



NARSTO News

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NARSTO News Feature: Models-3

This **NARSTO News** edition features the Models-3 project, an activity that has occupied a major portion of EPA's model-development effort during the past several years. Models-3 is a comprehensive air-pollution "modeling system," which incorporates all necessary computational features for regional pollution modeling, including emissions, meteorology, chemical-transport, and deposition. It also includes extensive post-processing capabilities, and will incorporate online sensitivity and uncertainty analysis in future versions.

Models-3 has been built from the "ground-up," using modern programming techniques, including object-oriented programming, which allow rapid and convenient interchange of computational modules. The system is designed for widespread application and will be freely distributed to the user community. Although it is a large system, it is designed to operate on selected work stations as well as on supercomputers.

Our feature article on Page 3 introduces Models-3's structure and operating interface, and provides a brief description of its current and future capabilities. Our next (Winter/Spring 2000) **NARSTO News** will present a similar feature on an emerging Canadian modeling system, the ACS Unified Regional Air-Quality Modeling System (AURAMS).



NARSTO Technical Conference on Aerosol Science: Querétaro, Mexico, October 2000

A NARSTO symposium, entitled **Aerosols: Science and Decisions in an International Community**, is scheduled for the Mexico City area during late October 2000. Addressed primarily to atmospheric-science aspects of aerosols, this conference is designed to feature the "payoff" of such research to national and international decision processes, as well as its "intersections" with the policy and health-sciences communities. Members of the policy and health-sciences communities are encouraged to attend.

The symposium is scheduled for the Hotel Real d Minas, a resort hotel and convention center located in Querétaro, about two hours north of Mexico City. A preliminary Call for Papers, as well as other material for the meeting appears on pages 17 and 18.

The NARSTO Home Page

<<http://www.cgenv.com/Narsto>>

will present updated information on the symposium as it develops. In addition, it will include a forum for electronic submission of abstracts.



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The NARSTO News is published biannually for the purpose of communicating NARSTO activities and progress to members of the extended NARSTO community. Persons wishing to comment on the newsletter or submit material for publication are invited to do so by contacting either Diane Fleshman or Jake Hales in the NARSTO Management Coordinator's office, at the following address:

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NARSTO's New Logo

Ever since NARSTO expanded to incorporate aerosol research (and modified its Charter to accommodate similar expansions in a relatively painless fashion, should these be deemed necessary in the future), the old logo,



has struck many of us as being a little off the mark. It seemed that we needed something that did not imply a limitation to just ozone, and that more obviously and strongly represented the tri-national cooperative spirit of the NARSTO organization.

So, after some discussion, the Executive Steering Committee Co-Chairs approved the image appearing here. In addition to giving a strong tri-national message, the logo connotes the overarching, cooperative nature of the NARSTO organization.

It'd make a pretty lapel pin. Anyway, we'll be expecting to use this image frequently to represent our organization in the future.





Models-3/CMAQ

A revised version of the U.S. EPA's Models-3/CMAQ system was released on June 30, 1999. Models-3 consists of a sophisticated computational framework for environmental models allowing for much flexibility in the communications between component parts of the system, in updating or replacing components, and in the graphical-user interface. The revised Models-3 framework (Version 3.0) is operational on SUN workstations (OS: Solaris 5.6, development version), contains Vis5D and PAVE visualization packages, and utilizes the IBM DX Explorer graphics/analysis software which is now freely available. Testing of the Models-3 framework on a single Windows NT platform is in progress, as well as a version which requires both a Silicon Graphics (SGI) platform and a Windows NT platform. The Models-3 framework will be limited to those platforms presently being tested.

The science code which comprises the Community Multiscale Air Quality (CMAQ) model can be used outside the Models-3 framework and users can adapt code to be compiled and executed on their UNIX computing platform. The capabilities of the CMAQ model are described later.

Overview of Models-3 Framework

The Models-3 framework is installed from a set of five 8 mm tapes or a single tape for those with a Digital Linear Tape (DLT) drive. The installation must be done carefully and a help desk has been established with this release to assist users with the installation. Each site has a unique four digit identifier and users must place an order. Arrangements for Orbix runtime licenses must be in place before tapes will be provided. Tapes are shipped along with an installation manual (System Installation and Operation Manual for the EPA Third-Generation Air Quality Modeling System (Models-3 Version 3.0), EPA-600/R-99/057, June 1999) and a user manual (User Manual for the EPA Third-Generation Air Quality Modeling System (Models-3 Version 3.0), EPA-600/R-99/055, June 1999). Both documents are also available at the Models-3 web site (www.epa.gov/asmdnerl/models3/). Adequate memory (256 MB) and disk space (46 GB) are required for the installation.

The main window of the Models-3 framework (Figure 1) and the main components of the framework are described in the user manual cited above. Programs may be registered in **Program**

Manager and datasets may be registered in **Dataset Manager**. Automatic registration is done when programs and datasets are generated in the framework. **Science Manager** is where the details of the science to be used are defined: chemical mechanism, vertical-layer definitions, geographic domain and horizontal size of the grid cell, and nested domains. **Model Builder** is required to create executable components for the science selected for a particular application. **Strategy Manager** is used for the emissions strategies and interactive emissions processing. **Study Planner** enables the user to establish a sequence for execution of the multiple executable components from **Model Builder**. All output datasets are automatically registered by the framework for later retrieval along with log files. The directory structure is unique so that output from each executable component may be examined. The emissions processing can also be done with **Study Planner**, except for the first day of a sequence of days for a new domain or grid resolution. The first day must be done interactively to build tables that are then applicable to the subsequent days being modeled. The final Models-3 component in the main window is the **Tools Manager** which is the gateway to the visualization and analysis tools available in the Models-3 framework.

Users who intend to generate new applications using the Models-3 framework should have a good understanding of UNIX. Users who intend to modify the science source code must have command of FORTRAN as well. Users who are only interested in visualizing and analyzing the results of applications generated by others will need to become familiar with the visualization packages they want to use. Tutorials of some visualization and analysis capabilities may be found at the website.

Overview of Community Multiscale Air Quality (CMAQ) Model

The CMAQ model is a set of fortran-based science codes that includes the CMAQ chemical transport model and its upstream driver models and processors. The structure of the system, including the component models, is presented in Figure 2. They include the MM5 meteorological model (run outside the Models-3 framework), the Meteorology-Chemistry Interface Processor (MCIP), the Models-3 Emissions Processor and Projection System (MEPPS), the Emissions-Chem-

(Continued on page 4)



Models 3 . . . Continued



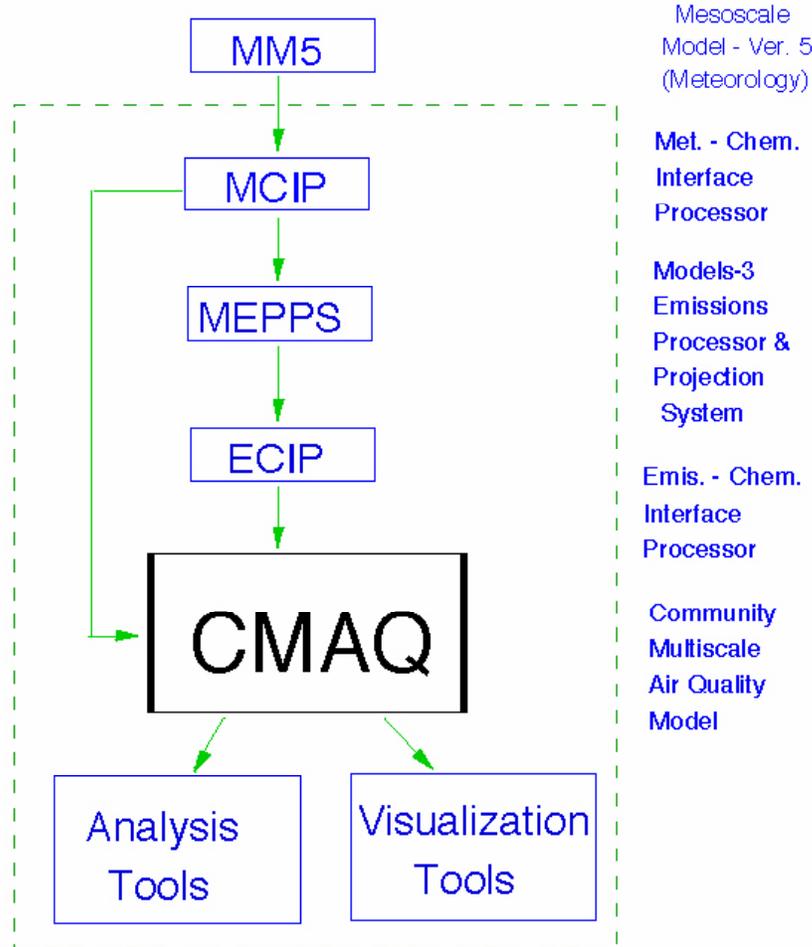
Figure 1. Models-3 Framework main window for version 3.0.

istry Interface Processor (ECIP), and the CMAQ chemical-transport model. At present the modeling system is capable of simulating the ozone and the other criteria pollutants, fine particles, visibility, and acid deposition pollutant regimes. Over the course of the next year, air toxics capabilities will be added including mercury and atrazine. The CMAQ is a multiscale model typically used in a nested grid mode. Current applications employ one-way grid nesting at 36-, 12-, and 4-km resolutions.

The CMAQ system was designed to facilitate the inclusion of alternative scientific descriptions and simulation processes in a relatively easy manner. There exist user options for chemical, transport, and numerical schemes in the CMAQ. The generalized

coordinate system employed makes it possible to tightly couple the CMAQ with different meteorological models without resorting to interpolation to adjust for differing model structures.

Complete scientific documentation exists on the CMAQ and its related models. This documentation is available as "Science Algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling System," EPA-600/R-99/030, (D.W. Byun and J.K.S. Ching, Eds.), March 1999, and can be accessed on the Models-3 website (www.epa.gov/asmdnerl/models3/).



Models-3 Framework

Figure 2. Schematic diagram of the Models-3/CMAQ air quality system. Dashed line represents the domain of control of the Models-3 framework.

The CMAQ and its upstream processors can be run utilizing the Models-3 computational framework, described earlier, or in a more traditional manner through the use of Unix scripts for stand-alone models. Except for the MEPPS, the model components are fortran-based and can be run on a variety of scalar, vector, and parallel computer architectures. The MEPPS is based on the SAS programming language and requires ARC/INFO, a geographic information system, to process the emissions into a grid structure for the model domain. The stand-alone models do not require Orbix licenses and are available at the website.

The following is a summary of the attributes of the principal modeling components of the Models-3/CMAQ system now and expected for the release next year (2000 version):

MM5 METEOROLOGICAL MODEL

- MM5-Version 2.10 with modifications
- Non-hydrostatic - 30 vertical layers in current applications
- One-way nested
- Surface-PBL currently uses Blackadar High Resolution scheme; new Pleim-Xiu (PX) land-surface model will be included in

(Continued on Page 6)



Models 3 . . . Continued

2000 version (will include vegetation, soil moisture, and the Asymmetric Convective Model)

- FDDA - Newtonian analysis nudging at 36-, 12-km resolutions; no nudging at 4-km resolution; observation nudging at 4-, 12-km resolutions will be included in 2000 version

METEOROLOGY-CHEMISTRY INTERFACE PROCESSOR (MCIP)

- Performs 30 — 21 layer collapse for use in current CMAQ applications
- Dynamic consistency is assured
- PBL parameters are rediagnosed; will include MM5 pass-through option in 2000 version
- Dry deposition uses RADM/Wesely algorithm, with high-resolution land use database; stomatal resistance algorithm; coupled to MM5 PX-land-surface model, in 2000 version

MODELS-3 EMISSIONS PROCESSOR AND PROJECTION SYSTEM (MEPPS)

- Source categories by SCC codes
- RADM-2 and CB-IV organic emission splits; will include SAPRC-99 in 2000 version
- Mobile5a model for mobile source emissions; PART 5 for mobile source particulate emissions
- BEIS2 model for biogenic emissions
- 36/12/4 km resolutions
- 2000 version may contain Mobile 6, BEIS 3 if available
- SMOKE implementation in Models-3 (work is ongoing)

EMISSIONS-CHEMISTRY INTERFACE PROCESSOR (ECIP)

- Linked to MEPPS for emissions data
- Linked to MCIP for meteorological data
- Computes plume rise
- Creates input files for Plume Dynamics Model
- Combines separate point and area emissions into single file for input into CMAQ chemistry transport model

PLUME DYNAMICS MODEL (PDM)

- Plume dynamics (trajectories and shapes) for major elevated point sources; required by plume-in-grid algorithm in CMAQ

BOUNDARY CONDITIONS

- Clean tropospheric boundary conditions (bc's) adapted from RADM
- 36-km domain - bc's are temporally constant with a unique profile for each (N-S-E-W) boundary
- bc's for 12- and 4-km domains obtained from 36- and 12-km domain simulations, respectively

INITIAL CONDITIONS

- Model is initialized at least 2 days prior to period of prime interest
- Clean tropospheric initial conditions (ic's) for 36-km domain
- ic's for 12- and 4-km domains obtained from 36- and 12-km domain simulations, using staggered start dates

PROCESS ANALYSIS (PA)/INTEGRATED PROCESS RATES (IPR)/ INTEGRATED REACTION RATES (IRR)

- PA/IPR - calculates incremental contribution to rates from all major modeled processes
- PA/IRR - calculates individual contribution to chemical rates of major chemical pathways

CMAQ CHEMICAL TRANSPORT MODEL

- Dynamics
 - Generalized coordinate capability
 - Hydrostatic/non-hydrostatic capability, depending upon meteorological input
- Chemical Mechanisms
 - RADM2
 - CB-IV
 - SAPRC-99 to be added in late 1999
- Chemical Solvers
 - Quasi-Steady State Approximation (QSSA)
 - SMVGEAR (CRAY; other vector machines)



- Cloud Processes
 - Aqueous chemistry, adapted from RADM
 - RADM-cloud scheme (sub-grid, based on Kuo scheme) at 36-, 12-km resolutions
 - Simple grid-resolved cloud scheme at all grid scales
 - Integrated grid-resolved microphysics and aqueous chemistry (work in progress)
- Advection
 - Piecewise-Parabolic Method (PPM)
 - Bott scheme
- Vertical Diffusion
 - Eddy-Diffusivity (K)
 - Asymmetric Convective Model (ACM) late 1999
- Horizontal Diffusion
 - Eddy-Diffusivity (K)
 - Constant for a single resolution (nest); variable across resolutions
- PM-fine
 - 2 size ranges (0-0.1 μm , Aitken mode; 0.1-2.5 μm , accumulation mode)
 - 9 "species" in each size range: sulfate, nitrate, ammonium, organic - primary anthropogenic, organic - secondary anthropogenic, organic - biogenic, elemental carbon, other primary, number of particles; surface area to be added in 2000 version
 - Aqueous-PM (as in RADM/RPM)
 - Size-dependent dry deposition
- PM-coarse
 - Primary
 - Size-dependent dry deposition
- Plume-in-Grid
 - Algorithm from TVA/ University of Alabama-Huntsville based on horizontal plume segments
 - Explicit sub-grid modeling of major point source plumes
 - Uses a photochemical Lagrangian plume model
- Photolysis Rates - Look-up table, with cloud attenuation

- Regional Haze
 - b_{ext} is calculated: directly from aerosol size distribution; and indirectly from IMPROVE "reconstructed" technique using mass
 - Visibility estimates: deciviews ($= 10 \ln(b_{\text{ext}}/0.01)$); and visual range

Figures 3 and 4 illustrate results from a recent demonstration run of the CMAQ model for a July 1995 pollution episode in the eastern United States. Model simulation was conducted for the period July 6-15, 1995 with a 36-, 12-, 4-km horizontal nested grid configuration focused on the northeastern United States, with 21 vertical layers. Results shown in these figures are from the 36-km runs for July 13, 1995. These figures show the elevated ozone and fine particle concentrations over the region associated with the evolution of a stagnating high pressure zone.

Concluding Remarks

Tutorials have been developed for the Models-3/CMAQ, one for the RADM2 chemical mechanism, and another for the carbon bond IV. Both tutorials are distributed on the installation tapes provided with the framework. Only the carbon bond IV tutorial is found in the stand-alone version at the website.

Installation tapes have been distributed to nearly 50 sites, including a wide variety of users, Federal, State, local, academic, industrial, and research organizations, including many from outside the United States. Use of the stand-alone version available from the website is not known, as it cannot be tracked. From questions which have been received, it is known that at least ten sites acquired and executed at least some of the code during the first month it was available.

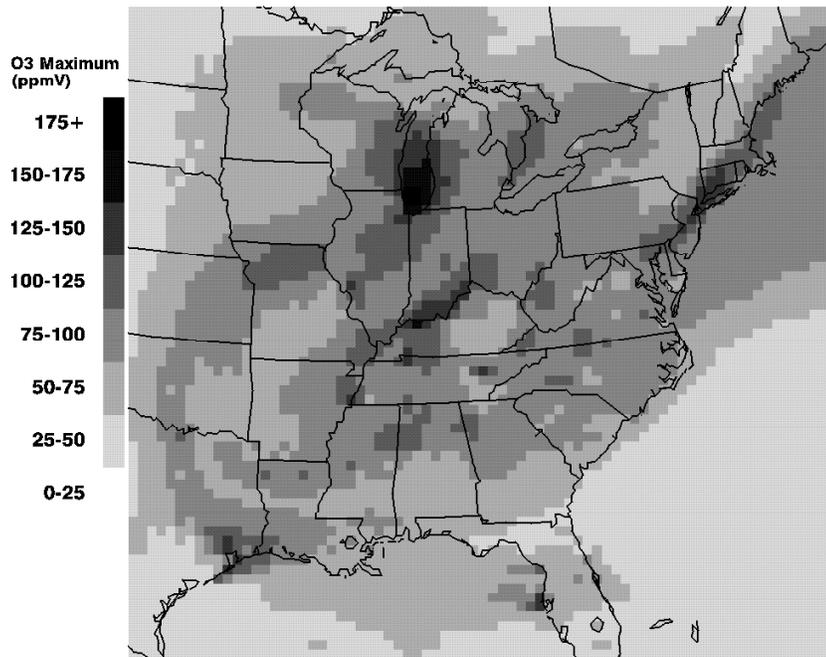
NARSTO News contribution by Sharon LeDuc, Daewon Byun, and Ken Schere

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Maximum O3 (36km Grid)

Jul 13, 1995 11:00:00 to Jul 14, 1995 04:00:00 GMT

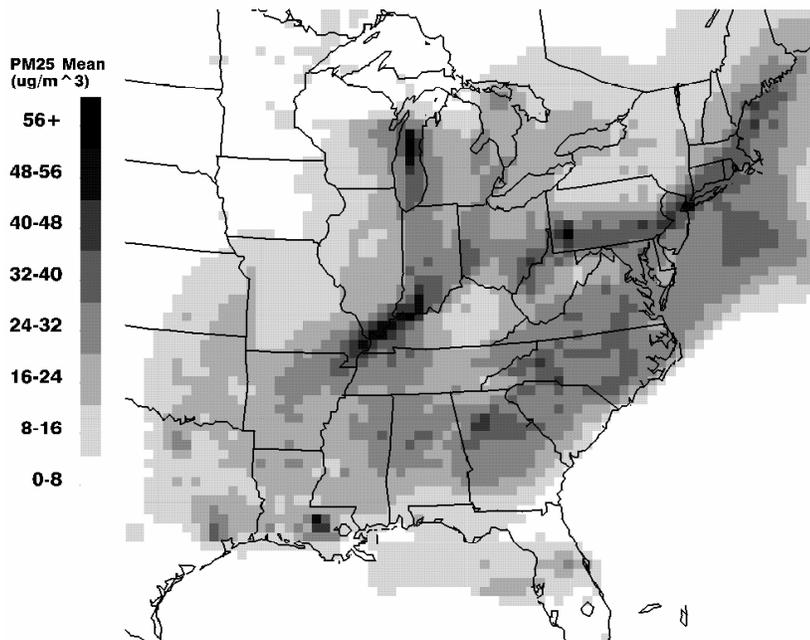


Layer: 1 (0 to 33 m)

Figure 3. CMAQ model results for ozone on July 13, 1995 for model layer 1. Concentrations are maximum (hourly) predicted for each grid cell on that day.

Mean PM25 (36km Grid)

Jul 13, 1995 04:00:00 to Jul 14, 1995 03:00:00 GMT



Layer: 1 (0 to 33 m)

Figure 4. CMAQ model results for fine particles (PM-2.5) on July 13, 1995 for model layer 1. Concentrations are 24-h average predicted for each grid cell on that day, as summed over chemical-specified components.



NARSTO/SOS: A Tale of Two Cities Act One – Nashville

The curtain has come down on the first act of this summer's Southern Oxidants Study's two-act play. The Nashville field campaign has been completed and the Atlanta (Act 2) portion has just begun.

The Nashville intensive, which ran from June 15 through July 15, employed both ground-based and airborne measurements to study the processes responsible for the formation and transport of ozone and fine particles at a level of detail that has hitherto not been possible. The primary focus of the Atlanta intensive is a comparison of aerosol measurement technologies and techniques. The extensive array of aerosol, gaseous pollutant, and meteorological measurements being conducted at the Atlanta, Jefferson Street site should provide a very rich data set.

It was the best of times...

All indications are that the Nashville intensive was a great success. The four instrumented aircraft (NOAA P-3, DOE/PNNL G-1, NOAA O₃/aerosol lidar aircraft (deHavilland Caribou), and the TVA Bell helicopter) were used to great effect, performing regional, land use studies and power plant and urban plume studies. The search for contrasting conditions, both in terms of meteorology and emissions, led the P-3 far afield with missions to North Carolina, the Upper Midwest, and Atlanta. The combination of detailed measurements of atmospheric dynamics and chemistry at the ground sites was extremely powerful, resulting in lots of exciting new data.

Early looks at the data suggest important new insights into the role of rural power plants in regional ozone and particulate-matter formation; nighttime chemistry and transport; and ozone formation under high NO_x conditions. Subsequent modeling and analyses should be very fruitful.

It was the worst of times ...

Unfortunately, the DOE/PNNL G-1 was an early casualty. On June 25 the G-1 experienced engine trouble shortly after takeoff and was forced to return to Nashville airport. It was subsequently determined that one of the engines would have to be replaced, a process that took several weeks and ended its participation in the study. The G-1 was able to get in 4 research flights, focusing mainly on urban plume studies under day/night conditions.

The success of this endeavor is a tribute to the innovation and hard work of the more than 150 scientists that participated. These scientists represented 5 Federal agencies (DOE, EPA, NOAA, NSF, and TVA) and 14 universities, as well as several industry and regulatory groups. The study was a confederation of groups from both the public and private sector, joined by a common interest and focussed on a common goal. We look forward to working together on the analysis of this wonderful data set.

More information? Visit the web sites for these two NARSTO/SOS studies:

- **Nashville:**

<http://www.al.noaa.gov/WWHD/pubdocs/SOS/sos99.main.html>

- **Atlanta:**

<http://www-wlc.eas.gatech.edu/supersite/>

NARSTO News contribution by Jim Meagher

Ozone and its Measurement: Comments and Discussion

Last month's **NARSTO News** published a discussion of ozone-measurement issues, entitled *One Step Forward and . . . : Some Cautionary Notes on Urban Ozone Measurements*. This note was rooted heavily in the Critical Review Paper by Dave Parrish and Fred Fehsenfeld entitled *Methods for Gas-Phase Measurements of Ozone, Ozone Precursors and Aerosol Precursors*, which is available on the NARSTO Web site, and is slated for publication in the special NARSTO issue of *Atmospheric Environment*.

Our **NARSTO News** note generated some considerable reader interest, and in the following articles we publish two responses — one by Frank McElroy and David Gemmill, and the other by Joel Maddy, presenting some alternative viewpoints on a number of ozone-measurement issues. These responses are followed by a short reply from Dave and Fred.

We express our appreciation to these correspondents for their insights and their comments. We hope that, by providing a forum for objective discussion of all aspects of issues such as this, we can contribute to our community ability to enhance quantitative, definitive, and reliable measurements.



Comments and Discussion: McElroy and Gemmill

Dear Dr. Hales:

This letter is in response to an article in the Winter/Spring, 1999, issue of *NARSTO News* regarding urban ambient ozone measurements (*One Step Forward and...: Some Cautionary Notes on Urban Ozone Measurements*). The article contains several quotations from a critical review paper entitled, *Methods for Gas-Phase Measurements of Ozone, Ozone Precursors and Aerosol Precursors* by David D. Parrish and Fred C. Fehsenfeld, and expresses concerns about the integrity of ambient ozone measurements using the UV absorption monitoring method. The potential measurement errors cited were calibration uncertainties, ambient interferences, and anomalous operating conditions.

We are concerned that the article may have given an overly pessimistic impression of the integrity of the Nation's ambient ozone measurements obtained using the UV monitoring method. This method is, by far, the most commonly used method in the States' ozone compliance monitoring networks. However, we are confident, based on data quality assessment systems reports, that the vast majority of the ozone monitoring data collected nationwide are of high quality and suitable for attainment/non-attainment determinations. At the same time, we acknowledge that there are some measurement uncertainties and anomalies associated with the UV ozone method (as mentioned below), as there are with other methods for measuring air quality, and we continually strive to reduce these uncertainties. Further studies are being undertaken to better characterize the nature, frequency, and impact of any potential measurement uncertainties encountered with the UV method for ozone. It is currently thought that the magnitude of these uncertainties is low and their impact minimal. Nevertheless, any updated quality assurance guidance determined to be appropriate, based upon the results of these studies, will be provided to assist monitoring agencies minimize potential measurement errors.

Calibration Uncertainties

Parrish and Fehsenfeld note that the UV absorption measurement technique is "...a particularly efficient technique for ambient moni-

toring of O₃..." then cite its further advantage as an "absolute measurement" and indicate that it is "curious" that EPA procedures specify independent calibration for UV ozone monitors.¹ They suggest that independent calibration (i.e. conventional calibration using a primary ozone UV photometric standard or an independently certified ozone transfer standard) is "inadequate" and "...can at worst perpetuate serious measurement problems since the ozone standard itself is merely a similar UV absorption measurement system coupled to an ozone generator."¹

EPA formally recognized the value of the UV absorption measurement technique as an "absolute" measurement for ozone in 1979 when a calibration procedure based on the UV measurement technique was promulgated as part of the federal reference method for ozone monitoring (40 CFR Part 50, Appendix D) and became, in effect, a *primary standard* for ambient ozone measurement. However, EPA did *not* specify the UV technique as the measurement principle for ozone reference methods, for a very significant reason. That reason is that other common gases absorb UV light at the same wavelength band used to measure ozone and can interfere with the ozone measurement. When one or more of these other gases is present, as is quite possible in ambient air, the UV measurement is no longer "absolute." These interferences are minimized in ambient air measurements by a differential process that uses a gas scrubber to create a reference gas sample from which the ozone is removed but other potentially interfering gasses remain. But the performance of this scrubber can be less than perfect. Also, UV ozone analyzers in every-day use are subject to other operational problems, including buildup of dirt in inlet lines, inlet filters, the solenoid valve, and the optic components², and scrubber deterioration or malfunction. Thus there is a substantial difference between using the UV absorption technique for calibration and using it for routine ambient air monitoring. The UV technique clearly makes a good calibration standard, when interfering gases can be avoided, no scrubber is used, and instrument components are not exposed to atmospheric contaminants. But

¹This particular language from the **NARSTO News** quotation is absent or changed in the November 20, 1998 version of the document obtained recently from the NARSTO web site, but the implication is similar.

²Dirt on cell interior surfaces and optical windows and mirrors should be compensated by the differential measurement process, but field reports indicate significant effects under some circumstances that may be reduced by cleaning.



using UV analyzers for routine monitoring without independent calibration is considerably more problematic.

Parrish and Fehsenfeld go on to suggest that (in lieu of conventional, independent calibration) the span adjustment of a UV analyzer should be maintained at its standard setting (*i.e.* the theoretical value based on the absorption coefficient of ozone), and the instrument's measurements should be frequently compared with another ozone analyzer that is in good repair, using ambient air. We believe that independent calibration of the UV analyzers is better for several reasons. First, independent calibration can compensate, at least to some extent, for some of the problems mentioned in the previous paragraph, such as some possible diminution of ozone in inlet lines and particulate filters as they become dirty in normal use and for when these components are, from time to time, cleaned or replaced. Second, the "reference" instrument that would be used for comparison with the primary monitoring instrument would likely be another UV type instrument, since chemiluminescence type instruments are now all but unavailable. Thus the "reference" instrument would likely be subject to the same interferences as the primary instrument and possibly some of the other problems as well, unless it was frequently cleaned and scrupulously maintained. Therefore, it may not be as reliable or credible as a "reference" measurement as we would like. Third, the comparison of the two instruments would likely often occur over a rather limited range of fairly low ozone concentrations. Such comparisons may be affected by otherwise minor zero offset errors and, while useful for assessment of precision, in general provide a rather limited quantitative assessment of analyzer accuracy, particularly for the higher ozone concentrations which are critical in attainment/non-attainment determinations. Longer-term collocated instrument comparisons to gain a wider range of ambient concentrations would profoundly raise costs to monitoring agencies and would gain only a modest advantage in assessing data quality. Of course, collocation of ozone analyzers is often useful for purposes other than calibration verification.

Independent calibration of ozone analyzers with certified ozone standards is certainly not infallible. But we believe conventional, independent calibration of UV ozone analyzers is advantageous for a variety of reasons. For example, independent calibration...

- Is a conventional, familiar concept that is widely used for most measuring instruments,
- Is consistent with calibration of other ambient gaseous pollutant analyzers, using certified concentration standards,
- Is uniformly applicable to any type of ozone analyzer, not just the UV-absorption type,
- Allows all measurements to be *independently* related to common, NIST-traceable ozone standards,
- Avoids uncertainties from UV-method ambient air interferences and routine operational degradation,
- Provides an accurate and precise calibration over the full measurement scale range, and
- Provides credible and readily quantitative assessment (audit) of analyzer accuracy.

EPA provides a network of NIST-traceable ozone standard reference photometers by which ozone calibration standards can be verified or certified. We are convinced that conventional calibration of UV ozone analyzers with certified ozone standards leads to very accurately calibrated ozone monitoring instruments at reasonable cost, provides readily documented and highly credible quantitative audit assessments of ozone monitoring data quality, and, we believe, is substantially superior to the verification assessment technique alternatively proposed by Parrish and Fehsenfeld. We do agree with them that adjustment of the span setting of UV-type ozone instruments for calibration should be limited to small adjustments, as any large difference from the natural or theoretical setting should be taken as an indication of some problem in either the instrument or the calibration equipment. We have made that recommendation for decades, and it appears in many UV monitoring instrument manuals.

Interferences

As noted above, UV ozone analyzers depend upon a scrubber to provide a reference air sample from which ambient ozone is removed but other potential interfering gasses in the ambient air sample remain to minimize measurement interferences. This scheme is generally quite successful, but not perfect—particularly for gases such as mercury and some aromatic hydrocarbon compounds that have large absorption coefficients relative to ozone (at 254 nm wavelength). Humidity does not appear to cause a direct interference but may af-

(Continued on page 12)



McElroy and Gemmill, . . . Continued

fect susceptibility to other interferences. Unusually high concentrations of particulate matter can also cause interference, since PM may not pass through the scrubber undiminished.

These positive interferences have been known all along and are believed to be a generally insignificant problem at most ozone monitoring sites, particularly when the scrubber is replaced periodically according to the manufacturer recommendations. Parrish and Fehsenfeld state that "even though significant evidence of interferences in the UV absorption technique has been reported, such interferences are not always observed, even in urban plumes." They go on to cite a 1998 report by Ryerson et al. describing simultaneous measurements of ozone by UV and chemiluminescence instruments in an aircraft and indicate that "...excellent correlations were found between the measurements of the two instruments..." and "there was never any indication (<1%) that the UV instrument measured systematically higher in the urban plume."

Nevertheless, EPA has always cautioned against siting a UV-type ozone analyzer in an area where interferences could be problematic, such as in the vicinity of potentially high mercury concentrations, asphalt plants or large asphalt-paved surfaces, gasoline stations or transfer facilities, heavy automobile traffic, etc. Years ago, UV ozone monitoring sites could be checked for the presence of such interferences quite easily by collocating a chemiluminescence ozone analyzer with the UV analyzer for some period of time and comparing the measurements. Now, with chemiluminescence ozone analyzers becoming increasingly difficult to obtain, this means of checking for interferences—as well as an alternative to a UV-type analyzer to use at an interference-plagued site—may be no longer available. We thus share some concern with Parrish and Fehsenfeld on this issue, but we believe that careful siting of UV ozone analyzers will minimize this problem.

Anomalous Operating Conditions

As noted above, the accuracy of UV ozone measurements critically depends on the performance of the chemical scrubber, which must remove all ozone from a representative air sample without altering the concentration of any

potentially interfering substances. Accumulating evidence from several state monitoring agencies indicates occasional measurement anomalies in UV analyzers, with a return to apparently normal measurement performance at other times. These anomalies may result in either positive or negative error and are generally associated with periods of high ambient temperatures, high humidity, and possibly other associated atmospheric conditions. Unfortunately, these conditions are also typical during periods when ozone concentrations peak and measurement accuracy is crucial. Further, these anomalies are often not detected by conventional ozone span checks or audits.

We are also concerned about this potential problem, but so far it has proved elusive and difficult to (1) reproduce in the laboratory, (2) determine the specific conditions under which it occurs or may occur, (3) predict the monitoring sites where it may occur, (4) define its specific manifestations, and (5) establish differences in susceptibility, if any, among different models of UV analyzers. Laboratory studies of this phenomenon have been inconclusive, and field studies are very expensive and difficult to carry out when resources are limited. Recent work by Joel Maddy of West Virginia appears to confirm our suspicions that the effect may be related to temporary partial failure of the scrubber, but that it also involves temporary effects in the optical cells, mirrors, and other internal surfaces. He has developed a test which appears to be able to identify UV analyzers that are most susceptible to anomalous measurements. His work further suggests that use of a heated silver wool scrubber (as opposed to other types), along with use of Teflon-coated stainless steel (rather than glass or quartz) absorption cells, will greatly reduce a UV analyzer's susceptibility to this effect. However, he acknowledges that these suggestions are based on empirical observations and not on an understanding of the mechanism that gives rise to the anomalies.

We are currently addressing this problem on three fronts. First, we are attempting to assess the extent and severity of these measurement anomalies by surveying monitoring agencies and monitoring agency associations. Second, we are collaborating with the American Petroleum Institute and state and local agencies by providing contract funding to conduct studies to better document the performance differences among various configurations of UV ozone analyzers. And third, we will evaluate Mr. Maddy's test for analyzer



susceptibility and the use of the heated silver wool scrubbers in minimizing the impact of anomalous analyzer performance and, if warranted, implement or promote their use among monitoring agencies. We intend to provide any updated quality assurance guidance resulting from these activities to help monitoring agencies minimize any potential measurement errors from them.

Conclusion

We hope that this additional information might provide some further perspective. We remain confident that the vast majority of ozone monitoring data collected nationwide is of high quality. And we agree with the need Parrish and Fehsenfeld identified for additional field inter-comparisons of the UV technique with other ozone measurement techniques, particularly during conditions typical of ozone exceedences, to better define the scope and impact of any potential UV ozone measurement uncertainties. We hope to be able to pursue such studies, but current resources for this activity appear to be insufficient. We will continue to pursue other means of investigating these potential uncertainties.

Sincerely,

Frank F. McElroy (MD-46)
 David B. Gemmill (MD-46)
 Atmospheric Methods & Monitoring Branch
 Human Exposure & Atmospheric Sciences
 Division
 U. S. Environmental Protection Agency

**Comments and Discussion:
 Maddy**

Dear Dr. Hales:

The State of West Virginia, Office of Air Quality (OAQ) would like to address some of the concerns expressed about ambient ozone monitoring in the article titled "One Step Forward and...: Some Cautionary Notes on Urban Ozone Measurements" found on page 16 of your Winter/Spring 1999 newsletter. Though West Virginia is considered rural for ambient air modeling purposes, all of the issues raised in the article; calibration uncertainties, interferences and anomalous operating conditions, pertain to ambient ozone monitoring in general.

In short, OAQ feels that its ozone calibration uncertainties are well within prescribed tolerances; that OAQ's observed ozone monitor anomalous behavior is remedied by heated silver/metal scrubbers; and that other than unknown contaminants associated with anomalous behavior, interferences have not been observed.

Not having observed interference effects does not mean they don't exist. West Virginia is rural and OAQ uses only UV method ozone monitors, while Leston and Ollison's¹ reported interference effects, cited in Parrish and Fehsenfeld's paper, were detected by comparing collocated UV and chemiluminescent method ozone monitors in urban areas.

Parrish and Fehsenfeld recognize the ability of Ultra Violet (UV) photometry to accurately assess ozone concentrations. This method serves as the National Institute of Science and Technology (NIST) authoritative standard for ozone, having a measurement uncertainty of 1%. But one of the article's quotes (though not found in the version of Parrish and Fehsenfeld's paper on NARSTO's web site at the time of this writing, page 40, lines 16 through 19) implies that the NIST traceable authority of transfer standard photometer calibrators is an issue. Quoting the article "This approach is inadequate; it can at worst perpetuate serious measurement problems since the ozone standard itself is merely a similar UV absorption measurement system coupled to an ozone generator", referring to adjusting monitors to photometer calibrators. OAQ's practical experience in calibrating ozone monitors, following Environmental Protection Agency (EPA) Quality Assurance (QA) guidelines, produces ozone data accuracy that typically appears to fall within +/- 5% of the NIST authoritative standard for ozone. A detailed overview of the chain of NIST traceable authority conferred on ozone monitoring data may help allay concerns about this perceived "calibration uncertainty".

Starting at the top of the NIST traceable "chain" of authority we find that Standard Reference Photometer (SRP) inter-comparison curve slopes are within +/-1% of 1.0. SRPs have no calibration adjustments; they are inherently accurate, operating in accordance with ideal Beer-Lambert theory. SRPs serve as the authoritative NIST standard for ozone and are increasingly being adopted world wide for such service.

In the second "link in the chain" the authority

(Continued on page 14)



Maddy, . . . Continued

of an air monitoring organization's local primary standard photometer is established by inter-comparison with an SRP. Inter-comparison curve slopes must be within +/-5% of 1.0. Local primary standards typically have adjustments which are set to theoretical ideal Beer-Lambert operating parameters, no zero offset correction and an absorption coefficient of 308 (or equivalent arbitrary settings supplied by the factory). This forces them to rely on the UV method's inherent accuracy. As a side note, it seems intuitive that ozone data accuracy would improve if local primary standards, having been established as precise and repeatable, were calibrated to the SRP.

The third "link" has a transfer standard calibrator's authority and accuracy established by comparison to a local primary standard photometer and the resulting calibration curve. At least six different methods for ozone calibration transfer standards exist, UV photometers and ozone generators being the most commonly used. Transfer standards need only be precise and repeatable, not inherently accurate.

A transfer standard UV photometer's "span" and "zero" can be adjusted to calibrate its ozone readings to those of the local primary standard photometer. Doing so eliminates the possibility of human error when manually calculating corrected readings. Although transfer standard photometers employ the same UV method as SRPs and primary standards, they differ by employing a device called a scrubber or deozone (more will be said about this device later); often generate and sample their own zero air and ozone; and are transported to the field monitors.

In the fourth and final "link" the field monitor's "span" and "zero" can be adjusted to calibrate its ozone readings to those of a transfer standard. Again, there are two different types of EPA equivalent method ozone monitors and the reference method monitor. UV absorption is used almost exclusively. No matter the method used for a monitor it need only be precise and repeatable, not inherently accurate. Field monitor calibration checks resulting in errors greater than +/- 15% result in void data; greater than +/- 10% indicates that a problem likely exists and should be remedied; and greater than +/- 5% indicates that the monitor should be re-calibrated.

UV method monitors, unlike all of the calibration

instruments discussed earlier continuously sample ambient air which has had most particulate matter filtered out and employ scrubbers as part of a process that compensates for interferences which can be present in ambient air.

What are the results of the calibration process described above? Over the past two years EPA audits have been performed at four OAQ ozone sites using a transfer standard photometer whose authority is traceable to EPA region II's SRP. OAQ uses this same SRP to establish the authority of its local primary standard photometer, which in turn is used to establish the authority of OAQ's transfer standards (both photometers and ozone generators) and finally the monitors in the field. With one exception (a monitor requiring maintenance as indicated by OAQ's instrument log records) the audits' inter-comparison curve slopes have fallen within the +/- 5% of 1.0 tolerance considered good.

Better still are the audit results when EPA region III's audit photometer is corrected back to EPA region II's SRP. Inter-comparison curve slopes then fall within a +/- 2% range, often within +/- 1%. Considering that EPA region II SRP's inter-comparisons with other SRPs yield curve slopes of 1.0 +/- 1% it would appear that the accuracy of OAQ's ozone data typically falls within +/- 5%, or better, of NIST's authoritative standard.

Another quoted "calibration uncertainty" was adjusting an UV equivalent method ozone monitor's "span". Again there is a discrepancy between the article's quote and the current version of the paper. The article quote saying "This approach is inadequate..." referring to "...adjusting the "span" control of the monitor until the instrument reading agrees with the output of a standard ozone generator". But their paper concedes to calibrations "limited to only small adjustments". In essence, Parrish and Fehsenfeld are suggesting that field monitors be operated as SRPs, producing readings with inherent "absolute" accuracy, taking full advantage of the UV absorption method. It is an admirable goal that would seem very arduous and expensive to implement bearing in mind that SRPs and local primary standards are laboratory instrumentation, with no scrubbers, that sample only zero air and ozone.

Why would an UV equivalent method ozone monitor need to be adjusted to any setting other than the theoretical ideal? An informal poll of several ozone monitor manufacturers cited mass production realities such as dimensional toler-



ances, precision of sensors for temperature and pressure, switching solenoid induced stray electromagnetic fields, and so on. More than one company engineer felt that it is unrealistic to apply the theoretical ideal Beer-Lambert parameters to mass produced UV method ozone monitors, suggesting an approach of using arbitrary initial manufacturer calibration parameters. One company's monitor does not reference the absorption coefficient of ozone as an adjustable or displayed parameter, allowing span and zero to be adjusted by no more than +/- 10% and +/- 10 ppb, respectively. Arbitrary operational parameters, preferably initial factory settings, will suffice as long as a monitor is precise, repeatable and has its authoritative NIST traceable accuracy established. All that's left to do is assign a realistic range of allowed adjustments.

It seems that the primary goal of Parrish and Fehsenfeld's suggestion to take "advantage" of UV method field monitors producing inherently accurate "absolute" ozone measurements, is as an indication of a monitor's need for maintenance.

OAQ accomplishes this same goal by keeping field logbooks of weekly site visits to track the performance of each monitor and graphing daily calibration check results. Monitors requiring excessive re-calibrations or exhibiting excessive drift are considered in need of maintenance. At OAQ nightly automated zero, precision and span calibration checks are performed with an Environics 9100's certified transfer standard ozone generator; the checks are enhanced by the presence of collocated monitors. Calibration check results are entered into a historical graph and tracked by site operators. OAQ has operated monitors that over their seven-month ozone season needed no re-calibration. Barring failures, some monitors may require as many as three. In the off season all ozone monitors are refurbished and performance tested before being re-deployed.

Parrish and Fehsenfeld also suggest "a much more critical assessment" of keeping a monitor's parameters set to produce "absolute" ozone measurements while occasionally collocating a known good "reference" monitor for comparison during ambient sampling. It appears a more significant goal of collocating ozone monitors for comparison during ambient sampling, aside from another form of calibration check, would be to detect any anomalous monitor behavior (one of their stated uncertainties) that may go undetected by standard calibration checks. The OAQ also considers the collocation of monitors a good idea for this and

several other reasons. Since 1993 a collection of different manufactures' ozone monitors have been collocated during the entire season, throughout OAQ's monitoring network. Doing so increases the percentage of valid data collected and has revealed malfunctions and anomalous monitor behavior that may have otherwise gone undetected. Two OAQ papers that document the anomalous behavior Parrish and Fehsenfeld's paper appears to be describing (page. 39, lines 8 through 14), and solutions for it can be downloaded at <http://www.dep.state.wv.us/oaq/airmon/field/field.htm>.

Collocation has also allowed OAQ to observe that virtually all of their ozone monitor malfunctions and conditions requiring maintenance result in reduced ozone readings. The anomalous behavior OAQ has observed during hot and humid ambient sampling can cause false high ozone readings, as well as low, with some manufacturers' configurations of ozone monitors. Only one brand of monitor known to OAQ exhibits a consistent bias in ozone readings when experiencing this anomalous behavior; its readings are biased low. Fortunately a new type of ozone scrubber, heated silver/metal, effectively eliminates OAQ's observed anomalous behavior and there is speculation that it may address two other documented MnO₂ scrubber humidity/interference related anomalies as well (Kleindienst et al., 1997² and Hudgens et al, 1994³).

Ozone monitoring concentrations biased either high or low, produce "critical uncertainties with large economic and societal implications". As progress brings new technologies and practices that further improve on the current high quality of ozone monitoring data, they should be evaluated, and if found valid made available to the ozone monitoring community. At present an air monitoring organization operating within the framework established by EPA can take extra measures, such as collocation, to further enhance the accuracy and quality of their reported ozone data.

Sincerely,

Joel A. Maddy
Supervisor, Air Monitoring Field Section
State of West Virginia Office of Air Quality

REFERENCES:

1 Leston, A. and Ollison, W. M., (1993), "Estimated Accuracy of Ozone Design Values: Are They Compromised by Method Interferences?", in Tropospheric Ozone: Nonattainment and Design Values Issues, TR-23, Air and Waste Management Association, Pittsburgh, PA, pp.

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2 Kliendienst, T. E., McIver, C. D. and Ollison, W. M., (1997), "A Study of Interferences in Ambient Ozone Monitors", VIP-74, proceedings A&WMA Measurement of Toxic and Related Air Pollutants Conference, RTP, NC, pp. 215-225.

3 Hudgens, E. E., Kliendienst, T. E., McElroy, F. F. and Ollison, W. M., (1994), "A Study of Interferences in Ozone UV and Chemiluminescence Monitors", in Measurements of Toxic and Related Air Pollutants, VIP-39, Air and Waste Management Association, Pittsburgh, PA, pp. 405-415.

Response: Parrish and Fehsenfeld

Dear Dr. Hales,

We are pleased that your article has generated interest and the discussion included in this newsletter. The importance of uncertainties in ambient ozone measurements clearly is an important question. Intercomparisons of ambient ozone measurements by different techniques, under field conditions, during photochemically active periods are critical to ensure that important exceedences are in fact captured with minimal danger of "false alarms." During the recently completed SOS 1999 Nashville Field Intensive, a UV absorption instrument and a chemiluminescence instrument were compared for approximately one month at an urban site. The chemiluminescence instrument was calibrated against the UV instrument using prepared ozone mixtures in clean, dry air. Preliminary analysis indicates excellent agreement during ambient measurements that spanned 0 to 130 ppbv. No evidence for any systematic differences was found (although the UV instrument showed anomalous behavior for a few days following the formal test period).

Sincerely,

David D. Parrish
Fred C. Fehsenfeld
Aeronomy Laboratory
National Oceanic and Atmospheric Administration

NARSTO Welcomes New Members

During the past few months several organizations have joined NARSTO as new members. These include:

New Sponsoring Members:

Chemical Specialties Manufacturers Association
Lyondell Chemical Company
Penreco

New Participating Members:

Atmospheric and Environmental Research, Inc.
Atmospheric Research & Analysis, Inc.
Lamar University, Gulf Coast Hazardous Substance Research Center
Radtech International North America
Saskatchewan Research Council

NARSTO welcomes these organizations to the

Texas 2000 Formally Links as a NARSTO Component

Recently the Texas 2000 ozone and fine-particle study (see Texas 2000 article on page 14 of the Winter/Spring '99 **NARSTO News**) petitioned NARSTO with the request to become listed formally as an official NARSTO program. The Science and Resource Planning Group and the Executive Steering Committee unanimously concurred with this petition, and so now Texas 2000 is "officially NARSTO."

Texas 2000 will be a challenging study in a chemically and meteorologically complex environment. It has tremendous potential for significantly increasing our understanding of atmospheric photochemistry and aerosol production, and we wish the research team well on this important endeavour.





CALL FOR PAPERS

Aerosols: Science and Decisions in an International Community

24-26 October 2000 (training courses on 23 October)
Hotel Real D Minas, Queretaro, Mexico (transportation to be provided from Mexico City)

This is an exciting time for scientific research on tropospheric aerosols. Much has been learned, and yet the tasks before us are challenging. Areas of investigation include not only the basic chemistry and physics of aerosol formation and dispersion, but also measuring and monitoring methods, issues in human health, weather and climate, and transboundary pollution.

This symposium is being conducted under the auspices of the NARSTO cooperative, a public/private partnership whose membership spans government, industry, the utilities, and academia throughout North America. The objective of the symposium is to bring together recent research findings in the context of science and decision-making needs to better understand tropospheric aerosol issues that may be of concern for the urban and regional environment.

Submit abstracts for either **Presentations** or **Posters** in the topic areas listed below or in others relevant to the conference theme. Each abstract must include a statement of how the material covered in the presentation or poster could be used by decision makers in the international community. Note that the conference language is English. You may submit abstracts electronically at on the Conference Web Page <<http://www.cgenv.com/Narsto>> or by email to normanm@dri.edu or by sending both hard copy and diskette to Norman Mamkim, Desert Research Institute, 2215 Raggio Parkway, Reno, NV 89512-1095.

To be included in the program, your abstract must be submitted in the format provided below by 15 December 1999. You will be notified of the status of your abstract by April 1, when a preliminary conference program will be available.

Abstracts are being solicited in the following areas (please identify the area for your abstract on the form):

Fine Particle Emission and Formation
Fine Particles, Exposure, and Human Health
PM Health Effects
PM Measurements
Air Quality Monitoring
Transboundary Issues
Visibility Impact and Assessment

Field Studies
Science-Policy Linkages
Stationary Sources and Control Alternatives
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Aerosol Satellites
Source Characterization

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US Environmental Protection Agency
Instituto Mexicano del Petróleo
Universidad Nacional Autónoma de México
Desert Research Institute

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Call for Papers . . . , *Continued*

Conference Chairs:

- Mexico: Adrian Fernandez, Director General for Environmental Management, Instituto Nacional de Ecologia
- United States: Jake Hales, Management Coordinator, North American Research Strategy for Tropospheric Ozone (NARSTO)
- Canada: Don McKay, Public Sector Chair, North American Research Strategy for Tropospheric Ozone (NARSTO)

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(775) 674-7050

Sylvia A. Edgerton and Elizabeth Malone
Pacific Northwest National Laboratory, 901 D St. S.W., Suite 900, Washington DC 20024
(202) 646-5236

Format for Abstracts being submitted to the NARSTO Symposium “Aerosols: Science and Decisions in an International Community”

Queretaro, Mexico, on October 24-26, 2000

This is the suggested format for abstracts of papers that are being submitted to the “Aerosols: Science and Policy in an International Community” conference to be held in Mexico City in October 2000. Your abstract should be 300 words or less. Please email your abstract to normanm@dri.edu. We prefer that you send a Microsoft Word for DOS/Windows file, but a WordPerfect for DOS/Windows or ASCII file is also acceptable.

You can use these instructions as a guide to typing your abstract, but a few details about formatting follow. Please use one-inch margins on all four sides of a letter- or A4-size page. The title should be in 14-point bold Times New Roman font, and everything else should be in 12-point normal Times New Roman font. Center the title on the first line. Center the author’s name(s) on the second line below the title. Center the author’s affiliation and address below the author’s name. Begin the text of your abstract on the fourth line below the author’s affiliation. Type the text single-spaced with one blank line between paragraphs. At the bottom of the page, please provide the name, address, phone number, fax number, and email address of the primary contact author. Also indicate your first and second choice of sessions in which you would like your paper to be included.

Contact:

Primary author:
Institution:
Address:

Session Preference:

1. _____
2. _____

phone:
fax:
email:



“Words of Encouragement” to Prospective *NARSTO* News Authors

As indicated on our masthead, the *NARSTO News* is printed as a service to the NARSTO community and its stakeholders, and we encourage any interested persons to submit articles, announcements, open letters and other suitable material for publication in future issues.

We also encourage submission in electronic form (preferably by e-mail to jake@cgenv.com). We can handle output from almost any word processor, and do a fair job with graphics, although we obviously can't “do” color on our hardcopy edition. Those individuals who do submit graphics should ensure that they are transmitted either in PostScript (or eps) form, or else in bit-mapped formats having sufficiently high resolution to print well (at least 300 dpi; preferably more, especially for complex graphics). TIFF, JPEG, GIF, or PICT will do fine. We can print photographs, but don't encourage highly complicated scenes because of the resultant image quality.

Anyway, this note is intended to encourage interested persons to use our newsletter as an announcement medium and as a forum for pertinent scientific discussions. We hope that you'll take this opportunity!

This Just In: Tom Feeley to Chair Fine-Particle Symposium at 2000 ACS Meeting

Just before going to print we received an email note from Tom Feeley at FETC, saying that he's been asked to organize and chair a symposium on Particulate Matter and Fossil-Fuel Combustion at the 2000 American Chemical Society Meeting in San Francisco, March 26-31, 2000.

This day-and-a-half meeting should give sufficient time to cover the numerous technical, scientific, and regulatory issues related to the emission, control, and impacts of PM. Tom has prepared a Call for Abstracts for the symposium, and is encouraging abstracts for prospective presentations. Abstracts are due 10/15/99 and final papers on 11/15/99. ACS Books has also asked that a Symposium Series Volume from the symposium be put together.

Tom can be reached at 412/386-6134 for further information and to obtain the Call for Abstracts. We'll hope to provide further updates on this on the NARSTO Web site.



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