Continuous Ammonia Monitoring

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Measurement Challenges

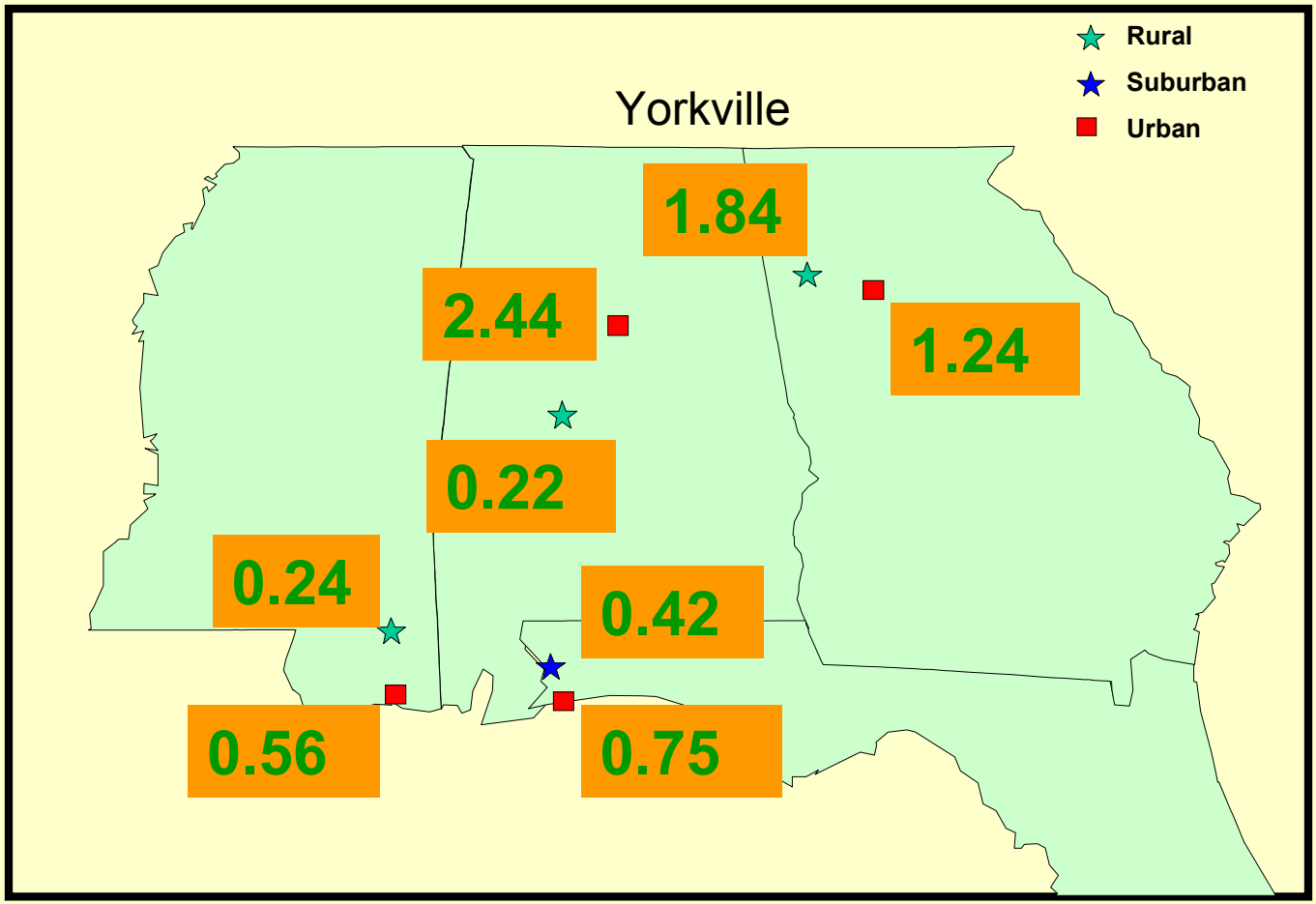
- Low concentrations – generally near or less than 1 ppbv, except near sources
- Highly reactive – sticks to surfaces, especially those that are “wetted” or covered with water molecules
- Oxidized nitrogen species (NO, NO_2, HNO_3, etc.) are generally much more abundant – it can be difficult to “see” the reduced nitrogen species against this background.

Integrated Methods

- Passive Samplers
  - Tube
  - Badge
- Active Samplers
  - Denuders
    - Annular
    - Honeycomb
    - Tubular
  - Filter Packs (ACID-MODES)
  - Fabric Mesh Filters (Dennis Fitz, UCR)

Source: Eric Edgerton

Mean NH_3 at SEARCH Sites (ppb) CY 2004 – Annular Denuder Method



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Continuous Methods

- Research Methods
  - Tunable Diode Laser – TDLAS
  - Wet Effusive Diffusion Denuder (WEDD)
  - Wet Scrubbing Long Path Absorption Spectrometer – WS-LOPAP
  - Wet Scrubbing IC analysis (URG AIM 9000, Dionex GP-IC?)
  - MARGA – Steam Jet Collection – IC
- Potential Routine Methods
  - Ion Mobility Spectrometer
  - Laser Acousto-Optical Detection
  - Chemiluminescence
    - SEARCH TRN
    - API Model 201E or Thermo Model 17C (1 ppb LDL)
  - AiRRmonia – ECN, Netherlands, Mechatronics Instruments, b.v.

SEARCH Continuous NH_3 Method (TRN)

- 2-channel oxidized AND reduced nitrogen chemiluminescence analyzer
- Channel 1 samples ambient air through a sodium carbonate denuder (TN), then two heated converters
- Channel 2 samples ambient air through dual sodium carbonate and citric acid denuders (TN*), then through a single moly converter
- NH_3 operationally defined as TN-TN*

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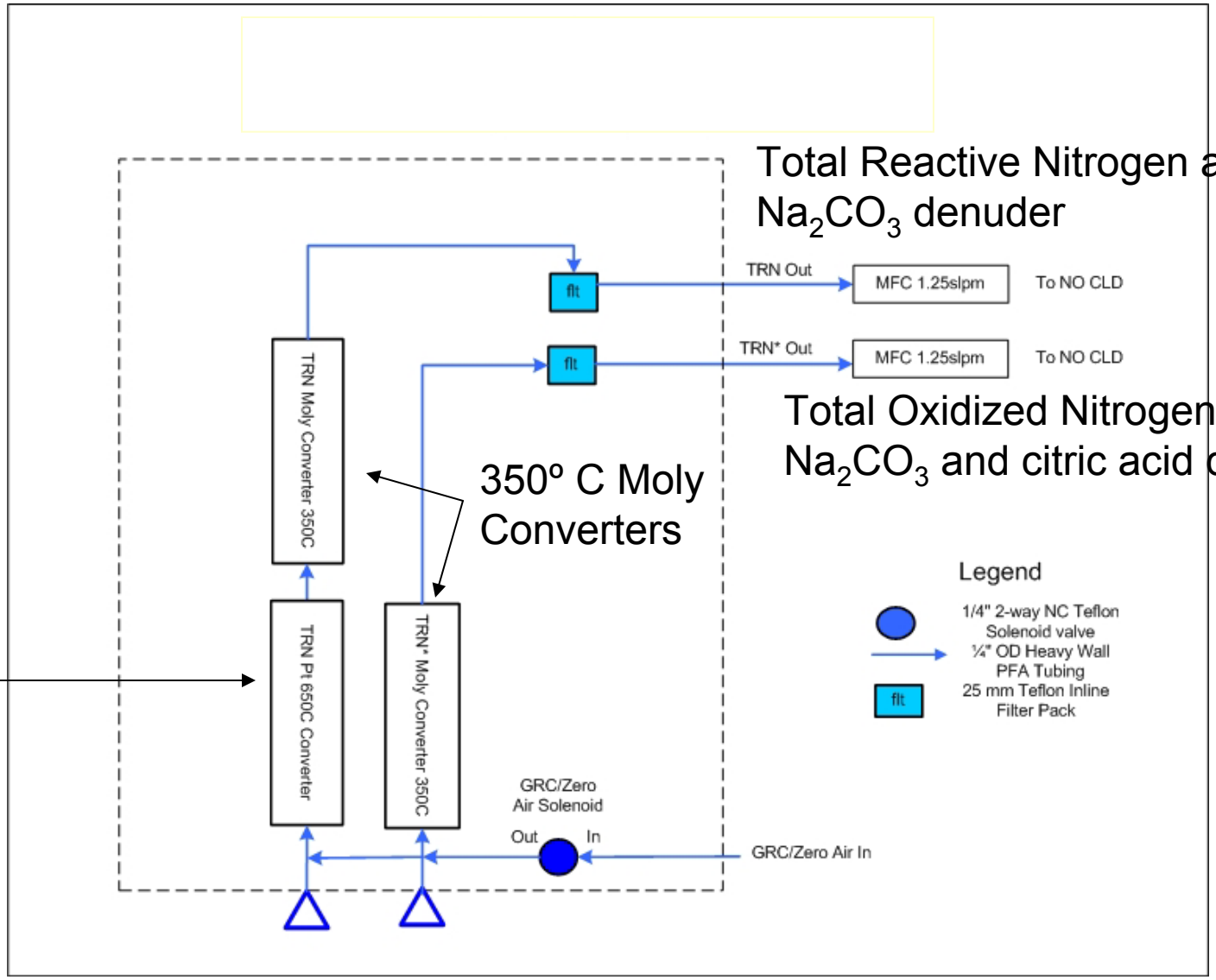
Total Reduced Nitrogen (TRN) Analyzer



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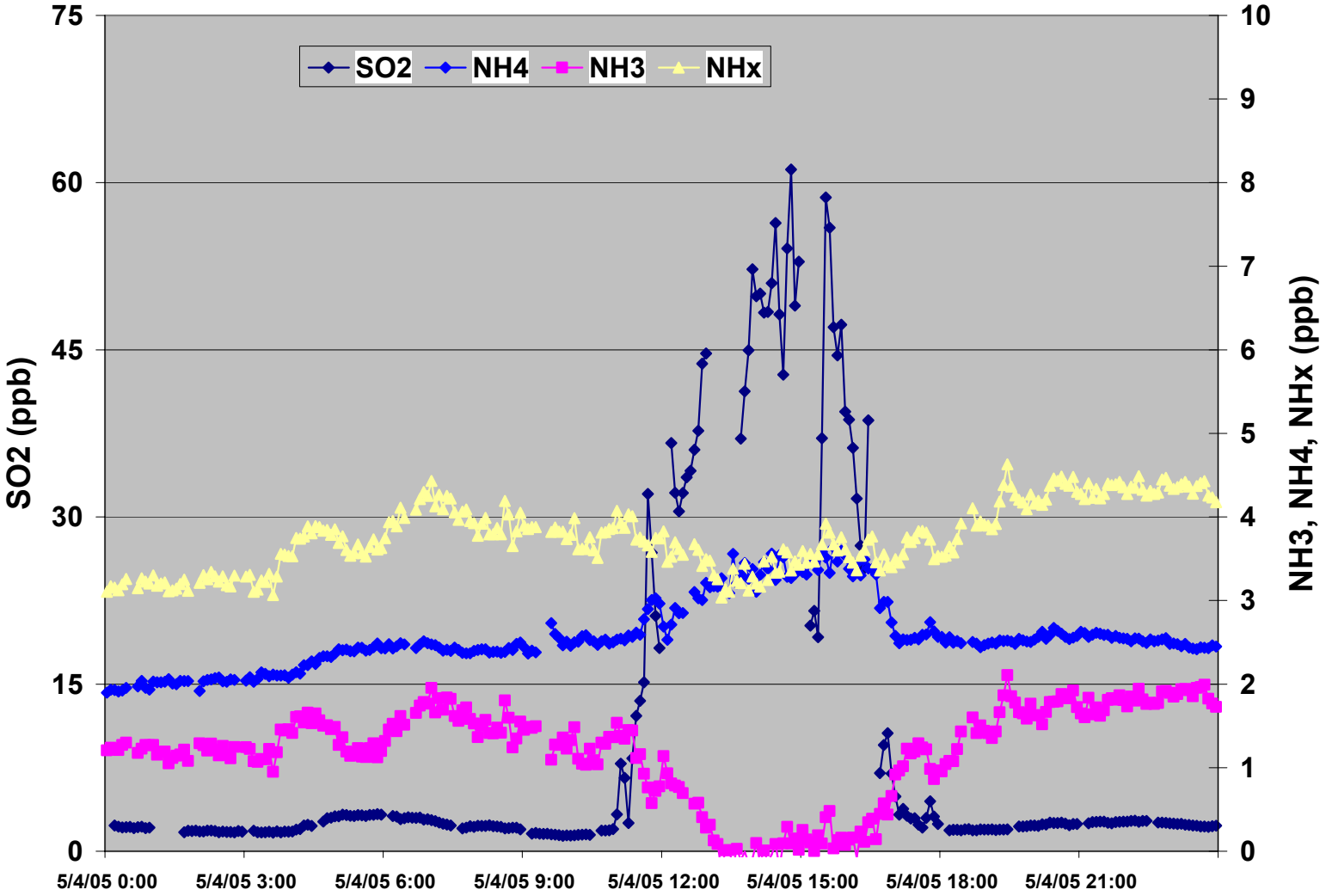
NH_3 and NH_4^+ during CFPP Plume Event



NH_4^+ increases; NH_3 disappears; NH_x conserved

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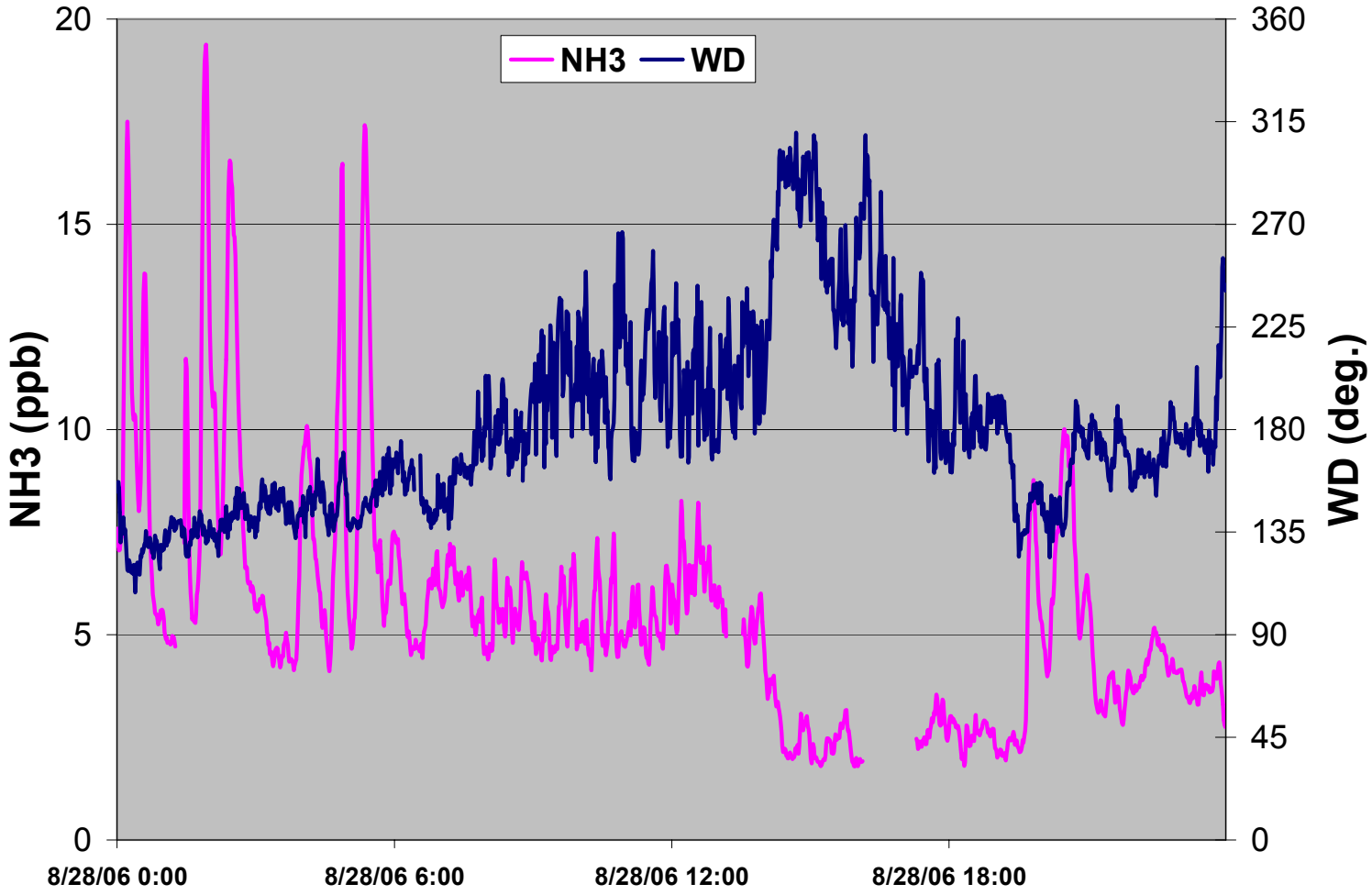
1-minute NH_3 and WD at Yorkville



Spikes between 90 and 180 degrees suggest nearby NH_3 sources.

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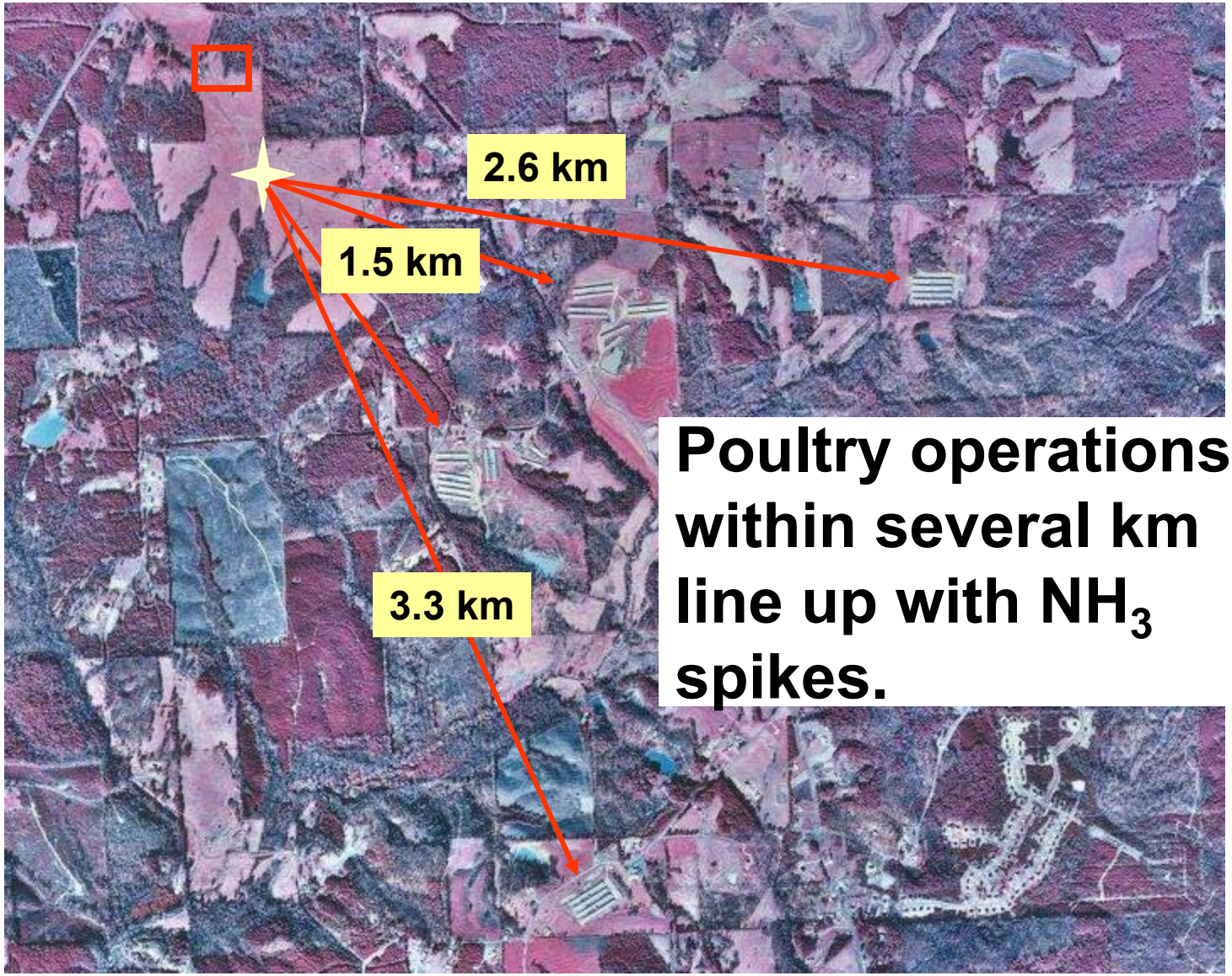
Local Sources of NH_3 at YRK



Poultry operations within several km line up with NH_3 spikes.

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Method 2 - IMS

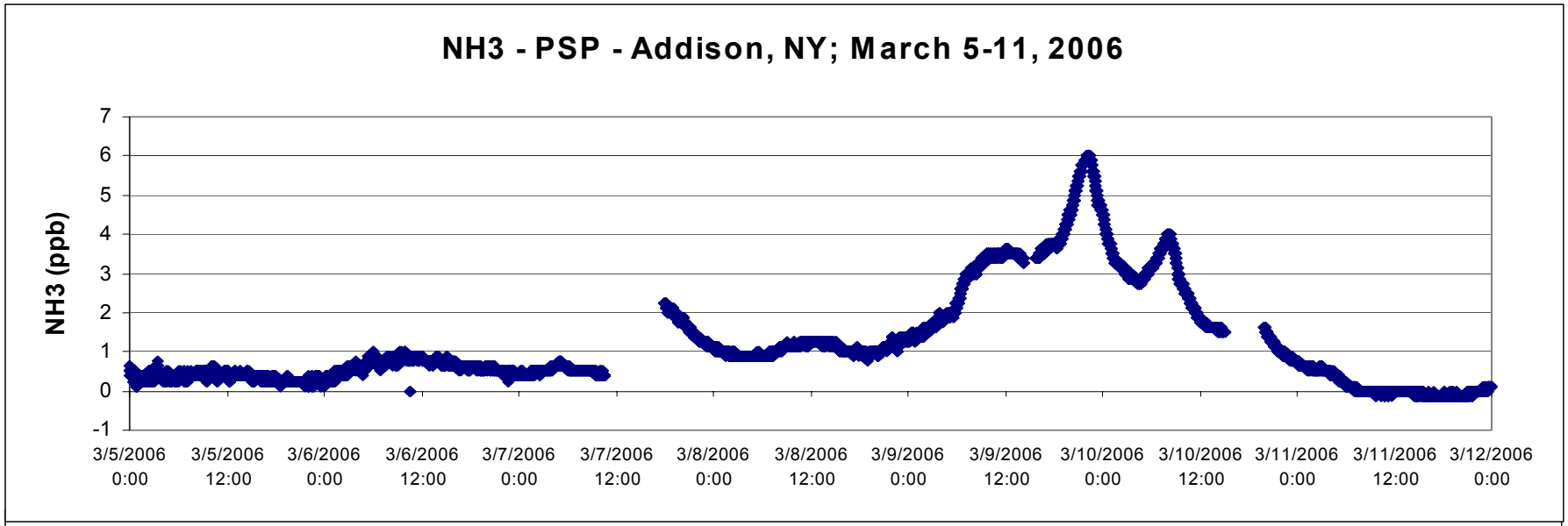
- Candidate for routine monitoring
- IMS – Ion Mobility Spectrometer (AirSentry-IMS Ammonia Analyzer, Particle Measuring Systems, Boulder, CO)
- Ionization based time-of-flight technique performed at atmospheric pressure
- Instruments are targeted to a specific molecule in a specific concentration range
- Range for this instrument: 0–300 ppb (Lab Intercomparison); 0-100 ppb (Field Deployment)
- Cost (with OBC) ~ $26 K

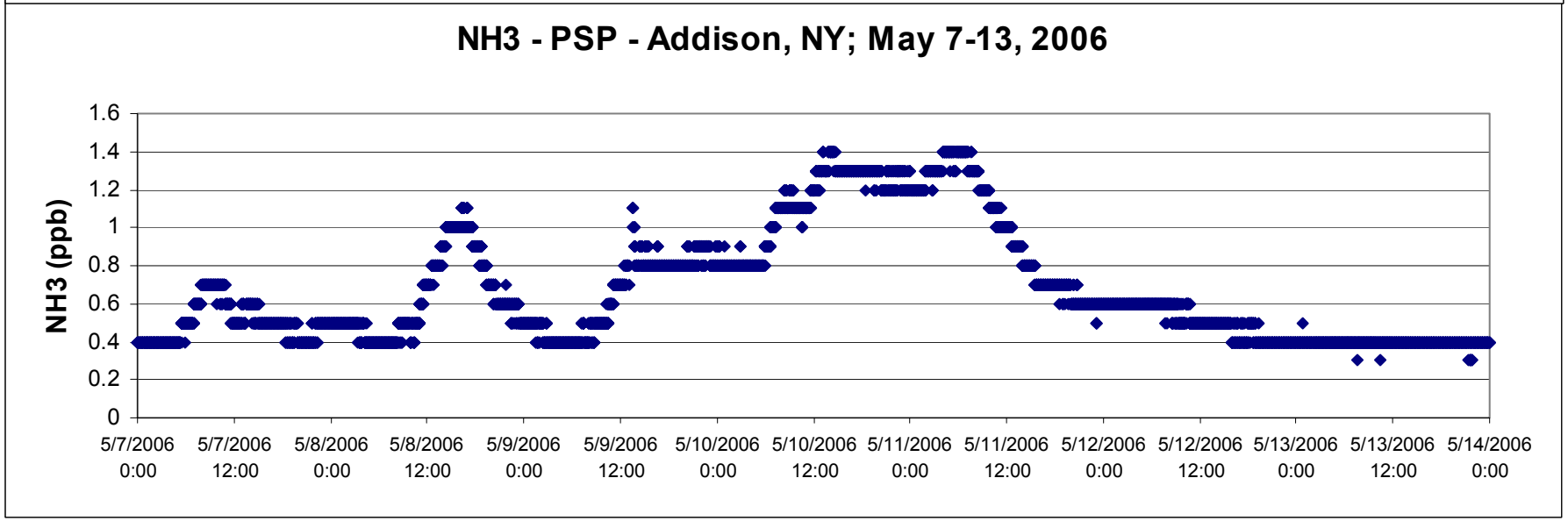

AirSentry-IMS®
Molecular Analytics
Ammonia Analyzer

Operational Details

- Requires up to 5 li/min of clean, dry instrument air (dewpoint ≤ -40º C)
- Internal sample pump option
- Factory default “Smoothing Factor” (8) should be increased for minute (or longer) averaged data
- Optional “On Board Calibration” - integral permeation oven set up (recommended)
- Nickel 63 sealed radioactive source (less than .005 microcuries) – ionization source

IMS Field Data





Preliminary data: do not cite or quote!

Laboratory Intercomparison

- September 12-30, 2005 at ASRC
- Six measurement Methods – seven instruments in all (Chemiluminescence method not included in analysis due to “conversion problem”)
- Heated glass manifold for uniformity of sampling environment
- Synthetic air and calibration system
- “Ambient” sample for two extended periods

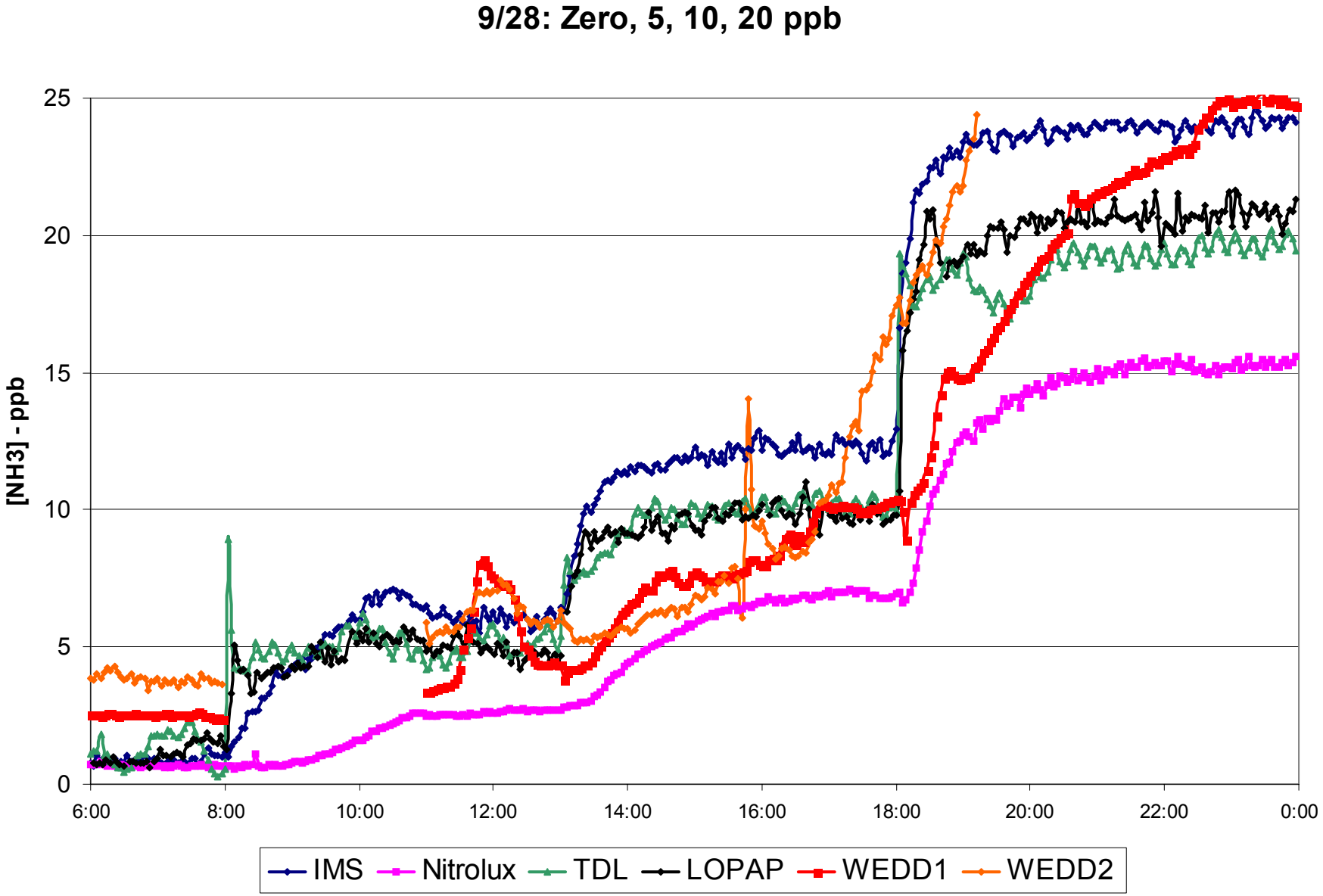
Pranalytica Nitrolux NH3 Analyzer

Note: Instrument used was one of the first sold by Pranalytica and company claims to have made significant improvements to later (i.e. current) instruments

- Photoacoustic spectroscopy
- CO_2 laser
- Low-noise microphone
- In-line particle filter (40 µm)
- LDL and cost depend on model
  - Model 1000 – LDL ~ 1 ppb; Cost ~$24K
  - Model 200 – LDL ~ 0.2 ppb; Cost ~$38K
  - Model 100 – LDL ~ 0.1 ppb; Cost ~$72K

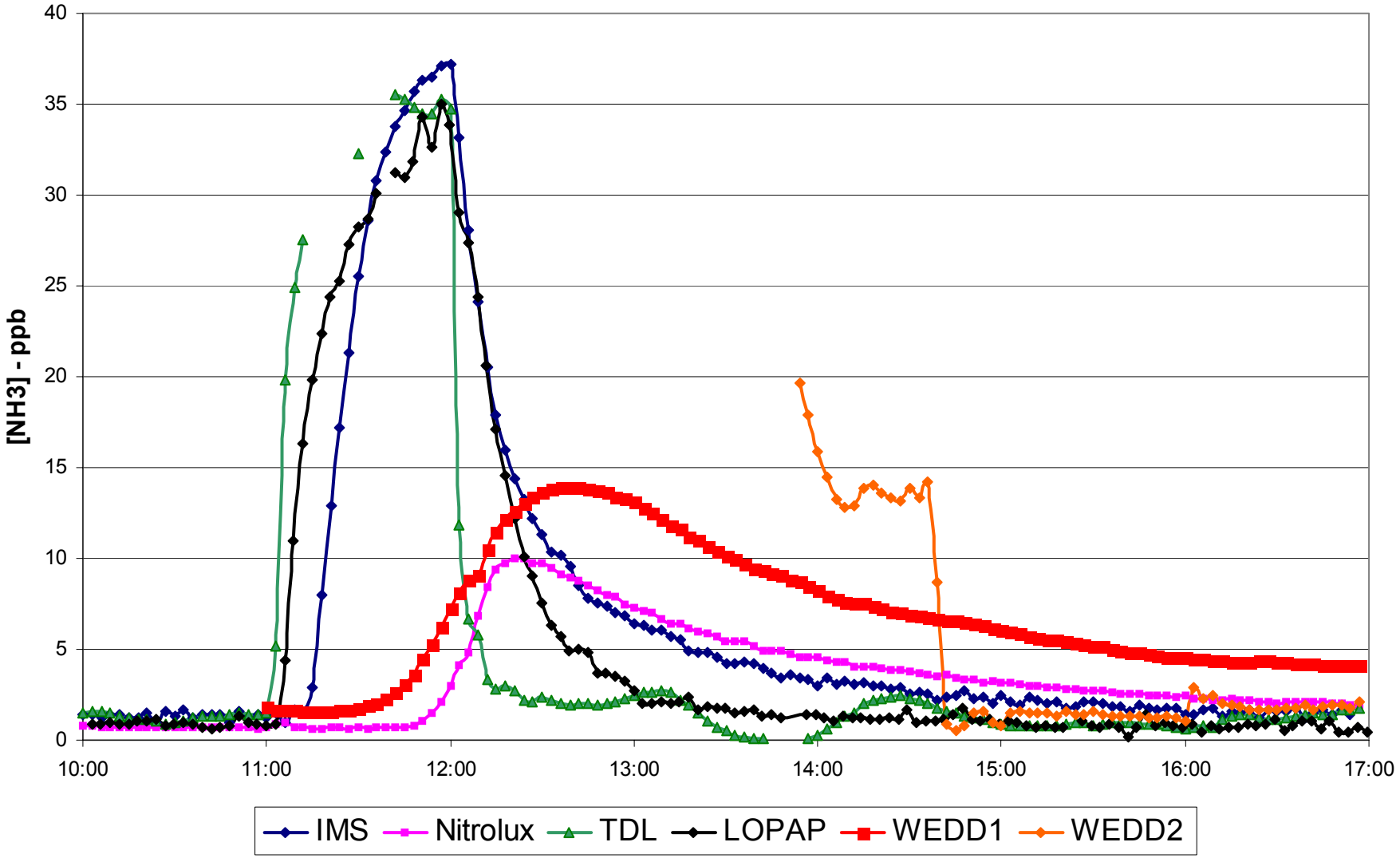
Method Characteristics Tested during Intercomparison

- Response to known [NH_3] – accuracy and precision of calibration
- Time Response – to step changes and “spikes”
- Comparability during ambient sampling
- Potential interferences



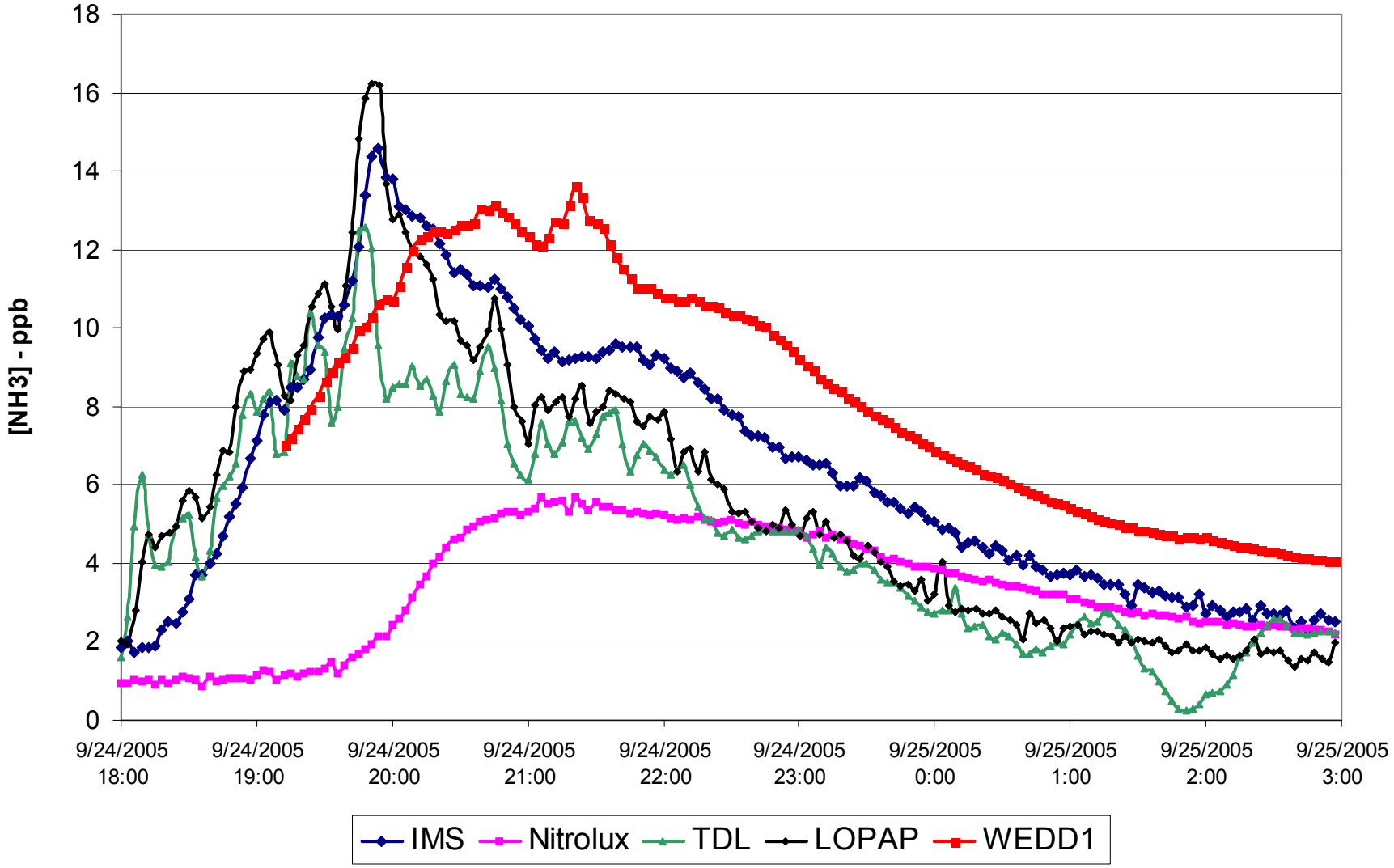
Preliminary data: do not cite or quote!

9/26: 40 ppb spike from zero



Preliminary data: do not cite or quote!

9/24: Ambient Spike



Preliminary data: do not cite or quote!

Sampling and response time

- This is an important issue for gaseous ammonia measurement – it clearly affects methods detecting gaseous ammonia directly and ammonium after scrubbing.
- The TDL is the system of choice for quick and accurate response – but it is not a “routine” method!

Best Candidate Methods for Monitoring – and their Major Shortcoming(s) (Editorial Opinions!)

- ARA TRN (chemiluminescence)
  - Not ammonia specific
  - Three heated converters – difference
  - Custom implementation of proven analyzer
  - Response time?
- AirSentry IMS (Particle Measuring)
  - Response Time
- Nitrolux 200 (or 100) (Pranalytica)
  - Response Time (worst of all tested instruments, but should be better in current versions)
  - Cost – Highest of “routine monitoring” candidates (for sufficiently low LDL)

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