Update on the Office of Research and Development’s Monitoring and Methods Research Priorities

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Office of Research and Development
Ambient Measurement Methods
Research in ORD’s Air Climate and Energy (ACE) Research Program

- Renewed Focus on Ambient Methods Development
  - Increase in resources (despite reductions in most activities) - ~$500K/FY
  - Clear on what we are going to deliver (and what we are not going to deliver)

- Methods to Inform Policy
  - ACE Task 176 – NAAQS Methods: Federal Reference Methods (FRMs) and Federal Equivalent Methods (FEMs)
    - FRM: Ozone, Lead, NO₂
    - Reference and Equivalent Methods Program: applications review

- Other Methods Research in ACE
  - ACE Task 135 – Innovative techniques for quantifying acrolein and other air toxics
  - ACE Task 245 – Use of satellite and aircraft remote sensing observations to diagnose aerosol and trace gas gradients and concentrations associated with National Ambient Air Quality Standards
  - ACE Task 071 – Development of low-cost, real-time sensors for fence line monitoring and community exposure assessment
Federal Reference Methods (FRMs) and Federal Equivalent Methods (FEMs)

Federal Reference Methods (FRM)

• A FRM is a method, sampler or analyzer that utilizes the measurement principles and calibration procedures specified in 40 CFR Part 50

• A candidate method (CM) must be shown to satisfy all applicable requirements of Part 53, Subparts A (documentation) and B (performance testing).

Federal Equivalent Methods (FEM)

• A FEM is an ambient air monitoring method that has been tested under 40 CFR Part 53 and designated by EPA as an FEM under Part 53.

• A CM must be shown to satisfy all applicable requirements of Part 53, Subparts A (documentation), B (performance testing), and C (testing for comparability to the FRM).
EPA AIRS Sampling Sites

Ambient air Innovative Research Site (AIRS)
- Site located on EPA RTP, NC campus
- Instruments calibrated according to operation manuals in accordance with FRM/FEM requirements
- Nightly, automated zero and span checks
- Glass inlet with sampling height @ 5 m above ground level and common sampling manifold

Not Shown
- 2B 202 & 205 Ozone
- CRDS & CAPS NO₂
Update on Ozone Federal Reference and Equivalent Methods Research Activities

Research Managed by Dr. Russell Long
U.S. EPA, Office of Research and Development
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Federal Reference Method for Ozone

- An O₃ FRM (Federal Reference Method) is an analyzer that utilizes the measurement principle and calibration procedure specified in Part 50, Appendix D
  - Ethylene Chemiluminescence

Discussion

- Technical performance of existing FRM has proven to be very sound, no other ambient ozone measurement technique has emerged as clearly superior.
- FRM is currently unavailable commercially, instrument maintenance becoming increasingly difficult due to unavailability of components

Federal Equivalent Methods for Ozone

- An O₃ FEM (Federal Equivalent Method) is an ambient air monitoring method (usually an analyzer) that has been tested under 40 CFR Part 53 and designated by EPA as an FEM under Part 53.

Discussion

- UV Photometric – most widely used FEM for O₃
- FEMs based on other measurement methods also available
**FRM Analyzer Resurrection**

- 3 Bendix 8002 FRMs – all non-operational
- OK electronically
- Replaced PMTs – no longer available commercially from manufacturer
- Appeared to successfully zero and span instrument

**Result**

- Source of noise and low span reading not yet identified

**Instrument supplied with 100 ppb ozone over 3 day period**
- Analyzer did not reach span value
- Significant noise observed
- Calibrator/ozone generator eliminated as source of noise
O₃ Results from EPA AIRS Site

Wintertime 1-hr ozone FEM results from the EPA AIRS sampling site
Ozone Research Initiatives and Next Steps

- Obtain a working ozone FRM analyzer
- Continued collocated ambient monitoring with FRMs and FEMs
  - EPA AIRS site – ongoing
  - Houston, TX (Summer 2013) – NASA DISCOVER-AQ Study
- Laboratory based method evaluations
  - 40 CFR Part 53 performance testing for FRM and FEMs
  - Detailed interference testing
- Develop and document performance criteria including calibration and challenge procedures
- FRMs and FEMs use as reference analyzer for sensor/apps assessment
Update on Lead Federal Reference Method Research Activities

Research Managed by Dr. Robert Vanderpool
U.S. EPA, Office of Research and Development
National Exposure Research Laboratory

Presented during Criteria Pollutant Methods Issues & Updates Session
Date/Time: Wednesday May 16, 2012, 3:30 PM
Room Colorado F
Summary of Pb NAAQS: Sampling and Analytical Techniques

The two different sampling FRMs (Pb-TSP and Pb-PM$_{10}$) have correspondingly different analytical FRMs associated with them.

Hi-Vol TSP Sampling (~ 50 cfm)
- Sampling at source-oriented sites
- Analytical FRM involves extraction of Pb on 8” x 10” glass fiber filters using acid extraction followed by flame AA analysis

PM$_{10}$ Sampling (16.7 Lpm)
- Sampling at non-source-oriented sites and at selected source-oriented sites where ultra-coarse emissions are expected to be minimal
- Analytical FRM involves XRF analysis of Pb on 46.2 mm diameter teflon filters

Source-oriented sites tend to produce high concentrations of large Pb-bearing particles.
Design Features for a New Pb FRM Sampler

- New FRM designed to replace both the hi-vol and PM10 sampler with a single sampler and a single analytical method
- Fixed inlet dimensions, fixed flow rate, and omnidirectional inlet
- Acceptable variation in size selective performance as a function of ambient wind speeds (2 to 24 km/hr)
- Cutpoint in the 18 to 20 µm size range would quantify all Pb-bearing particles currently measured by the Pb-PM$_{10}$ FRM while accounting for a portion of Pb-bearing particles above 10 µm
Proposed New Analytical FRM for Pb in TSP – ICP-MS

- Designed to meet lower detection limit requirements of new Pb NAAQS
- Based on two recently designated FEMs (EQL-0510-191 and EQL-0710-192)
- Extraction options: Heated ultrasonic with HCl/HNO₃ or hot block with HNO₃
- Applicable to glass fiber, quartz, and teflon filters
- Interlaboratory results from RTI, ERG, ORIA, and ORD are favorable for precision and comparability
Lead Research Initiatives and Next Steps

• Develop generation and measurement techniques for wind tunnel calibration aerosols (ongoing)

• Optimization of EPA’s aerosol wind tunnel for upcoming size selective tests (ongoing)

• Develop, wind tunnel evaluate, and finalize design of a new candidate inlet for the Pb FRM

• Conduct any necessary field evaluation of the proposed Pb FRM
Update on NO$_2$ Federal Reference and Equivalent Methods and “True” NO$_2$ Methods Research Activities

Research Managed by Dr. Melinda Beaver
U.S. EPA, Office of Research and Development
National Exposure Research Laboratory

Presented during Criteria Pollutant Methods Issues & Updates Session
Date/Time: Wednesday May 16, 2012, 3:30 PM
Room Colorado F
## Current NO₂ Regulations

<table>
<thead>
<tr>
<th>NO₂ Primary Standards</th>
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<tr>
<td><strong>level</strong></td>
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<tr>
<td>53 ppb</td>
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<tr>
<td>100 ppb*</td>
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* The monitoring locations for the new primary standard will be sited near roadways to capture areas of maximum concentration.
- Continuous monitors capable of hourly data are now necessary.
**Automated Federal Reference Method**

- Gas-phase chemiluminescence
- Indirectly measure NO₂ by conversion to NO, then NO is detected by chemiluminescence (NO + O₃ → NO₂*)
- Converter also capable of reducing other NOₓ species to NO resulting in a positive artifact, NO₂ determination is considered an upper limit
- Teledyne-API T200U, Thermo 42C
Replace the molybdenum converter with a photolysis cell to photolyze NO$_2$ to NO (NO$_2$ + $h\nu$ → NO + O)

- Use high-power light sources to maximize conversion to NO
- Advantage → more specific to NO$_2$
- Disadvantages → low, and variable (but stable) conversion efficiency; still indirect
- Teledyne-API 200EUP, T200UP, FEM designation imminent
Direct Optical Techniques

Cavity Ringdown Spectroscopy (CRDS)
- Instrument manufactured by Los Gatos Research, Inc.
- 10 s time resolution
- Advantage $\rightarrow$ DIRECT measurement
- Disadvantages $\rightarrow$ not-necessarily specific to NO$_2$, but to any molecule that absorbs light at 407 nm

Cavity Attenuated Phase Shift spectroscopy (CAPS)
- Instrument manufactured by Aerodyne Research, Inc.
- 2 versions: fast response (1 s) and ambient (10 s)
- Advantage $\rightarrow$ DIRECT measurement
- Disadvantage $\rightarrow$ not-necessarily specific to NO$_2$, but to any molecule that absorbs light at ~450 nm
Results from EPA’s AIRS site, NC

Wintertime FRM, photolytic, and direct measurement method 1-hr NO₂ results

March 2012
NO\textsubscript{2} Research Initiatives and Next Steps

- Ambient method inter-comparison through the summer
- Develop and document calibration and challenge procedures for direct measurement techniques
  - NO\textsubscript{2} cylinder vs GPT
- Detailed laboratory based assessments
  - Interference testing
  - 40 CFR part 53 subpart B performance testing
- Evaluate optical monitors in a near-roadway environment
- New NO\textsubscript{2} methods as reference analyzer for sensor/apps assessment
FRM/FEM Applications Review

• The most recent (Oct. 12, 2011) list of designated Reference and Equivalent Methods can be found at the AMTIC site:


• 5 new designations were made during the past year
  • Class III PM\(_{2.5}\) (1) - Grimm Model 180 PM\(_{2.5}\) monitor
  • PM\(_{10}\) (2) - Thermo 2000-D PM\(_{10}\) sampler and Thermo 2025-D PM\(_{10}\) sampler,
  • Lead (1) - US EPA/OAQPS TSP Pb by ICP-AES
  • Ozone (1) - Teledyne API Model T265 ozone analyzer

• 27 modification requests to existing designations were reviewed and approved in the past year.

• 11 new applications are currently undergoing review (2 for Class III PM\(_{2.5}\), 2 for Class III PM\(_{10-2.5}\), 2 for PM\(_{10}\), 2 for Pb, 1 for CO, 1 for O\(_3\), and 1 for NO\(_2\))
Summary

- EPA is currently performing research on methods for the measurement of ozone, lead, and NO$_2$ in ambient air.

- Further research is needed both in laboratory and field settings to develop and assess methods for NAAQS criteria pollutants including the identification of potential sampling interferences and/or challenges and to evaluate their use in routine monitoring.

- The results of this research may serve an informative role in the NAAQS review process for the corresponding criteria pollutants including the measurement methods used for its regulatory determination.
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Disclaimer

Although this work was reviewed by EPA and approved for presentation, it may not necessarily reflect official Agency policy.