Preliminary Comments from Members of the Clean Air Scientific Advisory Committee CASAC Air Monitoring and Methods Subcommittee (AMMS) As Of May 16, 2011

In Preparation for Public Teleconferences on May 16 - May 17, 2011

Purpose: To review and provide advice and ideas on how to improve EPA's Photochemical Assessment Monitoring Stations (PAMS) Network Re-engineering project and program.

Preliminary Comments from Members of CASAC AMMS Review Panel

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Preliminary Comments from Mr. George Allen

These comments are brief and primarily point to existing resources that are relevant to the general topic.

1. Last year I led a 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/

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

2. A written public comment has been submitted by CT-DEP regarding 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 comments on new PAMS GC technologies are posted with other public comments for this meeting, at:
http://yosemite.epa.gov/sab/sabproduct.nsf/bf498bd32a1c7fdf85257242006dd6cb/6a62b0219d19df358525785c0064e71b!OpenDocument&Date=2011-05-16

His experience with new GC methods is encouraging, and is important to consider during discussion of this charge question.

Preliminary Comments from Dr. Linda Bonanno

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

EPA should consider the following additional objectives for the PAMS program at this time:

1. Standardize the QA/QC procedures particularly on a regional basis (vs. state by state)

2. Promote use of the data either by providing funding to do analysis or recommending that regionally, someone is designated to do analysis of PAMS data

3. Improve emissions inventory

4. Standardize instrumentation and SOPs for a better comparison among regions and labroratories, interlab comparisons

5. Make the PAMS network to be more in line with air toxics monitoring to allow for comparison of short term sampling (hourly, 3 hr) to the 24 hr samples collected at the air toxics monitoring sites. Use PAMs data for exposure modeling.

5. Track trends in precurors

6. ID key constituents in ozone formation and don't analyze for the others'

7. Characterize transport

8. Use of PAMS data in modeling/forecasting

9. Enhance special studies

10. Measurement of SOA precursors

Preliminary 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.

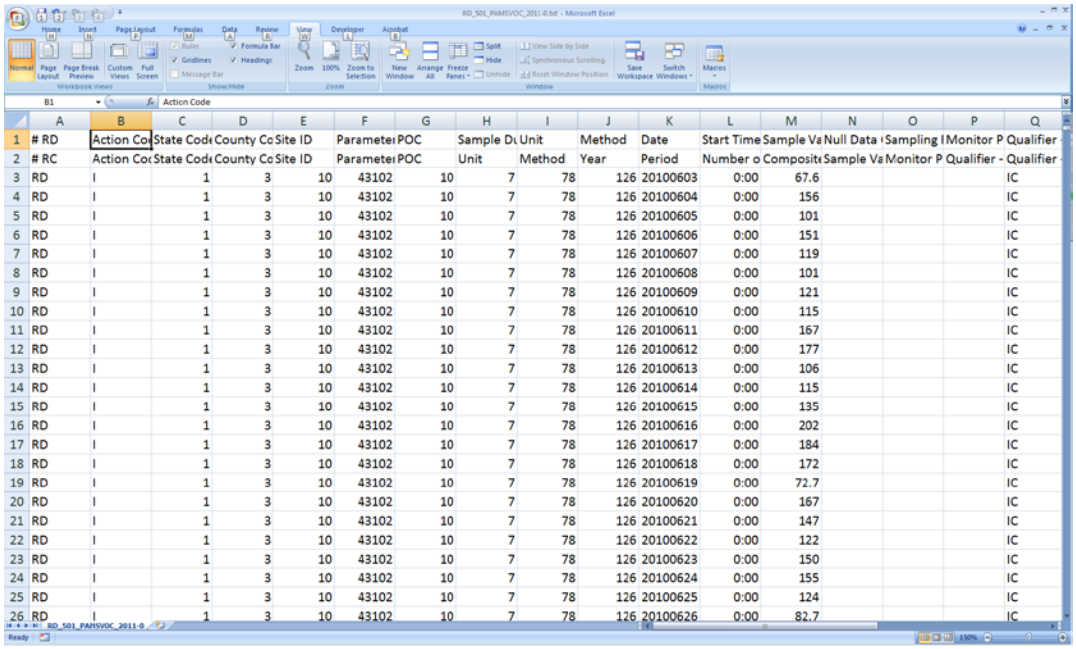
Preliminary Comments from Dr. Judith Chow

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

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.

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. 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 (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).

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

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).

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?

The suggestions for improving forecasting, understanding secondary organic aerosols, air toxics, and climate forcing substances are all good 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 needn’t 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. The fast-expanding extraction of natural gas in Wyoming and Pennsylvania, for example, 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.

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 that obtains higher time resolution and a 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 domain 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.

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

The following criteria need to be considered:

- Compounds in VOC profiles from existing sources in the domain: needed for tracking trends when emissions are reduced, 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. In addition, 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 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]	Coke oven emissions[c]	Mercury compounds
Acrolein[b]	1,3,-Dichloropropene[b]	Methylene chloride [b]
Acrylonitrile[b]	Diesel particulate matter[c]	Nickel compounds
Arsenic compounds	Ethylene dibromide[b]	Perchloroethylene[b]
Benzene[b]	Ethylene dichloride[b]	Polychlorinated biphenyls[c]
Beryllium compounds	Ethylene oxide[b]	Polycyclic organic matter[c]
1, 3-Butadiene[b]	Formaldehyde[b]	Propylene dichloride[b]
Cadmium compounds	Hexachlorobenzene[b]	Quinoline[b]
Carbon tetrachloride[b]	Hydrazine[b]	1,1,2,2-Tetrachloroethane[b]
Chloroform[b]	Lead compounds	Trichloroethylene[b]
Chromium compounds	Manganese compounds	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. VOC canisters contain enough air to be submitted to many different analyses that meet the criteria of Question 9, but they are labor intensive, and some of the VOCs deteriorate with storage time. VOC canister data doesn't provide reliable results for heavier hydrocarbons above C_{12} that aren't so important for O_3, but are very important for photochemical secondary organic aerosol formation (Pandis et al., 1992). Their time resolution 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 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. Not all of the VOCs are efficiently collected on the substrate by auto-GC and the interpretation of the peaks is not subject to expert judgment, however. 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 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.

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?

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, and contamination. These biases can be minimized through appropriate precautions and procedures (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).

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?

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. 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 65% to 90%, but 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 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 at PAMS sites?

Yes. 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 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 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 answer to Question 1.

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Preliminary Comments from Dr. Kenneth Demerjian

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.

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. That being said, my experience has been that states typically know best, 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?

Compound specific criteria should include:
The VOC is a good emissions source marker
The VOC has high reactivity (high ozone forming potential)
The VOC has high 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.

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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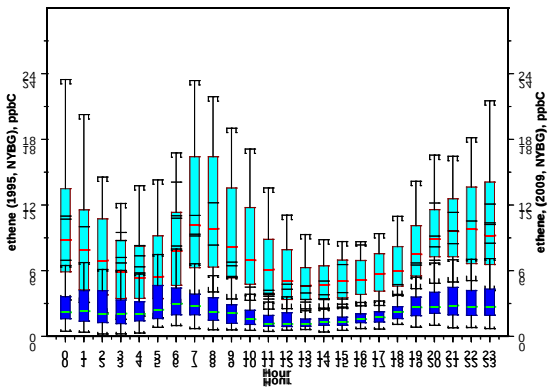
Figures:

ethene diurnal NYBG 1995 vs. 2009



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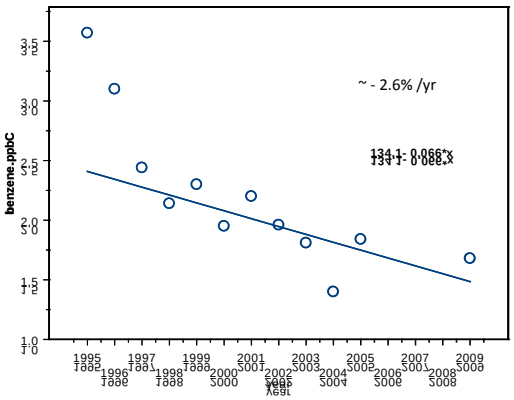

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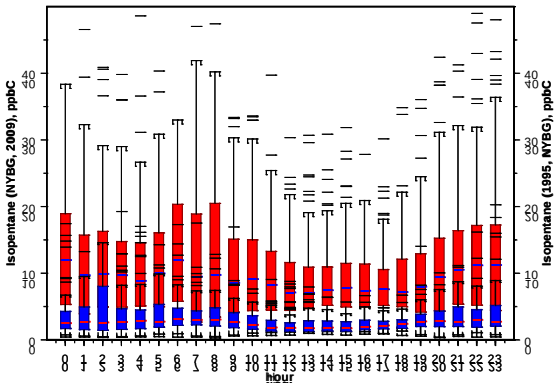

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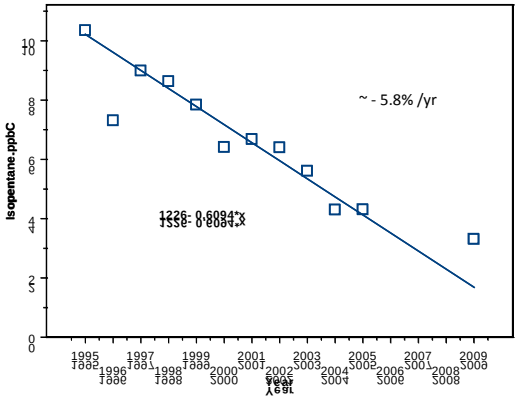

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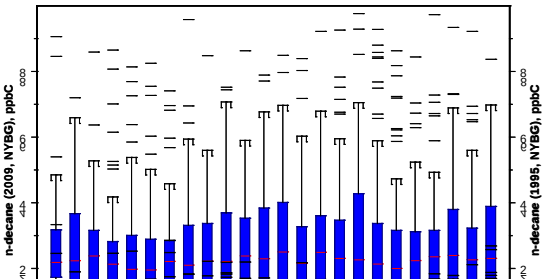

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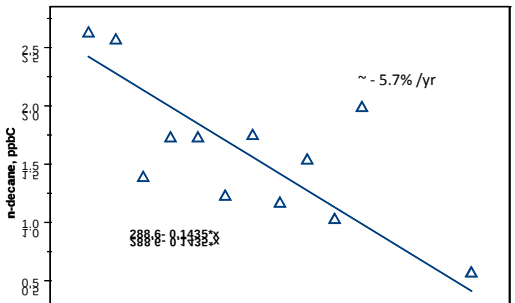

Preliminary Comments from Mr. Dirk Felton

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 a source emissions impact to evaluate 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 objectives should include a determination of natural biogenic precursors that are not subject to mitigation strategies which should be considered to be true background vs anthropogenic precursors and biogenic precursors resulting from anthropogenic activities such as agricultural fertilizing practices, CAFOs and eutrified water bodies.

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 have 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 or depending on the level of the NAAQS may soon be 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 existing PAMs areas which at one time had been classified as serious. PAMs measurements may be needed in order to determine the causes and potential control strategies for these 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?

Short-term monitoring should be undertaken 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.

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:

Monitoring and Data Collection

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

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.)
- Continuous Carbonyl

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.

<u>Charge Question 8:</u> 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.

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

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

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?

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?

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?

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 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 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 DIAL could be utilized in the special study category of PAMs to assess unconventional sources.

Surface based measurements must include Ozone and if possible the precursors which are most significant for the region.

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 near the marine boundary.

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?

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

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

Preliminary 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?

Given the ever tighter ozone NAAQS, issues such as continental background, biogenic VOC emissions, and interstate transport will become much more 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.

Preliminary 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 both 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. 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.

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

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 is not 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.

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. 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 development, but I have not followed their testing.

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.

Additional Comment: 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.

Preliminary 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?

Given the gradual tightening of ozone NAAQS, the permissible ozone levels are getting 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?

Preliminary Comments from Dr. Peter H. McMurry

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

My preliminary 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 preliminary 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, preliminary 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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Preliminary 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

"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 site. A subset of these sites could be used extend the trends but continuing to run all of the historical sites to continue the trends seems like overkill.

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.

Both of these objectives seemed to be poorly defined / catchall.

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 approach. For example, secondary organic aerosol precursors, air toxics, and indicators of global change are all worthy objectives.

A concern is that there are not sufficient resources to meet all of these 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 primary 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.

Measurement of important precursors and tracking trends of these precursors and analyzing PAMS data with an eye towards developing effective strategies to reduce secondary organic aerosol exposures.

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?

No preliminary comment.

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 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 single 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?

Consistent QA/QC procedures is 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 seems 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.

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.

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 important 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?
Lead Discussants:
Dr. Allen Robinson
Dr. James Schauer

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?

Charge Question 16: What other methods should be considered as an alternative to the manual TO-11A method for carbonyl sampling?
Lead Discussants:
Dr. Allen Robinson
Dr. Linda Bonanno

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 preliminary 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 preliminary 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 preliminary comments.

Charge Question 21: How can PAMS data best be used? What specific data analyses should be conducted?
Lead Discussants:
Dr. Allen Robinson
Dr. Kenneth Demerjian

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 which seem to do a lot more data analysis for models of how to do this. 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.

Preliminary 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 needs 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 preliminary comments

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

No preliminary 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 preliminary 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 preliminary comments

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

No preliminary 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.

Preliminary 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[1] (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.

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

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 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. [2,3] 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.

[2] See D.D. Parrish and F.C. Fehsenfeld (2000) *Atmos. Environ.*, **34**, 1921-1957 and references therein for work prior to 2000.
[3] C. Hak et al. (2005) *Atmos. Chem. Phys. Discuss.*, **5**, 2897–2945.

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.

Preliminary 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. 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. Met data is not unique to PAMS network, recognizing that PAMS network can contribute more met data. 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 is the adjustment. 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. 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. 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 wide spread 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). 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 result in a relatively small coverage on the U.S. map (maybe just Texas and California). It may not improve spatial coverage. It may even reduce spatial coverage from the current PAMS network. 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). One alternative could be maintain the current PAMS coverage even an area has been reclassified as less than serious under either 8-hour standards to be consistent with the anti-backsliding policy.

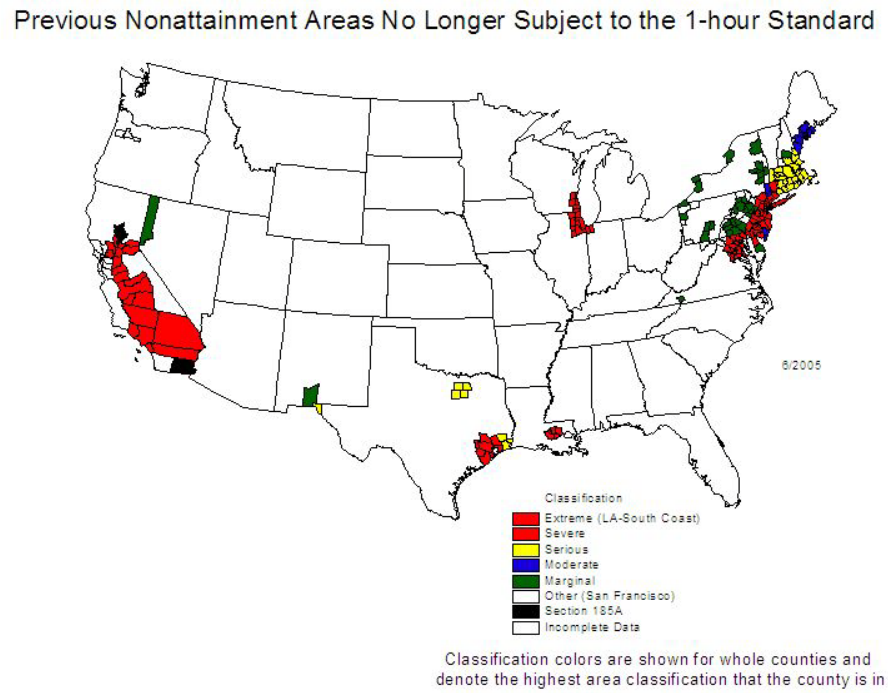

Figure CQ4-1. Classifications of ozone nonattainment areas under previous 1-hour standard.

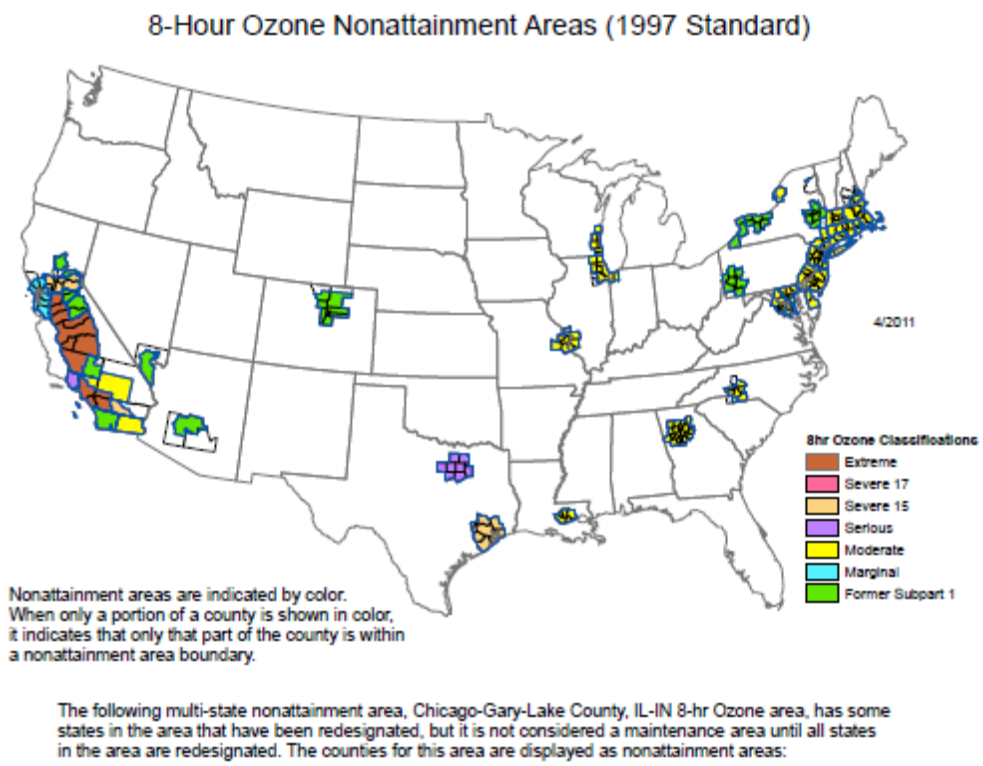

Figure CQ4-2. Classifications of ozone nonattainment areas under 1997 8-hour standard.

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 for 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 later responses to 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).

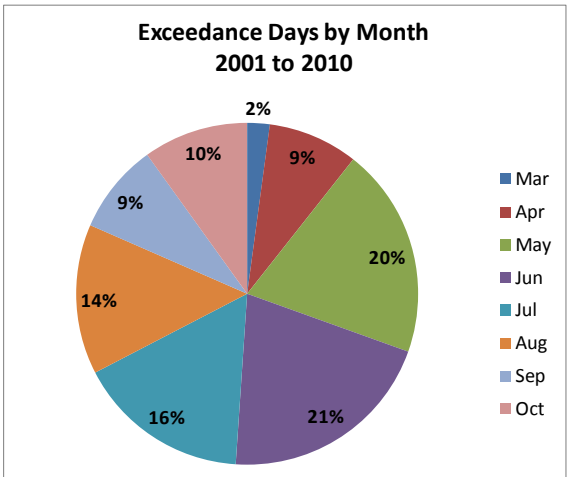

Figure CQ8-1. Ozone exceedance days by month in the Baton Rouge nonattainment area (courtesy of Tim Bergeron, Louisiana Dept. of Environmental Quality)

Although June-August may have a higher temperature, more thunderstorms and rain are likely to occur during these months, which minimizes 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 1997 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.

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

Response: The criteria recommended in my response to Charge Question 9 above should be used in the decision of adding or subtracting compounds. Based on MIR and detectability, the following subtraction (Table CQ10-1) and additions (Table CQ10-2) should be considered. Table CQ10-1 is based on detectability in the San Joaquin Valley PMAS data and may not be applicable to other regions. These two tables are provided as an illustration without a systematic review of MIR and analytic feasibility. EPA can perform a similar analysis systematically at national level and adjust the list.

Table CQ10-1. Candidate compounds for delisting (as an example)

Compound	MIR	% detectable (based on San Joaquin Valley PAMS data from 1994-2007)

Table CQ10-2. Candidate compounds for addition (as an example)

Compound	MIR

These two tables will be completed later.

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

Response: A summary of advantages and disadvantages of canister sampling vs. auto-GC has been made in a poster presentation at the 2006 National Air Monitoring Conference in Las Vegas (Zeng & Zhou, 2006). Because the poster presentation may not be available in publications and is referenced in multiple places in my responses to Charge Questions, it is included as Attachment 1 to this document.

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 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 in Attachment 1, 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. See Attachment 1 for more detailed explanations.

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 on more generic lab GC’s. 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 trade off is a lower performance.
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 auto-GC is awkward because they are fundamentally a lab bench top instrument designed for manual operations (the Ecotech AirmOzone may not have this issue). Data acquisition is very cumbersome and cannot be easily integrated into typical ambient air monitoring data acquisition system.
- *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 (see Attachment 1).
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 precursors.

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 in 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 a important role and should be included in the PAMS program.

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

Response: Aldehydes generally have high MIR values (Carter, 2009) and several of them are fairly common in ambient air (e.g., formaldehyde with MIR of 9.24, acetaldehyde with MIR of 6.34, etc.). 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. 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.

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?

Response: No preliminary comments.

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

Response: No preliminary 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?

Response: No preliminary 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?

Response: No preliminary comments.

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.
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 preliminary comments.

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. 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. The PAMS program should be either re-engineered so that the data collected from the program is systematically analyzed and useful information is extracted to support ozone attainment effort in each nonattainment area, or eliminated 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. 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 2 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 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 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 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 level consistent with the nonattainment area where the PAMS sites are designed to cover. The analysis should be done by the agency with the jurisdiction over 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, completing a PAMS data analysis should be tied to PAMS annual funding.

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 there should be about $583,333 in total PAMS funding and $145,833 for data analysis in each area. The 25% for data analysis seems adequate *if* this amount is actually used for data analysis.
Allocation of fund for data analysis should not 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.

1 Bibliography

Carter, W. P. (2009). *Updated Maximum Incremental Reactivity Scale and Hydrocarbon Bin Reactivities for Regulatory Applications.* Sacramento, CA: California Air Resources Board, Contract 07-339.

Providence. (2010). *Analysis of PAMS Data 1994-2007.* Fresno, California: San Joaquin Valley Air Pollution Control District, Contract 08-10-07.

Zeng, Y., & Zhou, L. (2006). Dual Applications of Automated GC – On-going Exposure Monitoring and Episodic Event Monitoring. *The 2006 National Air Monitoring Conference.* Las Vegas: Sponsored by EPA and STAPPA/ALAPCO.

Zhou, L., Zeng, Y., Hazlett, P., & Matherne, V. (2007). Ambient air monitoring with Auto-gas chromatography running in trigger mode. *Analytica Chimica Acta* , 156-163.

Attachment 1

Dual Applications of Automated GC

On-going Exposure Monitoring and Episodic Event Monitoring

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Abstract

Gas chromatography (GC) has been used to monitor speciated volatile organic compounds (VOC) either as ozone precursors or as air toxics in the ambient air. Due to low concentrations of these species in typical ambient air, a pre-concentrator is used to collect and concentrate samples for the GC analysis. The time for pre-concentration and the time for the GC analysis make the analytical cycle long – typically one hour. Such a system operates continuously (it can be referred to as "continuous Auto-GC") and is suitable for on-going exposure monitoring. However, continuous Auto-GC is not well suited for monitoring episodic events when the VOC plume is in transit and has a small footprint. The footprint of a plume is small when it is not far away from its source. This issue is more important when the emphasis of monitoring includes impact of local sources. In this situation the continuous Auto-GC system may miss or dilute the plume depending on the time the plume reaches the monitor in relation to the steps in the analytical cycle. A new configuration, referred to as "triggered Auto-GC", has been successfully developed and deployed. The triggered Auto-GC operates in a standby mode. It will start sampling only when an aggregated VOC level monitored by a simpler device exceeds a pre-determined trigger level. Triggered Auto-GC is more capable in capturing the episodic samples and better preserving their characteristics for further study of source-receptor relations. This presentation will include an analysis of both configurations and propose the third one – a combination of the two by adding an extra pre-concentrator and more sophisticated automatic controls. By doing so, an Auto-GC can have dual functions – monitoring of on-going average exposure and episodic events. The third configur is referred to as "dual-mode Auto-GC".

Introduction

- Ambient air monitoring for speciated VOC
  - Main applications
    - VOC ozone precursors – EPA PAM program
    - Air toxics
  - Most common methods
    - Canister sampling (EPA Methods TO-14 & TO-15)
      - Scheduled
      - Triggered
    - Auto-GC

Canister vs. Auto-GC

- Canister
  - Simple
  - Grab samples
  - Low cost for small number of samples; the cost advantage diminishes as sampling frequency goes up
  - Delayed results

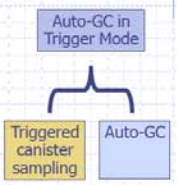
- Auto-GC
  - Sophisticated
  - Continuous operation
  - High capital cost; it becomes more cost effective when there are a lot of samples
  - Quick turnaround; near real-time if automated

Scheduled vs. Triggered Sampling

- Scheduled
  - Sampling at scheduled time, either at set periods or continuous
  - Application: routine air quality surveillance, receptor/exposure-oriented, community scale or larger
- Triggered
  - Event driven: sampling only when certain events happen, e.g. high VOC, wind in certain direction, etc.
  - Application: source characterization, source-receptor relation study, near sources
  - Typically canister sampling only

Auto-GC in Trigger Mode

- Project needs:
  - Event-driven (triggered by high levels of TNMOC), source-receptor relation study
  - Near-real time
- Combine features of canister and auto-GC
- More features realized after implementation – to be discussed later



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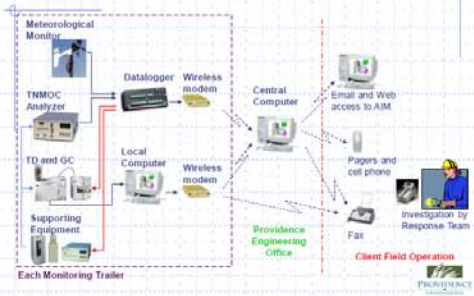
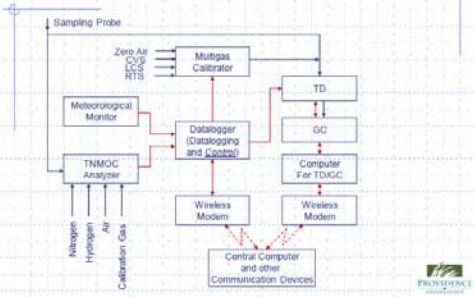
System Description

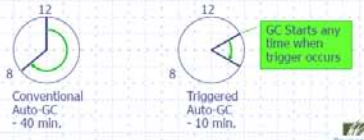


System Schematic



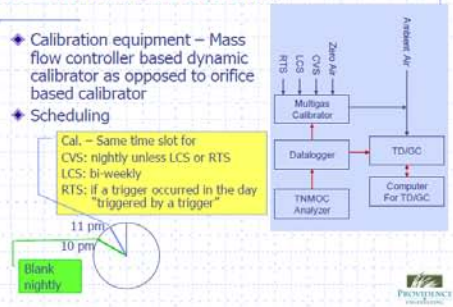
GC Sampling Time

- Ten min. as opposed to 40 min. in conventional Auto-GC because in trigger mode VOC concentrations are expected to be higher



GC Calibration Scheme

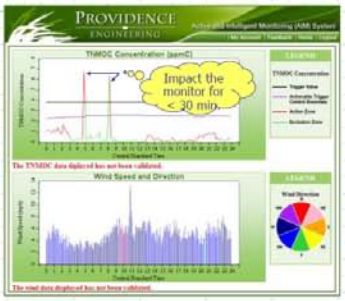
- Calibration equipment – Mass flow controller based dynamic calibrator as opposed to orifice based calibrator
- Scheduling



GC Performance When in Trigger Mode

- Performance study based on one station
- Method Detection Limit (MDL)
  - For Benzene, MDL=3.55 ppbC (0.59 ppbv)
  - For Propane, MDL=3.19 ppbC (1.06 ppbv)
- Precision
  - Coefficient of variance (CV, %)=(SD/Mean)*100
  - CV in a range of 3.84-11.98% for 12 compounds
- Accuracy
  - Recoveries in a range of 90-120% for most compounds and 80-140% for 3 compounds during a few sample runs

Transient Plume



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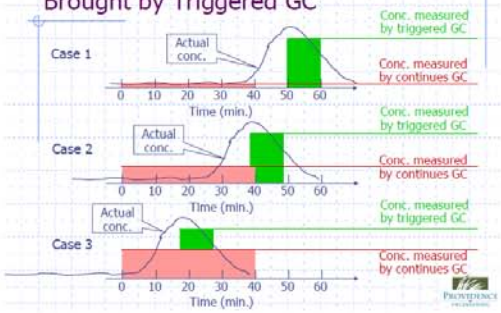
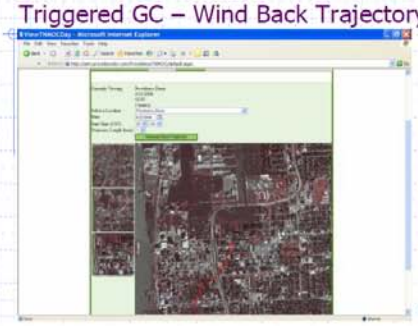
New Feature Brought by Triggered GC



On-line Tool in Conjunction with Triggered GC – Wind Back Trajectory



On-line Tool in Conjunction with Triggered GC – Scatter Plot

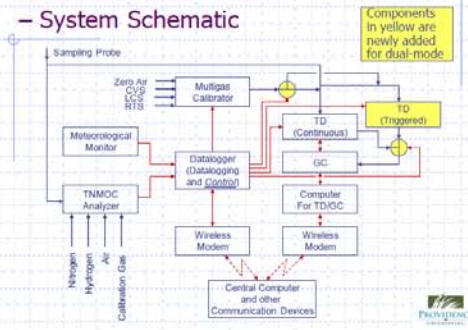
Summary for Trigger Mode

- Good performance
- RTS "triggered by triggers" – improve QC of compound ID
- Compared to triggered canisters – near real-time
- Compared to continuous Auto-GC,
  - Less sampling time and volume, less susceptible to moisture effect due to reduced sample volume
  - Better in capturing transient plumes with small footprint (monitors near sources) – better in preserving source characterizations, highlighting impacts, and studying source-receptor relations
- Very useful in studying source-receptor relations especially when used with real-time wind back trajectory
- The trigger can be other parameters, such as:
  - Ozone levels
  - Wind conditions
  - Other criteria at the same station
  - Conditions at up-wind stations in the monitoring network

Auto-GC in Dual-Mode – Design Objectives

- Maximize the investment in monitoring equipment and realize the benefits of both continuous and triggered modes
- Auto-GC normally in continuous operation mode to collect data for long-term exposure assessment
- When a VOC spike occurs, the system promptly capture a strike sample in a separate sorbent tube for 10 min. After the current continuous hourly sample is completed, the GC suspends the continuous mode for one hour to analyze the strike sample. After the strike sample is analyzed and if there is no other strike sample waiting, the GC resumes continuous mode.

Auto-GC in Dual-Mode – System Schematic



Summary
Canister
Low capital investment
Long waiting time for results
Auto-GC
High capital investment
Immediate sample analysis
Can be configured in three ways:
Continuous mode – conventional Auto-GC - best for monitoring on-going exposure
Triggered mode - best for studying episodic events
Dual-mode – combining the benefits of the above two modes with minimal investment
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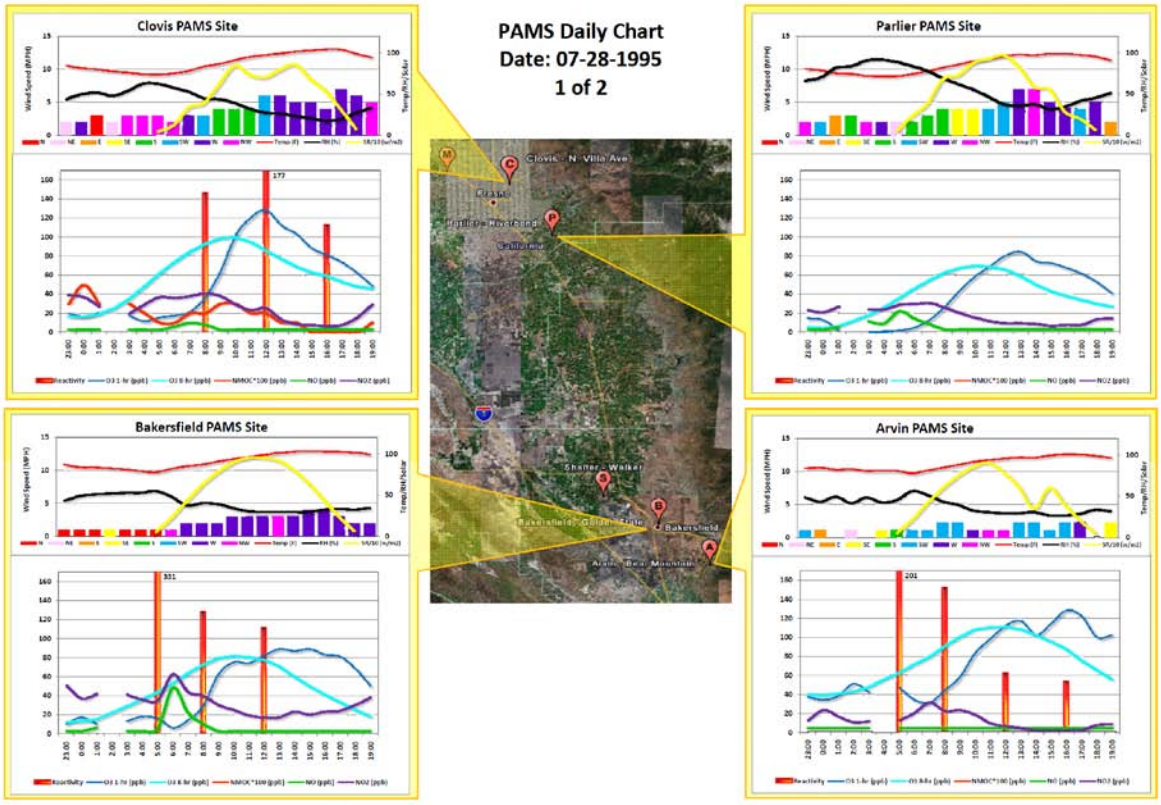
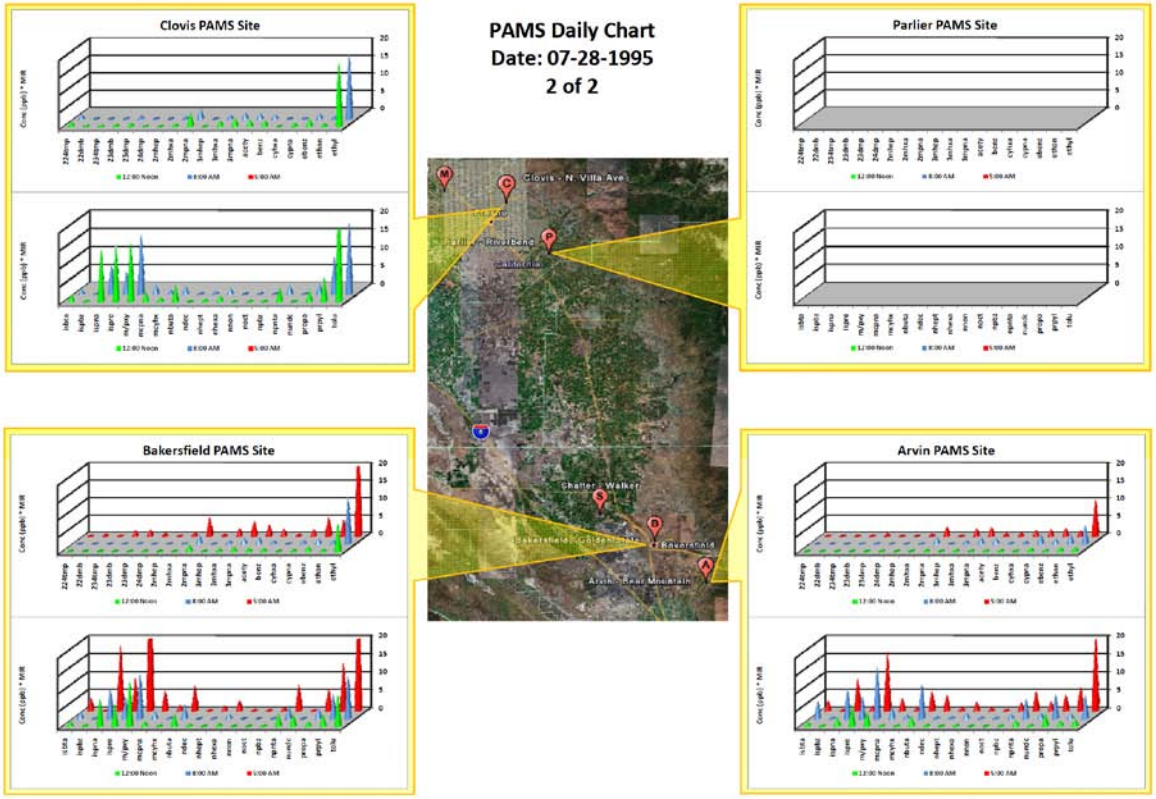
Attachment 2


Clovis PAMS Site
PAMS Daily Chart
Date: 07-28-1995
1 of 2
Parlier PAMS Site
Bakersfield PAMS Site
Arvin PAMS Site


PAMS Daily Chart
Date: 07-28-1995
2 of 2
Clovis PAMS Site
Parlier PAMS Site
Bakersfield PAMS Site
Arvin PAMS Site
Clovis - N. Villa Ave
Shafter - Walker
Bakersfield - Golden Hills
Bakersfield
Arvin - Bear Mountain