Comments to EPA's CASAC/AMMS Subcommittee regarding PAMS Re-engineering Project As noted in Federal Register / Vol. 76, No. 73 / April 15, 2011, pp. 21345-21346

Prepared by:

Alan R. Leston
Principal Scientist
AirQuality Research & Logistics, LLC
1026 Goshen Hill Rd.
Lebanon, CT 06249

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

Response: EPA's notes[1] that the Photochemical Assessment Monitoring Stations (PAMS) network came on-line in 1994 but the earliest reference to the "Objectives" for that program is listed as 1998[2]. It is difficult to comprehend how State, Local and Tribal (S/L/T) monitoring agencies selected monitoring sites, installed highly complex monitoring equipment and reported relevant data between 1994 and 1998 without clearly stated objectives. However, it is assumed that the Objectives cited by EPA in 1998 (listed below) are indeed "…the current…." PAMS objectives on which comments are sought;

(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 <u>evaluating population exposure to air toxics</u> as well as criteria pollutants. (Note: Underlining provided for emphasis by the author.)

The above list PAMS Objectives appears to minimize the use of ozone data to determine air quality standard attainment in light of the changing form and level of revised ozone NAAQS. Historically, PAMS sites were established in areas where ozone non-attainment designations of "serious" or above had been determined. However, Charge Question 4 (below) raises the issue of whether non-attainment areas with designations below "serious" should be required to install PAMS monitoring.

Objective (5) notes that "…additional selected criteria pollutants…." are possibly useful for "maintenance plan" creation but not for "implementation plan" modification. Monitoring areas which do <u>not</u> meet the NAAQS must develop an Implementation Plan which requires modeling which requires an Emission Inventory. Forthcoming changes to the form and level of the ozone NAAQS requires alterations to existing implementation plans. And any new PAMS sites would have to rely on historical ozone data (at least three years) regardless on its designated severity level. Therefore, Objective (5) above should be modified to include the use of PAMS data to support creation of and changes to existing implementation plans.

If prioritization is important, PAMS Objectives should focus on the following questions:

1) Is the current ozone NAAQS attained?
2) Does the data support specific control strategies?
3) Are trends evident in the data or resulting metrics (i.e., the Design Value)?
4) Is there significant exposure to Air Toxics?
5) Is the data useful in control strategy modeling exercises?
6) How well do modeled Emission Inventory levels agree with the ambient data?

S/L/T monitoring organizations <u>may</u> use PAMS data for other uses but the PAMS program should not require them to do so.

Additional suggestions include the following:

1) S/L/T monitoring agencies should design PAMS networks to best suit their needs and draft a Strategic PAMS Plan (with an appropriate Quality Assurance Project Plan) to identify how they propose to establish/modify a PAMS network, the length of the PAMS monitoring "season," and employ collected PAMS data. This Strategic Plan would address measurements of parameters deemed vital to the agency (e.g., ozone, NOx, volatile organic compounds (VOCs), semi-volatile organic compounds, meteorological parameters).

Although most ground level ozone comes from photolysis of NO_2**,** the precursor levels and atmospheric conditions leading up to the creation and photolysis of NO_2 vary greatly. Many areas are driven into non-attainment by mobile source emissions in concert with high afternoon temperatures, although some areas experience high biogenic emissions; many areas are subject to medium/long range transport, although a few areas experience high warm weather industrial emissions (or during cold weather under strong surface inversions). Most non-attainment areas

experience more than one of the above scenarios but virtually all S/L/Ts in the U.S. now understand the major drivers of high ozone within their domain(s). It is this knowledge that will allow them to create effective PAMS Strategic Plans (PSP).

2) EPA would review the proposed PSPs for applicability to PAMS Objectives, degree and nature of Quality assurance, and expected usefulness of proposed data analyses.

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

Response: Given the evolving nature of ambient air measurements, the PAMS sites can provide valuable platforms for testing emerging ozone and ozone-precursor measurement techniques. Although S/L/T monitoring agencies have limited (and in many cases, declining) resources it is possible that by providing a secure "platform" with adequate utilities and baseline measurements, S/L/T monitoring organizations can help advance improved measurement techniques. Therefore, S/L/T agencies can, and should be, encouraged to provide real-world PAMS test bed platforms for new monitoring techniques and to investigate emerging data collection and analysis hardware/software.

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 advantage of the current PAMS network is that it establishes comparable measurement platforms in areas crucial to understanding the formation and transport of ground level ozone although the cost disadvantage is very high. Although it's imprudent to reduce the number of sites, some changes noted below in monitoring methodology may be in order.

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**:* EPA is required to provide uniform, national ambient air monitoring strategies and that approach should apply to the PAMS program. However, some S/L/T agencies have already collected significant quantities of VOC/NOx data and actively used that data to develop control strategies. These S/L/Ts should be allowed to "opt out" of <u>some</u> PAMS monitoring requirements regardless of their level of non-attainment. This option should apply to agencies that have collected and analyzed large quantities of short-term VOC data where they would not gain appreciably from additional data.

Regarding use of "severity labels," it will be difficult for EPA to identify additional PAMS monitoring sites until promulgation of the final Implementation Rule designating ozone nonattainment areas and this action does not appear imminent.

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: Recently portions of Western States have recorded 8-hour ozone concentrations exceeding the NAAQS during very cold wintertime periods, thought by some related to the extraction/pipelining of natural gas although other possible sources have not been ruled out. Should this prove true, EPA should require PAMS monitoring stations in resource extraction areas exceeding NAAQS or showing increasing pollutant/precursor trends. At the same time, EPA should evaluate potential artifacts in current federal equivalent monitors (FEMs) under such extreme meteorological conditions.

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

Response: Given the current cost and complexity associated with fixed PAMS sites, EPA should not mandate that temporary or mobile sites be established but should encourage S/L/Ts to develop such approaches.

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: See response above to Charge Question 1.

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 length of the PAMS season drives program costs and vice versa. Some agencies, for example, with in-house laboratory canister-analysis facilities may have longer canister "seasons" for the same cost than other agencies running automated gas chromatographs (AGCs). For many S/L/Ts that have collected enough PAMS data to understand causes high ground-level pollutant concentrations in their areas, a reduced season is adequate. Therefore, S/L/Ts should be allowed to propose their own monitoring seasons in the "Strategic PAMS Plan" (see Response to Charge Question 1).

S/L/Ts could determine their PAMS season length by:

1) reviewing historical ozone/NOx/VOC data,
2) determining trends in ozone/NOx data,
3) indentifying source classes of VOCs (mobile, stationary, biogenic, etc.) and determining trends in each source.

With such information on current and projected ozone/precursor data available, monitoring agencies would be better able to decide both how long to monitor precursors and to a large extent which precursors to monitor.

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

Response: The first step for revision of the PAMS VOC target list should be an analysis of existing VOC data, collected either from PAMS program or other (e.g., air toxics, special studies) initiatives. EPA should compile and review such analyses before revising the PAMS target list.

The second step should focus on the percentage of non-detects (ND) associated with reactive compounds (e.g., alkenes, aromatics) known for producing more O3 than other classes[3]. If a highly reactive compound is not detected consistently (e.g., < 25% of attempted measurements) during the morning hours (5-11 AM) when ozone forming potential is greatest, then that compound can be assumed to play a minor role in daily ozone formation and should be excluded from mandatory PAMS reporting requirements. Understanding the increasing frequency of ND for each PAMS precursor is especially important because the concentration of VOCs in many areas is declining.

The bulk of ozone forming VOCs emitted by mobile sources burning reformulated gasoline (RFG) can be monitored by GC-FID[4]. Therefore, gas chromatographs measuring either speciated or total non-methane hydrocarbons appear to be appropriate tools for VOC data collection at ozone-focused PAMS sites.

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

Response: As noted in the "Response to Charge Question 9", if a relatively non-reactive compound appears as a "non-detect" 75% or more of the time, then EPA should allow S/L/T PAMS operators the option of dropping that compound from the required list of VOCs.

Although not a "compound" *per se*, EPA should consider adding measurement of the ultraviolet "A" band to the PAMS program. Radiation in the UVA band is chiefly responsible for photolysis of the NO_2 molecule which leads to the formation of most urban ground-level ozone. UVA should be measured at Type 2 sites in order to gauge the impact of day-to-day ultraviolet radiation on ozone formation.

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

Response: The main advantage of AGCs is that they provide real-time data on an hourly basis that can be correlated with hourly NAAQS monitors and can "finger print" unusual atmospheric events (forest fires, local fires/spills, industrial releases) that would be next to impossible to capture with time-averaged canisters. The main disadvantage is the large man-power requirement to operate the instrument and to quality assure resulting data. AGCs also suffer from retention time drift related to differences in the relative humidity of ambient samples and calibration gases.

Canisters require much less floor/rack space and support equipment and so can be employed at a wider range of sites. Most canisters also have sufficient sample volume to be re-analyzed if necessary or to be analyzed by more than one method. Sample water management for canister

analysis allows for the capture of more "unknowns" which results in a higher total non-methane organic compound (TNMOC) value.

Additional topic: In addition to auto-GCs and canisters, S/L/T monitoring organizations might be encouraged to consider multisorbent tubes for ambient VOC sampling when biogenic compounds are prevalent. Sorbent tubes[5] can collect and store a wide range of compounds up to 30 days. In addition to the TO-14a target list, isoprene and several terpenes can be recovered at high efficiency.

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: New auto-GCs are available (e.g., Synspec) that may be suitable for use at PAMS sites. However, given the Charge Questions regarding speciation vs. TNMOC, dropping/adding VOCs to the PAMS target list (as well as the possible need for inclusion of polar compounds) makes it difficult to lay out an evaluation program at this time. A major flaw in the field-based auto-GC program to-date has been the under-reporting of total non-methane hydrocarbon (TNMH) values due to the loss of polar compounds in the permeation dryer system needed to keep ambient humidity form plugging the cold trap[6]. A field-based Auto-GC with superior TNMH performance would be useful to the PAMS program. An Auto-GC which could perform routine TNMH analyses but switch to a speciated mode when high TNMH levels are detected would be extremely useful. Alternatively a TNMH monitor could be used to track diurnal patterns of non-methane hydrocarbons but trigger a canister sampler (or AGC) when pre-determined conditions are met.

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

Response: See response to CQ 12 above.

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?

Response: Direct measurement of NO2 is highly desirable and a photolytic (LED-based) system is available that may be suitable for deployment at this time. Because the conversion efficiency of LED converters is low and lamp life is limited (~5,000 hours)[7] the stability of the converter must be fully characterized. Collocation testing of two LED-based monitors with two FEM NOx monitors at several sites should commence. This "four monitor" approach is essential due to the possible malfunction of one or more monitors, which would lose critical seasonal data and require extending the comparison to an unacceptably long period of time.

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?

Response: Most important is data collection leading to a better understanding of mid- to long-range transport. For vertical profiles aircraft platforms and satellites would provide the most cost

effective solutions due to their higher frequency of data capture and ability to loft complex, heavy instrument packages. However, ground-based stations that gather data on mixing height and wind speed/direction aloft are also important due to their ability to detect low altitude "micro-jets" that drive overnight pollutant transport.

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

Response: Knowledge of upper air wind data and mixing height is crucial to the understanding of ozone (and other pollutant) transport. Upper air met profilers should be operated wherever transport is an issue but not necessarily at PAMS sites. Airports would be appropriate locations for such profilers especially those which already host Automated Surface Observation Systems (ASOS) and/or ceilometers.

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

Response: NOAA upper air profiler data is only available from stations in the central US and Alaska[6] and lack sufficient low elevation sensitivity. Therefore, that data is not useful to the PAMS program. However, as noted in the Response to CQ 19, ASOS data includes information from a Cloud Height Indicator (CHI) which is essentially a ceilometer. CHI data in conjunction with other meteorological parameters can provide very useful information on mixing height and atmospheric stability.

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

Response: A technical report to EPA[8] cited 5 additional proposed Data Quality Objectives (DQOs) to be met by speciated VOC data from the PAMS program. The DQOs were generated in part by the "PAMS Work Group" established by EPA. The proposed DQOs were;

1) Detect the presence of a diurnal pattern.
2) Detect a change in the diurnal pattern from one year to another.
3) Detect a 3% annual trend over a five-year period of time.
4) Detect a 20% change in the seasonal average between consecutive years.
5) Detect a 3% downward trend over a ten-year period.

The Technical Report examined six chemical compounds (acetylene, benzene, butane, ethylene, and isoprene) from multiple sites in the Boston area and San Joaquin Valley area for the years 1994-1997 and concluded that;

a) DQO 1 could be easily met,
b) DQOs 3 and 5 could not be met and,
c) mixed results (by site and parameter) were noted for DQOs 2 and 4.

The Technical Report concluded that "… PAMS data are not suitable for detecting a very small linear trend in mean chemical concentration from year to year…." and then suggested the following modifications so that the DQOs would read:

1) "*…For a 0.20-level test of the null hypothesis that no diurnal pattern exists, the data for any given pollutant measured at a PAMS site must generate an estimation of diurnal pattern change that is precise enough to reject the null hypothesis with a probability of at least 0.80, when the true change is 20% or more*…."

2) "*…For a 0.20-level test of the null hypothesis that no change in diurnal pattern exists, the data for any given pollutant measured at a PAMS site must generate an estimation of diurnal pattern change that is precise enough to reject the null hypothesis with a probability of at least 0.80, when the true change is 20% or more…."*

3) "*…For a 0.20-level test of the null hypothesis that no annual trend exists, the data for Total Volatile Organic Compound (TVOC) concentrations measured at Type 2 sites over a 5-year period must generate an estimation of annual trend that is precise enough to reject the null hypothesis with a probability of at least 0.80, when the true annual trend is 3% (upward or downward) or more*…."

4) "*…For a 0.20-level test of the null hypothesis that no change in the seasonal average between two consecutive years exists, the data for speciated VOC concentrations measured at a Type 2 site, when pooled by class, must generate an estimation of seasonal average change that is precise enough to reject the null hypothesis with a probability of at least, 0.80, when the true change is 20% (upward or downward) or more…."*

5) "*…For a 0.20-level test of the null hypothesis that no yearly downward trend exists, composite ozone, NOx and speciated VOC data for a given MSA/CMSA must generate an estimation of yearly downward trend that is precise enough to reject the null hypothesis with a probability of at least 0.70, 0.80, or 0.90 under Type-1, Type-2 or Type-3 site compositing, respectively, when the true downward trend is 3% or more…."*

Given the extensive data sets involved and rigorous statistical tests employed in this analysis, these revised DQOs should be included in any revision of PAMS objectives.

So many types of PAMS data analyses have already been performed that it is not possible to note them here. And as previously noted, S/L/Ts are generally aware of the specific ozone-related issues in their domains and do not need instruction as to how proceed. However, it is noted that in addition to quality assurance-related analyses such as the DQOs noted above most data assessments/analyses fall into the following categories; 1) air quality characterization, 2) biogenic emission investigation, 3) ozone forming potential studies, 4) emission inventory comparison to O3 precursors, 5) source apportionment studies, 6) air quality model evaluation, 7) precursor/precursor and precursor/product correlation studies, 8) transport analysis and 9) trend studies. S/L/T monitoring agencies must be given the flexibility to choose the most appropriate assessments and analyses for their domains and the order in which to perform them.

For example, ethane is a ubiquitous atmospheric component almost always present in speciated PAMS data sets that has both geogenic/biogenic sources and changes its concentration slowly in

a different pattern than primarily anthropogenic or biogenic compounds. These attributes give ethane a higher usefulness during data analysis than other VOCs even though ethane does not participate to a large extent in ozone formation. For example, if ethane displays the same diurnal pattern as anthropogenic or biogenic compounds it is likely that there has been a misidentification in the ethane (or other peak) identification; isoprene is emitted by mobile sources and although its traffic signature is obscured by biogenic isoprene during warm months, it re-emerges during the colder months.

Although collecting hourly data on these two species outside of the normal PAMS season has marker value each S/L/T must determine whether the value received for additional monitoring is worth the price paid.

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

Response: Primary analysis of PAMS data should rest with the S/L/T monitoring agency responsible for collecting the data. In most cases, ozone is a regional issue and therefore data analysis of a regional nature is almost always mandatory. Regional PAMS analyses can be performed by EPA Regional staff or by Multi-State Organizations (MSO) after individual S/L/Ts have quality assured the data and performed initial assessments and analyses.

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

Response: More analysis of PAMS data is in order but it is not clear that allocating more funds to analysis will actually accomplish that goal. Perhaps EPA should allocate some of the existing PAMS data analysis funding to a series of multi-day workshops where PAMS data (on a regional basis?) and data tools are made available on several PCs. Interested analysts would be given training/instruction during some portion of each morning of the workshop and then allowed to explore the data with emphasis on understanding/exploring data quality as well as issues such as source profiling, transport, or events leading to episodes. The day would end in a plenary session where results, problems and insights would be explored. a workshop would encompass 4-5 days so that analysts could immerse themselves fully in the data, tools and techniques.

References

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