NOy Monitoring – Issues and Auditing

MARAMA Monitoring Meeting
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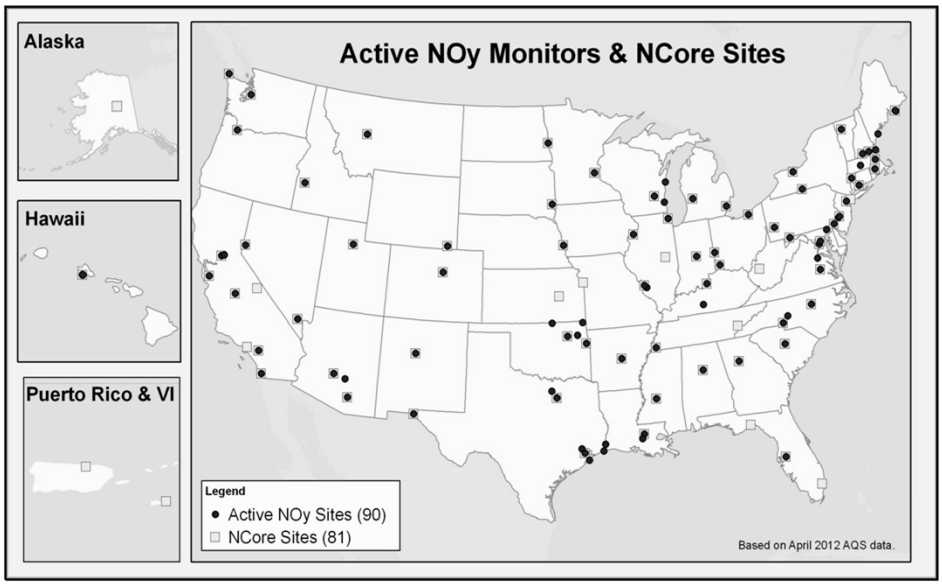
Kevin A. Cavender
EPA/OAR/OAQPS

Objectives

- Review NOy monitoring network
- Review chronology of EPA guidance on NOy monitoring
- Discuss “current” guidance on operations and recommended QA/QC
- Future of NOy monitoring
- NOy operational issues discussion
- Auditing



EPA Guidance Chronology

1998

- First EPA guidance on NOy monitoring was part of the "TAD for Sampling and Analysis of Ozone Precursors" issued September 1998 (http://www.epa.gov/ttn/amtic/pams.html)
  - NOy was 'strongly encouraged' as part of an enhanced ozone monitoring program (~PAMS) and data was to be used to evaluate and improve photochemical models
  - Detailed instructions on converting a NOx box to an NOy box, where changes in the location of the **converter, particulate filter(s), flow control capillary, and the 3-way solenoid valve** make the difference
  - All QA checks including converter efficiency were using NO_2; converter efficiency check suggested to be >96%
  - NPN and nitric acid are mentioned as challenge agents, but not elaborated upon

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EPA Guidance Chronology

2005

- NCore TAD Recommendations
  - External converter to be at 10 meters (primarily to reduce potential for HNO_3 loss)
  - Inlet to be made of PFA Teflon
  - Inlet allowed to use part of a Teflon filter holder as a bug screen
  - Only a heated Molybdenum converter could be used (versus Au) at 350˚ C
  - Use opaque lines and reduce residence times

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EPA Guidance Chronology

2005

- NCore TAD Recommendations (continued)
  - Quarterly multipoint NO calibrations (zero, 3 span levels)
  - Quarterly multipoint NO_2 calibrations (zero, 3 span levels, close to those used for NO)
  - Two week precision checks; with NO, target 20 ppb
  - Daily (Level 1) zero/span check; span gas unspecified, but target level to be 70 to 90 percent of scale
  - Detailed MDL determination procedures
  - *Monthly* single-point converter efficiency tests --- TAD has two targets listed in different places: 95% and 96%
    - Converter efficiency test language suggests using NPN

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EPA Guidance Chronology

2006 & 2007

- In the 2006 'Monitoring Rule', NCore sites were required, which included requirements for NOy
- NOy guidance resurfaced in 2007 as part of EPA – OAQPS' Precursor Gas Training workshops (http://www.epa.gov/ttnamti1/precurtr.html)
  - Reiterates external converter at 10 meters
  - Initial Calibration and zero/span recommended using NO and NO_2
  - Converter efficiency checks recommended to use NPN or IPN (targeting 96% efficiency)
  - Recognized loss of NO_Z species within different inlet materials (SS, Teflon, silicon steel) – Teflon still preferred

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EPA Guidance Chronology

2010

- EPA issued an AQS Technical Note (http://www.epa.gov/ttn/amtic/files/NAAQSReportingUpdate11032010.pdf)
- Noted creation of new parameter code for use with NOy instruments: NOy – NO
  - NOy – NO has the parameter code 42612
  - Some submissions erroneously were labeling such data as NO_2
  - Document also listed method codes

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EPA Guidance Chronology

2011

- EPA gives advice on NOy operations issues and QA reporting in the December 2011 "QA Eye" - Issue 12 (http://www.epa.gov/ttn/amtic/qanews.html)
- For NO data from an NOy analyzer:
  - Daily zero/span (Level 1 check)
  - 1 – point QC check (a.k.a precision check) for NO, at least every two weeks (higher frequency suggested)
- For NOy:
  - 1 – point QC check (a.k.a precision check) every two weeks, using NPN or IPN (*do not report NO 1 – point check data for these data*)
  - Converter efficiency check: TAD suggested monthly check; however, MQO tables suggested every two weeks
  - Since we have a biweekly 1 – point QC check with NPN or IPN, converter efficiency check still recommended to be monthly

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Summary & Discussion of ***Current*** NOy Guidance

- Instrument Set-up & Operation
  - Use PFA Teflon materials, opaque lines, and strive to reduce residence times
  - Molybdenum converter between 315 & 350° C (vendor specific)
  - Inlet at 10 meters; use Teflon bug screen

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- Summary & Discussion of Quality Control Procedures

Data Channel	QC Function	Challenge Gas	Suggested Gas Level	Minimum Frequency	Is it Needed?
NO	Zero/Span	NO	0 & 70- 90% of scale	Daily	Yes
NO	1-pt QC check (precision)	NO	~20 ppb	Biweekly	Yes
NOy	1-pt QC check (precision)	NPN or IPN	?	Biweekly	Yes
NOy	Converter Efficiency	NPN or IPN	?	Monthly	Yes
NO	Multipoint Calibration	NO	Zero, 3 levels	Quarterly	Yes
NOy	Multipoint Calibration	NPN or IPN or NO_2 ?	Zero, 3 levels	Quarterly	?
NOy	MDL determination	NPN or IPN?		Annually?	?

NOy as an FRM

- EPA is pursuing the potential designation of NOy analyzers as FRMs, pursuant to commitments made in the recent Secondary NOx/SOx NAAQS rulemaking
- February 2011, EPA submitted evaluation plans to CASAC AMMS for NOy and other methods
  - CASAC AMMS responded supportively
- EPA – ORD is currently evaluating the commercially available NOy analyzers

Approach

- Upon completion of the evaluation and compilation of the generated data and information on the NO_y measurement method, ORD will be able to describe the accuracy, precision, and reliability of the NO_y instruments and their applicability as FRM.
- ORD will provide a technical summary of the data and supporting information and develop the basis/rationale for adopting it as an FRM.
- ORD will prepare docket materials, proposal preambles, response to comments, and the FRM in regulatory text format.

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Auditing Trace-level (TL) NOy

Old Auditing Procedure

- Non-Trace Level NPAP Auditor Values for NO_2, CO and SO_2 have been based on CO calibrations, followed by audit gas CO analyses.
- Historically, diluted multi-blend (MB) cylinders of CO, SO_2, and NO were used; GPT was used to create NO_2 from NO
- Issues with the Trace Level (TL) NO_y and CO analyzers, the calibrator, and the zero air generator may require another approach, based on NO_y calibration; testing CO/NO_y now

Issues with Old Method

- NO_y - Convertor requires separate flow path; either need twice the calibration/audit gas, or have to do at different times
- Variable zero and span drift in trace-level CO causes problems with reliable low (0-50 ppb) levels
- Problems observed in reliable O_3 generation for low NO_2 levels (1-5 ppb) by GPT

New NO_y Audit Approach

- Generation: Multi-Blend, 200 ppm CO,1 ppm NPN
- Dilution:0-20 cc/min (NPN) and 30 LPM Zero air (ZA)
- 30 LPM ZA
- Two audit points:
- High Span: 160 ppb NPN + 4 ppm CO
- Low Span: 40 ppb NPN and 1 ppm CO

NPN Audit Advantages

- Quicker - NO GPT needed
- No low-level ozone needed to do low audit points
- Easy to do MDL when desired
- Truer test of NO_y than by GPT, which is for NO_2
- If NO_2 convertor efficiency is desired, will not add a lot of time to do both GPT and NPN

Will This New Calibration Method Work for TL NO_y?

- If it can be shown that NPN (and simultaneous CO)-based calibration, instead of CO (?+ GPT)-based calibration, works reliably and accurately
- Local field testing is currently underway;1st try seems OK
- NPN vs IPN: Gallon of liquid NPN has new safety issues; some vendors will suggest the use of IPN.
- But the low and high span cylinders for the trace level calibration method only take about 5 µl (micro liters)/cylinder of either NPN or IPN

Can We Still Use CO-Based Audit?

- Will the old method work for TL NO_y?
  - Maybe, down to each agency's method practical stable point for CO; but, ***NOT*** at the same time
  - Using GPT, ***only*** down to the agency's low point limit for stable (non-drifting), accurate O_3 generation
- What will work for TL NO_y?
  - Using the more stable NPN for the MB (with or without CO); depending on stability, as indicated by 6 month re-certifications