Preliminary Comments from Members of the Clean Air Scientific Advisory Committee CASAC Air Monitoring and Methods Subcommittee (AMMS) As Of May 13, 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.

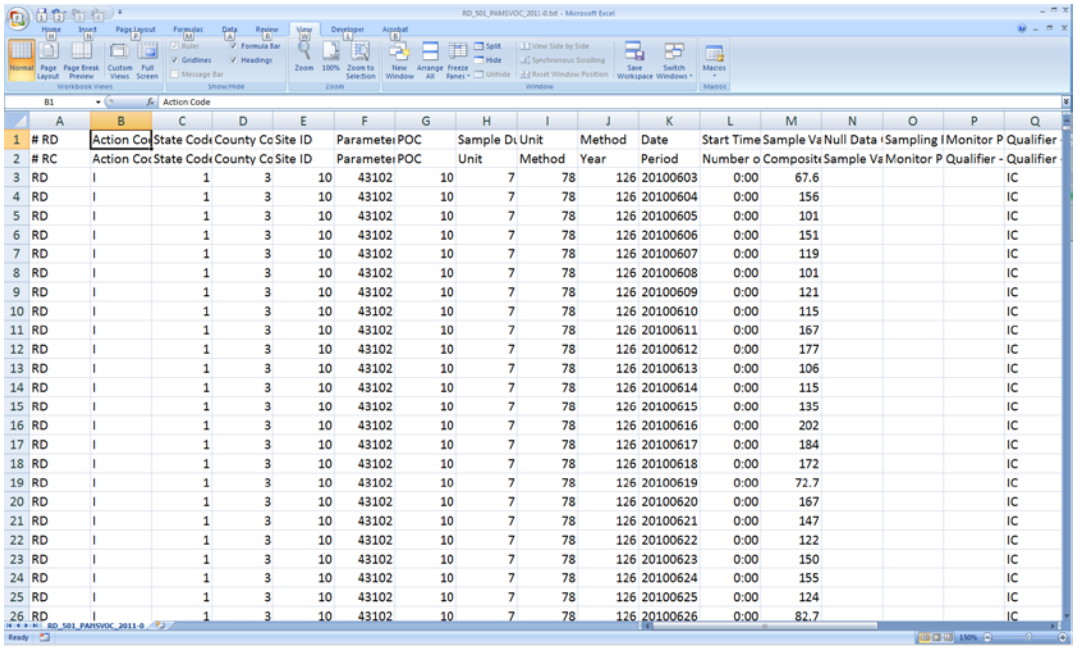
Preliminary Comments from Dr. Judith Chow

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. 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. 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. 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.

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. 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.

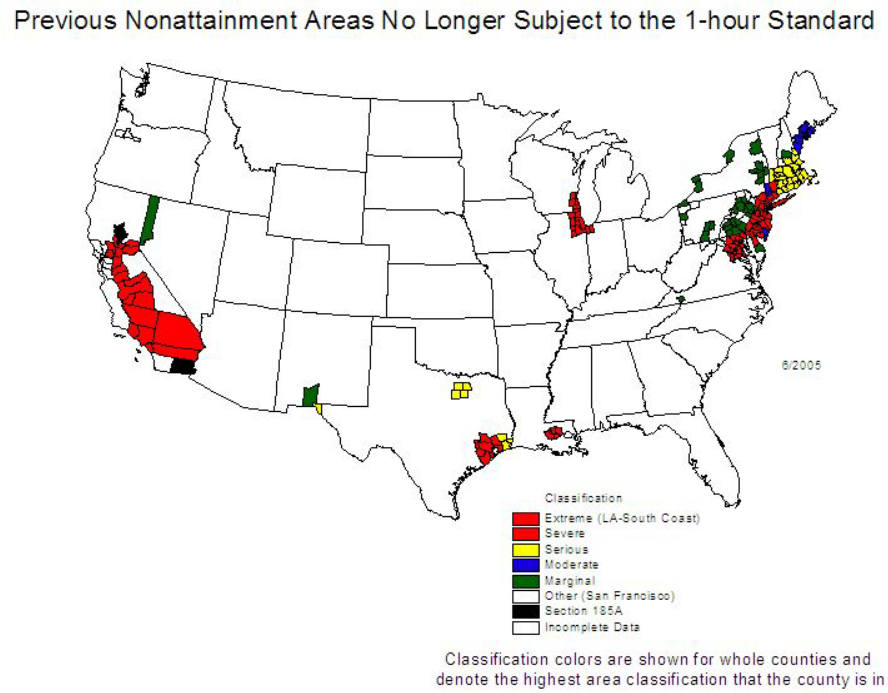

Figure CQ4-1. Classifications of ozone nonattainment areas under previous 1-hour standard.

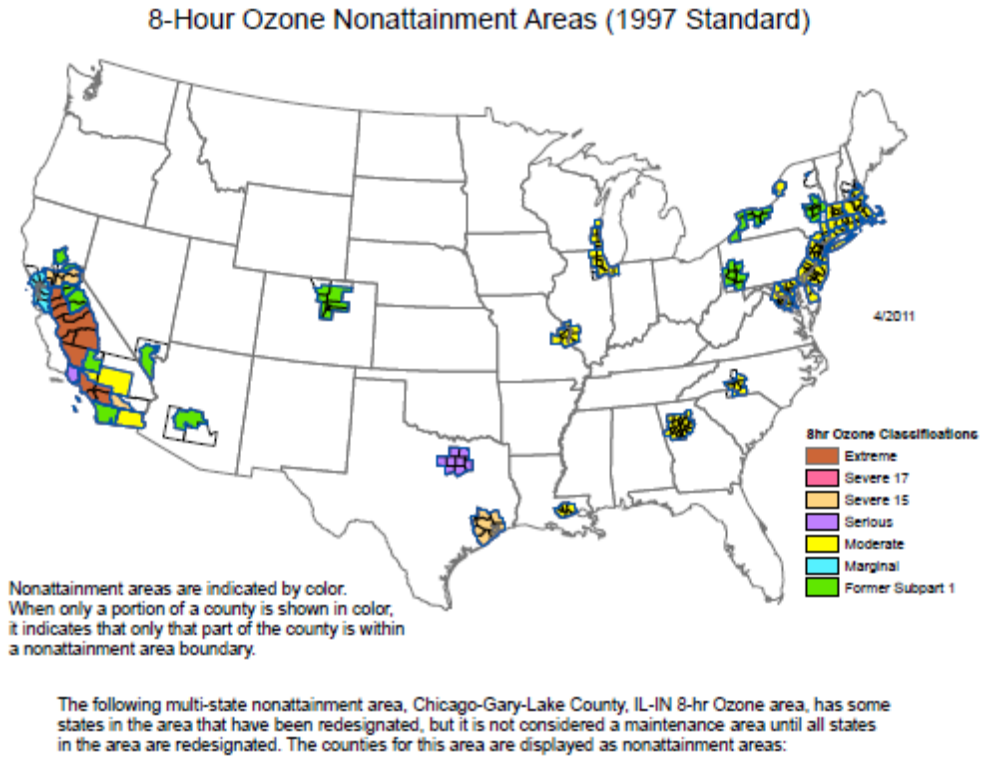

Figure CQ4-2. Classifications of ozone nonattainment areas under 1997 8-hour standard.

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).

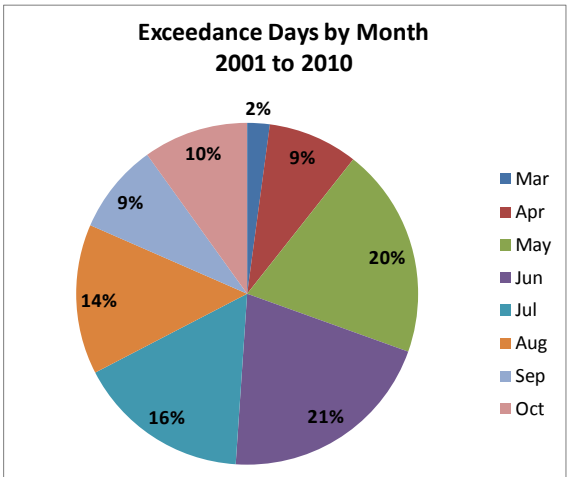

Figure CQ8-1. Ozone exceedance days by month in the Baton Rouge nonattainment area (courtesy of Tim Bergeron, Louisiana Dept. of Environmental Quality)

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.

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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 configuration 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

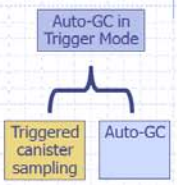
- Auto-GC
  - Sophisticated
  - Continuous operation
  - High capital cost; it becomes more cost effective when there are a lot of samples
  - Quick turnaround; near real-time if automated

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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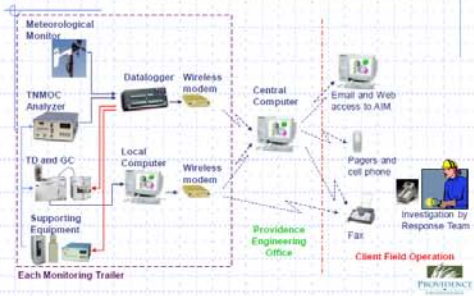
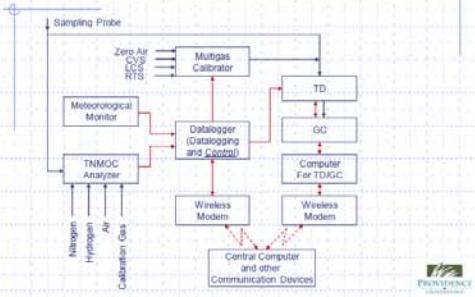
System Description

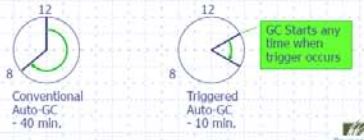


System Schematic



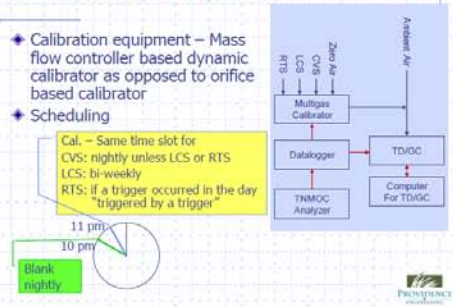
GC Sampling Time

- 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

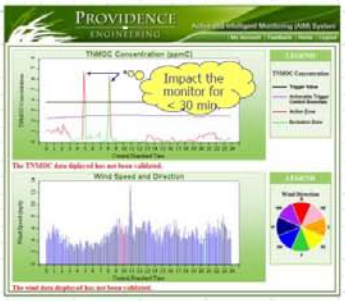
- Calibration equipment – Mass flow controller based dynamic calibrator as opposed to orifice based calibrator
- Scheduling



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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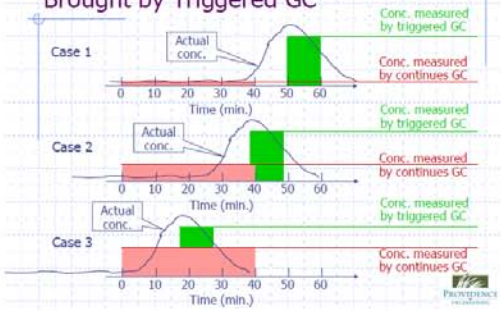
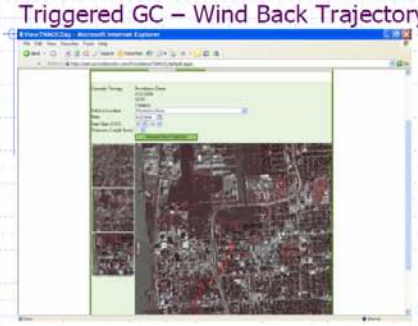
New Feature Brought by Triggered GC



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



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

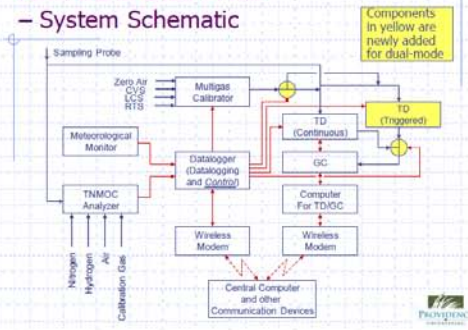
Summary for Trigger Mode

- 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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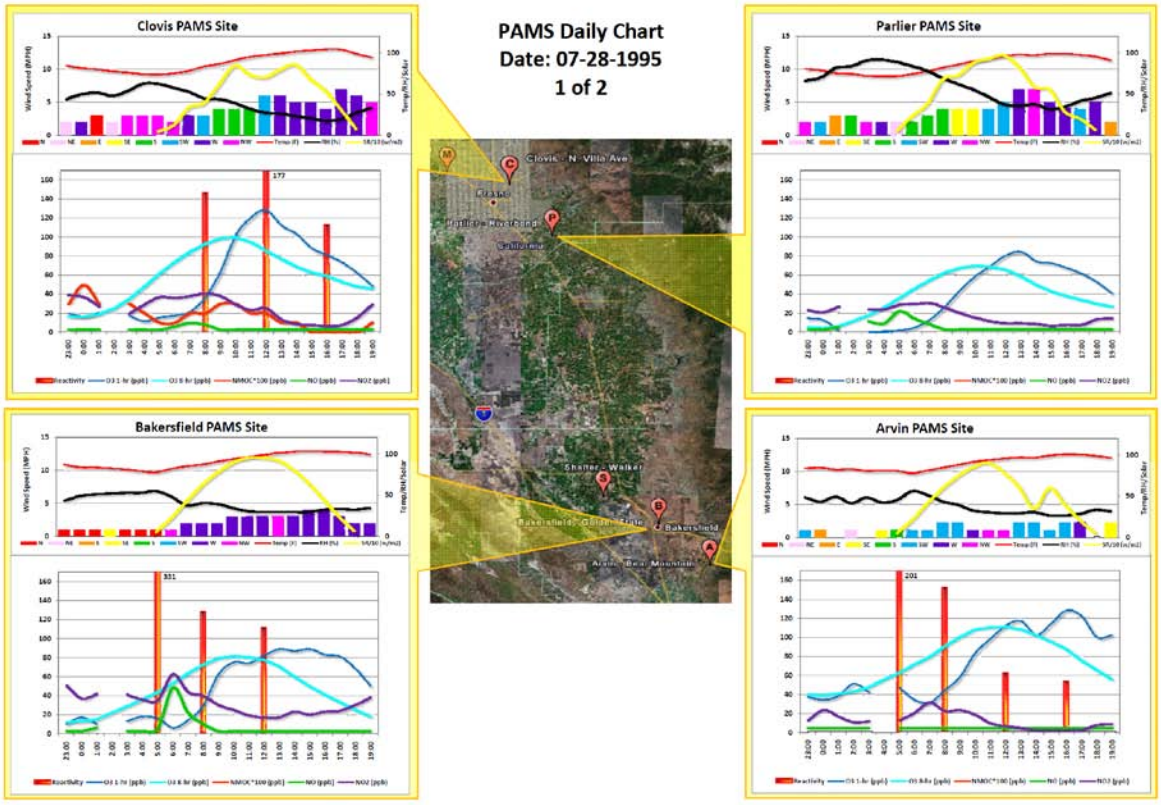
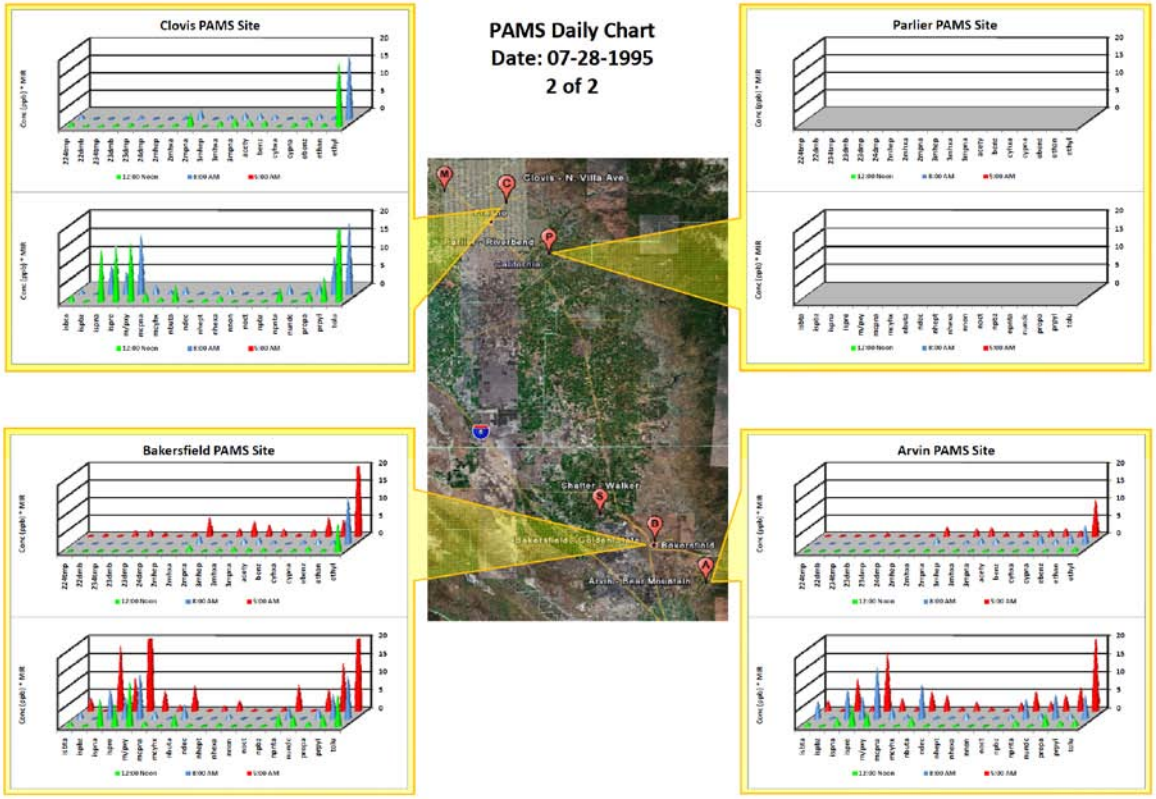
Attachment 2


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


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