ELECTRIC POWER RESEARCH INSTITUTE

Inorganic Continuous Aerosol Monitoring System (ICAMS):

Handout for US EPA Integrated Nitrogen Committee

May 14, 2009
Washington, D.C.

Eladio Knipping
Senior Technical Manager

Stephanie Shaw
Project Manager

Motivation

- Real-time data on reactive nitrogen species are needed at multiple locations to understand fluxes, dynamics of $PM_{2.5}$, and to constrain atmospheric models, etc.

- Existing methods (research and commercial) have proven problematic for widespread deployment.

© 2009 Electric Power Research Institute, Inc. All rights reserved.

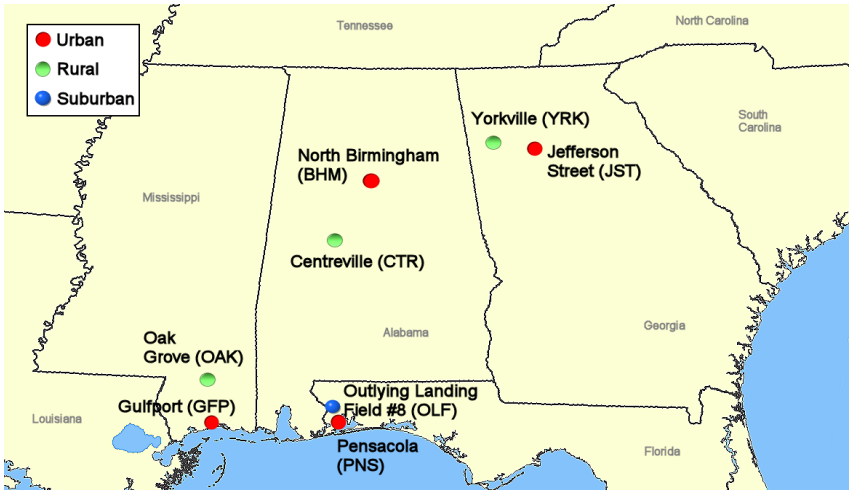
Proposed Approach

- Modify SEARCH research-grade analyzers for routine operation and conformance with routine monitoring resources (data system, etc.)

- Use SEARCH sites as a test-bed for demonstrating comparability of routine analyzers, both with research-grade analyzers and "gold standard" integrative samplers.

© 2009 Electric Power Research Institute, Inc. All rights reserved.

iCAMS Study Sites



Southeastern Aerosol Research and Characterization Network (SEARCH)

EPRI – Southern Company

© 2009 Electric Power Research Institute, Inc. All rights reserved.

EPRI ELECTRIC POWER RESEARCH INSTITUTE

Jefferson Street (JST): Atlanta, GA

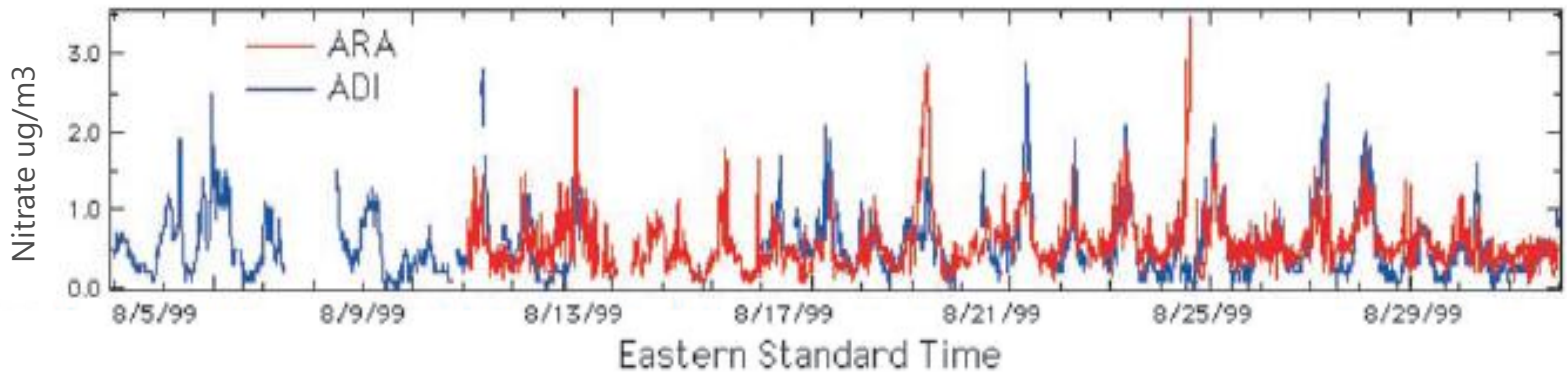
Jun 1998 to Present

Location of EPA SuperSite: Aug 1999

© 2009 Electric Power Research Institute, Inc. All rights reserved.

ELECTRIC POWER RESEARCH INSTITUTE

iCAMS Predecessor for Atlanta Supersite Experiment (1999)



- Captured time resolution and magnitude similarly to other available instruments, e.g., integrated collection and vaporization cell; Aerosol Dynamics, Inc.; Stolzenburg & Hering (2000)
- Some differencing errors at low nitrate concentrations; subsequent versions were substantially improved through NOx suppression

Weber et al. 2003 10.1029/2001JD001220

© 2009 Electric Power Research Institute, Inc. All rights reserved.

ELECTRIC POWER RESEARCH INSTITUTE

SEARCH Measurements: 8 Sites

- Discrete Particles and Gases (24-hour)
  - FRM: $PM_{2.5}$
  - PCM and Dichot: $PM_{2.5}$, PM_{10} and Speciation
  - Annular Denuder: NH_3
- Continuous Particles (1-min to 1-hr)
  - TEOM: fine mass
  - Sunset Laboratories: OC/EC/TC
  - Aethelometer: BC
  - SEARCH/ARA: Ammonium/Nitrate
  - Modified HSPH: Sulfate
- Trace Gases (1-min)
  - O_3, NO, NO_2, NOy, HNO_3, SO_2, CO, NH_3
- Meteorology and Visibility (1-min)
  - WS, WD, T, RH, BP, SR, rainfall, dry scattering, dry absorption

© 2009 Electric Power Research Institute, Inc. All rights reserved.

Further Development: SEARCH Continuous Measurements (2000-2006)

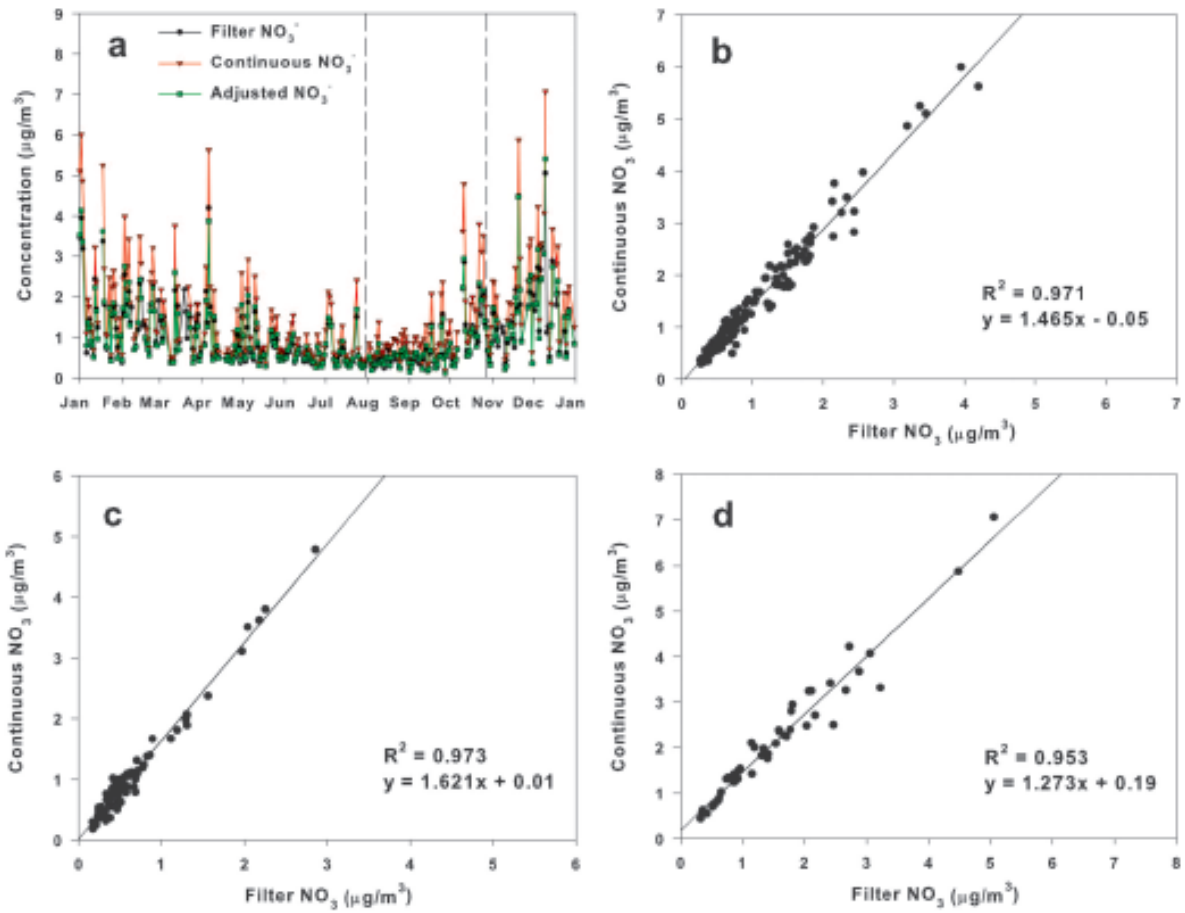


Figure 1. Example data adjustments for NO_3^- at JST. (a) Daily time series for 2002; (b) continuous NO_3^- vs. filter NO_3^-, January 1 to July 30, 2002; (c) continuous NO_3^- vs. filter NO_3^-, August 2 to October 25, 2002; (d) continuous NO_3^- vs. filter NO_3^-, October 26 to December 31, 2002.

Edgerton et al. 2006 JAWMA 56, Sept

© 2009 Electric Power Research Institute, Inc. All rights reserved.

ELECTRIC POWER RESEARCH INSTITUTE

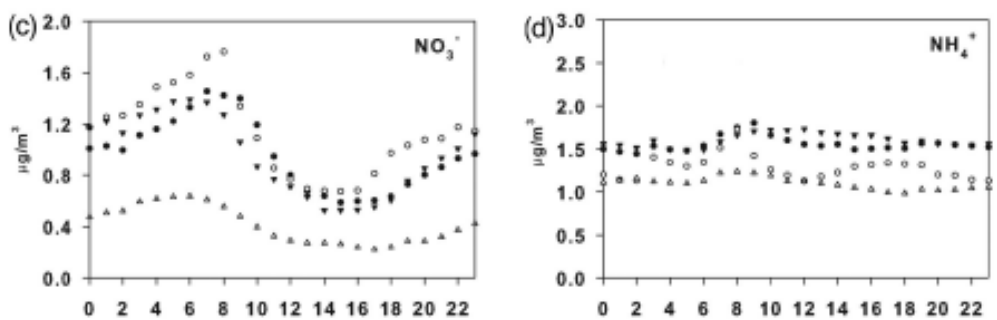
Further Development: SEARCH Continuous Measurements (2000-2006)

NOx suppression with activated carbon honeycomb denuders (MAST 'monolith')

Table 3. Statistical summary of continuous $PM_{2.5}$ measurements (adjusted) at JST.

Analyte	n	Filter (μg/m³) Mean	Filter (μg/m³) SD	Continuous (μg/m³) Mean	Continuous (μg/m³) SD	Absolute Error (μg/m³) Mean	Absolute Error (μg/m³) SD	Relative Error (%) Mean	Relative Error (%) SD
$PM_{2.5}$[a]	304	15.93	7.01	16.16	7.25	1.22	1.06	8.1	6.8
SO_4^{2-}	312	4.43	3.24	4.46	3.25	0.32	0.32	8.5	8.7
NO_3^-	307	0.84	0.85	0.85	0.84	0.09	0.11	13.9	13.2
NH_4^+	315	1.53	0.99	1.53	0.98	0.13	0.11	11.1	11.5
TC[a]	271	5.78	3.11	5.86	3.27	0.97	0.83	18.1	14.0
OC[a]	256	4.47	2.39	4.51	2.68	1.00	0.79	24.3	17.4
BC[a]	339	1.31	0.81	1.20	0.86	0.25	0.22	21.2	15.2

Notes: SD = standard deviation; Absolute Error = continuous − filter; % Relative Error = 100*(continuous − filter)/filter. Absolute and relative error statistics refer to individual data points. [a]2002 data, otherwise 2003.



Hour

Hour

Edgerton et al. 2006 JAWMA 56, Sept

© 2009 Electric Power Research Institute, Inc. All rights reserved.

ELECTRIC POWER RESEARCH INSTITUTE

ARA iCAMS: Research Prototype

- Modify SEARCH research-grade analyzers for routine operation and conformance with routine monitoring resources (data system, etc.)

- Use SEARCH sites as a test-bed for demonstrating comparability of routine analyzers, both with research-grade analyzers and "gold standard" integrative samplers.

© 2009 Electric Power Research Institute, Inc. All rights reserved.

HNO_3 Method

- Two Channel (CH) total oxidized nitrogen (NOy) analyzer
- Channel 1 directly samples ambient air through a Mo converter (NOy)
- Channel 2 samples ambient air through a KCl denuder then a Mo converter (NOy*)
- HNO_3 operationally defined as NOy-NOy*

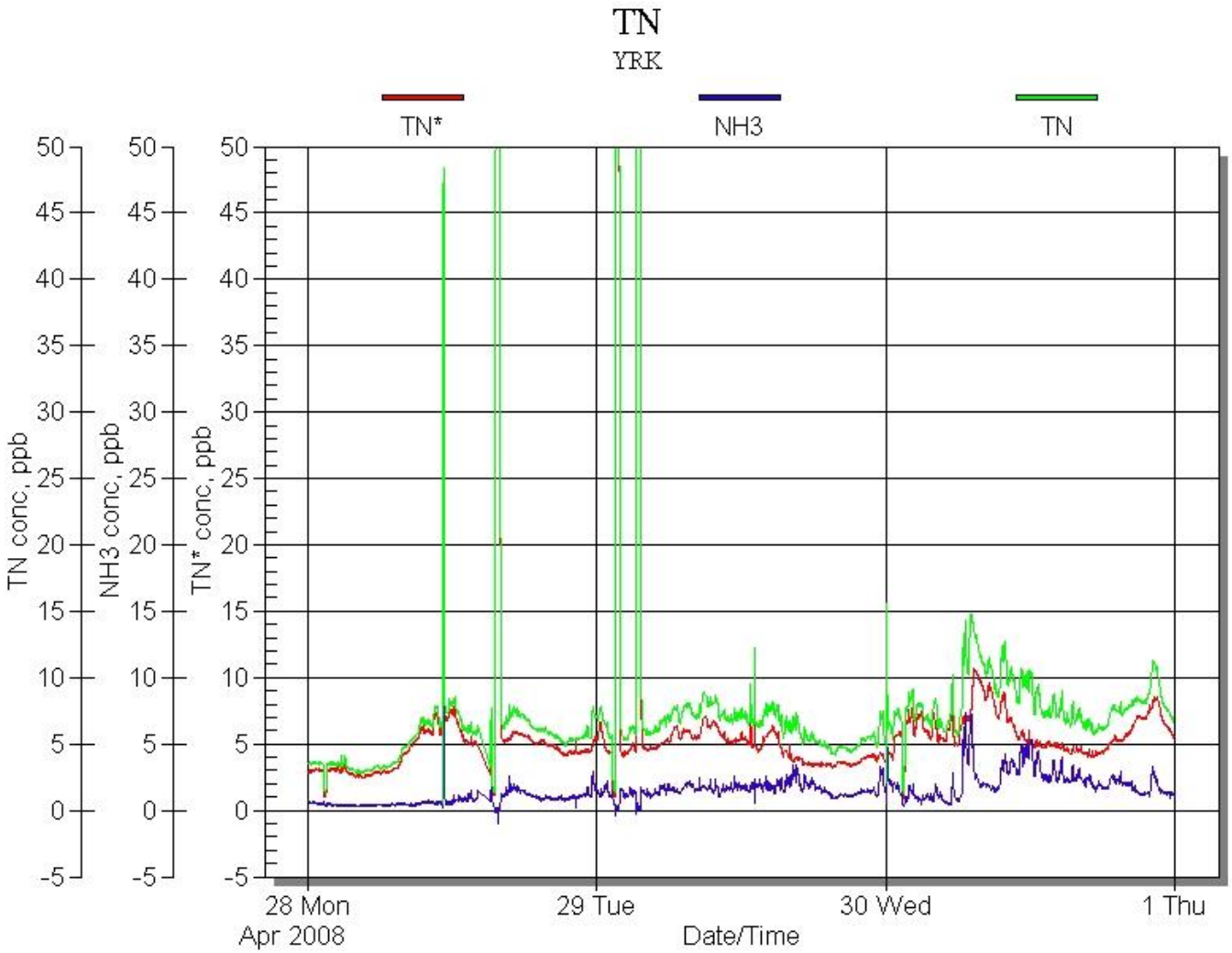
© 2009 Electric Power Research Institute, Inc. All rights reserved.

NH_3 Method

- Two channel oxidized AND reduced nitrogen (TN) analyzer
- Channel 1 samples ambient air through a sodium carbonate denuder then Pt/Mo converters in series (TN)
- Channel 2 samples ambient air through dual sodium carbonate and citric acid denuders then Pt/Mo converters in series (TN*)
- NH_3 operationally defined as TN-TN*

© 2009 Electric Power Research Institute, Inc. All rights reserved.

Raw TN/TN*/NH_3 Trace at YRK



© 2009 Electric Power Research Institute, Inc. All rights reserved.

ELECTRIC POWER RESEARCH INSTITUTE

$PM_{2.5}$ NO_3^- and NH_4^+ Method

- Three channel (CH) analyzer: background NO_x denuded at common inlet
  - CH1 - KCl filter/NOy converter
  - CH2 - Mo converter only
  - CH3 - Pt and Mo converters in series
- NO_3^- operationally defined as CH2-CH1
- NH_4^+ operationally defined as CH3-CH2

© 2009 Electric Power Research Institute, Inc. All rights reserved.

Advantages to Proposed Approach

- Uses commercial O_3-NO CL analyzers to measure target species
- Analyzers are routinely used by the monitoring community for criteria pollutants (i.e., well-known technology)
- Uses time-tested denuder techniques to separate gases and particles
- No messy liquids or potentially dangerous chemicals

© 2009 Electric Power Research Institute, Inc. All rights reserved.

Disadvantages to Proposed Approach

- Indirect technique: only measures oxidized and reduced forms of nitrogen, not specific compounds (positive biases). For example, to the extent NO_2 is removed by a KCl denuder, it will be interpreted as HNO_3.

- Differencing technique: quantifies target species based on difference between two channels of the NOx analyzer
  - Noisy when background NOx highly variable (single detector issue)
  - Noisy when background NOx is high (needle in haystack issue)

© 2009 Electric Power Research Institute, Inc. All rights reserved.

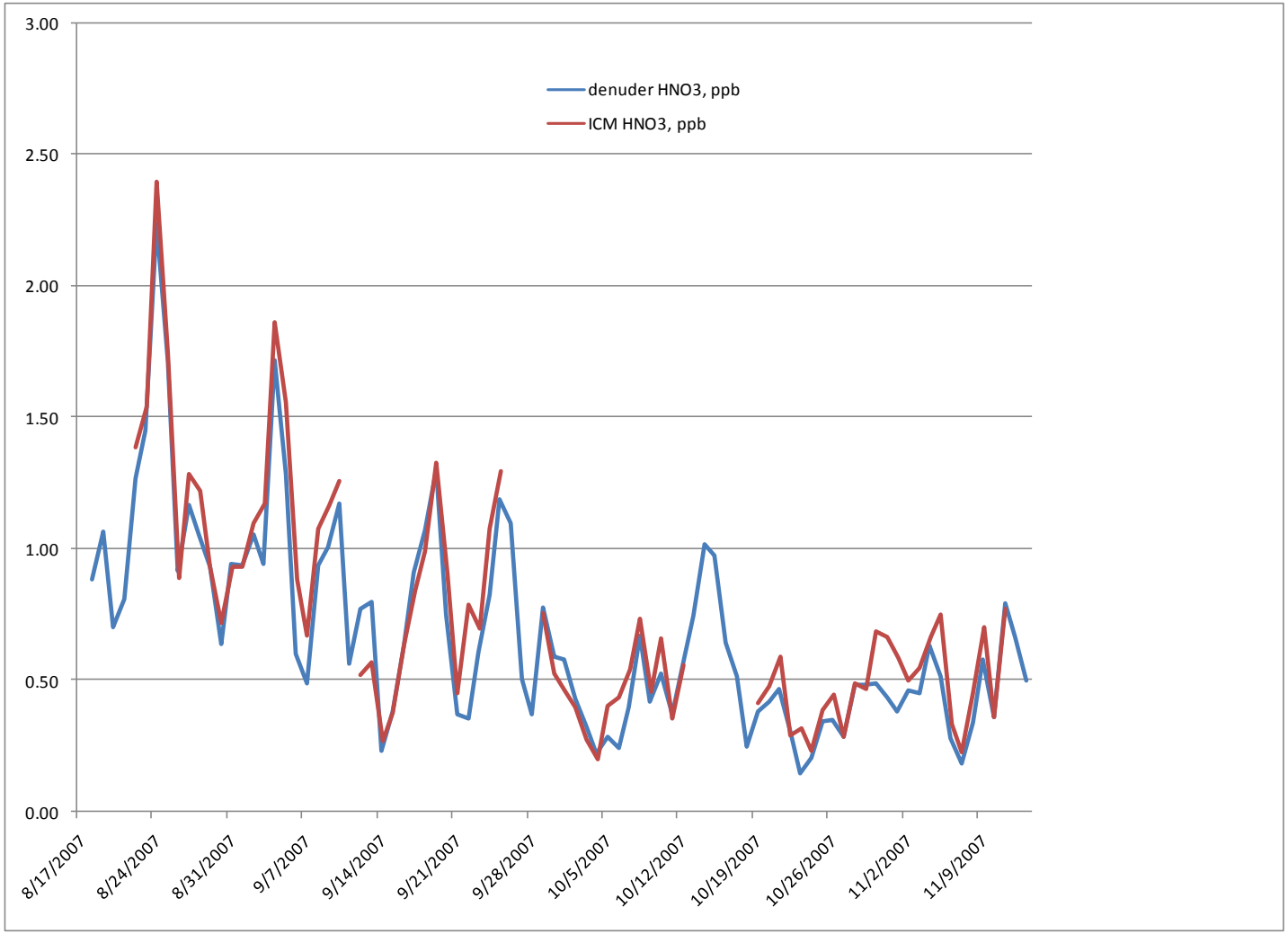
ARA iCAMS Study Timeline

- 3/06-7/07: design and fabrication
- 8/06-11/07: field testing, Atlanta, GA (JST)
- 11/07-12/07: field testing at YRK

- 2008: Further refinements (Air Quality Design, Inc.) and field testing with PILS at YRK

© 2009 Electric Power Research Institute, Inc. All rights reserved.

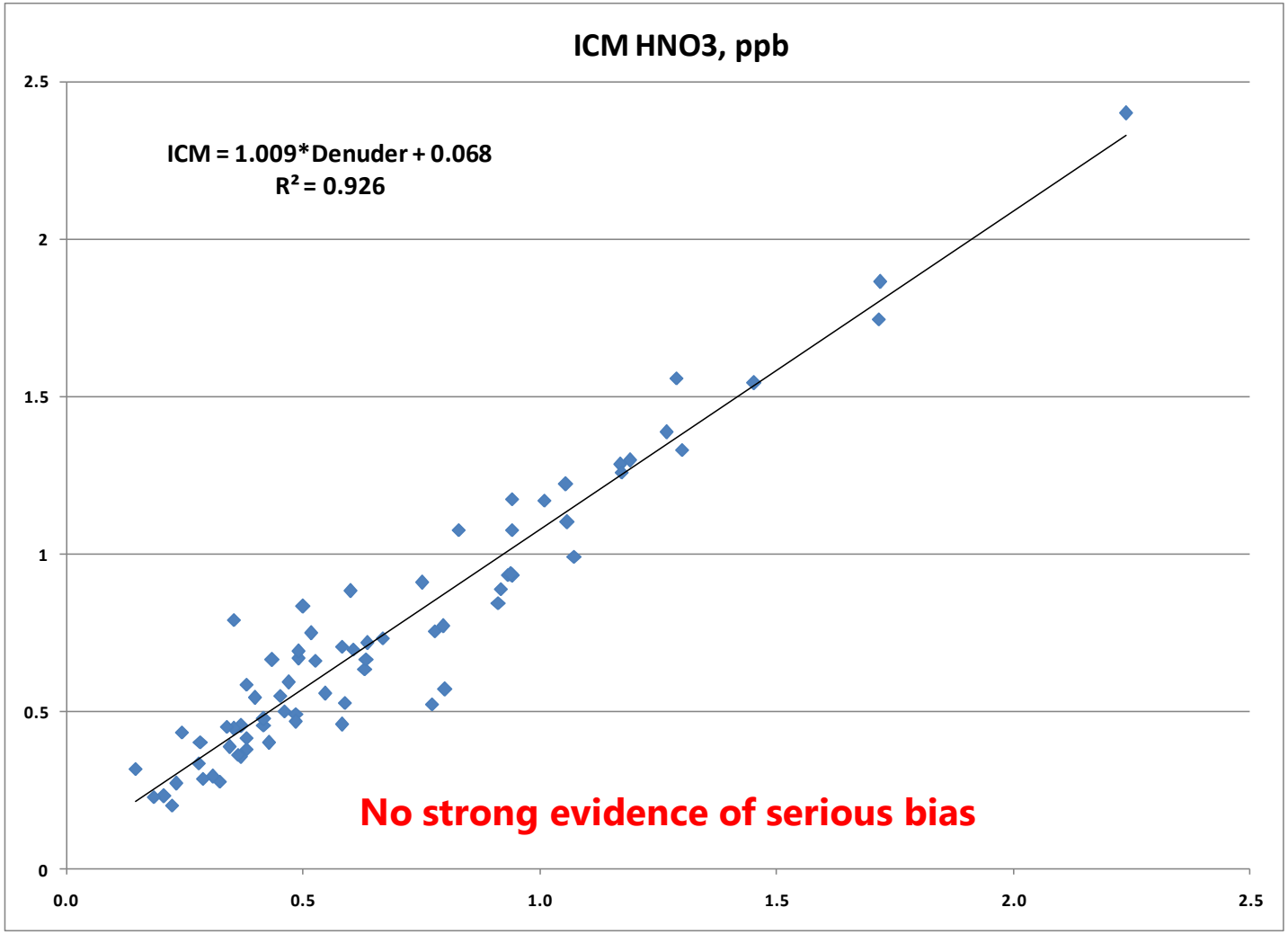
ARA iCAMS and Denuder HNO_3 at JST



© 2009 Electric Power Research Institute, Inc. All rights reserved.

ELECTRIC POWER RESEARCH INSTITUTE

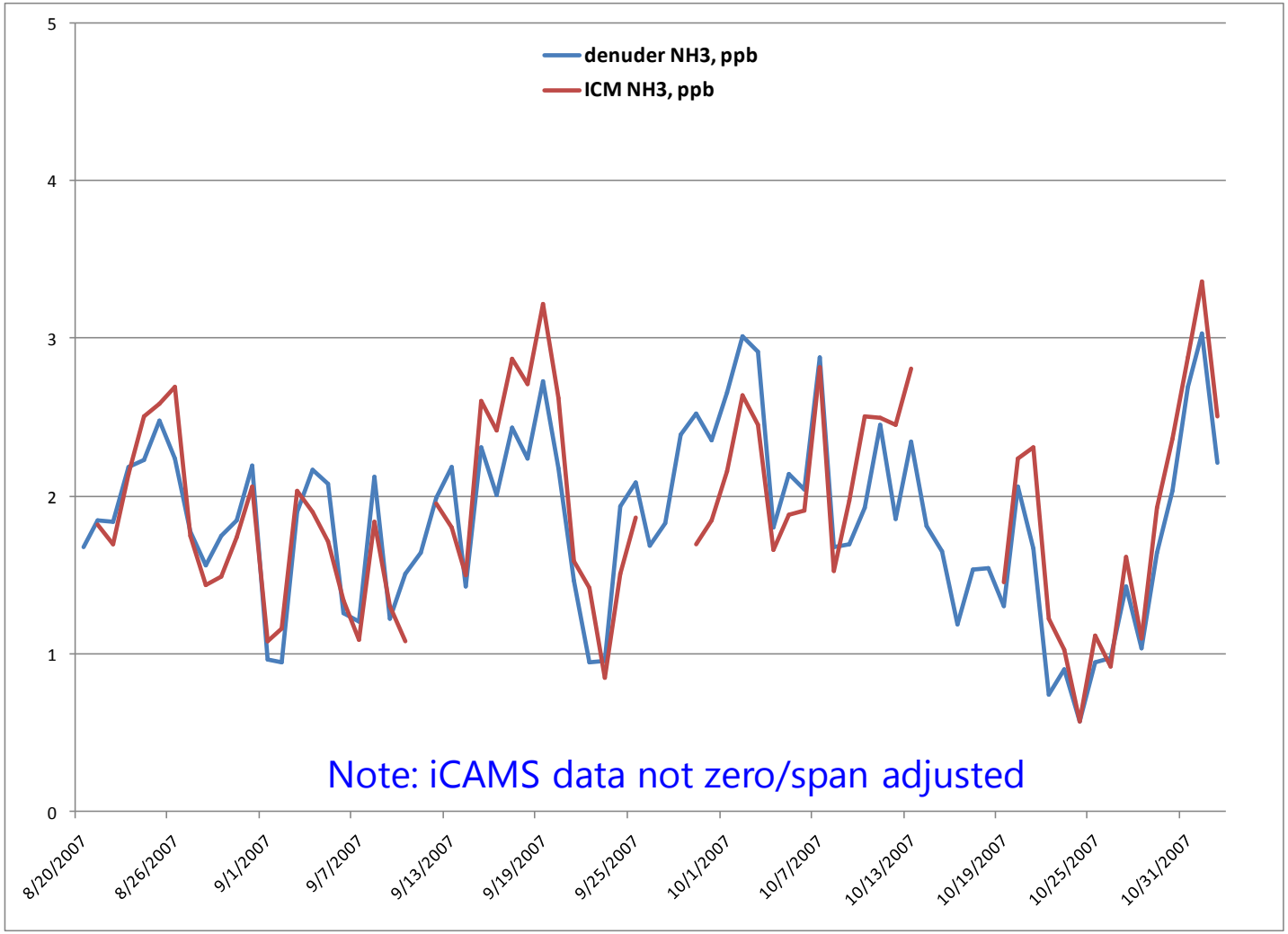
ARA iCAMS vs. Denuder HNO_3 at JST



© 2009 Electric Power Research Institute, Inc. All rights reserved.

ELECTRIC POWER RESEARCH INSTITUTE

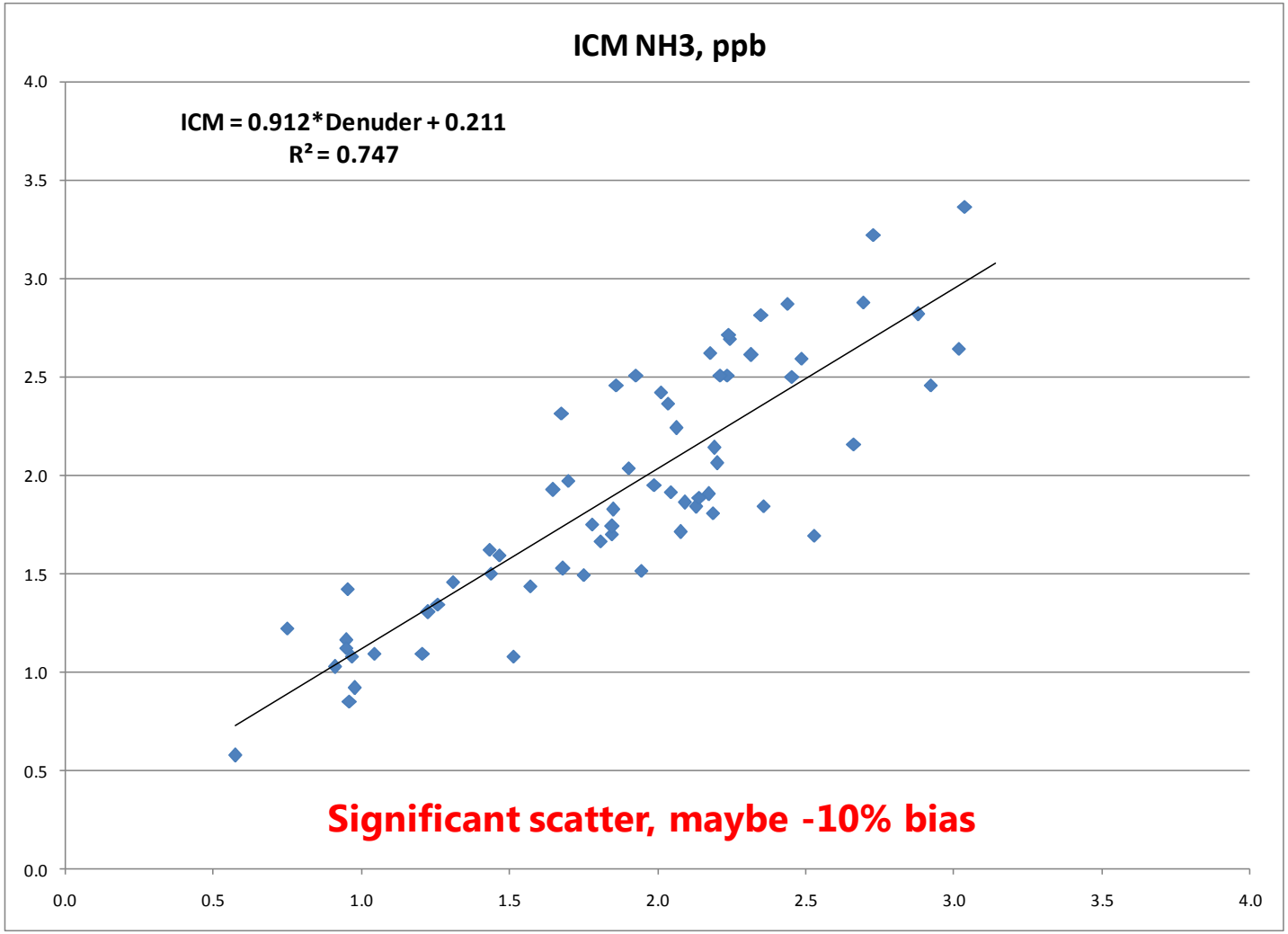
ARA iCAMS and Denuder NH_3 at JST



© 2009 Electric Power Research Institute, Inc. All rights reserved.

ELECTRIC POWER RESEARCH INSTITUTE

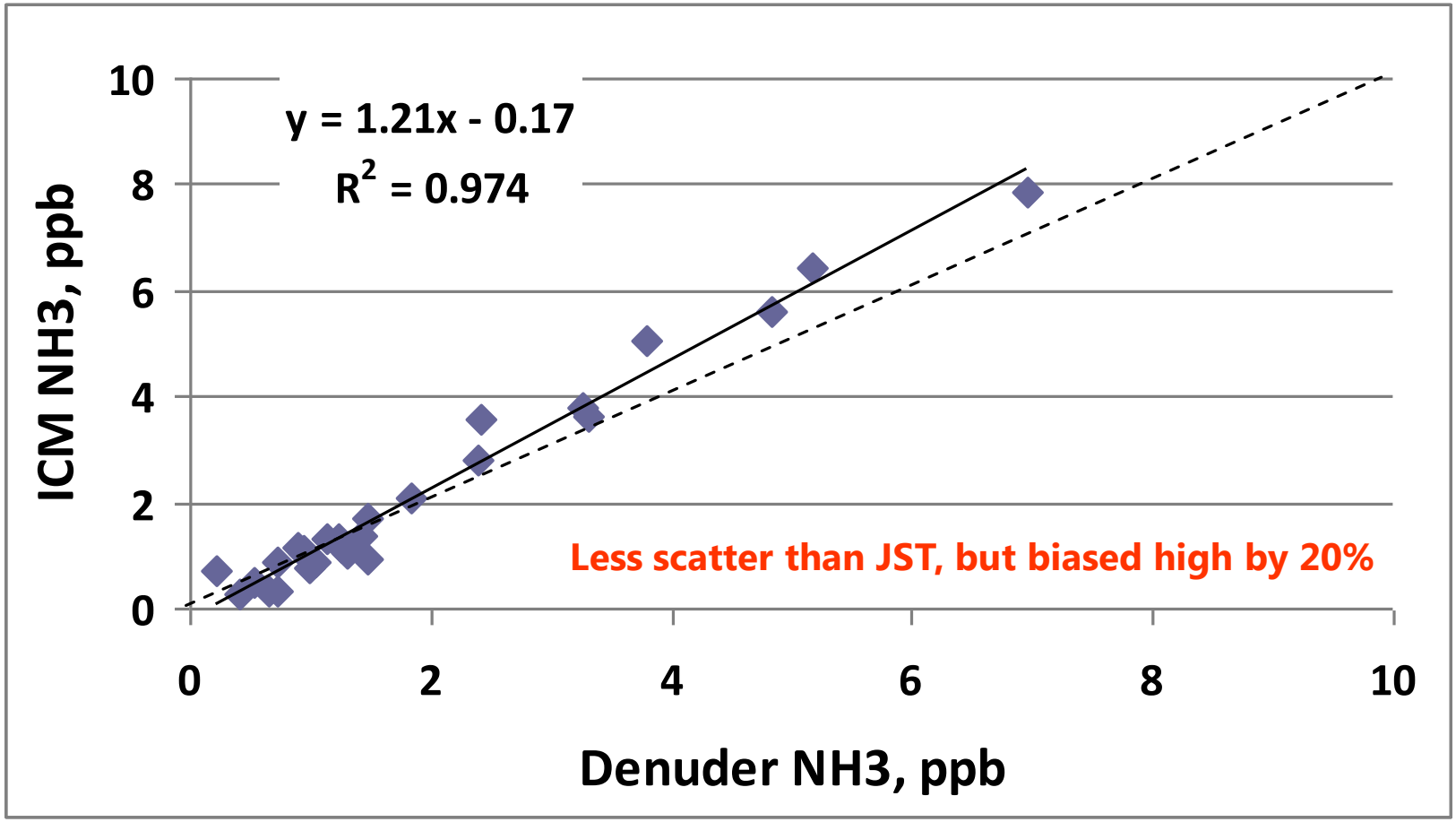
ARA iCAMS vs. Denuder NH_3 at JST



© 2009 Electric Power Research Institute, Inc. All rights reserved.

ELECTRIC POWER RESEARCH INSTITUTE

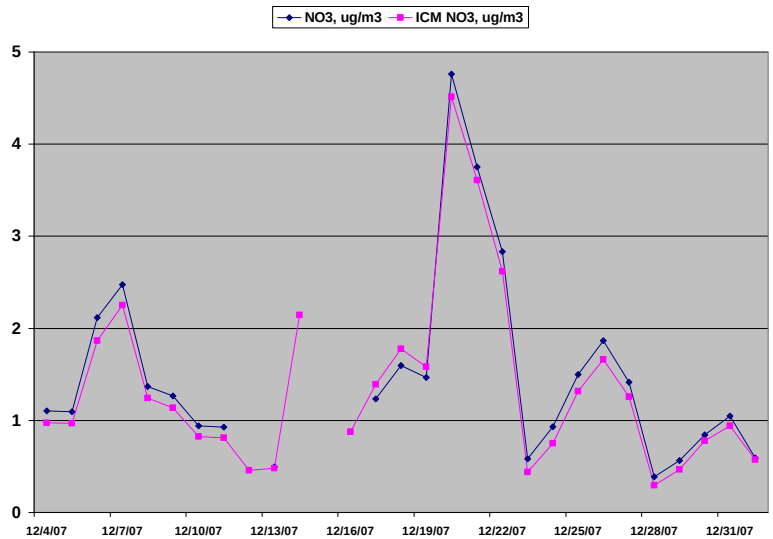
iCAMS vs. Denuder NH_3 at YRK

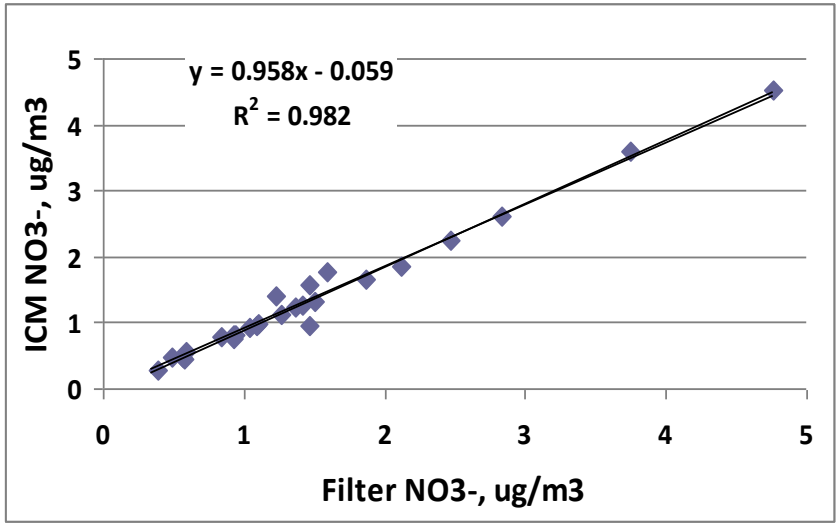


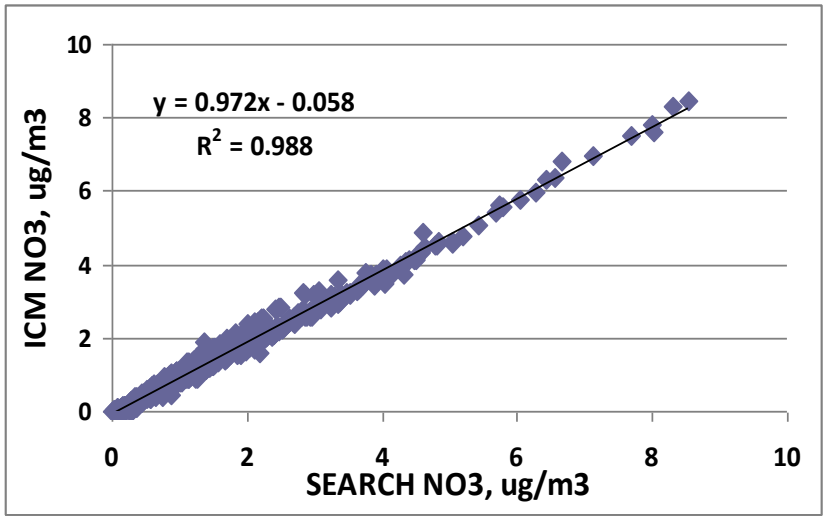
© 2009 Electric Power Research Institute, Inc. All rights reserved.

ELECTRIC POWER RESEARCH INSTITUTE

NO_3^- Measurements at YRK: 24-Hour





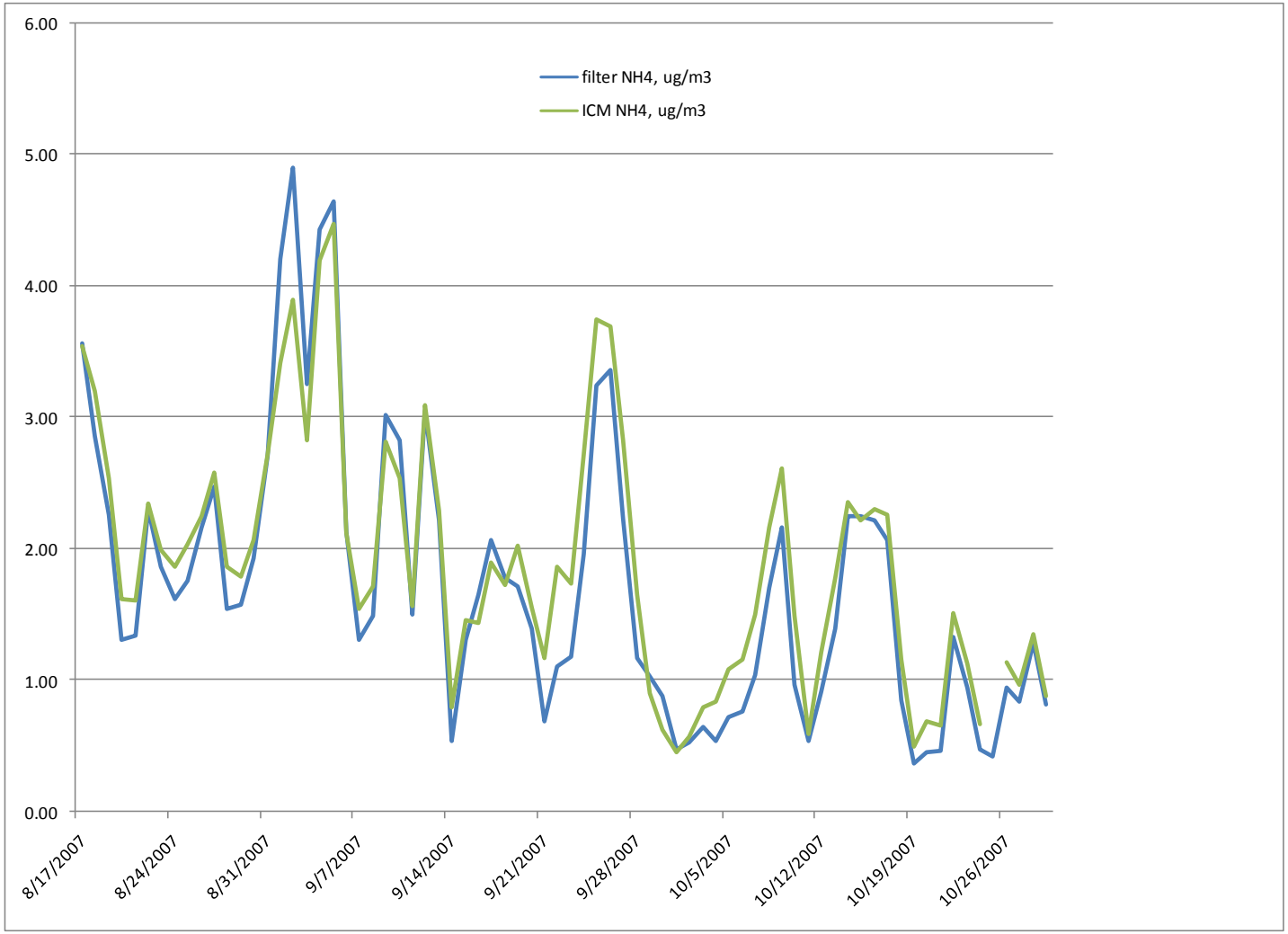


Hourly data

© 2009 Electric Power Research Institute, Inc. All rights reserved.

ELECTRIC POWER RESEARCH INSTITUTE

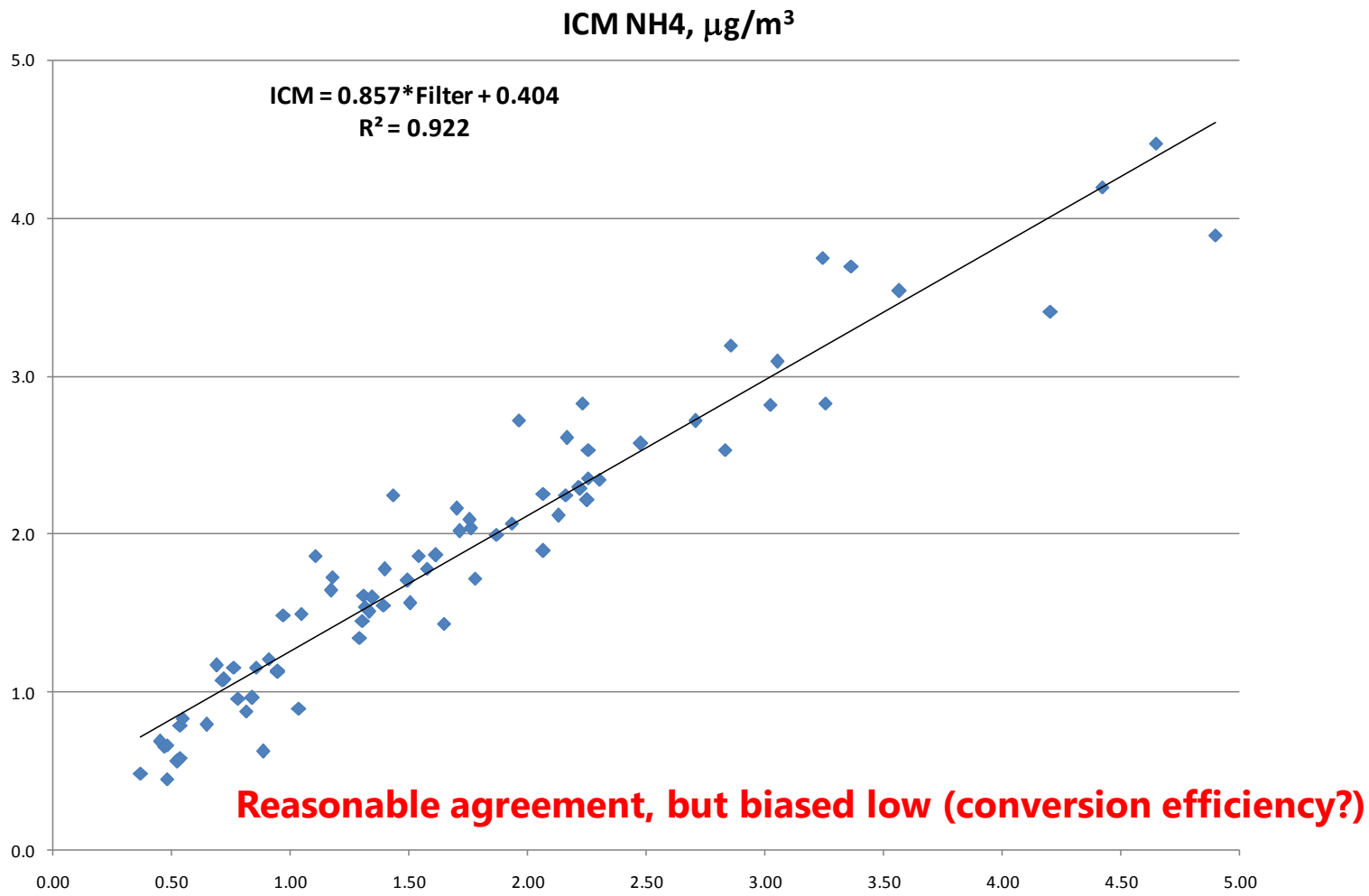
ARA iCAMS and Filter-based NH_4^+ at JST



© 2009 Electric Power Research Institute, Inc. All rights reserved.

ELECTRIC POWER RESEARCH INSTITUTE

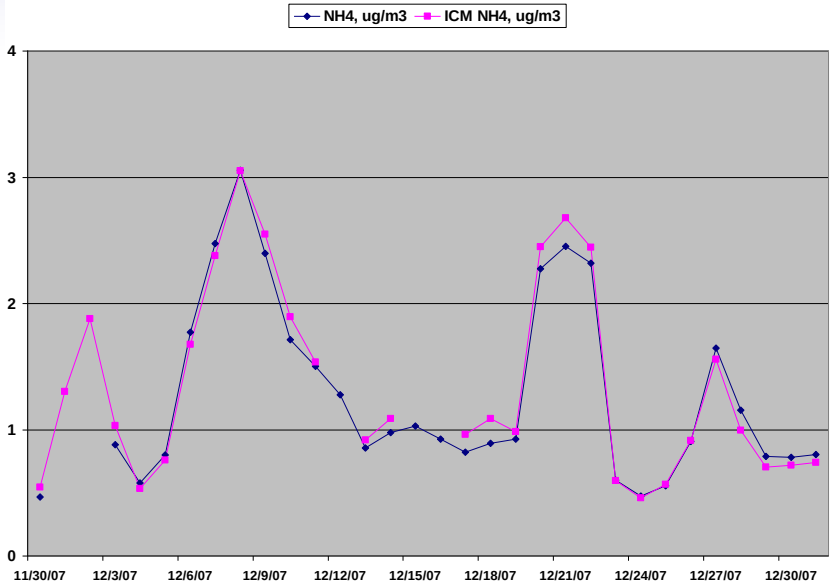
ARA iCAMS vs. Filter-based NH_4^+ at JST

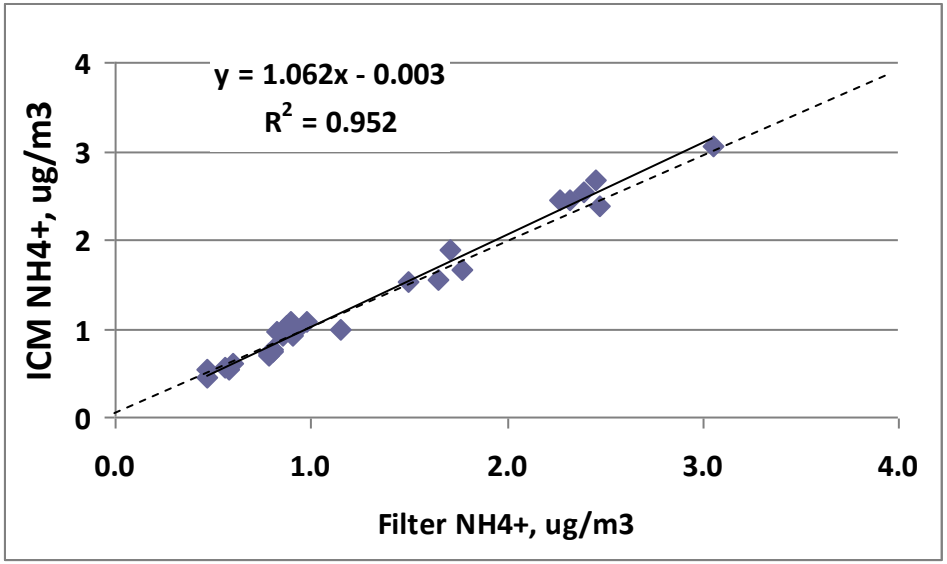


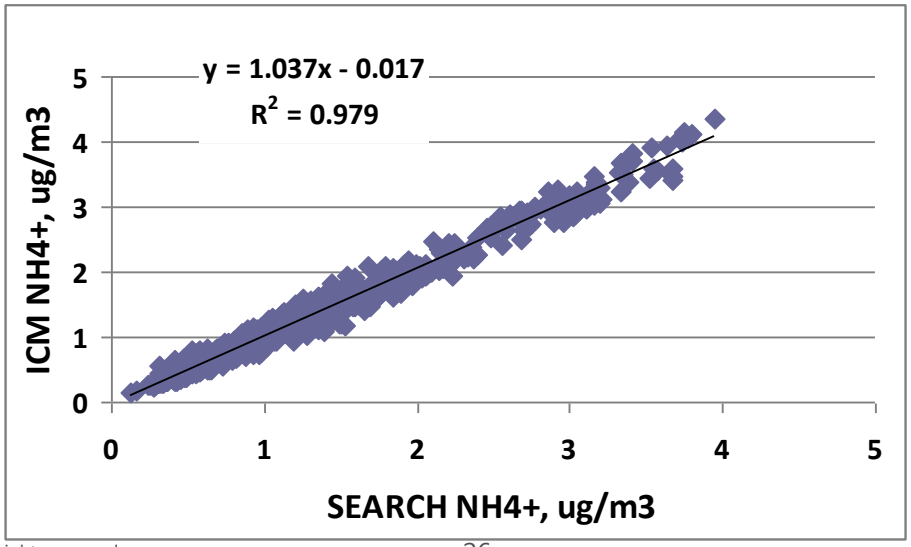
© 2009 Electric Power Research Institute, Inc. All rights reserved.

ELECTRIC POWER RESEARCH INSTITUTE

NH_4^+ Measurements at YRK







Hourly data

© 2009 Electric Power Research Institute, Inc. All rights reserved.

ELECTRIC POWER RESEARCH INSTITUTE

Summary of 2007 ARA iCAMS Field Tests

Var.	Site	Det. Lt.[a]	Slope	Int.[a]	r^2	Prec. (%)
HNO_3	JST	85	1.01	68	0.93	15
	YRK	36	0.82	105	0.88	18
NH_3	JST	107	0.91	211	0.75	22
	YRK	48	1.21	-170	0.97	14
NH_4^+	JST	99	0.86	404	0.92	8
	YRK	45	1.06	3	0.95	9
NO_3^-	JST	58	1.03	-48	0.96	11
	YRK	58	0.96	59	0.98	12

a – units for gases are ppt, units for particles are ng/m^3

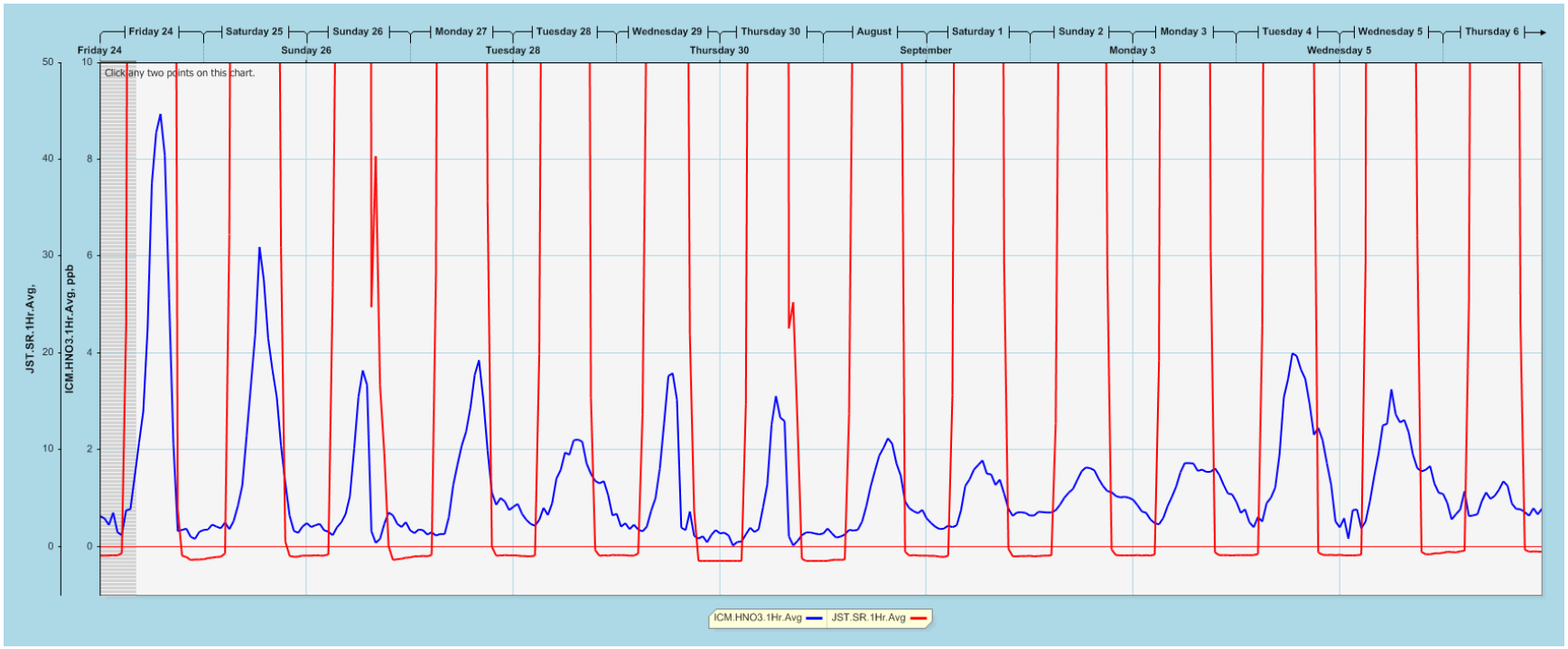
© 2009 Electric Power Research Institute, Inc. All rights reserved.

ARA iCAMS: Short-Term Variability

- Important for deducing what analyzers are really measuring

© 2009 Electric Power Research Institute, Inc. All rights reserved.

Hourly HNO_3 and SR at JST



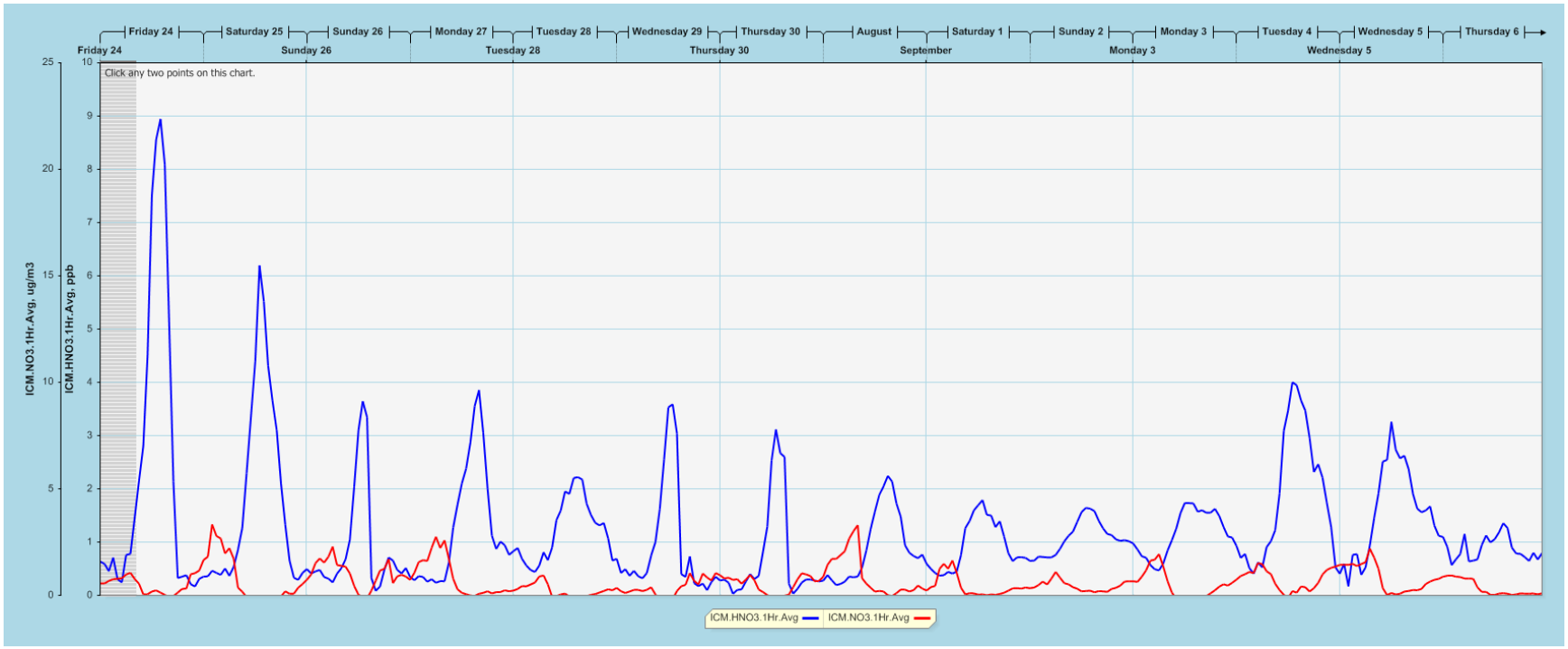
Note several hour delay between sunrise and HNO_3 increase. Suggestive that HNO_3 signal is not grossly contaminated by sunrise photochemistry.

© 2009 Electric Power Research Institute, Inc. All rights reserved.

ELECTRIC POWER RESEARCH INSTITUTE

Hourly HNO_3 and NO_3^- at JST

(Different scales used to show molar equivalent concentrations)

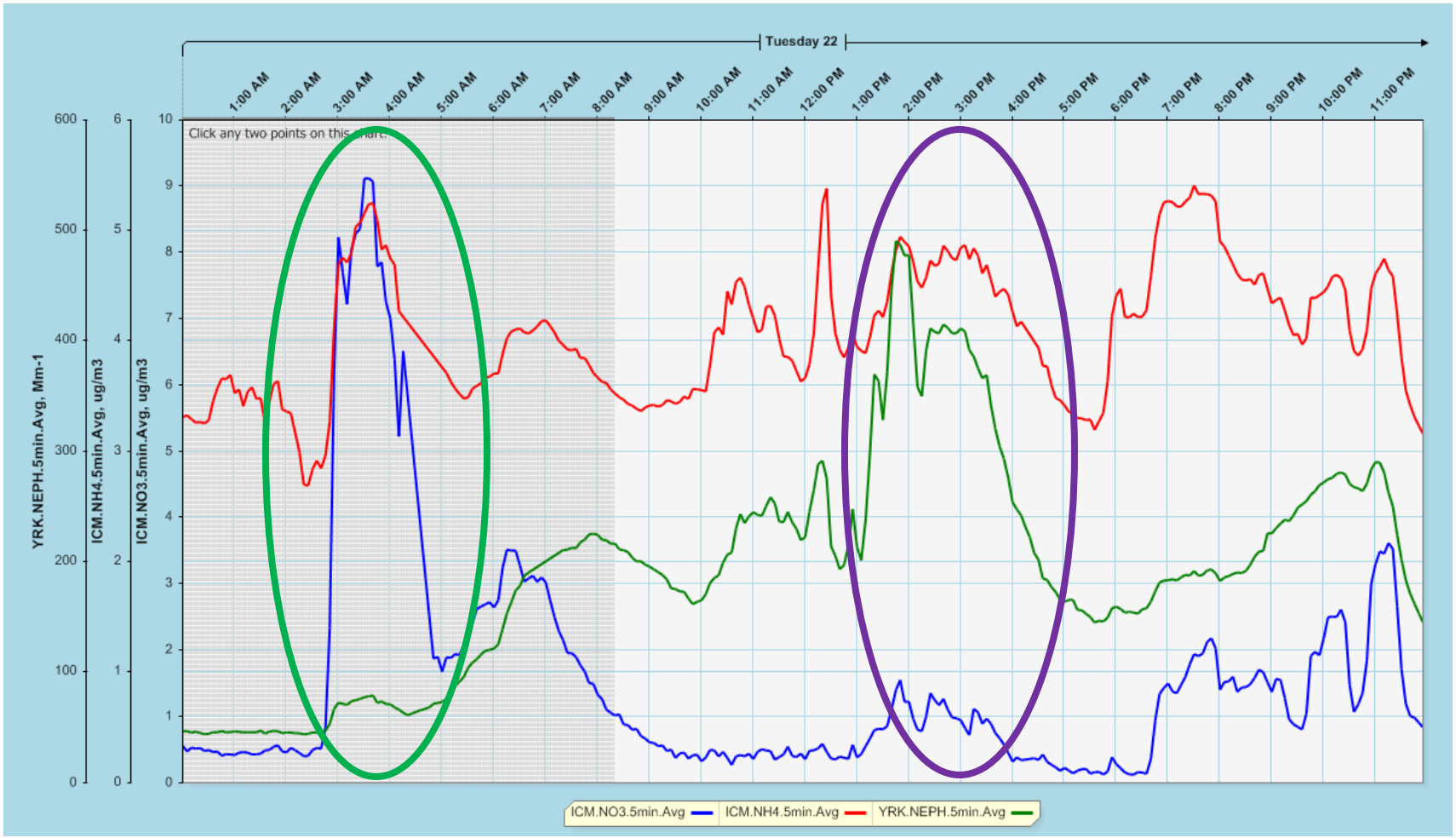


Note opposing diel cycles. Suggests that only a small fraction of HNO_3 is locally converted to particle phase.

© 2009 Electric Power Research Institute, Inc. All rights reserved.

ELECTRIC POWER RESEARCH INSTITUTE

Two different events same day

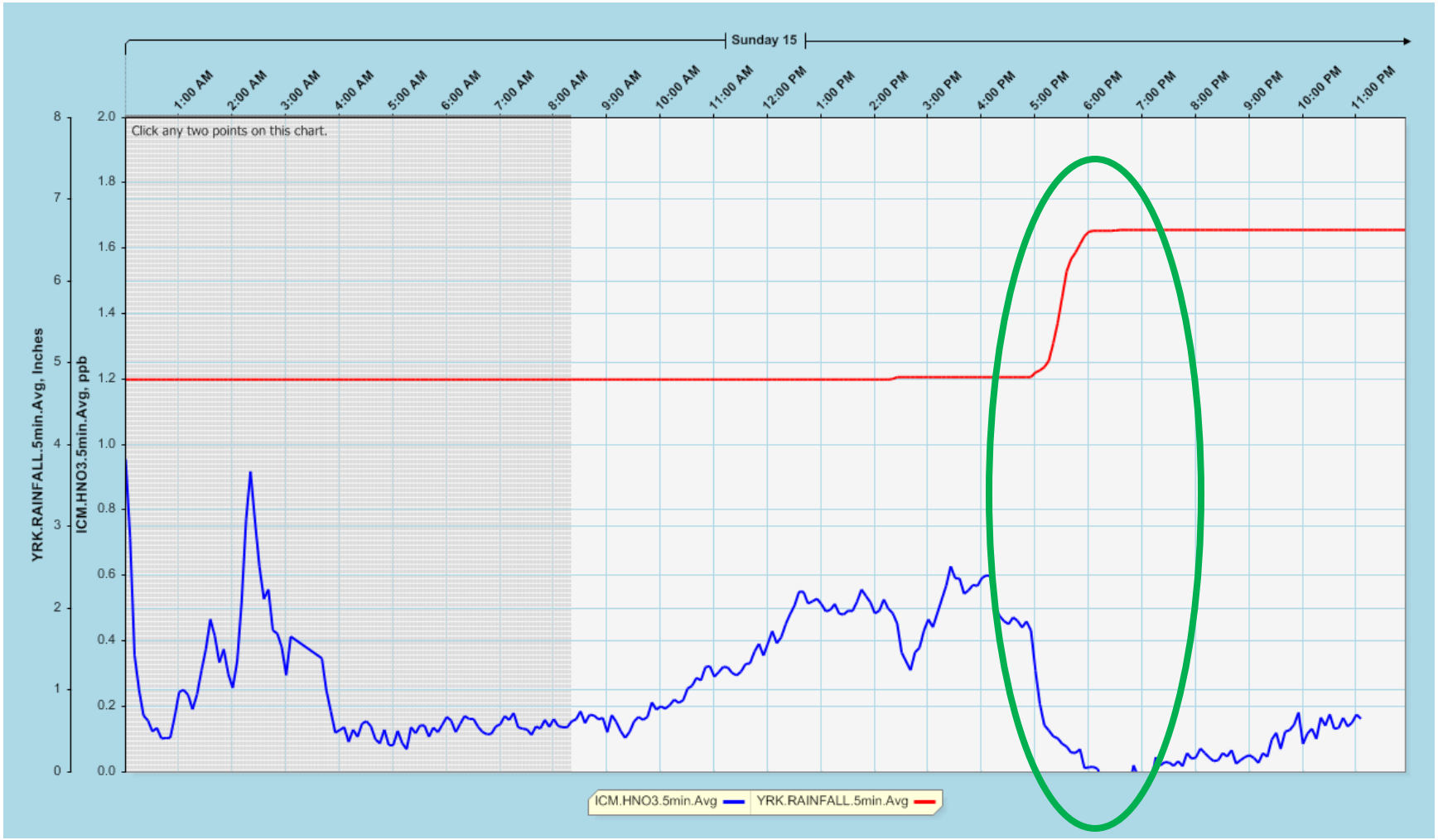


Early peak (green ellipse) exhibits dNH_4^+/dNO_3^- of 0.31 versus 0.29 for pure NH_4NO_3 ; Late peak (purple ellipse) shows only minor increases in NO_3^- and NH_4^+ during major smoke event (B_{sp} >400 Mm^{-1}).

© 2009 Electric Power Research Institute, Inc. All rights reserved.

ELECTRIC POWER RESEARCH INSTITUTE

Rainfall Event at YRK



For significant events, HNO_3 driven below 100 ppt.

© 2009 Electric Power Research Institute, Inc. All rights reserved.

ELECTRIC POWER RESEARCH INSTITUTE

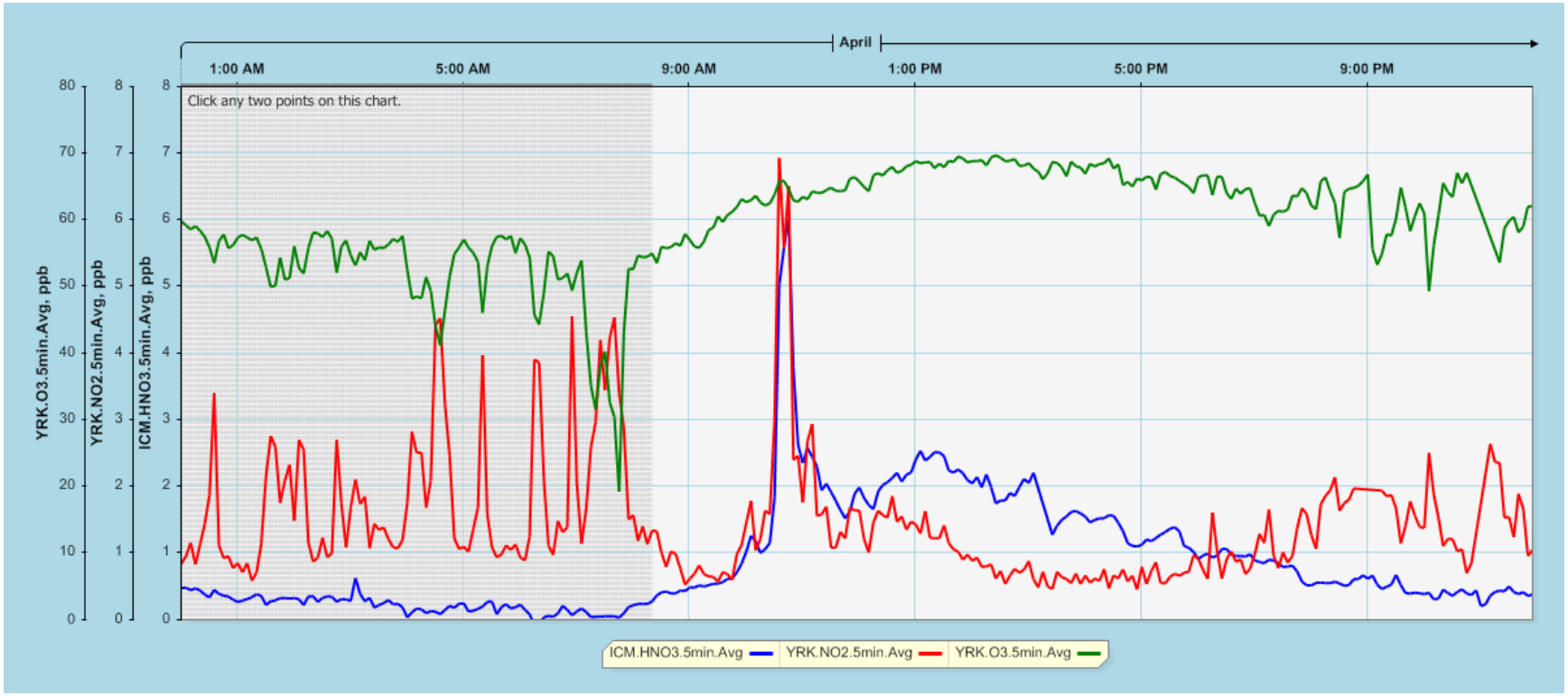
NH_3 Time Series at OAK

Similarly for NH_3 at a rural-forested site.

© 2009 Electric Power Research Institute, Inc. All rights reserved.

ELECTRIC POWER RESEARCH INSTITUTE

5-minute HNO_3, NO_2 and O_3 at YRK
Note: NO (not shown) is dead zero overnight



Absence of correlation between HNO_3 and NO_2 suggests the HNO_3 signal is not appreciably contaminated by NO_2 (and probably also not by N_2O_5)

© 2009 Electric Power Research Institute, Inc. All rights reserved.

ELECTRIC POWER RESEARCH INSTITUTE

ARA iCAMS: Summary and Next Steps

- Real-time analyzers for gas phase and particulate nitrogen species have been built and field tested
- Initial findings indicate good agreement (<+/- 25%) with filter/denuder measurements
- 5-minute and 1-hour data show very interesting (and encouraging) short-term behavior

Next Steps (2008 to Present)

- Refine/Consolidate inlets
- Summer 2008 Field Testing
  - hourly averages vs. IC-based systems
- Commercialize analyzers

© 2009 Electric Power Research Institute, Inc. All rights reserved.

Integrated Continuous Aerosol Monitoring System (First Commercial Prototype 1)

Air Quality Design, Inc.
AQD iCAMS

Gas and Particle Nitrogen by Denuder Difference

- First commercial-grade instrument for routine regulatory monitoring of

- Gas HNO_3 and NH_3
- Particle NO_3^- & NH_4^+
- Semi-continuous (hourly)
- Easy to use & maintain
- 3 component design for flexibility

© 2009 Electric Power Research Institute, Inc. All rights reserved.

iCAMS Development Overview: 1999-Present

Supersite Predecessor (1999)

NO_3^-

Described in Weber et al. 2003

Dual sodium hypochlorite-coated annular denuders to suppress NOx background

NH_4^+

Described in Edgerton et al. 2006 and Solomon & Sioutas 2008

Used a Pt/Alumina catalyst

HNO_3

Described in Solomon et al 2003

2 channel NOy and NOy–HNO_3 difference with KCl denuder

Also NOy

NH_3

Not measured

SEARCH and ARA-ICAMS

NO_3^-

Described in Edgerton et al 2006 and Solomon & Sioutas 2008

2 activated carbon honeycomb denuders (MAST 'monolith') for suppression of NOx background

NH_4^+

Described in Edgerton et al. 2006 and Solomon & Sioutas 2008

2 activated carbon honeycomb denuders (MAST 'monolith') for suppression of NOx background

Pt/Alumina in shot form for NH_4^+ oxidation (cheaper, conversion at low T, maintains high conversion efficiency longer)

HNO_3

Unchanged from Supersite

NH_3

Described in Saylor et al, to be submitted and 2008 AWMA Visibility Meeting Abstract (Edgerton et al.)

Other

Ballasts to synchronize flows
All annular denuders (all denuders but carbon) were URG (SEARCH version) or Sunset (ARA-ICAMS)

AQD-ICAMS: Prototype 1

NO_3^-

Zero calculation in software

NH_4^+

Zero calculation in software

HNO_3

Unchanged from ARA-ICAMS

NH_3

Unchanged from ARA-ICAMS

Other

Robust & compact packaging (1/2 to 2/3 less inlet volume)

Ethernet controlled

Plumbed for easy maintenance

Reduced # ovens

Post-process sample averaging

© 2009 Electric Power Research Institute, Inc. All rights reserved.

EPRI ELECTRIC POWER RESEARCH INSTITUTE

2008 AMIGAS:
August Mini-Intensive Gas and Aerosol Study

7 Labs and ~15 Datasets Beyond SEARCH

- Day vs. night chemistry
- Effects of manmade emissions on natural aerosols
- Effects of natural emissions on manmade aerosols

Account for Nitrogen in Air =

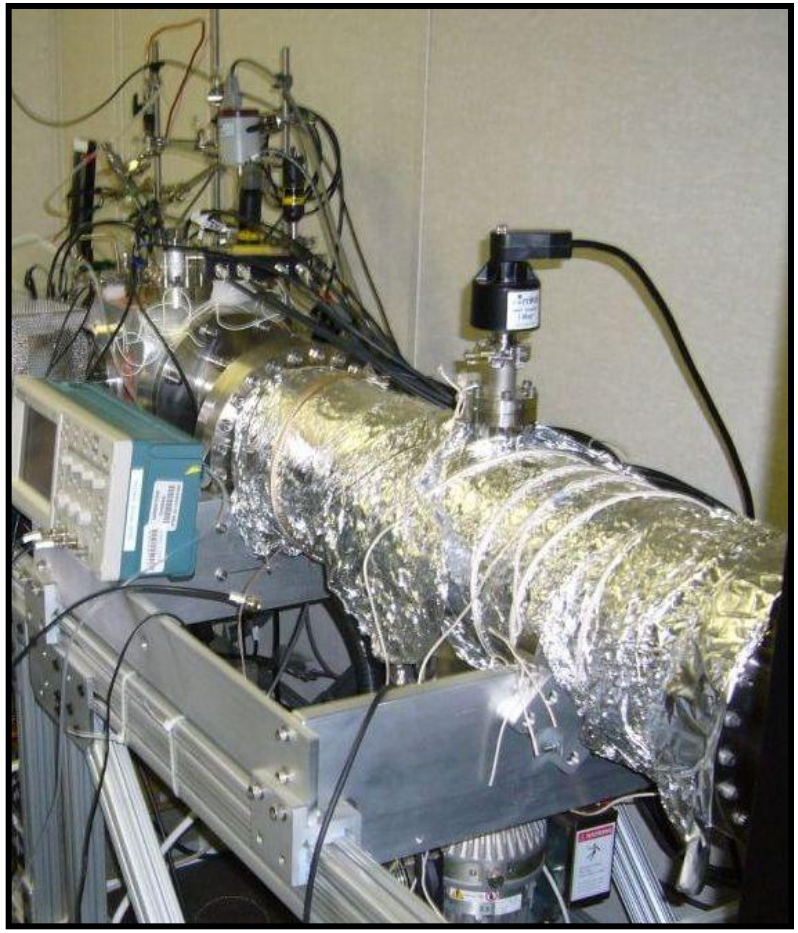
Gases and Particles; Oxidized and Reduced; Inorganic and Organic

© 2009 Electric Power Research Institute, Inc. All rights reserved.

Chemical Ionization – Aerosol Time-of-Flight Mass Spectrometer

Novel Research Instrument Quantifies Organic Nitrogen

- Previous instrument very sensitive to detecting amines and oligomers, but qualitative; provided particle formation information
- CI-ATOFMS can accurately and quantitatively confirm chemical identity
- Developed by Prof. Kimberly Prather, University of California, San Diego, with seed funding from EPRI



© 2009 Electric Power Research Institute, Inc. All rights reserved.

Extensive Instrument Evaluation in Field

- **August Mini-Intensive: CI-ATOFMS and ICAMS**
- Cross-calibration to determine unique features and biases
- iCAMS comparison essential for consistency with current long-term network measurements

- Analysis underway

© 2009 Electric Power Research Institute, Inc. All rights reserved.

Commercial-Grade iCAMS (Pre-Production Prototype under Development)

This instrument fills a monitoring gap

- Several minute time resolution
- Robust & compact packaging
- Ethernet controlled
- Plumbed for easy maintenance
- Minimal # of ovens
- Post-process sample averaging

AIR QUALITY DESIGNS

© 2009 Electric Power Research Institute, Inc. All rights reserved.

Relevant Publications (1/2)

- Solomon, P.; Sioutas, C., Continuous and semicontinuous monitoring techniques for particulate matter mass and chemical components: A synthesis of findings from EPA's particulate matter supersites program and related studies. *Journal of the Air & Waste Management Association* **2008,** 58, (2), 164-195.
- Edgerton, E. S.; Saylor, R. D.; Hartsell, B. E.; Jansen, J. J.; Hansen, D. A., Ammonia and ammonium measurements from the southeastern United States. *Atmospheric Environment* **2007,** 41, (16), 3339-3351.
- Edgerton, E. S.; Hartsell, B. E.; Saylor, R. D.; Jansen, J. J.; Hansen, D. A.; Hidy, G. M., The Southeastern Aerosol Research and Characterization Study, Part 3. Continuous measurements of fine particulate matter mass and composition. *Journal of the Air & Waste Management Association* **2006,** 56, (9), 1325-1341.
- Edgerton, E. S.; Hartsell, B. E.; Saylor, R. D.; Jansen, J. J.; Hansen, D. A.; Hidy, G. M., The southeastern aerosol research and characterization study: Part 2. Filter-based measurements of fine and coarse particulate matter mass and composition. *Journal of the Air & Waste Management Association* **2005,** 55, (10), 1527-1542.

© 2009 Electric Power Research Institute, Inc. All rights reserved.

Relevant Publications (2/2)

- Hansen, D. A.; Edgerton, E. S.; Hartsell, B. E.; Jansen, J. J.; Kandasamy, N.; Hidy, G. M.; Blanchard, C. L., The southeastern aerosol research and characterization study: Part 1. Overview. *Journal of the Air & Waste Management Association* **2003,** 53, (12), 1460-1471.
- Solomon, P.; Baumann, K.; Edgerton, E.; Tanner, R.; Eatough, D.; Modey, W.; Marin, H.; Savoie, D.; Natarajan, S.; Meyer, M. B.; Norris, G., Comparison of integrated samplers for mass and composition during the 1999 Atlanta Supersites project. *Journal of Geophysical Research-Atmospheres* **2003,** 108, (D7).
- Weber, R.; Orsini, D.; Duan, Y.; Baumann, K.; Kiang, C. S.; Chameides, W.; Lee, Y. N.; Brechtel, F.; Klotz, P.; Jongejan, P.; ten Brink, H.; Slanina, J.; Boring, C. B.; Genfa, Z.; Dasgupta, P.; Hering, S.; Stolzenburg, M.; Dutcher, D. D.; Edgerton, E.; Hartsell, B.; Solomon, P.; Tanner, R., Intercomparison of near real time monitors of PM2.5 nitrate and sulfate at the US Environmental Protection Agency Atlanta Supersite. *Journal of Geophysical Research-Atmospheres* **2003,** 108, (D7).
- Fehsenfeld, F.; Huey, L.; Leibrock, E.; Dissly, R.; Williams, E.; Ryerson, T.; Norton, R.; Sueper, D.; Hartsell, B., Results from an informal intercomparison of ammonia measurement techniques. *Journal of Geophysical Research-Atmospheres* **2002,** 107, (D24).

© 2009 Electric Power Research Institute, Inc. All rights reserved.

Contact Information

Stephanie Shaw, Electric Power Research Institute (EPRI)

Phone: 650.855.2353

Email: slshaw@epri.com

Web: www.epri.com

Eric Edgerton, Atmospheric Research and Analysis, Inc. (ARA)

Phone: 919.522.8565

Email: eedgerton@atmospheric-research.com

Web: www.atmospheric-research.com

Martin Buhr, Air Quality Design, Inc. (AQD)

Phone: 303.225.0287

Email: marty@airqualitydesign.com

Web: www.airqualitydesign.com

© 2009 Electric Power Research Institute, Inc. All rights reserved.