

Clean Air Scientific Advisory Committee (CASAC) Air Monitoring and Methods Subcommittee (AMMS) Advice on EPA's draft plans for Photochemical Assessment Monitoring Stations (PAMS) Network Re-engineering.

Rationale for Re-engineering of PAMS

The first PAMS sites began operation in 1994, and as such, have been in operation for over 15 years. Many changes have occurred during those times that have changed the ozone problem in the US as well as our understanding of it. The following paragraphs provide some of the reasons the EPA feels it is necessary to review the PAMS program at this time.

The ozone standard has been revised since the PAMS program was implemented. On July 18, 1997, the EPA revised the ozone NAAQS to a level of 0.08 parts per million (ppm), with a form based on the 3-year average of the annual fourth-highest daily maximum 8-hour average O₃ concentration (68 FR 614). On March 28, 2008, the EPA again revised the ozone standard to a level of 0.075 ppm, with a form based on the 3-year average of the annual fourth-highest daily maximum 8-hour average O₃ concentration (73 FR 16436).¹

These changes in the level and form of the ozone NAAQS, along with notable decreases in ozone levels in most parts of the US, have changed the landscape of the ozone problem in the US (see Figure 1). The initial nonattainment designations for the previous 1-hour ozone standard (in 1991) reflected 21 areas classified as serious (or above), while the initial nonattainment designations for the new 8-hour ozone standard (in 2005) reflected only 5 areas classified as serious (or above). While the number of serious and above areas decreased, the number of non-attainment areas remained nearly the same. This indicates the current 8-hour ozone problem is geographically broader compared to the previous 1-hour ozone problem, although extreme concentrations occur less frequently.

¹ This revision is currently under reconsideration, and the EPA has proposed that the level of the ozone NAAQS be set in a range between 0.060 and 0.070 ppm (75 FR 2938). It is unclear at this time when this proposal will be finalized.

Ozone Air Quality, 1980 - 2009
 (Based on Annual 4th Maximum 8-Hour Average)
 National Trend based on 255 Sites

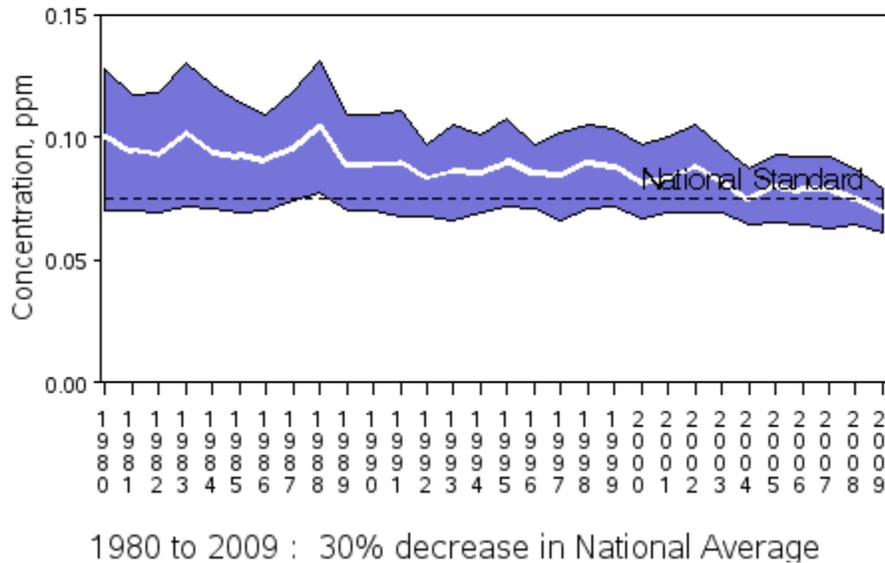


Figure 1. Ozone Trends in the United States²

As discussed above, the PAMS program has been in operation for more than 15 years, and has developed a large database of precursor and meteorology measurements. However, concerns are often voiced at various stakeholder meetings that PAMS data are not being used enough. Considering the resources dedicated to the PAMS program (EPA provides \$14 million annually in STAG 105 funding), the EPA feels it is important to determine if improvements to the PAMS program could be made to make the data more useful to its intended users. Various stakeholders including NACAA and state/local monitoring and modeling staff have been asking for a review of the PAMS program.

Furthermore, much of the equipment used at PAMS sites is old and in need of replacement. Before recapitalizing the network we believe we should reevaluate the equipment used at PAMS. New technologies have been developed since the inception of the PAMS program that should be considered for use.

For these reasons, the EPA has undertaken a project to re-evaluate the PAMS program. The remainder of this memorandum discusses the following aspects of the PAMS program and contains charge questions for the CASAC AMMS:

- Program objectives,
- Network design,

² Source: EPA Air Trends website, <http://www.epa.gov/airtrends/ozone.html>

- Monitoring period,
- VOC measurements,
- Nitrogen measurements,
- Meteorological measurements,
- Pollutant profile measurements, and
- Data analysis needs.

Program Objectives

We believe it is important to start this process with an evaluation of the program objectives and their associated data needs. The following objectives for the PAMS program were established during the initial implementation of the PAMS program (EPA, 1998):

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

During the evaluation of objectives for PAMS, new monitoring objectives should be considered that may add value to the program by supporting other monitoring program objectives (e.g., improving ozone forecasting, measurement of secondary organic aerosol (SOA) precursors, air-toxics measurements, and global climate change).

The program objectives will determine the data needs and strongly influence selection of network design and measurement technology. With this in mind, please consider the following charge questions.

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

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

Network Design

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

- ***Type 1 Sites: Upwind and background characterization site.*** These sites are established to characterize upwind background and transported ozone and its precursor concentrations entering the area and will identify those areas which are subjected to overwhelming incoming transport of ozone. The #1 sites are located in the predominant morning upwind direction from the local area of maximum precursor emissions and at a distance sufficient to obtain urban scale³ measurements. Typically, these sites will be located near the upwind edge of the photochemical grid model domain.
- ***Type 2 Sites: Maximum ozone precursor emissions impact site.*** These sites are established to monitor the magnitude and type of precursor emissions in the area where maximum precursor emissions representative of the MSA/CMSA are expected to impact and are suited for the monitoring of urban air toxic pollutants. The #2 Sites are located immediately downwind (using the same morning wind direction as for locating Site #1) of the area of maximum precursor emissions and are typically placed near the downwind boundary of the central business district (CBD) or primary area of precursor emissions mix to obtain neighborhood scale measurements. Additionally, a second #2 Site may be required depending on the size of the area, and should be placed in the second-most predominant morning wind direction.
- ***Type 3 Sites: Maximum ozone concentration site.*** These sites are intended to monitor maximum ozone concentrations occurring downwind from the area of maximum precursor emissions. Locations for #3 Sites should be chosen so that urban scale measurements are obtained. Typically, these sites are located 10 to 30 miles from the fringe of the urban area.

³ Urban scale defines concentrations within an area of city-like dimensions, on the order of 4 to 50 kilometers. Within a city, the geographic placement of sources may result in there being no single site that can be said to represent air quality on an urban scale. Neighborhood scale defines concentrations within some extended area of the city that has relatively uniform land use with dimensions in the 0.5 to 4.0 kilometers range. The neighborhood and urban scales have the potential to overlap in applications that concern secondarily formed or homogeneously distributed air pollutants.

- Type 4 Sites: Extreme downwind monitoring site. These sites are established to characterize the extreme downwind transported ozone and its precursor concentrations exiting the area and will identify those areas which are potentially contributing to overwhelming ozone transport into other areas. The #4 Sites are located in the predominant afternoon downwind direction from the local area of maximum precursor emissions at a distance sufficient to obtain urban scale measurements. Typically, these sites will be located near the downwind edge of the photochemical grid model domain.

As discussed earlier, in 2006 the EPA revised the minimum PAMS monitoring requirements to allow PAMS monitoring to be more customized to local data needs and to use the associated resources for other types of monitoring they consider more useful. The minimum network design requirements were decreased from requiring a minimum of four PAMS sites per PAMS area to a minimum of two sites in each PAMS area. A Type 2 site is required as well as either a Type 1 or Type 3 site. However, most PAMS areas currently have more than the minimum required number of sites. Figure 2 provides a map of the current PAMS network.

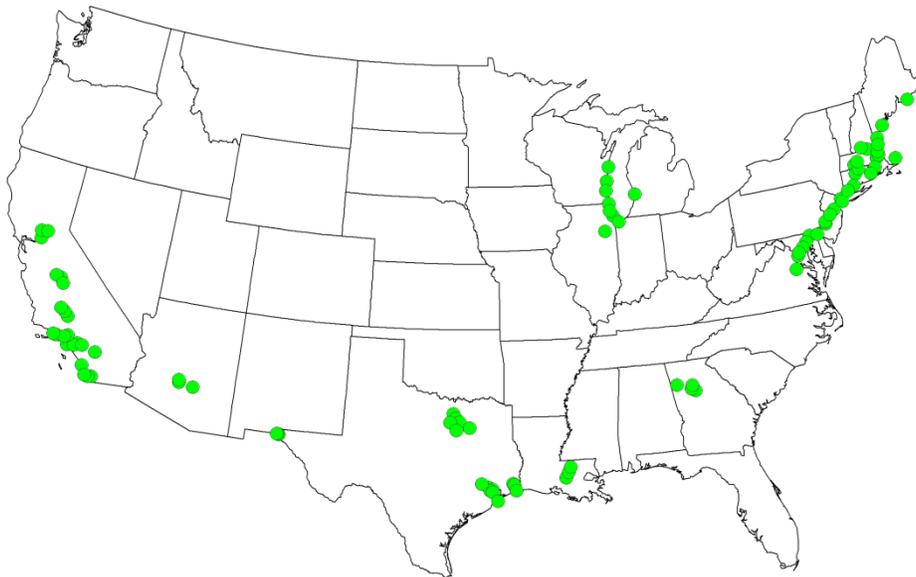


Figure 2. Map of Current PAMS

As can be seen in Figure 2, the location of the PAMS areas also strongly influences the current network design. Most PAMS areas are near the coasts, resulting in limited spatial coverage for the rest of the US.

The current network design appears well suited for some of the program objectives but is less well suited for others. For example, the data collected appears most useful to data users evaluating control strategies for specific PAMS areas (e.g., SIP planners). However, the

usefulness of the data for model development and evaluation may be limited due to the poor spatial coverage and proximity to coastal environments.

Also, with data from a relatively few fixed sites per PAMS area, the spatial coverage of a PAMS-based emissions inventory evaluation may be limited. Supplemental special purpose measurements, such as mobile monitoring, may help provide greater spatial coverage, but may only be possible in situations where resources permit.

Considering the priority of the various objectives discussed earlier, please address the following charge questions.

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?

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?

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)?

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

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?

Monitoring Period

PAMS precursor monitoring must be conducted annually throughout the months of June, July and August (as a minimum) when peak O₃ values are expected in each area. Alternate precursor monitoring periods may be submitted for approval to the Administrator as a part of the annual monitoring network plan. Limiting the PAMS season to these three months saves resources by not requiring sampling during the off season. However, the usefulness of the data for model development and evaluation again may be limited due to only measuring when conditions favor high ozone formation.

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?

VOC Measurements

PAMS Target List

Creating a database of VOC measurements is one of the main goals for the PAMS program. A list of VOCs to measure was identified early in the implementation of the program, and only a few minor changes have been made to the list since (EPA/OAQPS, PAMSgram Volume 9, 1998). Table 1 lists the current target VOC compounds being measured at PAMS sites (EPA/OAQPS, PAMSgram Volume 18, 2000).

Table 1. PAMS Target Volatile Organic Compounds

AQS Code	Target Compound Name	AQS Code	Target Compound Name
43203	Ethylene	43249	3-Methylhexane
43206	Acetylene	43250	2,2,4-Trimethylpentane (Isooctane)
43202	Ethane	43232	n-Heptane
43205	Propylene	43261	Methylcyclohexane
43204	Propane	43252	2,3,4-Trimethylpentane
43214	Isobutane	45202	Toluene
43280	1-Butene	43960	2-Methylheptane
43212	n-Butane	43253	3-Methylheptane
43216	trans-2-Butene	43233	n-Octane
43217	cis-2-Butene	45203	Ethylbenzene
43221	Isopentane	45109	m/p-Xylene
43224	1-Pentene	45220	Styrene
43220	n-Pentane	45204	o-Xylene
43243	Isoprene (2-Methyl-1,3-Butadiene)	43235	n-Nonane
43226	trans-2-Pentene	45210	Isopropylbenzene
43227	cis-2-Pentene	45209	n-Propylbenzene
43244	2,2-Dimethylbutane	45212	m-Ethyltoluene (1-Ethyl-3-Methylbenzene)
43242	Cyclopentane	45213	p-Ethyltoluene (1-Ethyl-4-Methylbenzene)
43284	2,3-Dimethylbutane	45207	1,3,5-Trimethylbenzene
43285	2-Methylpentane	45211	o-Ethyltoluene (1-Ethyl-2-Methylbenzene)

43230	3-Methylpentane	45208	1,2,4-Trimethylbenzene
43245	1-Hexene ⁴	43238	n-Decane
43231	n-Hexane	45225	1,2,3-Trimethylbenzene
43262	Methylcyclopentane	45218	m-Diethylbenzene
43247	2,4-Dimethylpentane	45219	p-Diethylbenzene
45201	Benzene	43954	n-Undecane
43248	Cyclohexane	43141	n-Dodecane ⁴
43263	2-Methylhexane	43102	TNMOC
43291	2,3-Dimethylpentane	43000	PAMHC

As part of the review, EPA wishes to revisit the PAMS target list. At this point we have collected over 15 years of concentration data on these target compounds. A review of concentrations seen in the Northeast has been initiated by NESCAUM. This review indicates that a number of target compounds are rarely seen at concentrations that would significantly impact ozone formation. As part of this review, EPA intends to perform similar analyses for the remainder of the PAMS areas. Based on this review, we hope to identify a smaller list of compounds. A smaller list may be desirable for two reasons. First, a small amount of savings may be had due to a decrease in analysis and reporting costs due to the lower number of compounds. More importantly, as will be discussed in the next section, a dual GC-detector is needed to analyze the complete list of target compounds. It may be possible to reduce the complexity and the cost of the GC needed with a shorter list of priority compounds.

In addition to removing compounds, we are also considering adding compounds as a number of additional compounds can be measured using the same technology used to measure the target VOCs. A number of biogenic compounds play an important role in ozone formation. Isoprene is currently being measured; however, measurements of other important biogenic compounds such as monoterpenes, sesquiterpenes, and methyl butenol may also be important. We believe that the addition of certain compounds that may have importance for other non-ozone objectives such as air toxics, and SOA formation should also be considered as part of the overall PAMS framework.

Finally, as discussed earlier, carbonyls were removed from the list of compounds to be measured in serious PAMS areas and are just measured in severe and extreme non-attainment areas because of concerns with the uncertainty associated with the data due to monitoring methods. If solutions to the monitoring methods can be addressed, it may be desirable to add carbonyls to the PAMS target list for all required sites.

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

⁴ These compounds have been added as calibration and retention time standards primarily for the purpose of retention time verification. They can be quantified at the discretion of the user.

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

Speciated VOC Sampling Methods

Monitoring agencies are required to measure the target VOC species at two locations in each PAMS area during the PAMS monitoring period. Three options are currently allowed for making the required measurements:

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

While these options provide flexibility, they also add complexity to the data set which may hamper data usage. A number of commercially available field auto-GCs have been developed since the inception of the PAMS program that may make the use of auto-GCs a superior option over the canister options. These systems are smaller and easier to use than the auto-GCs available when the PAMS program was initiated.

Due to the mixture of compounds in the target VOCs list, a dual GC with multiple detectors is needed to measure the complete list of target VOCs. As discussed above, a review of the target list will be performed as part of this list. One reason for the review of the list will be to determine if a reduced target list can be developed that allows for a single GC/detector system which would be both less expensive and less complicated.

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

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

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

Carbonyls

Carbonyls were identified as an important precursor to ozone and were added to the original target list. Compendium Method TO-11A is used to measure carbonyl compounds. In this method, a cartridge containing a solid sorbent is used to capture the carbonyl compounds. Sample analysis is accomplished using high performance liquid chromatography with ultraviolet/visible detection. During the late 1990s, a review of the method was performed. A number of issues were identified, including:

- Effects due to temperature and relative humidity,
- Ozone interferences,
- Media affects,
- Sample duration and breakthrough issues, and
- Affects due to sampler design.

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

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

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

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

Nitrogen Measurements

Nitrogen oxides play a major role in ozone formation. As such, measurements of ambient nitrogen oxide (NO) and nitrogen dioxide (NO₂) are required at all Type 2 sites. In recognition of the importance of other reactive nitrogen compounds to the photochemical activity, measurements of total reactive nitrogen (NO_y) were added to the required measurements for Type 1 and/or Type 3 sites in 2006.

Nitrogen dioxide measurements from conventional NO_x monitors have been shown to be positively biased because the converters used are not selective to NO₂ but also convert some portion of other nitrogen species (PAN, HONO, HNO₃) to NO which is then reported as NO₂. Advances in NO₂ measurement techniques allow for the direct measurement of NO₂ or more selective conversion of NO₂ (i.e., photolytic converter) which would provide for a more accurate NO₂ measurement.

Total reactive nitrogen (NO_y) use a conventional molybdenum converter which has been moved to the inlet and operated at a slightly higher temperature in an attempt to convert all reactive nitrogen species to NO. While these systems provide a fuller understanding of total reactive nitrogen, they do not give a NO_2 measurement. Some effort has been made to develop a single analyzer capable of measuring NO, NO_2 , and NO_y .

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?

Pollutant Profile Measurements

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

One project that may be of particular interest to the PAMS program is *In-Service Aircraft for a Global Observing System* (IAGOS, <http://www.iagos.org/>) which is based on the prior *Measurement of Ozone, Water Vapor, Carbon Monoxide and Nitrogen Oxides Aboard Airbus In-Service Aircraft* (MOZAIC) program (1994-2010) that measured trace gases from instruments aboard Lufthansa, Air France, Austrian Airlines, Sabina Airlines and Air Namibia aircraft. IAGOS will establish and operate a distributed infrastructure for longterm observations of atmospheric composition, aerosol and cloud particles on a global scale from a fleet of initially 10-20 longrange in-service aircraft of non-US based internationally operating airlines. IAGOS deploys newly developed high-tech instruments for regular in-situ measurements of atmospheric chemical species (O_3 , CO, CO_2 , NO_y , NO_x , H_2O), aerosols and cloud particles. All IAGOS aircraft will contain instruments to measure O_3 , CO, relative humidity, and cloud droplet backscatter with the potential to host one additional instrument package to measure one of the following: 1) NO_x , 2) NO_y , 3) CO_2+CH_4 , or 4) particulate matter (PM) size distribution and composition (can detect soot, volcanic ash and dust). The data will be available in near real time to weather services and GMES service centers. Currently, the planes used in the IAGOS will be non-US carriers, but are expected to make transatlantic flights into the US such as the previous MOZAIC program. Destination airports are likely to be major airports such as Atlanta, Chicago, Los Angeles, New York City, Philadelphia, or Washington Dulles which are synergistic with the locations of the PAMS. However these destination airports may or may not receive enough profiles for continuous monitoring due to the fact that individual commercial aircraft undergo frequent route reassignments. IAGOS data are best suited for continuous monitoring above airports that serve as hubs for the host airline, as the planes serve these airports most frequently. EPA and NOAA along with other agencies are looking into options to expand this effort into US based aircraft, thus having US based airlines at US hubs to provide a

continuous monitoring capability on ozone and nitrogen oxide profiles over major US airports which are often coincident with PAMS.

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?

Meteorological Measurements

In addition to speciated VOCs and reactive nitrogen, state and local monitoring agencies are required to make both surface and upper-air meteorological measurements. Although the PAMS rule establishes a requirement for meteorological monitoring, it does not provide specifics; e.g., a list of the meteorological variables to be monitored. Discussions to develop such a list took place in the spring of 1994, and a recommended list of parameters was eventually included in the technical assistance guidance document. The current list of recommended parameters include wind direction, wind speed, temperature, humidity, atmospheric pressure, precipitation, solar radiation, UV radiation, and mixing height. While upper air wind speed and direction were not listed as recommended parameters, the PAMS TAD appears to strongly encourage such measurements.

At the time of the original PAMS requirements, a number of options were identified to obtain the upper air data. These options range from periodic rawinsondes (4 times per day) to continuous systems such as SODAR and RADAR profilers. However, most areas opted to install RADAR profilers due to the limitations of SODAR (limited vertical range) and the labor involved with rawinsondes. These RADAR profilers are now old and in need of expensive upgrades or replacement.

Due to the expense of RADAR profilers, we are interested in alternatives to collecting mixing height data and upper air wind speed data. Relatively less expensive alternatives have been developed since the initiation of the PAMS program which will provide continuous real time estimates of mixing height. For example ceilometers are capable of estimating mixing height by measuring the change in aerosol concentration at the boundary layer.

The National Oceanic and Atmospheric Administration (NOAA) maintains a network of upper air systems collecting data that may be suitable for use in the PAMS program (<http://www.profiler.noaa.gov/npn/>). However, the current network focuses on the south-west states to assist in forecasting and detecting severe weather. NOAA also runs a program dedicated to combining upper air data from multiple cooperating agencies (<http://madis-data.noaa.gov/cap/profiler.jsp>). We are interested in exploring if and how the NOAA upper air data can be used to meet the PAMS upper air data needs.

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

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

Data Analysis Needs

As part of the grant guidance EPA provides for how the PAMS grant money should be utilized, the EPA states that 25% of the PAMS funds should be spent on data analysis. However, over the years, states and EPA have been criticized for not using PAMS data more than it currently is.

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

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

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

References

EPA. (1998). *TECHNICAL ASSISTANCE DOCUMENT FOR SAMPLING AND ANALYSIS OF OZONE PRECURSORS*. Retrieved from AMTIC:
<http://www.epa.gov/ttn/amtic/files/ambient/pams/newtad.pdf>

EPA/OAQPS. (2000, June 2000). *PAMSgram Volume 18*. Retrieved from AMTIC:
<http://www.epa.gov/ttn/amtic/files/ambient/pams/pamsgrm18.pdf>

EPA/OAQPS. (1998, March). *PAMSgram Volume 9*. Retrieved from AMTIC:
<http://www.epa.gov/ttn/amtic/files/ambient/pams/gram9.pdf>

National Academy of Science. (1992). *Rethinking the Ozone Problem in Urban and Regional Air Pollution*. http://www.nap.edu/catalog.php?record_id=1889: National Academies Press.