

**A NEW APPROACH  
FOR DEMONSTRATING ATTAINMENT OF THE  
AMBIENT OZONE STANDARD**

**MODELING, ANALYSIS, AND MONITORING CONSIDERATIONS**

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## **I. PURPOSE**

Over the past 15 years photochemical air quality simulation models (PAQSMs) have played a major role in elucidating our understanding of the relationship between the emissions of ozone precursors (volatile organic compounds, or VOCs, and nitrogen oxides, or NO<sub>x</sub>) and meteorology with the formation of ozone and other photochemical oxidants. As a result of provisions of the Clean Air Act Amendments of 1990, photochemical modeling is now the cornerstone of the air quality management approach used in the development of emissions control strategies designed to bring into attainment areas in the United States that exceed the NAAQS for ozone.

While twenty five years of regulatory efforts have effected substantial improvements in ozone-related air quality in the United States, these improvements have fallen short of goals and expectations. The failure to meet the air quality standard for ozone in a timely manner has raised concern nationally and elicited considerable attention, one result of which was the commissioning of major scientific studies by the Office of Technology Assessment (1989) and the National Academy of Sciences (1991). These studies have identified several basic issues regarding the state of the science and the operational approaches used in the management of ozone air quality. Specifically, these studies find that:

- current pollutant monitoring networks are inadequate to measure and track the performance and progress of the ozone air quality management process,
- representations of the emissions of ozone precursors can have significant errors and uncertainties and have not been subjected to independent testing and evaluation procedures,
- uncertainties in biogenic emissions and their contributions to ozone air quality may mask unanticipated and in some cases unachievable control requirements,
- a single national control strategy for the control of VOC and/or NO<sub>x</sub> emissions may not apply uniformly in all areas, and
- regulatory expectations for the use of models in the state implementation planning (SIP) process exceed their performance capabilities.

The premise of this document is that we cannot and should not continue to rely on the use of PAQSMs alone (or even substantially) in developing plans for attaining the NAAQS for ozone. Rather, we should design and adopt a planning approach that (a) integrates attractive aspects of key elements - modeling (using PAQSMs), data analysis, and, especially, ambient and source monitoring - in continuing to pursue attainment of the NAAQS and (b) provides for accountability and feedback, so that

corrective actions may be taken as needed. Such an approach is intended to:

- take advantage of the strengths of each of these individual elements,
- minimize the impact on planning of their known limitations, and
- integrate the application of the elements so that planning is a continuing and efficient process.

In this document we propose a new approach for demonstrating attainment of the NAAQS for ozone.

## II. PERSPECTIVE

### A. The Decision Maker and Information

#### *The Needs of the Decision Maker*

A central objective of planning to improve air quality in an urban area or a larger region is to establish how best to attain the NAAQS for ozone. Specific information needed by a decision maker includes determining:

- requirements for emissions reductions,
- the extent of transport of pollutants into the region and the impact of these pollutants on air quality,
- the anticipated response of the air resource to widespread emissions reductions, both locally and upwind,
- the effectiveness of emissions controls imposed (i.e., the fraction of prescribed reductions actually achieved),
- the extent of progress toward attainment of the standard through the monitoring of air quality in a region, and
- the magnitude of export of pollutants out of the region and the potential for adverse impacts downwind.

#### *Technical Pursuits*

To address these informational needs, a variety of technical endeavors are conducted. These include:

- characterizing air quality through routine ambient monitoring of ozone, and in some instances, one or more precursor species. Ozone is monitored in all large urban areas, at varying network density and spatial coverage. VOCs are monitored in only a fraction of cities; however, with the introduction of PAMS sites, coverage is improving markedly. NO<sub>x</sub> monitoring varies widely, from the dense network of the South Coast Air Basin to the absence of NO<sub>x</sub> monitoring in the some metropolitan areas. Here, too, PAMS is improving coverage.
- conducting an intensive measurement campaign to acquire a comprehensive aerometric data base that will support analysis and modeling aimed at increasing understanding of the dynamic atmospheric processes associated with adverse air quality.

- planning air quality improvements through the use of PAQSMs. Needs include assessing if the reduction of VOC or NO<sub>x</sub> or both limits the formation of ozone, determining the magnitude of emissions reductions required, establishing the soundness and reliability of estimation procedures, and determining the geographical region over which emissions reductions are to be imposed.
- demonstrating progress toward attainment through ambient monitoring. Efforts include characterizing air quality improvements through the analysis of concentration trends for both primary and secondary pollutants, adjusting for meteorological variability.
- tracking emissions changes. Activities may include both ambient and source monitoring, sampling for categories of sources comprised of a large number of individual emitters (such as motor vehicles), undertaking special experiments (such as tunnel studies), and conducting surveys or audits of surrogates for source emissions. Source monitoring is now conducted for many but not all categories of sources.
- evaluating the effectiveness of emissions controls through the analysis of relevant data. Observational information acquired is used in the analysis of emissions trends and the assessment of the efficacy of control programs.
- estimating the impacts of pollutants transported into a region, also through modeling. Often, inadequate attention is given to this need. This information may be provided as an output of PAQSM simulations.

Note that these technical endeavors, as undertaken now, address only a portion of the decision maker needs listed above. Specifically, the first two and last items in the list merit greater attention than they now receive. An improved approach to attainment demonstration should address each of the needs listed and incorporate each pursuit described as effectively as possible.

In addition, there is need to evaluate and weigh the relative costs and benefits of alternative control strategies in light of uncertainty, preferably through the formalism of decision analysis. Due to the more limited scope of this effort, these topics are not now addressed. However, they merit inclusion as components in an overall framework, and should be considered in any subsequent scoping activities pertaining to attainment demonstration.



## *Air Quality Monitoring*

A key element of a new approach must include increased (in quantity) and expanded (spatially) use of air quality monitoring. The current dependency on modeling as the central element in air quality management suggests an acceptance of PAQSMs as accurate estimators of present and future air quality. In fact, as we shall discuss, modeling results virtually always possess a degree of uncertainty that limits or discourages confidence in the result. In contrast, monitoring, being frequently perceived as "ground truth", engenders a degree of confidence that is often not warranted. In particular, the lack of specificity of some measurements, such as for  $\text{NO}_2$ , and the lack of ability to monitor at very low concentrations, such as for  $\text{NO}$  and  $\text{NO}_2$ , account for the reservations. Nevertheless, with the use of improved instrumentation now becoming available, awareness of the pitfalls of monitoring, and application of a proper level of care in conducting measurements, monitoring provides a reasonably reliable adjunct to modeling in establishing knowledge of air quality and in providing feedback to a continuing planning process, one that allows for the improvement of PAQSMs through incorporation of newly gained knowledge and the revision or adjustment of their estimates based on "real world" measurement.

In general, we envision several consequences of an expanding role of ambient monitoring:

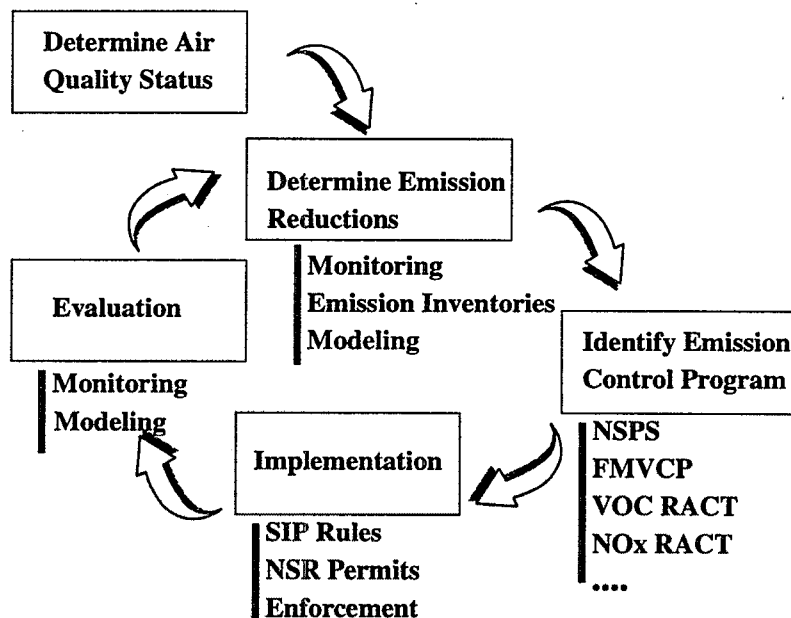
- Monitoring information is likely to be incorporated more fully in the planning process due to the continuing concern about the uncertainties and inaccuracies that attend modeling.
- Metropolitan areas that choose to expand their routine monitoring network because of inadequate spatial coverage or the absence or paucity of monitoring of selected pollutants will wish to take maximum advantage of their new investments.
- The introduction of PAMS sites in major cities is providing impetus to use the data in planning and assessment.
- Ambient monitoring of precursors in the vicinity of sources, coupled with in-source monitoring and special studies, will provide information on the efficacy of controls that is not now available to the extent needed.
- Tracking of progress and continuing assessment of accountability will be more feasible.

Overall, there is need for a shift in planning philosophy from a dependency on modeling results with little feedback to a commitment to a fully integrated planning effort based on modeling, expanded monitoring, and data analysis, with continuing

feedback of observational information into the analytical elements of the process.

## **B. Attainment Demonstration**

As discussed, models play a central role in the ozone air quality management process and are the operational tool used in state implementation planning to quantify the emission control requirements needed to achieve the ozone air quality standard. The air quality management approach defines the conceptual framework for linking pollutant emissions to ambient air quality, and the state implementation plan provides the operational context for carrying out the management approach. Schematics of the air quality management approach and the state implementation planning process are provided in Figures II-1 and II-2. Although it is possible to base the air quality management approach on elements other than models (e. g., technology-based emissions controls and/or monitoring), this has not been the case for ozone. Since ozone is not directly emitted into the atmosphere, but formed through photochemical reactions of primary emitted precursors (VOC and  $\text{NO}_x$ ), models are thought to be the most effective means for quantifying the complex chemical and meteorological interactions that relate precursor emissions to ozone production.



**Figure II-1. Air Quality Management Approach**

The state implementation planning process (Figure II-2) requires data for several purposes. First, ozone air quality data are needed to determine if the standard has been violated and to what extent. During the demonstration phase of the SIP process, air quality, meteorological and emission data must be acquired to support the operation of a modeling system and the evaluation of its performance in estimating air quality for the base case year. Models are then used to estimate the emission reductions (taking into consideration future emission projections) needed to

attain the ozone air quality standard. Once the control program for achieving the target year demonstration for ozone attainment is stipulated and all supporting documentation is prepared, the SIP is submitted for public comment and approval by EPA. This completes the demonstration phase of the SIP.

As part of the implementation phase of the SIP, a new provision under the Act requires the tracking of emissions to determine reasonable further progress (RFP). The RFP requires a 15% reduction in VOC emissions over the first 6 years and 3% reduction per year thereafter until attainment is achieved in all but "marginal" classified areas.

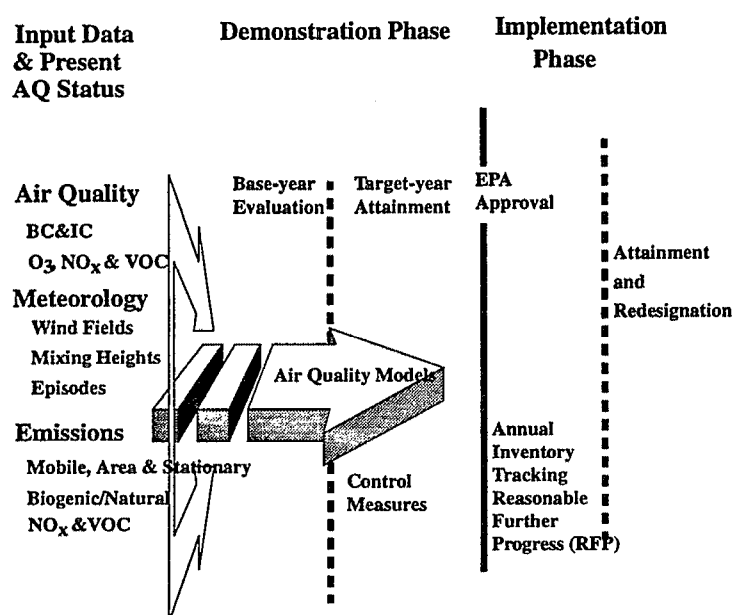


Figure II-2. State Implementation Planning Process

## C. Shortcomings of the Attainment Demonstration Process

### *The Overall Process*

As currently mandated under Clean Air Act Amendments of 1990, the air quality management approach and its use of photochemical air quality simulation models in the SIP process to develop control strategies for attainment of the ozone standard has, in effect, failed to meet its objectives. For a given geographical area, this lack of success stems from one or more of the following potential problems:

- The time and resources available are inadequate to support SIP modeling requirements.
- The availability of data are inadequate to support SIP modeling.
- Limitations inherent to PAQSMs strongly suggest that regulatory needs may exceed performance capabilities.
- Annual inventory tracking of reasonable further progress (RFP) frequently is "a paper exercise" with little or no substantive accountability.
- Although PAMS has the potential to establish monitoring as an effective means for tracking progress and introducing accountability in emission control programs, substantial implementation and operational issues remain unresolved.

Although the air quality management approach, in principle, appeared to be a viable methodology for addressing the problem of air pollution, it has encountered a number of failures as a result of flaws in execution and an insufficiency of means and incentives to track progress and account for the effects of emission control strategies on air quality. The future success of the ozone control program will depend strongly on the community's ability and willingness to address these shortcomings. Actions to be considered include:

- seeking to modify CAAA requirements and/or attendant regulations,
- developing improved guidelines for applying models,
- further developing, refining and testing empirically-based, observation-driven methods (ODMs),
- improving monitoring capabilities, including PAMS implementation, and refining PAMS-related methodologies to facilitate addressing existing problems.

The approach proposed here incorporates each of these responses.

### *Models*

We have expressed concerns about the extent to which modeling systems (i.e., comprised of air quality, emissions, and meteorological models) adequately portray the dynamics of atmospheric processes that govern ozone formation and thus about the accuracy of simulated air quality representations. These concerns include:

- deficiencies in knowledge of key dynamic processes and thus limitations in the formulations of these processes embodied in the model. Processes of concern are emissions, transport and dispersion, gas phase chemistry, and dry deposition. In the course of model development and application through the 1980s, notable improvements were made. These include the introduction of prognostic meteorological modeling in the mid-1980s, the incorporation of mechanistically-based dry deposition algorithms in place of more empirical relationships, and with the discovery of underestimation of VOC emissions in the late 1980s, efforts to correct for it, either through improved estimates or adjustments of the incorrect estimates based on independent evidence, the inclusion of NO<sub>x</sub> emissions from soils in 1993, and adjustment of the emissions rates of isoprene in 1994. Each improvement introduced significant alterations in model inputs or formulation and thus the potential for changes of similar significance in modeling results.

In recent years, regional scale modeling is receiving increasing attention. As spatial and temporal scales expand, the simulation of some dynamic processes becomes more critical and others less critical. For example, the simulation of biogenic VOC emissions and the deposition of pollutant species requires greater attention and accuracy. In most cases, the needed shifts in emphasis have yet to be adopted. Attention should be given to improvements in the representation of individual processes, insofar as demands for accuracy of depiction increase with increasing spatial scale.

- additional demands for data and improved performance created by the increasing complexity of model formulation. As greater attention is given to simulating the dynamics of individual processes, model complexity increases. Attending increased model complexity are (a) increased difficulty in simulating each individual process correctly, (b) the potential for greater cumulative uncertainty (while imprecision may increase, bias may be reduced) and (c) increased computational demands. Thus, the potential for uncertainty increases after a certain point, rendering overall acceptance of the model more difficult. Some feel that the "bottom of the complexity-uncertainty curve" has already been passed, and the community is being confronted with evaluation requirements that are increasingly difficult to meet.

- limitations in the availability of information needed as inputs to UAM. Typically, important data deficiencies exist for emissions estimates for VOCs and NO<sub>x</sub>, meteorological fields (wind velocities and vertical exchange rates), boundary conditions, and aerometric data aloft. Such limitations exist even when relatively rich data bases are available, but they are particularly severe when data are only routinely collected in an urban area. Most areas are lacking or deficient in data needed to estimate boundary conditions and meteorological and air quality conditions aloft. Relatively few areas monitor VOC concentrations. Moreover, due to limitations in measurement capabilities, monitored concentrations of NO, NO<sub>2</sub>, and other nitrogen-containing atmospheric pollutants are often inaccurate. Where data gaps of consequence exist, modeling accuracy suffers, and the prospects for identifying and reducing or eliminating the presence of compensating errors are diminished.
- limitations imposed in estimating the likelihood of attainment based on the results of simulations for only one or two episodes for which intensive data are acquired and intensive modeling is pursued. The number of episodes simulated today in preparing a SIP does not begin to meet the needs of representation of meteorological regimes of interest. Also, highly adverse episodes often are not captured in data collection programs. In addition, EPA guidelines permit the elimination from consideration of "hard to simulate" episodes.
- limitations imposed in estimating the likelihood of attainment that derive from the deterministic analysis of meteorological processes that are inherently stochastic and thus the inability to directly relate results to the standard (which is probabilistic in formulation). The results of PAQSM simulations do not and cannot tell us the probability of an area's exceeding the NAAQS in the future, once a stipulated control program is fully in place, given that modeling results indicate that attainment will be achieved.
- the potential for inaccuracy and imprecision in model-derived concentrations estimates devolving from the deficiencies and limitations noted above. Model imprecision for ozone concentrations typically ranges from 25-40%, inaccuracy (bias) from 5-30%. These uncertainties should be compared with a typical "signal" of 25-40% - the fraction of reduction in the peak ozone concentration for an area (150-170 ppb) that is needed to achieve attainment (at 120 ppb).

In most modeling exercises, the modeler adjusts inputs in attempting to improve performance. A key test of quality of performance is to evaluate the model for other episodes without adjustments, using the same rules for establishing model inputs for the second and third episodes as were used for the first. This type of test is rarely applied. When it is, performance typically is inconsistent.

- the potential for introducing compensating errors into the model as a

consequence of the inability to evaluate model components independently. It appears that compensating errors have been present in many past applications. Their presence introduces the potential for bias into the estimation of the impacts of emissions control strategies.

- the lack of availability and use of well founded emissions projections techniques. Complex socioeconomic forces drive population growth, industrial expansion, residential and commercial development, and emissions changes. Little effort has been made nationally to develop the capability to project future emissions based on a quantitative evaluation of alternative futures. Thus, uncertainties in projections of alternative futures made ten years or more in advance can significantly exceed inherent uncertainty levels. This deficiency in prediction capability is not likely to be rectified in the near future.

### *Implications*

These issues, in the aggregate, place into serious question the potential for the PAQSMs, including UAM-IV and UAM-V and related models, to provide accurate quantitative representations of the impacts of emissions reductions on peak ozone concentrations and thus of attainment demonstration. Given the unfavorable noise-to-signal ratios in model simulations and the frequent presence of compensating errors in the modeling systems, the high level of dependency being placed on this type of model seems inappropriate. If model performance is judged to be inadequate and cannot be improved, no alternatives for developing emissions control strategies will exist. It thus seems prudent to adopt an approach that either permits "back-up" or constitutes an alternative, such that a much lower probability of failure accompanies the use of these models. Unfortunately, today's guiding principle for the use of a PAQSM might be stated as, "The model is the best tool available," so let's use it, and not, "Is it good enough to meet the need?"

It is crucial to recognize that the history of air quality projection using PAQSMs is one of consistently overestimating the reductions in peak ozone concentrations that are to be realized in a specified period of time. A record of emissions reductions prescribed in the past and projections of future air quality now exists. SIPs prepared since 1979 and throughout the 1980s document this information. In the vast preponderance of situations, projections of air quality made in the past have not been achieved in the present. While there are many reasons for this, the inaccuracy of modeling systems (i.e., air quality, emissions, and meteorological models and their inputs) is a likely contributor to this failure in projection.

As discussed, a second notable deficiency in the SIP process also merits attention: the lack of (a) accountability for ensuring that plans are met and (b) evaluation and demonstration requirements. The current SIP process stipulates control programs



based on "engineering estimates" that are intended to achieve needed reductions in precursor emissions, as projected through model simulations. Unfortunately, the process has lacked requirements or procedures to track progress in reducing emissions, attaining emissions reduction goals, and achieving planned air quality improvements. In addition, it has lacked a requirement and a post-SIP effort to assess the accuracy and reliability of models used in estimating future air quality. There is a need to institute a process of retrospective analysis for determining cause(s) of failures in modeling, such as flawed formulations, erroneous emissions representations, inadequate data bases, and insufficiently effective implementation of emissions reductions, and to introduce improvements that will lead to reliable estimation of control needs.

#### **D. Improving the Process**

##### *Needs*

Models play a central role in the ozone air quality management process and are the operational tool used in state implementation planning to quantify the emission control requirements necessary to achieve the air quality standard for ozone. The air quality management approach defines the conceptual framework for linking pollutant emissions to ambient air quality, and the state implementation plan provides the management approach. The experience gained in SIP preparation and the subsequent failure to meet air quality standards in the time frame prescribed speaks strongly to the need for an improved planning process, one which, if conducted thoughtfully, will not experience failure in its outcome. Needs to be met that are not now being met include:

- oversight of SIP implementation, including tracking progress and demonstrating the extent to which the plan being implemented is being met,
- a mechanism for mid-course adjustment or correction, where emissions reductions fall short of targets as a function of time or where air quality improvements, adjusted for meteorological variability, fall short of targets as a function of time, and
- diagnostic analysis of modeling failures and improvement or correction of the modeling process.

### *A proposed direction*

We propose that a new process for attainment demonstration and SIP preparation be developed and adopted, taking advantage of the strengths of elements (such as modeling, data analysis, monitoring) now in use, minimizing the impacts of key limitations of these elements, introducing tracking and feedback, and requiring diagnostic analysis of the SIP process during the years following. Section III proposes such an approach, Section IV delineates its elements, Section V offers recommendations for research and development in support of the new approach, and Section VI suggests additional improvements that should be considered over the longer term.

### III. A PROPOSED APPROACH TO TRACKING PROGRESS AND DEMONSTRATING ATTAINMENT

#### A. A Schematic Depiction of an Improved Process

We now describe an alternative approach to attainment demonstration, one that de-emphasizes but retains the use of PAQSMs and adds other elements which, when taken together, constitute *a process for achieving attainment* rather than *an act of attempting to demonstrate attainment*. We refer the reader to Figures III-1a and III-1b, which present a detailed schematic diagram depicting the approach. We now briefly describe its elements and their purposes.

##### Conduct initial data acquisition

Supporting modeling and ODM use with a data base adequate to meet the input requirements of the methods is a requisite for reducing uncertainty, eliminating bias, and building confidence in the use of these tools in decision making. If formal air quality planning is contemplated for an area, the planning and implementation of ambient aerometric monitoring should begin as soon as possible. Sections IVD and VC of this report address monitoring needs.

##### Conduct modeling, using both PAQSMs and ODMs

PAQSMs should be used to simulate the temporal and spatial distributions of ozone concentrations that are anticipated to result from prescribed reductions in the emissions of VOC and NO<sub>x</sub>. However, their limitations should be recognized, and expectations associated with their use should not exceed their demonstrated performance capabilities. The following principles should be observed in applying photochemical modeling systems (air quality, emissions, and meteorological models):

- Acquire and use a suitable data base for performance evaluation, control strategy assessment, and sensitivity analysis.
- Require adequate testing and performance prior to use. Model evaluation protocols prepared for the Western States Petroleum Association (WSPA) (Reynolds, et al., 1994) and the San Joaquin Valley ozone study (Roth, et al., 1995 ) provide guidance on the conduct of model evaluations. Among the many issues meriting attention are the need (a) for "hands off" testing of the model for episodes after the first studied and (b) to examine the

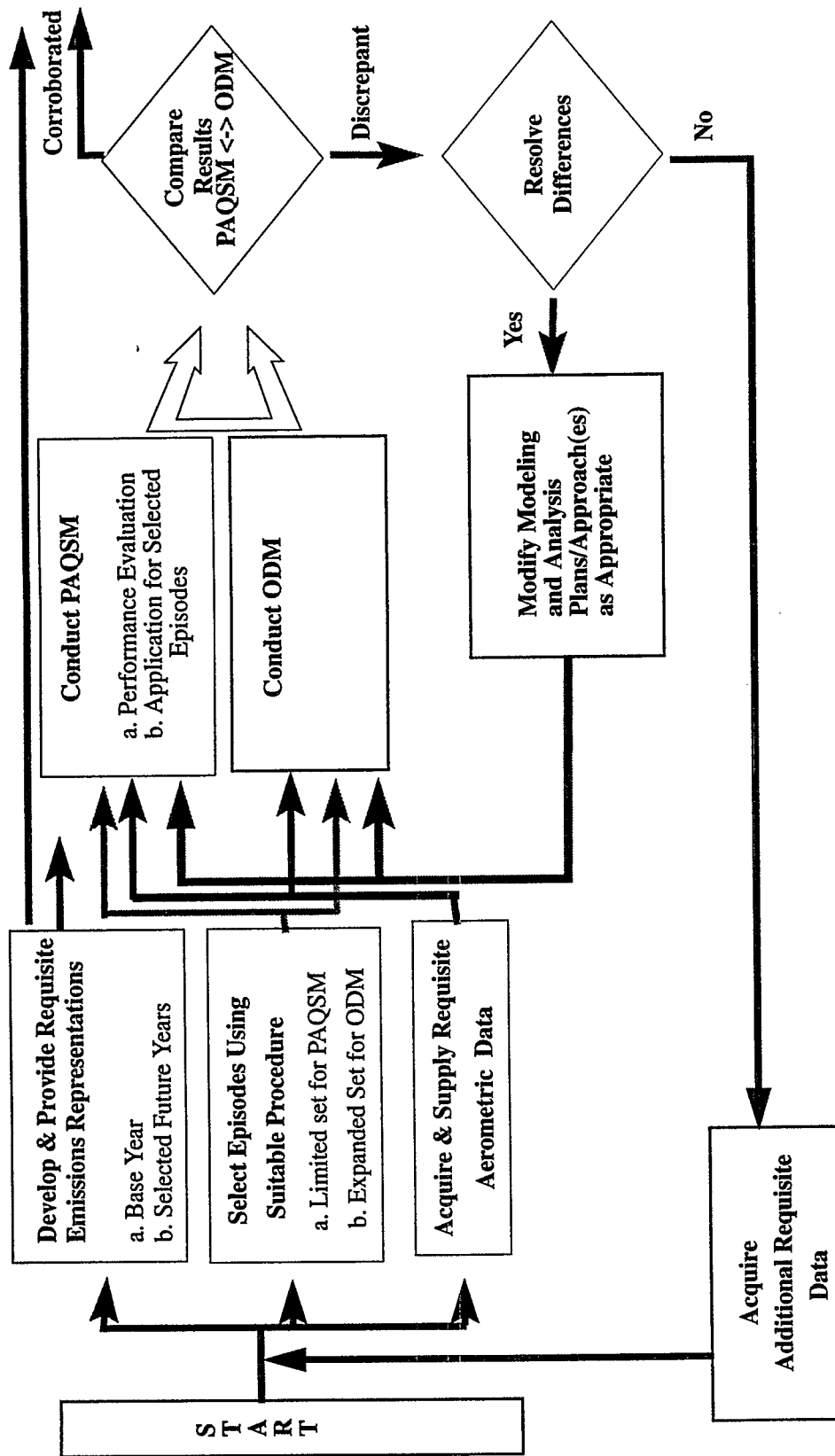


Figure III.1.A Schematic Depiction of the Attainment Demonstration Process

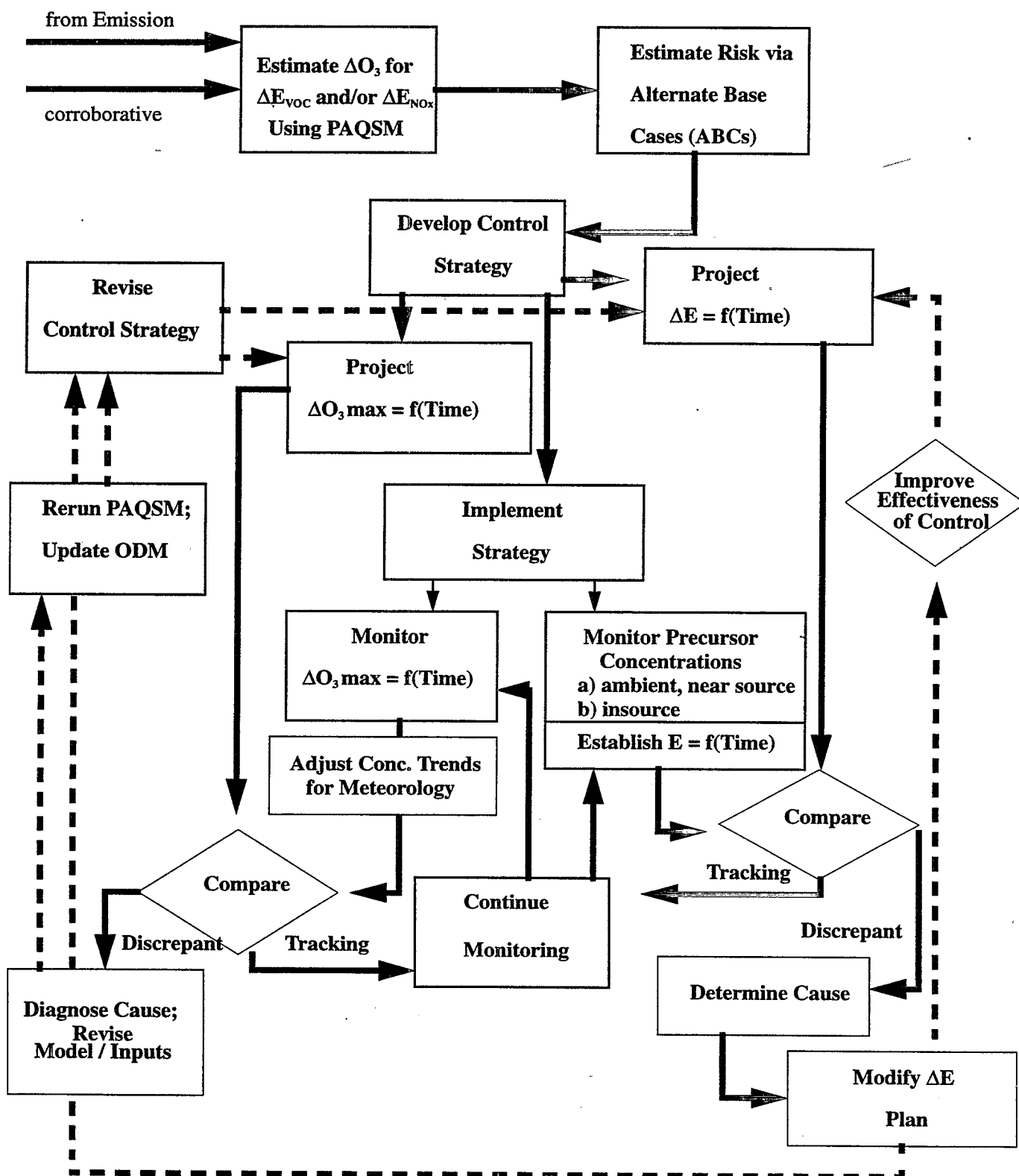


Figure III.1.B Schematic Depiction of Attainment Demonstration Process (continued)

adequacy of individual modules comprising the models in order to eliminate, to the extent feasible, the possibility of undetected compensating errors.

- Apply and test the model for episodes representing a satisfactory range of meteorological conditions.
- Give explicit consideration to the need to model an area upwind of the metropolitan area of interest in order to examine the impacts of upwind sources on ozone concentration in the metropolitan area and downwind.
- Conduct analyses of alternative base cases to determine the range of simulation outcomes that are consistent with the uncertainties of the modeling system.
- Provide estimates of uncertainties in outcomes to the extent that these can be developed.

One or more observation-driven methods (ODMs) should be used to estimate the spatial and temporal ranges of VOC versus NO<sub>x</sub> limitation for the atmospheric system and episodic conditions under study. Several ODMs are under development and evaluation. Some are available for use; of these, most are available in a preliminary form. All ODMs are discussed in Section IVB.

#### Establish corroboration among models and methods

Results should be compared directly with those of the PAQSM, to determine if areas of VOC and NO<sub>x</sub> limitation coincide. If significant discrepancies exist, diagnostic analyses should be conducted to determine possible causes. Corrections should then be made and the model and methods run again and compared. Proceeding further along paths on the schematic should be conditioned on the acceptability of comparisons for several episodes.

#### Develop alternative candidate emissions control strategies and identify the most attractive option

Once a successful evaluation of a PAQSM is conducted, following the guidance of the protocol cited, and the results are corroborated using one or more ODMs, the impacts of alternative emissions reduction scenarios should be estimated and compared. Emissions estimates should be developed using two or more independent estimation methods - source-oriented vs ambient and/or "top-down" vs "bottom-up", whenever possible to afford a means for reliably evaluating their soundness. Where estimates are discrepant, diagnostic analyses should be conducted to determine the causes, and corrections should be made. The attainment demonstration process should proceed further only when the accuracy of the emissions estimates is reasonably assured.

Emissions projections should be prepared for use for "future year" simulations. Unfortunately, effective procedures for projecting emissions to future years have not been developed for use in air quality modeling. See Chapter V for a discussion of needed research and development in the preparation of emissions projections.

#### Estimate uncertainties using alternative base case and sensitivity analyses

An alternative base case (ABC) is a simulation (a) having a set of inputs that differs from the reference base case and (b) displaying performance that does not differ statistically from that of the reference case. [See Reynolds, et al (1996) for a discussion of alternative base case (ABC) analysis.] Three or four base cases, consistent with the uncertainties in the modeling system, should be established and used as a basis for control strategy evaluation. Sensitivity and control strategy runs using each base case as a reference provide a basis for estimating a minimum uncertainty accompanying ozone concentration estimates derived for the preferred control strategy.

#### Finalize and implement control strategy

Based on the findings of control strategy, sensitivity, and ABC simulations, develop estimates of the extent to which one or more selected air quality indicators, such as peak ozone concentration or exposure, will be reduced. [A new, 8 hour standard, if adopted, can be accommodated in this structure as well] If the estimates suggest that attainment will be achieved, then adopt the control strategy for implementation. In evaluating the merit of the strategy, take into account the fact that past estimates of air quality improvement in a specified time frame have rarely been realized. If analysis of the historical record supports it, an adjustment should be made to account for a potential shortfall in improvement relative to projections.

If it appears that attainment may not be achieved, re-evaluate the merits of alternative strategies considered earlier and/or increasing the stringency of control measures in the strategy under consideration. Evaluate the likelihood of success of this alternative.

Once a decision is made to accept a strategy, implement it. [As noted earlier, consideration should be given in future work to the use of cost/benefit and decision analysis in comparing alternative strategies.]

#### Project changes in emissions and ambient ozone and precursor concentrations with time

Using emissions estimation and projection procedures in place and the PAQSM, project changes in emissions and air quality for several years in the future. Create projected trend plots for use as a reference, to be compared with data collected in the

field and near or at sources.

Compare projections with monitoring data

Compare projected and observed air quality data, for ozone and precursors.

If unacceptably discrepant, determine the cause and adjust the control strategy accordingly

Conduct diagnostic analyses to determine the causes of the discrepancies. Conduct modeling and analysis with inputs modified in accordance with the results of the diagnostic analyses. Project air quality as a function of time using the modified modeling system. Re-evaluate the anticipated effectiveness of emissions controls. Based on the findings, revise the control strategy. Implement it.

If projections comparable with observations, continue to monitor

In this case, we are on track. No need for changes.

Continue process

Continue process until attainment is achieved. Thereafter, continue process to maintain or further improve air quality in accordance with regulation.

## **B. The Primary Information Flows**

### *The Flows*

The initial effort centers on acquiring a sound and comprehensive data base, conducting traditional photochemical modeling, introducing the use of ODMs, establishing consistency in the results of the PAQSM and the ODM(s), estimating the uncertainties attending the calculations, and, based on all the information available, recommending a control strategy.

Once a strategy is implemented, observational data are used to gauge progress and to determine if the strategy implemented is likely to be successful. As soon as information is forthcoming that suggests otherwise, diagnostic, modeling, and data analysis are conducted to determine what modifications to strategy might be effective in increasing the rate of air quality improvement to coincide with the target trend line.



The cycle of comparing observation with estimates, noting discrepancies, conducting diagnostic investigation, repeating modeling and data analysis with modifications in place, and adjusting the control strategy to conform with the revised results constitutes a pattern that is followed until attainment is achieved and then thereafter to assure that attainment is maintained.

### *The Outputs*

The main outputs of the various analyses conducted include:

- PAQSM results,
- ODM results,
- estimated reductions in peak ozone concentrations for specified changes in VOC and NO<sub>x</sub> emissions,
- estimated uncertainties in control strategy simulations based on the results of ABC analyses,
- projections of emissions as a function of time,
- projections of air quality as a function of time (for ozone, VOC, and NO<sub>x</sub>), and
- revisions in all of the above, based on the results of diagnostic analyses and subsequent modifications in cases where observations and estimates are discrepant.

### *Comparisons and Corroboration*

Decisions or actions are based on the comparison of:

- PAQSM and ODM results,
- projected and observed air quality as a function of time, and
- projected and observed emissions as a function of time.

### *Feedback Loops*

Feedback loops are a distinguishing feature of the proposed approach. The primary loops are those instituted by:

- an inability to resolve differences between PAQSM and ODM results, leading to

acquisition of additional or more suitable data and modification of modeling and analysis efforts,

- discrepancies between projected and observed air quality, and
- discrepancies between projected and observed emissions.

### C. The Primary Elements: A Synopsis

The primary elements of the proposed approach to attainment demonstration include:

- Using photochemical models to (a) indicate where and if VOC or NO<sub>x</sub> controls, or both, are likely to be effective in reducing ozone concentrations; (b) assist in better representing process dynamics, (c) determine where controls should be applied for maximum effectiveness, and (d) estimate attainment requirements. *However, they would not be used explicitly for attainment demonstration.*
- Introducing observation-driven methods for determining if VOC and/or NO<sub>x</sub> are limiting. These methods, which do not depend on knowledge of emissions or boundary conditions, may be used to determine the choice of pollutant to control but not the magnitude of the control needed. In this approach, control requirements (i.e., magnitudes) are estimated using a photochemical modeling system, but actual determinations of concentration levels achieved will be made over time through monitoring.
- Monitoring primary and secondary pollutants downwind, including ozone, nitric oxide, nitrogen dioxide, nitric acid, PAN, and NO<sub>y</sub>, to determine current air quality and to provide historical information for estimating trends. Progress toward attainment is evaluated based on this information and that discussed under the element following.
- Monitoring VOC and NO<sub>x</sub> in near source areas and in-stack to determine if annual emissions reductions requirements prescribed by the CAAA are being met.

This four-element approach takes advantage of the strengths of photochemical air quality simulation models while avoiding the limitations of most concern. It also capitalizes on the attractive aspects of monitoring. Note that the approach does not place undue dependence on the accuracy of models; rather, it relies on monitoring to provide feedback for those determinations that are difficult to make using modeling.

In summary, the proposed approach stresses:

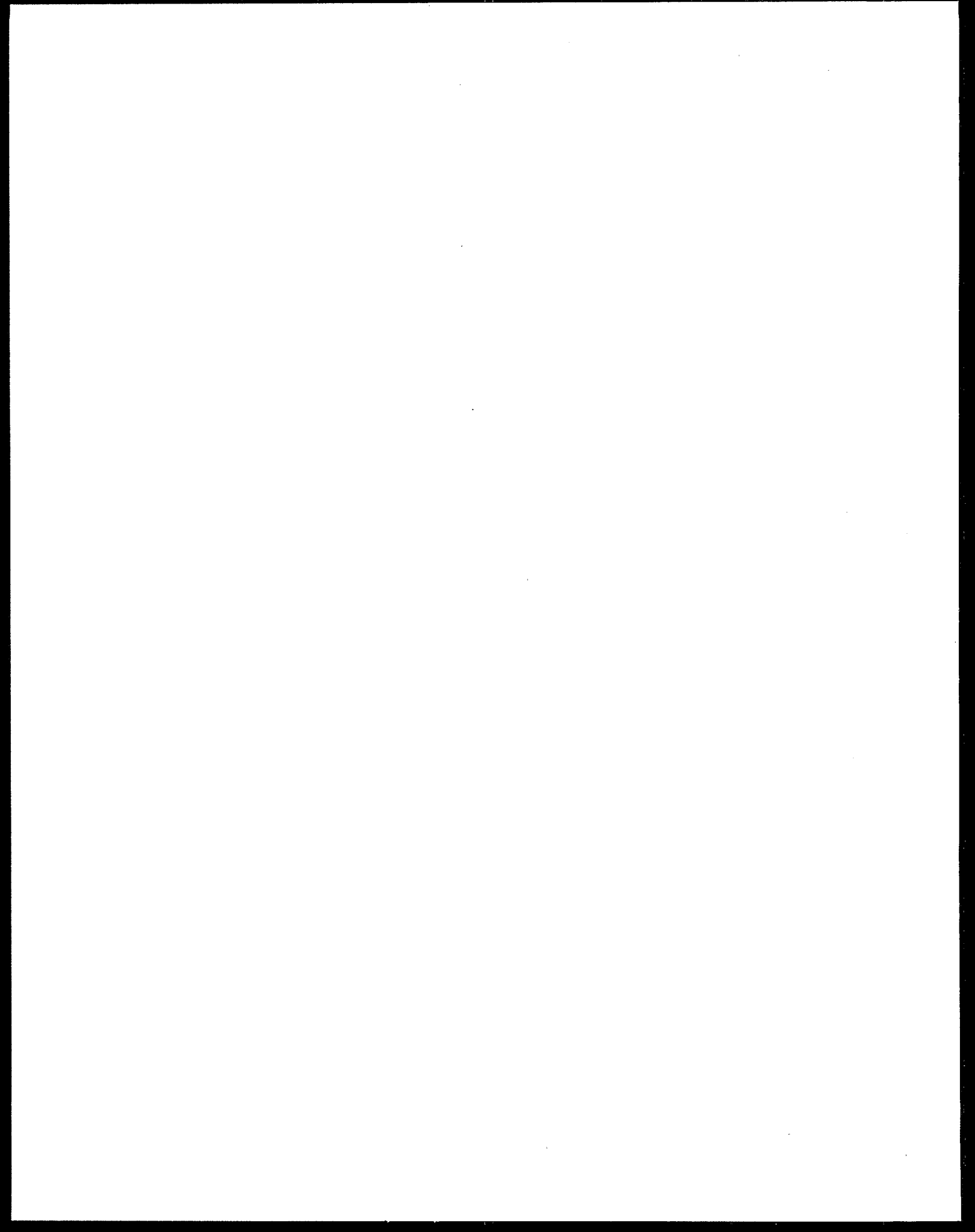
- demonstrating the comparability of the results of PAQSMs and observations-based analyses before proceeding;
- seeking high quality performance of the PAQSM, as established through testing;
- checking of emissions and air quality projections in the field through monitoring;
- allowing for feedback and correction in a reasonable time frame (1-3 years, as feasible); and
- assessing the uncertainties associated with the projection of future air quality through ABC analysis.

The overall approach outlined has the following advantages:

- reduced dependency on modeling results -- the accuracy of which cannot be assured.
- provision for correction of unfavorable variances from planned outcomes.
- increased assurance of meeting prescribed targets.

Its primary disadvantages are that:

- it is "less prognostic" in conception, and
- it provides no immediate answer; rather, it offers a process that is "distributed over time".



#### IV. ELEMENTS OF THE PROPOSED APPROACH

In this chapter we examine each major element of the proposed procedure: photochemical air quality simulation modeling, application of observation-driven methods, expanded monitoring, and analysis of data.

##### A. Photochemical Air Quality Simulation Modeling

A PAQSM is one of three models that comprise a system of models designed to simulate the formation of air pollutants and their transport, dispersion, chemical transformation, and removal from the atmosphere. The other two are a meteorological model and an emissions estimation capability (in recent times, also a model). The meteorological model is used to develop a representation of the three dimensional wind and temperature fields and the dispersion characteristics of the atmosphere. This information is then used as input to the emissions model, as emissions are influenced by temperature and winds. Both emissions and meteorological representations developed using the appropriate models are then supplied as input to the air quality model. The output of the air quality model is a three dimensional representation of the concentrations of air pollutants of interest as a function of time.

Basically, a PAQSM solves a series of equations that describe the conservation of mass for each pollutant species, taking into account emissions, transport, chemistry, dispersion, and deposition (and, in some, aerosol physics). The governing equations are approximated to permit numerical solution on a computer. The numerical integration method used is one that minimizes numerical error while attempting to maintain reasonable efficiency (i.e., computational time). Solution is effected on a three dimensional grid artificially imposed on the geographical area. A typical grid spacing for an urban area might be 5 km in the horizontal (x and y directions) and 0.02-0.4 km in the vertical (z direction); the number of cells might be (typically)  $30 \times 20 \times 8$ . For regional application, the horizontal dimension of individual grid cells will typically be larger, and the number of cells usually will be greater.

To evaluate model performance, estimated pollutant concentration fields are compared with observations. If performance is flawed, diagnostic analyses are conducted to determine the cause of the problem, and the problem is corrected if feasible. Performance evaluation is then repeated. Once a model is accepted for use, it may be applied for a variety of circumstances. The most common involves changing emissions in conformance with the anticipated outcomes of a control strategy, maintaining all other inputs constant (with the possible exception of initial and boundary conditions), and estimating the impact of the changes on the three dimensional distribution of pollutant concentrations.

Data required to support model evaluation and application are quite substantial. Emissions information for all types of sources is needed, including spatial and temporal distributions. Information should be provided at the spatial resolution of the modeling grid (typically 5 km x 5 km) and a one hour temporal resolution. For diagnostic wind models (i.e., analysis procedures based on interpolation of wind data), the availability of observed wind velocities at a number of sites is essential. For prognostic wind models (e.g., models based on the solution of fundamental governing equations), few input data are needed in principle. However, when used in the "data assimilation" mode, a common practice in attempting to achieve accuracy, sounding data are required to bring estimates in line with observations at regular time intervals. Pollutant concentration data are needed to establish initial and boundary conditions for air quality models and to compare with model estimates.

In general, the following key categories of aerometric data are often sparse or lacking (see also Section C):

- VOC concentrations,
- NO<sub>x</sub> concentrations (usually available, but often at too few sites, with too low a sensitivity and with ill-defined measurements interferences or artifacts),
- air quality and wind data aloft,
- mixing heights (for models that require them, such as UAM-IV), and
- upwind boundary conditions at the surface and aloft (for the air quality and meteorological models).

Reliance is usually placed on the availability and accuracy of routinely collected data. Often, this data base is inadequate to support model evaluation and application. When an area determines that it wishes to seriously pursue photochemical modeling, it augments routine monitoring for a short period (3 to 8 weeks) during the "smog season" with a suite of additional measurements selected to significantly enhance the range and quantity of data available. Generally, data for one to three episodes of interest are acquired through the monitoring effort, depending on the "favorability" of the meteorology at the time. Note, however, that these episodes may not include:

- the highest ozone concentrations observed,
- one or more categories of meteorological conditions of interest, or
- particular attributes of interest, such as high boundary concentrations or high concentrations of ozone aloft.

Thus, an adequate data base may not be acquired even when a special monitoring study is conducted.

The most advanced and attractive PAQSMs available for use today include the two latest versions of the Urban Airshed Model, UAM-IV and UAM-V, the CalTech model and variants, and the San Joaquin Valley Air Quality Simulation Model (SAQM, an advanced version of RADM).

While we have provided this brief background for those unfamiliar with PAQSMs, we recognize that most readers will be knowledgeable about the formulation, data requirements, performance characteristics, and other attributes of this class of models. Further, applications practice is well known and will not be discussed here. Limitations of the PAQSM are summarized in Chapter II. See Tesche et al (1992) for a detailed critical commentary on the UAM-IV; many of the topics discussed in this report pertain to other PAQSMs as well. See also Roth (1993).

In general, conducting a sound and well conceived photochemical modeling effort having a high probability of simulating atmospheric dynamics with reasonable fidelity requires giving attention to a broad list of needs, several of which may require significant funding, staff time, and calendar time. Historically, the extent to which these needs have been satisfied varies enormously - from the conduct of extensive multi-year research programs involving the acquisition of a comprehensive data base to several month efforts using what data are available. While comprehensive efforts have a greater chance of success, decision makers are sometimes confronted with budgets and/or schedules that are sufficiently tight that they view their only option as being to forge ahead, respecting existing constraints. The proposed procedure is intended to provide a general framework, one that will apply for the full range of situations encountered.

In the ideal situation, with adequate funding, time, and staff, it is desirable to:

- acquire a comprehensive aerometric (air quality and meteorological) data base,
- undertake a careful and detailed construction of an emissions representation, with corroboration of individual elements through at least two independent means of estimation,
- conduct detailed prognostic meteorological modeling with four dimensional data assimilation (FDDA), supported by adequate data acquisition,
- evaluate the estimation capability of the modeling system for a range of meteorological episodes,
- conduct "hands off" performance evaluation (i.e., conducting simulations without

adjustment of inputs in an attempt to improve performance) for at least half of the episodes,

- require high standards of performance for the full range of episodes studied (representing a variety of meteorological regimes),
- evaluate the performance of individual models (meteorological and emissions) and process modules (e.g., chemistry, boundary conditions, deposition) in an effort to minimize the potential for compensating errors remaining undetected and to correct errors as feasible,
- conduct ABC analyses to assess uncertainty, and
- use uncertainty information in decision analysis.

However, circumstances rarely permit this full range of efforts to be undertaken and completed. The press of time, the availability of data, and/or the limitations of budget inevitably restrict the extent of effort. To the extent that one must truncate or omit one or more of the activities listed, the risk increases that modeling results may not be reliable. The advantage of the proposed procedure is that it provides a means for detecting flaws in the control strategy, as implemented, and correcting for them, regardless of the accuracy of the modeling. In effect, a "safety net" is provided to offset the risks associated with conducting an incomplete or limited modeling effort. One might consider this aspect of the attainment demonstration procedure "modeling without guilt".

Consider the extremes. If a comprehensive modeling effort is conducted, the probability is reduced of developing an inaccurate air quality management plan and falling short of air quality targets. Perhaps a "one or two pass" emissions control effort might be required, minimizing the uncertainties attending the amounts of control needed and minimizing the costs associated with frequent revisitation of the control issue on the part of industry. If a limited modeling effort is conducted and/or if the supporting data base is limited or insufficient, the converse situation might be expected. In this case the probability of having to revisit the specification of an area's control strategy is increased in some relation to the shortfall in the modeling effort. Consequently, the overall cost of control to industry and regulators is likely to remain uncertain for a longer time and, in the long run, to be higher. In effect, then, the decision to conduct or not conduct a data acquisition program and to undertake a modeling program at a given level of effort is tantamount to weighing the trade off between the level of investment that might be made in planning and the uncertainty in control needs and, possibly, the overall costs of control and reassessment over time.



Finally, a particular issue in the use of PAQSMs is the design and conduct of a study such that proper attention is given to the emissions from sources in upwind areas that have a significant influence on air quality in the region of interest. Specifically, it is important to (a) characterize emissions of upwind sources (b) characterize their transport, transformation, and deposition downwind and (c) estimate the effect on downwind air quality of controls that might be placed on these sources. This need may be addressed in one of three ways:

- to model the entire region of interest, placing a grid of finer resolution on metropolitan areas that are not in attainment,
- to incorporate knowledge of upwind conditions in the boundary condition for the metropolitan area, omitting modeling of the upwind area, or
- to incorporate knowledge of upwind conditions in the boundary condition for the metropolitan area, and to derive their conditions through modeling the upwind area independently or properly coupled.

Data bases needed to support comprehensive regional modeling or modeling of the upwind area alone have been inadequate. Further, focusing on boundary conditions without analysis of the impacts of controls in upwind areas falls short of meeting needs. How best to address the regional scale impacts of upwind sources is a topic of considerable interest and a focus of the newly initiated NARSTO program. We thus will not pursue this topic further here, except to say that consideration of upwind sources can be accommodated in the proposed framework.

## B. Observation-Driven Methods

### *Definition and Capabilities*

Observation-driven methods (ODMs) use measurements from one or more monitoring locations to assess the relative sensitivities of ozone concentrations to reductions in VOC or NO<sub>x</sub> emissions. Four such methods are:

- the correlation between ozone and NO<sub>y</sub> or NO<sub>z</sub> (e.g, Trainer et al., 1993; Jacob et al., 1995),
- the Integrated Empirical Rate (IER) model of Johnson (1984), as revised by Blanchard et al. (1994) and Chang et al. (1995). [Blanchard et al. (1994) name their revised version the Smog Production (SP) algorithms],
- the use of indicator species and ratios (Sillman et al., 1990; Milford et al., 1994; Sillman, 1995; Watkins et al, 1995; Jacob et al., 1995), and
- the observation-based model (OBM) of Cardelino and Chameides (1995).

The ODMs vary in their degree of empiricism.<sup>1</sup> Correlation of ambient ozone and NO<sub>y</sub> is the most empirical of the methods; however, key chemical processes are responsible for the correlation and, thus, the method is linked to current understanding of ozone formation. The IER and SP algorithms are primarily but not exclusively empirical: they are sets of algebraic relationships that describe the formation of ozone in environmental chambers. Blanchard et al. (1994) show that the SP algorithms also describe the formation of ozone as calculated using a box model with an initial charge of pollutants and two different chemical mechanisms. The use of NO<sub>y</sub> concentrations (Milford et al., 1994) and indicator ratios (Sillman, 1995) was proposed based upon consideration of key chemical reactions; the values suggested by Milford et al. (1994) and Sillman (1995) as threshold criteria for distinguishing VOC from NO<sub>x</sub> control preferences were derived from one or more applications of one or more grid-based PAQSMs. However, this method could have a more empirical character as well, because the concepts are potentially verifiable using field data. The OBM, as its name suggests, is a model that utilizes ambient measurements rather than emissions estimates to drive a photochemical simulation.

Because the ODMs have in common the use of ambient measurements as inputs, we group them together under the title "Observation-Driven Methods." The ODMs are all diagnostic, rather than prognostic, tools. They are capable, in principle, of

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<sup>1</sup>As will be described below, some ODM's are themselves dependent on some of the same assumptions as photochemical models.

qualitatively estimating the sensitivity of ozone concentrations to VOC or NO<sub>x</sub> reductions.

The ODMs share some other characteristics as well. 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 upon the representativeness of the locations of the ambient monitoring sites, since they hold only for monitored locations (see Section C for further discussion).

Because most of the ODMs have been developed only recently, and because no comprehensive review of ODMs has been published, this section is somewhat more detailed than other portions of the report. We summarize and evaluate each of the four methods listed above according to the following categories:

- Description
- The key assumptions
- Nature and levels of uncertainty associated with the method
- The type of output of the method and the degree of consistency between this output and the types of information needed for regulatory applications
- Availability of data needed as input to the method
- Availability of equipment, computational algorithms, or software needed for implementing the method
- Potential value of the method as part of the proposed new attainment demonstration procedure (including for use in comparisons among ODMs)

Following the discussion of each method, this section discusses similarities and discrepancies among methods, where identifiable, and characterizes the potential for developing confirmatory cross-comparisons through applications of the methods to specific data bases. In Section V, recommendations are presented for the conditions of use of each ODM and for further research and development of the ODMs.

#### *Correlation Between Ozone and NO<sub>y</sub> or NO<sub>z</sub>*

Description. Unlike the other ODMs, this method was not originally proposed for use as a discriminator between VOC and NO<sub>x</sub> sensitivity of ozone. Rather, the method, which was applied primarily at sites where ozone concentrations were thought to be limited by the availability of NO<sub>x</sub>, was intended to help elucidate

aspects of ozone formation at low concentrations of  $\text{NO}_x$  (e.g., confirmation that ozone levels appeared to be related to  $\text{NO}_x$  concentrations at locations thought to be  $\text{NO}_x$  limited; estimation of rates of ozone formation with respect to  $\text{NO}_x$  consumption). However, the procedure appears to have value as a discriminator between VOC and  $\text{NO}_x$  sensitivity of ozone; moreover, it can be linked to the methods proposed by Milford et al. (1994) and by Sillman (1995).

The method consists of computing correlations and regression relationships between ozone and either  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ),  $\text{NO}_y$  (the sum of  $\text{NO}_x$  and its reaction products), or  $\text{NO}_z$  ( $\text{NO}_y - \text{NO}_x$ ). For example, Trainer et al. (1993) used measurements obtained from six rural sites in the eastern United States and Canada to show that ozone concentrations in photochemically aged air increased from about 30 to 40 ppbv at  $\text{NO}_y$  concentrations below 1 ppbv to values of 70 to 100 ppbv at  $\text{NO}_y$  concentrations of about 10 ppbv. The data were selected to reflect photochemically aged air through the choice of remote or rural monitoring locations (four of which were along the crest of the Appalachians), restriction to the hours from 1:00 to 5:00 p.m., and restriction to measurements where  $\text{NO}_x/\text{NO}_y$  was less than 0.40 (these two restrictions were not applied to the four mountain-top sites). Ozone was found to correlate more closely with  $\text{NO}_z$ , the products of the oxidation of  $\text{NO}_x$  (i.e.,  $\text{NO}_z = \text{NO}_y - \text{NO}_x$ ), than with  $\text{NO}_y$ . Earlier studies have shown correlations between ozone and  $\text{NO}_x$  (e.g., Fehsenfeld et al., 1983; Kelly et al., 1984; Parrish et al., 1986),  $\text{NO}_z$  (Spicer, 1977; Hanst et al., 1982; Tuazon et al., 1980, 1981) or  $\text{NO}_y$  (Fahey et al., 1986). In particular, Fehsenfeld et al. (1983) showed that the rate of daytime increase in ozone concentration at Niwot Ridge, Colorado, was proportional to the concentration of  $\text{NO}_x$  when  $\text{NO}_x$  was in the range of 0.4 to 3 ppbv.

The key assumptions. Ozone production in the troposphere requires the photolysis of  $\text{NO}_2$ . In turn,  $\text{NO}_2$  is produced by reaction of NO with either ozone or peroxy radicals. Ozone can accumulate only when sufficient peroxy radicals are present.  $\text{NO}_x$  is removed from the NO-to- $\text{NO}_2$ -to-NO cycle by reaction of  $\text{NO}_2$  with OH radical to yield  $\text{HNO}_3$ , which, in turn, may form aerosol nitrate; another reaction product of  $\text{NO}_x$  is PAN, formed by reaction of  $\text{NO}_2$  with peroxyacetyl radicals. Since radical reactions result in both ozone formation and conversion of  $\text{NO}_x$  to its reaction products, a correlation of ozone with  $\text{NO}_z$  should occur whether or not  $\text{NO}_x$  is the limiting precursor. However, because the number of ozone molecules produced per  $\text{NO}_x$  consumed decreases as  $\text{NO}_x$  concentrations increase (e.g., Liu et al., 1987), the relationship between ozone and  $\text{NO}_z$  appears to deviate from linearity when  $\text{NO}_z$  reaches about 5 to 10 ppbv (Trainer et al., 1993). The use of the correlation between ozone and  $\text{NO}_z$  as a discriminator between VOC and  $\text{NO}_x$  limited conditions thus requires that monitoring data exhibit statistically distinguishable slopes,  $\Delta\text{O}_3/\Delta\text{NO}_z$ , under conditions of VOC and  $\text{NO}_x$  limitation.

The correlation of ozone with  $\text{NO}_y$  should be observed when  $\text{NO}_x/\text{NO}_y$  is low; otherwise, concentrations of  $\text{NO}_x$  in excess of a few ppbv might obscure the

correlation. Ozone levels have been shown to correlate with  $\text{NO}_x$  concentrations when  $\text{NO}_x$  is less than a few ppbv (e.g., Fehsenfeld et al., 1983; Kelly et al., 1984; Parrish et al., 1986), but at higher  $\text{NO}_x$  concentrations the correlation can break down since  $\text{NO}_x$  need not be limiting the rate of ozone formation. Where ozone is scavenged by  $\text{NO}$ , the correlations described above would be expected to break down.

Nature and levels of uncertainty associated with the method. The existing measurement studies do not provide firm guidance for delineating the range of slopes,  $\Delta\text{O}_3/\Delta\text{NO}_x$ , that would be indicative of  $\text{NO}_x$  limitation. Trainer et al. (1993) reported two sets of regression results bearing on ozone production efficiency, i.e., on the ratio of ozone produced to  $\text{NO}_x$  consumed. For the site at Scotia, Pennsylvania, the data were well described by a line having an intercept of 35 ppbv ozone and a slope of 8.5 ppbv ozone per ppbv  $\text{NO}_x$  oxidized for  $\text{NO}_x$  concentrations up to 10 ppbv (Trainer et al., 1993). Data from the Los Angeles area, in which  $\text{NO}_x$  concentrations ranged from about 20 to 85 ppbv, showed a slope of about 5 ppbv ozone per ppbv  $\text{NO}_x$  (Trainer et al., 1993); because the  $\text{NO}_x$  concentrations excluded aerosol nitrate, the true slope was thought to be lower (Trainer et al., 1993). These two data sets represent extremes (i.e., high and low  $\text{NO}_x$  concentrations) on a continuum of precursor limitation, thus suggesting that application of the method to areas in which precursor limitations are less clearly defined would require discrimination between slopes somewhat exceeding 4:1 and those that were somewhat less than 8:1. Jacob et al. (1995) used the slope,  $\Delta\text{O}_3/\Delta\text{NO}_x$ , in conjunction with two other indicators described by Sillman (1995) to argue that data from a site in Shenandoah National Park exhibited a transition from  $\text{NO}_x$ - to VOC-limited conditions during September 1990. The slopes were 18:1 and 7:1. While no error bars were given for the slopes, the correlation coefficients were modest ( $r^2$  values were 0.49 and 0.23 for the two periods), thus suggesting that the slopes may not have been statistically different. Moreover, the value of the slope occurring under conditions that were asserted to be VOC-limited, 7:1, was almost certainly statistically indistinguishable from the 8.5:1 value reported by Trainer et al. (1993) for a  $\text{NO}_x$ -limited situation. It is possible that additional guidance could be derived from modeling studies. Sillman (1995) (see discussion below) presents ranges of  $\text{O}_3/\text{NO}_x$  for which modeling results showed sensitivity of ozone to reductions of VOC and  $\text{NO}_x$ .

While the existence of discernible correlations between ozone and  $\text{NO}_x$  (or  $\text{NO}_y$ ) at rural sites that are thought to be  $\text{NO}_x$ -limited does help to confirm the expected  $\text{NO}_x$  limitation, little or no guidance is available regarding the opposite situation. That is, while poor correlations could be indicative of VOC limitation, "poor" is not a well-defined criterion. Presumably, firm indication of VOC limitation might also require demonstration of a good correlation between ozone and either VOC concentration or radiation. Alternatively, as for the case of the correlation between ozone and  $\text{NO}_x$ , it is possible that additional guidance could be derived from modeling studies. Sillman

(1995) (see discussion below) presents ranges of  $O_3/NO_2$  and  $O_3/NO_y$  for which modeling results showed sensitivity of ozone to reductions of VOC and  $NO_x$ .

The regression relationships described by Trainer et al. (1993) use binned data, i.e., each data point shown is the average of ten percent of the data set. Time averages of the measurements range from 5 minutes to one hour. The results for the unbinned data show more scatter and would thus be more indicative of the uncertainties associated with application of the method to individual ozone episodes.

The type of output of the method and the degree of consistency between this output and the types of information needed for regulatory applications. Output of the method consists of regression relationships indicating linearity ( $r^2$  values) and changes in ozone with respect to changes in  $NO_x$ ,  $NO_y$ , or  $NO_z$ . To be of most use for regulatory applications, these outputs would need to be expressed in qualitative terms, i.e., as indicating VOC sensitivity,  $NO_x$  sensitivity, sensitivity to both precursors, or as being indeterminate. Criteria for making these qualitative distinctions would also need to be provided.

Availability of data needed as input to the method. Application of the method requires measurements of ozone,  $NO_x$ , and  $NO_y$ . Both  $NO_x$  and  $NO_y$  would probably need to be measured with accuracies of about one ppbv down to concentrations of about one ppbv; however, this need has not been explicitly demonstrated. Virtually no measurements of true  $NO_x$  or  $NO_y$  are available from routine monitoring programs at present. However, the technology exists for measuring both  $NO_x$  and  $NO_y$  at the stated concentration and levels of accuracy.

Availability of equipment, computational algorithms, or software needed for implementing the method. Application of the method requires only monitoring equipment. No specialized computational algorithms or software are needed, other than commercially available database or statistical software.

Potential value of the method as part of the proposed new attainment demonstration procedure (including for use in comparisons among ODMs). Use of the method appears promising. Measurements of both  $NO_x$  or  $NO_y$  at the stated levels of accuracy are technically feasible. Coupled with the indicator levels proposed by Milford et al. (1994) and the ratios suggested by Sillman (1995), the method appears capable of qualitatively identifying VOC or  $NO_x$  sensitivity. Additional research and development should be carried out, as described in Section V.

#### *The IER model and SP algorithms*

Description. The IER model was derived from environmental chamber experiments carried out at the Commonwealth Scientific and Industrial Research Organization

(CSIRO) in Sydney, Australia (Johnson, 1984; Johnson and Quigley, 1989; Johnson et al., 1990; Johnson and Azzi, 1992). Johnson (1984) defined smog produced (SP) as:

$$SP(t) = O_3(t) - O_3(0) + NO(0) - NO(t)$$

where all species are expressed in units of mixing ratios (not mass). [In situations in which  $NO_x$  ( $NO + NO_2$ ) enters a system over a period of time,  $NO(0)$  would be replaced by  $NO(i)$ , which denotes the concentration corresponding to the sum of  $NO_x$  inputs.] SP is a useful variable because: (1) the time derivative of SP is an indicator of the rate of NO oxidation by peroxy radicals and a robust measure of the time required to reach the NO- $NO_2$  crossover and the  $NO_2$  and  $O_3$  maxima in environmental chambers (Carter and Lurmann, 1991); (2) the environmental chamber studies carried out at the CSIRO in Sydney indicate that SP displays a linear relationship to cumulative light flux, provided sufficient  $NO_x$  is present to sustain ozone production; and (3) since ozone and NO react rapidly and reversibly, their concentrations are not independent (the definition of SP accounts for this dependence).

The original CSIRO environmental-chamber studies exhibited an empirical relationship between the maximum potential SP ( $SP_{max}$ ) and initial  $NO_x$  concentration (Johnson, 1984):

$$SP_{max} = \beta[NO_x(0)]$$

where the parameter  $\beta$  was assumed to be constant with a value estimated from the CSIRO experiments of  $4.1 \pm 0.4$ .  $\beta$  is an estimate of the maximum amount of SP potentially produced ( $SP_{max}$ ) per unit  $NO_x$  input.

The extent of reaction (E) was defined by Johnson (1984) as:

$$E(t) = SP(t) / SP_{max}$$

When the extent of reaction reaches one in Johnson's model, smog production ceases because virtually all of the  $NO_x$  has reacted. Subsequent photochemical formation of ozone is negligible because the system has consumed all of the  $NO_x$  and, therefore, can no longer produce ozone. Situations in which extent reaches one correspond to cases in which peak ozone concentrations could be lowered by reducing  $NO_x$  inputs to the system. Regions where the calculated extent of reaction is predominantly less than one during the periods of high ozone concentrations are classified as VOC (or light) limited, indicating that peak ozone concentrations could be lowered by reducing VOC inputs to the system. When extent approaches but does not reach one (e.g.,  $E > 0.8$ ), a system is usually in a transitional regime in which peak ozone might be responsive to reductions of either VOCs or  $NO_x$ .

Chang and Suzio (1995) modified the IER model using the relationship

$$(O_3)_{\max} = \gamma [NO_x(0)]^{1/2}$$

based upon the chamber data reported by Akimoto et al. (1979). Chang et al. (1995) further modified the IER through substitution of a parameterization of deposition for one of the parameters of Johnson's model.

Blanchard et al. (1994) re-defined SP as:

$$SP(t) = O_3(t) + DO_3(t) - O_3(0) + NO(0) - NO(t)$$

where they added the term  $DO_3(t)$  to the definition of SP to account for the cumulative ozone lost to deposition from time zero to  $t$  (i.e., ozone that has been produced but deposited). Further, Blanchard et al. (1994) proposed the following equation:

$$SP_{\max} = \beta [NO_x(0)]^\alpha$$

Data from environmental chamber experiments carried out at the University of North Carolina (UNC), the Statewide Air Pollution Research Center (SAPRC) at the University of California at Riverside, and the CSIRO were reviewed to identify those experiments that used a mixture of VOCs and that went to completion. Values of 0.680 to 0.721 were obtained for  $\alpha$ , depending upon the treatment of wall effects (Blanchard et al., 1994). Simulations carried out using a photochemical box model (OZIPR) (Gery and Crouse, 1992) with the Carbon Bond 4 Mechanism (CBM-4) (Gery et al., 1989) yielded  $\alpha=0.701$ ; with the Carter-Atkinson-Lurmann-Lloyd (CALL) mechanism (Lurmann et al., 1986),  $\alpha=0.658$  (Blanchard et al., 1994). Correlation coefficients were about 0.9 for the chamber data and greater than 0.99 for the box model, with no relationship to VOC concentration (Blanchard et al., 1994).

Blanchard et al. (1994) described further revisions of the model, which included the incorporation of a deposition algorithm to account for deposition losses of  $NO_y$  and ozone, and provided equations appropriate for use in applications to ambient data. A computationally tractable version of the equations was described, which used the value  $\alpha=2/3$ .

The key assumptions. The SP algorithms (Blanchard et al., 1994) are based on the analysis of environmental-chamber data and simulations carried out using a box model. These systems all have fixed volumes and an initial charge of  $NO_x$  and VOCs. Because the algorithms are not yet fully developed for systems subject to dilution and continuous injection of emissions, the application of the algorithms to ambient data is potentially subject to biases that have not yet been determined.



Additional work, which is now in progress, should help clarify the potential importance of these biases.

The value of the exponent proposed by Chang and Suzio (1995) (i.e.,  $1/2$ ) differs significantly from that proposed by Blanchard et al. (1994) (i.e.,  $2/3$ ). Since the former value ( $1/2$ ) was derived from single-species (propylene) experiments, whereas the latter ( $2/3$ ) was based upon both mixture experiments and box-model simulations using urban-mixture speciation, the value  $a=2/3$  appears to be more appropriate for application to ambient data. Although other details of the revisions proposed by Chang et al. (1995) and Blanchard et al. (1994) vary, the two versions appear to have converged in most respects.

Nature and levels of uncertainty associated with the method. The following sources of uncertainty could affect the accuracy and replicability of the calculated extent of reaction ( $E = SP/SP_{max}$ ):

- 1) inaccuracy of the functional form (i.e.,  $SP_{max} = f[NO_x(0)]$ ) that is used to derive the expression for  $E$ , including incomplete specification of the arguments of the function;
- 2) failure of the equations to adequately treat physical processes that are insignificant in smog chambers but that are of importance in the ambient atmosphere (e.g., dilution -- which is potentially testable in a chamber with dilution);
- 3) inaccuracy (i.e., bias) of measurements ( $O_3$ ,  $NO$ ,  $NO_2$ ,  $NO_y$ ), parameters ( $\alpha$ ,  $\beta$ ), and estimated or modeled quantities (deposition of  $O_3$ );
- 4) imprecision of measurements ( $O_3$ ,  $NO$ ,  $NO_2$ ,  $NO_y$ ), parameters  $\alpha$ ,  $\beta$ , and estimated or modeled quantities (deposition of  $NO_y$  and  $O_3$ );

The first three factors would introduce biases into the calculation of the extent of reaction, whereas the last factor would affect the replicability, or precision, of the calculated extent.

Although biases can be difficult to identify, the agreement between chamber experiments and chemical mechanisms described by Blanchard et al. (1994) suggests the absence of serious biases of the first type when applying the algorithms to fixed-volume, initial-charge systems.

The principal uncertainty associated with the method has to do with its applicability to ambient measurements, as described above. The potential for biases of the second type requires further investigation.

Because the SP algorithms are algebraic in nature, they lend themselves to direct analytical calculation of uncertainties deriving from the third and fourth items listed

above. Differentiation of the function defining E with respect to each of its arguments indicates the sensitivity of the calculated extent to variation in each measurement or parameter. These sensitivities, denoted  $\Delta E/\Delta M$ , where M is a measurement or parameter, are usually known as sensitivity coefficients. Sensitivity coefficients may be used to evaluate potential biases in E that would result from biases in the measurements or parameters and can also be used in determining  $s_E^2$ , the overall variance of the calculated extent.

At present, some but not all uncertainties have been estimated,<sup>2</sup> (see Blanchard et al., 1994). For example, a change of 10 ppbv in ozone concentration yields about a 0.01 to 0.02 change in extent. Measurements of  $\text{NO}_x$  that are accurate to approximately 2 ppbv at  $\text{NO}_x$  concentrations of about 2 to 5 ppbv permit the calculation of extent to be accurate to within about 0.02 to 0.1 units. If  $\text{NO}_y$  is accurate to within 10 percent, biases in E can be limited to about 0.05 units. Changes of 10 ppbv in the estimated background ozone concentration yield changes of about 0.01 to 0.02 when extent is calculated using the  $\text{NO}_x$  version of the algorithms; the changes are about 0.05 to 0.1 units for the  $\text{NO}_y$  version of the algorithms.

The type of output of the method and the degree of consistency between this output and the types of information needed for regulatory applications. The output of the method consists of calculations of the extent of reaction. Extent can be related to the sensitivity of ozone concentrations to precursor reductions, thus permitting a qualitative determination of control preferences.

Availability of data needed as input to the method. Application of the method requires measurements of ozone,  $\text{NO}_x$ , or  $\text{NO}_y$ . Both  $\text{NO}_x$  and  $\text{NO}_y$  should be measured with accuracies of about one ppbv down to concentrations of about one ppbv. Virtually no measurements of true  $\text{NO}_x$  or  $\text{NO}_y$  are available from routine monitoring programs at present. However, the technology exists for measuring both  $\text{NO}_x$  and  $\text{NO}_y$  at the stated concentrations and levels of accuracy. It is also possible to utilize present routine measurement of " $\text{NO}_x$ ", which are biased by the inclusion of unquantified levels of interference from PAN and other species, in the algorithms in a way that bounds the calculated extent of reaction (e.g., Blanchard et al., 1995).

Availability of equipment, computational algorithms, or software needed for implementing the method. Measurements of ozone,  $\text{NO}_x$ , or  $\text{NO}_y$  at the stated accuracy levels are technically feasible using existing measurement instruments. The computational algorithms are explicitly delineated in Blanchard et al. (1994). A software program is available that permits easy implementation of the method.

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<sup>2</sup>It should be noted that these estimates all presume the applicability of the algorithms to ambient measurements.

Potential value of the method as part of the proposed new attainment demonstration procedure (including for use in comparisons among ODMs). Use of the method appears promising. Additional research and development should be carried out, as described in Section V.

### *The Use of NO<sub>y</sub> and Indicator Ratios*

Description. Milford et al. (1994) concluded that ozone concentrations would be responsive to reductions of NO<sub>x</sub> where afternoon concentrations of NO<sub>y</sub> fall below a threshold ranging from about 10 to 25 ppbv NO<sub>y</sub>. The value of the threshold, which was derived from analysis of modeling results, was given as a range to reflect the ranges exhibited by the different modeling studies. Sillman (1995) proposed using several indicator species or ratios to distinguish between NO<sub>x</sub> and VOC limited situations: NO<sub>y</sub>, NO<sub>z</sub>, O<sub>3</sub>/NO<sub>y</sub>, O<sub>3</sub>/NO<sub>z</sub>, O<sub>3</sub>/HNO<sub>3</sub>, HCHO/NO<sub>y</sub>, H<sub>2</sub>O<sub>2</sub>/HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>/NO<sub>y</sub>, and H<sub>2</sub>O<sub>2</sub>/NO<sub>z</sub>. Ranges of threshold values were given by Sillman (1995) based upon variation of a number of model inputs.

The key assumptions. Milford et al. (1994) drew upon results from three PAQSMs, which used two different chemical mechanisms, applied to four geographical regions. The findings were based upon a range of models, modeling assumptions, and model applications to help reduce the possibility that the results would be overly dependent upon the accuracy of a single modeling application. Sillman (1995) used a single model [which was denoted as 'UMICH' by Milford et al. (1994)], applied to two regions with four cases per region (the cases were obtained by varying factors such as the base-case anthropogenic VOC emissions).

Nature and levels of uncertainty associated with the method. The uncertainty range of the NO<sub>y</sub> threshold was given by Milford et al. (1994) as 10 to 25 ppbv NO<sub>y</sub>. This range does not, however, encompass the full range of uncertainty that would have to be ascribed to the method. No applications of the UAM were included. Two of the models (ROM and UMICH) used relatively coarse grids (18.5 km horizontal and three-layer vertical grid for ROM; 20 km horizontal and two-layer vertical grid for UMICH), while the CIT model application to the Los Angeles basin used a finer grid resolution (5 km horizontal and 5-layer vertical resolution). The sharpness of the delineation of the NO<sub>y</sub> threshold varied among the models. The sharpest thresholds were obtained from the UMICH applications. The ROM application exhibited more scatter, while, for the CIT application, the sensitivities of ozone to its precursors exhibited so much scatter that no well-defined threshold appeared. The range of the threshold, 10 to 25 ppbv NO<sub>y</sub>, thus represents the range exhibited among the applications, considering for each application the average over all locations within the modeling domain. Were additional model applications considered, the range might be larger. Consideration of individual locations would also expand the uncertainty range, and would necessitate consideration of the large scatter shown by the CIT model application.

Although Sillman (1995) considered four base cases for each of two regions, the results were nonetheless obtained through application of a single model. The threshold values of the indicators varied by about a factor of two among the alternative cases. According to Sillman's (1995) results, the transition into  $\text{NO}_x$  sensitivity was observed for values of (a)  $\text{NO}_y$  less than 7 to 31 ppbv (i.e., the threshold depended upon the simulation), (b)  $[\text{O}_3 - 40]/\text{NO}_z$  greater than 3.6 to 6.4, (c)  $\text{HCHO}/\text{NO}_y$  exceeding 0.2 to 0.39, and (d)  $\text{H}_2\text{O}_2/\text{HNO}_3$  greater than 0.25 to 0.67. As noted earlier, were additional model applications considered, the ranges might be larger.

The type of output of the method and the degree of consistency between this output and the types of information needed for regulatory applications. The output of the method consists of concentrations ( $\text{NO}_y$  or  $\text{NO}_z$ ) or ratios of species, which would be compared to threshold values to determine if a particular location and time was VOC limited,  $\text{NO}_x$  limited, or indeterminate. The computations are straightforward and readily lend themselves to a qualitative determination of control preferences.

Availability of data needed as input to the method. Computation of all indicators considered by Sillman (1995) would require measurements of ozone,  $\text{NO}_x$ ,  $\text{NO}_y$ ,  $\text{HCHO}$ ,  $\text{H}_2\text{O}_2$ , and  $\text{HNO}_3$ . Both  $\text{NO}_x$  and  $\text{NO}_y$  would probably need to be measured with accuracies of about one ppbv down to concentrations of about one ppbv; however, this need has not been explicitly demonstrated. Virtually no measurements of true  $\text{NO}_x$  or  $\text{NO}_y$  are available from routine monitoring programs at present. However, the technology exists for measuring both  $\text{NO}_x$  and  $\text{NO}_y$  at the stated concentrations and levels of accuracy. The availability of adequate measurement methods for  $\text{HCHO}$ ,  $\text{H}_2\text{O}_2$ , and  $\text{HNO}_3$ , applicable on a routine basis, appears problematic. A number of methods are available for measuring  $\text{HNO}_3$ . Hering et al. (1988) showed that the differences in measurements obtained in a field study using different instruments exhibited a coefficient of variation of forty percent, and that concentrations could vary among instruments by a factor of four. A commonly used method is the denuder difference method (DDM), which generally requires sampling over a period of at least a few hours. Nitrate must then be extracted from filters and aqueous concentrations measured in the laboratory. The level of effort entailed can be substantial. Moreover, implementation of the DDM in one routine monitoring network, the California Acid Deposition Monitoring Program (CADMP), appears to have encountered difficulties having to do with the maintenance of the samplers (Watson et al., 1991; Blanchard and Michaels, 1994; Tuazon et al., 1995). Nitric acid can be measured continuously by means of either Fourier transform infrared spectroscopy (FTIR) or tunable diode laser absorption spectroscopy (TDLAS). However, the detection limits for FTIR are generally too high for the method to be of use in many (perhaps most) locations (Hering et al., 1988). The TDLAS appears promising, but may require further evaluation before it could be considered for routine application (Hering et al., 1988; Mackay, 1994; Tuazon et al., 1995). A variety of measurement methods have been used for  $\text{HCHO}$  and  $\text{H}_2\text{O}_2$ , including TDLAS,

DOAS, and instruments described by Watkins et al. (1995) and Munger et al. (1995). None of these methods may be considered tested and proven for routine application.

Availability of equipment, computational algorithms, or software needed for implementing the method. Application of the method requires only monitoring equipment. No specialized computational algorithms or software are needed. Although instruments for measuring  $\text{NO}_x$  and  $\text{NO}_y$  are available and could be used routinely, instruments for measuring  $\text{HCHO}$ ,  $\text{H}_2\text{O}_2$ , and  $\text{HNO}_3$  appear to require further development before they may be considered for use in routine monitoring networks.

Potential value of the method as part of the proposed new attainment demonstration procedure (including for use in comparisons among ODMs). Use of the method appears promising in part, although the stated ranges in the threshold values are large. While measurements of both  $\text{NO}_x$  or  $\text{NO}_y$  at the stated levels of accuracy are technically feasible, measurements of  $\text{HCHO}$ ,  $\text{H}_2\text{O}_2$ , and  $\text{HNO}_3$  may not be possible at present in routine monitoring networks. Additional research and development should be carried out, as described in Section V.

#### *The Observation-Based Model (OBM)*

Description. Cardelino and Chameides (1995) describe the use of a box model for calculating the sensitivity of ozone to VOC or  $\text{NO}_x$  reductions, which they name the "Observation-Based Model" (OBM). The model is an ODM because it uses ambient concentrations rather than emissions estimates to drive the calculations. The calculation is carried out separately for each monitoring location. Unlike a trajectory model, each box is fixed at the location of its monitor. The OBM utilizes some features of the OZIPM4 model to account for dilution and employs a modification of the CBM-4 (Cardelino and Chameides, 1995).

Cardelino and Chameides (1995) define a quantity,  $P^S_{\text{O}_3\text{-NO}}$ , which is the net ozone formed plus the net NO consumed over a 12-hour period (this quantity is similar to SP of the IER model but is computed as an integral over time rather than an instantaneous concentration). The fractional change in  $P^S_{\text{O}_3\text{-NO}}$ , divided by the fractional change in the "source strengths" of precursors, are used to define relative incremental reactivities (RIRs). For each measured species, instantaneous source strengths are calculated from the measurements and from production and loss terms using a set of coupled nonlinear equations resembling the continuity equations but which are expressed for a volume rather than an infinitesimal volume element. The RIRs for each site are (or can be) averaged to generate area-averaged RIRs. Cardelino and Chameides (1995) sum RIR terms so as to yield RIRs for NO, anthropogenic hydrocarbons (AHC), and natural hydrocarbons (NHC). The split between RIR-AHC and RIR-NHC is accomplished by summing RIRs for species arising from anthropogenic and biogenic emissions, respectively.

The key assumptions. Numerous assumptions are made in the procedure. Some of the assumptions that appear to have a potentially substantial effect on the calculations are listed here. As with any method, there is a concern that assumptions could lead to biases. Magnitudes of biases cannot be identified without carrying out specific analyses, nor can the likely direction of most biases be ascertained a priori. However, the following factors appear to introduce a potential bias toward overestimating the benefits of anthropogenic  $\text{NO}_x$  reductions:

- The OBM calculates RIRs for AHC and NHC, but does not separate  $\text{NO}_x$  into anthropogenic and natural components. In many cities, the natural  $\text{NO}_x$  source might be small; however, in some situations, e.g. where anthropogenic fertilizer use is high, soil emissions of  $\text{NO}_x$  can be a significant fraction of the total  $\text{NO}_x$  source. The OBM is able to compute RIRs for AHCs and NHCs because some chemical species can be identified as anthropogenic in origin, while others (e.g., isoprene) are known to be primarily of biogenic origin. However, no such subdivision of  $\text{NO}_x$  is possible.
- The RIRs are computed from the fractional changes in  $P^s_{\text{O}_3\text{-NO}}$ , divided by the fractional changes in the "source strengths" of precursors. The RIR for NO may, under some circumstances, not properly reflect the increases that can occur in ozone concentrations subsequent to  $\text{NO}_x$  reductions. For example, consider the following simplified case (assume a fixed volume). Let the initial ozone and NO concentrations be zero and 10 ppbv, respectively. After 12 hours, suppose the ozone and NO concentrations are 90 and zero ppbv, respectively. Now compare initial ozone and NO concentrations of zero and 5 ppbv, and suppose the final concentrations are again 90 and zero ppbv (i.e., the ozone concentrations at the end of 12 hours are identical for the two cases). The  $P^s_{\text{O}_3\text{-NO}}$  term is actually computed by integrating over the 12-hour period. However, for purposes of illustration, consider the 12-hour period as a single time step. Then, the numerator of the RIR-NO would be  $(90 + 10) - (90 + 5)$  divided by 100, which is a positive quantity (i.e., 0.05); hence, the RIR-NO will be positive. However, ozone was actually unchanged. Thus, an apparent sensitivity is obtained that is entirely due to the reduction in the amount of NO consumed. While this example is highly artificial, it does appear to indicate the potential for a generic bias arising from the definition of the RIRs in terms of the  $P^s_{\text{O}_3\text{-NO}}$  term. In more general terms, since  $P^s_{\text{O}_3\text{-NO}}$  integrates the areas under both the ozone and NO curves, any reduction in NO concentrations must translate into a positive contribution to the RIR-NO, thus potentially overstating the sensitivity of ozone to  $\text{NO}_x$ .

The effects of other assumptions and choices made in the development of the method appear difficult to predict. Some factors to consider include the following points; any consequent biases might range from inconsequential to substantial and cannot be determined without further study.

- Depending upon the choice of chemical mechanism, the reactivities of natural VOCs may be too high, thus affecting the computed RIRs for NHCs as well as the apparent relative benefits of controlling VOCs versus  $\text{NO}_x$ .
- In application to data from Atlanta, the RIR-NO and RIR-AHC were sensitive to the afternoon NO concentrations (Cardelino and Chameides, 1995); the crossover point occurred at 0.75 ppbv, a concentration below the detection limit of most currently-operating NO instruments. Thus, the value of the method may be limited until NO measurements can be made routinely with an accuracy of about 0.1 ppbv down to about 0.1 ppbv.
- Many assumptions appear to underlie the box modeling. The conditions under which the assumptions hold or fail are not obvious, nor is it apparent which conditions would occur for typical applications.
- Uncertainties appear to arise due to temporal and spatial averaging in the calculation of the source functions.
- The horizontal transport of calculated species, which includes  $\text{NO}_2$  and secondary paraffins, are treated as negligible (Cardelino and Chameides, 1995); the potential uncertainties cannot be identified at present.
- Only surface data are used to drive the calculations. Aloft concentrations are assumed to be those of the free troposphere. The effect may or may not be to limit the applicability of the procedure.
- Cardelino and Chameides (1995) do not explicitly describe the treatment of deposition, although the process may be incorporated into the loss terms.
- Area-averaged RIRs would appear to lump together potentially dissimilar sites. This effect, however, should be apparent through computation of the standard error function described by Cardelino and Chameides (1995) and through examination of the site-specific RIRs.

Nature and levels of uncertainty associated with the method. Analyses of uncertainty have not been carried out for the OBM. Taking into account the uncertainties deriving from factors such as those listed in the preceding section, as well as the inaccuracies and unavailability of data for typical nonattainment cities, there is a clear need to quantitatively characterize the resulting overall uncertainties in the model output. At present, some of the assumptions appear to generate biases that would enhance the apparent benefits of controlling anthropogenic  $\text{NO}_x$ .

The type of output of the method and the degree of consistency between this output and the types of information needed for regulatory applications. The output consists of RIRs for NO, AHC, and NHC. RIRs can also be output for anthropogenic area and point sources, as well as for other disaggregations that would be of use. The form of the output, as RIRs, can be directly translated into qualitative control preferences. However, RIRs derived from 12-hour  $P^S_{O_3-NO}$  terms may not be appropriate given the present form of the ozone standard, which requires compliance with a one-hour ozone average. Presumably, the time averaging could be modified should this appear necessary, though Cardelino and Chameides (1995) do not explicitly indicate that such modification is possible. Moreover, because the RIRs are expressed in terms of  $P^S_{O_3-NO}$  terms, it is unclear that the sensitivities of ozone are properly characterized, as described above.

Availability of data needed as input to the method. The method requires measurements of NO that are accurate at sub-ppbv concentrations (Cardelino and Chameides, 1995), which appears to exceed the capabilities of most instrumentation that has been, or will be, deployed in routine monitoring networks. The OBM also appears to require continuous gas chromatograph (GC) measurements of hydrocarbon species (multi-hour averages appear to be inadequate given the need to interpolate concentrations to relatively fine time resolution). Such data are largely nonexistent at present, although the technology is available.

Availability of equipment, computational algorithms, or software needed for implementing the method. As indicated above, equipment for measuring NO at sub-ppbv concentrations with sub-ppbv accuracies generally has not been deployed, although it is available. Presumably, the OBM consists of one or more computer programs that could be made available to interested parties. However, the availability and ease of use of these programs is unknown.

Potential value of the method as part of the proposed new attainment demonstration procedure (including for use in comparisons among ODMs). The OBM is a much more complex procedure than the other ODMs described here and involves a level of effort that appears to be on a par with the use of emission-based dispersion models. Several aspects of the OBM require further study and evaluation, as indicated above, before the method may be considered available, useful, and accurate in the guidance that it provides. The full range of assumptions underlying the OBM, and the attendant uncertainties, cannot be characterized as readily as for other ODMs; both assumptions and uncertainties should be clearly delineated. There is a need to determine if the uncertainties associated with the OBM are greater or less than those characterizing emissions-driven models; if the uncertainties are as large as for emissions-driven models, the level of effort involved in operating the OBM may not be warranted. Finally, the necessary measurements may be largely unavailable, both at present and in the near future, thus limiting the utility of the method even if it



otherwise appears attractive. Nonetheless, further research efforts are both needed and recommended, as discussed in Section V.

#### *Cross-comparisons Among the ODMs*

Both the SP algorithms (Blanchard et al., 1994) and the use of  $\text{NO}_y$  as an indicator species appear to be broadly consistent with the ozone- $\text{NO}_y$  (or  $\text{NO}_z$ ) correlations described by Trainer et al. (1993). However, the comparisons described here are limited and should be carried out in greater depth.

Trainer et al. (1993) selected measurements that indicated photochemically aged air (in which ozone levels would be limited by the availability of  $\text{NO}_x$ ). With the exception of a single day at one site, the  $\text{NO}_y$  and  $\text{NO}_z$  concentrations reported by Trainer et al. (1993) were less than 14 and 10 ppbv, respectively. In comparison, Milford et al. (1994) concluded that ozone concentrations would be responsive to reductions of  $\text{NO}_x$  where afternoon concentrations of  $\text{NO}_y$  fall below a threshold ranging from about 10 to 25 ppbv  $\text{NO}_y$ . A more exact comparison of consistency would require consideration of the sensitivities of the modeling results to the calculated deposition rates and of the comparability of model-calculated grid-cell average concentrations to ambient measurements (Milford et al., 1994).

As noted earlier, the data from Scotia were well described by a line having an intercept of 35 ppbv ozone and a slope of 8.5 ppbv ozone per ppbv  $\text{NO}_x$  oxidized for  $\text{NO}_z$  concentrations up to 10 ppbv; data from the Los Angeles area, in which  $\text{NO}_z$  concentrations ranged from about 20 to 85 ppbv, showed a slope of about 5 ppbv ozone per ppbv  $\text{NO}_z$  (Trainer et al, 1993). For the indicator  $[\text{O}_3 - 40]/\text{NO}_z$ , Sillman (1995) reported that values of 1.8 to 7.4 denoted VOC sensitivity, whereas values of 3.6 to 11 indicated  $\text{NO}_x$  sensitivity (see earlier discussion). Thus, the Scotia data fall within the  $\text{NO}_x$ -sensitive regime according to the Sillman indicator; the Los Angeles data are indeterminate.

The SP algorithms use the simple relationship  $\text{SP}_{\max} = \beta [\text{NO}_x(0)]^\alpha$ , with  $\beta = 19$  and  $\alpha = 2/3$ . For a fixed-volume system, the relationship implies a ratio of ozone [where  $\text{O}_3 = \text{SP} - \text{NO}(0)$ ] to  $\text{NO}_y$  of 7.8:1 when  $\text{NO}(0) = 10$  ppbv and  $\text{NO}_2(0) = 0$  ppbv, excluding consideration of depositional losses of ozone and  $\text{NO}_y$ . For systems in which  $\text{NO}_x$  concentrations have decayed to low (sub-ppbv) values, the ratio of ozone to  $\text{NO}_y$  would be approximately equal to that of ozone to  $\text{NO}_z$ . The corresponding ozone-to- $\text{NO}_z$  ratio at  $\text{NO}(0)$  of 55 ppbv is 4.0:1. These ratios would be somewhat higher if the deposition algorithm and the initial  $\text{NO}/\text{NO}_x$  fractions used in the SP algorithms were included in the calculation; as calculated, the ratios nonetheless appear broadly consistent with the data presented by Trainer et al. (1993). On the other hand, the SP algorithms use a nonlinear relationship even below 10 ppbv  $\text{NO}_x$ , whereas the data of Trainer et al. (1993) appear approximately linear below 10 ppbv  $\text{NO}_z$ .

No co-applications of the ODMs have been conducted (see recommendations in Section V).

### *Summary*

Four ODMs were reviewed. Each is under active development, and some are available for application in preliminary forms. Further development and evaluation of each of the ODMs is warranted (see Section V). The ODMs should be co-applied to several study areas to permit assessment of the consistency of the guidance provided (see Section V). Interim applications of the ODMs should be encouraged so as to facilitate familiarity with their use, provide incentives for developing the necessary monitoring information, and develop experience with their performance capabilities. The developers of the ODMs should provide users with clear guidance as to present capabilities and limitations so that the findings from interim applications may be interpreted appropriately.

Finally, one other caveat should be mentioned. With the exception of correlation analyses of the observation measurements, all other observations-driven methods can be traced back to empirical chamber data. This derivation is direct in the case of the IER method or indirect, through the use of chemical mechanisms, in the other two approaches, which use smog chamber data in their development. Therefore, should smog chambers have an undetected systematic bias which affects the quantitative relationship between ozone and its precursors, these methods could also be biased.

### **C. Analysis of Observations**

Analysis of air quality data has predominantly considered studies associated with ozone concentrations, and with the exception of the past few years, very little consideration given to ozone precursor concentrations (volatile organic compounds (VOC) and oxides of nitrogen (NO<sub>x</sub>)). This lack of analysis activity by the scientific and air quality communities was mainly the result of severe limitations in the availability of high quality concentration data of the requisite precursor species and to a lesser extent limited funds in support of this area. As a result of recent criticisms regarding this data and analysis void (NRC, 1991), the U.S. Environmental Protection Agency has initiated an extensive monitoring effort to be implemented by state agencies (U.S. EPA, 1993) within specified ozone Nonattainment areas. The Photochemical Assessment Monitoring Stations (PAMS) are to measure ozone, NO, NO<sub>2</sub>, NO<sub>x</sub>, formaldehyde, acetaldehyde and acetone and fifty-five (55) hydrocarbon species in and around the specified nonattainment areas.

With the onset of this data, come a variety of data analysis opportunities which historically were not possible or were so data limited as to be impractical for credible scientific inquiry. These new analysis opportunities, open new options for

consideration in the air quality management process as well as a rethinking of the role monitoring and analysis can play in the SIP processes. Using the PAMS network as a prototype, this section identifies some of the analysis tools and applications that will be possible with a "new generation" of air quality data and discusses the role such analyses can play in implementing the "Attainment Demonstration Process (ADP)" proposed in this report.

In a later section on monitoring, a discussion is presented regarding specific improvements in the PAMS program and its related operational infrastructure as well as additional monitoring activities which must be considered to augment the ADP.

#### *Basic Data Analysis Tools and Objectives*

Historically most air quality data analysis studies have been confined to characterizing ozone air quality and establishing its overall trend with time (U.S. EPA, 1974; Chock et al., 1982). Although these analyses have provided information on ozone air quality, exposure assessments and basic trend information within the monitored regions, they have shed little light on the reasons for the unexpected and limited progress made in mitigating ozone pollution in the region. In recent years, research measurement programs have collected data sets over limited time periods, which have provided detailed characterizations of the chemical composition of regional atmospheres. These data sets have resulted in the consideration of more ambitious data analyses studies that present new opportunities for understanding the photochemical processes associated with ozone formation and its quantitative relationship with VOC and NO<sub>x</sub> precursor emissions. These analysis techniques should become routinely possible with the availability of measurement data sets such as those being collected as part of the PAMS, SOS and NARSTO-NE programs.

The purpose is not to provide a critical review of all possible data analysis techniques available for air quality assessment, but to identify a select series of analysis approaches to address specific objectives identified within the ADP. As new analysis techniques are identified and accepted as better serving the analysis objectives outlined in the ADP, they should be incorporated into the process.

A summary of ADP needs and supporting data analysis techniques is presented in Table IV.C-1. Selected examples of the application of these techniques in addressing air quality related objectives identified as part of the ADP will now be discussed.

Table IV.C-1. Summary of ADP Needs and Supporting Data Analysis Techniques		
Needs	Techniques	Chemical Species
☛ characterizing ozone exposures and NAAQS attainment	Air Quality Characterization: 1) extreme value and exceedance statistics; 2) meteorological data adjustment	a) ozone b) ozone precursors c) target indicator species
☛ assessing effectiveness of emission control ☛ tracking air quality ☛ tracking (reasonable further progress) RFP	Ambient Trend Analysis: 1) time series of hourly, daily, monthly, and annual statistics 2) means and extreme values 3) detrended data	a) ozone b) ozone precursors c) target indicator species
☛ assessing effectiveness of emission control ☛ tracking RFP ☛ corroborating NO <sub>x</sub> and VOC emission budgets	Emissions Trend Analysis: 1) time series of hourly, daily, monthly, and annual statistics 2) means and extreme values	a) ozone precursors b) target indicator species
☛ assessing effectiveness of emission control ☛ corroborating NO <sub>x</sub> and VOC emission budgets	Source Attribution: 1) principal component analysis (PCA) 2) chemical mass balance (CBM) 3) source apportionment by factors with explicit restrictions (SAFER)	a) ozone precursors b) target indicator species
☛ corroborating of NO <sub>x</sub> and VOC emission budgets ☛ assessing effectiveness of emission control ☛ tracking RFP	Correlation Analysis: 1) NMHC and NO <sub>x,y</sub> , CO and NO <sub>x,y</sub> , NMHC and CO	a) ozone and its precursors b) target indicator species

### *ADP Emission Related Analysis Components*

The emissions related data analysis components identified within the ADP scheme must be concerned with the tracking of emissions changes, corroborating inventories, establishing the effectiveness of control programs, attributing source contributions to observed precursor levels and providing feedback and accountability to the emission control/projection process.

Example analyses include:

- Using ambient concentration ratios (i.e., NMHC/NO<sub>x</sub>, NMHC/NO<sub>y</sub>, CO/NO<sub>x</sub>, CO/NO<sub>y</sub>, SO<sub>2</sub>/NO<sub>x</sub>, SO<sub>2</sub>/NO<sub>y</sub>, NMHC/CO) to determine if the relative proportions of the precursor components of the emissions inventory are consistent (Parrish et al., 1991; Buhr et al., 1992; Fujita et al., 1992);

- Using ambient concentration ratios from early to midmorning measurements of NMHC/NO<sub>x</sub> and NMHC/NO<sub>y</sub> to provide insights with regard to expected ozone responses to hydrocarbon vs NO<sub>x</sub> emission control strategies within monitored regions (Wolff and Korsog, 1992);
- Using ambient concentration ratios from early to midmorning measurements of CO/NO<sub>x</sub>, CO/NO<sub>y</sub>, and NMHC/NO<sub>x</sub>, NMHC/NO<sub>y</sub> to identify sources of error in emission inventories (Fujita et al., 1992);
- Using ambient concentrations to detect trends in total NMHC, NO<sub>x</sub>, NO<sub>y</sub>, CO, NMHC/NO<sub>x</sub>, NMHC/NO<sub>y</sub>, CO/NO<sub>x</sub>, CO/NO<sub>y</sub> and target indicator hydrocarbon species for the purpose of tracking reasonable further progress (RFP) towards ozone attainment; the choice of the most appropriate analysis parameters will depend on the control strategies selected to meet the RFP for the monitored region, (e.g. if Reformulated Gasoline (RFG) were part of a region's RFP, ambient trends in NMHC, CO, NMHC/NO<sub>x</sub>, NMHC/NO<sub>y</sub>, CO/NO<sub>x</sub>, CO/NO<sub>y</sub>, benzene and benzene/NMHC would all prove to be relevant analyses for tracking the progress of emission reductions and the effectiveness of the RFG control strategy);
- Using ambient measurements of speciated hydrocarbons and ratios of indicator species to reconcile source contributions to ambient concentrations (Stephens and Burleson, 1967, 1969; Altsuller et al., 1971; Mayrsohn et al., 1976; Lonneman et al., 1968; Pilar and Graydon, 1973; Ioffe et al., 1979; Whitby and Altwicker, 1978; and McKeen et al., 1990; Jobson et al., 1994) and to derive specific source contributions source apportionment techniques (Henry et al., 1994)

#### *ADP Air Quality Trends and Control Strategy Evaluation Analysis Components*

Air quality monitoring to support feedback and accountability in the air quality management approach is a central feature of the ADP. Data analysis procedures to track and verify air quality responses to implemented control strategies and related emissions projections are used in the ADP: to assess the effectiveness of control programs; to provide the opportunity to evaluate the progress of the control program and consider mid-course corrections; to establish that the ozone response function to measured ambient precursor concentration changes is consistent with that predicted by the PAQSM. Example analyses include:

- Using linear regression, analysis of variance, and nonparametric statistical analyses of the means of early to midmorning measurements of NMHC, NO<sub>x</sub>, NO<sub>y</sub>, CO and target indicator hydrocarbon species concentrations within urban monitoring sites to evaluate trends in precursor air quality; using commensurate analyses of maximum O<sub>3</sub> concentrations at the respective downwind sites evaluate trends in ozone air quality (Chock et al., 1982, Kumar and Chock, 1984; Rao et al.,

1992);

- Using statistical filtering methodologies remove the influence of meteorological fluctuations on the concentrations of  $O_3$ , NMHC,  $NO_x$ ,  $NO_y$ , CO, and target indicator hydrocarbon species so as to detect changes in ozone air quality due to changes in precursor emissions and/or selective control strategies (Korsog and Wolff, 1991; Rao and Zurbenko, 1994);
- apply extreme value theory - chi-square distribution and Poisson process to evaluate and track trends in ozone summary statistics based on daily maximum ozone concentrations and the attainment of the NAAQS (Roberts, 1979; Smith, 1989; Shively, 1991)
- apply correlation analyses of the concentrations of  $O_3$  and  $NO_y$ ;  $O_3$  and  $NO_y - NO_x$ ;  $O_3$  and CO;  $O_3$  and NMHC to discriminate if region is  $NO_x$  or VOC limited with regard to ozone formation (Trainer et al., 1993; Parrish et al., 1993; Chin et al., 1994; Olszyna et al., 1994) These methods are discussed in further detail in Section IV.B.

#### D. Monitoring

##### *Siting and Analysis Objectives*

The successful application of measurement data to support analysis approaches, whether they be related to the evaluation of theoretical models or the development and application of diagnostic observational data analysis tools, are contingent upon the measurement/monitoring stations meeting specified data quality objectives and siting attributes. The PAMS program has identified four distinct site types, summarized in Table IV.C-2 and identified their intended monitoring objectives for each site type (U.S.EPA, 1991).

Table IV.C-2. PAMS Siting Criteria and Contributions to ADP			
	Attributes		Intended Contributions to ADP *
Type (1)	located in the predominant morning upwind direction from the local area of maximum precursor emissions		specifying pollutant inflow and trends; specifying model boundary conditions, present and future.
Type (2)	located immediately downwind of maximum precursor emissions		corroborating NOX and VOC emissions; tracking emissions and progress in implementation strategy; evaluating pollutant exposures, models, and NAAQS attainment.
Type (3)	located 10 to 30 miles downwind from the edge of the urban area		evaluating pollutant exposures, models, and NAAQS attainment; tracking emissions and progress in implementation strategy
Type (4)	located in the predominant afternoon downwind direction from the local area of maximum precursor emissions		evaluating ozone control strategies; specifying pollutant outflow and trends; specifying model boundary conditions, present and future.

\*The scope of the PAMS network, although ambitious, is inadequate for meeting all the intended contributions to ADP.

In the discussion which follow, the PAMS network is taken as a starting point from which modifications or additions will be considered to meet the goals and objectives of the proposed ADP. The establishment of the four designated site types identified under PAMS is critical to the successful implementation of key analysis procedures to be applied for tracking, feedback and verification of the ADP, but it is important to note that the network has significant limitations with regard to its coverage and spatial representativeness. In addition, there are currently no operational examples of State PAMS networks which considered all four site types nor are there demonstrated data analyses protocols to assess the representativeness of the PAMS sites which are operational. To some extent it has tried to serve too many masters and as a result has over stated its intended objectives. For example, a single upwind monitor is inadequate and potentially misleading for specifying model boundary conditions, as is its ability to specifying trends in pollutant inflow fluxes.

*Measurement Parameters, Methods and Data Quality Objectives*

Chemical parameters measured in PAMS sites include: NO, NO<sub>2</sub>, NO<sub>x</sub>, O<sub>3</sub>, formaldehyde, acetaldehyde, acetone and the fifty-five non-methane hydrocarbon species listed in Table IV.C- 3.

Table IV.C-3. PAMS Speciated Non-Methane Hydrocarbons		
Acetylene	2,3-Dimethylbutane	2,3,4-Trimethylpentane
Ethylene	2-Methylpentane	Toluene
Ethane	3-Methylpentane	2-Methylheptane
Propylene	2-Methyl-1-Pentane	3-Methylheptane
Propane	n-Hexane	n-Octane
Isobutane	trans-2-Hexene	Ethylbenzene
1-Butene	cis-2-Hexene	p-Xylene
n-Butane	Methylcyclopentane	Styrene
trans-2-Butene	2,4-Dimethyl pentane	o-Xylene
cis-2-Butene	Benzene	n-Nonane
3-Methyl-1-Butene	Cyclohexane	Isopropylbenzene
Isopentane	2-Methylhexane	n-Propylbenzene
1-Pentene	2,3-Dimethyl pentane	α-Pinene *
n-Pentane	3-Methylhexane	1,3,5,-Trimethylbenzene
Isoprene	2,3-Dimethylpentane	1,2,4-Trimethylbenzene
trans-2-Pentene	3-Methylhexane	β-Pinene *
2-Methyl-2-Butene	2,2,4-Trimethylpentane	
2,2-Dimethylbutane	n-Heptane	
Cyclopentane	Methylcyclohexane	Total Non-Methane HC

\* Recent testing and evaluation of the automated Gas Chromatographic hydrocarbon analysis method deployed in PAMS have reported that these species cannot be measured quantitatively and have been removed from the required species list.



Meteorological parameters to be measured at a height of 10 meters from the surface include: wind speed and direction, temperature, relative humidity, barometric pressure and solar radiation. The PAMS network must also have available regional representative upper air meteorological measurement data including: winds, temperature, dew point, and pressure which can be used to help characterize the synoptic flow and mixed layer dynamics of the region.

Measurement methods and techniques for PAMS are outlined in EPA reference methods and technical assistance documents (U.S. EPA, 1993; U.S. EPA, 1991), those associated with criteria pollutants (i.e.,  $O_3$ , NO,  $NO_2$ , and  $NO_x$ ) are reasonably well established, though, as we will discuss later, issues still remain regarding detection limits and accuracy. The measurement methods required for speciated hydrocarbons and carbonyls in PAMS are not well established and quality assurance procedures/standards for these methods are still under development.

A scoping study has been initiated in the northeast portion of the United States in 1995 as part of the North American Research Strategy for Tropospheric Ozone (NARSTO). This multi year program is designed to address a series of policy relevant scientific issues associated with oxidant control and ozone nonattainment in the northeast region. This summer a research measurement network was established, that is designed to augment PAMS monitoring through characterization of chemical backgrounds in the northeast region. In addition, several PAMS sites in the region were augmented with  $NO_y$  instrumentation. Chemical measurements and methods deployed at these research measurement sites are summarized in Table IV.C-4. The table also provides performance criteria and operating schedules for these measurements and is indicative of what should routinely be possible in air quality monitoring networks.

In addition, a standard complement of meteorological measurements (wind speed and direction, relative humidity, temperature, solar radiation and pressure) will be collected at site each from 10 meter towers. The program also has supplemented upper air meteorological measurements, through a network of acoustical and radar sites in the region.

Other chemical measurements of interest in support of model evaluations and diagnostic testing of chemical process relevant to the ozone precursor relationships include: radical termination products (e.g.  $HNO_3$ ,  $H_2O_2$ , ROOR, and  $RONO_2$ ); VOC oxidation products (e.g. PAN, MEK and MA); and oxygenated VOC sources ( $CH_3OH$ ,  $C_2H_5OH$ , and MTBE)

Aircraft platforms are capable of providing equivalent sets of measurements as identified in Table IV.C-4, but quality measurements from these platforms requires significantly more effort as a result of additional factors affecting instrumentation performance (e.g. air sampling inlet designs, pressure and temperature variations, in-

flight quality assurance procedures) .

TABLE IV.C-4. Typical Chemical Measurements Performed at Regional Enhanced Monitoring Sites in NARSTO-NE, 1995			
Measurement/ Method	Range/MDL	Averaging Times	Operation Schedule
NO/NO <sub>2</sub> /NO <sub>x</sub> Chemiluminescence	0 - 50 ppb 100 ppt	1 minute/hourly	Photochemical Season or Year Around
NO <sub>y</sub> - Mo/Au Conversion <sup>1</sup> Chemiluminescence	0 - 50 ppb 200 ppt	1 minute/hourly	Photochemical Season or Year Around
O <sub>3</sub> UV absorption	0 - 200 ppb 2 ppb	1 minute/hourly	Photochemical Season or Year Around
CO <sup>1</sup> Gas Filter Correl. Enh.	0 - 1000 ppb 20 ppb	5 minute/hourly	Photochemical Season or Year Around
Speciated Hydrocarbons GC-FID <sup>2</sup> ; dual column auto GC <sup>3</sup>	0 - 500 ppbC 0.2 ppbC	grab or integrate (1-6hr) cans, 4 to 6 samples/day; in line cryotrap continuous ~ 1 hr	Photochemical Season or Year Around (reduced sampling schedule)
Carbonyl Compounds DNPH Silica Gel & C-18 Cartridges <sup>4</sup> - HPLC	0 - 10 ppbC 0.5 ppb	integrated (1-6 hr) cartridges, 4 to 6 samples/day	Photochemical Season or Year Around (reduced sampling schedule)
SO <sub>2</sub> <sup>1</sup> Pulsed Fluorescence	0 - 10 ppb 100 ppt	1 minute/hourly	Photochemical Season or Year Around

<sup>1</sup>Chemical species currently not measured in PAMS network

<sup>2</sup>Hydrocarbon speciation C<sub>2</sub> - C<sub>10</sub>

<sup>3</sup>Automated dual column Gas Chromatographs are currently under evaluation

<sup>4</sup>DNPH cartridge sampling systems are currently under evaluation

The depolyment of instrumented aircraft to address the very important characterization of the vertical dimension of the air quality is very much dependent of the range, performance, and payloads of the aircraft. Even the most ambitious of aircraft measurement programs will characterizes only a few episodes well enough to be useful for selective model evaluation studies and provide an indication as to the importance boundary conditions may have on a designated modeling domain. There is critical need for routine chemical concentration data in the vertical, but the costs associated with aircraft measurement programs to provide the data are prohibitive.

Therefore the development of innovative techniques, ( remote sensing, instrumented tether balloons, instrumented unmanned aircraft) must be considered to support the future advancement of the field.

### *Ambient Monitoring in Support of PAQSM*

Ideally, the information needed to support the operation and evaluation of the entire photochemical air quality simulation modeling system, including all modules and preprocessor models requires a data base which completely characterizes the spatial and temporal features of requisite input variables and the final estimated concentration fields. The meteorological and air quality models provide estimates that represent spatial averages over volumes the size of a grid cell, which may have dimensions of several kilometers in the horizontal and several tens to a few hundred meters in the vertical. But in reality, current measurement technology typically provides observations at a "point" (i.e., the sampling volume is much smaller than that of a grid cell). Although the time averaging of fixed surface observations may be comparable to that of the model estimates (i.e., one-hour averages), measurements from instrumented aircraft typically represent averages over an interval of less than one minute. Thus, both the spatial and temporal scales of aircraft data are much smaller than those of the model estimates. This disparity of scales problem pervades all current observations. Using current measurement technologies, it is important to collect information in a way that allows the "point" observations to provide information that is as representative as possible of values averaged over larger spatial and time scales. Therefore, site selection criteria are a critical part of assuring data representativeness of the measurement site.

Ambient monitoring data in support of model evaluation activities may include: area-specific emissions measurements; combined chamber and air parcel tracking studies to assess the chemical mechanism; inert tracer releases and associated downwind monitoring to test treatment of pollutant transport; dry deposition experiments; and grid-averaged, time varying information on primary and secondary pollutant concentrations along upwind and downwind boundaries; and hourly- and grid-averaged concentrations of  $O_3$ ,  $NO_x$ ,  $NO_2$ , VOCs (speciated), PAN, and other secondary reaction products collected over all significant portions of the modeling region.

Initial pollutant concentrations for use in the air quality models are derived using interpolation techniques and available air quality data collected at the surface and aloft. Surface monitoring sites situated in the immediate vicinity of large sources may not be useful in establishing the subregional estimates of initial concentrations needed by the model. If significant amounts of pollutants reside aloft at the start of a simulation, their concentrations will be difficult to characterize in the absence of aircraft or other suitable measurements. Speciated VOC data are needed to specify the concentrations of organic species required by the kinetic mechanism and must

usually be collected as part of a supplemental field study. Alternatively, values must be derived based on an analysis of data collected in previous studies in other urban settings. In general, an attempt is made to minimize problems associated with specifying initial concentrations through the performance of multi-day simulations.

Boundary concentrations are derived using available local data at the sectors upwind of the modeling domain. These routine measurements of pollutant levels upwind of an urban area must characterize horizontal spatial distributions of the incoming concentration fields. The specifications of pollutant levels aloft are much more difficult to characterize. Instrumented aircraft flying along the upwind boundaries can be used to help establish boundary concentrations, but is important to recognize their limitation as well, since at best these data rarely provided more than a few periods during a day. The entrainment of pollutants from aloft, representative of the previous day's mixed layer, may also be estimated from upwind surface monitors, if they are not influenced by local source emissions. For example by reviewing the time rate of change in the diurnal profiles of species concentrations of  $O_3$ ,  $NO_x$  and CO during the morning periods, reasonable assumptions can be made of concentrations aloft.

As with the lateral boundary concentrations, measurement data for the top boundary of the modeling domain, are very limited. Though the exchange of background concentrations of ozone and its precursors in the free troposphere (or stratosphere) into the modeling domain can occur through significant larger scale convective activity, it is generally of secondary importance in photochemical ozone episodes. Data for this top boundary can be collected via aircraft or from elevated mountain-top sites in the region.

#### Routine Monitoring Networks

Federally mandated air quality monitor networks [State or Local Air Monitoring Stations (SLAMS) and National Air Monitoring Stations (NAMS) ] were not designed to support model evaluation studies, but to measure criteria pollutants in terms of characterizing 1) maximum concentrations, 2) population exposure, 3) source impacts, 4) background concentrations and 5) in the case of NAMS to track air quality. These monitoring sites are typically located in an urban, multi-source impacted areas with high population density. Their greatest value in model performance evaluations is in their ability to characterize the spatial distribution of ozone and its maximum concentration within an urban area.

These surface air quality measurements will generally be impacted by local sources, thus limiting their spatial representativeness for use in model performance evaluations. Also the networks have provided only limited data on VOC and  $NO_x$  concentrations, which are essential for model performance evaluations, moreover, sensitivity and specificity of the  $NO/NO_x$  instruments used in these networks is

insufficient to accurately determine low ambient concentration levels needed to effectively test the O<sub>3</sub>-VOC-NO<sub>x</sub> relationship.

As mentioned above, PAMS, the newest federally mandated measurements network, is intended to provide information to assist in control strategy development and evaluation, emission tracking, and trend analysis, and exposure. The ozone precursor measurements to be performed will be a vast improvement in the air quality data base and should significantly benefit the model performance evaluation processes. It is unlikely that the spatial coverage provided by PAMS will be sufficient to satisfy current requirements specified for model performance evaluations (Roth et al., 1992). Criteria for network design, including station density, areal coverage, chemical and physical parameters, and precision and accuracy of the measurements in support of the model performance evaluation process, have not been established. The choice of chemical and physical parameters and the required precision and accuracy of their measurement have been driven by what was available and not by the rational development of data quality objectives designed to meet specific model performance evaluation standards. This result is not surprising, since the establishment of unambiguous model performance standards, remains as elusive now as it did ten years ago. In a similar manner sample frequency and averaging time are generally driven by instrumentation capabilities or cost constraints. Current generation O<sub>3</sub>, NO/NO<sub>x</sub>, SO<sub>2</sub>, and CO instrumentation can deliver virtually continuous data and should be archived for averaging times of one minute, five minute and one hour. Speciated VOC and carbonyl compounds currently being measured under the PAMS program have minimum sampling times of one hour and three hours respectively.

We can clearly state that the attributes of the four types of sites identified under the PAMS program must be represented in any model domain being considered for evaluation. What is less clear is the number of each type of site required to provide acceptable spatial coverage of the modeling domain for the performance evaluation.

#### The Role of Intensive Field Measurement and Special Study Programs

In addition to routine monitoring data, intensive field study programs have been carried out to support regulatory applications of photochemical models. Programs such as the Southern Oxidant Study (SOS; Chameides and Cowling, 1995), Lake Michigan Ozone Study (LMOS; ENSR, 1991), Southern California Air Quality Study (SCAQ; Blumenthal, Watson, and Roberts, 1987), South Central Coast Cooperative Aerometric Monitoring Program (SCCCAMP; Dabberdt and Viezee, 1987), and SJVAQS/AUSPEX (Blumenthal and Watson, 1991) have been carried out in part to provide data needed to support the application and evaluation of photochemical models in these study areas because existing routine monitoring activities were inadequate.

The design for an intensive monitoring program begins with consideration of the overall modeling program objectives. Considering the existing routine monitoring network, various measurements are added to fulfill one or more modeling needs. The goal is to fully characterize important transport and chemical transformation phenomena in the study area of concern. There are three major categories of data which must be enhanced; meteorological, emissions inventory and air quality. The discussion here is limited to air quality data and the measurements/monitoring required.

Enhancements in surface air quality monitoring undertaken as part of these field intensives and typically operated continuously throughout one or more photochemical seasons include:

- supplementing existing networks with instrumentation to provide a complete complement of ambient air quality measurements, including ( $\text{NO}$ ,  $\text{NO}_x$ ,  $\text{O}_3$ , VOC, PAN, etc.);
- establishing new monitoring sites or even networks to provide regional coverage or a better characterization of the upwind and downwind areas;
- testing and evaluation of new advanced instrumentation capable of monitoring low level concentrations of species important to assessing the quantitative relationship between ozone and its precursors;
- establishing enhanced high sensitivity monitoring sites in rural areas, near the boundaries of the model domain to provide both boundary condition data for model inputs and also data to evaluate model performance, and perform diagnostic and corroborative analyses.

Intensive measurement programs, as part of these field intensives, are carried out on an intermittent basis, typically during episode periods. These programs typically measure air quality aloft through the use of aircraft and operate research instrumentation at selected surface monitoring site(s) to measure unique chemical species of importance to understanding photochemical oxidation processes and the ozone-VOC-  $\text{NO}_x$  relationship. Aircraft data provide initial and boundary concentration inputs for model applications and a three-dimensional characterization of air quality for use in model performance evaluation. Unfortunately the temporal and spatial limitations of aircraft data are significant. As a result, a very limited number of realizations are available to test/evaluate the model which leaves model performance testing in this region highly uncertain. Surface and airborne lidar have become increasingly useful for characterizing air quality conditions aloft and may help in establishing inputs as well as in evaluating model performance. One or more inert tracers may be released from key source areas to document actual transport phenomena; associated air sampling may be conducted at downwind surface locations and by instrumented aircraft.

The quality of a model performance evaluation is directly related to the availability of suitable meteorological, air quality, and emissions data. Routine measurement programs do not adequately characterize the spatial and temporal variability of key meteorological and air quality variables and thus cannot be relied upon to support the model evaluation effort. Thoughtfully designed intensive field measurement programs can provide the needed supplemental information. At a minimum, such programs should include additional meteorological and air quality monitoring (both at the surface and aloft), collection of day-specific emissions data for large industrial sources, VOC speciation measurements, and upwind monitoring of  $O_3$  and precursors at the surface and aloft.

#### *Ambient Monitoring in Support of Observation-Driven Methods*

The PAMS network should provide an excellent foundation for the support of observation-driven methods and related data analysis and diagnostic techniques. Several operational issues regarding PAMS and its supporting infrastructure remain unresolved and present some cause for concern. The deployment of PAMS is significantly behind schedule, though many sites are identified as operational, delivery of quality assured data is not forthcoming. This seems to be a systemic problem that can be traced to 1) a significant underestimation of the manpower resources and technical expertise required to maintain and operate the PAMS sites; 2) the inability of state agencies to commit sufficient manpower resources to the PAMS operation; 3) premature deployment of unproven instrumentation/measurement systems for routine operation; 4) limited infrastructures to support routine data assessment, analysis and distribution of the PAMS data to facilitate quality assurance and scientific interactions.

A fully deployed PAMS as prescribed in (U.S. EPA, 1993) must be maintained and operated for a minimum of ten years to meet the most important policy relevant and operational analysis objectives it was designed to address. The significant commitment required to maintain a high quality monitoring network like PAMS is a new and unprecedented challenge to the state agencies involved and suggests the need for external technical assistance in the deployment and operation of these sites as well as scientific assistance in the assessment and analysis of the data collected. The scientific community recognizes the potential value of the PAMS and has recommended augmentation of the network through the addition of complementary enhanced regional measurement sites and suggested instrumentation upgrades and measurement parameter additions to the existing PAMS networks (NARSTO, 1994). The community also recognizes the scientific and technical assistance needs of the state agencies and is in the process of building partnerships, mainly through university and federal research groups, to facilitate PAMS related operation and analysis activities with state agencies.

The measurements being performed under PAMS and the enhanced PAMS sites under the NARSTO program, should very likely meet the needs of the most ambitious observation-driven methods. The routine delivery of high quality assured data from these networks is currently not a reality, but should be possible with the proper infrastructure development and support.

Specific measurement requirements for ODMs were addressed in Section IV.B for each of the four methods reviewed. These requirements are summarized in Table IV.D-1, along with suggested siting and spatial representation requirements. It should be noted that the measurement requirements for emission-based models, even at the most rudimentary level of model application and performance evaluation, are far more demanding than ODM requirements. Although the full extent of the measurements requirements for the ODMs are not established at this time, since these methods are still under development, it is not likely that they will approach the needs of the PAQSM.

Finally, there are several measurement/instrumentation issues associated with critical parameters identified in the measurement requirements for both the ODMs and PAQSM as well as in the analysis of observations which will be addressed in Section V.

#### *Ambient Monitoring in Support of Analysis of Observations*

There are many similarities in the data needs in support of the analysis of observations approaches outlined in Section IV.C and those identified with regard to the ODMs. What is a somewhat unique objective identified in the analysis of observations approaches, but not emphasized in the other techniques are the emission analysis components which require near source and in-source measurements. Type(2) monitors identified under the PAMS network, can provide useful data for addressing these near source measurement needs (see Table IV.C-1 and Table IV.C-4). But intensive measurement programs designed to specifically target source categories will likely be needed to augment these sites.

In-source measurements have been mainly associated with special studies and research programs, and with the exception of the recent regulatory requirement (Clean Air Act, 1990) to provide continuous NO<sub>x</sub> measurements for point sources emitting more than 100 tons per year, the direct measurement of source emissions has not been considered in the monitoring programs.



Table IV.D-1 Measurement Requirements in Support of ODMs

Observation-Driven Method (ODM)	Parameters	Range/MDL <sup>1</sup>	Site Location and Spatial Representation <sup>2</sup>
Correlation; O <sub>3</sub> -NO <sub>y</sub> or O <sub>3</sub> -NO <sub>z</sub>	O <sub>3</sub>	0 - 200 ppb 2 ppb	1) one or more monitors (20-40 km) upwind and downwind of major urban emission regions; 2) several monitors in rural areas which characterize regional pollution events; 3) one or more monitors immediately downwind of major urban emission regions (<20 km)
	NO-NO <sub>2</sub> , NO <sub>y</sub>	0 - 200 ppb 500 ppt	
<sup>3</sup> Correlation; O <sub>3</sub> -CO, O <sub>3</sub> -NMHC, CO-NO <sub>x</sub> , CO-NO <sub>y</sub> ,	CO	0 - 1000 ppb 20 ppb	
	NMHC (speciated)	0 - 1000 ppbC 500 pptC	
Integrated Empirical Rate (IER)	O <sub>3</sub>	0 - 200 ppb 2 ppb	1) one or more monitors (20-40 km) upwind and downwind of major urban emission regions; 2) one or more monitors immediately downwind of major urban emission regions (<20km); 3) several monitors in rural areas which characterize regional pollution events
	NO-NO <sub>2</sub> , NO <sub>y</sub>	0 - 200 ppb 500 ppt	
Indicator Species and Ratios	O <sub>3</sub>	0 - 200 ppb 2 ppb	1) one or more monitors (20-40 km) upwind and downwind of major urban emission regions; 2) one or more monitors immediately downwind of major urban emission regions (<20km); 3) several monitors in rural areas which characterize regional pollution events
	NO-NO <sub>2</sub> , NO <sub>y</sub>	0 - 200 ppb 100 ppt	
	HCHO H <sub>2</sub> O <sub>2</sub> HNO <sub>3</sub>	0 - 10 ppb 200 ppt	
Observation-based Model (OBM)	O <sub>3</sub>	0 - 200 ppb 2 ppb	1) one or more monitors (20-40 km) upwind and downwind of major urban emission regions; 2) one or more monitors immediately downwind of major urban emission regions (<20km)
	NO-NO <sub>2</sub> , NO <sub>y</sub>	0 - 200 ppb 100 ppt	
	NMHC (speciated)	0 - 1000 ppbC 500 pptC	

<sup>1</sup> Ranges will vary with site location, values identified are typical for downwind urban sites

<sup>2</sup> Location requirements are in priority order

<sup>3</sup> Analyses identified in Section IV.C

The majority of emissions related characterization studies have been directed towards mobile source emissions, with many of these studies specifically design to evaluate the contribution of mobile source emissions of VOC and NO<sub>x</sub> to ambient concentrations in the region and assess the accuracy of mobile source emission models used in the ADP process. It is important to distinguish these studies from source emission factor studies which are associated with measurements made on various generic source types with the objective of establishing a quantitative relationship between the rate of pollutant emitted from the source and a set of appropriate operational and process parameters.

Special studies to characterize mobile source emissions have included:

#### Tunnel Studies

In these studies ambient measurement of hydrocarbons, carbon monoxide and NO<sub>x</sub> have been carried out in parking garages and roadway tunnels (Lonneman et al., 1974; Pierson, 1978; Gorse and Norbeck, 1981; Hampton, et al., 1983; Gorse, 1984; and Lonneman et al., 1986; Ingalls, 1989; Ingalls et al, 1989) to determine the emissions factors for the measured species for comparison with model estimated emissions for the vehicles mix observed in these somewhat controlled environments. The contained tunnel sample, has reduced uncertainties associated with chemical transformations and transport, and as a result of high concentration levels found in these environments reduced uncertainties in measurement. Tunnel studies have proven useful in identifying errors in the emission estimates derived from mobile source emission models (Pierson et al., 1990).

#### Roadside Measurements

In these studies ambient measurements immediately downwind or within the roadway environment are performed to determine emissions from the in-use vehicle mix sampled. Experimental studies have considered:

- measurements designed on the principals of conservation of mass, measuring the vertical concentration profile of chemical constituents and appropriate meteorological parameters upwind and downwind of the source region (roadway). Measurements determining the net mass flux due to vehicle emissions on the roadway have been used, (Bullin et al, 1980, and Hlavinka and Bullin, 1988) to determine CO emission factors along an interstate highway for comparison to emissions models.
- measurements using inert tracers releases within roadway traffic to determine dilution effects (Zweidinger et al., 1988, Cadle et al., 1976) have been applied to study on-road vehicle emissions and estimate the emission rate of the composite

vehicle fleet on the roadway.

- real-time in situ long path CO and CO<sub>2</sub> on-road measurements via remote sensing (Bishop et al., 1989; Bishop and Stedman, 1990; Lawson et al., 1990; Stephens and Cadle, 1991; Bishop et al., 1993; Bishop et al., 1994); have reported the CO emission rates for large populations of vehicles, indicating that a small percentage of the vehicle population ( $\leq 10\%$ ) is responsible for  $\sim 50\%$  of the total CO emissions, averaged on a gm CO per gallon of fuel burned basis.

Finally, analysis applications using the continuous emission monitoring (CEM) data that is now being collected as required under the Clean Air Act have not been addressed by the scientific community to date. This is likely the result of the data being very new and not readily accessible. But, once the data are in the main stream, analysis opportunities include:

- performing quality assurance checks on the major points source emission inventory estimates;
- evaluating projection and disaggregation techniques for estimating daily emission rates;
- providing feedback and coupling between point source emissions and receptor measurements for the purpose of monitoring emissions projections, tracking projected air quality improvements, diagnosing modeling and/or analysis failures, and monitoring transport impacts of point sources with changing meteorological conditions

#### *Data Management*

Current practice is that all data collected under federally mandated air quality networks be submitted to the EPA AIRS data base. AIRS is neither user friendly nor state of the art. It represents one of the major road blocks relating to the distribution and scientific application of air quality monitoring data compiled by EPA. It is highly likely that the PAMS data sets will be seriously underutilized, if AIRS remains the primary source for data compilation, access, and retrieval. A discussion in Section V.A provides suggestions as to how data assessment, analysis and distribution systems can be developed to resolve this problem.



## V. AN AGENDA FOR RESEARCH AND DEVELOPMENT

### A. Data Assessment, Archive, Distribution and Analysis System

The utility of measurement data and its successful application in emission-based and observation-driven methods is directly related to its demonstrated quality and its accessibility. The PAMS network has major deficiencies with regard to providing the necessary infrastructure needed to process the extensive data sets generated by the continuous automated gas chromatographic systems and other continuous gas phase. These processing needs include:

- performing routine visual quality assurance checks of gas chromatogram and concentrations time series;
- performing matrix scatter plots of paired hydrocarbon or chemical species, paired chemical species and meteorological parameters for the purpose of checking data quality, representativeness of the site and influence of local sources, and sample contamination

The generation of high quality data must be supported with an appropriate data archiving and distribution system. The data system must be user friendly, allowing the measurement community both easy access with respect to data entry as well as retrieval, be accessible on the internet, and have available to the data user a standard set of analysis tools, demonstrated to be useful in assessing data quality and supporting needs identified in the attainment demonstration process.

One approach for developing the required infrastructure to support data assessment, archiving, distribution and analysis is to establish regional data analysis center. These centers will act as the central repository for the PAMS data for the state agencies within the designated regions and will develop and maintain a client - server network which will provide the necessary training, access, and analysis tools to support the various analysis activities outlined in Section IV.B and IV.C. The regional centers would preferably be associated with Universities having active atmospheric-air quality research programs and computational expertise and facilities to support the development and operation of the data system.

## B. Modeling

### *Development and Evaluation*

No co-applications of the ODMs have been conducted. The general levels of agreement and disagreement among the ODMs could be much better evaluated were one or more co-applications to be carried out. At least one such co-application should be for an area for which results are available from one or more recent PAQSM applications. Several possible data bases exist. The 1995 Nashville study, which is not yet ready for analysis, may be one of the best data bases for comparing ODMs. Among the presently available data, the Southern California Air Quality Study (SCAQS) provides a unique data base in two respects: many different types of measurements were carried out, including for species such as  $\text{HNO}_3$ , PAN,  $\text{H}_2\text{O}_2$ , HCHO, and others, and the measurements were taken in highly urbanized locations [thus contrasting with the data presented by Trainer et al. (1993)]. Sillman (1995) uses one hour of data from the SCAQS by way of illustration; however, many days of data are available. A major shortcoming of the SCAQS data is that, to the best of our knowledge, true  $\text{NO}_y$  was not measured. Thus, the applicability of the correlational approach would need to be examined. Calculations using the SP algorithms have been, or could readily be, carried out for all SCAQS days (including both intensive and nonintensive sampling days). The SCAQS data base might lend itself to application of the OBM, although, as with the Atlanta study (Cardelino and Chameides, 1995), the detection limits for NO may not have been adequate to support the method fully (also, VOC samples were collected as one-hour averages 3 to 6 times a day using canisters).

Three other major data bases should be considered: the San Joaquin Valley Air Quality Study/AUSPEX (SJVAQS/AUSPEX), the Lake Michigan Ozone Study (LMOS), and the Coastal Oxidant Assessment for Southeast Texas (COAST) study data bases. The SP algorithms have been applied to the COAST data (Blanchard et al., 1995). Because species such as  $\text{HNO}_3$ ,  $\text{H}_2\text{O}_2$ , and  $\text{NO}_y$  were not measured in these three studies, the applicability of each of the other ODMs would need to be considered further.

Because the OBM has, to date, been applied only to the 1990 Atlanta study, the Atlanta data should also be evaluated using one or more of the other ODMs. The diagnostic value of these comparisons may be limited, however, because some of the data were of inadequate sensitivity or accuracy to drive the OBM (Cardelino and Chameides, 1995). Nonetheless, there appears to be value in carrying out the comparisons.

Finally, it may be possible to utilize one or more of the data sets included in Trainer et al. (1993) to drive ODMs other than the correlational method.

In the next section, we consider development and evaluation needs that are specific to each ODM.

Correlation Between Ozone and  $\text{NO}_y$  or  $\text{NO}_x$ . Because the procedure consists of reasonably straightforward regression analyses of ambient data, the statistical methods do not themselves require much further development. The two statistical topics that would benefit from some further development are, first, the treatment of data points as individual time periods (e.g., hourly) versus binned averages, and, second, the use of robust regression methods [e.g., Jacob et al. (1995) allude to the use of a different regression procedure without explanation; also, various types of robust procedures are described in the statistical literature].

Further attention should be devoted to delineating specific criterion values for differentiating  $\text{NO}_x$  and VOC-limited situations. For example, the existing measurement studies do not provide firm guidance for delineating the range of slopes,  $\Delta\text{O}_3/\Delta\text{NO}_x$ , that would be indicative of  $\text{NO}_x$  limitation. Moreover, the existence of good correlations between ozone and  $\text{NO}_x$  (or  $\text{NO}_y$ ) at rural sites does help to indicate  $\text{NO}_x$  limitation, no unambiguous definition of a "poor correlation", which would be indicative of VOC limitation, exists. Thus, there is a need to apply the method to a broad sampling of field measurements, representing a range of conditions from urban to remote, to help delineate empirically a range of slopes and correlation coefficients that could be used as guideline values.

Because this method is the only ODM that has been developed using exclusively ambient measurements, it is important to carry out the developmental procedures described above (they permit the method to remain independent of findings derived from modeling and chamber experiments). However, there is also merit in drawing upon modeling studies, such as Sillman (1995), that present ranges of  $\text{O}_3/\text{NO}_x$  and  $\text{O}_3/\text{NO}_y$  for which modeling results showed sensitivity of ozone to reductions of VOC and  $\text{NO}_x$  (see discussion below).

Guidance will also be needed for accounting for variability and uncertainty (see also the discussion below). A particular need specific to the correlational approach is to develop guidance for the indeterminate cases, i.e., those situations that cannot be clearly delineated as VOC- or  $\text{NO}_x$ -limited because the slopes or correlations fall into some intermediate range.

SP algorithms. The SP algorithms were derived from analyses of chamber experiments and box modeling using two existing chemical mechanisms. The accuracy of the algorithms, when applied to the lower concentrations that occur in the ambient atmosphere, is unknown. For example, the lowest initial  $\text{NO}_x$  concentrations in the UNC and UC Riverside chamber experiments were 90 to 100 ppbv; a limited number of the CSIRO experiments used 25 to 50 ppbv initial  $\text{NO}_x$ .

Some, though not all, of the same chamber experiments were used to develop the chemical mechanisms; thus, the accuracy of the mechanisms at low  $\text{NO}_x$  concentrations is essentially untested. In contrast, ambient  $\text{NO}_x$  concentrations are often in the range of 5 to 100 ppb. During the past few years, attempts have been made to carry out chamber experiments at increasingly lower  $\text{NO}_x$  concentrations. Results from such experiments should be obtained and used to further evaluate the SP algorithms.

The SP algorithms were derived from systems that all have fixed volumes and an initial charge of  $\text{NO}_x$  and VOCs. Because the algorithms are not yet fully developed for systems subject to dilution and continuous injection of emissions, the application of the algorithms to ambient data is potentially subject to biases that have not yet been determined. Additional work, which is now in progress, is needed to clarify the importance of these possible biases.

Additional applications of the SP algorithms should be carried out using data sets that would permit further evaluation of their performance under ambient conditions. For example, studies having a high density of monitors and sufficient meteorological information with which to construct trajectories could be used to evaluate the consistency of the calculations along trajectories (in the absence of fresh emissions, extent of reaction should increase with time and values of  $\text{SP}_{\text{max}}$  at earlier times should not be less than SP at later times, etc.).

The Use of  $\text{NO}_y$  and Indicator Ratios. To help reduce the possibility that results would be overly dependent upon the accuracy of a single modeling application, Milford et al. (1994) drew upon a range of models, modeling assumptions, and model applications, while, for the same reason, Sillman (1995) used a single model applied to two regions with varying assumptions. Nonetheless, the range of studies could be expanded, for example, by including applications of the UAM. The consistency of the findings should then be re-examined.

The utility of the indicator species and ratios should be examined using field data. Sillman (1995) provides three limited examples for illustrative, rather than evaluative, purposes. Similarly, Jacob et al. (1995) and Watkins et al. (1995) apply the concepts to two data sets, but, in each case, the application is largely illustrative rather than critical. A larger number of field studies should be selected, spanning a broad range of conditions, and indicator species and ratios computed for each. The consistencies among the different species should be examined for each field study. Where possible. Cross-comparisons should be made using the method of correlations, the SP algorithms, or independent modeling results.

At present, all indicator species and ratios are expressed as a range of threshold values, rather than tight crossover points. Further work is needed to determine if the widths of the ranges are artifacts of modeling assumptions or if such ranges also can



be demonstrated to characterize ambient field data. If the ranges cannot be tightened, additional guidance will be needed for interpreting cases that are indeterminate, i.e., those situations that cannot be clearly delineated as VOC- or  $\text{NO}_x$ -limited because the concentrations or ratios fall into some intermediate range.

The OBM. Several developmental and evaluational needs are apparent. First, there is a need to determine if the fundamental basis for calculating relative incremental reactivities (RIRs) provides information that is appropriate and relevant. RIRs derived from 12-hour  $\text{P}^{\text{S}}_{\text{O}_3\text{-NO}}$  terms may not be appropriate given the present form of the ozone standard, which requires compliance with a one-hour ozone average. Moreover, because the RIRs are expressed in terms of  $\text{P}^{\text{S}}_{\text{O}_3\text{-NO}}$  terms, it is unclear that the sensitivities of ozone are properly characterized, as described in Section IV.

Many assumptions appear to underlie the box modeling approach used in the OBM. Sensitivity analyses should be undertaken to clarify the consequences of the various assumptions. Once a sufficiently large set of sensitivity analyses becomes available, there will be a need to determine if the uncertainties associated with the OBM are greater or less than those characterizing emissions-driven models. If the uncertainties are as large as for emissions-driven models, consideration should be given to whether or not the level of effort involved in operating the OBM is warranted.

#### *Data Support*

For each of the ODMs, improvements are needed in sampling methods. In some cases, improvements in accuracy and detection limits are required for species that are currently sampled. In other cases, the methods require measurements of species that are not now routinely monitored.

Present measurements of NO are generally unbiased and many are sufficiently accurate for use in the correlational methods and the SP algorithms. The indicator species and ratios do not make explicit use of NO. However, the OBM requires measurements of NO that are accurate to about 0.1 ppbv at concentrations as low as 0.1 ppbv. While measurement technologies exist that are capable of providing NO measurements at concentrations as low as about 20 pptv, the performance of such high-sensitivity instrumentation when used in routine monitoring networks may degrade considerably.

Measurements of true  $\text{NO}_y$  and  $\text{NO}_2$  are needed for use in the correlational methods, the SP algorithms, and the indicator species and ratios. At present, measurement of  $\text{NO}_y$  appears more feasible in a routine mode than does the measurement of  $\text{NO}_2$ . While each of these ODMs can be used with  $\text{NO}_y$  data only, better results could be obtained if  $\text{NO}_2$  were also measured (thus providing measurements of true  $\text{NO}_x$  and of  $\text{NO}_2$ ). The development of accurate routine measurements of both  $\text{NO}_y$  and  $\text{NO}_2$  is of considerable importance. Such measurements are expected to be of value

regardless of the state of development of the ODMs reviewed here.

The use of indicator species and ratios other than  $\text{NO}_y$  and  $\text{O}_3/\text{NO}_y$  requires measurements of  $\text{HNO}_3$ ,  $\text{H}_2\text{O}_2$ , or  $\text{HCHO}$ , none of which are measured routinely at present. As noted in Section IV, measurement of nitric acid has been problematic in at least one routine monitoring network. Because it appears that substantial effort would be required to develop routine measurement capabilities for these species, the focus of effort at present should be on the evaluation of the utility of the indicator ratios using special data sets (see earlier discussion).

The OBM may require continuous GC instrumentation to provide speciated hydrocarbon measurements with appropriate time resolution (the adequacy of, e.g., one-hour average concentrations from canisters is not known to us). At present, efforts to improve VOC measurement methods are under way. With respect to the use of the OBM, the need is to evaluate the accuracy of the method given current VOC measurement capabilities.

For each of the ODMs, additional effort should be devoted to providing guidance regarding the necessary numbers and locations of monitoring stations needed for reliable results.

### *Analysis of Uncertainty*

Analyses of uncertainties are needed for each of the ODMs. In each case, uncertainties fall into two broad categories. The first category consists of methodological limitations and uncertainties that should be addressed as previously described under the heading "Development and Evaluation." Addressing this type of uncertainty is necessary for eliminating methodological biases. The second category consists of the irreducible uncertainties that exist even for fully developed methods that may be considered fundamentally sound and accurate. Such uncertainties can generally be quantified through statistical methods or sensitivity analyses; a necessary assumption is that the ODMs are accurate and appropriate for the intended applications.

The development of the ODMs should proceed so that outputs always consist of both findings and associated uncertainty estimates. In some cases, the statistical form of the procedures lends itself to the calculation of a confidence limit. For example, the regression analyses of the correlational procedures fall into this category. Similarly, the computation from ambient measurements of mean values for indicator species or ratios generates a straightforward confidence band. In other cases, such as for the SP algorithms, the simplicity of the method permits a direct calculation of an uncertainty in the result as a function of the uncertainties in measurements and parameters.

Uncertainty analyses should, however, be translated into a format that would be of more utility when the ODMs are used to help evaluate emission control strategies. That is, the output of the ODM analyses needs to be expressed so as to qualitatively indicate the precursor (VOC or NO<sub>x</sub>) whose control would be most effective in reducing peak ozone concentrations; similarly, the uncertainty analyses should be expressed in a manner that indicates the probability that the stated conclusions are erroneous. Additional efforts are needed to translate the confidence intervals mentioned above into the type of probability statements that are actually needed.

Finally, further attention should be devoted to the treatment of variability. Because differing conclusions may result for different days or locations, guidance is needed for both presenting and interpreting results that exhibit substantial day-to-day or site-to-site variability. This need applies equally to all ODMs and should be addressed generically.

### C. Monitoring

Significant measurement issues remain with regard to supporting the modeling, analysis, and monitoring considerations in support of the attainment demonstration process. These measurement issues fall into three general classes.

- Measurements involving standard commercial monitoring instrumentation, where questions remain regarding their performance, sensitivity and specificity in routine operational monitoring.
- Measurements involving new commercially available instrumentation or methodologies which have not been fully demonstrated or evaluated for routine monitoring
- Measurements which require instrumentation development and or advancement in new technologies

#### *Monitoring of the Oxides of Nitrogen*

Historically routine monitoring of the oxides of nitrogen has been quite limited. The method of choice for NO measurements has been chemiluminescence detection, based on the chemiluminescent reaction of O<sub>3</sub> with NO. Coupling this method with a catalytic convertor to reduce NO<sub>2</sub> to NO, it is possible to infer NO<sub>2</sub> concentrations by difference between the NO<sub>x</sub> and NO detection channels of the instrument. These monitors, when used in routine networks, have had two major shortcomings which affect their use in analysis related activities outline in this report

- The catalytic convertor is not NO<sub>2</sub> specific and measures some unquantifiable fraction of organic nitrates and nitric acid resulting in measured NO<sub>2</sub> concentrations which are biased systematically high
- The detection limit and sensitivity for NO is insufficient to measure the critical NO<sub>2</sub>/NO ratio during peak ozone production periods.

High sensitivity commercial NO<sub>x</sub> instruments are now available which can provide NO detection limits of 100 ppt, but it remains to be demonstrated that such measurements can be routine performed in operational monitoring networks. Programs like SOS and NARSTO-NE are currently evaluating these systems and developing the necessary methodologies to quality assure data at these low levels.

The development and evaluation of NO<sub>y</sub> research instrumentation has proceeded for almost a decade, but it was not until this year that a commercial instrument become available in the U.S. This technology, which is an extension of the NO<sub>x</sub> technology mentioned above, takes care to deliver all the oxides of nitrogen immediately to the catalytic convertor and assure that they are reproducibly and efficiently reduced prior to entering the chemiluminescence detector. Programs like SOS and NARSTO-NE are currently evaluating these systems and developing the necessary methodologies to quality assure data at low concentration levels (i.e. 100 ppt).

The current state of monitoring science for the oxides of nitrogen indicates that further work is needed in the following areas:

- develop NO<sub>2</sub> specific instrumentation technologies, promising areas include photolytic reduction, spectroscopic methods using tunable diode laser absorption and differential optical absorption spectroscopy and luminol chemiluminescence detection
- test and evaluate low level, high sensitivity NO chemiluminescence instruments to quenching effects of water vapor and other trace gases found in polluted environments
- test and evaluate the sensitivity of NO<sub>y</sub> convertor efficiencies to water vapor and other trace gases found in polluted environments
- develop instrumentation technologies for research measurements of HNO<sub>3</sub> and organic nitrates (including PAN) and which provide opportunities for the development of routine continuous monitors

## *Monitoring of Speciated Hydrocarbons and Volatile Organic Compounds*

The measurement of hydrocarbons in the atmosphere has historically been performed as part of research and special study programs. Routine, continuous monitoring of speciated hydrocarbons has never been performed mainly due to the lack of acceptable instrumentation. As a result of the PAMS initiative and its requirements for speciated hydrocarbons, instrument vendors developed and introduced several automated gas chromatographic hydrocarbon analysis systems. These systems have been deployed in PAMS somewhat prematurely and have not undergone rigorous field testing and evaluation, nor have acceptable SOPs or quality assurance programs been established for these systems. The measurement of carbonyl compounds has followed a similar track and is likely even less established than the hydrocarbon methods. The SOS and NARSTO-NE programs have performed some testing and evaluation of these systems in the field during the summer of 1995, but much remains to be done.

Further work is needed in the following areas:

- establish the detection and speciation limits for operational automated continuous gas chromatographic hydrocarbon analysis system
- develop low cost continuous speciated NMHC and VOC instrumentation
- evaluate current technologies and develop new techniques for the measurement of carbonyls and other oxygenated hydrocarbons (e.g. alcohols, ethers, organic acids)
- develop SOPs and quality assurance programs for the automated continuous gas chromatographic hydrocarbon analysis system

One or more commercial instruments have recently become available which use luminescence reactions in the liquid phase to measure concentrations of formaldehyde and hydrogen peroxide on a continuous basis. These techniques should be evaluated both for their application for research as well as routine measurement programs.

### **D. Longer Term Needs**

#### Recognizing the stochastic nature of the system in the attainment demonstration process

Simulating stochastic atmospheric processes using deterministic models is clearly a simplifying approximation. The primary output of a deterministic approach, for a simulation of an air quality episode, is one realization of the dynamic processes of

interest. If two or three episodes are studied, the overall output will be simulated results for two or three determinations. The ambient standard, however, is probabilistic. Comparing the results of PAQSM simulations with the standard is at best artificial and, in some circumstances, is an inadequate exercise that can be misleading. Were a probabilistic model available for use, results could be compared in terms of estimated and observed frequencies of occurrence of concentrations at monitoring sites in an area. Relative to deterministic modeling little research and development effort has been devoted to stochastic modeling. We recommend that NARSTO consider pursuing the development of this type of modeling system.

### Assessing risk

Once modeling studies have been conducted, decision makers have to interpret their results in light of the uncertainties that accompany them. Adopting a conservative approach to control will lead to greater protection of the public and higher costs of control, which eventually are absorbed by the larger community. Adopting a more lenient approach will give more weight to economic concerns. Stated otherwise, the decision maker must weigh the risks of underprotection of health and overexpenditure for control. As now conducted, balancing risk is a wholly subjective pursuit. While human judgment is irreplaceable, the scientific community can develop and provide tools for use in clarifying decision options, quantifying and assessing risks, and presenting information in ways that are readily communicated. [See, for example, Clemen (1991).] We recommend that research and development be conducted to provide analytical tools that will aid the decision maker in evaluating risk.

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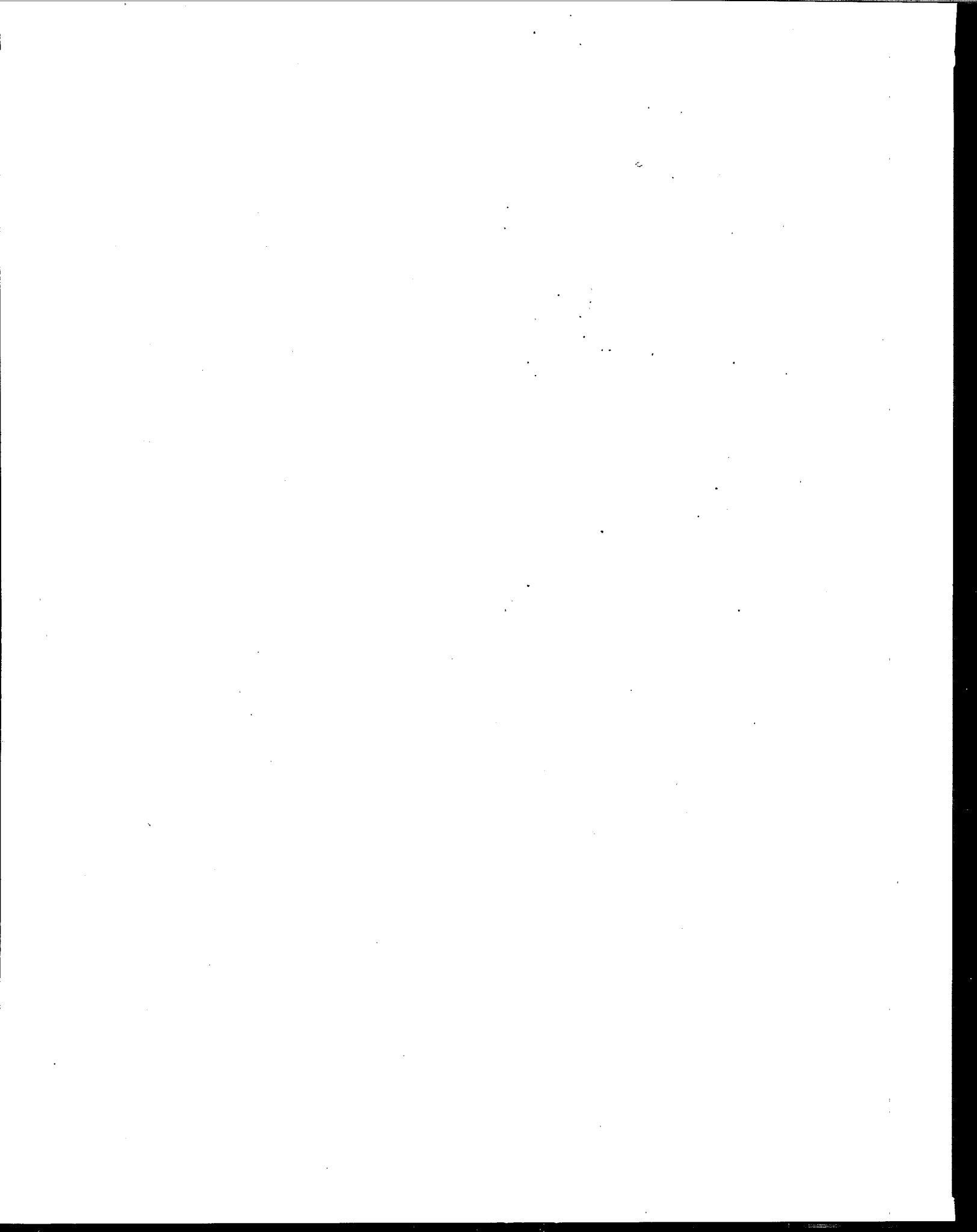
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