



*Photochemical Assessment Monitoring Stations (PAMS) Issue Summary*

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## **Preface**

This document contains information compiled from feedback provided by a work group of EPA and Regional EPA staff involved in Photochemical Assessment Monitoring Stations (PAMS) implementation. The role of the work group was to discuss and identify issues related to PAMS, identify goals related to each issue, and communicate current activities in each area. Comments on this document are invited. Please address comments to:

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## PAMS Issue Summary

Since the PAMS (Photochemical Assessment Monitoring Stations) program officially began in 1994, a tremendous amount of data has been generated from ozone, oxides of nitrogen (NO<sub>x</sub>), meteorological, carbonyl and hydrocarbon measurements. Having successfully progressed through the planning and implementation phases, the PAMS program is has shifted in focus to the analysis and interpretation of the data generated. As the first national ozone precursor monitoring network that is routine in nature, the PAMS network has become a model network for the collection of ozone precursors and also afforded a variety of opportunities for the data analysis community. Not only is the data from this network being used by the PAMS community for establishing trends, evaluating ozone nonattainment conditions, developing ozone control strategies, and model input and evaluation, but it is also of interest to the expert community. For example, PAMS data is of interest to the PM<sub>2.5</sub> species data analysis community in understanding the photochemical oxidation process leading to ozone formation and the identification of possible relationships between the chemistry of particle formation from precursor gases such as sulfur oxides, NO<sub>x</sub>, and volatile organic compounds (VOCs).

The network is a success; however, issues remain that need to be addressed in order to continue improving the quality of the data being generated. Review of the PAMS network and identification of key issues provides an opportunity to make improvements to the program and continue improving upon the data collection and data quality efforts. This review process is an informal beginning to the Data Quality Assessment (DQA) phase of the program, a phase of a maturing program that logically follows the planning and implementation phases. A work group was formed by the OAQPS (Office of Air Quality Planning and Standards) that consists of Regional PAMS contacts, OAQPS PAMS team members, and the ORD (Office of Research and Development). The role of this work group was to discuss and identify the key PAMS issues, identify goals, and communicate current activities in each of the areas. This issue summary paper is based on the work group's efforts.

The top ten issues compiled from input provided by the PAMS Review work group are as follows:

**Carbonyl Measurements**  
**Data Quality Assessment**  
**NO<sub>y</sub> Measurements and Guidance**  
**Canister versus Continuous, Automated GC Measurements**  
**Measurements of "true" NO<sub>2</sub>**  
**Precision and Accuracy (P&A) Guidance**  
**Data Validation**  
**VOC Measurements**  
**Improving Data Accessibility**  
**Regional Data Analysis**

The following includes an expanded discussion and the primary goals for each of the top ten issues. Although not specifically identified, there are currently several activities on-going in almost all ten areas as a result of EPA, Regional and State efforts. This document will be used as a starting point for the development of a short and long-term OAQPS, EMAD (Emissions, Monitoring, and Analysis Division) plan for PAMS.

## **Carbonyl Measurements**

The integrity of the field sampling devices and lack of field audit and sampling protocols are key carbonyl sampling issue for PAMS. Failures of the sampling equipment as a result of leaks have been recently experienced as the network and equipment is aging. Carbonyl sampling equipment leaks are often extremely difficult to detect and often go unnoticed until data quality or other quality assurance (QA) issues indicate a problem. Collocated sampling with duplicate equipment is sometimes used to aid in problem diagnosis but State agencies often do not have the equipment or expertise needed to perform this sampling. There is currently no field audit procedures for carbonyl sampling at PAMS; however, development of a procedure is currently being pursued by OAQPS.

Quality assurance is particularly important in light of disagreement between data obtained by sampling systems at some of the PAMS sites. The basis for disagreement has not been specifically identified but could be one of the documented problems associated with sample collection. Complete guidance for establishing quality assurance using existing equipment needs to be developed. Alternatives to the dinitrophenylhydrazine (DNPH) approach include a real-time formaldehyde monitor which is being tested beginning in June 1998 by the ORD.

The current carbonyl sampling method will also benefit from improved precision and accuracy (P&A) measurements. The lack of required measures for P&A can lead to sampling problems going unnoticed for extended time periods or not being noticed at all. Collocated sampling with duplicate equipment is sometimes used to detect a problem but State agencies and EPA Regions often do not have the equipment or the expertise to quickly diagnose, troubleshoot and fix the problem. A sampler bias may be identified between collocated samplers at a site but the source of the problem may not be found before the PAMS season ends, since the season is short and data analysis turnaround time is long. Any potential solutions tried in the field may prove ineffective since data may not be readily available.

***Goal:*** *Develop guidance and standardized procedures for carbonyl measurements and field QA at PAMS. Implementation of real-time formaldehyde monitoring will be considered as this technology develops.*

## **Data Quality Assessment (DQA)**

A Data Quality Assessment (DQA) is the scientific and statistical evaluation of data to determine if the data obtained are of the right type, quality, and quantity to support the intended use. The DQA process naturally follows the program planning and implementation phases. Questions to be addressed during the DQA process include: What is the quality of the data generated? Does the data meet the original data quality objectives (DQOs)

established for the program? Are changes to the program warranted, such as revision to the target list, methods, DQOs, etc?

Those issues raised by the work group that logically fit under the DQA process are the following:

- **Review Program Objectives** - Review the intended data uses and clarify relationships to other programs (e.g. toxics). Restate or update PAMS program objectives.
- **Revised/updated data quality objectives (DQO)** - Restate or update PAMS DQOs to encompass the revised program objectives and expectations of the PAMS program.
- **Network review** - Evaluate the network design and evaluate the spatial representativeness of the monitors. For example, is more emphasis on VOC monitoring in source (urban) regions and less on downwind areas needed?
- **Validate Data** - Evaluate the data base quality.
- **Sampling frequency, especially for carbonyls** - Review sampling frequency in conjunction with network design to determine if program objectives and DQOs are met. For example, does the re-engineered minimum sampling frequency for carbonyls meet the data use needs?
- **Review target list and expand measurements** - Expansion or reduction of the PAMS target list to include naturally occurring aldehydes (i.e. butanal-decanal, biogenics, aldehydes), NO<sub>2</sub>, CO, methane, and SO<sub>2</sub>; or remove compounds no longer important to photochemical processes. Need agreement on prioritization of species (NO, NO<sub>y</sub>, NO<sub>2</sub>) to incorporate into PAMS. Other compounds may be outside of the program objectives for PAMS and more suited as ORD research priorities.

**Goal:** *Perform a DQA in accordance with QA/G-9.*

## **NO<sub>y</sub> Measurements and Guidance**

There is a need to develop more detailed guidance for NO<sub>y</sub> instrument calibrations and measurements. There is increasing concern regarding the suitability of NO<sub>y</sub> reduction methods due to possible interferences from reduced nitrogen species which are not associated with NO<sub>x</sub> or its oxidation products. It has been suggested that through-the-inlet additions of HNO<sub>3</sub> and HCN or NH<sub>3</sub> be performed to evaluate the methodology.

**Goal:** *Develop standardized procedures for the measurement of NO<sub>y</sub> (including calibration and operational procedures).*

## **Canister Versus Hourly GC Measurements**

One of the PAMS DQOs is to provide additional measurements that can be used to evaluate population exposure to air toxics. Collection of one 24-hour canister every sixth day, year round, is a requirement of PAMS Type #2 sites. Annual mean toxic air pollutant concentrations can be calculated to help estimate the average exposure of the population in urban environments to individual VOCs which are considered toxic. By measuring the target PAMS

VOCs a subset of toxic pollutants are also measured. The additional use of PAMS for air toxics monitoring allows for the consideration of air toxics impacts in the development of future ozone control strategies. The comparability of these techniques for the PAMS target analytes has not been fully evaluated.

**Goal:** *Determine the comparability between data collected by the two measurement techniques for a select group of representative species.*

### **Measurements of “true” NO<sub>2</sub>**

The measurement of NO<sub>2</sub> is a primary data need expressed by the modeling community. This measurement is based on surface conversion of NO<sub>2</sub> to NO and the subsequent detection of NO using the well characterized chemiluminescence technique. Though simple and rugged, surface conversion techniques have proven relatively non-specific for NO<sub>2</sub>. Because these surfaces can convert other nitrate compounds to NO, these techniques tend to overestimate NO<sub>2</sub>. The combined chemiluminescence of NO present in the ambient sample as well as the photolysis-generated NO from the sampled NO<sub>2</sub> are detected. Because the conversion of NO<sub>2</sub> to NO by photolysis is less than unity, a separate, accurate, parallel determination of NO must be made if NO<sub>2</sub> is to be measured accurately.

**Goal:** *Work with ORD to develop and implement a research strategy for obtaining "true" NO<sub>2</sub> measurements.*

### **Precision and Accuracy Guidance**

Although precision and accuracy (P&A) checks are required for all types of PAMS monitors, guidance has not yet been issued for conducting and reporting VOC P&A checks due to the significant number of target compounds and the non-trivial issues associated with collocated measurements or dual analyses. Since guidance is pending, no VOC P&A data has been reported to AIRS. However, many reporting organizations utilize some form of P&A audits in their quality assurance program. More prescriptive guidance is needed to ensure national consistency.

**Goal:** *Develop guidance for collecting and submitting precision and accuracy data to AIRS-AQS.*

### **Data Validation**

Quantify/assess/validate the quality of existing data in AIRS and take actions to assure that future PAMS data is of acceptable quality before uploading to AIRS. Develop the appropriate metrics and guidance for use by States to validate PAMS data. Review methods of quality assuring and archiving PAMS data so that the user community is assured of having a readily accessible high quality data base.

**Goal:** *Develop guidance and metrics for validating and ensuring the quality of data prior to AIRS submittal.*

### **VOC Measurements**

Concentrate on providing the highest quality VOC database possible by optimizing the sampling, analysis, and data processing systems currently in place. Several potential problems inherent in the current sampling and analytical approaches have been identified. These typically deal with sample conditioning which includes two stages: (1) the reduction of the water content of the ambient sample; and (2) the preconcentration of VOCs prior to compound separation on the column. Misidentification of compounds separated by gas chromatography on a non-specific detector such as the flame ionization detector (FID) is always a potential problem especially if retention time shifts occur. Software packages to adjust the database for baseline shifts are available commercially.

**Goal:** *Work with ORD to develop and implement a research strategy for VOC measurements.*

### **Improving Data Accessibility**

Lack of real-time or near-real-time access to data has been frustrating to the data use community. There is a need to improve the accessibility and capability to download data as it becomes available from the reporting organizations. Improvements include access to PAMS data via the Internet.

**Goal:** *Provide accessibility of the PAMS data base through the use of the Internet and AIRS data base tools.*

### **Regional Data Analysis**

Carry out routine PAMS data analysis at the Regional level. A part of this effort is the continuing assessment of the quality of the data. As far as data analysis is concerned, many of the objectives have already been stated in general terms and many of the tools and techniques have been identified. Many of the Regional Office staffs have delivered first class work. Foster an interest to share results among the offices which will result in national consistency. Such Regional analyses will also be needed for the PM<sub>2.5</sub> program.

**Goal:** *Regional data analysis reports prepared and distributed annually by all PAMS regions.*