

**LITERATURE REVIEW IN SUPPORT OF
PAMS PROGRAM ASSESSMENT**

**FINAL REPORT
STI-900860-2039-FR**

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PREFACE

This report summarizes a literature review performed as Task 1 of a project for the Northeast States for Coordinated Air Use Management (NESCAUM) and the Mid-Atlantic Regional Air Management Association (MARAMA) to aid in analyzing and interpreting Photochemical Assessment Monitoring Station (PAMS) data and in recommending improvements to PAMS operations. In this task, we reviewed PAMS-related scientific literature, government reports, and previous literature reviews pertaining to analysis of PAMS and PAMS-like data in the NESCAUM and MARAMA regions, in other regions, and in other research and field studies. The report includes summaries of selected key analysis report, recommendations concerning specific data management or analysis techniques that could be applied to PAMS data, and a bibliography.

The goal of this task is to investigate how PAMS (and similar) data have been—or could be—used to meet PAMS objectives, with special emphasis on evaluating potential modifications to the existing network.

This literature review was used in later tasks of the project to help us formulate recommendations concerning monitoring, data management, and data analysis methods that could be applied to PAMS data to meet the PAMS program objectives.

Please refer to Main and Roberts (2001) for final recommendations to the Northeast and Mid-Atlantic States PAMS program.

Main H.H. and Roberts P.T. (2001) Recommendations for the PAMS network in the Northeast and Mid-Atlantic states. Final report prepared for NESCAUM, Boston, MA, by Sonoma Technology, Inc., Petaluma, CA, STI-900860-2067-FR, June. Also available at <http://www.nescaum.org/committees/pams.html>.

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1. INTRODUCTION

This report summarizes a literature review performed as Task 1 of a project for the Northeast States for Coordinated Air Use Management (NESCAUM) and the Mid-Atlantic Regional Air Management Association (MARAMA) to aid in analyzing and interpreting Photochemical Assessment Monitoring Station (PAMS) data and in recommending improvements to PAMS operations.

1.1 TASK OBJECTIVES

The goal of this task is to investigate how PAMS (and similar) data have been – or could be – used to meet PAMS objectives, **with special emphasis on evaluating potential modifications to the existing network**. We reviewed scientific literature, government reports, and previous literature reviews pertaining to analysis of PAMS and PAMS-like data in the NESCAUM and MARAMA regions, in other regions, and in other research and field studies. We provide a review of selected key analysis reports, recommendations concerning specific data management or analysis techniques that could be applied to PAMS data in the NESCAUM and MARAMA regions, and a bibliography.

1.2 PAMS PROGRAM BACKGROUND

1.2.1 Monitoring Information

State and local air pollution control agencies operate the PAMS sites. The PAMS networks typically monitor 56 target hydrocarbons and 2 carbonyl compounds, ozone, oxides of nitrogen (NO_x and/or NO_y), and meteorological measurements. Sample speciation may vary among sites as some agencies report more hydrocarbons and/or carbonyl compounds than the PAMS target list. Differences among analytical techniques also can alter the list (e.g., co-eluters).

The sampling frequency varies among regions, states, and sites in the PAMS program. For example, hydrocarbons are sampled on a 1-hr or 3-hr average basis; may or may not cover a 24-hr period; and are collected every day, every third day, or on an episodic basis. Carbonyl compounds are typically collected as 3-hr averages every third day but other sampling variations exist. Most sites take surface meteorological measurements, including wind speed, wind direction, and temperature reported hourly. PAMS program upper-air meteorological measurement requirements may be met in a number of ways, including using rawinsondes, radar profilers, or twice daily National Weather Service soundings.

The number of PAMS sites varies among metropolitan statistical areas (MSAs). Ozone precursors (volatile organic compounds [VOC] and NO_x) and surface meteorology are required to be measured at two to five sites in an MSA, depending on the MSA population. Upper-air meteorology must be monitored at one representative site in an MSA. PAMS measurements

(U.S. Environmental Protection Agency, 2001) are made at different site types that have different measurement objectives:

- Type 1 – Upwind and background characterization site.
- Type 2 and 2A – Maximum ozone precursor emissions impact site.
- Type 3 – Maximum ozone concentration site.
- Type 4 – Extreme downwind monitoring site.

It is convenient to use the site types as defined by the EPA to discuss the PAMS data in this report because the PAMS monitoring and analysis community is familiar with the designations. In a geographic region such as the Northeast and Mid-Atlantic, the site types may be clearly defined from a political boundary point of view but may be less clearly defined in the region as a whole. For example, a Type 4 site may also be a Type 1 site for another MSA. For this project, the data from each site were analyzed with respect to the proximity of the site to sources, age of air mass, diurnal characteristics, etc. rather than solely relying on site type.

1.2.2 PAMS DATA ANALYSIS OBJECTIVES

Analyses of PAMS data were originally intended to fulfill eleven objectives:

National Ambient Air Quality Standard (NAAQS) Attainment and Control Strategy Development

1. Attainment/nonattainment determinations
2. Assessment of the relative contributions of local and upwind sources
3. Boundary conditions for photochemical modeling
4. Episode selection
5. Model evaluation

State Implementation Plan (SIP) Control Strategy Evaluation

6. Evaluation of the effectiveness of implemented control strategies

Emissions Tracking

7. Corroboration of nitrogen oxides (NO_x) and volatile organic compound (VOC) inventories and trends
8. Corroboration of VOC species source profiles
9. Analysis of air toxics

Ambient Trend Appraisals

10. Trends for ozone (O₃), NO_x, total and speciated VOC, including adjustments for variations in meteorological conditions

Exposure Assessment

11. Estimation of risk levels and the size of affected populations

A set of refocused objectives was developed in a recent State and Territorial Air Pollution Program Administrators/Association of Local Air Pollution Control Officials (STAPPA/ALAPCO) PAMS workshop (STAPPA/ALAPCO, 2000). We have structured our review according to the refocused objectives. For convenience, we have mapped the original goals to the refocused objectives. The numbers in brackets below identify the original PAMS objectives, mapping each to one or more of the newer objectives. In addition, we have added one objective [see (v) below] that more explicitly includes the original PAMS objectives pertaining to photochemical model development and evaluation. The refocused objectives are to

Help assess ozone control programs by

- (i) tracking trends [10],
- (ii) assisting in improving emission inventories [7, 8],
- (iii) identifying key constituents and parameters involved in photochemical ozone formation [6],
- (iv) characterizing transport [2],
- (v) providing data for model application and evaluation [3, 4, 5], and
- (vi) assisting in forecasting episodes [new].

Use PAMS data to benefit other programs by

- (vii) helping to characterize ambient air toxics for exposure modeling and trend analyses [9, 11],
- (viii) helping to characterize emissions and ambient concentrations of nitrogen species [7, 10],
- (ix) providing data for evaluation of particulate matter [new], and
- (x) enhancing special studies [3, 4, 5].

Our review focuses on the first six objectives (i-vi) – those pertaining to the use of PAMS data for evaluating the effectiveness of ozone control programs. Although these six primary objectives are of broad interest, in the context of the PAMS program we consider them principally in relation to the ongoing assessment of control strategies. For example, trend assessment is a key PAMS data-analysis objective because it is the principal means for documenting rates of progress toward attainment of the federal 1-hr or proposed 8-hr ozone standards. Similarly, accurate emission inventories are needed to focus control efforts on the most important sources; the PAMS data can be used to improve emission inventories. In addition, our understanding of the atmospheric processes involved in photochemical ozone formation, while of general scientific interest, is of specific regulatory interest as to how it affects decisions about sources to control and the levels of emissions control required.

1.3 APPROACH

We first defined PAMS data analysis objectives (Section 1.1.2). For each objective, we

1. describe applicable data analysis methods,
2. give example applications,
3. discuss limitations of the methodologies,
4. discuss limitations of the data (focusing on the capability of the data for supporting methodologies), and
5. provide recommendations for PAMS.

1.4 REVIEW OF LITERATURE AND EVALUATION OF OBJECTIVES

The types of data and data analyses needed to support the six primary, refocused PAMS analysis objectives are identified in summary form in Table 1. This table lists the six primary PAMS data analysis objectives and identifies specific technical questions associated with each objective. For each technical question, the table identifies one or more data analysis approaches (indicated as “x”s in the row for each question). By following the column for each approach to the second page, the table identifies specific measurements, techniques, or computer software (indicated as “x”s in the column for each data analysis approach). These approaches and techniques are discussed in detail in the following sections. A recent draft report (U.S. Environmental Protection Agency, 2000) documents 38 studies that have recently been completed using PAMS data. One or more of each of eleven types of analyses described in the PAMS workbook was conducted in the set of 38 studies. Some of those studies are included as examples in later sections of this report.

Table 1-1. Decision matrix to be used to identify example activities that will help the analyst address scientific/technical questions and objectives. To use the matrix, find your technical objective at the left. Follow this line across to identify activities that are useful for meeting the objective. For each activity, look down the column to identify data and data analysis tools.

| SCIENCE/TECHNICAL QUESTIONS/OBJECTIVES | APPROACHES, TOOLS | | | | | | | | | | | | | | | | | | | |
|---|--|---|---|---|---------------------------------------|---------------------------|--|---|-----------------------------|--|--|--------------------------|-------------------------------|---------------------------------|------------------------------|--|---------------------------------|------------------------------------|--------------------------------------|---|
| | Describe & display spatial & temporal O ₃ distributions | Describe & display spatial & temporal precursor distributions | Describe trends & assess statistical significance | Perform climatological, synoptic analyses | Compare surface and upper-air AQ data | Estimate pollutant fluxes | Describe & display met characteristics | Perform case study of met & AQ at strategic sites | Perform trajectory analyses | Compare ambient & emissions ratios, fractions, composition | Interpretative & case study analyses for model input, evaluation | Develop conceptual model | Perform VOC receptor modeling | Apply Smog Production Algorithm | Apply emissions-based models | Develop statistical relationships among pollutants | Characterize reaction chemistry | 2D and 3D displays and evaluations | Analysis of model simulation results | |
| Assess ozone trends | | | X | | | | | | | | | | | | | | | | | |
| Assess precursor trends | | | X | | | | | | | | | | | | | | | | | |
| Evaluate emissions inventories | | | | | | | | | | X | | | X | | | | | | | X |
| Perform source attribution | | | | | | | | | X | | | | X | | | | | | | X |
| Assess O ₃ concentration distributions | X | | | | X | | | | | | | | | | | | | | | |
| Characterize precursor concentration distributions | | X | | | X | | | | | | | | | | | | | | | |
| Characterize meteorological processes | | | | | X | | X | X | | | | | | | | | | | | |
| Describe climatological patterns | | | | X | | | | | | | | | | | | | | | | |
| Ascertain VOC sources (natural vs. anthropogenic) | | | | | | | | | | | | | X | | | | | | | X |
| Assess VOC and/or NO _x reduction influence on O ₃ | | | | | | | | | | | | | | X | X | X | X | | | X |
| Estimate fluxes into and within region | | | | | X | X | | | | | | | | | | | | | | X |
| Assess contribution of subregions, carryover | | | | | | | | | | | | X | | | | | | | | X |
| Obtain data for model initial, boundary conditions | | | | | | | | | | | | X | | | | | | | | |
| Evaluate air quality models | | | | | | | | | | | | X | X | | | | | X | X | X |
| Evaluate meteorological models | | | | | | | | | | | | X | X | | | | | | X | X |
| Determine met & AQ phenomena to be reproduced | | | | | | | | | | | | X | | | | | | X | X | X |
| Forecast episodes | | | | | | | | | | | | | | | | | | | | |
| Assess precursors with respect to O ₃ concentrations | X | X | | X | | | | X | | | | | | | | | X | | | |

Table 1-1. Decision matrix to be used to identify example activities that will help the analyst address science/technical questions and objectives. To use the matrix, find your technical objective at the left. Follow this line across to identify activities that are useful for meeting the objective. For each activity, look down the column to identify data and data analysis tools.

| | APPROACHES, TOOLS | | | | | | | | | | | | | | | | | | |
|--|--|---|---|---|---------------------------------------|---------------------------|--|---|-----------------------------|--|--|--------------------------|-------------------------------|---------------------------------|------------------------------|--|---------------------------------|------------------------------------|--------------------------------------|
| | Describe & display spatial & temporal O ₃ distributions | Describe & display spatial & temporal precursor distributions | Describe trends & assess statistical significance | Perform climatological, synoptic analyses | Compare surface and upper-air AQ data | Estimate pollutant fluxes | Describe & display met characteristics | Perform case study of met & AQ at strategic sites | Perform trajectory analyses | Compare ambient & emissions ratios, fractions, composition | Interpretative & case study analyses for model input, evaluation | Develop conceptual model | Perform VOC receptor modeling | Apply Smog Production Algorithm | Apply emissions-based models | Develop statistical relationships among pollutants | Characterize reaction chemistry | 2D and 3D displays and evaluations | Analysis of model simulation results |
| MEASUREMENTS | | | | | | | | | | | | | | | | | | | |
| Surface | | | | | | | | | | | | | | | | | | | |
| O ₃ | X | | X | | X | | | X | | | X | X | | X | X | X | X | X | X |
| NO, NO _x or NO _y | | X | X | | X | | | X | | X | X | X | | X | X | X | X | X | X |
| NMHC, carbonyls | | X | X | | X | | | X | | X | X | X | X | X | X | X | X | X | X |
| Meteorology | | | X | X | | | | X | X | X | X | X | | X | X | | | X | X |
| Upper-air | | | | | | | | | | | | | | | | | | | |
| Meteorology | | | X | X | | X | X | X | | | X | X | | | X | X | | X | X |
| Non-PAMS | | | | | | | | | | | | | | | | | | | |
| CO | | | X | | | | | | | X | X | | X | X | | X | | | X |
| Emission inventory | | | | | | | | | | X | | | | X | | | | | X |
| UAM model output | | | | | | | | | | | | | | | | | | | X |
| Aloft air quality | X | X | | | X | X | X | | | | X | X | | | | X | X | X | X |
| USEFUL TOOLS | | | | | | | | | | | | | | | | | | | |
| AMDAS | X | X | | X | X | X | | | | | X | X | | | X | | X | | |
| VOCDat | | X | | | | | | | | | X | X | | | | | X | | |
| Time series analysis with and w/o met adjustment | | | X | | | | | | | | | | | | | | | | |
| Other statistical methods | X | X | X | X | X | X | X | | | X | X | X | | | X | | X | | |
| Voyager | | | | | | | | | | | X | X | | | X | | | | |
| Ozone M.A.P.P.E.R. | | | | | | | | | | | | | | X | | | | | |
| Trajectory methods | | | | | X | X | | | X | | X | | X | | X | | | X | |
| Factor, cluster analyses | | | | | | | X | | | | | | X | | | X | X | X | |
| Advanced factor analyses (e.g., PMF) | | | | | | | | | | | | | | | | X | X | X | |
| UNMIX | | | | | | | | | | | | | | | | X | X | X | |
| CMB | | | | | | | | | | | | | | | | X | X | | |
| SPECIATE | | | | | | | | | | | | | | | X | X | X | X | X |

2. SUMMARY OF LITERATURE REVIEW

2.1 TRACKING TRENDS

2.1.1 Applicable Data Analysis Methods

Rates of progress toward attainment of the ozone standard are tracked by analyzing trends in ozone concentrations. Indeed, quantifying rates of progress is a necessary part of the SIP process. However, understanding the factors that are responsible for the observed trends requires additional analyses, including characterizations of trends in precursor concentrations. Moreover, because ozone formation is highly nonlinear, examining trends in precursor concentrations is the most direct way to investigate the effects of emission control programs. Trends in precursor concentrations may be used to corroborate changes in emission inventories.

While many statistical techniques have been employed to detect air pollutant trends, they may be conveniently categorized using the following dichotomies:

- Analysis of hourly concentration data versus seasonal or monthly statistics, such as the annual maximum hourly concentration.
- Analysis of statistics closely related to the ozone standard versus more robust air-quality indicators. For example, the fourth-highest hourly ozone maximum during each three-year period is closely linked with the expected-exceedance form of the federal 1-hr ozone standard, but is known to exhibit considerable year-to-year variability. To improve the signal-to-noise ratio, the California Air Resources Board (ARB) includes analyses of trends in the average of the top 30 daily ozone 1-hr maxima each year.
- Incorporation versus no incorporation of adjustments for year-to-year variations in meteorological phenomena that influence the rate of ozone formation.

Because ozone concentrations are highly correlated from hour to hour and even from day to day, analyses based upon hourly or daily data must be carried out using reasonably sophisticated statistical time series techniques. Besides accounting for the correlation structure within the data, such techniques also incorporate filtering (Rao and Zurbenko, 1994; Rao et al., 1999) or smoothing (Sirois, 1993) procedures for extracting linear, nonlinear, or step changes that are typically small in relation to the wide variations observed in the hourly or daily ozone concentrations. Simpler regression techniques are appropriate for annual statistics. Usually, either substantial averaging of the data (e.g., the top 30 ozone maxima) or adjustment for meteorological variations that influence the annual extreme concentrations (e.g., fourth-highest hourly maximum during each three-year period) is needed to obtain detectable trends over periods of less than ten years.

Twelve recent analyses of ozone or precursor trends using PAMS data are documented in the draft PAMS data usage report (U.S. Environmental Protection Agency, 2000).

2.1.2 Limitations of the Methods

Trends in ozone and other species of interest are difficult to quantify because the majority of the day-to-day, and even year-to-year, variation in concentrations is attributable to variations in weather. This variation cannot be removed by simply adding more monitoring locations because all locations within a particular area experience the same weather patterns and tend to show highly correlated variations in concentrations.

Because ozone is a secondary pollutant, concentration variations are affected by changes in the concentrations of many other chemical species. Therefore, documenting the effects of an emission rule is more readily accomplished by examining trends in specific primary pollutants, rather than in ozone.

The utility of trend analyses depends upon the magnitudes of emission reductions, the quality and length of record of the monitoring data, and the relative magnitudes of the emissions- and weather-driven variations in ambient pollutant concentrations (Blanchard, 2000). For a signal-to-noise ratio of 1:1, about two to four years of monthly data are needed to detect a linear trend with high probability (90%) at a 95% confidence level, whereas 10 to 20 years of data are needed when the signal-to-noise ratio falls to 0.1:1 (Weatherhead et al., 1998). Variations in urban ozone concentrations are dominated by weather; temperature variations, random variation, and emissions-related trends have been shown to account for 70%, 20%, and 10%, respectively, of the total variance of ozone concentrations at several monitoring locations (Rao and Zurbenko, 1994; Rao et al., 1999). Given such an unfavorable ratio of signal to noise (~0.1:1), ozone trend analyses have typically incorporated procedures for adjusting for variations in temperature and other meteorological factors (e.g., Rao and Zurbenko, 1994; Rao et al., 1999; Kolaz and Swinford, 1990; Kuntasal and Chang, 1987; Cassmassi and Bassett, 1993; Zeldin et al., 1991; Stoeckenius, 1991; Cox and Chu, 1993; Shively, 1991; Bloomfield et al., 1996); used statistics (e.g., median, 90th percentile) that are less sensitive to meteorological variations than are the extreme ozone concentrations (Fiore et al., 1998; Korsog and Wolff, 1991; Curran and Frank, 1991; Chock et al., 1982); or have averaged data spatially and temporally (Fujita, 1993). The capabilities of the methods that have been employed to account for the effects of weather variations on ozone concentrations have not been systematically compared, so none can be identified as superior (Rao et al., 1999). Although some success has been achieved in identifying trends and demonstrating their qualitative consistency with the magnitudes of emission reductions, ozone trend analyses generally have not been able to link ambient concentrations with specific source types or locations. An exception is time series analyses that have demonstrated step changes in urban ozone concentrations occurring when new emission control procedures were implemented, thus quantifying a relationship between the controlled sources and ambient ozone concentrations (Milanchus et al., 1998.; Rao and Zurbenko, 1994; Box and Tiao, 1975).

2.1.3 Adequacy of PAMS Data to Support Methods

The single most important factor affecting the success of trend analyses is the quality of the data record. A long and continuous record is needed, with reasonably complete sampling

during each ozone season. One site with a high-quality record is more valuable than many sites with short records or incomplete sampling.

Data are needed to support analyses of trends in ozone and ozone precursor concentrations. Accurate, high-resolution measurements of NO_x (or NO_y), carbon monoxide (CO), and total nonmethane hydrocarbons (NMHC) are desirable for this purpose and are not particularly resource-intensive because they are continuous, hourly measurements. Continuous CO (ppbv detection limits) and NMHC (50 ppbv detection limits) are not measured at PAMS sites. For tracking total hydrocarbon concentrations, the continuous NMHC measurements (i.e., not speciated) may be a reasonable, and less resource-demanding, substitute for total nonmethane organic compounds (NMOC) (speciated canister samples or gas chromatograph [GC]). The exception is the need to document changes in specific compounds in relation to the adoption of new emission rules. For example, Main et al. (1998; 1999) showed that statistically significant decreases in ambient benzene weight fractions occurred between 1994 and 1995, coinciding with the reduction of benzene amounts in the reformulated gasoline that was introduced in 1995. For total NMHC, detection of significant changes is not necessarily expected in a data set of five to six years; thus, it is important to continue to gather data to compile a longer record.

Spatial representativeness of measurements is an issue for trend analysis when there is reason to suspect that trends differ among locations. For example, urban center trends may differ from trends in suburban areas due to growth and development, which has largely occurred in suburbs. Nationwide, CO monitors, most of which are in center-city locations, recorded peak 8-hr CO concentration declines averaging 39% from 1990 to 1998, a greater than proportional decline than the 16% reduction of total CO emissions during the same period (U.S. Environmental Protection Agency, 2000). The data suggest that the CO emission reduction was more prominent in the urban centers (i.e., reductions were not offset by growth in vehicle miles traveled near urban-center monitors). It is possible that some areas experiencing high growth rates may have experienced increases in local emission rates. For comparison, peak ozone monitors are generally located in downwind areas where growth of commute traffic may have resulted in locally higher ozone precursor loading rates. During the period 1989-98, 104 of 139 Metropolitan Statistical Areas (MSAs) exhibited statistically significant declines in the second maximum 8-hr CO concentration, whereas only 25 of 198 MSAs showed statistically significant declines in the fourth maximum 8-hr ozone concentration (U.S. Environmental Protection Agency, 2000). (Trends were based upon spatial averages of all monitors within each MSA.) Ozone concentrations increased at 17 of 24 National Park Service sites where ozone is monitored (U.S. Environmental Protection Agency, 2000). Anecdotal evidence suggests that at some sites, declines in peak ozone concentrations appear to be associated with rising NO_x levels, and possibly titration of ozone by NO, rather than resulting from reductions of ozone formation.

2.1.4 Recommendations

Trends, and the relationship of ozone to precursor trends, will be best recognized using continuous, complete, and long-term sampling for ozone, CO, NO_x (or NO_y), and total NMHC (or speciated NMOC) at Type 2 and Type 3 PAMS locations. The principal program needs for PAMS sites are to ensure the continuity of monitoring at existing locations, to add high-resolution (ppbv) CO (which will serve other purposes, as discussed in Section 2.2), and to

replace speciated NMOC with accurate continuous measurements of total NMHC (50 ppbv or better resolution) at locations where speciated hydrocarbons might be discontinued for other reasons (see Section 2.2). Comparability of NMHC to total NMOC measurements should be established through a period during which collocated NMHC and NMOC measurements are made. If trends in carbonyl concentrations are deemed of sufficient interest, an attractive cost option is to replace cartridge sampling with continuous formaldehyde monitors at some Type 2 or Type 3 locations.

2.2 IMPROVING EMISSION INVENTORIES

2.2.1 Applicable Data Analysis Methods

PAMS data can be used in two general ways to help evaluate emission inventories:

- Compare ratios of ambient measurements of species with corresponding ratios in emission inventories to evaluate the relative composition of inventories. For example, comparisons of ambient to emissions ratios of TNMOC/NO_x,¹ CO/NO_x, and TNMOC/CO have helped identify shortfalls in estimates of hydrocarbon emissions. The speciation of hydrocarbon emission estimates has been examined using ratios such as acetylene/benzene.
- Apply receptor models to resolve the composition of ambient hydrocarbon concentrations into components related to different types of emission sources. Receptor modeling may be enhanced through trajectory analyses to confirm that the identified source types are, in fact, located along calculated back trajectories.

The first approach is sometimes known as a “top-down” inventory evaluation. As noted, top-down emission inventory evaluations can be divided into two parts: (1) comparison of ambient- and emission inventory-derived hydrocarbon/NO_x and CO/NO_x ratios and (2) comparison of chemical species groups and/or individual chemical species. Comparison of ambient- and emission inventory-derived hydrocarbon/NO_x and CO/NO_x ratios provides a means of comparing the relative mass of emissions in the ambient air quality and the emission inventory. Comparisons of the individual chemical species in the ambient air quality and in the emission inventory can serve as an indicator of the accuracy in the speciation of the inventory because individual chemical compounds are characteristic of emissions from specific source categories.

Top-down inventory evaluation is typically combined with a “bottom-up” evaluation. The latter uses data or estimates from sources other than the PAMS monitors, such as census information or activity data, to investigate the accuracy of the calculations used for generating emission estimates. Since “bottom-up” approaches are not carried out using PAMS data, they are not discussed further here. The “top-down” approach is especially useful for providing an independent assessment of the emission estimates.

¹ Conventional terminology often refers to the "VOC/NO_x" ratio. However, ambient measurements report TNMOC/NO_x. We have used the terms "TNMOC" and "hydrocarbon" in most discussions.

Receptor modeling provides an important tool for attributing ambient hydrocarbon concentrations to their emission source types (source attribution). This information then is useful for re-evaluating the relative contributions of different source types as specified by emission inventories. At present, over a dozen different types of receptor models have been developed. The U.S. Environmental Protection Agency (EPA) Office of Air Quality Planning and Standards (OAQPS) recognizes two models as part of its SIP development guidance documentation. They are the chemical mass balance model (CMB) and a multivariate statistical procedure known as principal components analysis (PCA). Other methods currently under investigation by EPA include positive matrix factorization (PMF) and UNMIX.

Three recent emission inventory evaluations using PAMS data are documented in the draft PAMS data usage report (U.S. Environmental Protection Agency, 2000).

2.2.2 Limitations of the Methods

Top-down inventory evaluation. Top-down emission inventory evaluation is used to identify areas of an emission inventory that appear suspect. The methodology can compare the relative amounts of pollutants in the inventory and in the ambient atmosphere, but it cannot quantify absolute errors in the inventory; it complements, but does not substitute for, a bottom-up evaluation.

Comparisons of ambient air quality data and emission inventory estimates for hydrocarbon, CO, and NO_x are based on the premise that ambient concentrations are primarily influenced by fresh emissions emitted in the vicinity of the monitor. However, precursor transport, carryover effects, and chemical reactions can also influence concentrations. The influence of these confounding effects on the comparison can be minimized (but not eliminated) by selecting monitoring sites located in areas with high emission rates and by examining data collected when emission rates are high and reaction rates are low. Using early morning sampling periods is most appropriate when making emission comparisons because, typically, emissions are high while wind speed, atmospheric mixing height, temperature, and chemical reactivity are low. Data from early morning sampling periods are most likely to contain minimal effects from upwind transport and photochemistry. Because anthropogenic hydrocarbon emissions come from combustion, fugitive, and evaporative sources, estimating hydrocarbon emissions can be very difficult; in contrast, anthropogenic NO_x is emitted only by combustion sources and is therefore assumed to be the more accurate of the two.

Comparisons between ambient- and emissions inventory-derived ratios can be made reasonably robust by matching individual chemical species in the ambient air quality data to the emission inventory prior to the analysis. The emission inventory and ambient air quality data are then compared for the same early morning time period and are matched spatially by grid cells corresponding to the predominant wind speed and direction at each ambient air quality monitoring site. Wind analyses are performed to calculate air parcel travel distances during the morning ambient air quality sampling period.

Receptor modeling. The earliest applications of receptor modeling were oriented to apportioning aerosol mass to its emission source types; receptor-modeling methods were later

extended to hydrocarbons selected on the basis of having lower rates of reaction with hydroxyl radical (OH) (Watson et al., 1999; Tombach, 1982; Scheff et al., 1989; Scheff et al., 1993; Scheff et al., 1996; Fujita et al., 1994; Fujita et al., 1995). Aerosol and hydrocarbon receptor modeling serve different purposes. For aerosols, receptor modeling is typically used to estimate the contributions of different source types to the aerosol mass; emission reductions required from each source type are then estimated by determining the difference between aerosol mass and the level of the particulate matter (PM) NAAQS and applying linear rollback. In contrast, there are no NAAQS for hydrocarbons. Hydrocarbon receptor modeling is used to apportion the total ambient TNMOC concentration to different sources, and this information is then used to evaluate emission estimates. Apportionment of hydrocarbons using CMB analysis has consistently shown that ambient motor vehicle contributions are two to three times their proportions in emission inventories while contributions from coatings (e.g., paints), solvents, and biogenic emissions are lower than indicated by inventory estimates (Watson et al., 1999). Applications of hydrocarbon receptor modeling are subject to important uncertainties arising from the assumptions of the methodologies.

The important assumptions underlying the CMB model are that emissions compositions are constant over the periods of source and receptor sampling; all chemical species are nonreactive; all source types have been identified and included; the number of source types is no greater than the number of chemical species measured; the source profiles are linearly independent; and measurement uncertainties are independent, random and normal in distribution (Watson, 1982; Watson, 1997). In practice, deviations from assumptions always occur and the true uncertainties of the estimated source strengths exceed the uncertainties predicted by the CMB model (Watson, 1997); for hydrocarbon receptor modeling, the assumption of nonreactivity is not met. Because few or no sources can be tagged uniquely by a single compound, the method depends upon measuring many species whose relative proportions differ in the emissions from different source types (Watson, 1997). The availability of accurate, area-specific source profiles is an important limitation. Statistical methods, such as PCA, PMF, and UNMIX, do not require source profiles, but large quantities of data are required and the results must be interpreted to associate source types with statistically derived quantities (factors).

2.2.3 Adequacy of PAMS Data to Support Methods

Inventory evaluation. Top-down emission inventory evaluation uses measurements to generate ratios, the most common of which are TNMOC/NO_x, CO/NO_x, and TNMOC/CO. When inconsistencies between ambient- and emission inventory-derived ratios exist, the availability of all three ratios can help indicate which pollutant is over- or underestimated. Thus, there is a need to add measurements of CO to PAMS Type 2 sites (i.e., at locations best suited to inventory evaluation). Ratios of individual hydrocarbons, or groups of species, can be used to check the relative species composition of inventories. Chinkin et al. (1999) used ratios of paraffins, olefins, and aromatics, computed from PAMS measurements taken in southern California, to show that ambient paraffin content was slightly greater, and ambient olefin content slightly less, than the emission inventory proportions. The match between PAMS species and the species contained within emission inventories is imperfect, though, so emissions of carbonyls, alcohols, ethers, acetates, glycols, esters, formates, organic amines, organic oxides,

phenols, terpenes, organic acids, C11+ hydrocarbons, and halogenated species cannot be checked.

Receptor modeling. The speciated hydrocarbon data provided by the PAMS network are well suited for application of receptor models because they include a variety of species that provide multi-species fingerprints of different emission source types. Examples of some of the species that are typically used to define source profiles are automobile exhaust (e.g., ethylene, acetylene, benzene, and toluene), gasoline evaporative emissions (e.g., n-butane), liquid fuel (e.g., isobutane, isopentane, and toluene), petroleum refining (e.g., isobutane, n-pentane, and C6-C8 compounds), and architectural and industrial coatings (e.g., n-hexane, cyclohexane, toluene). At present, PAMS speciation does not permit diesel and gasoline exhaust to be distinguished well; measurements of elemental carbon or semi-volatile compounds could potentially improve discrimination.

The number of PAMS sites appears sufficient for receptor modeling. In many urban areas, hydrocarbon compositions and, by implication, relative source contributions appear to be similar among most or all of the locations where speciated hydrocarbon data have been collected. For example, the spatial and temporal variations in the relative hydrocarbon composition during the 1987 Southern California Air Quality Study (SCAQS) were small, and overall composition was indicative of a predominant contribution from light-duty motor vehicles (Lurmann and Main, 1992). Later analyses of the 1997 Southern California Ozone Study (SCOS) data indicated that higher relative concentrations of lower-reactivity species occurred at some downwind locations and were indicative of more aged air masses (Main et al., 1999). Within the MARAMA region, some variations of composition occurred among PAMS Type 2 sites, but all Type 2 sites exhibited hydrocarbon compositions and diurnal variations indicative of fresh emissions at all times (Main et al., 1999). From the standpoint of receptor modeling, no compelling need for more sites is apparent.

2.2.4 Recommendations

High-sensitivity hourly CO monitors (ppbv detection limits) should be added to PAMS Type 2 sites to aid the evaluation of emission inventories through computation of a complete set of TNMOC/NO_x, CO/NO_x, and TNMOC/CO ratios.

Preliminary review of the data obtained to date suggests a general similarity of source composition among Type 2 and Type 2A, or other near-source, sites. If further analyses indicate that hydrocarbon speciation at PAMS Type 2A sites is closely similar to speciation at PAMS Type 2 sites, consideration should be given to reducing the amount of data acquired at Type 2A sites. In view of the resource-intensiveness of speciated hydrocarbon measurements, hydrocarbon speciation at PAMS Type 2A sites may be dispensable.

2.3 IDENTIFYING KEY CONSTITUENTS AND PARAMETERS INVOLVED IN PHOTOCHEMICAL OZONE FORMATION

2.3.1 Applicable Data Analysis Methods

Methods for identifying key constituents and parameters involved in ozone formation may be conveniently grouped into two general categories: descriptive data analyses and interpretive, or process-oriented, data analyses. Descriptive analyses include statistical summaries of ozone and precursor concentration distributions, as well as descriptive evaluations of meteorological processes and climatological variables. Descriptive analyses often provide the "raw material" for interpretive data analyses and for conceptual models of ozone formation.

Interpretive analyses include various techniques of graphic display. For example, plots of mean diurnal profiles of species concentrations can yield insights into the times of occurrence of fresh emissions, their effects on ozone formation rates, and transport of ozone and precursor species.

Species ratios provide insights into air mass age, the presence of fresh emissions, and deposition rates. Some ratios may involve the same species that are used for emission-inventory evaluation, but the purpose and methods differ from those of inventory evaluation. For example, the ratio of CO/NO_x at Type 2 sites is useful for inventory evaluation; the same ratio, or the ratio of CO/NO_y, at Type 3 or Type 4 sites can provide insight into the rates of reaction of NO_x or deposition of nitric acid (HNO₃) and other components of NO_y.

Various approaches for characterizing the reaction rates of different hydrocarbons have been proposed, including the maximum incremental reactivity (MIR) and maximum ozone reactivity (MOR) (Carter and Atkinson, 1987). There have been some disagreements about the merits of different approaches to assessing reactivity or the implications for control strategies; however, considerations of reactivities have helped bring more perspective to the relative importance of different species in contributing to ozone formation than was the case when only species mass, or concentration levels, were considered. Vukovich (2000), for example, combined PAMS speciated hydrocarbon measurements made in Baltimore with literature values of the species reactivities with OH to evaluate the relative contributions of the measured species to ozone formation; Vukovich found that the 10 hydrocarbons with the highest OH reactivities accounted for 78% to 82% of the total reactivity, but only 24% to 27% of the total hydrocarbon concentration.

Other interpretive, or process-oriented, data analyses that are carried out independently of modeling applications may provide results of direct applicability to control strategy evaluations and ozone attainment demonstrations. The most well-developed techniques of this type are "data-driven" techniques designed to provide a qualitative assessment of the relative utility of hydrocarbon versus NO_x emission reductions (e.g., Cardelino and Chameides, 1995; Sillman, 1995; Chang et al., 1997; Blanchard et al., 1999, 2000). Observation-driven methods (ODMs) use measurements from one or more monitoring locations to qualitatively assess the relative sensitivities of peak ozone concentrations to reductions in hydrocarbon or NO_x emissions. In general, qualitative equivalency exists among these methods (Chameides et al., 2000).

The extent to which ozone levels respond to decreases in the emissions of nitrogen oxide (NO) or hydrocarbons depends on many factors. An important, though coarse, indicator of the relative benefits of controlling the two precursors is the ratio of ambient TNMOC/NO_x concentrations upwind of locations experiencing exceedances of the ozone standard (both surface and aloft concentrations are of relevance). The basis for this indicator lies in the ozone isopleth diagrams derived from smog-chamber studies and from modeling. An ozone isopleth diagram, which shows peak ozone concentration as a function of initial hydrocarbon and NO_x concentrations, concisely summarizes the results of single-day smog chamber experiments (the peak ozone concentrations plotted on an isopleth diagram are implicitly a function of a larger number of controlling variables that are held fixed). Ozone isopleth plots can also be produced using the calculations from a chemical mechanism. Isopleth plots are extremely useful for conveying qualitatively the key features of the systems under study. Such plots show the importance of the initial hydrocarbon/NO_x in determining the directional response of peak ozone as a function of changes in initial hydrocarbon, NO_x, or both. In some cases, hydrocarbon/NO_x ratios are thought to be misleading as indicators of ozone sensitivity, but when used in conjunction with some of the other ODMs, it is possible to use ratios of hydrocarbons/NO_x to derive consensus findings.

Thirteen recent descriptive or interpretive analyses of ozone or precursor species using PAMS data are documented in the draft PAMS data usage report (U.S. Environmental Protection Agency, 2000).

2.3.2 Limitations of the Methods

Descriptive and interpretive analyses. The insights obtained from purely descriptive analyses are typically limited, but such analyses are nonetheless important for providing key material for interpretation. Hales et al. (1993) describe limitations associated with the MIR and MOR scales. The limitations associated with other interpretive methodologies are illustrated in the following discussion of the methods for delineating hydrocarbon and NO_x sensitivity.

Hydrocarbon and NO_x limitation.² Essentially all regional or multiday nonattainment problems involve complex situations with multiple source regions and complicated transport patterns. Examples of such cases include the Northeast Corridor, the southern Lake Michigan area, and California's San Joaquin Valley. Many of these nonattainment cases of particular concern pose difficult challenges to data-driven techniques designed to provide a qualitative assessment of the relative utility of VOC versus NO_x emission reductions methods, including methods based on the ratio of hydrocarbons/NO_x. Applications should employ cross-checks using multiple methods and comparisons with other data analyses.

Observation-driven methods for delineating areas of VOC and NO_x limitation share a number of characteristics. Because they are all driven by ambient measurements, the accuracy of their findings depends upon the precision and accuracy of the ambient measurements, as well as upon the details of the formulation of the methods. Moreover, conclusions are also dependent

² Conventional terminology refers to "VOC-limitations". We have used "TNMOC" and "hydrocarbon" to refer to ambient data.

upon the representativeness of the locations of the ambient monitoring sites. With the exception of the ozone-NO_y correlation method (Trainer et al., 1993), all the ODMs can be traced back to environmental chamber experiments, either directly or indirectly through chemical mechanisms that were developed from chamber data. Should chambers have an unknown systematic bias affecting the applicability of findings to the ambient atmosphere, the ODMs could also be biased.

Ambient TNMOC/NO_x ratios are highly variable; this variability potentially obscures the discriminatory capabilities of the TNMOC/NO_x. It is helpful to think of the comparison of ambient TNMOC/NO_x to a criterion value as a statistical test: if the mean (or median) TNMOC/NO_x is sufficiently greater than the criterion, considering the variability in both measurements and criterion, then one control strategy is indicated (i.e., NO_x control). If the TNMOC/NO_x ratio is sufficiently smaller than the criterion, again considering variability, another strategy is indicated (i.e., VOC control). However, if the TNMOC/NO_x and the criterion are insufficiently different, considering the variability in each, the outcome is ambiguous. Wolff and Korsog (1992) argued that correlations between peak ozone and morning VOC/NO_x are statistically insignificant or weak, implying that the variability in VOC/NO_x is unrelated to high ozone concentrations. Moreover, Wolff and Korsog (1992) point out that ambient TNMOC/NO_x ratios suggest VOC-only control strategies for Atlanta, Baltimore, Cleveland, New York/New Jersey, Philadelphia, and St. Louis (based on current EPA guidance), whereas grid-based modeling suggests benefits of NO_x control for Atlanta and disbenefits for New York.

2.3.3 Adequacy of PAMS Data to Support Methods

Descriptive and interpretive analyses. The PAMS network provides a rich database for describing and relating ozone concentrations to the concentrations of its precursor hydrocarbon and NO_x species, and to products of photochemical oxidation. Existing compliance monitors generally suffice for providing descriptive statistical summaries of ozone concentrations with adequate spatial resolution. The PAMS data, however, are a source of time-resolved measurements that are not otherwise collected. In this regard, the auto-GC data are especially useful for providing hourly resolution, continuous data that may be analyzed for diurnal patterns or interpreted using time series analysis. In contrast, the 3-hr canister samples collected every third day typically do not provide a very sharp resolution of diurnal patterns or a record amenable to time series analysis. Those measurements do, however, contribute to a fuller statistical description than would otherwise be available in the absence of PAMS.

Hydrocarbon and NO_x limitation. The PAMS data support application of several methods for delineating VOC and NO_x limitation. With measurements of ozone, NO, and NO_y, the methods of Trainer et al. (1993), Blanchard et al. (1999), Milford et al. (1994), and Sillman (1995) can be used. However, the correlational approach of Trainer et al. (1993) is more useful when ozone is correlated with NO_z (NO_y-NO_x) than with NO_y; also, the data support computation of Sillman's (1995) indicator ratio of O₃/NO_y, but not O₃/NO_z, nor the potentially more useful ratio of H₂O₂/HNO₃. For all these methods, both NO_x and NO_y should be measured with accuracies of about 1 ppbv down to concentrations of about 1 ppbv.

Cardelino and Chameides (1995) describe the use of a box model (Observation-Based Model or OBM) for calculating the sensitivity of ozone to VOC or NO_x reductions. The method requires measurements of NO that are accurate at sub-ppbv concentrations (Cardelino and Chameides, 1995) which are not provided by the PAMS or other routine monitoring networks. The OBM also may require continuous GC measurements of hydrocarbon species (documentation is not clear on this point). Multi-hour averages appear to be inadequate given the need to interpolate concentrations to relatively fine time resolution.

Ozone formation is difficult to understand and describe because it is governed by non-linear processes with numerous feedback effects. "Real-world" data have the most compelling weight for establishing an event or process and revealing its dynamics. Unfortunately, such data may be insufficient for explaining the spatial or temporal patterns of ozone concentrations, due to the lack of certain measurements (e.g., precursor species concentrations) or to insufficient temporal or spatial resolution or coverage.

Typically, a transition between VOC and NO_x limitation occurs between urban areas and their rural surroundings. Delineation of this transition is valuable for assessing how areas might respond to projected emission controls and clarifying the implications for population exposure.

The PAMS network has too few sites, and compliance networks have too few sites with measurements of NO_x or NO_y, to delineate the transitions between VOC and NO_x limitation in any of the PAMS domains. Most PAMS Type 2 sites are VOC-limited, while Type 1, Type 3, and Type 4 sites are NO_x-limited during ozone episodes (**Figure 2-1**). In the figure, where the extent of reaction is less than ~0.6, ozone formation is usually VOC-limited. As ozone formation becomes NO_x-limited, the extent approaches 1; for the types of averages shown in Figure 2-1, extent values exceeding ~0.8 indicate where ozone is likely responsive to changes in NO_x levels. The sites have been grouped according to their PAMS or AIRS site types. The results show that nearly all sites were more NO_x-limited on days having peak 8-hr ozone concentrations exceeding 80 ppbv than on other days. Ozone formation was most NO_x-limited during hours having ozone concentrations exceeding 124 ppbv. Nine of the 12 Type 1, Type 3, and Type 4 sites were NO_x-limited on all episode days (sites classed as 1/3 or 1/4 are listed here as 3 or 4, respectively). Seventeen of the 23 Type 2, or other urban, sites were VOC-limited, averaged over all episode days. Nine of the 16 suburban sites were transitional, averaged over all episode days. The transition between VOC and NO_x limitation generally occurs somewhere in suburban or surrounding rural areas. Delineation of the transition is possible if NO_x or NO_y monitors are added to some of the numerous ozone compliance monitoring locations that are presently operational downwind of every major urban area. While this augmentation does not involve PAMS sites, greater coordination between the PAMS and compliance monitors would enhance the value of the data that are presently being acquired by both networks.

2.3.4 Recommendations

To reduce the analytical workload, speciated hydrocarbon measurements at PAMS Type 3 sites could be replaced with continuous NMHC (with better than 50 ppbC detection limit) during most times. Occasional samples could be collected for speciation. These data might be

used for analyses of air mass age and possible comparison with predictions of VOC and NO_x sensitivity obtained from other analyses.

Within each of the PAMS urban domains, NO_x or NO_y monitors could be added at three to six downwind suburban or rural compliance monitoring locations where ozone is presently measured to improve the delineation of the transition from urban, VOC-limited ranges to NO_x-limited regions.

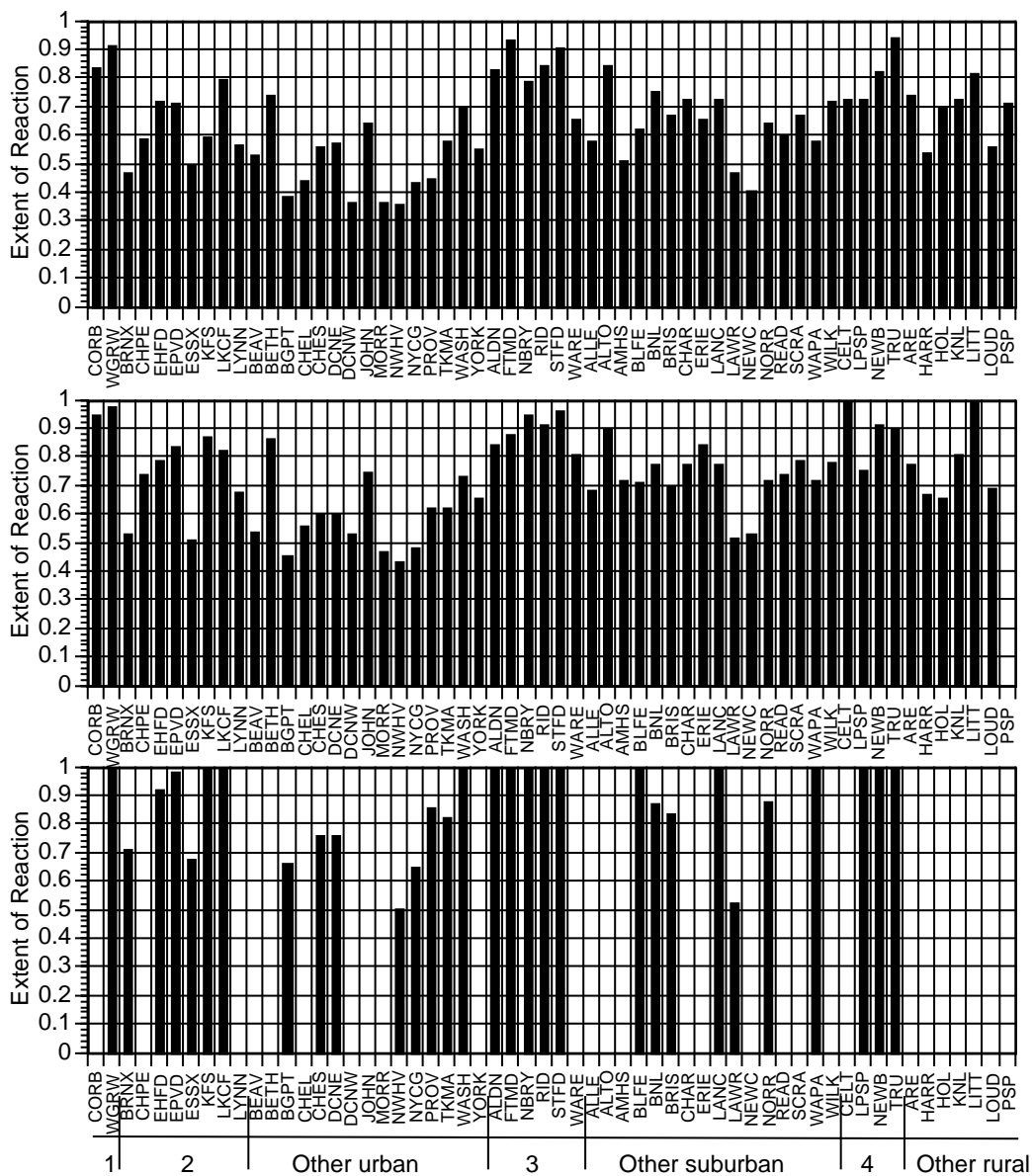


Figure 2-1. Summary statistics describing an indicator of VOC or NO_x limitation during the 1995 NARSTO-Northeast study: (top) mean afternoon extent of reaction on all 13 episode days, (middle) mean extent during 8-hr periods with ozone averages exceeding 80 ppbv, and (bottom) mean extent during hours with 1-hr ozone concentrations exceeding 124 ppbv. Site key is provided in **Table 2-1**. Source: Blanchard, 1998.

Table 2-1. Site key for Figure 2-1.

| Site Code | State | Location | Site Type (PAMS 1-4, or rural [R], urban [U], suburban [S]) |
|-----------|-------|-----------------------------------|---|
| CORB | VA | Corbin | 1 |
| WGRW | RI | West Greenwich | 1 |
| BRNX | NY | New York City Bronx | 2 |
| CHPE | MA | Chicopee | 2 |
| EHFD | CT | East Hartford | 2 |
| EPVD | RI | East Providence | 2 |
| ESSX | MD | Essex | 2 |
| KFS | ME | Kittery | 2 |
| LKCF | MD | Lake Clifton | 2 |
| LYNN | MA | Lynn | 2 |
| BEAV | PA | Beaver Falls | U |
| BETH | PA | Bethlehem | U |
| BGPT | CT | Bridgeport | U |
| CHEL | MA | Chelsea | U |
| CHES | PA | Chester | U |
| DCNE | DC | Washington DC 34th & Dixon Sts NE | U |
| DCNW | DC | Washington DC 24 & L Sts NW | U |
| JOHN | PA | Johnstown | U |
| MORR | NY | Morrisania Center | U |
| NWHV | CT | New Haven | U |
| NYCG | NY | New York City Greenpoint Ave | U |
| PROV | RI | Providence | U |
| TKMA | DC | Washington DC Takoma | U |
| WASH | DC | Washington DC McMillian Res | U |
| YORK | PA | York | U |
| ALDN | MD | Aldino | 3 |
| FTMD | MD | Fort Meade | 3/1 |
| NBRY | MA | Newbury | 3 |
| RID | NJ | Lawrence (Rider College) | 3 |
| STFD | CT | Shenipsit State Forest | 3 |
| WARE | MA | Quabbin Summit | 3 |
| ALLE | PA | Allentown | S |
| ALTO | PA | Altoona | S |
| AMHS | NY | Amherst | S |
| BLFE | DE | Bellefonte | S |
| BNL | NY | Brookhaven National Laboratory | S |
| BRIS | PA | Bristol | S |
| CHAR | PA | Charleroi | S |
| ERIE | PA | Erie | S |

Table 2-1. Site key for Figure 2-1.

| Site Code | State | Location | Site Type (PAMS 1-4, or rural [R], urban [U], suburban [S]) |
|-----------|-------|---------------------------------------|---|
| LANC | PA | Lancaster | S |
| LAWR | PA | Lawrenceville | S |
| NEWC | PA | Newcastle | S |
| NORR | PA | Norristown | S |
| READ | PA | Reading | S |
| SCRA | PA | Scranton | S |
| WAPA | PA | Washington | S |
| WILK | PA | Wilkes-Barre | S |
| CELT | ME | Cape Elizabeth | 4 |
| LPSP | DE | Lums Pond State Park | 4/1 |
| NEWB | NJ | New Brunswick (Rutgers Research Farm) | 4/1 |
| TRU | MA | Truro | 4 |
| ARE | PA | Arendtsville | R |
| HARR | PA | Harrisburg | R |
| HOL | PA | Holbrook | R |
| KNL | PA | Kunkletown | R |
| LITT | PA | Little Buffalo State Park | R |
| LOUD | NY | Loudonville | R |
| PSP | NY | Pinnacle State Park | R |

2.4 CHARACTERIZING TRANSPORT

2.4.1 Applicable Data Analysis Methods

A variety of techniques have been used to characterize the transport of ozone and ozone precursors. As described in more detail in this section, upper-air measurements of ozone and ozone precursors are the most straightforward means for characterizing transport. Techniques that employ surface measurements are also useful. Such techniques include assessment of air mass ages using VOC species ratios that differ in reactivity; analysis of surface wind speeds and directions; calculation of recirculation factors based upon average and vector-averaged winds; and analyses of the times of occurrence of peak ozone values along trajectories.

In some situations, successive monitoring sites located along the orientation of the prevailing surface wind direction may show ozone peaks occurring at progressively later times, with the product of the times between peaks and the average wind speed approximately equal to the distances between sites. Direct transport is indicated in such situations. However, many of the most significant ozone problems involve much more complicated patterns of transport. For example, Roberts et al. (1994) showed that data from the 1991 Lake Michigan Ozone Study were inconsistent with direct transport northwards from Chicago toward Milwaukee; rather, the lake-

breeze–land-breeze circulation appeared to transport emissions over Lake Michigan, returning them later in the day, with daytime south-to-north transport occurring over the water. The times of occurrence of peak ozone values were similar for many of the sites located along the lakeshore because the lake breeze moved emissions-laden air masses from over the lake onshore at approximately the same times.

Recirculation can be quantified using a ratio derived from vector-average and scalar-average winds. Particularly informative results can be obtained using rawinsonde or radar wind profiler data to generate a vertical profile of recirculation factors (e.g., Ray, 1998).

Various research studies have used aloft measurements (aircraft, ozonesondes) of ozone and precursors to characterize transport. **Figures 2-2 and 2-3** provide examples of aircraft measurements made during the 1995 NARSTO-Northeast study. Above approximately 400 to 600 m elevation, ozone concentrations were ~80 ppbv within spirals flown between 0400 and 0700 EST. Thus, substantial concentrations of ozone were available over an extended region for carryover into the daytime. These data also show that in the air aloft, ozone levels had reached their maximum potential—the air masses were aged and had too little NO_x to sustain further ozone production after sunrise. However, at the urban locations, ozone levels below ~400 m were depleted relative to concentrations aloft, and the presence of higher concentrations of NO_y implied that ozone had been depleted by reaction with fresh emissions of NO. With sunrise, sufficient NO_x was present to then generate much higher ozone concentrations, as indicated by the maximum potential ozone values in Figures 2-2 and 2-3, though of course these higher concentrations would be diminished following vertical mixing with air aloft having ozone concentrations of ~80 ppbv.

When aloft ozone or precursor measurements are combined with measurements of wind speeds and velocities, estimates of ozone transport across flux planes are possible. Example applications include Roberts et al. (1994) and Blumenthal et al. (1997).

Tracer studies are also useful for characterizing atmospheric transport; in addition, tracers are used to quantify dispersion characteristics of plumes, providing empirical data for evaluating long-range trajectory models and conducting material balances for use in quantitative source apportionment. Both planned tracer releases, using inert, nondepositing gases such as sulfur hexafluoride (SF_6) or perfluorocarbons, and tracers of opportunity have been used. Atmospheric transport studies are logistically less demanding than other types of tracer applications since documentation of tracer locations and travel times typically suffices to meet the objectives of such studies (Rappolt and Teuscher, 1995). Caution must be exercised in inferring transport distances because the deposition rates of the pollutants of interest exceed those of the tracers by many orders of magnitude. Planned tracer releases have been used to qualitatively track the transport of pollutants from the Los Angeles metropolitan area into the Mojave Desert (Reible et al., 1982), from a power plant south of Las Vegas into Arizona (Green, 1998), within the Los Angeles area (Horrell et al., 1989), and from sources near ground level compared with tall stacks (Englund et al., 1989). During the 1990 San Joaquin Valley Air Quality Study (SJVAQS), perfluorocarbon tracer releases revealed transport from the San Francisco Bay area approximately 250 km down the length of the San Joaquin Valley (Rappolt and Quon, 1995). The SJVAQS operated 72 tracer monitoring sites within a domain of approximately

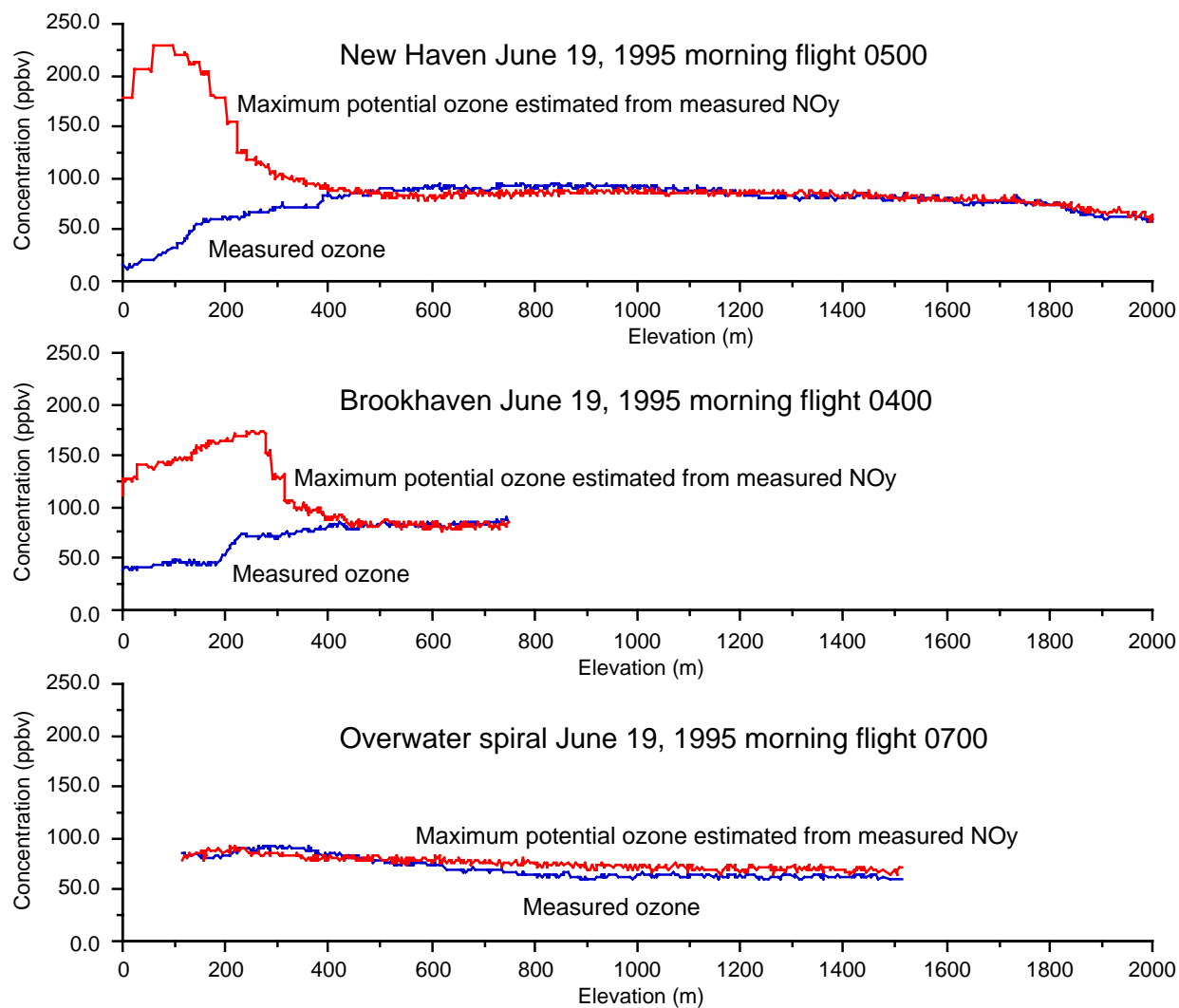


Figure 2-2. Aloft ozone concentrations on the morning of June 19, 1995 at three locations. The maximum potential ozone concentrations were predicted using the method of Blanchard et al. (1999). Data were obtained by STI aircraft. Source: Blanchard, 1998.

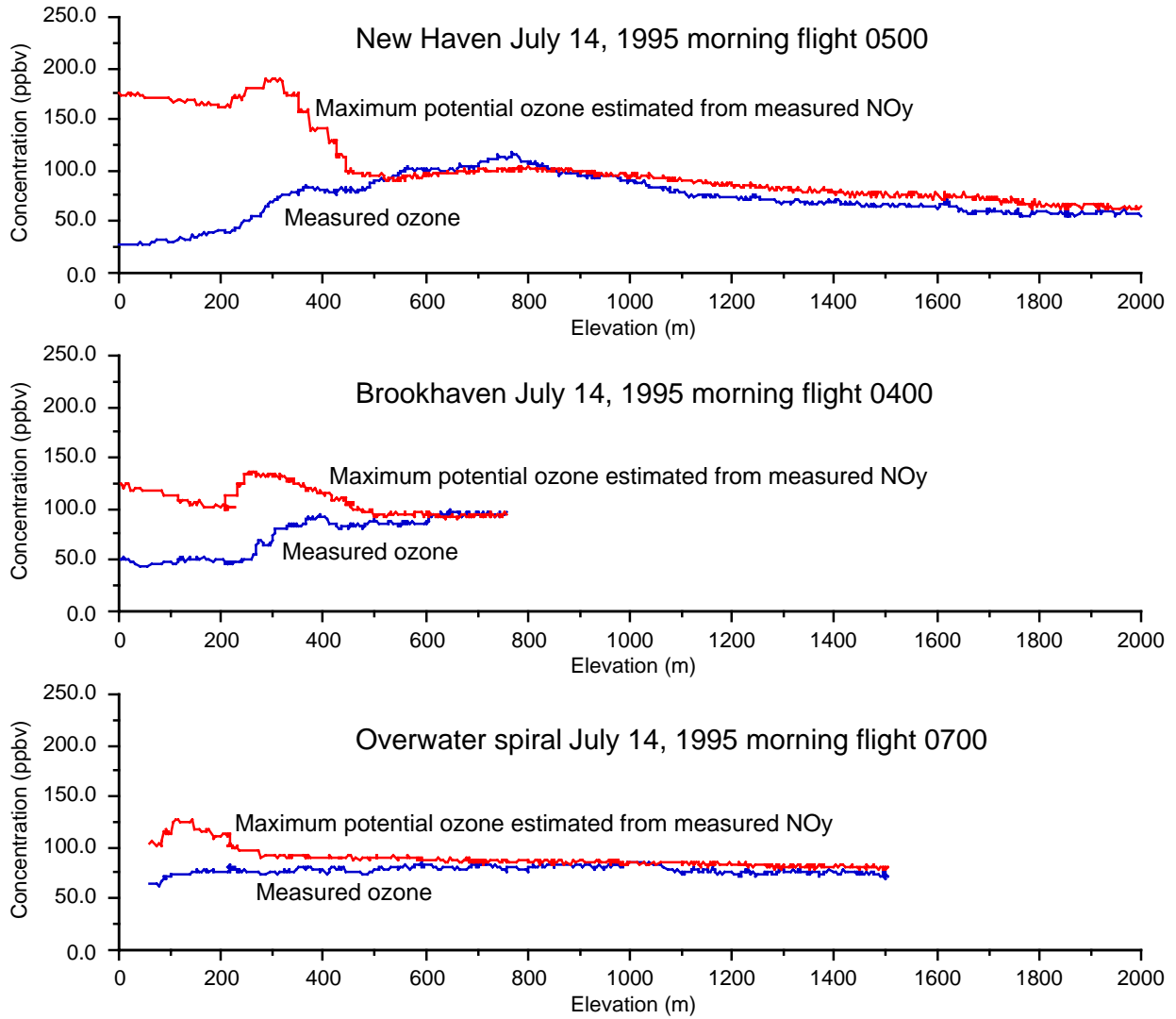


Figure 2-3. Aloft ozone concentrations on the morning of July 14, 1995 at three locations. The maximum potential ozone concentrations were predicted using the method of Blanchard et al. (1999). Measurements were made by STI aircraft. Source: Blanchard, 1998.

150 km x 250 km (Rappolt and Teuscher, 1995); the 72 sites provided density sufficient for revealing atmospheric transport distances, transport times, and the relative magnitudes of transported versus fresh emissions (Smith and Lehrman, 1995).

Two recent analyses of ozone or precursor transport using PAMS data are documented in the draft PAMS data usage report (U.S. Environmental Protection Agency, 2000).

2.4.2 Limitations of the Methods

Transport analyses using either surface or aloft data generally cannot be carried out in a routine manner; typically, such analyses require a substantial amount of interpretation, time, and effort.

Planned tracer studies are expensive and provide limited temporal coverage. In contrast, tracers of opportunity sometimes provide temporally extensive data sets at low cost. However, neither planned tracers nor tracers of opportunity can provide quantitative assessment of the relative magnitudes of transported and locally generated ozone. The reason for this limitation is that tracers do not have the same deposition rates or rates of chemical reaction as do ozone or its precursors, so quantitative estimation of transport contributions is not possible. Tracers of opportunity are rare, and PAMS data do not provide measurements of species that might be suitable as unique tracers.

2.4.3 Adequacy of PAMS Data to Support Methods

Transport analyses generally rely upon meteorological data from a fairly extensive network of stations. The PAMS surface measurements can contribute to the surface meteorological databases. To date, studies have not shown that PAMS species data provide any tracers of opportunity.

Aloft ozone measurements are not incorporated into the PAMS network, nor into other routine monitoring networks. PAMS upper-air meteorological data are a valuable resource for interpreting variations of surface-level concentrations. At present, these data are not as accessible as they could be, nor are the measurements compiled and reviewed uniformly.

2.4.4 Recommendations

Upper-air meteorological measurements are valuable and should be continued. It would be of great value to implement improvements in validation, data access, and the tools available for using the upper-air data. Aloft measurements of ozone may be acquired during special research studies.

2.5 PROVIDING DATA FOR MODEL APPLICATION AND EVALUATION

2.5.1 Applicable Data Analysis Methods

Four principal methods have been employed for evaluating modeling accuracy: performance evaluation, sensitivity analysis, diagnostic evaluation, and corroborating analyses. PAMS data potentially can contribute to both performance evaluation and diagnostic evaluation. In addition, PAMS data can be used for conducting complementary corroborating analyses using techniques such as delineating VOC and NO_x limitation.

Performance evaluation is the process of comparing model predictions to observed ambient data. For Eulerian models, comparisons of predictions to observations are complicated by an important incommensurability: model predictions are concentration averages over the dimensions of a grid cell, whereas ambient measurements are concentrations recorded at a specific location and time. Thus, perfect agreement is not expected. The existence of multiple monitoring stations within the dimensions of a typical model grid cell (i.e., 4-5 km horizontal scale) is helpful for characterizing the variability across stations. When the predicted ozone values of urban- and regional-scale Eulerian models have been compared with ozone measurements, mean errors of about 35% have been typical, along with biases of about 5% to 15%, usually toward underprediction of ozone peaks

A more demanding test of model performance than comparing predicted and measured ozone concentrations is to compare predicted and observed concentrations of precursor species, such as NO, NO₂, TNMOC, or some hydrocarbon or carbonyl species. Because precursor species are not monitored as extensively as is ozone, past comparisons of predicted and measured precursor concentrations have been limited, but they typically revealed discrepancies on the order of 30% to 50% (Roth et al., 1989). PAMS measurements provide a rich database with which to test model applications more thoroughly.

Performance evaluation, through comparison of predicted and measured concentrations, is necessary but not sufficient for evaluating model accuracy. A serious limitation of model performance evaluation is that predicted and measured species concentrations may agree reasonably well if compensating errors exist. Thus, additional tests are needed. Model evaluation typically also includes sensitivity analysis, which is the process of determining a model's response, or sensitivity, to variations in key model inputs, parameters, or equations. One approach to sensitivity analysis is to simply alter input or parameter values, rerun the model, and determine the effects. Model sensitivities to variations of input or parameter values can also be determined more directly through several mathematical techniques. The primary procedure that has been used in photochemical air quality models is known as the direct decoupled method (Dunker, 1981, 1984). This method has been applied to identify the sensitivity of the predicted mixing ratios of ozone and other species to uncertainties in the rate constants and stoichiometric coefficients of the chemical reactions used in a gas-phase chemical mechanism (Gao et al., 1995a, 1995b). Sensitivity analyses typically do not require ambient measurements, so PAMS data are not critical for this aspect of model testing.

A third approach to model evaluation employs techniques for diagnostic evaluation of simulations. Diagnostic evaluations typically examine the capacity of a model application to reproduce a variety of atmospheric processes that are thought to substantially influence ambient pollutant concentrations. Emphasis is placed on designing tests to reveal flaws in the model, if present. For example, a performance evaluation protocol (Roth et al., 1998) developed for an Eulerian modeling application (SARMAP) to central California (Chang et al., 1997; Lu and Chang, 1998) establishes a series of diagnostic steps, beginning with a review of the scientific formulation of the model and concluding with comparisons to other modeling studies. A key step is the evaluation of individual components of the model, which is accomplished through a series of three emissions-related tests, thirteen meteorological tests, and eight air-quality tests.

One recent photochemical model evaluation using PAMS data is documented in the draft PAMS data usage report (U.S. Environmental Protection Agency, 2000).

2.5.2 Limitations of the Methods

Thorough performance and diagnostic evaluation of a model, or modeling system, requires substantial effort and commitment of the necessary resources. When completed, the modeling system is expected to be of known reliability and capable of providing levels of accuracy commensurate with its intended uses. In practice, such a rigorous evaluation process is more comprehensive in scope and consumptive of time and effort than the process typically adopted for use. Schedule, financial, and technical resource constraints usually limit the ability to carry out some aspects of the evaluation program. In this regard, it appears unrealistic to design the PAMS network around a complete set of model evaluation needs. However, some of the data required for model evaluation may be acquired within the existing PAMS protocol, or with modest changes, and at reasonable program cost.

2.5.3 Adequacy of PAMS Data to Support Methods

A complete model evaluation process normally requires data that can only be acquired during special field studies. Routine measurements, including those of the PAMS network, should be considered as a supplement to the more extensive databases that are designed specifically for model evaluation.

The EPA Office of Research and Development (ORD) has recently identified a set of measurements needed for diagnostic model evaluation (**Table 2-2**). The EPA then compared these measurement needs with available PAMS data. Three changes to the PAMS measurement protocol were considered possible: (1) addition of some continuous formaldehyde monitors, (2) addition of NO₂-specific monitors, and (3) addition of some high-sensitivity (ppbv detection limits) CO monitors. These recommendations are consistent with recommendations derived from consideration of other uses of the PAMS data. In addition, for performance and diagnostic model evaluation, maintaining hydrocarbon speciation at as many Type 2 and Type 3 sites as possible would be highly desirable. Note that other PAMS data analyses do not necessarily require speciation at all Type 3 sites. The measurement of other species, such as HNO₃, H₂O₂, HONO, OH or nitrate radicals, and other compounds, was considered useful from a modeling perspective but too expensive or difficult to do on a routine basis.

Table 2-2. EPA ORD priorities for use of PAMS data for model evaluation (reproduced from ORD memo).

| Priority | Locations | Recommended Parameters | Reason For Need |
|----------|----------------|---|---|
| 1 | All sites | NO ₂ NO _y (with preference of NO ₂ over NO _y if forced to choose one or the other) NO O ₃ speciated VOC* Total NMHC | To check ratios over time as the character of the atmosphere changes due to controls and other forces |
| 2 | Selected sites | HCHO (formaldehyde–continuous/short term) | |
| | | H ₂ O ₂ (1 hr routinely, but capability in special study to achieve 5 minute average) | To check on regime change and style of O ₃ production |
| | | PANs (n-PAN, PPN, total PAN); HNO ₃ | To track trends over time |
| 3 | Special sites | H ₂ O | |
| 4 | Special sites | CO (need to determine which PAMS sites also have CO monitors)–need ppb resolution, however | |
| 5 | Special sites | Other VOC compounds (e.g., oxygen-containing compounds) | Needed for other model mechanism testing |
| 6 | Special sites | Other aldehydes–if high enough (surface reactions on particles?) | |

*VOCs needed for aging studies–27 VOCs for emission check purposes; some of those and another 10 (total of 37) needed for diagnostics. Data needed downwind of downtown. ORD expressed concern about dropping compounds even at upwind and downwind sites for aging study purposes.

PAN = peroxyacetylnitrate

PPN = peroxypropionynitrate

One of the stated PAMS objectives is to provide hydrocarbon measurements appropriate for evaluating the initial or boundary conditions of modeling studies. However, regional, and even urban-scale, modeling studies all locate the model domain boundaries far upwind of the main areas of study. PAMS Type 1 sites typically are not close to model boundaries. Thus, the usefulness of PAMS data for constraining model boundary concentrations appears limited.

2.5.4 Recommendations

Type 3 sites should be reviewed for replacement of carbonyl measurements with continuous formaldehyde monitors. NO₂-specific monitors should be added to some Type 3 sites and the usefulness of the data evaluated. High-sensitivity (ppbv detection limits) CO monitors should be added to Type 2 and Type 3 sites. VOC speciation should be maintained at Type 2 and Type 3 sites.

2.6 FORECASTING EPISODES

2.6.1 Applicable Data Analysis Methods

Ozone forecasting has typically relied upon analyses of meteorological data to predict the occurrence of conditions conducive to ozone formation. In part, synoptic analyses have been used to identify, for example, the locations of high pressure systems or blocking ridges. In different parts of the country, various specific measured or derived meteorological quantities have been found useful as predictors of high-ozone days. Such quantities include upper-air temperatures, certain pressure gradients, or other indicators of stagnation conditions. Recently, some forecasting techniques applied to the Atlanta area have made use of pinene and selected olefin concentrations. Morning concentrations of other species may also prove useful. Another recent approach has been to use the Urban Airshed Model (UAM) to forecast next-day peak ozone concentrations (Chang and Cardelino, 2000). In general, most forecasting approaches are likely to rely primarily on analysis of meteorological conditions. The availability of real-time sounding data will aid such methods. Such data are also needed for UAM forecasting if that approach proves feasible.

2.6.2 Recommendations

Enable real-time access to PAMS auto-GC and surface and upper-air meteorological data.

2.7 OTHER USES OF PAMS DATA

PAMS data potentially are useful for purposes that are auxiliary to the original objectives of the network, including

- characterizing ambient air toxics for exposure modeling and trend analyses,
- characterizing emissions and ambient concentrations of nitrogen species,
- providing data for evaluation of particulate matter, and
- enhancing special studies.

To be most useful for these other purposes, further consideration should be given to the types of measurements made and the time periods sampled. For example, ambient toxic assessment realistically requires year-round measurements. Typical sampling routines involve collection of 24-hr samples once every 6 or 12 days throughout the year. Other sampling regimens are employed for studies of PM. Potentially, PAMS speciated VOC measurements might provide research-level information relevant to the formation of secondary organic carbon aerosol. Further assessment is needed. Conversely, measurements of elemental carbon, typically included within sampling of PM, could be useful in VOC receptor modeling for distinguishing diesel from gasoline exhaust if they were carried out with adequate time resolution (hourly or multi-hour).

Two recent analyses of air toxics exposure using PAMS data are documented in the draft PAMS data usage report (U.S. Environmental Protection Agency, 2000).

3. RECOMMENDATIONS

In reviewing the literature, we have prepared general recommendations for the PAMS network and specific recommendations for the Northeast and Mid-Atlantic PAMS sites. These recommendations should be considered preliminary as we have not yet completed our analyses of the data. We suggest these recommendations be used as a place from which to begin discussions and analyses.

3.1 GENERAL RECOMMENDATIONS FOR THE PAMS NETWORK

3.1.1 Number of sites of each type

1. Examine the possibility of eliminating speciated hydrocarbon sampling at the second Type 2 site in many large cities. Preliminary data analyses suggest that in many cities, source composition is similar at both Type 2 sites, so little new information is being generated from speciated hydrocarbon measurements at the second site. However, it would generally be useful to maintain monitoring of ozone, NO, NO_x, and CO at the second Type 2 site, depending upon the existing spatial density of monitoring. If speciated hydrocarbon measurements are discontinued at Type 2A sites, optionally replace speciated hydrocarbon sampling with continuous total NMHC (+/- 10 ppbC at 50 ppbC). The continuous measurements are less resource-intensive and yield information on primary pollutant emission levels and changes over time, the spatial distribution of which is valuable to understand.
2. Maintain a long and continuous data record with good data quality and a high level of data completeness at one or a few sites; this record is more important than broad spatial coverage for the purpose of trend analysis. However, the representativeness of sites requires assessment. A good example is the possibility of opposing trends at some Type 2 and Type 3 sites. In some areas, Type 2 sites may have experienced declining levels of ozone precursors. However, downwind sites may have experienced less or no change in precursor levels as suburban growth counterbalanced emission controls. Sufficient spatial coverage is needed to capture all trends.
3. Maintain a sufficient density of monitoring sites with measurements of ozone, NO, and NO_x in areas between Type 2 and Type 3 sites so that the transition from VOC to NO_x limitation, which typically occurs somewhere in the near-to-far downwind area, could be identified to within 10 km. This recommendation pertains more to the whole compliance network than to PAMS sites. Nonetheless, it is an important design consideration.

3.1.2 Species measured at each site

1. Measure NO₂ and NO_y at Type 3 and Type 4 PAMS sites with +/- 1 ppbv in the range 1 to 10 ppbv. In addition, maintain a conventional NO_x measurement at all sites during some periods, and at some sites continuously, to facilitate comparison with NO_x data from other monitoring sites.

2. Add high sensitivity (ppbv detection limits) hourly CO monitors to PAMS Type 2 or Type 2A sites for aiding the evaluation of emission inventories.
3. Add high sensitivity (ppbv detection limits) hourly CO monitors to PAMS Type 3 sites for assessing the loss rates of NO_x and NO_y and improving evaluations of the relationship between ozone formation and NO_x levels.
4. Standardize upper-air meteorological measurement reporting and make data more widely accessible.
5. Add semivolatile measurements to Type 2 sites on the morning of every sixth day, or add continuous elemental or black carbon measurements, to better estimate the diesel emissions contributions.
6. Eliminate use of the Nafion dryer, if possible, to allow expansion of the PAMS target list to include more species such as pinenes and to improve accuracy of measurements of C₂-C₆ alkenes, including isoprene.
7. Replace some Type 3 or Type 4 monitors with continuous total NMHC (+/- 10 ppbC at 50 ppbC). Collocate continuous NMHC and speciated measurements for a sufficient time to establish a relationship. Then use occasional canisters to check speciation.
8. Tailor the PAMS target species list to permit summing of closely related compounds. For some groups of compounds, summing could improve the accuracy of values close to detection limits and eliminate possible misidentification of close peaks. Candidate compounds for summing are (1) 2,2-dimethylpentane, 2-methylpentane, and 3-methylpentane, (2) o-, m-, and p-ethyl toluenes, and (3) o-, m-, and p-diethyl benzenes.
9. Consider “lumping” C2 and C3 compound concentrations at selected sites to simplify the analytical demands.

3.1.3 Frequency and resolution of measurements

1. Reduce carbonyl measurement requirements to afternoon samples at downwind sites and morning samples at Type 2 sites. Expand the list of carbonyls measured to be more complete (including heavier carbonyls) OR use continuous formaldehyde monitors at selected sites.
2. Eliminate or reduce measurements at some Type 3 or Type 4 sites.

3.2 SPECIFIC RECOMMENDATIONS FOR THE NESCAUM AND MARAMA REGIONS—PRELIMINARY AND CONTINGENT UPON COMPLETION OF DATA ANALYSES

Based on the general recommendations of Section 3-1, we provide a set of specific recommendations for the PAMS monitors in the NESCAUM and MARAMA regions. These recommendations are presented for consideration and further evaluation by NESCAUM. They are not intended to be final, nor are they meant to be implemented without careful review of all their implications by NESCAUM, MARAMA, EPA, and other parties involved with the PAMS network.

3.2.1 Number of sites of each type

1. Review site typing. Preliminary analysis of the PAMS data suggests that some sites exhibit characteristics similar to sites of other types (see **Table 3-1**). The recommendations that follow should be reconsidered upon review of the existing site types.
2. If further data analyses reveal highly similar hydrocarbon speciation between Type 2 and 2A sites in some areas, consider eliminating speciated hydrocarbon sampling at Type 2A sites: Long Island MA, Hamden CT, Queens Com. College NY, Living Classroom MD, Camden NJ, Ft. Lee School VA. Consider if any of these Type 2A sites provide more representative data than the Type 2 sites. Maintain ozone and NO_x or NO_y monitors. Optionally replace speciated hydrocarbon sampling with continuous NMHC.
3. Review AIRS for coverage near Type 3 sites and in downwind suburban and rural areas. Within each of the PAMS urban domains, add NO_x or NO_y monitors to three to six downwind suburban or rural compliance monitoring locations where ozone is presently measured.

3.2.2 Species, frequency, and resolution of measurements at each site

1. Add NO₂ and/or NO_y instrumentation at the following Type 3 sites: Newbury MA, Stafford CT, Borderland MA, Ware MA, Sherwood Island CT, Aldino MD, Rider College NJ, and Fort Meade MD. Add NO₂ and/or NO_y to the existing NO_x instrumentation at the following Type 4 sites: Acadia ME, Cape Elizabeth ME, Truro MA, New Brunswick NJ. In the NESCAUM area, all Type 3 and Type 4 sites except Newbury now have NO_y. Maintain existing NO_x instruments, or add them where possible, to allow comparisons between NO_x and NO_y.
2. Add high-sensitivity (ppbv detection limits) hourly CO monitors to the following PAMS Type 2 and Type 2A sites: Lynn MA, Long Island MA, Bronx NY, Queens Community College NY, Kittery ME, East Providence RI, Chicopee MA, McMillan Reservoir DC, Essex MD, Clifton Park MD, Living Classroom MD.
3. Add high-sensitivity (ppbv detection limits) hourly CO monitors to PAMS Type 3 sites: Newbury MA, Stafford CT, Borderland MA, Ware MA, Sherwood Island CT, Aldino MD, Rider College NJ, and Fort Meade MD.
4. Replace some Type 3 or Type 4 monitors with continuous total NMHC (+/- 10 ppbC at 50 ppbC). Type 3 sites are Newbury MA, Stafford CT, Borderland MA, Ware MA, Sherwood Island CT, Aldino MD, Rider College NJ, and Fort Meade MD. Type 4 sites are Acadia National Park ME, Cape Elizabeth ME, Truro MA, and Lums Pond DE. Use occasional canisters to check speciation. Consider lumping C2 and C3 compounds where speciation is done.
5. Install continuous formaldehyde instruments at Type 2 (Lynn MA, Long Island MA, Bronx NY, Queens Community College NY, Kittery ME, East Providence RI, Chicopee MA, McMillan Reservoir DC, Essex MD, Clifton Park MD, Living Classroom MD) and Type 3 sites (Newbury MA, Stafford CT, Borderland MA, Ware MA, Sherwood Island CT, Aldino MD, Rider College NJ, and Fort Meade MD). If continuous formaldehyde

monitors are installed, reduce cartridge measurement requirements to occasional spot checks with afternoon samples at Type 3 sites and morning samples at Type 2 sites. If spot checks are done, expand the list of carbonyls measured to be more complete (heavier carbonyls) at Type 3 and Type 4 sites; eliminate expanded carbonyl sampling at Type 2 sites (data analyses to date indicate that formaldehyde is an adequate predictor of acetaldehyde, and higher carbonyls are present at low concentrations).

Table 3-1. PAMS monitoring sites in the NESCAUM and MARAMA regions.

| Area | State | Site | Type | Known concerns |
|---------------------------------|-------|-------------------------|------|----------------------------|
| Boston-Lawrence-Worcester | MA | Borderland | 1/3 | |
| | MA | Lynn | 2 | |
| | MA | Long Island | 2A | |
| | MA | Newbury | 3 | |
| | ME | Acadia National Park | 4 | |
| Connecticut | CT | Sherwood Island | 1 | |
| | CT | East Hartford | 2 | |
| | CT | Hamden | 2A | |
| | CT | Stafford | 3 | |
| | ME | Cape Elizabeth | 4 | |
| New York-New Jersey-Long Island | NJ | New Brunswick | 1/4 | Data resemble Type 2 or 3? |
| | NY | Bronx Botanical Gardens | 2 | |
| | NY | Queens Comm. College | 2A | |
| | CT | Sherwood Island | 3/1 | |
| Portsmouth-Dover-Rochester | NH | Brentwood | 1 | |
| | ME | Kittery | 2 | |
| Providence-Pawtucket-Fall River | RI | West Greenwich | 1 | |
| | RI | East Providence | 2 | |
| | MA | Borderland | 3/1 | |
| | MA | Truro | 4 | |
| Springfield | MA | Agawam | 1 | Urban character? |
| | MA | Chicopee | 2 | |
| | MA | Ware | 3 | |
| Baltimore | MD | Fort Meade | 1/3 | |
| | MD | Essex | 2 | |
| | MD | Clifton Park | 2A | |
| | MD | Living Classroom | 2A | |
| | MD | Aldino | 3 | |
| | DE | Lums Pond | 4/1 | |
| Philadelphia-Wilmington-Trenton | DE | Lums Pond | 1/4 | |
| | PA | East Lycoming Lab | 2 | |
| | NJ | Camden | 2A | |
| | NJ | Rider College | 3 | |
| | NJ | New Brunswick | 4/1 | Data resemble Type 2 or 3? |
| Washington | VA | Corbin | 1 | |
| | DC | McMillan Reservoir | 2 | |
| | MD | Fort Meade | 3 | |
| | DE | Lums Pond | 4 | |

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