# An Instrument for Real Time Speciation of Water Soluble Tracers in Atmospheric Particulate Matter


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# Project Goal

Configure, validate and deploy cost-effective, robust "real-time" (1h) instruments to measure water-soluble components of $PM_{2.5}$ at network sites.

**Analytical Method Development** → **Integration with PILS, Field Trials & Ambient Studies**

**(A)** Inorganic species: Methods to replace IC.

**(B)** New techniques for online measurements of metals.

- Combine with existing WSOC method.

# Study Overview – $PM_{2.5}$ Component Matrix

| Module or Analyte Group | | | |
|---|---|---|---|
| Bulk Components (Major Ions) | Cations & Anions (Source Tracers) | Redox Active Metals | Water Soluble Organic Carbon |
| Ammonium ($NH_4^+$) | Calcium ($Ca^{2+}$) | Iron (Fe) | WSOC |
| Nitrate ($NO_3^-$) | Potassium ($K^+$) | Manganese (Mn) | |
| Sulfate ($SO_4^{2+}$) | Sodium ($Na^+$) | Copper (Cu) | |
| | Chloride ($Cl^-$) | Chromium (Cr) | |

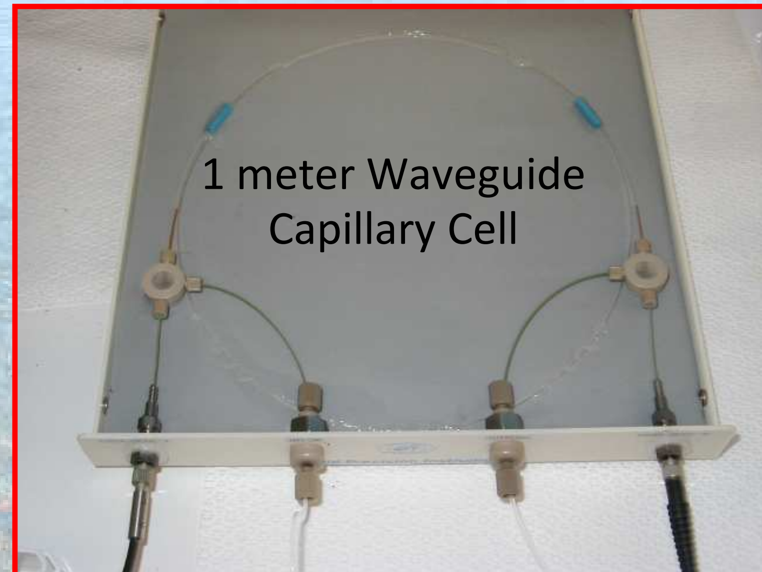
**GOALS - for each species:**

- **Develop an "on-line" compatible analytical method**
- **Validate the new methods using real-world filter-based samples.**
- **Conduct field trials of the on-line implementation for selected species.**

# Analytical Methods Explored

## Ion-Selective Electrodes (ISE)

## Long Optical Path Spectrophotometry with Liquid Wave Guides (LWCC)





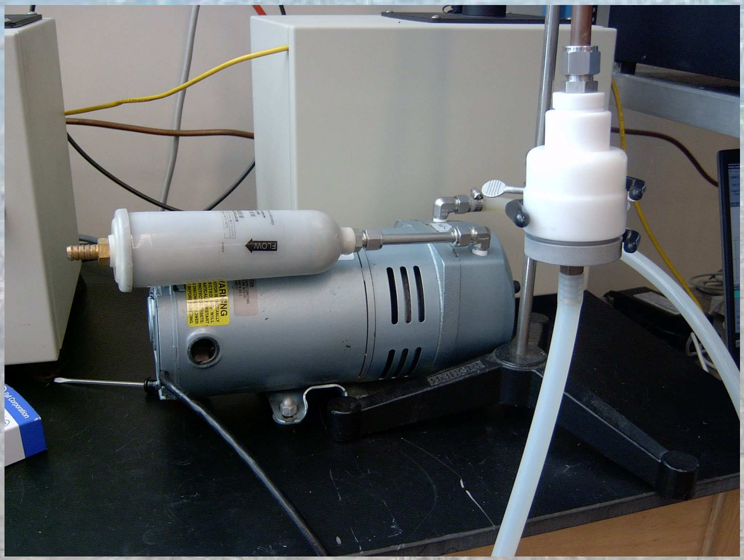
**For Both Methods**

- Low Sample Volume Requirements
- Minimal Sample Pretreatment
- Low Cost
- Field Portable & Real-Time Configurable

# Filter and Online System for Collecting Particles

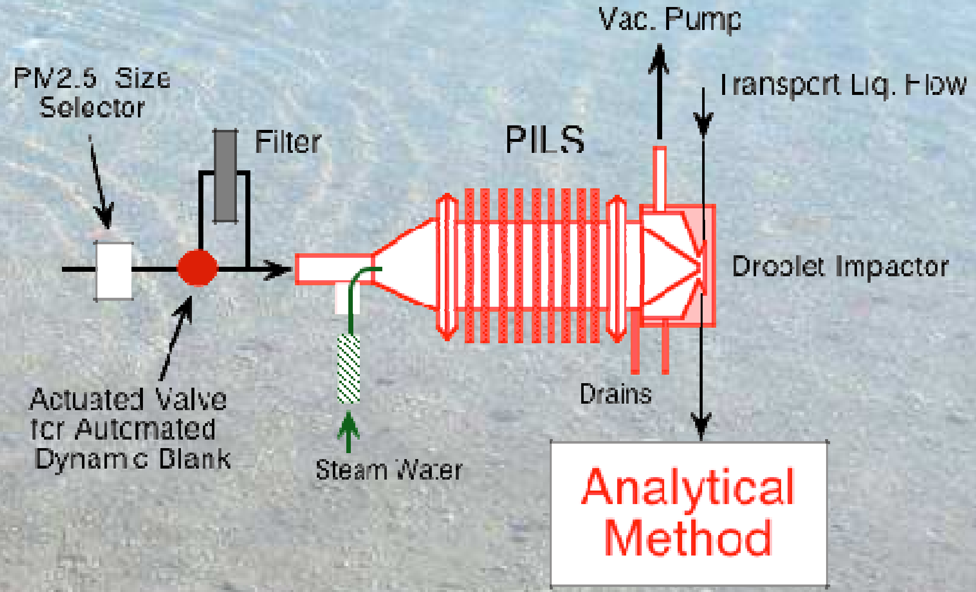
## Filter Collection

Off-line Water-Extraction and Analysis



## Particle-Into-Liquid Sampler

Automated On-line Analysis



# (A) Cations & Anions
# Summary of Method Evaluation Status

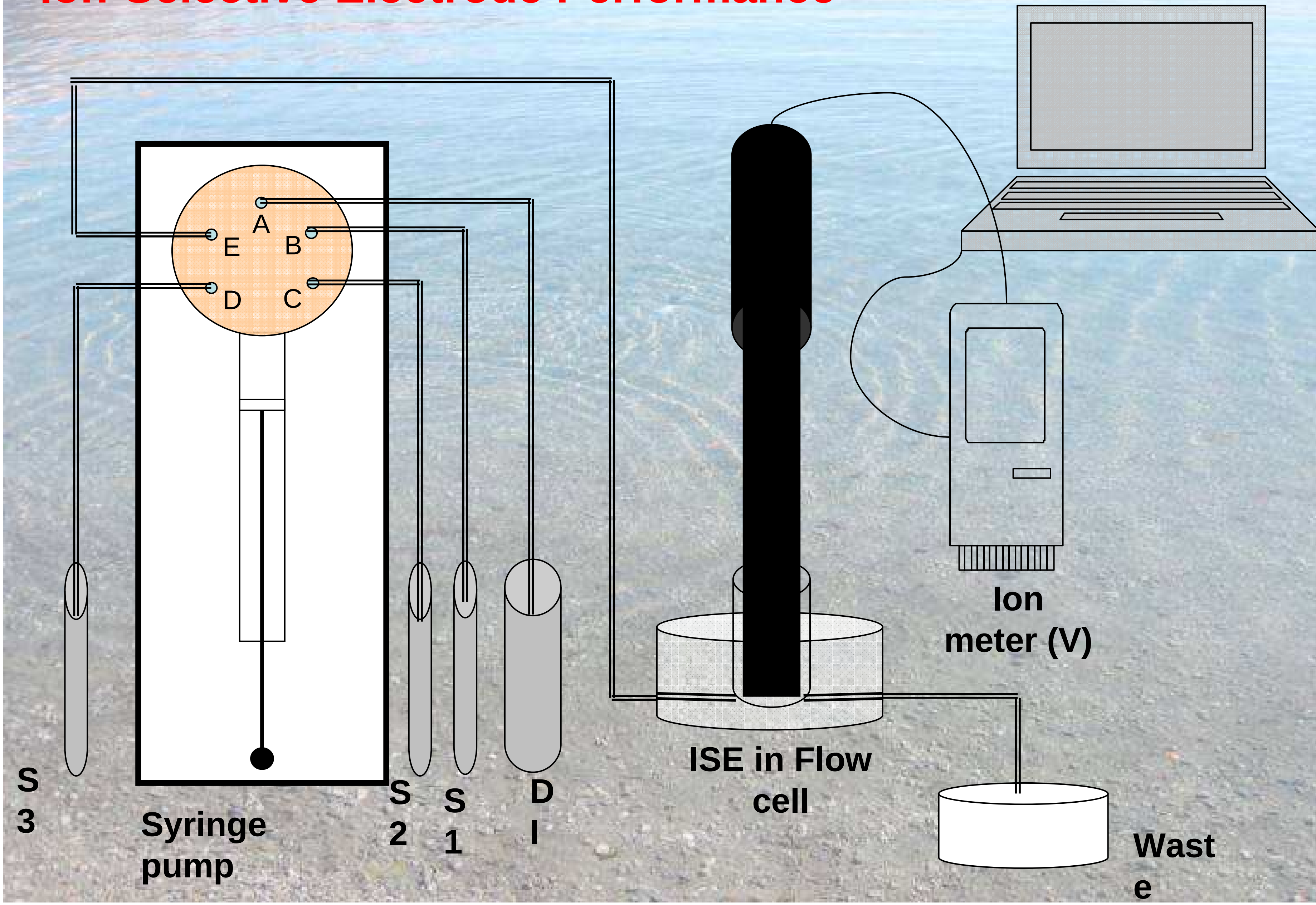
| Species | Method Investigated | Field Filter Validation | Field PILS Validation | Acceptable for Filter | Acceptable for PILS |
|---|---|---|---|---|---|
| **Ammonium** | ISE | Yes | No | Likely | Likely |
| **Nitrate** | UV-Optical | Yes | Planned? | Yes | Likely |
| **Sulfate#** | Attempted | No | No | No | No |
| | | | | | |
| **Calcium** | ISE | No | No | Maybe | Maybe |
| **Potassium** | ISE | Yes | Attempted | Yes | Yes |
| **Sodium** | ISE | Yes | In Progress | Yes | Likely |
| **Chloride** | ISE | No | No | Maybe | Unlikely |

**#A barium sulfate precipitation - ligand exchange method was evaluated, however the method proved unreliable.**

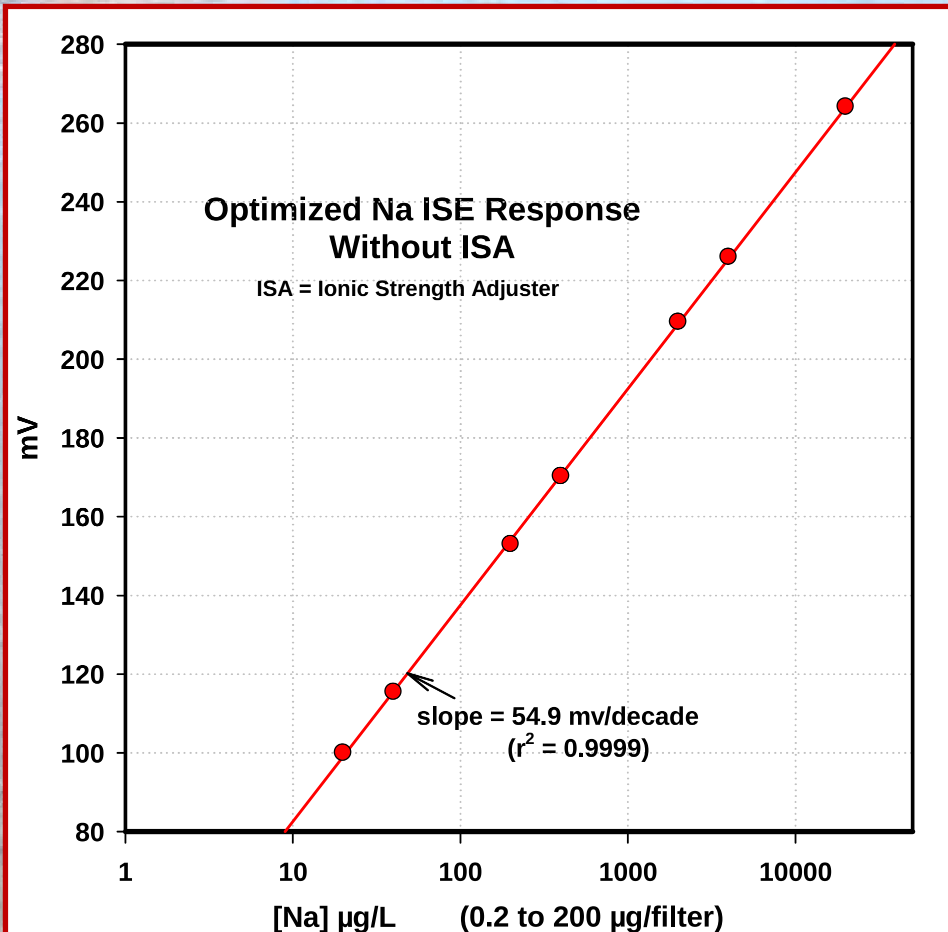
- **Acceptable for Filter:** Method appropriate for typically-loaded 12-24 hr filter collection.
- **Acceptable for PILS:** Method appropriate for shorter-term (hours) on-line use in typical atmosphere.

Maybe = in certain high-concentration atmospheres.

# (A) Schematic Diagram of Laboratory System for Evaluating Ion-Selective Electrode Performance



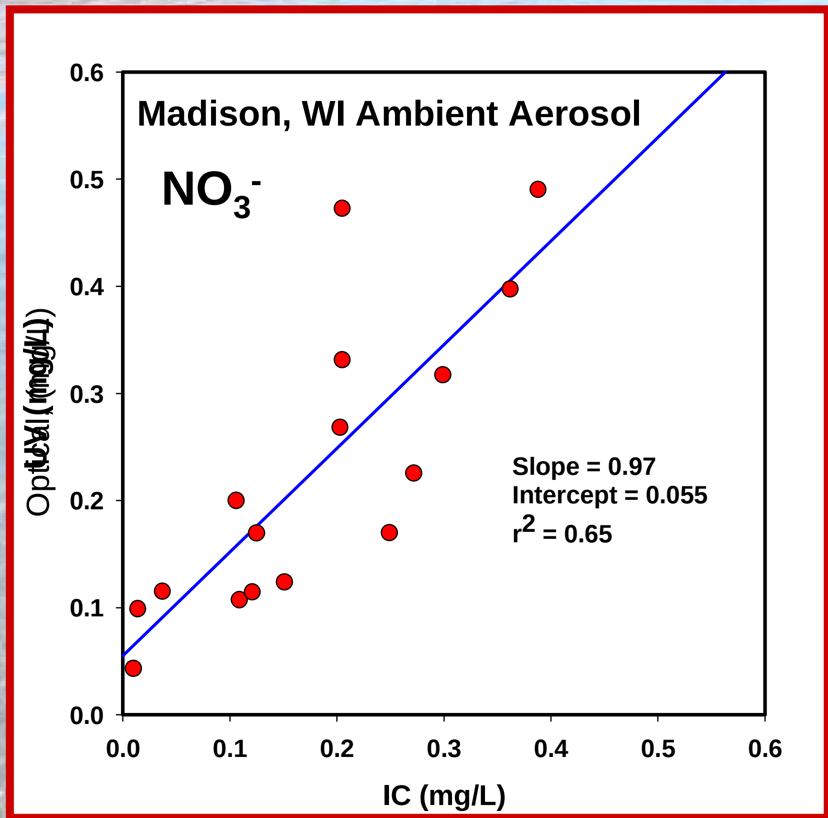
# (A) Example of ISE Method Cal's: $Na^+$ Summary

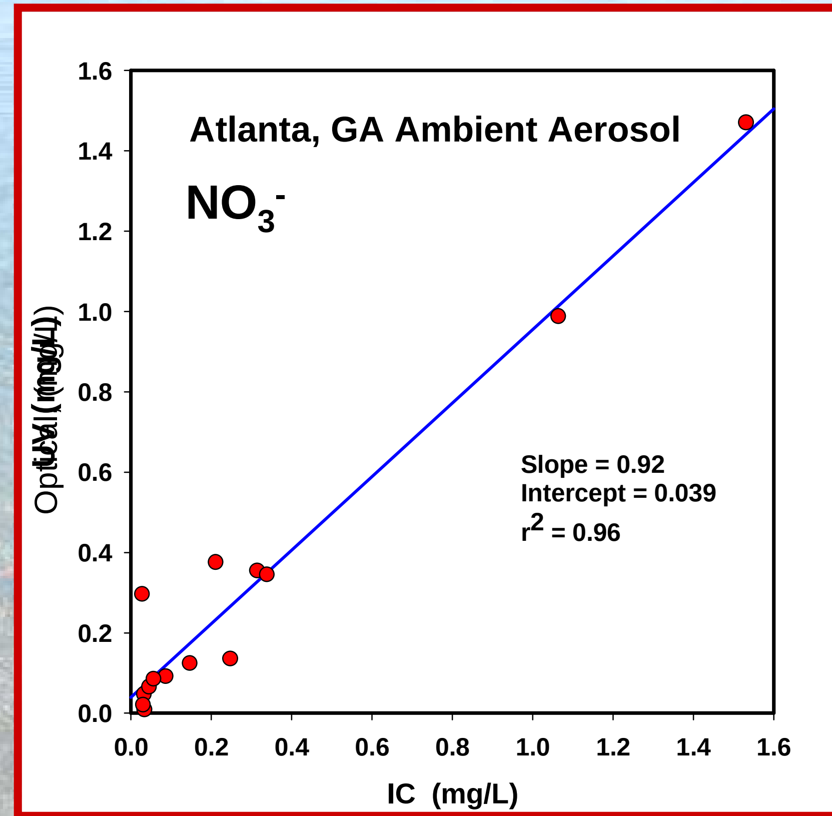



- Linear over full range of environmental concentrations
- Sensitivity likely adequate for hourly measurements in some environments (e.g. marine influenced)

Field validation deployment scheduled for Los Angeles in May/June 2010.

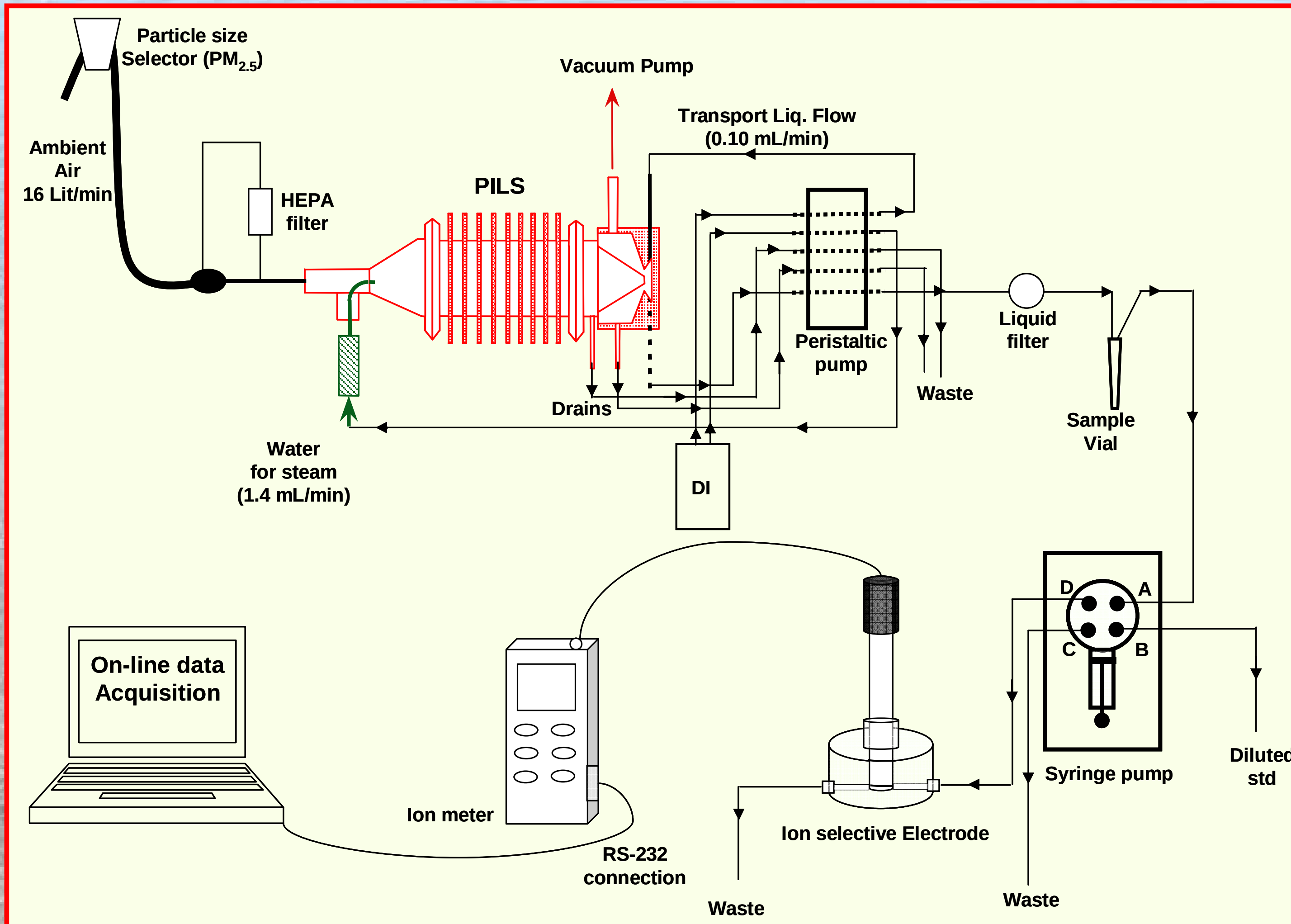
# (A) Example of Optical Method Cal's: Nitrate – Comparison with Filter-Based IC Measurements



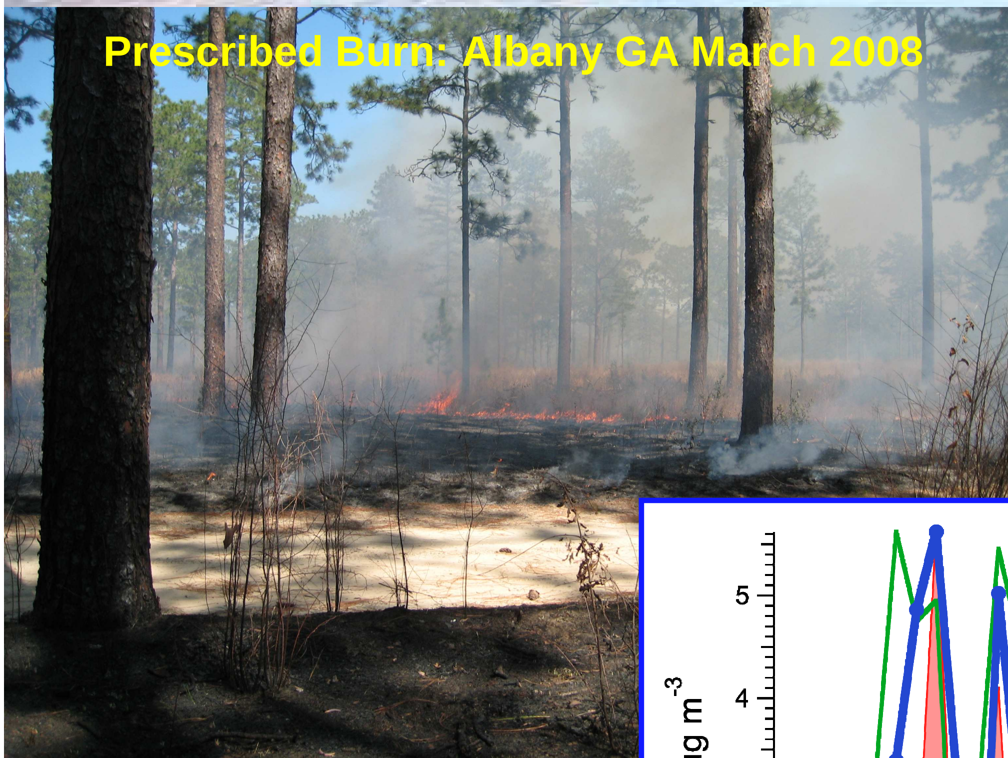




**Nitrate by the UV-method (with interference correction) vs IC on extracts of ambient aerosols from Madison, WI (24 hr – 12 $m^3$ samples) and Atlanta, GA. Room for improvement, but reasonable agreement.**

# (A) Schematic Diagram of Field Deployment of PILS Ion-Selective Electrode System (e.g., $K^+$)

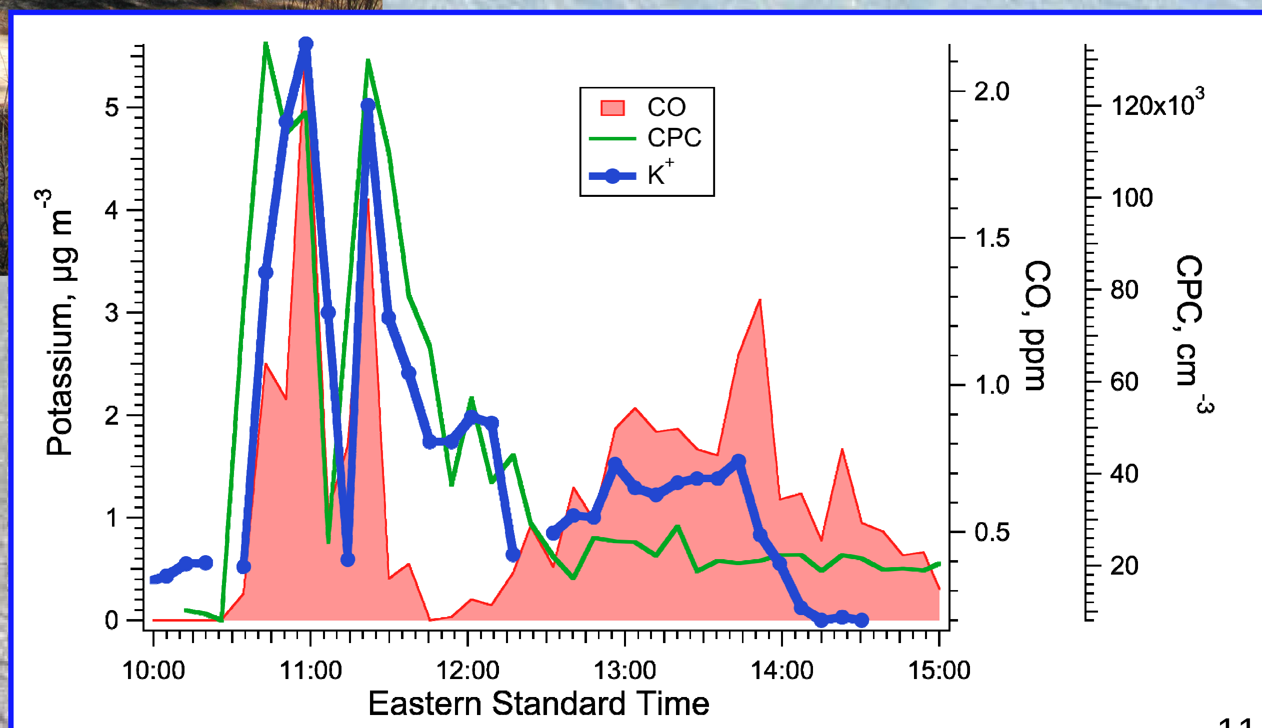


# (A) Preliminary Field Testing of $K^+$ ISE



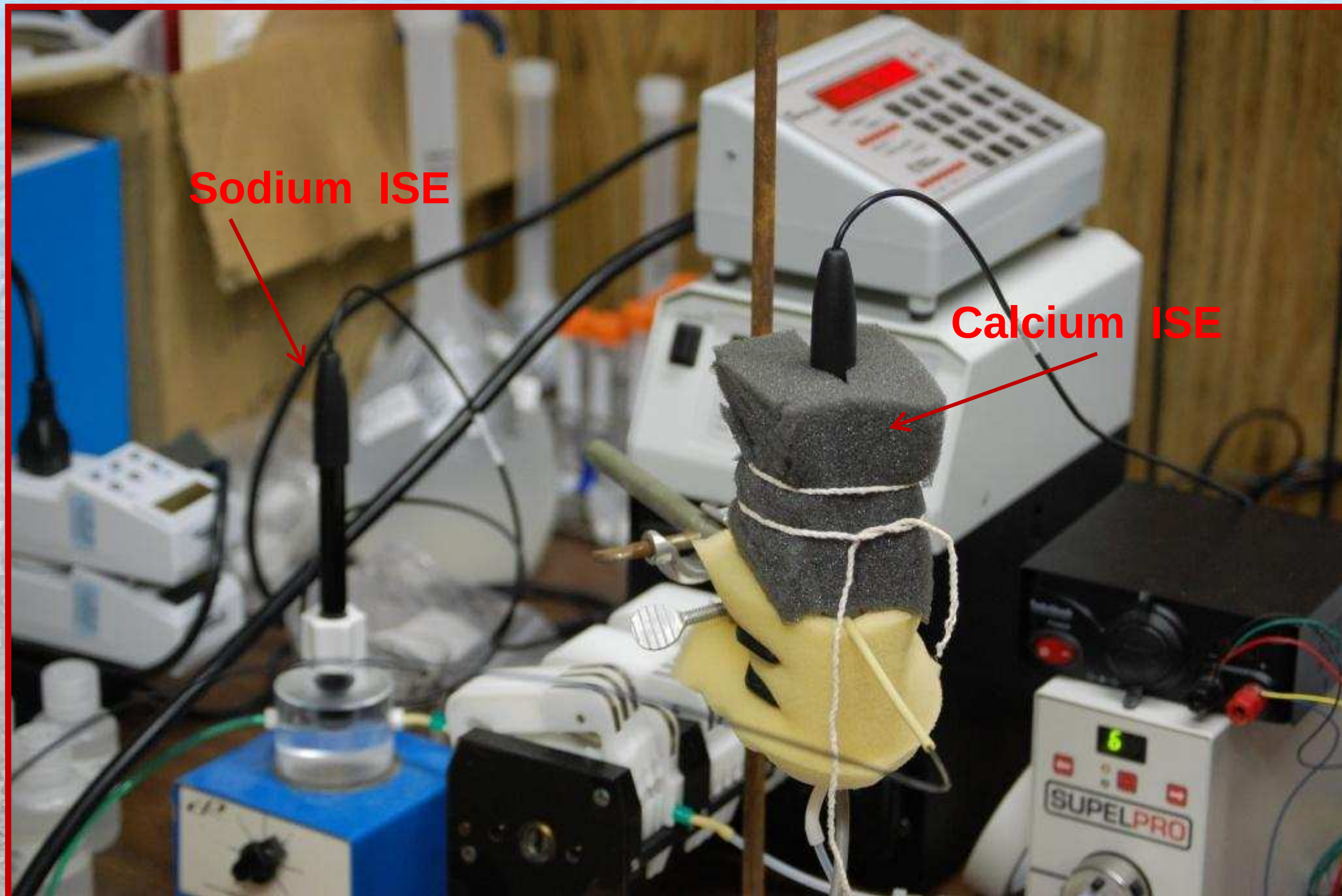

Site of high $[K^+]$ and test of dynamic range

$K^+$ ISE tracks smoke concentrations, but possible issues with $NH_4^+$ Interferences




***Paper in prep. 2010***

# (A) Field Deployment of Sodium and Calcium Ion-Selective Electrodes (ISE) (in-series)



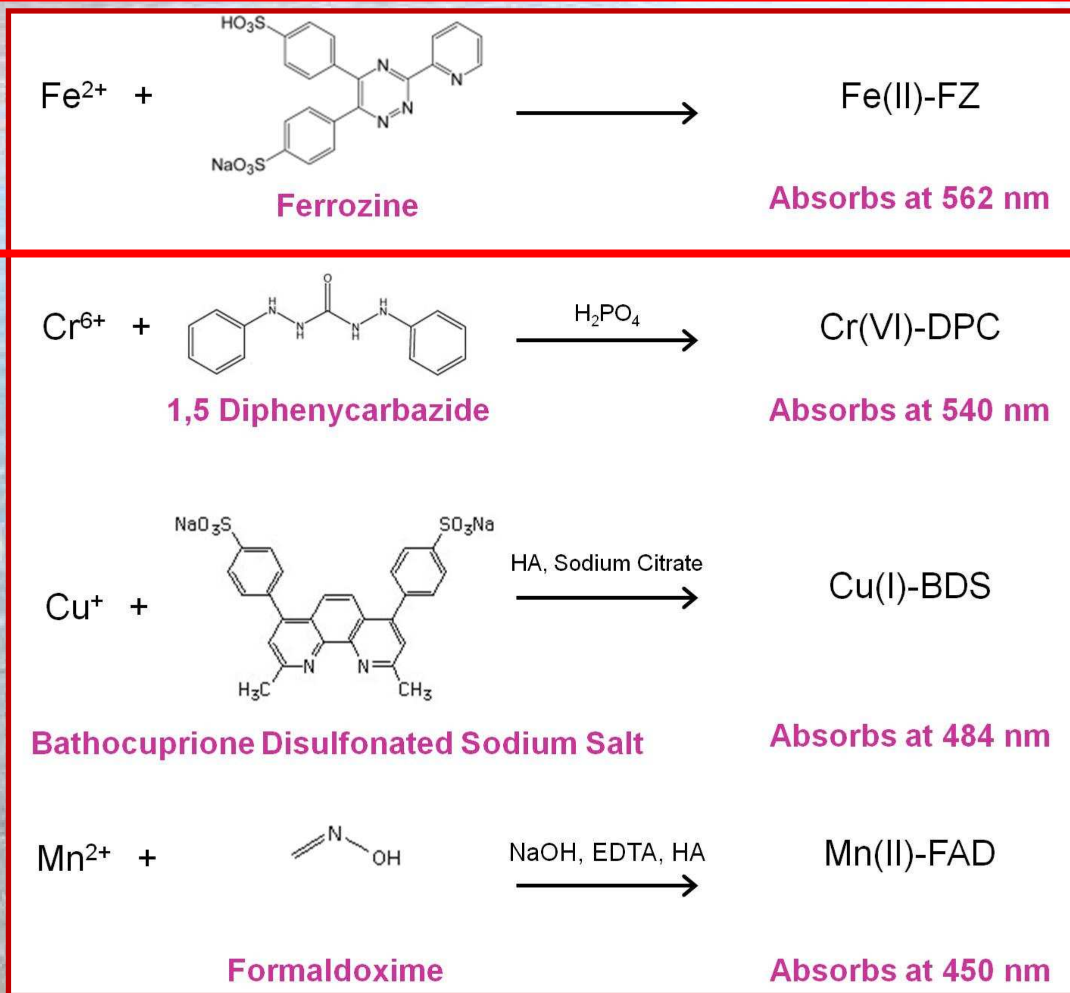

**Comparison of PILS-ISE vs PILS-IC during CalNex June 2010**

# (A) Summary: Current Status of Method Development

| Module or Analyte Group | | | |
|---|---|---|---|
| Bulk Components (Major Ions) | Cations & Anions (Source Tracers) | Redox Active Metals | Water Soluble Organic Carbon |
| Ammonium ($NH_4^+$) | Calcium ($Ca^{2+}$) | Iron (Fe) | WSOC |
| Nitrate ($NO_3^-$) | Potassium ($K^+$) | Manganese (Mn) | |
| Sulfate ($SO_4^{2+}$) | Sodium ($Na^+$) | Copper (Cu) | |
| | Chloride ($Cl^-$) | Chromium (Cr) | |

| PILS deployment completed or planned | Successful implementation of method with filter-based samples | Successful method development |
|---|---|---|

# (B) Trace Metal Chemistries Adapted for the LWCC




Methods are oxidation state sensitive and can be adapted to quantify multiple redox states of a given metal.

| Species | Ligand | Absorptivity $LM^{-1}cm^{-1}$ | Additional Reagents |
|---|---|---|---|
| Chromium VI | Diphenylcarbazide | 40,000 @ 540 nm | $H_2SO_4$ , ($KMnO_4$) |
| Copper II + I | Bathocuproine-DS | 14,200 @ 484 nm | $NH_2OH$-HCl |
| Iron II (III) | Ferrozine | 25,300 @ 562 nm | ($NH_2OH$-HCl) |
| Manganese | FAD | ~30,000 @ 450 nm | EDTA , HA , NaOH |

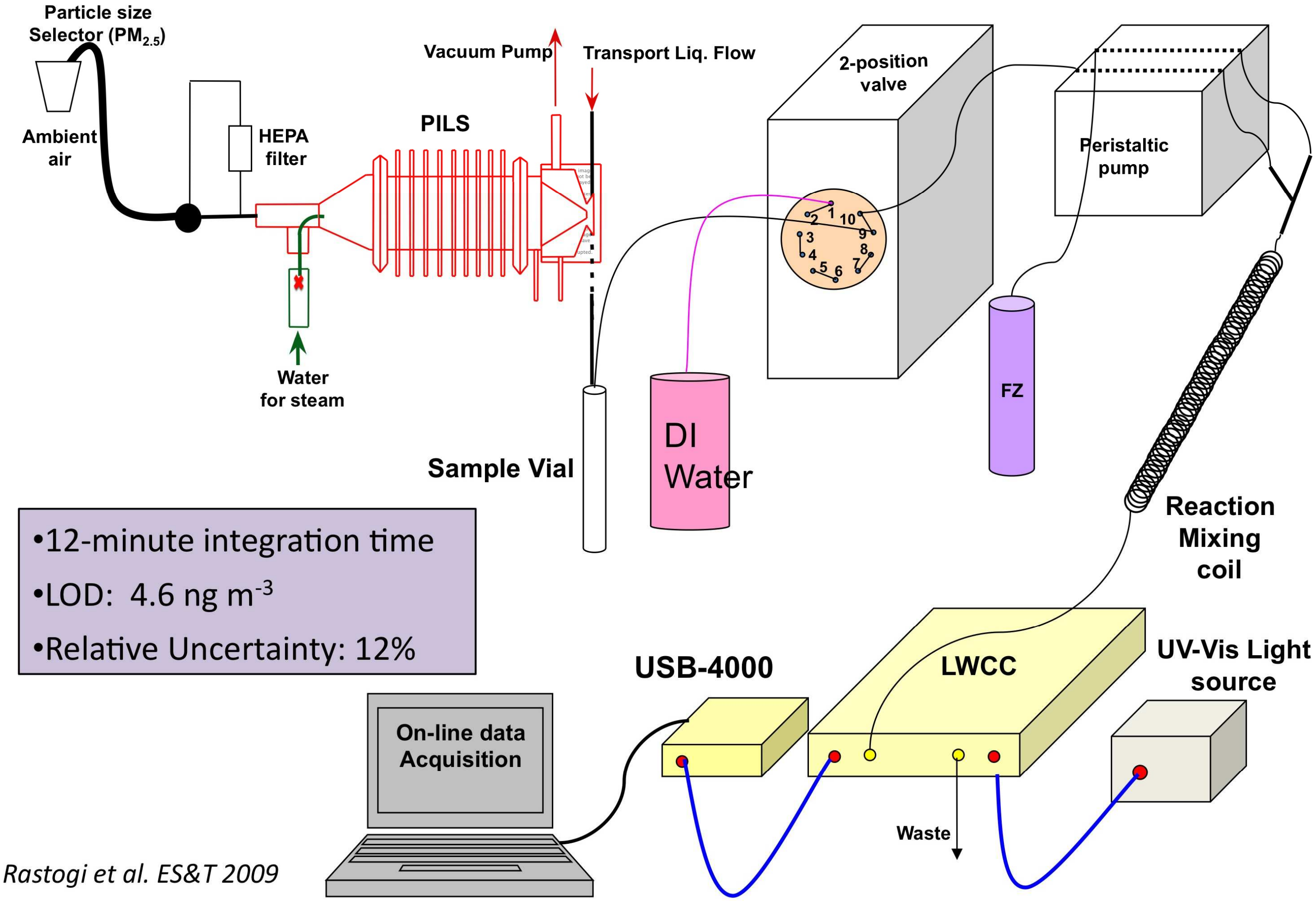
# (B) Trace Element (redox active metals) Summary of Method Evaluation Status

| Metal | LWCC Method Developed | Field Filter Validation | Field PILS Validation | Acceptable for Filter | Acceptable for PILS |
|---|---|---|---|---|---|
| **Cr** | Yes | No | No | No | No |
| **Cu** | Yes | Yes | No | Yes | Maybe |
| **Mn** | Yes | Yes | No | Yes | Likely |
| **Fe** | **Yes** | **Yes** | **Yes** | **Yes** | **Yes** |

- **Acceptable for Filter:** Method appropriate for typically-loaded 12-24 hr filter collection.
- **Acceptable for PILS:** Method appropriate for shorter-term (hours) on-line use in typical atmosphere.

Maybe = in certain high-concentration atmospheres.

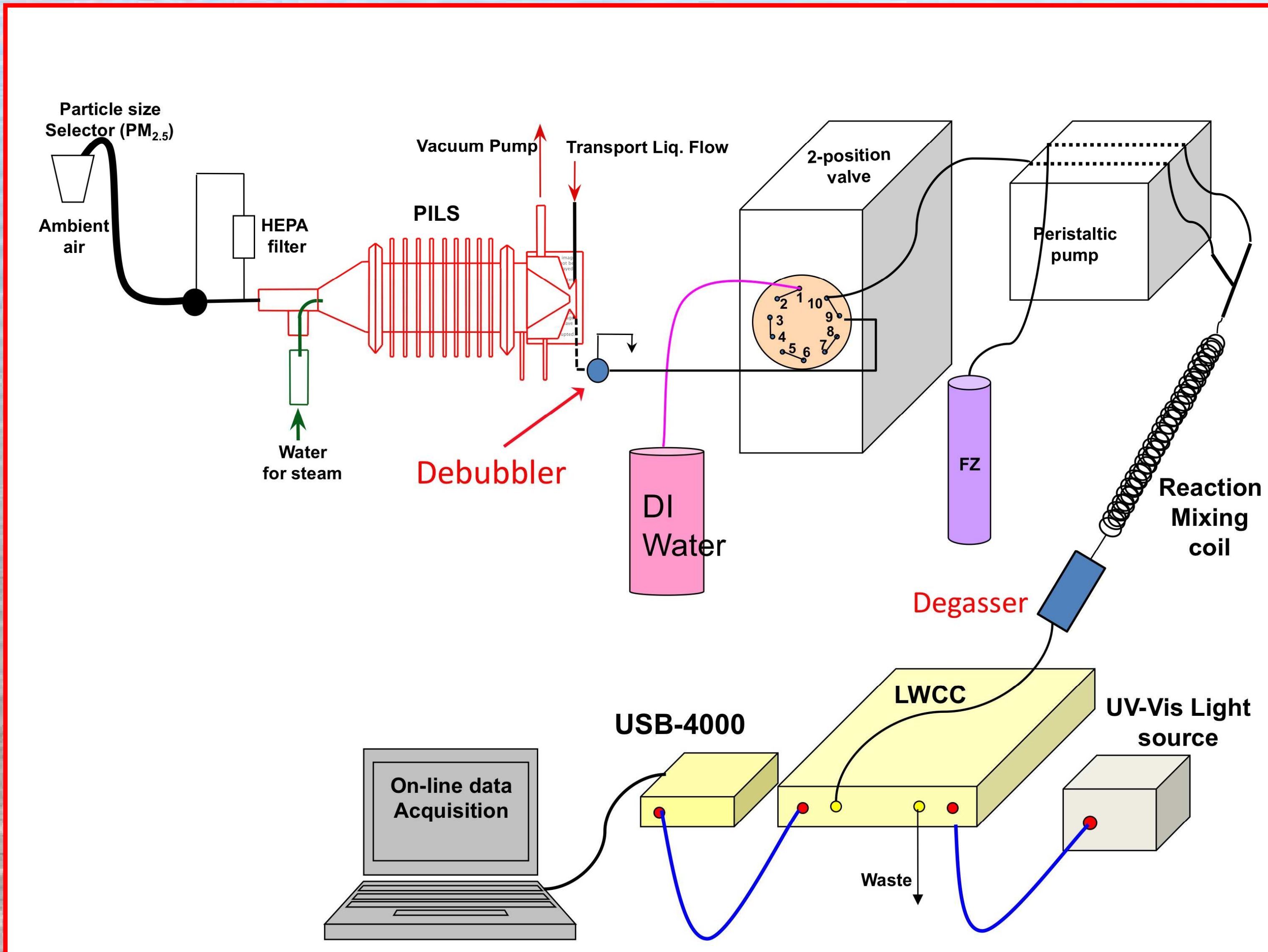
# (B) V1: PILS-LWCC for On-line Measurement of Water-Soluble Fe(II): Non-Continuous Gas Segmented Flow



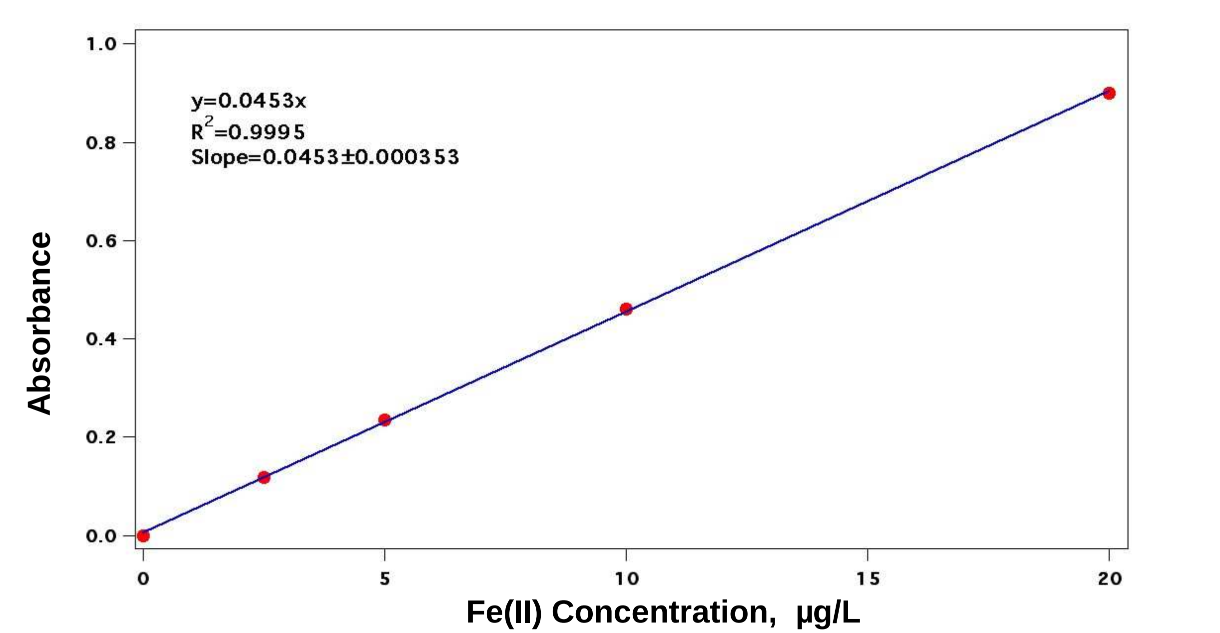

- 12-minute integration time
- LOD: 4.6 ng $m^{-3}$
- Relative Uncertainty: 12%

*Rastogi et al. ES&T 2009*

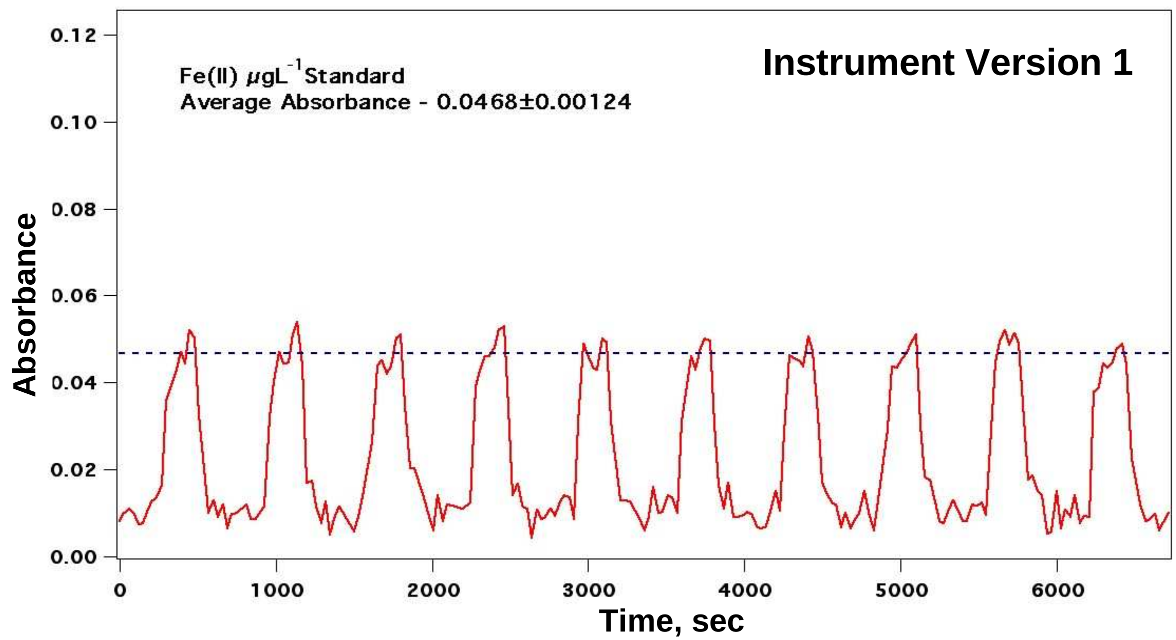
# (B) V2: PILS-LWCC for On-line Measurement of Water Soluble Fe(II): Continuous Sample/Water Blank Flow



# (B) WS_Fe(II) Calibration and Liquid Flow Analytical Method Performance




**Highly linear calibration**




**Good analytical precision <3% (std vs water blank)**

*Rastogi et al, ES&T 2009*

# (B) Urban and Biomass Burn Trial Studies: Verification and WS_Fe(II) Results

**Dearborn MI**
**Jan 13 - Feb 10, 2008**

**Urban Atlanta**

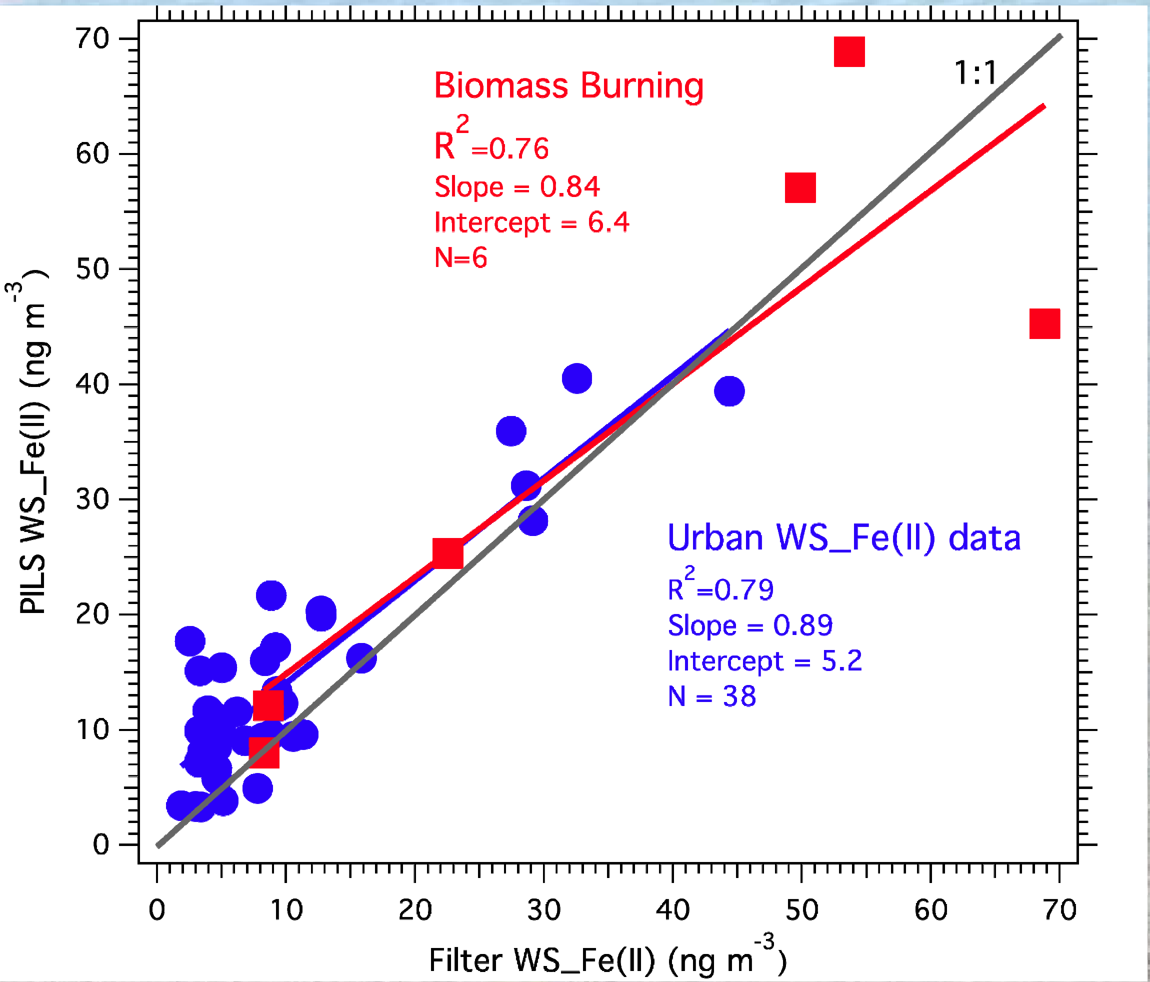
**EPRI AMIGAS**
Jeff. St. Aug 2008

**Fire Station 8**
2007-2010
Selected 1-mnth studies in different seasons

**Prescribed Burn: Albany GA**
**March 2008**

# (B) WS_Fe(II) Method Validation: PILS vs. Teflon Filter

**Urban Atlanta (6/08, 8/08, 6/09, 1/10) + Prescribed Burn**

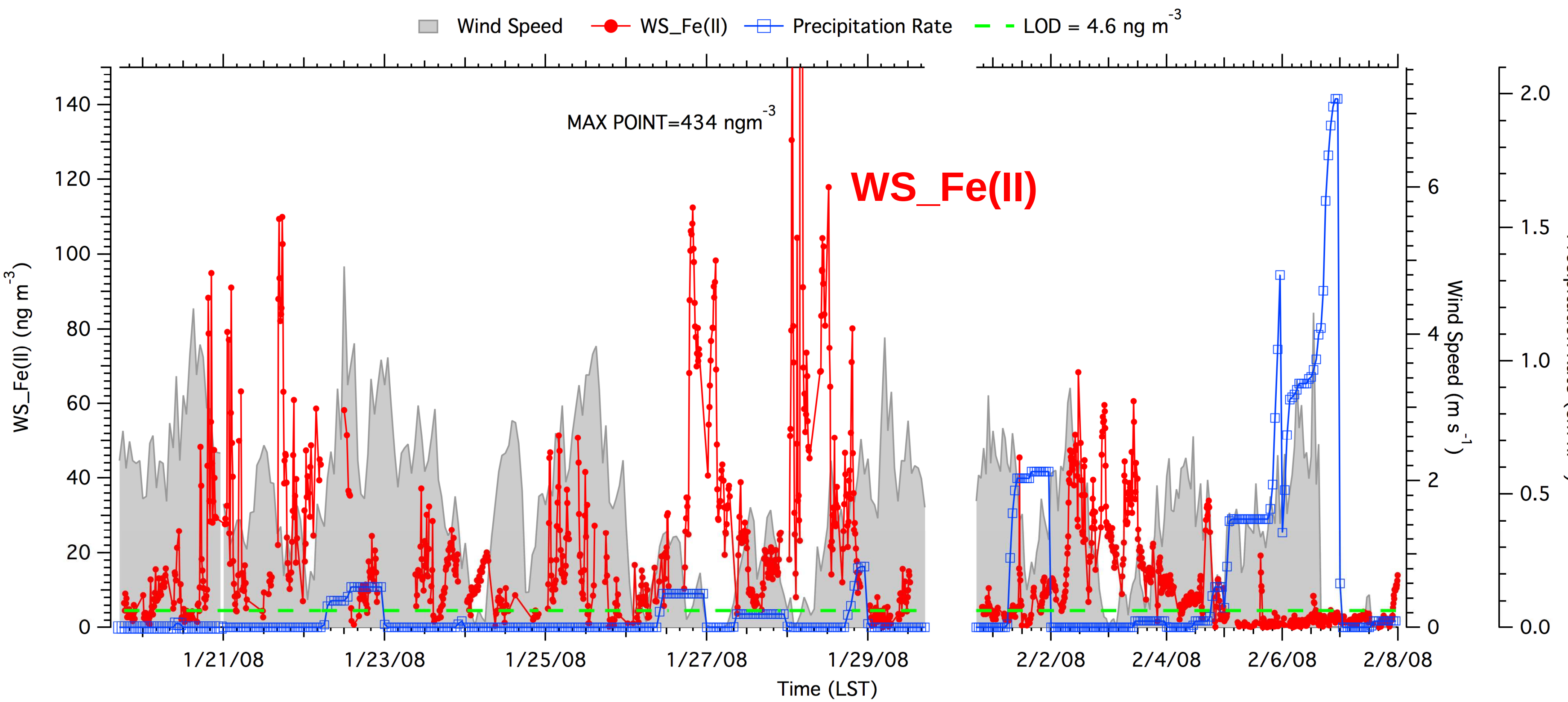



**Teflon filter extract with same analysis**

**PILS_LWCC WS_Fe(II) agrees with 24-h Teflon filter WS_Fe(II).**

**No FS-8 transient events**

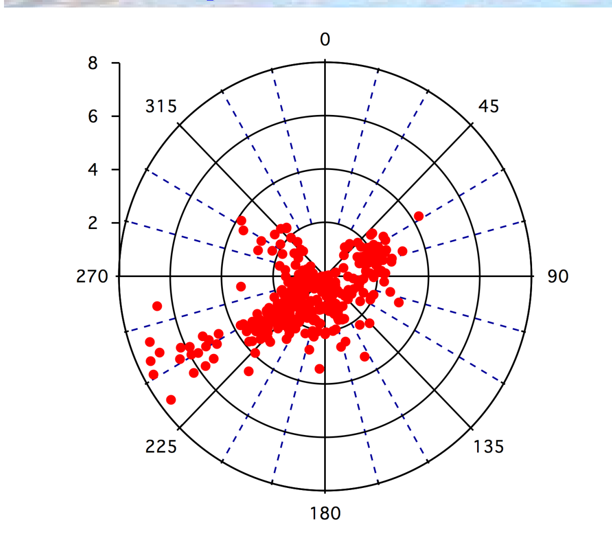
# (B) Winter in Dearborn
# WS_Fe(II) and Industrial Sources



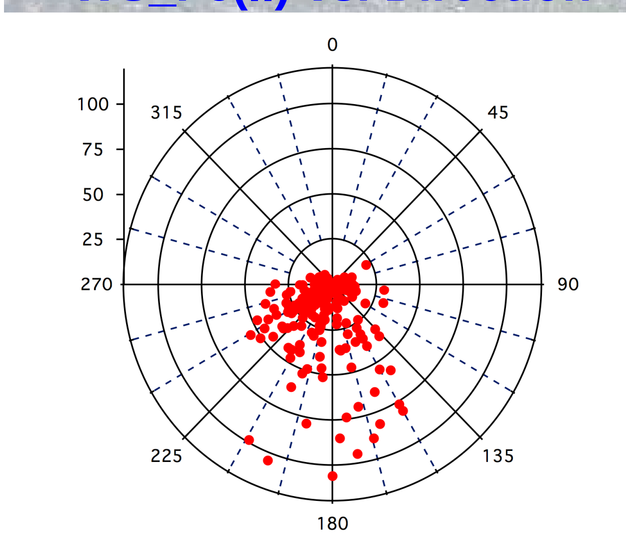

- WS_Fe(II) high during low wind speeds (local sources)
- WS_Fe(II) vs EC $R^2 = 0.03$ and vs OC $R^2 = 0.12$, not mobile sources.
- No correlation between WS_Fe(II) and PM2.5 mass ($R^2$=0.004), no association with any other significant PM2.5 component.

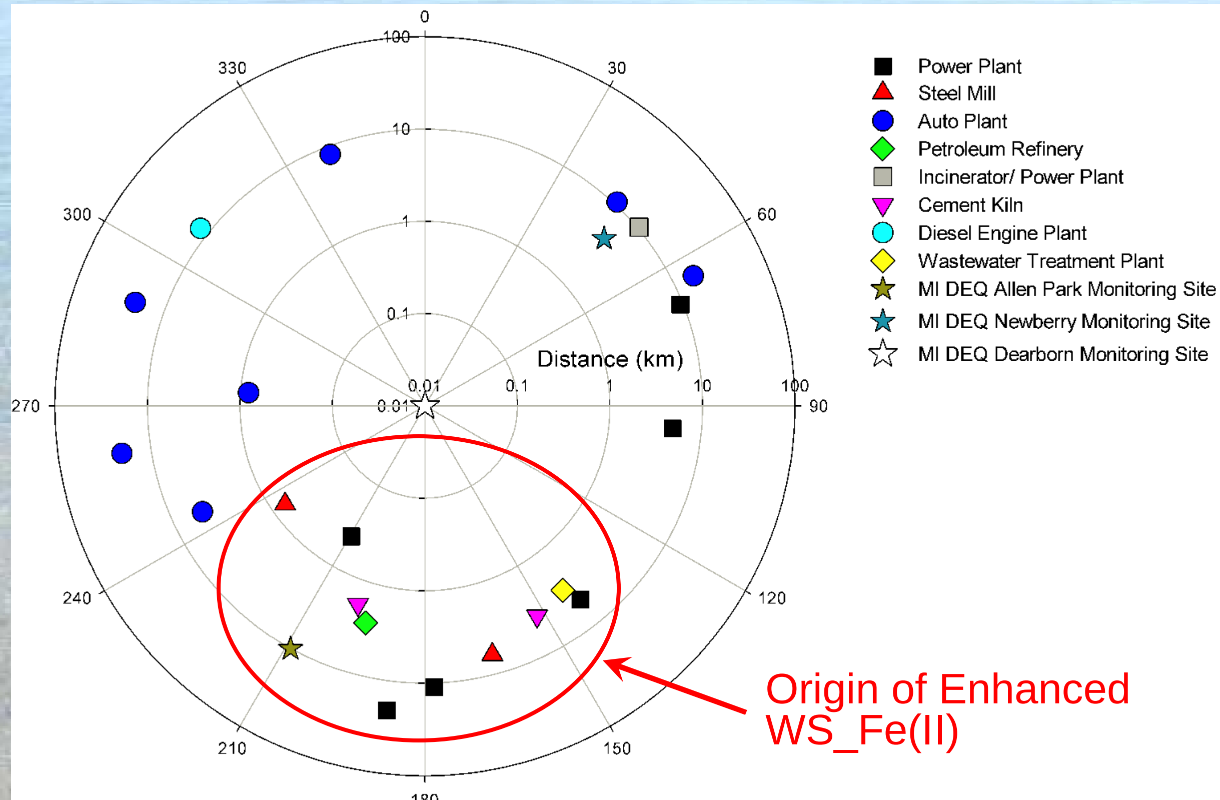
# (B) Winter in Dearborn
# WS_Fe(II) and Industrial Sources

## Wind Speed vs Direction




## WS_Fe(II) vs. Direction

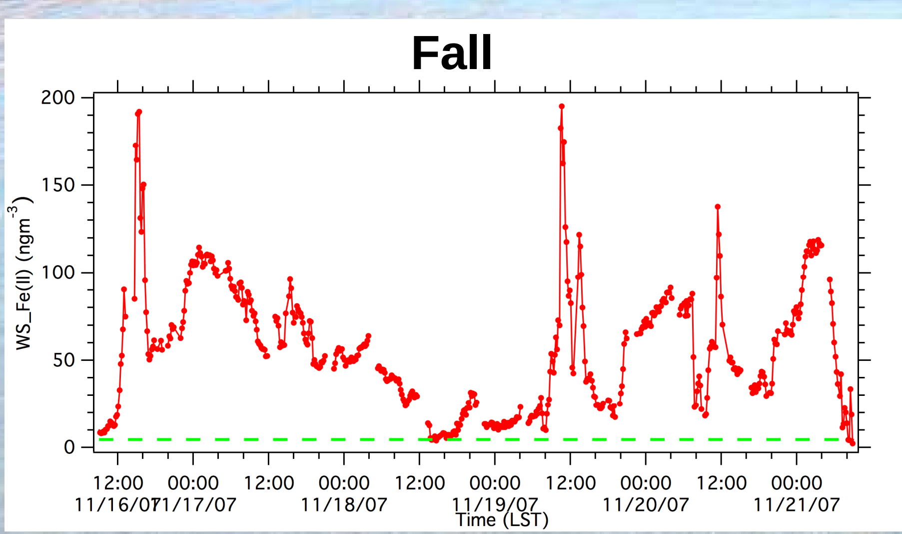


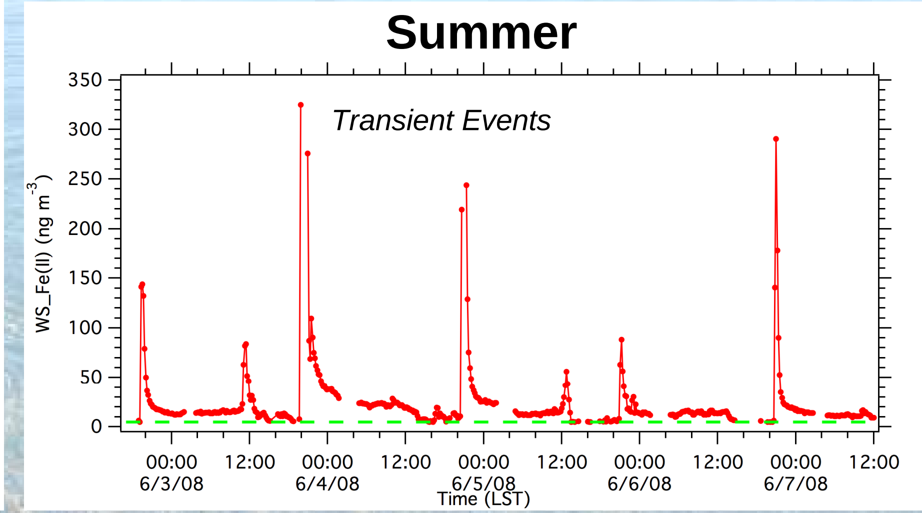




**WS_Fe(II) and industrial sources to the south**

*Oakes et al, JGR, 2010*

# (B) WS_Fe(II) Seasonal Variability In Atlanta



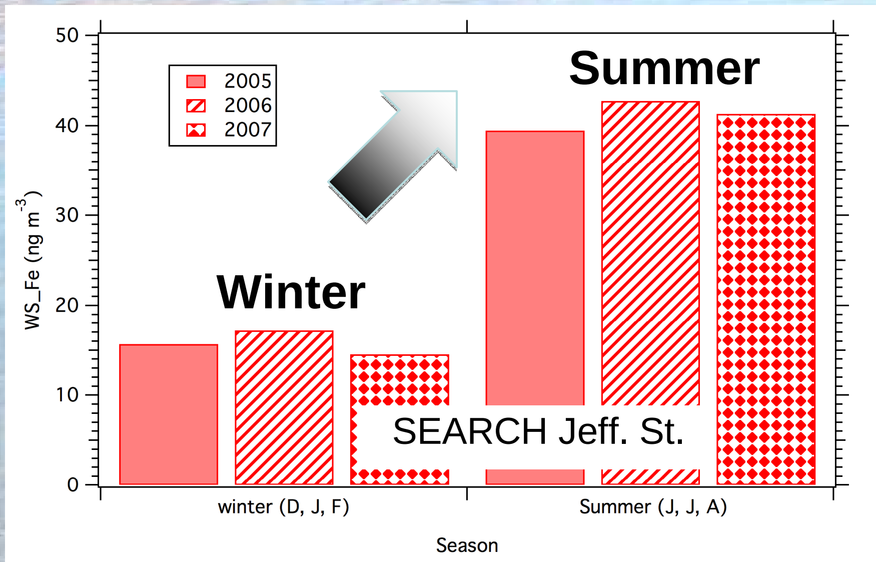

•Concentrations in ng $m^{-3}$

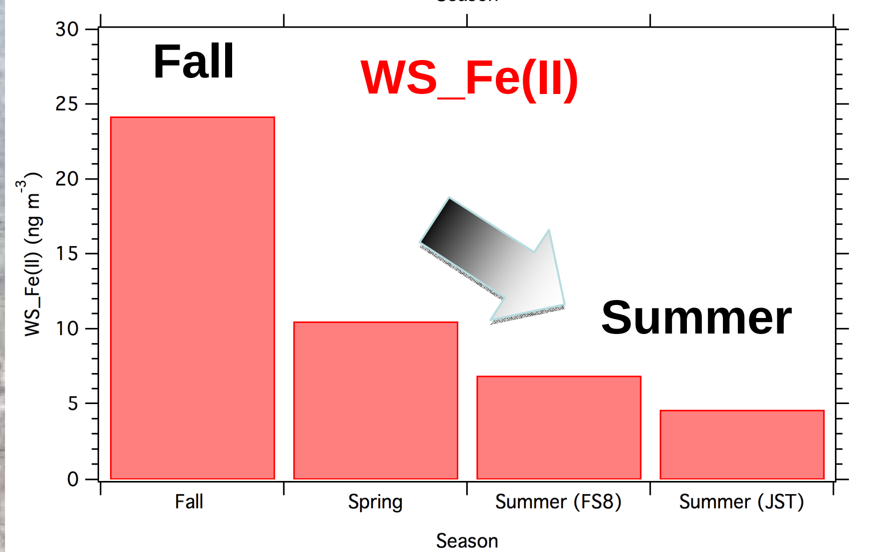
| Season | Site | % <LOD | Mean | Med | Stdev | N |
|---|---|---|---|---|---|---|
| Fall | FS8 | 4.6 | 34.8 | 24.2 | 30.5 | 1401 |
| Spring | FS8 | 27.0 | 14.8 | 10.5 | 13.7 | 456 |
| Summer | FS8 | 36.7 | 13.4 | 6.9 | 28.3 | 2050 |
| Summer | JST | 49.7 | 5.1 | 4.6 | 3.6 | 1278 |

*Oakes et. al., 2010*

# (B) WS_Fe(II) Seasonal Variability In Atlanta

**Total WS_Fe: Fe(II)+Fe(III)**




In Summer Total WS_Fe is higher

Mostly in form of WS_Fe(III) ?

**Oxidation**

$Fe^{2+} + H_2O_2 \rightarrow Fe(III) + \bullet OH + OH^-$

$Fe^{2+} + HO_2\text{-}H^+ \rightarrow Fe(III) + H_2O_2$

$Fe^{2+} + O_3\text{-}H^+ \rightarrow Fe(III) + OH^* + O_2$

Etc . . .

**Reduction**

$Fe^{3+}\text{-}Org + hv \rightarrow Fe^{2+} + Org^*$

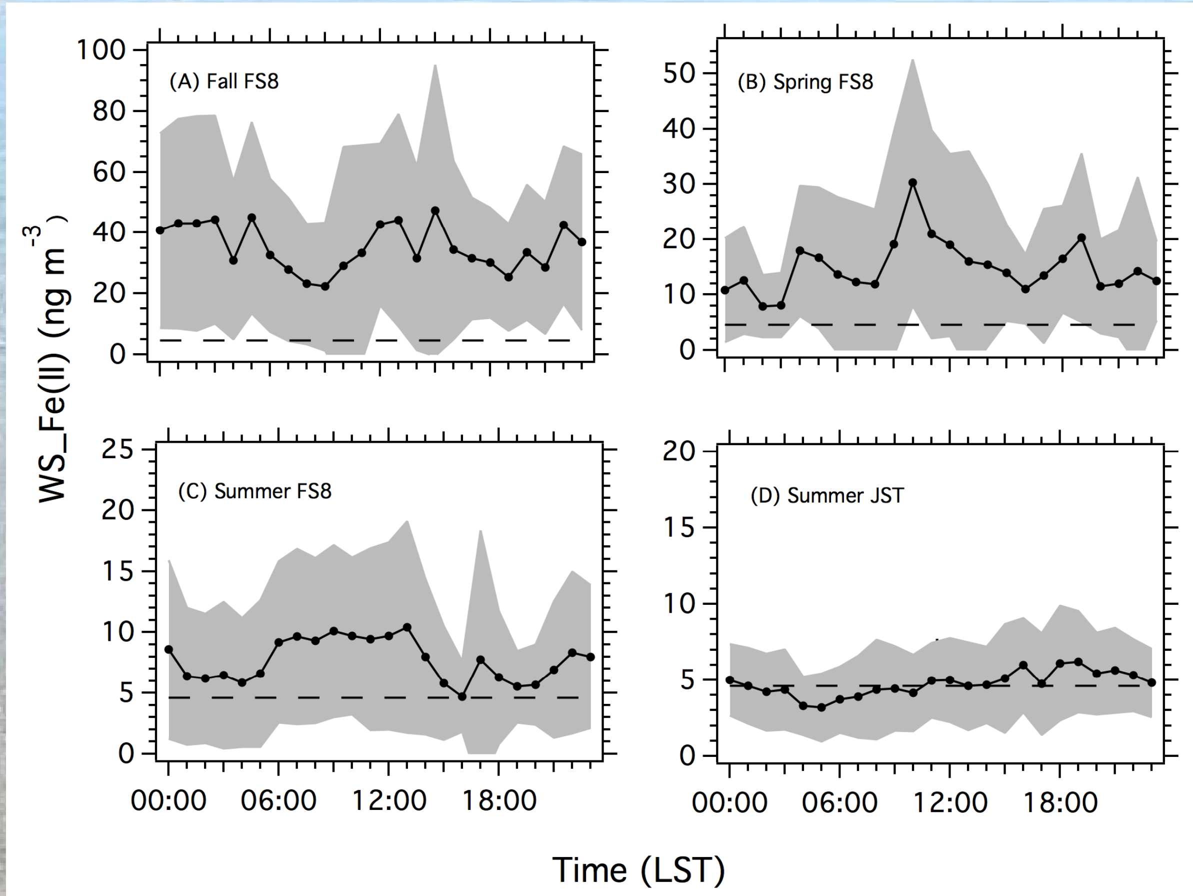
$Fe(III) + O_2^- \rightarrow Fe(II) + O_2$

$Fe(III) + S(IV)\text{-}O_2 \rightarrow Fe(II) + S(VI)$

Etc . . .

# (B) WS_Fe(II) Diurnal Trends in Atlanta

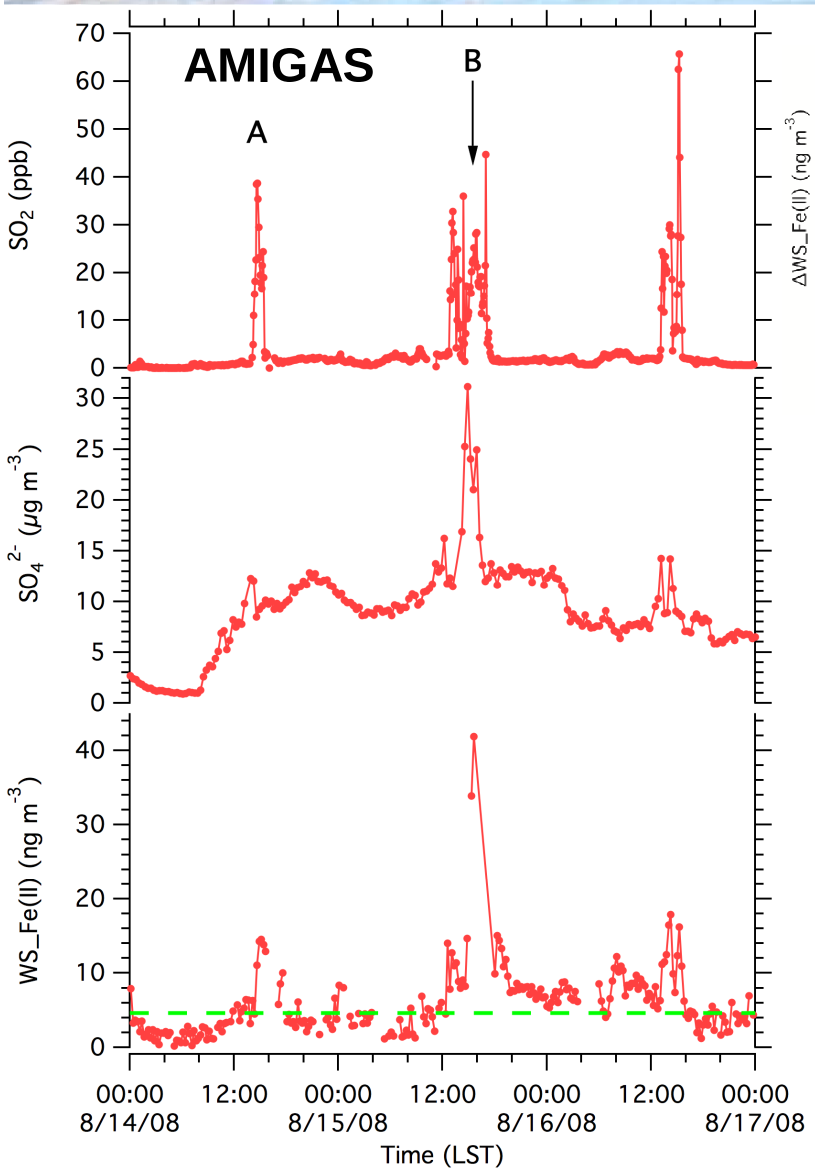
**BUT NO EVIDENCE FOR A DAY/NIGHT PATTERN**

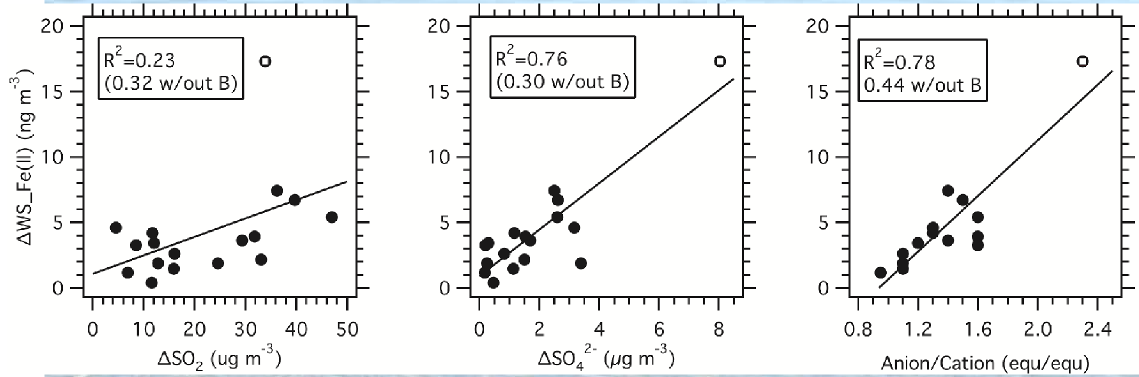



*Oakes et. al., 2010*

- **Photo-reductive processes do not impact the net concentration in Atlanta ? Possible red-ox chemistry (e.g. re-oxidation)?**

# (B) Evidence for WS_Fe(II) and Acid Aerosol Linkage

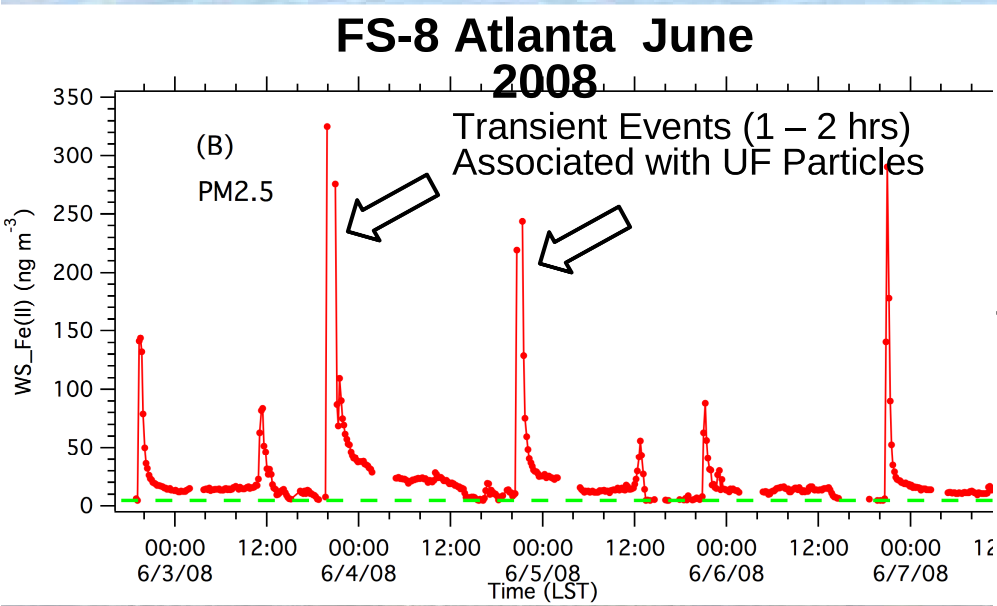


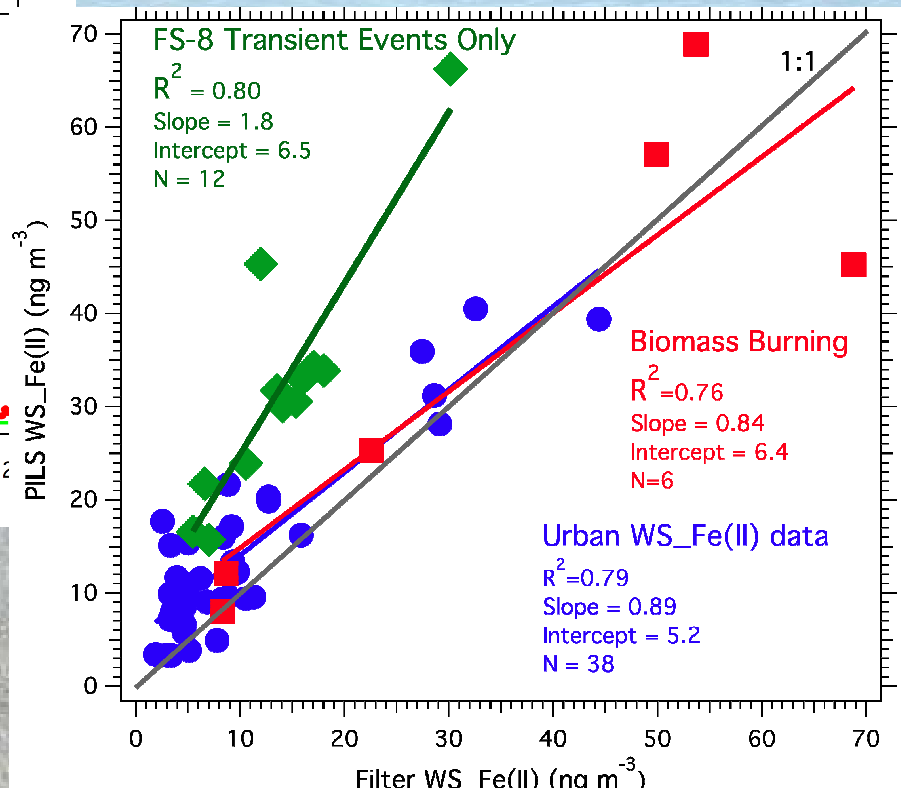




- Transient WS_Fe(II) tracked $SO_2$ and $SO_4^{2-}$
- Fresh (Plume A) vs. Aged (Plume B) Coal-fired power plant plume
- Evidence for acid-processing:
  - $\Delta$WS_Fe(II) correlates better with $\Delta SO_4^{2-}$ and particle acidity than $\Delta SO_2$
- Origin of iron particle?
  - Co-emitted and later processed
  - Other source of Fe.

*Oakes et. al., 2010*

# (B) Filter WS_Fe(II) Negative Artifacts In Unique Emissions?




**Also observed in spring 2010**

Filter WS_Fe(II) consistently lower than PILS C during unique transient events
Sampling artifact inherent with the filter-based method.

# (B) Current Status of Method Development (Redox Active Metals)

| Module or Analyte Group | | | |
|---|---|---|---|
| Bulk Components (Major Ions) | Cations & Anions (Source Tracers) | Redox Active Metals | Water Soluble Organic Carbon |
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| | Chloride ($Cl^-$) | Chromium (Cr) | |

| | | |
|---|---|---|
| PILS deployment completed or planned | Successful implementation of method with filter-based samples | Successful method development |

# Summary

Configure, validate and deploy cost-effective, robust "real-time" (1h) instruments to measure water-soluble components of PM2.5 at network sites.

## Inorganic Species:

1. Configuring and validating methods took longer than expected, LODs in practice (PILS-ISE) are an issue.
2. Demonstrated ***PILS-ISE online method*** with $K^+$ and $Na^+$. Nitrate PILS-Optical LWCC is also viable alternative to IC.

## Water-Soluble Metals:

1. PILS-Optical/LWCC for WS_Fe(II) is a proven robust method. Application to other metals is straight-forward extension, but only viable in high concentration atmospheres (LOD limitations).

# Products

## Current Status of Manuscripts

1. Optical-LWCC Nitrate Method; Shafer et al., in progress.
2. Optical-LWCC Cu Method; Shafer et al., in progress.
3. ISE Method Overview Paper, Shafer et al., in prep.
4. PILS-ISE $K^+$, $Na^+$ paper (Revision to Rastogi et al. AS&T 2009).
5. PILS-WS_Fe(II) Method; Rastogi et al. ES&T, 43, 2425-2430, 2009.
6. WS_Fe(II) Ambient Results using Real-Time Data; Oakes et al., J. Geophys. Res., 10.1029/2009JD012638, 2010.
7. WS_Fe(II) transient events and filter artifacts, Oakes et al, in prep.
8. Oakes et al. PhD Thesis

## 8 Conference Presentations

## Training of 2 Post Docs, 3 grad. students, undergrad assistants.