short-term precursor/Ozone studies (spatial, elevation and temporal)
  Mobile GC, temporary site (up to 1-Yr) or canister deployment,
  Canister collected by threshold from TNMHC analyzer
- Emission/source characterization: (stack test, Biogenic flux measurements, etc.)
- OH measurements in Ozone production regions
- Continuous Carbonyl
- Evaluation of newer GCs without Nafion dryers
- Evaluation of NO2 methods

Category 3: Data Analysis Studies:

- Atmospheric Chemistry investigation
- Model sensitivity, boundary studies
- Model development: individual VOC reaction rates

The efficient implementation of a more flexible PAMs program could be problematic because States can't effectively institute the program on their own if a needed monitoring or special study effort has to take place in an up or downwind State or Country. To help make the PAMs program as useful as possible, the selection of monitoring parameters and data analysis objectives must be made on a multistate, regional basis. It would be helpful if the RPO model was re-instituted to help coordinate this effort.

Charge Question 8: Should the current PAMS monitoring season framework be retained or should the period for required measurements be revised (e.g., lengthened or determined on a case-by-case basis) based on analyses of ambient data, meteorology, climatology, or other factors?

The PAMs monitoring season must at a minimum cover the period for the local Ozone season. There is no guarantee that a mitigation strategy that works for an August exceedence will also work for one that occurs in March. It would be helpful if at least one Type 2 site in each Ozone Region operated year-round. The data will improve the understanding of patterns of emissions and could provide useful air toxics data.

Charge Question 9: What criteria should EPA consider when re-evaluating the PAMS target VOC list?

This question is difficult to answer due to the large percentage of unknown compounds that cannot be measured with the current Auto-GCs. The newer compact field GC's that do not have a Nafion dryer may be able to resolve some of these compounds. The target list should be relatively flexible so species can be added if tracers are found for source categories. It is also likely different target lists will be appropriate for different areas. The VOCs and NOx species prevalent in industrial cities will vary from those found in the Northeast or the Southwest or in rural areas.

Charge Question 10: Are there specific compounds that EPA should consider adding or subtracting from the target list?

The EPA should try to identify more compounds that can be used to characterize emissions sources including biogenics.

Charge Question 11: What are the advantages and disadvantages of manual canister sampling versus field deployed auto-GCs?

The hourly Auto-system data is more appropriate for model evaluation due to the diurnal profile of data. The canister data can be used to quality assure the auto-system data and to expand the geographic representativeness of the auto-system data.

Charge Question 12: Are the new commercially available auto-GCs appropriate for use at PAMS sites? What additional evaluations are necessary to determine the suitability of auto-GC's for use in the PAMS network?

EPA ORD should conduct a 1-Yr side by side comparison of the auto-system with the newer compact field GCs. This comparison should be conducted in an east coast city, a west coast city and in a rural area. The study should include an evaluation of the data, the ability of each method to identify compounds currently listed as unknown, as well as each instrument's robustness and the necessary level of operator training.

Charge Question 13: What role, if any, should TNMH monitors play in the PAMS program?

The TNMH monitors are relatively inexpensive and are particularly useful for investigating the patterns of overall VOCs emissions. Since the data from these instruments are not speciated, the data are most useful in areas where the VOCs are already well characterized such as near existing Type 2 sites or near specific industrial facilities.

Charge Question 14: Should carbonyls be required at all VOC speciation sites?

Charge Question 15: What issues have been addressed, and what issues still need to be addressed with the current TO-11A method for carbonyl sampling?

The method needs improvement. The collection efficiency, susceptibility to humidity and Ozone and field quality assurance procedures are all areas that must be addressed. The field samplers have not been part of the PAMs program's quality assurance procedures. At a minimum, the quality assurance procedures should include quarterly flow audits and requirements for the preparation, heating set point and replacement interval for the sampler denuder.

Charge Question 16: What other methods should be considered as an alternative to the manual TO-11A method for carbonyl sampling?

The newer technology methods are not suitable for routine use but certainly could be part of a special study. The TDL and wet chemical methods could be employed where high frequency data are needed.

Charge Question 17: Are direct measurement NO2 or photolytic NO2 analyzers suitable for deployment in the PAMS network? What additional evaluations are necessary to determine the suitability for use in the PAMS network?

NO2 is important for the PAMs program but this is complicated by the need for NOy as well. A solution for routine operation should include a modification of the existing instrumentation that could provide NO, NO2 and NOy. For non-routine special studies, the TDL or the ring down spectrometer could be used where accurate high frequency data are required.

Charge Question 18: What observational approaches (surface based sondes and optical remote sensing, aircraft platforms, satellites) are best suited to assist such assessments? What routinely collected surface measurements and in what locations would complement vertical profile and total column observations?

The regional nature of Ozone including Ozone's precursors and the atmospheric conditions that contribute to Ozone formation make Ozone a better candidate for non-traditional monitoring approaches than other typically primary pollutants. Observational approaches are particularly well suited for determining the atmospheric conditions for forming Ozone. Solar radiation, temperature, mixing height, snow cover/reflectivity/cloud, land use and fog cover are all parameters that are well suited to vertical or remote measurement techniques. These measurements require little ground-truthing and should be automated to the extent possible using existing satellite, airport and aircraft measurement platforms. Profilers are almost too expensive to be a routine part of the PAMs program. The EPA should consider the newer less expensive vertical temperature based radiometers/ceilometers that can provide mixing height data. This information is needed particularly in mountain regions and in places such as coastal regions where atmospheric models have difficulty in determining the hour to hour mixing height. Accurate mixing height data can also make the interpretation of vertical column data more straightforward.

Remote sensing techniques can also be useful for source characterization for area wide sources such as marine and airports, railyards, and large industrial facilities. Some of the more expensive of these such as FTIR, DOAS and DIAL could be utilized in the special study category of PAMs to assess unconventional sources.

Surface based measurements made below and above the mixing height such as at the base and summit of a mountain are very effective at evaluating vertical column data. The surface sites should at a minimum include the species that tend to remain close to the ground.

Charge Question 19: Is it necessary to collect upper air wind speed and wind direction data at PAMS sites?

Not all PAMs sites require upper air measurements. It would be useful to have at least one in each region with additional locations where the models have difficulty such as in mountain regions and near the marine boundary. Ceilometers may be adequate in coastal regions.

Charge Question 20: How should NOAA data be incorporated into the PAMS program?

Charge Question 21: How can PAMS data best be used? What specific data analyses should be conducted?

Data analysis should be tailored to each region so requiring specific data analyses may be counter-productive. The EPA should make the data easily accessible which would encourage its use by the outside community.

Charge Question 22: How should any recommended data analyses be implemented? Should these analyses be conducted at the state, regional, or national level?

It is difficult to implement a viable research program and control strategy development initiative within the boundaries of one state in a larger Ozone region such as the northeast corridor. It makes sense to use the RPO model to organize and direct the multi-state research effort towards a workable goal. This may not apply to States which encompass the Ozone area such as California and Texas.

Charge Question 23: Should more or less of the PAMS funding be allocated to data analysis?

This is an issue that should be discussed with NACAA. They will be able to weigh the opinions of the respective State and Local Agencies. It would not be appropriate for the EPA to take these funds without the consent of the Agencies that ultimately have to submit an approvable SIP.

Comments from Dr. Phil Fine

Charge Question 1: How should EPA prioritize the current PAMS objectives? What current objectives, if any, should be deemphasized or eliminated?

All the current PAMS objectives listed in the white paper still express valid and important needs towards a better understanding of ozone chemistry, transport, modeling, and attainment demonstration. The prioritization of these objectives, however, will be region or air shed specific. Different non-attainment areas will have different outstanding questions to be answered, whether it is more VOC data and trends, or inventory uncertainties, or background conditions, or upper air meteorology. Any attempt to prioritize objectives on a national level would be ignoring these regional differences. A one-size-fits-all approach would lead to unnecessary measurements and thus a potential waste of resources.

Charge Question 2: What additional objectives should EPA consider for the PAMS program at this time?

Issues such as continental background, biogenic VOC emissions, and interstate transport are critical. So an objective recognizing the need for a better understanding of natural vs. anthropogenic ozone precursor emissions and transport from upwind or off-shore areas beyond a State’s authority to implement controls would be appropriate.

Charge Question 3: What are the advantages and disadvantages of the current design with multiple sites per PAMS area? What changes, if any, should be made in the number and spatial distribution of required sites?

The general framework of the PAMS Type 1-4 sites is scientifically sound, but as mentioned in the white paper and implemented in recent PAMS program changes, different ozone non-attainment areas will have different needs, and a high priority site may not fit perfectly into one of the PAMS site type categories. There may also be some overlap of Type 4 sites in one area and Type 1 sites in the neighboring area that may cause redundancies.

The advantage of this approach is to provide regulatory assurances, beyond mere guidance, to PAMS agencies as to the important criteria in choosing a set of PAMS sites. This can also be considered a disadvantage if it causes a lack of flexibility to site PAMS stations where state and local agencies feel they need to site them. The number of sites and spatial distribution within a state or region may also be better determined by local needs. If a better national distribution is desired for VOC precursors, then perhaps other programs not tied to ozone attainment status, such as NCore or NATTS, would be better suited to provide that coverage.

Charge Question 4: Should EPA consider requiring PAMS measurements in areas other than areas classified as serious and above for the ozone NAAQS to improve spatial coverage?

As stated above, if a better national distribution is desired for VOC precursors, then perhaps other programs not tied to ozone attainment status, such as NCore or NATTS, would be better suited to provide that coverage. Lowering the ozone status threshold for PAMS to below serious would likely lead to too numerous and often unnecessary measurement sites.

Charge Question 5: Should EPA consider requiring PAMS measurements at a new subset of ozone sites in addition to the traditional PAMS (e.g., maximum concentration sites in all non-attainment areas, all urban NCore sites)?

The answer should depend on both the local data needs as well as the desire for national spatial coverage. Dictating that every ozone non-attainment area implement PAMS measurements may not be a wise allocation of resources if those areas on the edge of attainment understand the problem and/or are expected to be in attainment as control programs take effect. Perhaps PAMs measurements could be optional in some of these areas. However, the NCore and NATTS could provide the desired national coverage and consistency while limiting the resource requirements.

Charge Question 6: What role, if any, should mobile or temporary sites play in the PAMS program?

If a state or local agency can develop a sampling plan utilizing such an approach that would help to address their particular ozone issues, then this approach may be useful and should be supported. But given the complexity in deploying this type of monitoring, there should be no national-level requirements for mobile or temporary sites.

Charge Question 7: EPA has received feedback that the PAMS program needs to be as flexible as possible to help states meet specific needs. In consideration of this potential objective, what are the committee's views on the relative merits of revising PAMS to be a very flexible program with relatively few requirements versus a program that is highly specified? If the more flexible model were adopted, what minimum requirements, if any, should be included?

Flexibility will be key to a successful PAMS program that meets the stated objectives in the most efficient way. There are advantages to a highly specified program, such as national consistency in methods and ensuring spatial coverage for national assessments and modeling efforts. However, there is a lot of room in the current PAMS requirements to relax some requirements while still achieving these national-level goals. Current sampling requirements for sub-daily periods, frequencies, and seasons may result in many more samples (and resources expended) than is really needed to achieve both local and national goals. Resources saved by relaxing these requirements could be put towards other monitoring more relevant to local needs.

Charge Question 8: Should the current PAMS monitoring season framework be retained or should the period for required measurements be revised (e.g., lengthened or determined on a case-by-case basis) based on analyses of ambient data, meteorology, climatology, or other factors?

The PAMS monitoring seasons should be determined on a case-by-case basis based on local factors such as those listed (ambient data, meteorology, climatology), but also based on other local needs such as model evaluation and inventory checks. If there exists a need to perform these measurements year round to fully evaluate models and inventories, then it should be supported within the PAMS framework.

Charge Question 9: What criteria should EPA consider when re-evaluating the PAMS target VOC list?

The EPA should continue to look at historical data regarding ambient levels, and eliminate compounds that are rarely found above detection limits. This may have to be done on a regional basis. The EPA should also consider what is known about reactivity of the VOCs, and possibly develop a reactivity weighted index to help further reduce the size of the target list. The EPA should not preclude the measurement or reporting of VOCs not on a smaller target list if the local agency has a specific need to measure that VOC. Adding in additional biogenic VOCs, given their abundance in certain areas and their reactivity, is recommended.

Charge Question 10: Are there specific compounds that EPA should consider adding or subtracting from the target list?

In general the target list should be greatly reduced or even eliminated entirely, and allow the state and local monitoring agencies to develop a target list based on their needs. As stated above any VOC that is mostly below detection or has a low reactivity weighted importance for ozone production should be eliminated. The known biogenic and reactive VOCs such as mono-terpenes should be added. Carbonyls should be retained if a full assessment of the sampling and analytical issues shows the data to be reliable.

Charge Question 11: What are the advantages and disadvantages of manual canister sampling versus field deployed auto-GCs?

If a field deployed auto-GC is a reliable, robust, instrument that can run continuously with minimal field staff time, then there can be considerable resource savings. However, this is rarely the case with current instrumentation, and the fact that they provide hourly data leads to the need for extra staff resources in fully validating this much larger data set. The extra value in hourly vs. 3-hour samples is questionable.

Charge Question 12: Are the new commercially available auto-GCs appropriate for use at PAMS sites? What additional evaluations are necessary to determine the suitability of auto-GC's for use in the PAMS network?

A full evaluation of these new auto-GCs is highly recommended, not just for accuracy, precision, specificity, and target analyte capabilities, but also for ease of deployment, reliability, robustness, and cost of operation. If these new instruments can be shown to perform well given these criteria, then they should be considered for deployment at PAMS sites.

Charge Question 13: What role, if any, should TNMH monitors play in the PAMS program?

TNMH analyzers may have a role and their utility to meet local PAMS objectives should be determined by the state or local PAMS agency.

Charge Question 14: Should carbonyls be required at all VOC speciation sites?

To the extent that the methods can be evaluated and shown to be reliable, then they should be part of the PAMs program. They are a very important part of ozone chemistry almost everywhere. However, whether or not they should be required should depend on the local ozone problem and whether there is a need for that specific data in that specific area.

Charge Question 15: What issues have been addressed, and what issues still need to be addressed with the current TO-11A method for carbonyl sampling?

Many of the issues related to TO-11A have not been addressed, such as breakthrough, low precision levels, reactions occurring during sampling (i.e. ozone interferences), and the accuracy of formaldehyde measurements. A full assessment of all PAMS carbonyl measurements taken to data, along with comparisons to other programs such as NATTS, should yield important information on lab-to-lab and sampler-to-sampler biases.

Charge Question 16: What other methods should be considered as an alternative to the manual TO-11A method for carbonyl sampling?

Canister methods such as TO-15 should be re-examined for some of the carbonyls, and perhaps some of the field auto-GCs are better suited for carbonyl analysis vs. the traditional lab-based GCs.

Charge Question 17: Are direct measurement NO_2 or photolytic NO_2 analyzers suitable for deployment in the PAMS network? What additional evaluations are necessary to determine the suitability for use in the PAMS network?

They may be suitable if a particular area has a need for true NO2 readings. Further evaluations comparing NO2 to traditional NO/NOx and NO/NOy may be necessary before wide-scale deployment.

Charge Question 18: What observational approaches (surface based sondes and optical remote sensing, aircraft platforms, satellites) are best suited to assist such assessments? What routinely collected surface measurements and in what locations would complement vertical profile and total column observations?

All approaches and technologies should be considered and may be appropriate for PAMS assessments in specific areas. The state or local agency should propose and justify the need for such approaches to be funded under the PAMS program. National requirements for the use of such approaches would probably not be appropriate given their limited availability in some areas

Charge Question 19: Is it necessary to collect upper air wind speed and wind direction data at PAMS sites?

The necessity, frequency, and spatial coverage of such measurements are completely dictated by local modeling needs. National requirements are not warranted, but the PAMs program should support such efforts if justified by state and local agencies that have the need for upper air data.

Charge Question 20: How should NOAA data be incorporated into the PAMS program?

If available and applicable, NOAA data should be considered for use by state and local agencies in testing and improving model performance.

Charge Question 21: How can PAMS data best be used? What specific data analyses should be conducted?

The PAMS data is useful for most of the stated PAMS objectives, including trend analysis, model evaluation, inventory validation, and determining background conditions for the models. Specific data analysis efforts will depend upon the specific objective of the effort. PAMS databases should be considered a resource to be used as needed to answer specific questions. Less focused, routine analyses of PAMS data may only be useful for national or local trends assessments or for identifying biases dependant on sample type or laboratory.

Charge Question 22: How should any recommended data analyses be implemented? Should these analyses be conducted at the state, regional, or national level?

Local, state or regional analyses should be conducted as needed to answer specific questions related to ozone formation and attainment demonstration. There is little need for a national program dictating the types or frequency of analyses to be conducted. Routine analyses can be performed at a national level to examine trends or any analytical or sampling biases.

Charge Question 23: Should more or less of the PAMS funding be allocated to data analysis?

No PAMS funding needs to be specifically allocated to data analysis. There is no need to perform some of these analyses annually, so allocating a fraction of funding every year would not be productive. State and local agencies should justify the configuration and utility of their PAMS programs, and part of that justification will necessarily be how the data will be used, what analyses will be conducted, and how much funding will be needed for those analyses.

Additional Comment

An important potential part of the PAMS program may be additional ozone and NOx measurements to provide spatial resolution beyond the EPA minimum monitoring requirements for PAMS or those criteria pollutants. It is one of the stated PAMS objectives, but was not part of the Charge Questions. If a state or local agencies believe a larger network of these criteria pollutants will help address their understanding of their particular ozone issues, then such efforts should be specifically supported by the PAMs program.

Comments from Dr. Phil Hopke

Charge Question 1: How should EPA prioritize the current PAMS objectives?

Charge Question 2: What additional objectives should EPA consider for the PAMS program at this time? What current objectives, if any, should be deemphasized or eliminated?

These questions are probably best answered collectively. The current objectives are

1. Provide a speciated ambient air database which is both representative and useful for ascertaining ambient profiles and distinguishing among various individual VOC. These data can later be used as evaluation tools for control strategies, cost-effectiveness, and for understanding the mechanisms of pollutant transport.
2. Provide local, current meteorological and ambient data to serve as initial and boundary condition information for photochemical grid models. These data can later be used as a baseline for model evaluation and to minimize model adjustments and reliance on default settings.
3. Provide a representative, speciated ambient air database which is characteristic of source emission impacts. These data can be particularly useful in analyzing emissions inventory issues and corroborating progress toward attainment.
4. Provide ambient data measurements which would allow later preparation of unadjusted and adjusted pollutant trends reports.
5. Provide additional measurements of selected criteria pollutants. Such measurements can later be used for attainment/nonattainment decisions and to construct NAAQS maintenance plans.
6. Provide additional measurements of selected criteria and non-criteria pollutants from properly-sited locations. Such measurements can later be used for evaluating population exposure to air toxics as well as criteria pollutants.

These objectives are uniformly simplistic in the context of an oxidative atmosphere of varying capacity to modify the composition of organic emissions on a relatively short time scale. The “ambient profile” depends on the local emissions, transport, and physical chemical characteristics (temperature, particle surface area and oxidant concentrations). A better idea would be to look at distributional characteristics characterized by meteorological regimes developed from multiple years of data.

The objective “Initial and Boundary Conditions” to grid models give no indication as to what scale? PAMS provides point measurements and grid models are typically 12 km x 12 km (can be as small as 4 km x 4 km) so what are they looking for? An important unasked question is how spatially representative are the measurements at any given PAMS site. Also if the measurements are to provide initial and boundary conditions, they cannot also serve to evaluate the model. These objectives need to be separated and two independent sets of data need to be developed: One that represents inputs to the mode and another that can be used for evaluation purposes.

“Provide a representative, speciated ambient air database which is characteristic of source emission impacts.” Source apportionment has and can be done on such data, but the problems related to varying species reactivity. Our experience is to work with nighttime values when their stability is much greater. Also plumes represent significant problems. In many locations, the background of reacted materials and modified profiles makes source identification very difficult.

The development of “trends” also has to take short-term reactive variability into account.

The installation of additional monitors should really be at the discretion of the state or local agency based on their analysis as to whether additional data would provide better planning to be achieved.

For a research objective, it is always desirable to have population exposure measurements. Some of the PAMS species are also HAPS so to some extent their hazard could be assessed. However, the question is whether there are additional resources available beyond the monitoring necessary to protect public health with an adequate margin of safety.

Charge Question 3: What are the advantages and disadvantages of the current design with multiple sites per PAMS area? What changes, if any, should be made in the number and spatial distribution of required sites?

It is not clear that the specification of the multiple sites is connected to the modeling that it supposed to support.

Charge Question 4: Should EPA consider requiring PAMS measurements in areas other than areas classified as serious and above for the ozone NAAQS to improve spatial coverage?

Potentially. If we are concerned with transported ozone from Asia having an impact on the US, then transport is clearly much more important than we thought when setting up the PAMS network 15 to 20 years ago. There needs to be modeling to estimate transport with reaction to determine the relative impacts of local and distant sources. If VOC sources and transport are important sources of VOC in the non-attainment areas, then it may be important to have data for the transported component to identify a strategy to reduce the local ozone.

Charge Question 5: Should EPA consider requiring PAMS measurements at a new subset of ozone sites in addition to the traditional PAMS (e.g., maximum concentration sites in all non-attainment areas, all urban NCore sites)?

Only if there is *a priori* indications (like model results) that having these data will actually contribute to improving the modeling and control strategy development. It has seem that the PAMS data have been underutilized in the past and thus, expanding the monitoring without a clear indication that the cost will provide adequate benefits in better models and control strategies, then there is no justification for the expansion.

Charge Question 6: What role, if any, should mobile or temporary sites play in the PAMS program?

Mobile measurements might be helpful in finding local sources and assessing the emissions factors, but those are specific studies that should be left to the authorities who are developing the SIP. It is hard to see a lot of value of short-term measurements except for source characterizations.

The presentation on the IAGOS was intriguing in its possibilities to help to look at spatial variability of ozone and likely locations for ground level non-urban PAMS sites.

Charge Question 8: Should the current PAMS monitoring season framework be retained or should the period for required measurements be revised (e.g., lengthened or determined on a case-by-case basis) based on analyses of ambient data, meteorology, climatology, or other factors?

There are advantages of winter measurements when oxidant levels are lowest and reactions are slowest because of decreased temperature. If assessment of dispersion or source identification/apportionment is the goal, winter sampling can be useful. Otherwise, it is hard to see it is likely to be very helpful.

Charge Question 9: What criteria should EPA consider when re-evaluating the PAMS target VOC list?

It may be useful to assess the role of VOCs in producing SOA as well as ozone. Thus, species that represent significant SOA precursors could assist in PM strategy development and provide additional value to the PAMS measurements.

Charge Question 10: Are there specific compounds that EPA should consider adding or subtracting from the target list?

I do not know. I know when we analyzed data, there were a number of species that were BDL for most samples. Thus, it is a good idea to do a useful data inventory to see what the typical number of times that data are greater than the MDL and above the limit of determination. If all the data are just below or just above the MDL, then there is no information content and it is not worth including them. However, this would be on a site-by-site basis.

We have also mined data from Houston and found several of the peaks in the chromatograms were well related to ozone. However, we have no idea what they are. There needs to be some flexibility to carefully look at the data and decide what species are likely to be useful in control strategy development.

Charge Question 11: What are the advantages and disadvantages of manual canister sampling versus field deployed auto-GCs?

It really depends on the objectives. The increased time resolution of the auto-GC is advantageous for the source apportionment. However, for just providing input into the models, the increased time resolution may not worth the worth the cost and effort so canisters probably makes more sense.

Charge Question 12: Are the new commercially available auto-GCs appropriate for use at PAMS sites? What additional evaluations are necessary to determine the suitability of auto-GC's for use in the PAMS network?

With modern GCs and computers, it is hard to imagine that better systems could not be implemented, but it is not something I have done or looked at.

Charge Question 13: What role, if any, should TNMH monitors play in the PAMS program?

It is not clear to me that non-specific measures of organic vapor species concentrations are very useful. There is such a wide range of reactivity that a TNMH measurement is not likely to be strongly related to ozone formation potential. If monitors were available that mimicked the lumping of compound types that occurs in the chemical transport models, then they might have value.

Charge Question 14: Should carbonyls be required at all VOC speciation sites?

No. It should be possible to use models and some screening measurements to ascertain the impact of carbonyls and their photolysis on ozone formation. If the *a priori* data suggests a limited role in a given geographical area, why spend money on additional analyses?

Charge Question 15: What issues have been addressed, and what issues still need to be addressed with the current TO-11A method for carbonyl sampling?

I do not have any useful insights into this problem.

Charge Question 16: What other methods should be considered as an alternative to the manual TO-14A method for carbonyl sampling?

I do not have any useful insights into this problem.

Charge Question 17: Are direct measurement NO2 or photolytic NO2 analyzers suitable for deployment in the PAMS network? What additional evaluations are necessary to determine the suitability for use in the PAMS network?

There were several in developments, but I have not followed their testing.

Should EPA pursue the development of a single analyzer capable of measuring NO, NO2 and NOy?

Obviously if everything can be rolled into a single instrument, it reduces the cost of operation and calibration and potentially capital costs. First step is to have definitive systems for measurement of NO2 and NOy to start with.

Charge Question 19: Is it necessary to collect upper air wind speed and wind direction data at PAMS sites?

I do not see this to be very useful if it is ONLY a PAMS site. If it is a more comprehensive monitoring site, it is generally useful to have additional vertical profiling if it can be afforded.

Charge Question 20: How should NOAA data be incorporated into the PAMS program?

Not clear. We can certainly do trajectory ensemble analyses (PSCF, RFA, SQTBA, etc) to look at likely source areas of transported VOCs although again variable reaction rates makes such analyses more problematic.

Charge Question 21: How can PAMS data best be used? What specific data analyses should be conducted?

There are various multivariate calibration methods that can be applied to explore the relationships between specific VOCs and current or future ozone. These methods could be used to look at the sensitivity of ozone to the VOC concentrations.

The objectives need to be sharpened and then specific data analysis tasks can be developed to address those objectives. Right now, there is a disconnect between the data uses and the panoply of objectives.

Charge Question 22: How should any recommended data analyses be implemented? Should these analyses be conducted at the state, regional, or national level?

It needs to be done on the scale necessary to answer the specific questions related to the elevated ozone in a particular area.

Charge Question 23: Should more or less of the PAMS funding be allocated to data analysis?

It is hard to see where the money has gone. There does not seem to be a lot of obvious uses of the data as reflected in the scientific literature. We have explored the data for source apportionment and there can be some results obtained, but it has not proven very insightful in terms of helping to improve control plans. In particular, we have not seen a lot of efforts to relate the PAMS data to the ozone values. We have done some work in this area that actually provided some reasonable predictive capability for ozone forecasting,[3,4] but given the amount of funding that is being devoted to data analysis, there does not appear to be much return.

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[3] Application of Artificial Neural Networks to Modeling and Prediction of Ambient Ozone Concentrations, L. Hadjiiski and P.K. Hopke, J. Air Waste Manag. Assoc. 50:894-901 (2000).

[4] Data Mining of the Relationship Between Volatile Organic Components and Transient High-Ozone Formation, F. Gan and P.K. Hopke, Anal. Chim. Acta 490 153–158 (2003).

Comments from Dr. Rudolf Husar

Charge Question 1: How should EPA prioritize the current PAMS objectives? What current objectives, if any, should be deemphasized or eliminated?

If the ozone NAAQS is tightened, the permissible ozone levels would become comparable to the ozone levels due to 'extra-jurisdictional' source, i.e. not controllable by correct management procedures. Identifying the corresponding Policy-Relevant Background (PRB) of O3/Precursors is becoming an increasing challenge. Hence, characterization of PRB should be given a high priority of the re-designed PAMS program.

Charge Question2: What additional objectives should EPA consider for the PAMS program at this time?

Better characterization of Policy Relevant Background. PRB ozone/precursors are those that are not due to anthropogenic emissions within the US, Canada or Mexico. The primary PRB contributions are forest fires, biogenic emissions and anthropogenic emissions from outside North America.

Charge Question 4: Should EPA consider requiring PAMS measurements in areas other than areas classified as serious and above for the ozone NAAQS to improve spatial coverage?

Yes, measurements near sources that contributes to Policy Relevant Background.

Charge Question 5: Should EPA consider requiring PAMS measurements at a new subset of ozone sites in addition to the traditional PAMS (e.g., maximum concentration sites in all non-attainment areas, all urban NCore sites)?

PAMS measurements at locations that elucidate Policy-Relevant Background (PRB) ozone and precursors would be desirable. These include regions of smoke emissions, NW US and SW US. Both regions have non-industrial, seasonal VOC emissions that significantly impact on downstream receptor areas.

Also, regions impacted by long-rage transported O3 and precursors would also need to be characterized. The regions include the Mexico and Canada border regions. The trans-pacific transport of O3/precursors fro East Asia would also require characterization.

Charge Question 6: What role, if any, should mobile or temporary sites play in the PAMS program?

Very specialized mobile sampling may be useful for source characterization of ozone precursors for special cases such as major fires. However, mobile sampling should not be used for routine monitoring.

Charge Question 7: EPA has received feedback that the PAMS program needs to be as flexible as possible to help states meet specific needs. In consideration of this potential objective, what are the committee's views on the relative merits of revising PAMS to be a very flexible program with relatively few requirements versus a program that is highly specified? If the more flexible model were adopted, what minimum requirements, if any, should be included?

More flexible approach is desired. The minimum requirement is that major geographic and seasonal ozone regimes be identified; each ozone regime to be defined by seasonal/regional extent; source pattern; chemical integrations and transport pattern.

Charge Question 8: Should the current PAMS monitoring season framework be retained or should the period for required measurements be revised (e.g., lengthened or determined on a case-by-case basis) based on analyses of ambient data, meteorology, climatology, or other factors?

The April-September ozone season would need to be evaluated based on detailed analysis of the available PAMS and FRP ozone monitoring data. Such analysis would probably identify the regions where monitoring should be extended or shortened.

Charge Question 9: What criteria should EPA consider when re-evaluating the PAMS target VOC list?

The target VOC list should include the best-available tracers/indicators for fires, biogenic emissions and as well as for anthropogenic emissions.

Charge Question 18: What observational approaches (surface based sondes and optical remote sensing, aircraft platforms, satellites) are best suited to assist such assessments? What routinely collected surface measurements and in what locations would complement vertical profile and total column observations?

Satellite remote sensing of some O3 precursors appear to be the most promising observations to improve the understanding of ozone precursor emissions, ozone formation, and transport. The daily coverage of satellites along with ~10km spatial resolution constitutes a consistent global-scale dataset for several atmospheric chemical constituents.

In particular, the OMI spectral reflectance sensor on Aura satellite platform offers column-concentration measurement of NO2 and formaldehyde (a biogenic emission tracer) and ozone. The OMI data, available since 2004, constitute a unique contribution, particularly to the estimation of organic emissions from biogenic and fire emissions.

The MOPITT and MODIS sensors on Aqua/Terra satellite platforms produce column-concentrations data for CO and aerosol respectively. These observations available since 2001 have improved our understanding of non-industrial sources and emissions, primarily from episodic fire sources.

Satellite sensors have numerous limitations in accuracy, precision and spatio-temporal coverage. The column-concentrations measurements are difficult to calibrate and have interferences from clouds, other chemicals and surface reflectance. Hence, satellite observations are best used in conjunction with other observations and/or chemical transport models.

Surface-based column observations e.g. for ozone (Dobson instruments) and aerosol optical thickness (Sun-photometers) provide suitable, high-grade ground-truth for the satellite sensors. These should be utilized in conjunction with the satellite data.
At this time I am not ware of a systematic effort to fuse the surface-based measurements with satellite columnar observations. Evidently, the methodologies for such multi-sensory data fusion need to be developed before one can take advantage of the new observation platforms.

Charge Question 19: Is it necessary to collect upper air wind speed and wind direction data at PAMS sites?

I doubt that adding profilers or radiosondes at PAMS sites would improve the understanding of transport significantly. My reasoning is that I don't see how these observations are incorporated or assimilated into the current analysis or modeling efforts. Hence, rather than adding new sites, I would focus on developing techniques for the assimilation of observations into the MM5/CMAQ models.

Charge Question 20: How should NOAA data be incorporated into the PAMS program?

The variety of NOAA atmospheric observations and models could be incorporated into different types of analyses. Surface meteorological observations are helpful for local transport and removal analyses. Upper air observations (Raisosonde and Profilers) along with the NOAA regional met that assimilates these observations could be used in the regional CMAQ model.

Charge Question 21: How can PAMS data best be used? What specific data analyses should be conducted?

There should be more emphasis on diagnostic modeling as an approach to data analysis.
Currently, emission control actions rely heavily on the CMAQ model but the model performance for ozone simulations is rather marginal. In fact, it is said that the CMAQ O3 simulation performance has not improved over the past decade. Hence, it may be time for newer ideas such a combined analysis/modeling approach rather than the usual separate modeling and observation-based analysis.

Charge Question 22: How should any recommended data analyses be implemented? Should these analyses be conducted at the state, regional, or national level?

Clearly, the PAMS analysis approaches of the past were inadequate. Maybe a participatory process would be more productive and beneficial. It would be helpful to (1) identify the key PAMS stakeholders (e.g. EPA/Regions, states, observations community, modeling community, data analysts/researchers..(2) seek to understand and *their* needs and possible contributions (3) collectively formulate the analysis plans of which outcome would benefit all stakeholder participants.

EPA could be the catalyst in organizing and facilitation such a participatory process. EPA could use multiple vehicles including the STAR research grant program. The approach would include a prudent combination of regional (e.g. local source characterization) and national-scale analyses (e.g. modeling, transport).

Charge Question 23: Should more or less of the PAMS funding be allocated to data analysis?

More funding should be allocated for analysis. However, the related question is how could EPA catalyze more PAMS analysis? The recognition that PAMS data are under-analyzed and under-utilized has been on OAQPS radar for at least 15-20 years but remedies were scares. Is the NESCAUM PAMS analysis effort a possible approach? How did it happen? Could it be replicated by other states/regions?

Comments from Dr. Peter H. McMurry

Charge Question 6: What role, if any, should mobile or temporary sites play in the PAMS program?

My thinking is that mobile measurements might best be used in research studies aimed at understanding factors (emissions and spatial patterns of emissions from anthropogenic and natural sources, meteorology, etc.) that affect local ozone concentrations. For example, aircraft measurements carried out during the Texas 2000 Air Quality Study, together with models, provided information that was used to assess causes of high ozone levels that have been observed in the Houston area (Kleinman et al. 2002; Tanaka et al. 2003; Jiang and Fast 2004; Lei et al. 2004; Berkowitz et al. 2005; Murphy and Allen 2005; Fast et al. 2006). Similar studies have been done elsewhere, such as in the San Joaquin valley (where the interplay between ozone and agricultural emissions was a focus), Los Angeles, New York, etc. In his comments, Dr. Yousheng Zheng gave good examples of ways in which mobile PAMS measurements were effectively used for diagnostic purposes in the Baton Rouge area.

Temporary sites may also be useful for modifying PAMS network design to meet needs associated with changes in emissions patterns. Changes can occur as a result of successful implementation of emissions controls programs, population growth, or new industrial sources.

Thought should be given to the most effective approach for using temporary or mobile sites. Much has been learned from short-term, intensive research programs that include state-of-the art measurements and modeling. Such studied can be designed, for example, to use specialized aircraft platforms that have been developed at considerable expense and with the benefit of decades of experience. One possibility might be to make more use of intensive campaigns coordinated by state and local agencies rather than mobile PAMS sites operated by state and local agencies.

Charge Question 13: What role, if any, should TNMH monitors play in the PAMS program?

I do not have direct experience with the collection or use of TNMH data.

However, comments by other Subcommittee members make a convincing case that TNMH monitors can provide valuable supplemental information for PAMS networks. For example, Yousheng Zheng pointed out that since TNMH measurements can be completed in about one minute, TNMH data can be used to trigger more expensive PAMS sampling when high concentrations are detected. Furthermore, TNMH and NOx can be measured at similarly high time resolution. This information on ozone precursor gases provides essential information for models.

Charge Question 20: How should NOAA data be incorporated into the PAMS program?

I have looked at the NOAA web site (http://madis-data.noaa.gov/cap/profiler.jsp), and it seems clear that this information would be of some value to chemical-transport modelers, who need to understand relationships between chemical transformations, emissions, and the ozone formation.

I do not have sufficient experience with air quality modeling to know how these data would be incorporated into models. Other Subcommittee members will be better equipped to elaborate on potential uses of these data.

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Comments from Dr. Allen Robinson

Charge Question 1: How should EPA prioritize the current PAMS objectives? What current objectives, if any, should be deemphasized or eliminated?

Most important objectives are those directly related to photochemical assessment, and model and inventory evaluation.

“Provide a speciated ambient air database which is both representative and useful for ascertaining ambient profiles and distinguishing among various individual VOC. These data can later be used as evaluation tools for control strategies, cost-effectiveness, and for understanding the mechanisms of pollutant transport.”

“These data can later be used as a baseline for model evaluation and to minimize model adjustments and reliance on default settings.”

“Provide a representative, speciated ambient air database which is characteristic of source emission impacts. These data can be particularly useful in analyzing emissions inventory issues and corroborating progress toward attainment.”

Inventory and model evaluation seem especially important since these are core tools for developing control strategies.

Medium important objective

“Provide ambient data measurements which would allow later preparation of unadjusted and adjusted pollutant trends reports.”

Pollutant trends are important. At this point we have 15 years of trends from PAMS sites. A subset of these sites could be used to extend the trends but continuing to run all of the historical sites to continue the trends seems like overkill. It would be a better to shift resources to new sites to more spatial resolution of the data.

Least important objectives:

“Provide local, current meteorological and ambient data to serve as initial and boundary condition information for photochemical grid models.”

There are many sources of meteorological data; not clear why that is a priority for PAMS. Not clear how important the data are for initial and boundary conditions for grid models. The data are very important for evaluating models.

The following two objectives seemed to be poorly defined / catchall. They seem to apply to any monitoring site and are not particular to PAMS. I would recommend deleting them.

“Provide additional measurements of selected criteria pollutants. Such measurements can later be used for attainment/nonattainment decisions and to construct NAAQS maintenance plans.”

“Provide additional measurements of selected criteria and non-criteria pollutants from properly-sited locations. Such measurements can later be used for evaluating population exposure to air toxics as well as criteria pollutants.“

Charge Question 2: What additional objectives should EPA consider for the PAMS program at this time?

Redesigning PAMS to meet a broader set of objectives is consistent with the growing emphasis on multi-pollutant approaches. For example, PAMS could add explicit objectives around secondary organic aerosol precursors, air toxics, and indicators of global change. These are all worthy objectives.

A concern is that there are not sufficient resources to meet the current objectives never mind additional objectives. Therefore, broadening the goals of PAMS may reduce its effectiveness at photochemical assessment. Photochemical assessment seems like a critical goal since O3 and fine particle pollution are the most challenging criteria pollutants. Using PAMS to improve our understanding of inventories, models, control strategies, etc. for these secondary pollutants seems more important than air toxics.

A broader set of objectives likely could be achieved by more focused analysis of the existing PAMS data. My sense is the lack of data analysis is a real weakness of the PAMS program. There needs to be specific data analysis tied to each PAMS objectives, including explicit analyses to determine whether the objective has been achieved.

Charge Question 3: What are the advantages and disadvantages of the current design with multiple sites per PAMS area? What changes, if any, should be made in the number and spatial distribution of required sites?

A disadvantage is that PAMS resources are concentrated in relatively small numbers of areas. Given the more regional nature of the O3 problem today, a more widely distributed network would make sense. For example, one could considering putting a PAMS sit in each O3 non-attainment area.

Charge Question 4: Should EPA consider requiring PAMS measurements in areas other than areas classified as serious and above for the ozone NAAQS to improve spatial coverage?

The coverage of the existing PAMS network is very geographically limited. Given the evolving and more regional nature of the O3 problem today (compared to early 90s) it makes sense to broaden the spatial distribution of PAMS.

There may also be specific areas that warrant more monitoring, such as areas of rapid development of oil and gas industry in PA, WY, and TX or rapidly expanding urban areas.

Charge Question 5: Should EPA consider requiring PAMS measurements at a new subset of ozone sites in addition to the traditional PAMS (e.g., maximum concentration sites in all non-attainment areas, all urban NCore sites)?

Yes, but a simple rule of all non-attainment areas or all urban NCore sites probably does not make sense.

Charge Question 6: What role, if any, should mobile or temporary sites play in the PAMS program?

Given the very limited spatial coverage of the current PAMS network, transportable sites that could be deployed in different locations might make a lot of sense, especially given current resource constraints. One would want to maintain a subset of fixed sites to continue to determine long term trends at a subset of locations.

Charge Question 7: EPA has received feedback that the PAMS program needs to be as flexible as possible to help states meet specific needs. In consideration of this potential objective, what are the committee's views on the relative merits of revising PAMS to be a very flexible program with relatively few requirements versus a program that is highly specified? If the more flexible model were adopted, what minimum requirements, if any, should be included?

Consistent QA/QC procedures are important in order to facilitate regional or national analysis.

Charge Question 8: Should the current PAMS monitoring season framework be retained or should the period for required measurements be revised (e.g., lengthened or determined on a case-by-case basis) based on analyses of ambient data, meteorology, climatology, or other factors?

The current PAMS monitoring season is too constrained: do June, July and August make the most sense in all locations? What about September? In the end it makes sense to define monitoring effort to match the specific characteristics of the area. This should be up to the state and local agencies operating the network and writing the SIPS. EPA should require them to justify whatever period they decide to monitor.

Charge Question 9: What criteria should EPA consider when re-evaluating the PAMS target VOC list?

Each compound should be justified in the context of photochemical assessment. For O3 we are worried about the combination of abundance and reactivity. EPA should consider the historical PAMS data through that lens and rank order the existing list of compound. EPA should consider adding compounds based on these criteria.

For SOA, the critical precursors are less clear. The traditional view is that single ring aromatics are the most important anthropogenic precursors and monoterpenes are the most important biogenic. Therefore those would make sense to measure. However, there is still significant uncertainty about the relative importance of different compounds as SOA precursors.

Carbonyl and other small oxygenated compounds can provide substantial insight into atmospheric oxidation.

NATA provides risk rankings for various carbonyls and other air toxics.

Charge Question 10: Are there specific compounds that EPA should consider adding or subtracting from the target list?

EPA should consider adding some additional biogenic VOCs, e.g. monoterpenes. They contribute significant to atmospheric reactivity in certain locations. Long-term trends of biogenic VOC would also provide insight into the effects of land use changes and climate change on emissions and atmospheric reactivity.

Charge Question 11: What are the advantages and disadvantages of manual canister sampling versus field deployed auto-GCs?

Advantages for auto-GC are richer datasets (more time resolution theoretical without gaps). Auto-GC may have some sampling advantages relative to canister in terms of losses and reactions with canister walls.

Advantage of canister is that it is a well-established technique that air monitoring agencies are comfortable with. Therefore, there is not significant uncertainty with respect to performance and cost.

Disadvantages with auto-GC seem largely uncertainty. How well will the next generation of instruments work? How much will it cost? What is cost of QA/QC of the larger volume of data?

Charge Question 12: Are the new commercially available auto-GCs appropriate for use at PAMS sites? What additional evaluations are necessary to determine the suitability of auto-GC's for use in the PAMS network?

Additional evaluations:

Technical performance – intercomparison with establish methods across full range of atmospheric conditions.

Cost – technician time, maintenance, etc. required to run and analyze data in a PAMS context.

Charge Question 13: What role, if any, should TNMH monitors play in the PAMS program?

I think that measurement TNMH is valuable since the suite of PAMS VOCs only constitutes a fraction (often a minority of total reactive organic gases). Therefore having a measure of the total allows one to quantify the total fraction of organics covered by the speciated measurements.

Alternatively one could consider a measure of total reactivity (e.g. techniques of Bill Brune and others). These are research measurements today, but have a lot of bearing on the photochemistry assessment. One would carefully need to assess practicality for a PAMS application.

Charge Question 14: Should carbonyls be required at all VOC speciation sites?

Carbonyls are an important part of ozone chemistry essentially everywhere. For example, aldehydes such as formaldehyde and acetaldehyde are ubiquitous and have relatively high MIR. Therefore, scientifically, there are compelling reasons to include them in PAMS. Furthermore, data on reactive intermediates can provide significant insight into oxidation mechanisms.

Some carbonyls are also air toxics, providing an additional motivation for measuring them.

A challenge is that carbonyls comprise a very broad class of atmospheric organics. In order to make an informed decision EPA should evaluate the relative importance of carbonyls to the general ozone reactivity based on existing data. This exercise could also help identify which carbonyls to target. Identifying target carbonyls based on abundance and reactive (i.e. importance to ozone problem) may help with method development.

If there are not adequate data to evaluate the relative importance of carbonyls to ozone problem then EPA should considering obtaining such data in order to make an informed decision before requiring them in PAMS.

However, no matter how scientifically attractive, there needs to be a robust a robust and inexpensive method for measuring them. My perception is that there are legitimate concerns with TO-11A and I am not aware of another method. Given the importance of carbonyls it seems like priority should be better evaluation of current methods (e.g. TO-11a) or the development of new methods.

Charge Question 15: What issues have been addressed, and what issues still need to be addressed with the current TO-11A method for carbonyl sampling?

No comment

Charge Question 16: What other methods should be considered as an alternative to the manual TO-11A method for carbonyl sampling?

Robust measurement of a broad spectrum of carbonyls is a challenging problem. The suitability of canister, auto-GC, and potentially other in situ measurements should be (re-)evaluated. Certainly there are more robust in situ measurements for individual carbonyls such as formaldehyde in the research community. The research methods typically target individual carbonyls. Given the importance of carbonyls it seems like method development and evaluation should be a priority. Robust measurements of one or two carbonyls may be of more use than poor quality data for a lager number.

Charge Question 17: Are direct measurement NO_2 or photolytic NO_2 analyzers suitable for deployment in the PAMS network? What additional evaluations are necessary to determine the suitability for use in the PAMS network?

No comment.

Charge Question 18: What observational approaches (surface based sondes and optical remote sensing, aircraft platforms, satellites) are best suited to assist such assessments? What routinely collected surface measurements and in what locations would complement vertical profile and total column observations?

No comment.

Charge Question 19: Is it necessary to collect upper air wind speed and wind direction data at PAMS sites?

Charge Question 20: How should NOAA data be incorporated into the PAMS program?

No comments.

Charge Question 21: How can PAMS data best be used? What specific data analyses should be conducted?

There are many interesting and important ways to use the PAMS data –

Evaluation of chemical transport models and inventories

Trends in secondary organic aerosol precursors

Trends in biogenic compounds as indicators of land use change and climate change

Evaluation of NATA and estimate of air toxics exposures (e.g. Logue et al. AE 2010)

It is not clear that the data are being used extensively in this fashion

Charge Question 22: How should any recommended data analyses be implemented? Should these analyses be conducted at the state, regional, or national level?

I would look at some at the procedures that IMPROVE and other monitoring networks have implement to encourage data analysis. Regional or national analysis of monitoring network such as IMPROVE, AEROCOM that seem to be much more successful with having) for ways in which to increase

Charge Question 23: Should more or less of the PAMS funding be allocated to data analysis?

I was surprised to see that 25% of PAMS funding is allocated for data analysis. I see very few studies utilizing PAMS in the peer review literature. Given the nature of the data I find this surprising. Therefore this raises the question in my mind of whether really 25% is being spent and if so what is it being spent on. My sense is there could be much more value from the PAMS data given appropriate analysis.

The IMPROVE data are widely used. There are likely some lessons learned from IMPROVE about how data analysis. IMPROVE data are available through a well-organized website which allows researchers easy access. The IMPROVE “staff” also actively work on the data to answer scientific questions and improve methods.

Comments from Dr. Armistead (Ted) Russell

Attached are some plots from a project conducted about 7 years ago that used PAMS data. I think you might find the comparison of interest. It is important to note, however, that this type of analysis takes a bit more time to get the data and work with it.

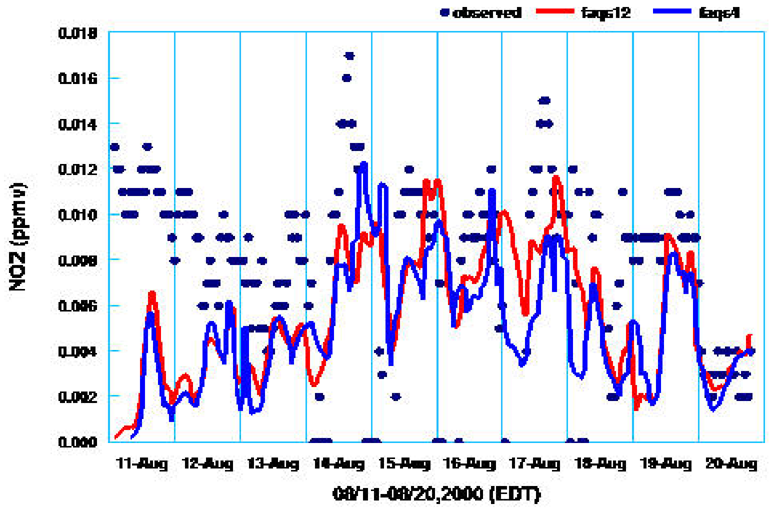

Figure 0.1 Time Series Plot of Simulated and Observed Surface NOZ Concentrations at PAMS Station with AIRS code of 130890002 in Atlanta

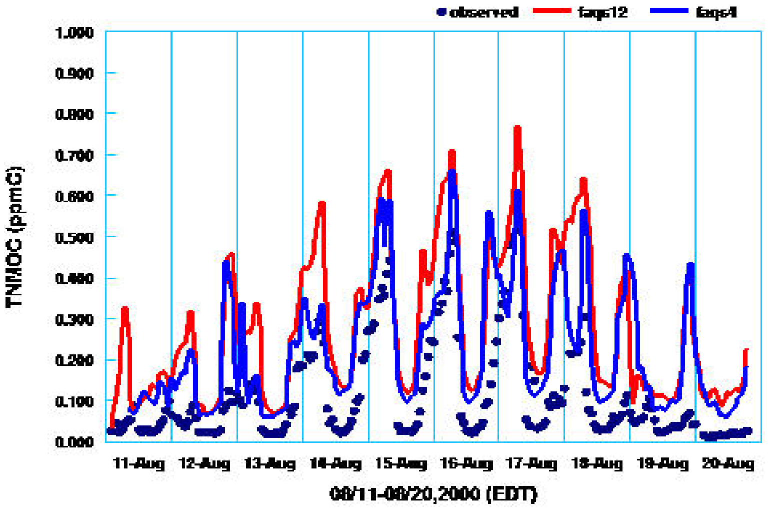

Figure 0.2 Time Series Plot of Simulated and Observed Surface Total Nonmethan Organic Compounds Concentrations at PAMS Station with AIRS code of 130890002 in Atlanta

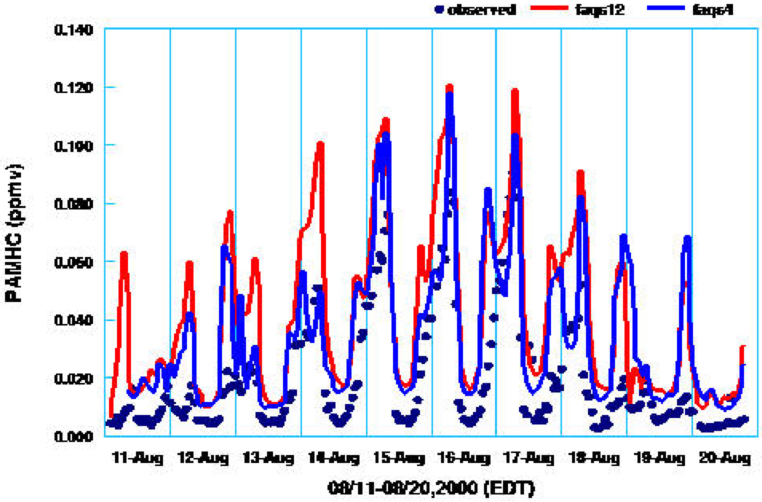

Figure 0.3 Time Series Plot of Simulated and Observed Surface PAMS Hydrocarbons Concentrations at PAMS Station with AIRS code of 130890002 in Atlanta

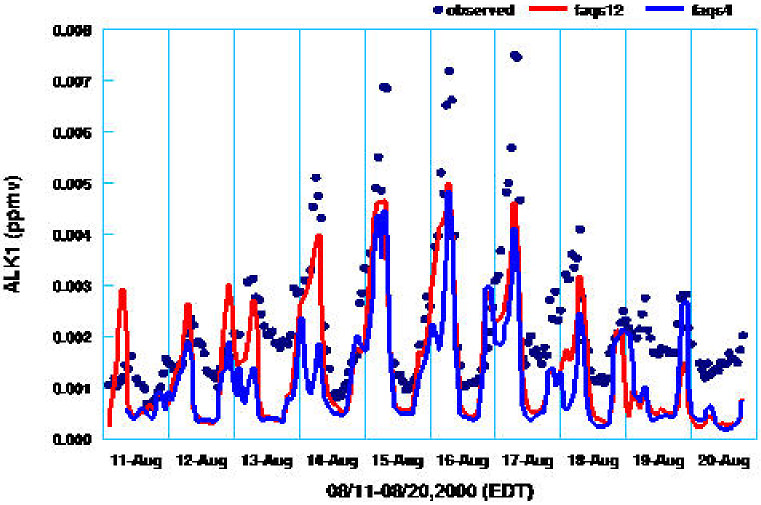

Figure 0.4 Time Series Plot of Simulated and Observed Surface ALK1 Concentrations at PAMS Station with AIRS code of 130890002 in Atlanta

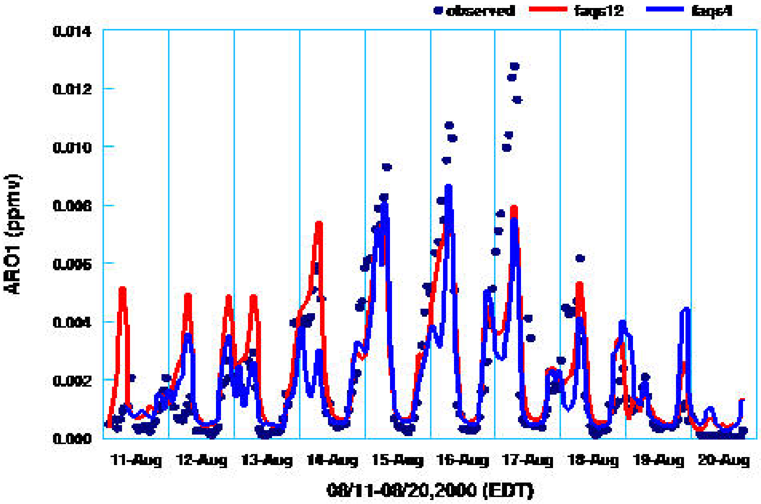

Figure 0.5 Time Series Plot of Simulated and Observed Surface ARO1 Concentrations at PAMS Station with AIRS code of 130890002 in Atlanta

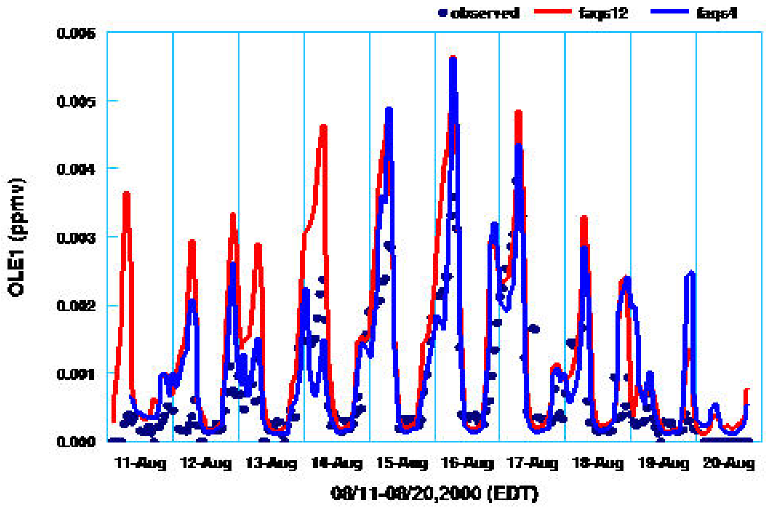

Figure 0.6 Time Series Plot of Simulated and Observed Surface OLE1 Concentrations at PAMS Station with AIRS code of 130890002 in Atlanta

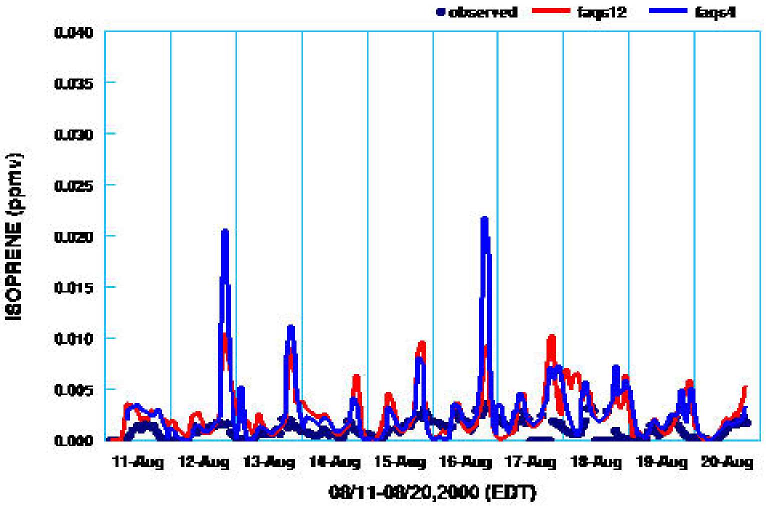

Figure 0.7 Time Series Plot of Simulated and Observed Surface ISOPRENE Concentrations at PAMS Station with AIRS code of 130890002 in Atlanta

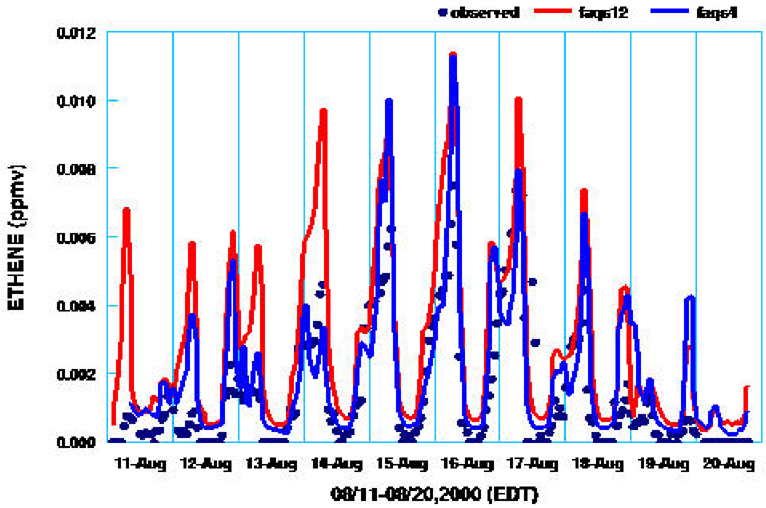

Figure 0.8 Time Series Plot of Simulated and Observed Surface ETHENE Concentrations at PAMS Station with AIRS code of 130890002 in Atlanta

Comments from Dr. Jamie Schauer

Charge Question 1: How should EPA prioritize the current PAMS objectives? What current objectives, if any, should be deemphasized or eliminated?

The original PAMS objectives need to be evaluated by EPA to determine the incremental benefits of additional PAMS monitoring in the context of exiting time series of data. Objectives 1 and 3 use the word "useful" and it is not clear that the incremental measurements at most PAMS sites are indeed very useful. Likewise, Objective 2 and 4 address baseline data and trends, which after 15 years should be largely met if a large change in speciation is not observed at a specific the site.

Charge Question 2: What additional objectives should EPA consider for the PAMS program at this time?

The PAMS Program objectives should be updated to address critical monitoring needs to address uncertainties in ozone modeling and uncertainties in the sources of key species that impact ozone chemistry. In addition, the PAMS program should extend to address data needs for air toxics, SOA precursors, and gases important to climate change.

Charge Question 3: What are the advantages and disadvantages of the current design with multiple sites per PAMS area? What changes, if any, should be made in the number and spatial distribution of required sites?

To the degree that the multiple sites can continue to reduce the uncertainty in ozone modeling or add information that can advance the understanding of VOC sources, the multiple site approach should continue.

Charge Question 4: Should EPA consider requiring PAMS measurements in areas other than areas classified as serious and above for the ozone NAAQS to improve spatial coverage?

Given the need to better improve the modeling of ozone at background sites to provide boundary conditions for ozone modeling, select PAMS sites should be considered to better understand VOCs in areas other than serious or above designation.

Charge Question 5: Should EPA consider requiring PAMS measurements at a new subset of ozone sites in addition to the traditional PAMS (e.g., maximum concentration sites in all non-attainment areas, all urban NCore sites)?

Additional PAMS measurements at a subset of ozone sites needs to be driven by the ability to advance the understanding of VOC sources or improvement of ozone models.

Charge Question 6: What role, if any, should mobile or temporary sites play in the PAMS program?

There is a great need for both mobile and temporary sites but it does not seem wise to address this need within a monitoring network program. The infrastructure and knowledge base for using mobile and temporary sites would be different than that of existing PAMS data analysis in most instances.

Charge Question 7: EPA has received feedback that the PAMS program needs to be as flexible as possible to help states meet specific needs. In consideration of this potential objective, what are the committee's views on the relative merits of revising PAMS to be a very flexible program with relatively few requirements versus a program that is highly specified? If the more flexible model were adopted, what minimum requirements, if any, should be included?

Flexibility is good but the PAMS data needs to meet the needs of other stakeholders than just the states even if the states are the primary users of the PAMS data. To this end, adequate guidelines are needed to assure integration of PAMS data across different states and that the data can be used to meet the data analysis needs of diverse stakeholders.

I think regional and some national coordination is critical. As you indicate, giving each state a flexible program is probably not workable. The data needs to meet the needs of a variety of stakeholders and support national trends to the degree that the revised PAMS objectives warrant. I like the RPO coordination as I do not see the state led flexible programs as workable given the point that you outline and the fact that many states would not be able to effectively manage and support such a flexible program from a planning and technical perspective. I think the RPO model could do a good job with the ozone goals and the potentially added air toxics goals if indeed this was added. However, any added objective associated with climate relevant gases probably need to have a more nationally coordinated effort that focuses on trends.

Charge Question 8: Should the current PAMS monitoring season framework be retained or should the period for required measurements be revised (e.g., lengthened or determined on a case-by-case basis) based on analyses of ambient data, meteorology, climatology, or other factors?

In the context of broader objectives addressing air toxics, SOA precursors, and gases important to climate change, the period of monitoring should be expanded.

Charge Question 9: What criteria should EPA consider when re-evaluating the PAMS target VOC list?

Re-evaluation of the PAMS target list should be conducted in the context of ozone modeling uncertainty, source apportionment of VOCs, and monitoring needs to air toxics, SOA precursors, and gases important to climate change

Charge Question 10: Are there specific compounds that EPA should consider adding or subtracting from the target list?

Not sure. Need to consider the revised or prioritized objectives to make this assessment.

Charge Question 11: What are the advantages and disadvantages of manual canister sampling versus field deployed auto-GCs?

Auto-GCs may present a problem for some states in terms of manpower of field staff and expertise of field staff. However, auto-GCs have the potential for advancing source attribution efforts.

Charge Question 12: Are the new commercially available auto-GCs appropriate for use at PAMS sites? What additional evaluations are necessary to determine the suitability of auto-GC's for use in the PAMS network?

This needs to be assessed in the context of the skill sets of air monitoring field staff at diverse states.

Charge Question 13: What role, if any, should TNMH monitors play in the PAMS program?

The TNMH measurement is a good reference metric and should be maintained. Since all VOCs are not measured, the TNMH provides an important reference for measurements.

Charge Question 14: Should carbonyls be required at all VOC speciation sites?

The requirement of carbonyls needs to be driven by modeling needs and air toxic data needs.

Charge Question 15: What issues have been addressed, and what issues still need to be addressed with the current TO-11A method for carbonyl sampling?

No comments

Charge Question 16: What other methods should be considered as an alternative to the manual TO-11A method for carbonyl sampling?

No comments

Charge Question 17: Are direct measurement NO2 or photolytic NO2 analyzers suitable for deployment in the PAMS network? What additional evaluations are necessary to determine the suitability for use in the PAMS network?

No comments

Charge Question 18: What observational approaches (surface based sondes and optical remote sensing, aircraft platforms, satellites) are best suited to assist such assessments? What routinely collected surface measurements and in what locations would complement vertical profile and total column observations?

No comments

Charge Question 19: Is it necessary to collect upper air wind speed and wind direction data at PAMS sites?

No comments

Charge Question 20: How should NOAA data be incorporated into the PAMS program?

Integration across agencies is important and will become more important as climate change needs to be addressed. Incorporating NOAA data will help these efforts in the short and long run.

Charge Question 21: How can PAMS data best be used? What specific data analyses should be conducted?

I am not sure that this is a good question. PAMS monitoring needs to be driven by regulatory and scientific questions and should not happen in reverse. If data analysis needs cannot be identified then it seems hard to justify the PAMS network, Likewise, if the existing PAMS network cannot meet the data analysis needs than changes in PAMS is needed.

Charge Question 22: How should any recommended data analyses be implemented? Should these analyses be conducted at the state, regional, or national level?

There should be common goals that develop year to year that should be directed nationally or regionally but adequate flexibility is needed within the states to assure that local needs are being met.

Charge Question 23: Should more or less of the PAMS funding be allocated to data analysis?

Seems about right but given the use of PAMS data that I have seen, it seems hard to believe the 25% of the funds are being used for useful data analysis. It may be that these analysis results are not being made available to the broader community but like a bigger visibility and impact of PAMS data is needed.

Comments from Dr. Jay Turner

Charge Question 12: Are the new commercially available auto-GCs appropriate for use at PAMS sites? What additional evaluations are necessary to determine the suitability of auto-GC's for use in the PAMS network?

There have been promising developments in the auto-GC technology over the past fifteen years. One example is the Syntec Spectras Ozone Precursor Analyzer[5] (Synspec BV) which is an example of a dual GC/detector system with one analyzer for C2-C5 compounds and another analyzer for C6-C10 compounds. While I am not personally familiar with these analyzers, they share a measurement platform with the Syntec Spectras Benzene/BTEX analyzer that has a favorable reputation. Several other makes and models of field auto-GC units are available. As noted in the white paper, in addition to the conventional dual GC/detector system there might be merit in simplifying the target analyte list to permit use of a single GC/detector. At least one state briefly brought on board a third party to operate a GC/MS system for one seasons of PAMS measurements. Given the advantages of continuous hourly data over periodic, more time-integrated data – especially for applications such as chemical transport model validation and source apportionment – there is merit in documenting their current capabilities. There are many factors to be considered including but not limited to data quality, field robustness, required level of expertise to operate and maintain the analyzers, and cost.

I strongly believe a technical and operations evaluation is warranted, and I suggest a two-phase approach. First, users of auto-GCs for PAMS and related applications should be surveyed. This user group includes state/local agencies and also several other organizations engaged in long-term monitoring projects. While this survey might capture relatively little experience with the newer instruments, it would serve to document what has – and has not – worked well in the past. Second, a field evaluation should be conducted, ideally at one of the PAMS sites and ideally for at least a month. The challenges to this evaluation should not be underestimated; while it would be ideal to have a third party operate the instruments, this might be impractical depending on the scope of the study. It is appreciated that such an evaluation does not adequately capture certain important components of a field evaluation, such as long-term performance and maintenance requirements, but could be very useful towards elucidating instrument performance under ideal conditions.

Charge Question 15: What issues have been addressed, and what issues still need to be addressed with the current TO-11A method for carbonyl sampling?

First, the carbonyls target analyte list must be evaluated – is the goal to keep the focus on formaldehyde, acetaldehyde, and acetone, or to expand the list of analytes? My understanding is that several additional carbonyls are often detected and reported by the analytical laboratories but only these three are typically reported to AQS.

The TO-11A method collects carbonyls using DNPH cartridges. Potential issues include positive and negative artifacts from contamination, reaction with ambient oxidants (especially ozone), collection efficiency and carbonyl generation on the substrate. It was my impression that most of these issues can now be controlled. For example, an ozone scrubber is now typically integrated with the DNPH cartridge

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[5] No endorsement should be inferred from any mention of specific manufacturers or consulting firms.

and is swapped out with each sample. This approach places the quality control burden on the analytical laboratory preparing the sampling cartridges rather than on the field operators. Improved handling protocols have presumably lowered blanks concentration values and reduced the frequency of contamination.

The most-recent NATTS QA Annual Summary (calendar year 2008) demonstrates network-wide overall precision of ~20% for formaldehyde which is similar to many of the canister-based VOC precisions. However, five of the 15 stations with precision data exceeded the 15% MQO and one station was nearly 50%. Many states perform the analysis in house, and proficiency testing of a single sample across fourteen laboratories exhibited a mean bias within the 25% MQO. Of course, these QA assessments do not inform us about the impact from many of the aforementioned sources of artifacts.

While initially it was my impression that most the DNPH-based carbonly sampling and analysis issues can now be controlled, a cursory review of the literature suggests otherwise and a more-detailed review is needed. [6,7] To my knowledge there has not been a recent formal evaluation of the DNPH-based method(s) and it is warranted. Also, previous work has focused on formaldehyde and we need better documentation of performance for the other target carbonyls. Several research groups and analytical laboratories have extensive experience with carbonyl sampling and their perspectives would be valuable.

Charge Question 22: How should any recommended data analyses be implemented? Should these analyses be conducted at the state, regional, or national level?

This is a very important question that is tied back to the monitoring objectives. Since the objectives might be revised through the PAMS re-engineering process, it might be necessary to cycle back to this question after such changes have been defined.

Analyses would likely be implemented at all of the above levels. It would be very helpful to have EPA (perhaps through a subcontractor) prepare annual summaries including an independent evaluation of the data quality and some basic trends analyses (e.g. descriptive statistics, spatiotemporal patterns, etc.). Previous PAMS data analyses (including but not limited to the series of work products by Sonoma Technology, Inc., for various clients) and network assessments can be used as a starting point to define the candidate analyses. Part of this effort could include repackaging the data in a few of the more common formats likely to be used by stakeholders such as regional planning organizations and state/local agencies.

To promote more widespread use, the data must be available through a user-friendly portal. While a VEIWS- or DataFed-like platform is ideal, there other options such as the AQS data polls periodically performed by EPA and made available (in AQS format) through a web site. The latter is a bit clunky and requires substantial reformatting by the user, but I have found these packaged data sets to be invaluable.

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[6] See D.D. Parrish and F.C. Fehsenfeld (2000) *Atmos. Environ.*, **34**, 1921-1957 and references therein for work prior to 2000.

[7] C. Hak et al. (2005) *Atmos. Chem. Phys. Discuss.*, **5**, 2897–2945.

Comments from Dr. Yousheng Zeng

Charge Question 1 - How should EPA prioritize the current PAMS objectives? What current objectives, if any, should be deemphasized or eliminated?

Response: In general, some of the current objectives are vague and subject to different interpretation. Through this re-engineering effort, the objectives should be stated more clearly. My comment on each of the current PAMS objectives is provided below:

- *Provide a speciated ambient air database which is both representative and useful for ascertaining ambient profiles and distinguishing among various individual VOC. These data can later be used as evaluation tools for control strategies, cost-effectiveness, and for understanding the mechanisms of pollutant transport.*
    - I think this objective is still valid. However, I have some concern on the word "representative". The kind of speciated VOC monitored by current PAMS network indicate a strong spatial variability and typically there are only a small number of PAMS sites in a nonattainment airshed. It will be difficult to make the data "representative" unless EPA is willing to allocate significantly more fund for the PAMS program and add more stations. I think that the data is still "useful" and I would give this objective a **high priority**.

- *Provide local, current meteorological and ambient data to serve as initial and boundary condition information for photochemical grid models. These data can later be used as a baseline for model evaluation and to minimize model adjustments and reliance on default settings.*
    - The meteorological data (met data) are collected by various air monitoring networks (e.g., SLAMS) that typically provide more data points in a given airshed than the met data generated by PAMS sites. Although PAMS network can contribute more met data, met data is not unique to PAMS network, The phrase "ambient data" should be clarified. If it refers to a large number of speciated VOC and some speciated NOx, that would be specific to PAMS network, but I am not sure these data have been used as initial and boundary condition for photochemical grid models. The data points provided by PAMS' limited number of sites in an urban airshed are isolated and scant, and they may represent very localized condition due to atmospheric lifetime of the speciated VOC and spatial variability. These scant data points may not be representative for a model that has 2-km or larger grid spacing. Depending on clarification of "ambient data", I would either **eliminate** this objective **or** give it a **low priority**.

- *Provide a representative, speciated ambient air database which is characteristic of source emission impacts. These data can be particularly useful in analyzing emissions inventory issues and corroborating progress toward attainment.*
    - I think this objective is valid and I would give it a **high priority**.

- *Provide ambient data measurements which would allow later preparation of unadjusted and adjusted pollutant trends reports.*
    - Again, it is not clear as to what "ambient data" this objective is referring, and what the adjustment is. If it is for trending, this objective could be covered by the first objective above.

- *Provide additional measurements of selected criteria pollutants. Such measurements can later be used for attainment/nonattainment decisions and to construct NAAQS maintenance plans.*
    - This should not be considered as an objective for PAMS. A PAMS site should have ozone and PM2.5 measured for a study of their relationship with their precursors measured at the site. These ozone and PM2.5 measurement may be used, along with other monitoring data, for attainment/nonattainment determination; but it is not an objective of PAMS. If EPA or a monitoring agency wants to have an additional measurement of a criteria pollutant (e.g., SO_2), they can co-locate an SO_2 monitor at the PAMS site; but it is not an objective of PAMS. I would **eliminate** this objective.

- *Provide additional measurements of selected criteria and non-criteria pollutants from properly-sited locations. Such measurements can later be used for evaluating population exposure to air toxics as well as criteria pollutants.*
    - The "P" in PAMS is for *photochemical* assessment. Its main objective should be to provide information that can help achieve ozone (now maybe $PM_{2.5}$ too) attainment, which is a widespread issue across the country. Some VOC ozone precursors monitored by PAMS are also air toxics. As a by-product or collateral benefit, these measurements yield additional information on air toxics. However, air toxics are typically a localized issue and can be addressed more effectively if it is not tied to the PAMS program. This objective should have a **low priority**.

Charge Question 2 - What additional objectives should EPA consider for the PAMS program at this time?

Responses: The main objective of the PAMS program is ***P**hotochemical **A**ssessment*, which helps bring an ozone (and maybe to some degree $PM_{2.5}$) nonattainment area into attainment through better understanding of ozone precursors and their relationship with ozone formation. Everything else should be at most secondary. Some additional objectives may be stated if they are more specific or explicit, and address different facets or derivatives of the same basic relationship between ozone and its precursors (e.g., improving ozone forecasting).

The scope of PAMS program should not be broadened beyond the photochemical assessment and the relationship between ozone (maybe $PM_{2.5}$) and their precursors. The ozone nonattainment is the most widespread problem in the nation's air quality and has a far reaching economic impact. The PAMS program should focus on solving this problem and not be diluted by other objectives. If other pollutants (e.g. air toxics) are measured as a by-product of the PAMS program, that is fine. However, it should not be an objective of the program. When other objectives are considered, certain program elements, such as siting criteria, resources for measurement, etc., will likely be compromised to accommodate competing objectives. For example, air toxics may be a local issue. It may not be relevant or cost effective to make air toxics a PAMS program-wide objective. If EPA wants to gain some additional benefits and cost savings by leveraging an existing program, the consideration should be given holistically (including all air monitoring programs) in a manner similar to the approach discussed in the January 2010 draft report "Air Quality Observation Systems in the United States" prepared by Committee on Environmental and Natural Resources (CENR)/Air Quality Research Subcommittee (AQRS) rather than just considering the PAMS program.

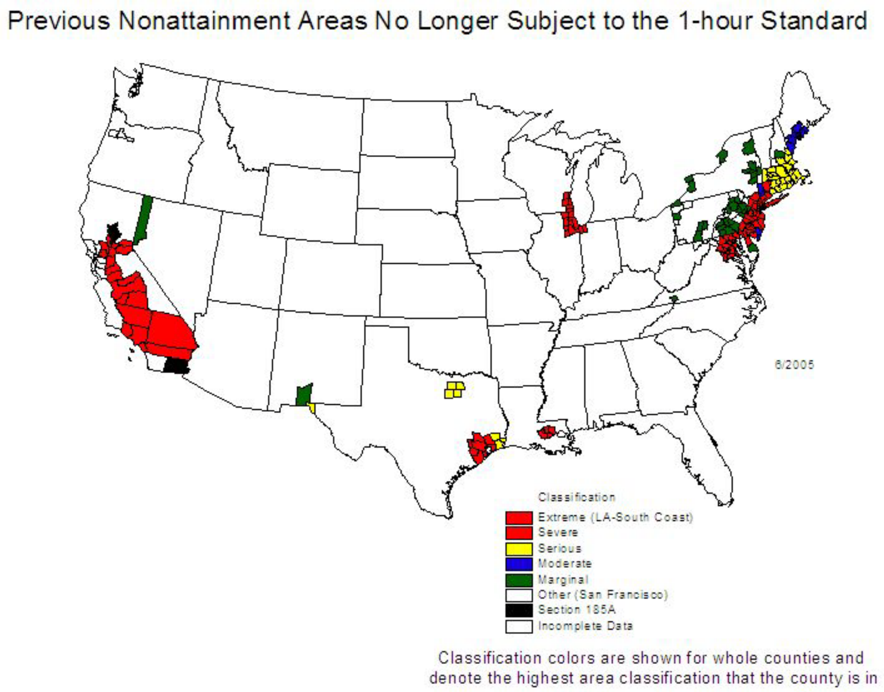
Charge Question 3 - What are the advantages and disadvantages of the current design with multiple sites per PAMS area? What changes, if any, should be made in the number and spatial distribution of required sites?

Response: The current four types of sites are useful as a guideline. They do not need to be a requirement. Some flexibility should be given to state and local agencies so that they can use this guideline and consider their specific situations and needs to set up PAMS sites.

The function of Type 3 sites (maximum ozone concentration sites) may be covered by regular ozone monitoring station because by the time ozone level reaches its maximum concentration, many precursor species (particularly VOC precursor species) have been depleted to a minimal level that may not be detectable (Providence, 2010). With respect to Type 2 sites, see my responses to Charge Questions 6 and 8.

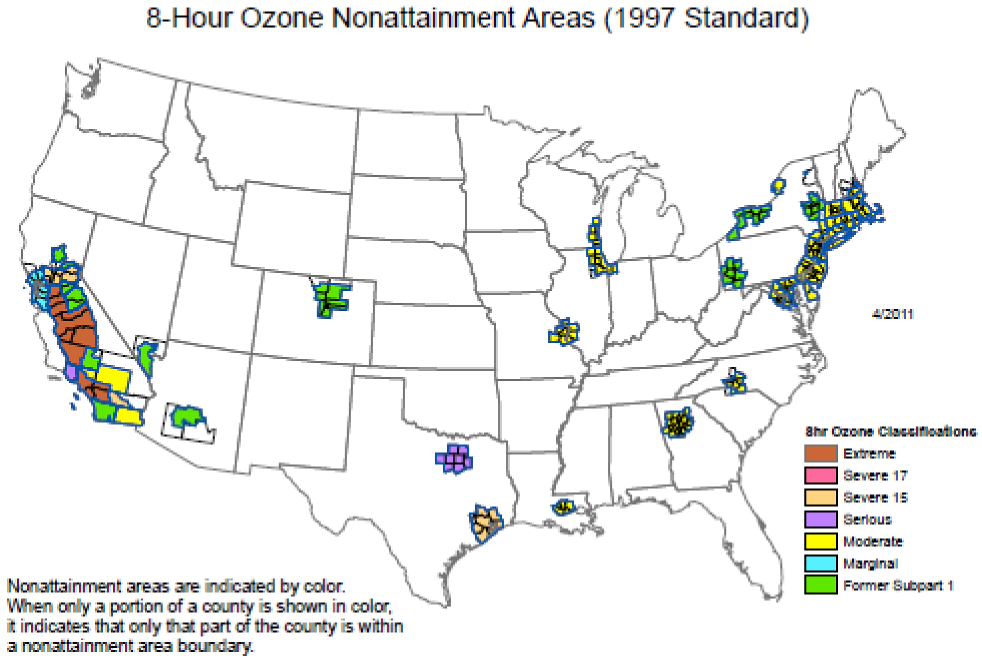
Charge Question 4 - Should EPA consider requiring PAMS measurements in areas other than areas classified as serious and above for the ozone NAAQS to improve spatial coverage?

Response: When the PAMS program was initiated, the ozone standard was based on 1-hour averaging. Under the 1-hour ozone standard, there were more areas falling into the serious and above classifications (see Figure CQ4-1). Under the 1997 8-hr ozone standard, there are only seven areas classified as serious and above (two in Texas and five in California) see maps below (Figures CQ4-2). The PAMS network established under the 1-hour standard is still maintained due to the anti-backsliding policy. I don’t have classification information under the 2008 ozone standard (EPA should have this information and could provide the information to the panel for this discussion). The impression I have is that although there are more non-attainment areas under the 2008 standard, there may not be many more areas classified as serious and above. If that is the case, requiring PAMS monitoring only in the areas classified as serious and above will not improve spatial coverage compared to the current coverage. If there is a reason to improve spatial coverage, PAMS measurements may be required in areas below serious, e.g., moderate and above or some other criteria (a classification map under the 2008 standard, if available, will help formulate the criteria), or even some strategically selected rural areas.



Classification colors are shown for whole counties and denote the highest area classification that the county is in

Figure CQ4-1. Classifications of ozone nonattainment areas under previous 1-hour standard.



Nonattainment areas are indicated by color. When only a portion of a county is shown in color, it indicates that only that part of the county is within a nonattainment area boundary.

The following multi-state nonattainment area, Chicago-Gary-Lake County, IL-IN 8-hr Ozone area, has some states in the area that have been redesignated, but it is not considered a maintenance area until all states in the area are redesignated. The counties for this area are displayed as nonattainment areas:

Figure CQ4-2. Classifications of ozone nonattainment areas under 1997 8-hour standard.

Charge Question 5 - Should EPA consider requiring PAMS measurements at a new subset of ozone sites in addition to the traditional PAMS (e.g., maximum concentration sites in all non-attainment areas, all urban NCore sites)?

Response: No, at least not at the maximum concentration sites – see my response to Charge Question 3.

Charge Question 6 - What role, if any, should mobile or temporary sites play in the PAMS program?

Response: Mobile or temporary (or referred to as transportable) sites can play an important role in the PAMS program. Long-term/fixed sites can provide trends where as mobile or temporary sites are much more effective and cost efficient for diagnostic purposes, making them particularly suitable for Type 2 sites. In 2005-2007, about two dozens of temporary ozone precursor monitoring stations were used around 16 suspected major precursor sources in the Baton Rouge ozone nonattainment area after the area was bumped up from serious to severe classification under the 1-hour standard. Some of these monitors were transportable (on a trailer platform) and they were moved seasonally based on prevailing wind direction. This temporary monitoring program provided very valuable data to either identify/confirm major precursor sources or exonerate other sources. The information helped the state agency in control strategy development and the ozone level in the area has been declining.

Mobile or transportable monitors offer great flexibility. They can be deployed to a particular area of interest for a relatively short period of time. During this period, enough data can be collected to evaluate the levels and relationship of ozone, its precursors, and sources; whether the location is precursor dominating (earlier stage of the ozone formation process) or ozone dominating (later stage of ozone formation process); and how much more information could be obtained if the monitoring period is extended. After a period of time (e.g., one ozone season), the incremental gain in useful information tends to diminish (unless the main purpose is long-term trending). The stations can be re-deployed to another location.

With transportable monitors, a PAMS network for an air basin can be designed more effectively and cost-efficient. It can consist of two fixed long-term sites (one for upwind urban scale monitoring, i.e., a Type 1 site, and the other for downwind urban scale monitoring, i.e., a Type 4 site) and two mobile/transportable monitors that will be deployed near major sources (i.e., function as Type 2 sites) or/and high ozone concentration areas (i.e., function as Type 3 sites). Compared to truly mobile (vehicle based) platform, transportable trailer based platform will be more cost effective because once deployed, these monitors will stay in a location for months. Truly mobile vehicle based monitors are more suitable to incident response applications. Two transportable units are desirable because they can be deployed as a pair, one for upwind and the other for downwind from suspected major precursor sources in Type 2 applications. For Type 3 applications, one or both units can be deployed. The ozone monitoring results from the transportable monitors will not be used for NAAQS attainment/nonattainment designation purpose because they may not have long enough monitoring time at a location.

Charge Question 7 - EPA has received feedback that the PAMS program needs to be as flexible as possible to help states meet specific needs. In consideration of this potential objective, what are the committee's views on the relative merits of revising PAMS to be a very flexible program with relatively few requirements versus a program that is highly specified? If the more flexible model were adopted, what minimum requirements, if any, should be included?

Response: One of the advantages of a highly specified program is consistency, i.e., the data produced will be more comparable. Compared to other monitoring programs, the most important differentiator of the PAMS program is that it covers a much larger number of precursor species to help understand the ozone issues in specific areas. Comparability is more important for criteria pollutants (rather than precursors) and it has been achieved by other monitoring networks. I believe that getting useful data to help solve the ozone problem is the most important objective for PAMS and the comparability across multiple air basins or across the country is not as important. Therefore, I would favor a more flexible program. As far as siting is concerned, the 2 fixed sites plus 2 transportable sites model discussed in my response to Charge Question 6 could be used as minimum requirements. Significant flexibility can be obtained through the 2 transportable sites. Flexibility in other aspects of PAMS (e.g., target compounds, monitoring periods, etc.) is discussed in responses to later charge questions.

Charge Question 8 - Should the current PAMS monitoring season framework be retained or should the period for required measurements be revised (e.g., lengthened or determined on a case-by-case basis) based on analyses of ambient data, meteorology, climatology, or other factors?

Response: The current minimum requirement of 3 months (Jun., Jul., & Aug.) are not representative for some areas. For example, in the Baton Rouge nonattainment area more ozone exceedances occurred in May than in July or August (see Figure CQ8-1).

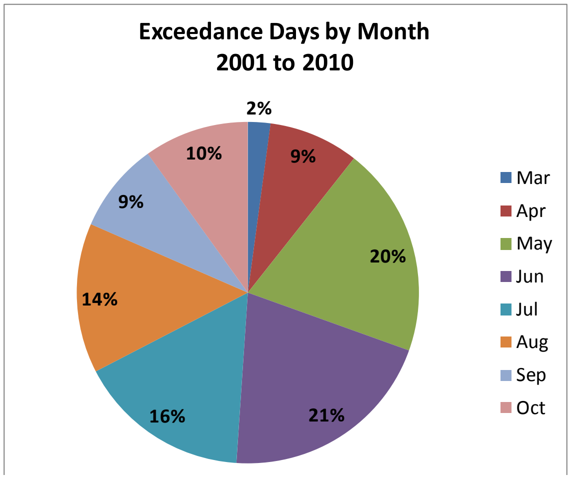


Figure CQ8-1. Ozone exceedance days by month in the Baton Rouge nonattainment area (courtesy of Tim Bergeron, Louisiana Dept. of Environmental Quality)

Although June-August may have a higher temperature, more thunderstorms and rain are likely to occur during these months, which reduce ozone formation. In late spring and early fall, thunderstorms and rain are less frequent and the temperature is high enough to cause ozone formation. In 2010, 8 exceedances occurred in October, 4 in September, 4 in May, 1 in April, and only 1 or 0 occurred in each of the months from June through August.

Ozone precursor data in non-ozone season can actually be very informative and useful. For many sources, emission rates are in the same order of magnitude throughout a year. In winter season, atmospheric physical and chemical process is less intense (less turbulent, less photochemical reactions, etc.). As a result, more precursors (particularly VOC precursors) are “preserved” better for monitors to pick up. This kind of data can be insightful in evaluating sources that could play a significant role in ozone formation when the temperature is higher and UV light is stronger in summer.

For these reasons, a case-by-case approach seems to be appropriate. I understand that EPA could retain the minimum requirement of 3 months (Jul-Aug) and let state and local agencies to expand the period if they need to. However, this minimum requirement will likely result in insufficient funding that will make it impractical for these monitoring agencies to expand the monitoring period even it is beneficial and justified.

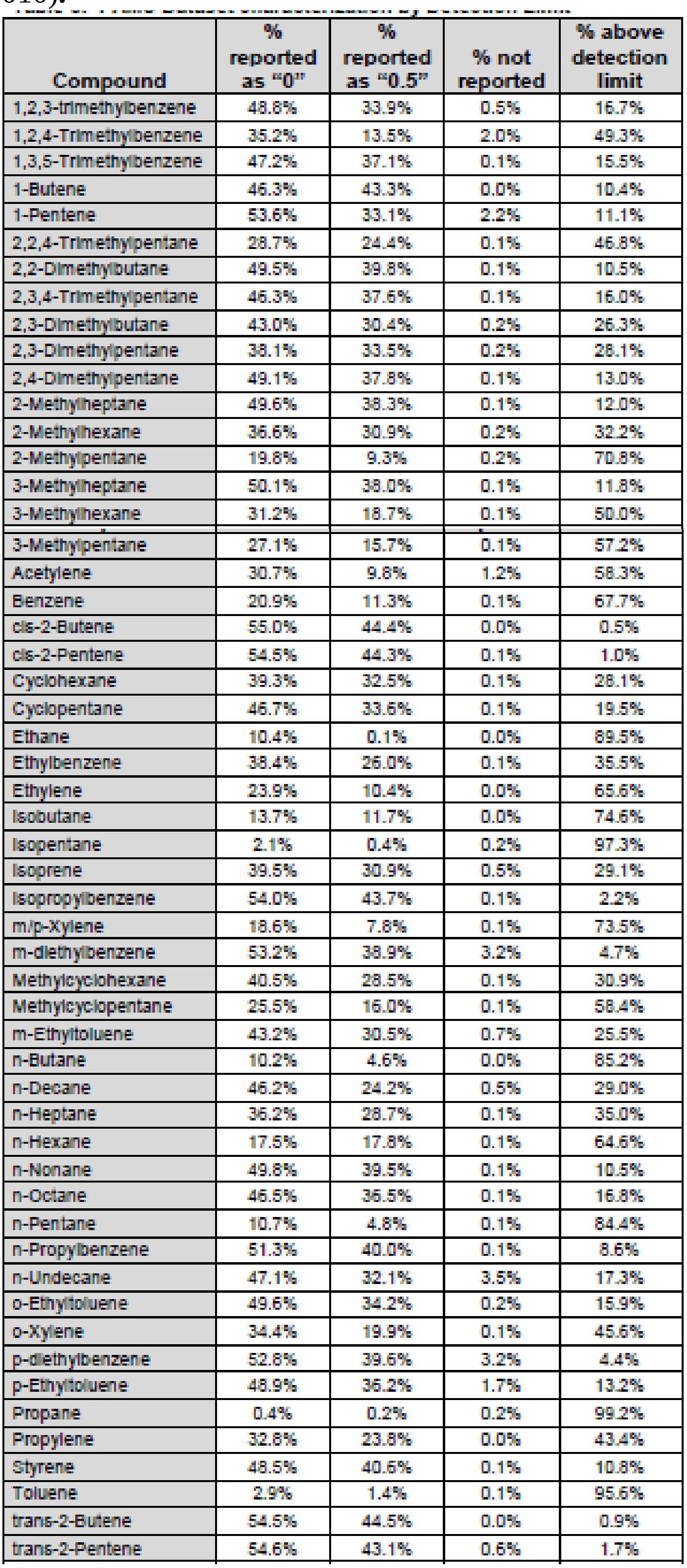
Charge Question 9 - What criteria should EPA consider when re-evaluating the PAMS target VOC list?

Response: The following criteria should be considered in selecting PAMS target VOC list:

Reactivity in contribution to ozone formation: It is obvious that the VOC target list should include compounds that play an important role in ozone formation. The importance of individual organic compounds in ozone formation may be evaluated through atmospheric photochemical models such as CMAQ. A simple approach could be to use the Maximum Incremental Reactivity (MIR) (Carter, 2009). MIR is a way to measure incremental ozone impacts of VOCs under a set of scenarios representing conditions where ozone is most sensitive to VOC emissions. Different VOC species have different MIR values. For example, the MIR for propene is 11.57 g O_3/g propene, and the MIR for propane is only 0.56 g O_3/g propane. MIR can also be expressed as mol O_3/mol VOC species. Compounds with high MIR values should be given more weight than the ones with low MIR values in selecting target VOC for the PAMS program.

Expected concentrations: If the expected concentration of a VOC compound is below or near detection limit, there is limited value of including it in the target list. Based on the analysis of 14 years of PAMS data collected in San Joaquin Valley, there are multiple compounds barely detectable. Table CQ9-1 is a summary of PAMS VOC detectablity in San Joaquin Valley (Providence, 2010).

Table CQ9-1. Detectability of PAMS VOC in San Joaquin Valley from 1994-2007 (Providence, 2010).



Compound	% reported as "0"	% reported as "0.5"	% not reported	% above detection limit
1,2,3-trimethylbenzene	48.8%	33.9%	0.5%	16.7%
1,2,4-Trimethylbenzene	35.2%	13.5%	2.0%	49.3%
1,3,5-Trimethylbenzene	47.2%	37.1%	0.1%	15.5%
1-Butene	46.3%	43.3%	0.0%	10.4%
1-Pentene	53.6%	33.1%	2.2%	11.1%
2,2,4-Trimethylpentane	28.7%	24.4%	0.1%	46.8%
2,2-Dimethylbutane	49.5%	39.8%	0.1%	10.5%
2,3,4-Trimethylpentane	46.3%	37.6%	0.1%	16.0%
2,3-Dimethylbutane	43.0%	30.4%	0.2%	26.3%
2,3-Dimethylpentane	38.1%	33.5%	0.2%	28.1%
2,4-Dimethylpentane	49.1%	37.8%	0.1%	13.0%
2-Methylheptane	49.6%	38.3%	0.1%	12.0%
2-Methylhexane	36.6%	30.9%	0.2%	32.2%
2-Methylpentane	19.8%	9.3%	0.2%	70.8%
3-Methylheptane	50.1%	38.0%	0.1%	11.8%
3-Methylhexane	31.2%	18.7%	0.1%	50.0%
3-Methylpentane	27.1%	15.7%	0.1%	57.2%
Acetylene	30.7%	9.8%	1.2%	58.3%
Benzene	20.9%	11.3%	0.1%	67.7%
cis-2-Butene	55.0%	44.4%	0.0%	0.5%
cis-2-Pentene	54.5%	44.3%	0.1%	1.0%
Cyclohexane	39.3%	32.5%	0.1%	28.1%
Cyclopentane	46.7%	33.6%	0.1%	19.5%
Ethane	10.4%	0.1%	0.0%	89.5%
Ethylbenzene	38.4%	26.0%	0.1%	35.5%
Ethylene	23.9%	10.4%	0.0%	65.6%
Isobutane	13.7%	11.7%	0.0%	74.6%
Isopentane	2.1%	0.4%	0.2%	97.3%
Isoprene	39.5%	30.9%	0.5%	29.1%
Isopropylbenzene	54.0%	43.7%	0.1%	2.2%
m/p-Xylene	18.6%	7.8%	0.1%	73.5%
m-diethylbenzene	53.2%	38.9%	3.2%	4.7%
Methylcyclohexane	40.5%	28.5%	0.1%	30.9%
Methylcyclopentane	25.5%	16.0%	0.1%	58.4%
m-Ethyltoluene	43.2%	30.5%	0.7%	25.5%
n-Butane	10.2%	4.6%	0.0%	85.2%
n-Decane	46.2%	24.2%	0.5%	29.0%
n-Heptane	36.2%	28.7%	0.1%	35.0%
n-Hexane	17.5%	17.8%	0.1%	64.6%
n-Nonane	49.8%	39.5%	0.1%	10.5%
n-Octane	46.5%	36.5%	0.1%	16.8%
n-Pentane	10.7%	4.8%	0.1%	84.4%
n-Propylbenzene	51.3%	40.0%	0.1%	8.6%
n-Undecane	47.1%	32.1%	3.5%	17.3%
o-Ethyltoluene	49.6%	34.2%	0.2%	15.9%
o-Xylene	34.4%	19.9%	0.1%	45.6%
p-diethylbenzene	52.8%	39.6%	3.2%	4.4%
p-Ethyltoluene	48.9%	36.2%	1.7%	13.2%
Propane	0.4%	0.2%	0.2%	99.2%
Propylene	32.8%	23.8%	0.0%	43.4%
Styrene	48.5%	40.6%	0.1%	10.8%
Toluene	2.9%	1.4%	0.1%	95.6%
trans-2-Butene	54.5%	44.5%	0.0%	0.9%
trans-2-Pentene	54.6%	43.1%	0.6%	1.7%

As shown in Table CQ9-1, eight compounds were detectable in less than 10% of samples. This is based on data from 1994 to 2007. Concentrations were higher in early years of this 14-year period. For more recent years, more compounds were below detection limits. Some compounds were barely above their

detection limits and the usefulness of the data is limited. Combining the detectability and MIR, a number of compounds could be eliminated from the target list.
Mobile or temporary monitoring platform discussed in Charge Question 6 can be an effective tool for screening detectability of compounds in a particular airshed.

Charge Question 10 - Are there specific compounds that EPA should consider adding or subtracting from the target list?

Response: Instead of listing specific compounds, a systematic approach should be used in selection of target compounds. The criteria recommended in my response to Charge Question 9 above should be used in the decision of adding or subtracting compounds. Because MIR values for compounds are the same regardless of location, EPA should provide a longer list of potential target compounds based on MIR. Monitoring agencies should be given flexibility to use this longer list as a starting point and select compounds to be monitored with additional consideration of detectability in their specific airsheds. Currently compounds from biogenic sources are underrepresented. In the new target compound selection process, more compounds from biogenic sources should be considered.

Charge Question 11 - What are the advantages and disadvantages of manual canister sampling versus field deployed auto-GCs?

Response: Below is a side-by-side comparison of canister sampling vs. auto-GC (Zhou et al, 2007).

Canister Sampling	Auto-GC
• Simple • Grab samples • Low cost for small number of samples; the cost advantage diminishes as sampling frequency increases • Delayed results	• Sophisticated • Continuous operation • High capital cost; it becomes more cost effective when sampling frequency increases • Quick turnaround; near real-time if automated

Auto-GC has been used in Texas, Baton Rouge nonattainment area, and other areas. Having hourly VOC precursor data that matches hourly NOx data and hourly ozone data is very helpful in understanding the ozone formation process and developing ozone strategies. Preliminary auto-GC data can be made available within an hour. Compared to the canister method, the data from auto-GC is much more timely and relevant. Part of reason that a vast amount of data is generated by current canister based PAMS sites but not effectively used is that the canister data is spotty (1-3 data points per day, a couple of days per week) and not timely (1-2 weeks after the samples are collected). Because of the 1-2 weeks of time delay, the data is not actionable and is not relevant to most operational function of an agency other than a few data analysts. The canister method is somewhat a halfway approach. It costs money, but does not produce the desired results. If EPA is committed to the PAMS program, auto-GC method should be given a high priority in its PAMS re-engineering effort.

As discussed by Zhou (Zhou et al, 2007), auto-GC can be further divided into two modes of operation, hourly mode and triggered mode. The hourly mode will be very suitable to Type 1, 3, and 4 sites.

However, it may miss or “flatten” the signal from precursor sources. It may not be representative of transit plumes. The triggered mode will minimize these shortcomings and better serve the purpose of Type 2 sites.

Charge Question 12 - Are the new commercially available auto-GCs appropriate for use at PAMS sites? What additional evaluations are necessary to determine the suitability of auto-GC’s for use in the PAMS network?

Response: GC configured for continuous or triggered ambient monitoring operations are commercially available from PerkinElmer and Agilent. Ecotech markets auto-GC that is specifically designed for continuous air monitoring. Currently majority of auto-GC deployed are PerkinElmer units. Agilent GC can be configured to achieve the same results. Both PerkinElmer and Agilent systems are built as more generic lab GC’s but used as continuous field monitoring instruments. Therefore there are many operational disadvantages associated with these instruments. The Ecotech AirmOzone is relatively new. I don’t know if EPA has evaluated the Ecotech system. It appears to be designed specifically for field application (as opposed to generic lab instrument) and therefore should be more durable for field deployment. However, I don’t know if the tradeoff is a lower performance. Through this review process, I became aware of another commercially available auto-GC made by Synspec. This instrument looks very promising.

It may be a good idea to invite vendors to participate in a comprehensive side-by-side performance evaluation (like EPA did for other monitors such as PM monitors). In addition to typical areas of such an evaluation (e.g., repeatability/precision, accuracy, linearity, detection limits, etc.), the following aspects specific to auto-GC for ozone VOC precursor monitoring should be addressed:

- *Moisture management*. Nafion dryers have been used to remove excess moisture in ambient air samples. Nation dryers may cause low recovery for some target compounds. In a triggered mode, the sample volume is smaller (because the VOC level is already elevated), and the moisture issue is less severe (Zhou, Zeng, Hazlett, & Matherne, 2007).
- *Field operability*. Compared to other ambient air monitoring analyzers (e.g., ozone, NOx, etc.), operations of PerkinElmer and Agilent auto-GC are awkward because they are fundamentally a lab bench top instrument designed for manual operations. Data acquisition is very cumbersome and cannot be easily integrated into typical ambient air monitoring data acquisition system. The Synspec ozone precursor analyzer and Ecotech AirmOzone may not have this issue. They all need to be field evaluated.
- *Capability for Additional Compounds*. As a result of this PAMS re-engineering effort, the target VOC list may be different from the current 56 compounds. The new compounds should be included in the evaluation. Separation of compounds is an important issue in any GC based measurement system.

Charge Question 13 - What role, if any, should TNMH monitors play in the PAMS program?

Response: PAMS VOC samples are collected either on a fixed schedule or when an elevated VOC is detected by a TNMH monitor (i.e., triggered sampling approach). In the cases of triggered sampling approach (mostly Type 2 sites for precursor source-oriented monitoring), the TNMH monitors play a critical role to generate a signal that triggers sample collection either by canisters or by auto-GC running in the triggered mode (Zhou et al, 2007).

In addition to acting as a trigger, TNMH (or Total Non-Methane Organic Compounds, TNMOC, or simply NMOC) gives a reasonable indication of total VOC present in the atmosphere. The TNMH monitors have a short analytical cycle (e.g., Model 55i manufactured by Thermo completes each analytical cycle in 70 sec.) and can be averaged over a hour to match the NOx hourly monitoring data so that the monitoring data for both precursors (VOC and NOx) can be in sync with hourly ozone monitoring data. This will help understand the relationship between ozone and its two precursor categories (VOC and NOx). The lack of specificity in the TNMH data regarding particular species sometimes is made up for by its abundant data points in a near real time basis. It is a very useful tool in routine, action-oriented data analyses.

The VOC compounds monitored by the current PAMS program are a subset of TNMH. Based on the San Joaquin Valley PAMS data analysis (Providence, 2010), the percentage of TNMH explainable by the sum of the VOC compounds monitored in the PAMS program can vary from 20% to over 100%. This suggests that the sum of VOC compounds monitored by GC in the PAMS program is not a good surrogate for VOC. TNMH monitors are universal monitors for hydrocarbon and they capture most, if not all VOC precursors. The difference between TNMH and the sum of VOC compounds measured by GC gives a clue on how much VOC is uncounted for in the current PAMS measurements.

Considering above factors, TNMH monitors serve an important role and should be included in the PAMS program. The shortcomings of TNMH analyzers should be recognized. The detector of the TNMH analyzer is a Flame Ionization Detector (FID), and it has different response factors for different compounds. This issue could be resolved unless hundreds of VOC species in the atmosphere were separated and calibrated individually. No instruments could do this. TNMH is the best method available to obtain some useful information on aggregated level of VOC in the atmosphere.

Charge Question 14 - Should carbonyls be required at all VOC speciation sites?

Response: Aldehydes generally have high MIR values (e.g., formaldehyde with MIR of 9.24, acetaldehyde with MIR of 6.34, etc.) (Carter, 2009) and several of them are fairly common in ambient air. As mentioned in response to Charge Question 13, up to 80% of TNMH is not counted for by current PAMS speciation. Significant portion of these unaccounted compounds could be carbonyls. Considering their high potential for ozone formation and common presence at levels comparable to other VOC species, carbonyls should be included in the PAMS program unless there are no adequate monitoring methods available. If carbonyls are added back to the PAMS program, some flexibility could be provided to monitoring agency. For a particular location, if 1-2 years of monitoring data show no significant carbonyls (indexed to MIR, or product of concentration and MIR), the monitoring agency can eliminate carbonyls from their PAMS program. Because instruments for carbonyl monitoring are different from other VOC species analyzed by GC, elimination of carbonyls can significantly reduce cost.

Charge Questions 15 – 18: No responses.

Charge Question 19 - Is it necessary to collect upper air wind speed and wind direction data at PAMS sites?

Response: Upper air wind data can be used for air monitoring, air modeling analysis, and air quality forecasting. One set of upper air data can reasonably cover a fairly large area (e.g., an area covered by a PAMS network for an urban area). I don't have specific comments on this charge question, but this seems to be an area where multiple air monitoring programs (even broader than air monitoring programs) can share resources. It appears that some other programs may have more critical needs for the upper air data than the PAMS program, and if so, it would make sense to leave the measurement of these parameters to another program and focus on parameters that are specific to PAMS.
The answer to this question also depends on how EPA plans to use this data in the PAMS program and what will be the new objectives of the PAMS program.

Charge Question 20 - How should NOAA data be incorporated into the PAMS program?

Response: No response.

Charge Question 21 - How can PAMS data best be used? What specific data analyses should be conducted?

Response: The PAMS program generates a large amount of monitoring data (over 50 VOC species in every sample). If these data are simply stored and not analyzed to the degree the program is designed for, the return on the investment in the PAMS monitoring effort is very small. It should be recognized that the PAMS program is a regulatory program. If the data generated by PAMS is only used for research, the program could be designed differently and managed by research organizations as special research projects. The PAMS program should be either re-engineered so that the data collected from the program is systematically analyzed and useful information is extracted regularly to support ozone attainment effort in each nonattainment area, or eliminated as a regulatory program all together.

In 1997 an EPA contractor prepared a PAMS Data Analysis Workshop Workbook for EPA (http://www.epa.gov/oar/oaqps/pams/analysis/). The Workbook addressed data validation, various specific data analysis techniques, and how the data could be used (primarily to support ozone attainment effort). However, the Workbook might not be instructive enough for some less experienced data analysts to follow and it has not been updated. As the EPA White Paper for this review stated, NESCAUM has performed a review of concentrations seen in the Northeast. Recently San Joaquin Valley Air Pollution Control District (SJVAPCD) commissioned a comprehensive analysis of PAMS data collected in 14 years from 1994 to 2007 (Providence, 2010). The report of this analysis (without appendices) is available online http://www.providenceeng.com/P/Files/othertechnicalinfo/455-002-001ER%20Final%20Report%20Narrative.pdf. There may be other systematic PAMS data analyses I am not aware of. It appears that these data analyses are not regularly done.

To help monitoring agencies in PAMS data analysis, EPA should consider using the 1997 Workbook as a starting point, updating the materials with more step-by-step instructions, incorporating other data analysis techniques (such as some used in the SJVAPCD PAMS data analysis), and providing monitoring agencies with a useful "toolbox" (a guidance document) for them to conduct PAMS data analysis.

The new guidance document should include two types of analyses:

Daily Data Analysis: Attachment 1 is an example of tools for this type of PAMS data analysis. This type of tools can be automated and accessible online to agency staff through intranet (or to the public with a note specifying “preliminary data, subject to change after further data validation” or “validated data”). This type of routine data can be analyzed along with daily ozone forecast. An agency data analyst can perform a very quick analysis on a daily basis. After a period of time with this repeated analysis, the analyst will have a very good idea as to what is going on in the airshed and provide insight to the agency decision makers. A similar daily data analysis was performed by Louisiana DEQ for the Baton Rouge nonattainment area in 2005-2007 and it helped the agency to reduce ozone precursors and reduce ozone level. This is an observation-based, episode-oriented analysis, and could lead to prompt actions. It can help validate (or provide feedback to) ozone forecast. It keeps PAMS information in the forefront and relevant in the effort to attain the ozone standard.

Seasonal or Annual Data Analysis: At the end of each ozone season (or end of each year), a data analysis should be performed to review the data collected during the season (or year). More data analysis tools should be used in the End of Season Analysis than the Daily Data Analysis described above. This analysis should reveal more information by examining the data set as a whole. It should also include previous years’ data for trending. Most of the data analysis tools included in the 1997 Workbook were designed for this type of long-term data analysis. This analysis should be done promptly at the end of an ozone season (or at least at the end of a calendar year) to keep it relevant and applicable to the coming ozone season.

Charge Question 22 - How should any recommended data analyses be implemented? Should these analyses be conducted at the state, regional, or national level?

Response: The most important objective of the PAMS program is to help ozone nonattainment areas to achieve attainment. The data analyses discussed above (Charge Question 21) should be conducted at the area consistent with the nonattainment area where the PAMS sites are designed to cover. The data analysis should be done by the agency or the regional planning organization responsible for the ozone nonattainment area. Unless two nonattainment areas are adjacent, the PAMS analysis for them should be performed separately. Neighboring agencies’ cooperation should be encouraged. EPA may conduct some data analysis at a high level covering regional or national trend.

The discussions for Charge Question 21 have touched on some implementation issues. In addition to generating high quality PAMS data, completion of PAMS data analysis should be part of PAMS annual funding requirements. Each monitoring agency should demonstrate how the PAMS data is used in the ozone attainment effort. EPA should consider annual workshop or symposium in winter or early spring to facilitate exchange of ideas/methods for data analysis among PAMS monitoring agencies and to demonstrate how PAMS data is used to help achieve ozone attainment.

Charge Question 23 - Should more or less of the PAMS funding be allocated to data analysis?

Response: The EPA White Paper for this review states that the current PAMS funding level is $14 million per year and EPA guidance is to use 25% of the funding for data analysis. According to PAMS website, there are 24 areas under the PAMS program. On average each area should receive about $583,333 for PAMS operations, of which $145,833 should be used for data analysis. The 25% for data analysis seems adequate *if* this amount is actually used for data analysis. This does not seem to be the case. PAMS is more of an investigative program than a compliance program or research program. The PAMS program should include sufficient and meaningful data analysis to provide information that can be used to solve the ozone attainment problem.

Allocation of fund for data analysis does not need to be proportional to the number of sites in each area. The level of effort to perform the same types of data analysis for an area with 2 PAMS sites is going to be more than a half of that for an area with 4 PAMS sites. In other words, the increment cost for adding one more site in an analysis will be less than the cost of performing the analysis for the first site. Although the same principle of economy of scale applies to sampling and chemical analysis aspect of PAMS operation, the effect for data analysis is more noticeable.
EPA should consider setting aside some data analysis fund at the national level and use this fund to:

- Develop useful data analysis tools in the PAMS data analysis tool box, including guidance documents, data analysis methods, online data analysis tools, and computer programs to automate the process of monitoring data analysis and visualization.
- Provide data analysis training and organize annual PAMS data analysis workshop or symposium.

1. Bibliography

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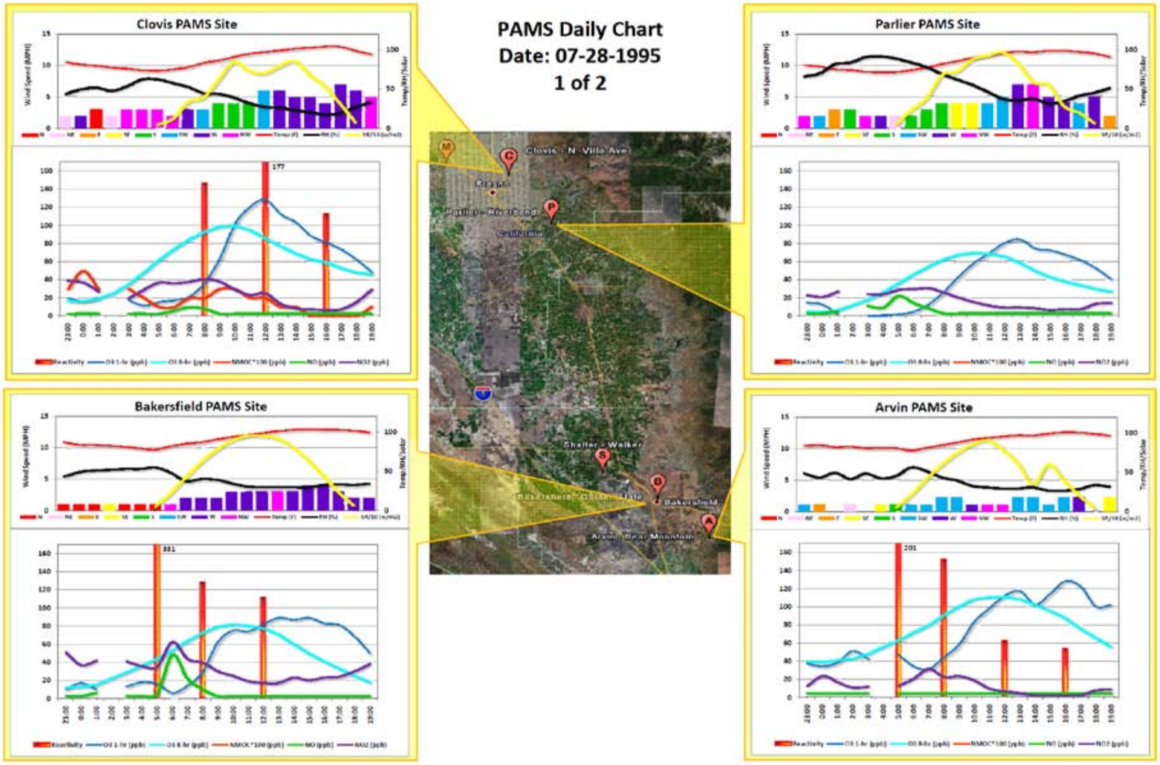
Attachment 1

PAMS Daily Chart
Date: 07-28-1995
1 of 2



PAMS Daily Chart
Date: 07-28-1995
2 of 2