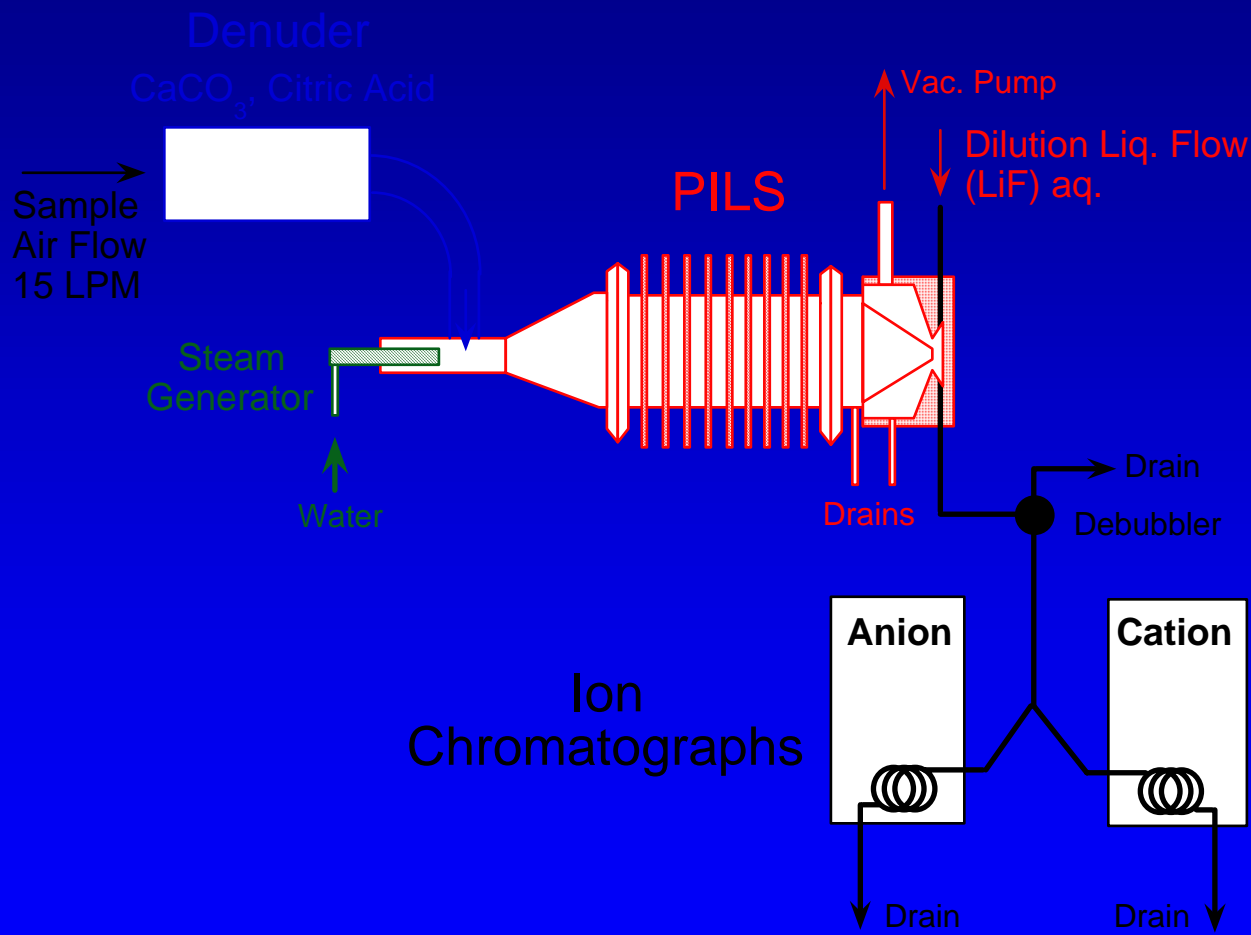


Preliminary Comparison of 2 Continuous PM Analyzers

**E. Edgerton and B. Hartsell, ARA
R. Weber, GIT**

AAAR 2002
Charlotte, NC

Aerosol Chemistry: Particle-Into-Liquid-Sampler



PILS Features

- 7.5 minute collection interval
- 8.5 minute analysis interval
- Analysis via IC: true SO₄, NO₃, NH₄
- Capability for faster response/add'l. analytes

SEARCH Continuous Trace Gas and Particle Measurements

<u>Species</u>	<u>Method</u>	<u>Time Resolution</u>	<u>Status</u>
O ₃ , NO, NO _y , SO ₂ , NO ₂ , CO	various	1-minute	commercialized
HNO ₃	denuder diff.	1-minute, 60-minute	routine
NH ₃ /TRN	cat. oxid. To NO	< 60-minute	drawing board
PM _{2.5} Mass	TEOM, dry, 30C	5-minute	commercialized
PM _{coarse} Mass	TEOM, dry, 30C	5-minute	developmental
Part. Black Carbon	optical absorption	5-minute	commercialized (aethalometer))
Part. Carbon	combustion to CO ₂	60-minute	commercialized
Part. SO ₄	reduction to SO ₂	5-minute	modified Harvard approach
Part. NO ₃ /NH ₄	cat. red./ox. to NO	5-minute	ARA

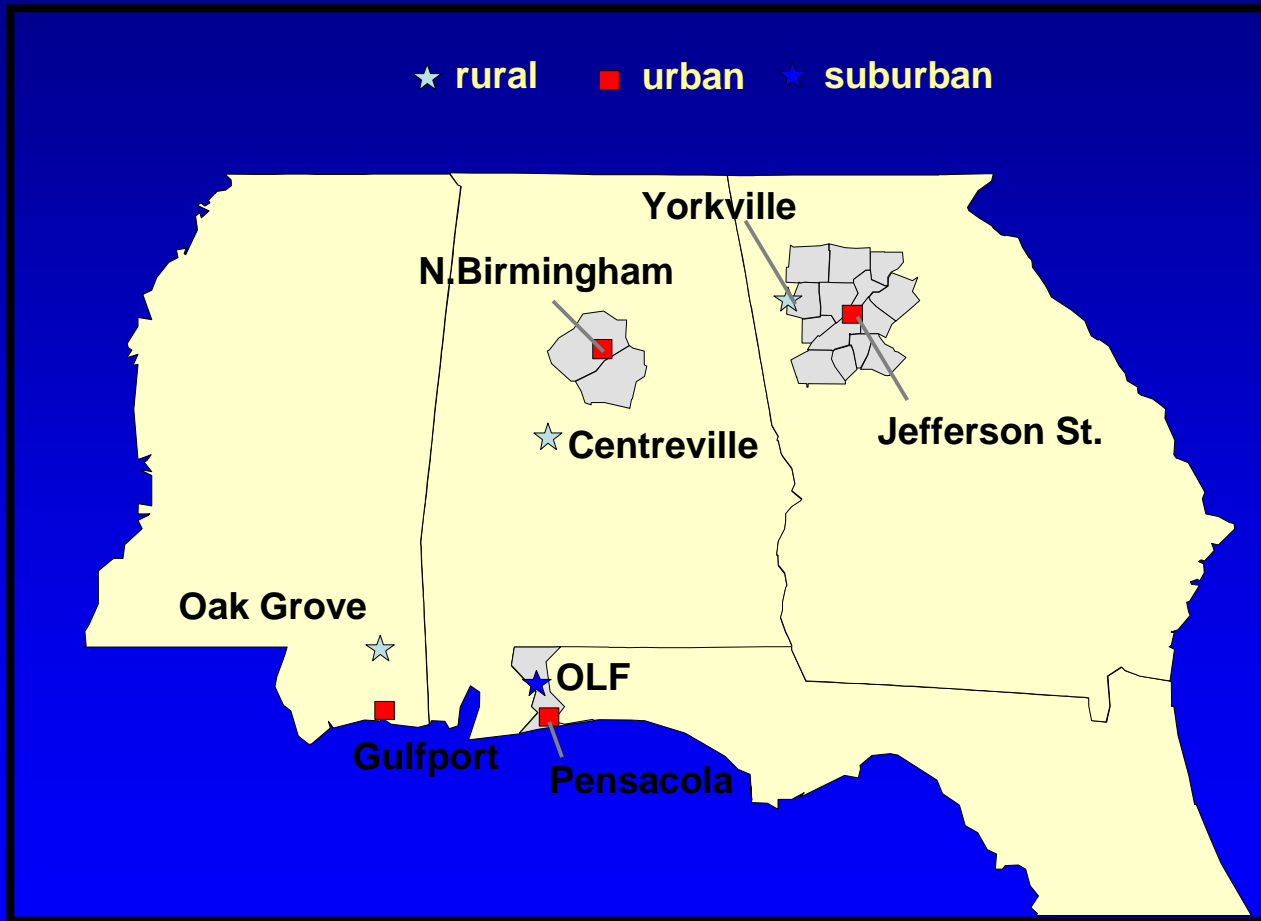
ARA Continuous PM

- Harvard SO₄ analyzer
 - Denuders to remove SO₂ (carbonate) and reduced S gases (C monolith)
 - Reduction of SO₄ to SO₂ on hot SS (850+C)
 - Automated zeroing every 90 minutes
 - 1-minute data acquisition
 - Mean and s.d. each averaging interval

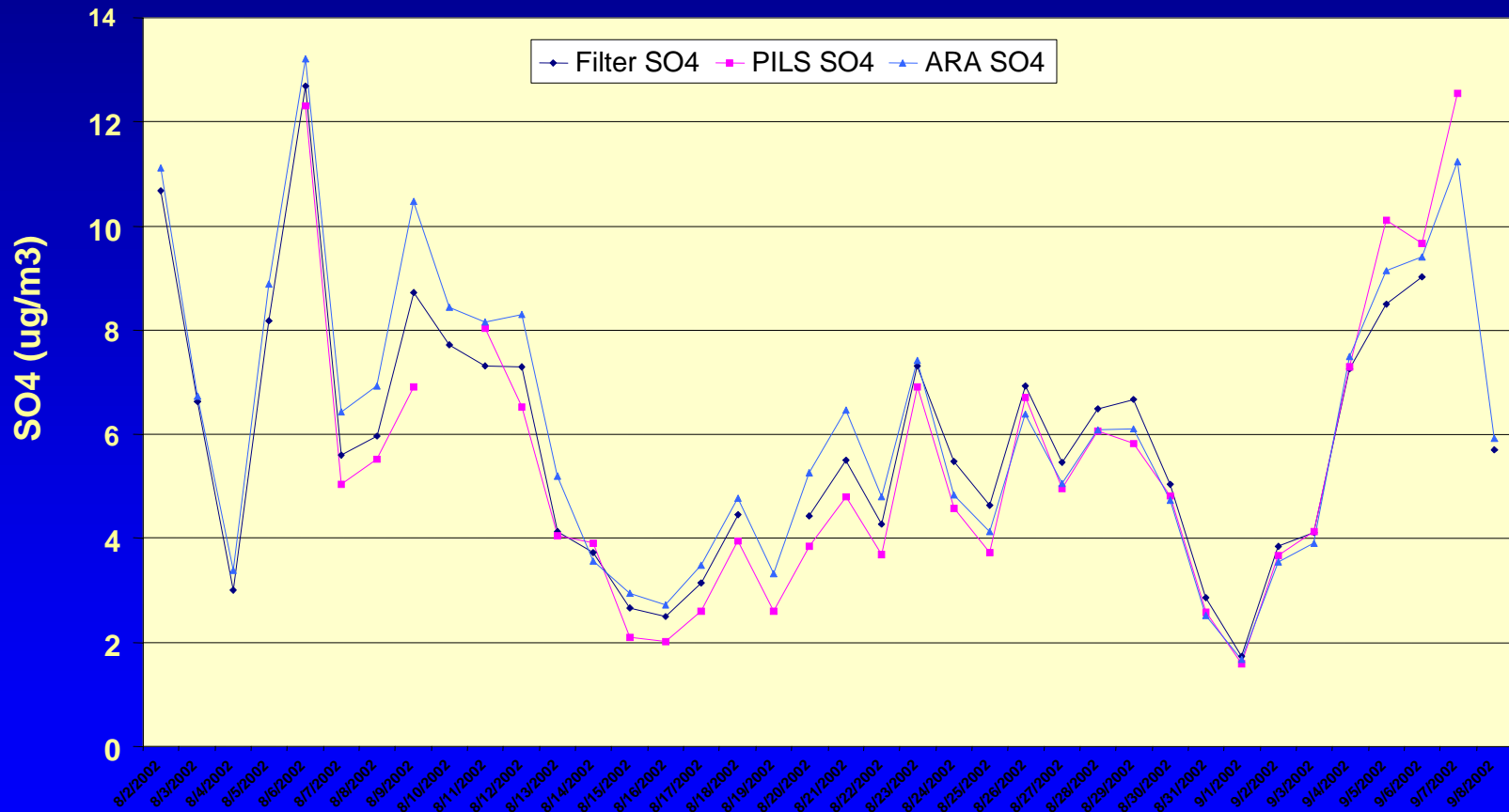
ARA Continuous PM (cont'd.)

- 3-channel analyzer for NH_4 and NO_3
- NH_4 via oxidation to NO on hot Pt
- NO_3 via reduction to NO on Mo
- Remove gas phase species with acid/base denuders and C monolith
- Detection via NO -ozone CL
- 1-minute data acquisition

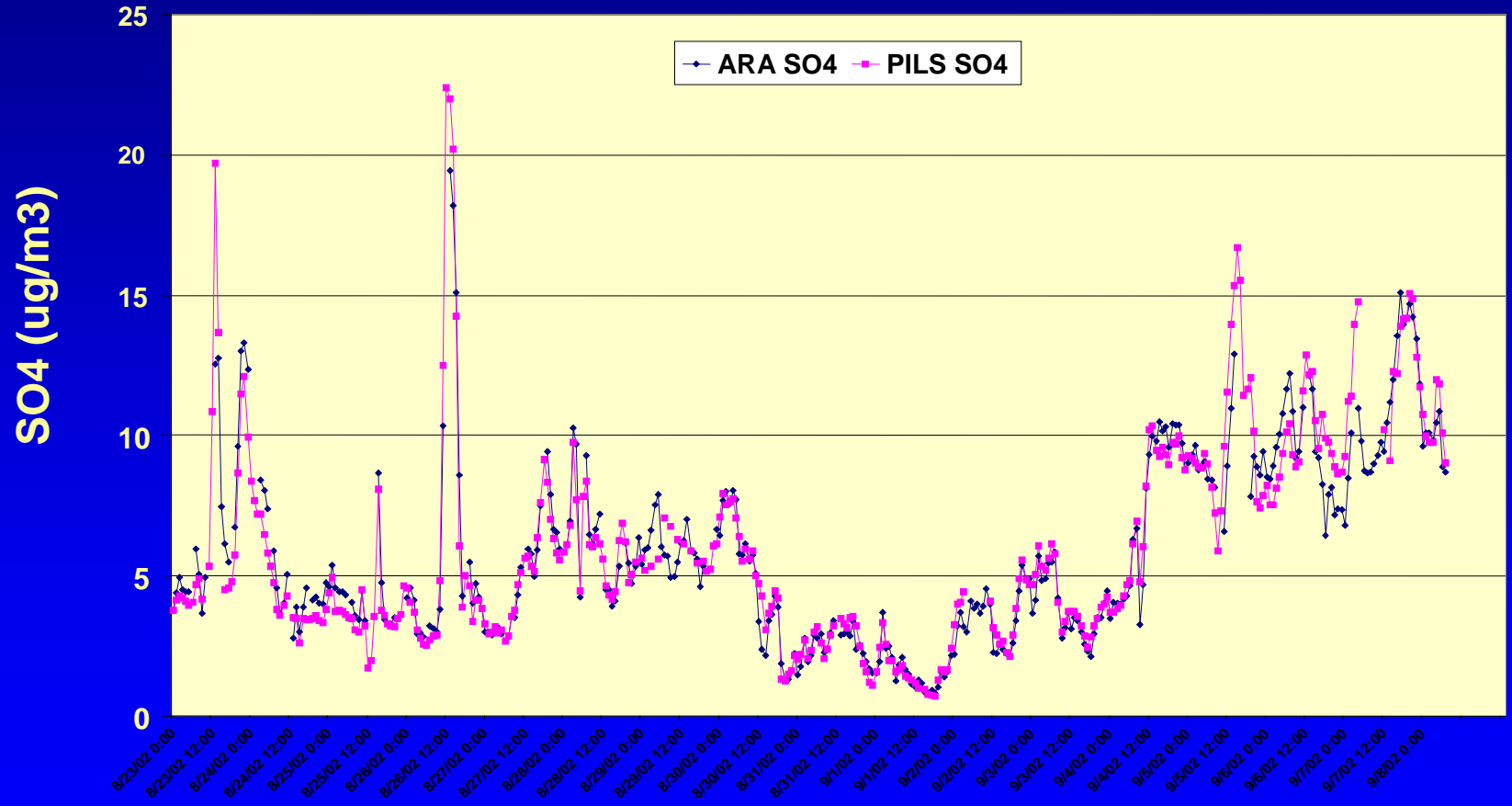
SEARCH Research Network



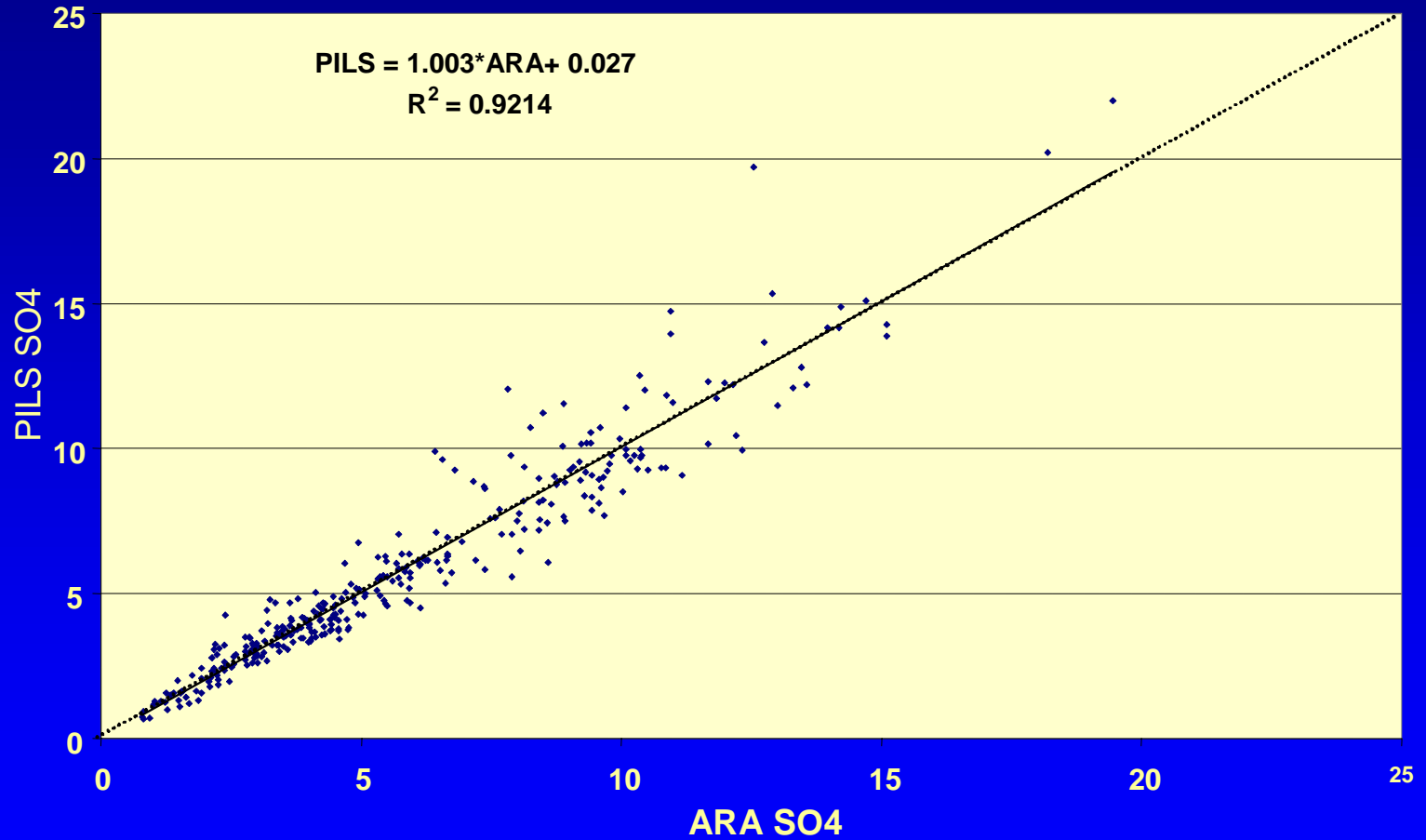
Time Series of 24-Hr SO_4^{2-}



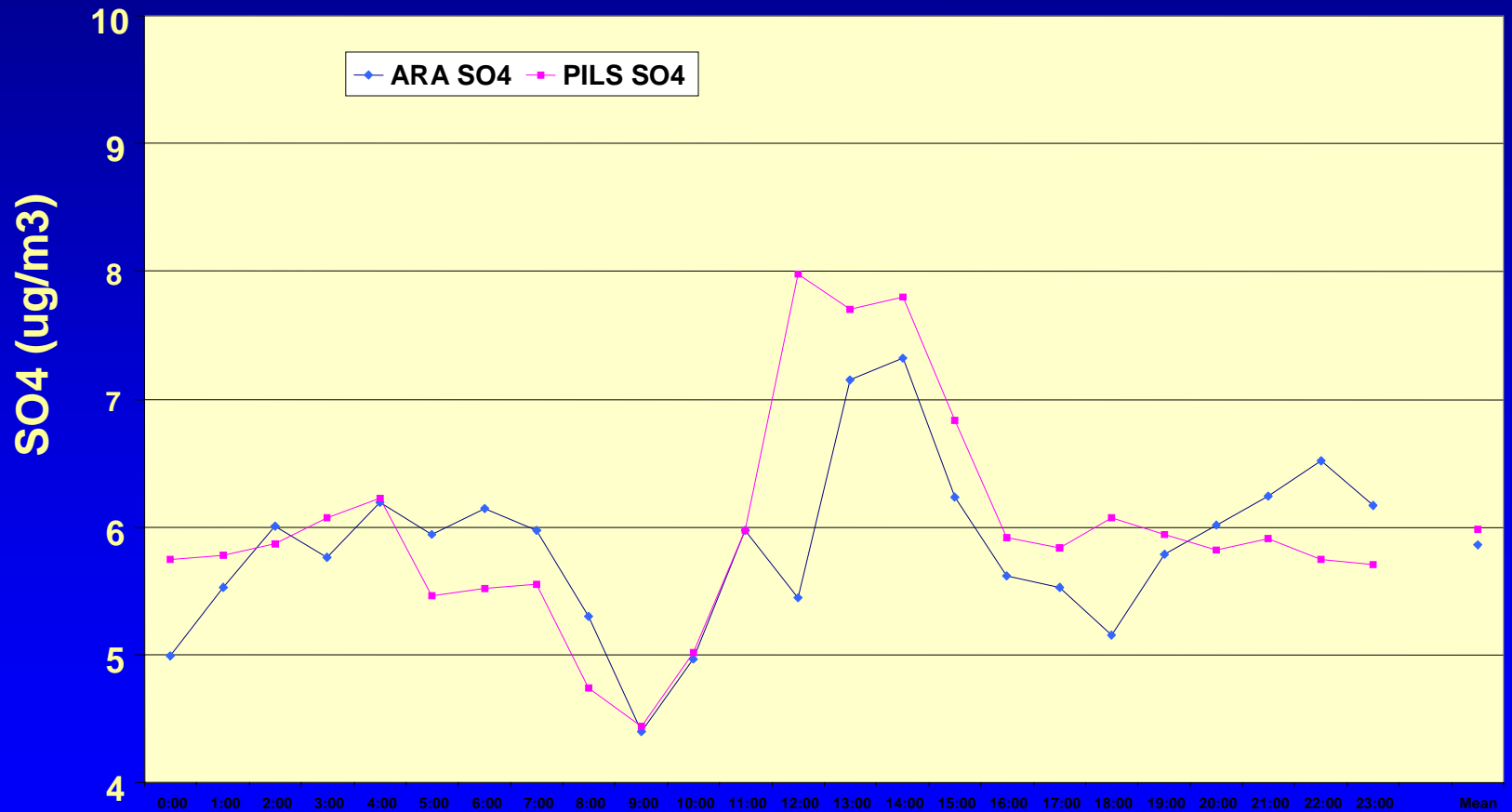
Time Series of Hourly SO_4^{2-}



Scattergram of Hourly SO_4^{2-}

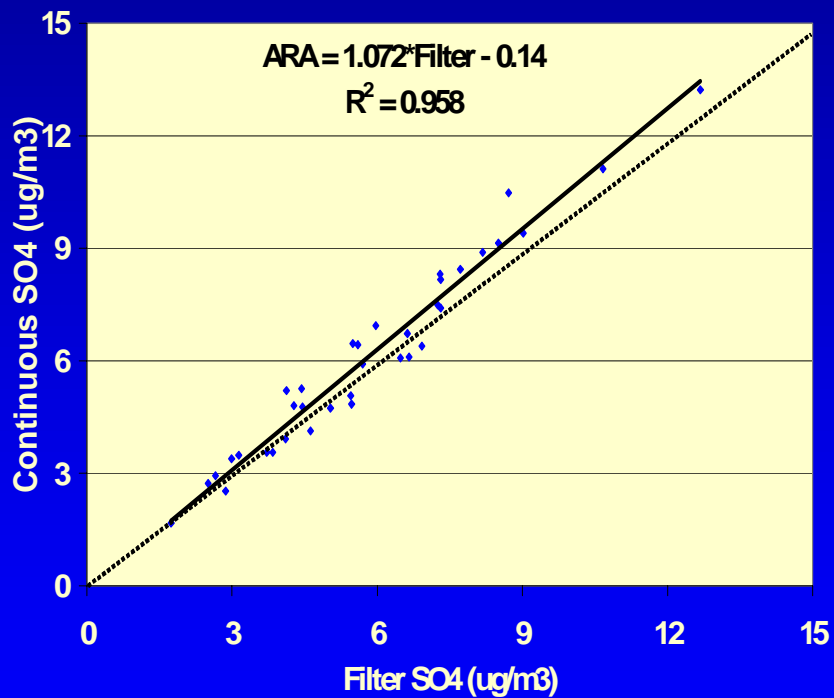


Diurnal Pattern for SO_4^{2-}

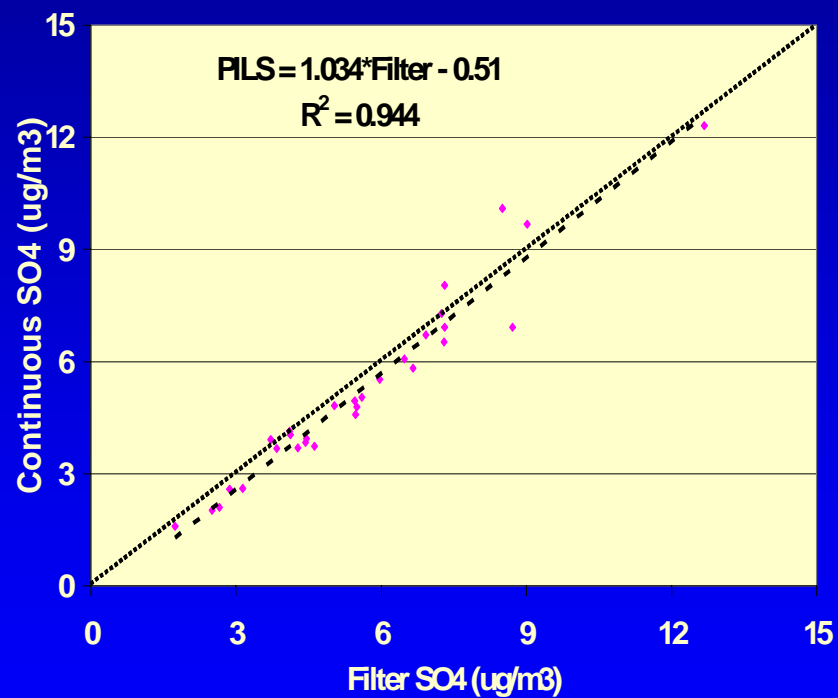


Continuous vs. Filter SO_4^{2-}

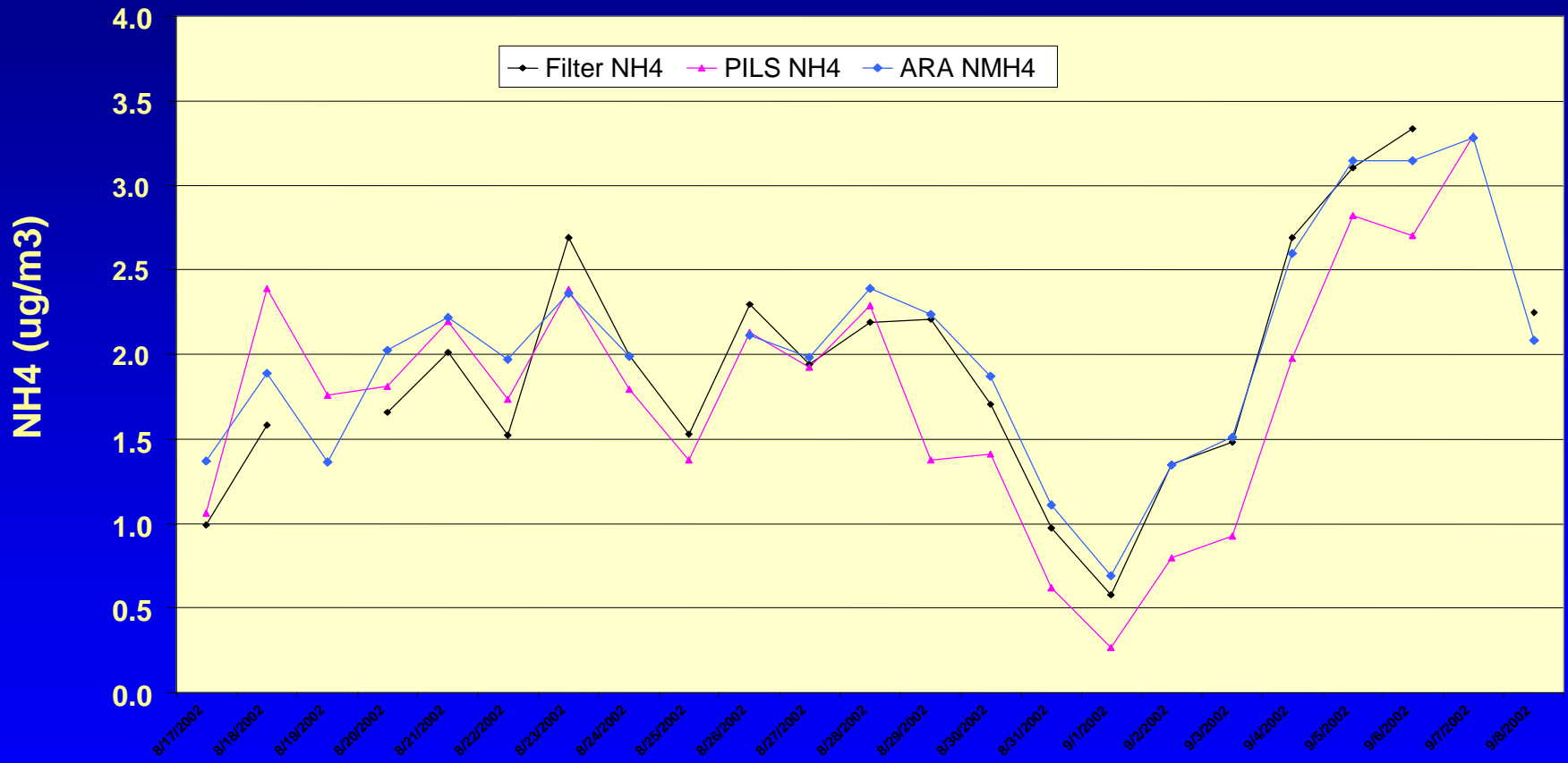
ARA



PILS

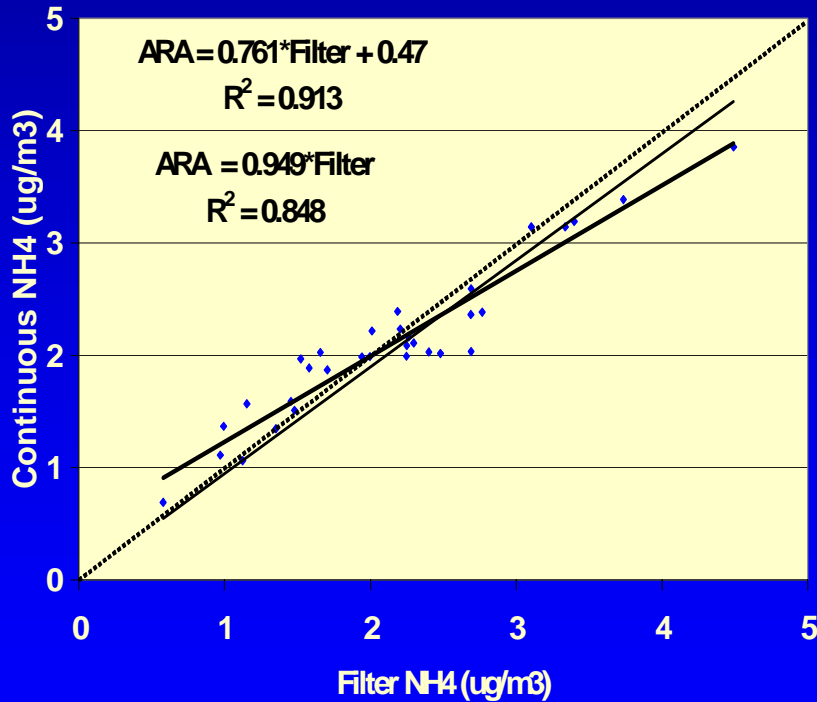


Time Series of 24-hr NH_4^+

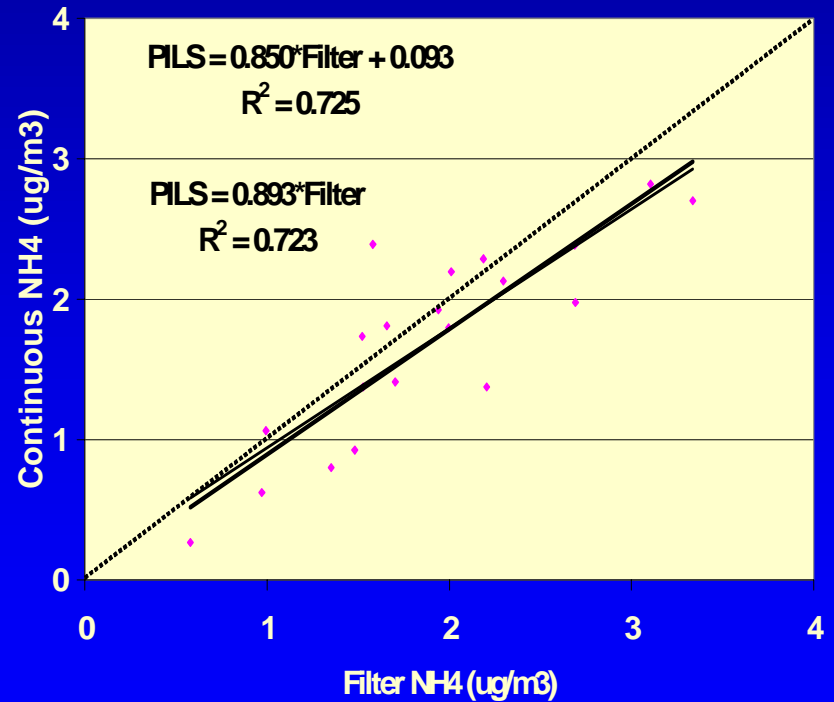


Continuous vs. Filter NH_4^+

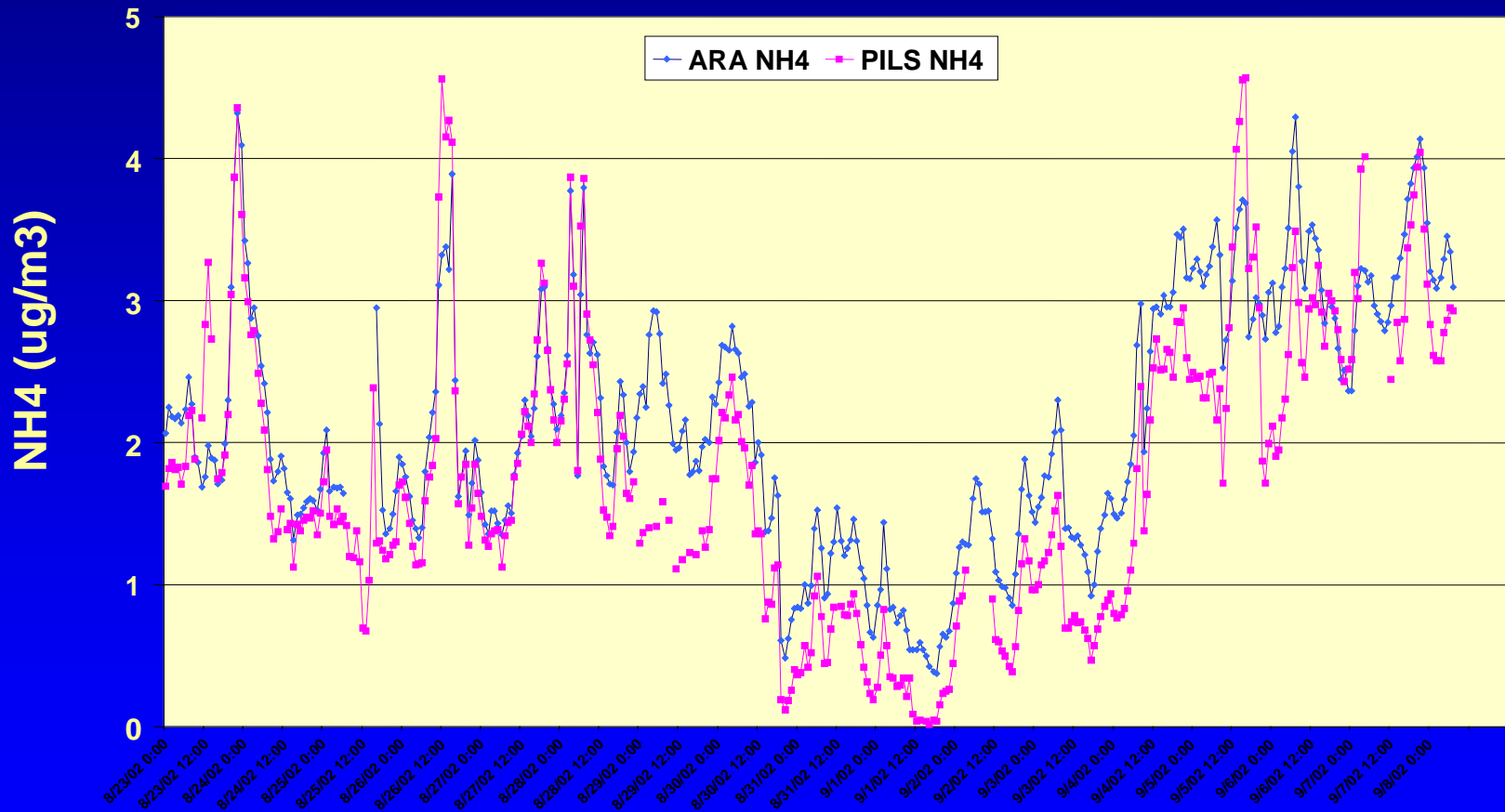
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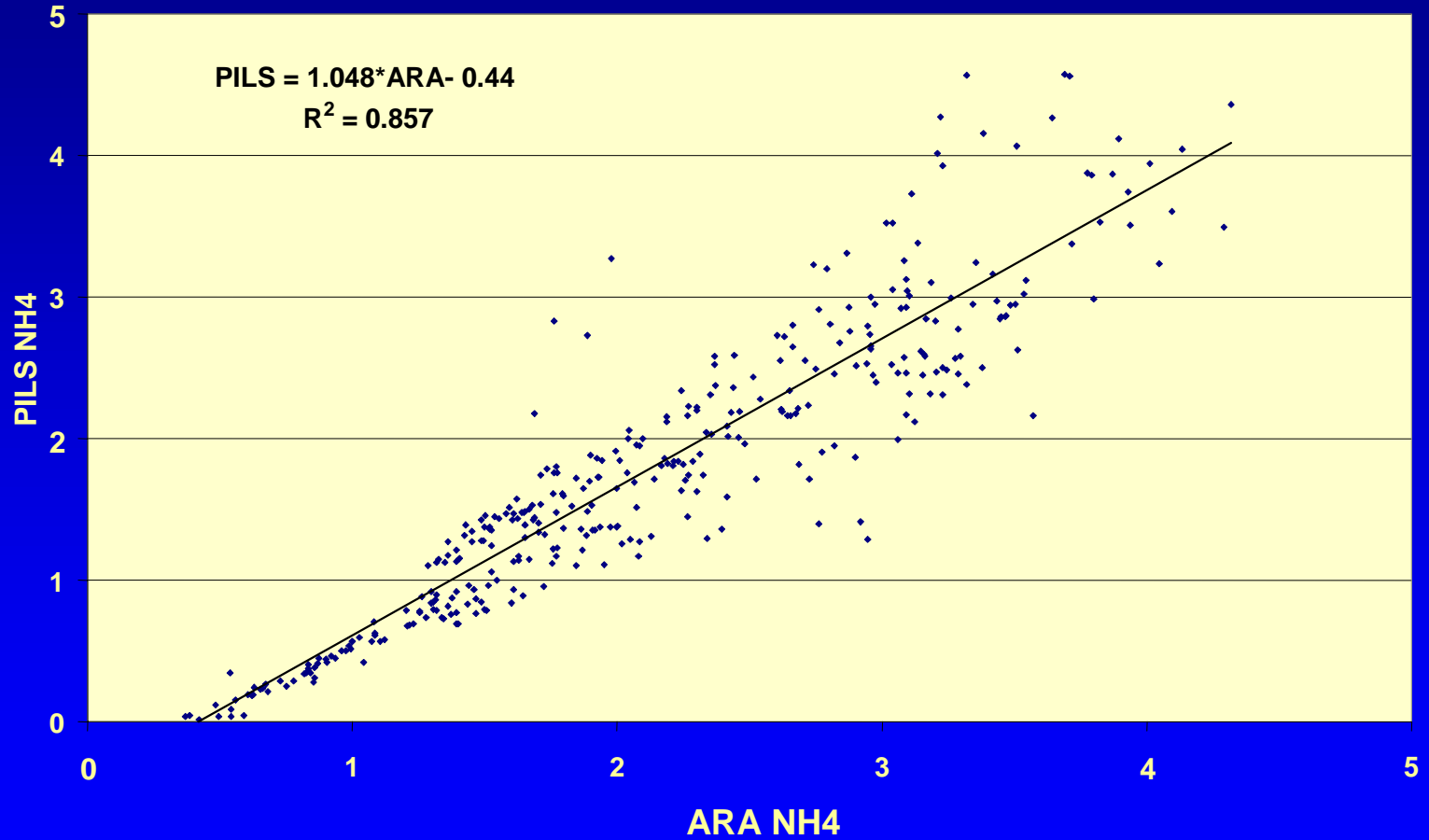
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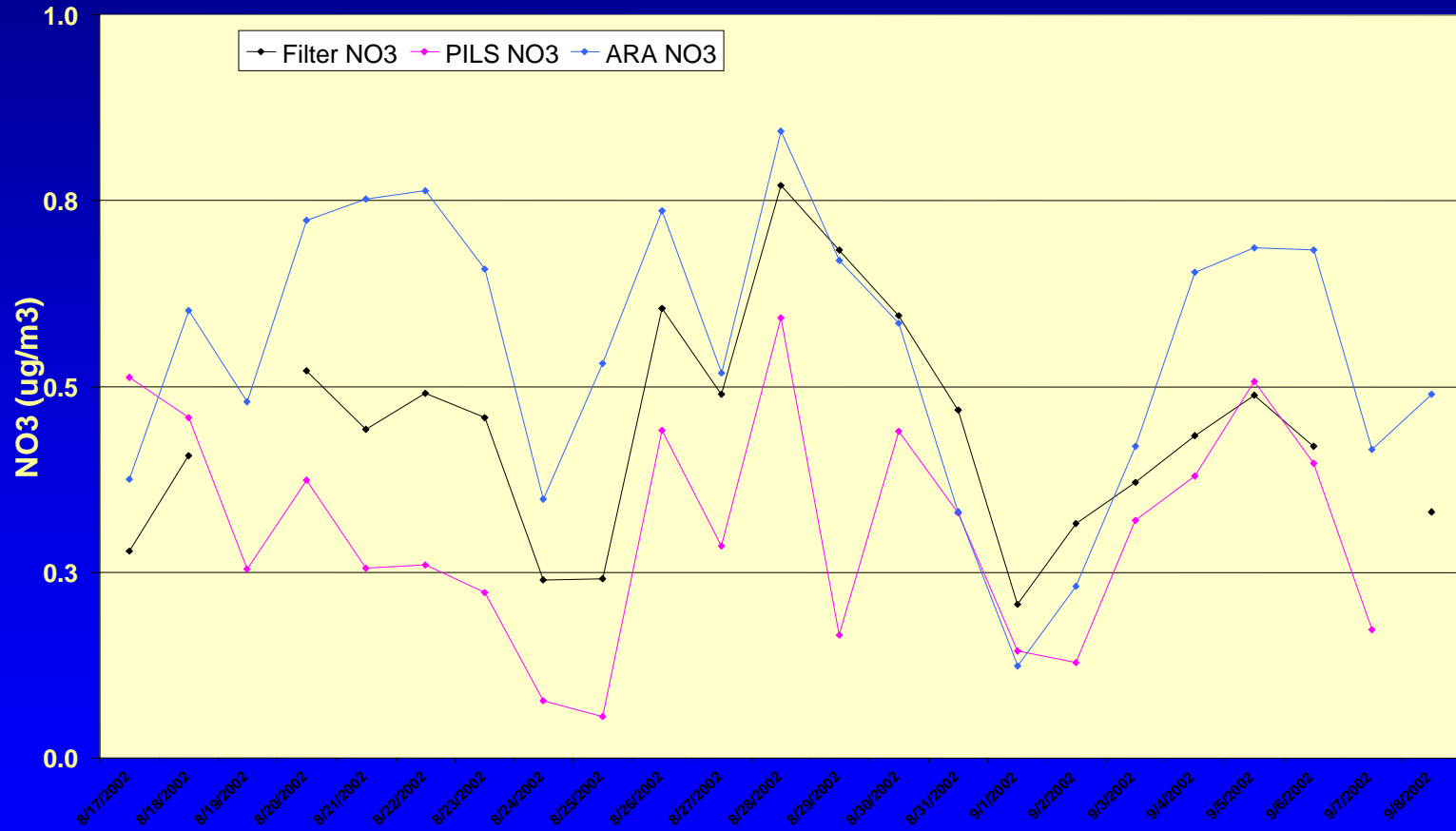
Time Series of Hourly NH_4^+



Scattergram of Hourly NH_4^+

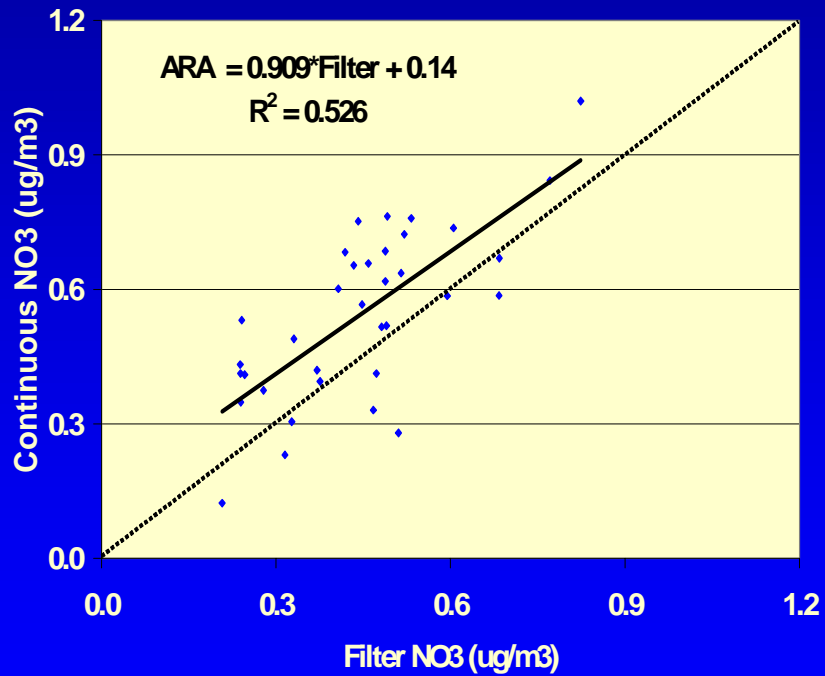


Time Series of 24-hr NO_3^-

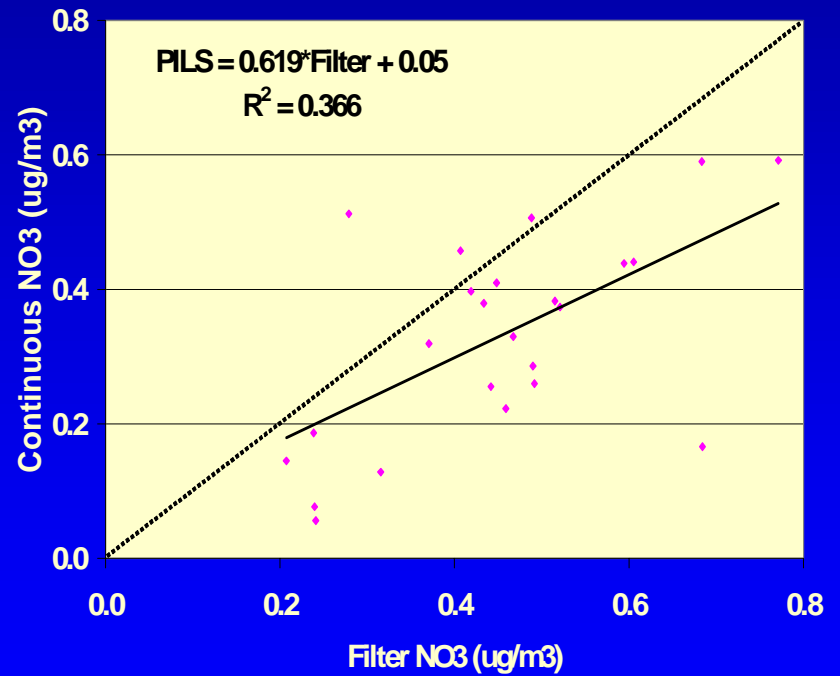


Continuous vs. Filter NO_3^-

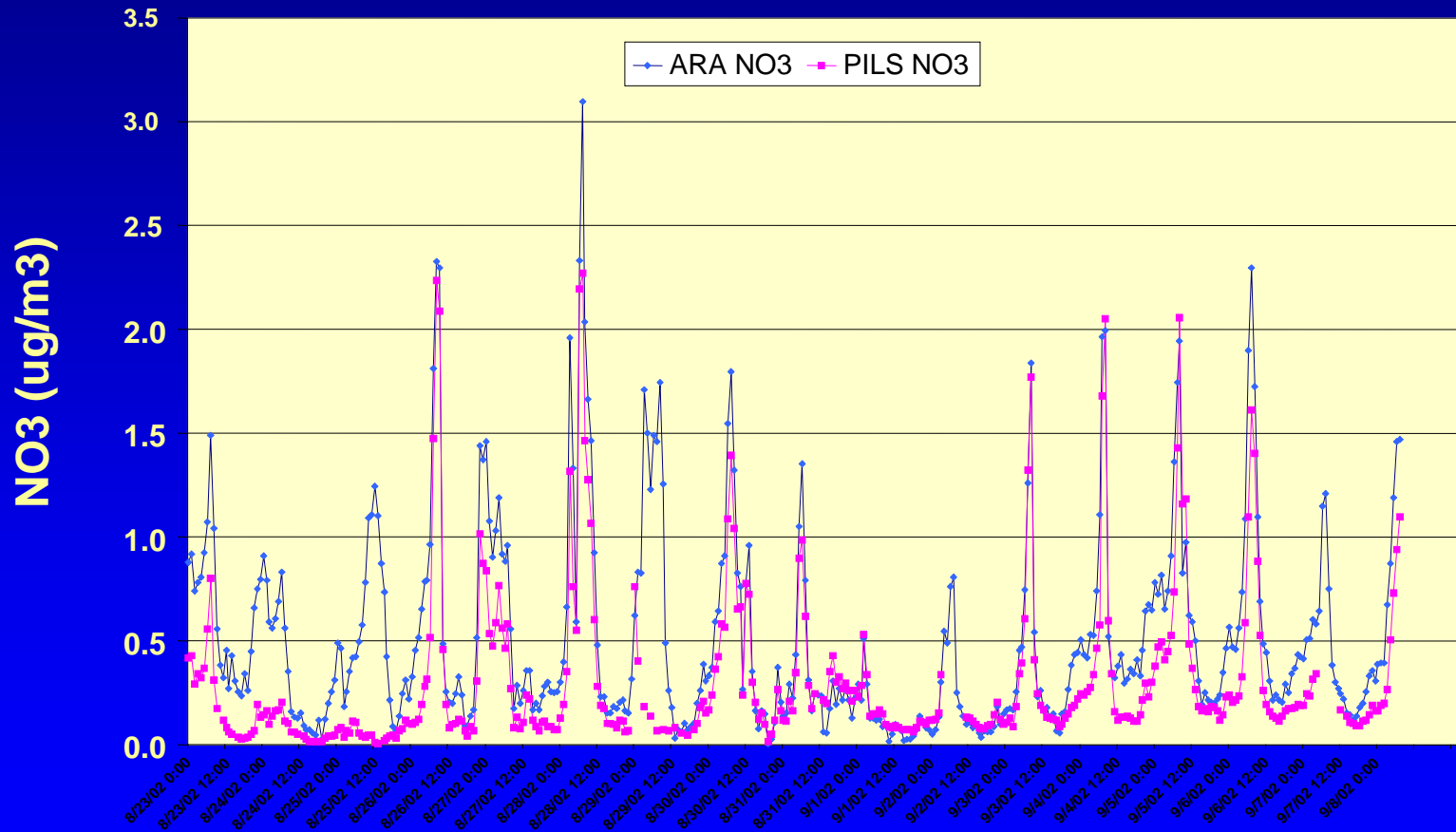
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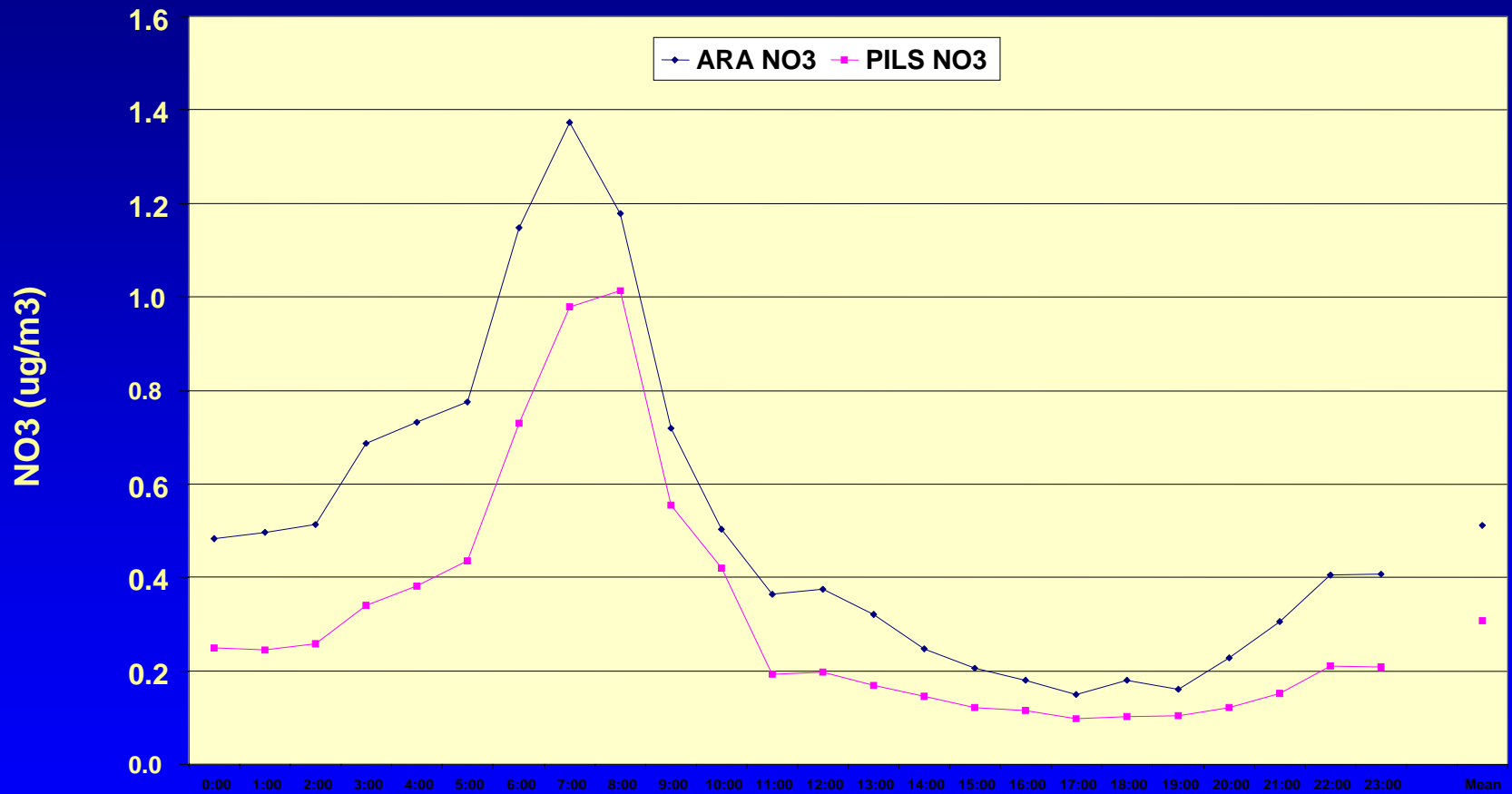
PILS



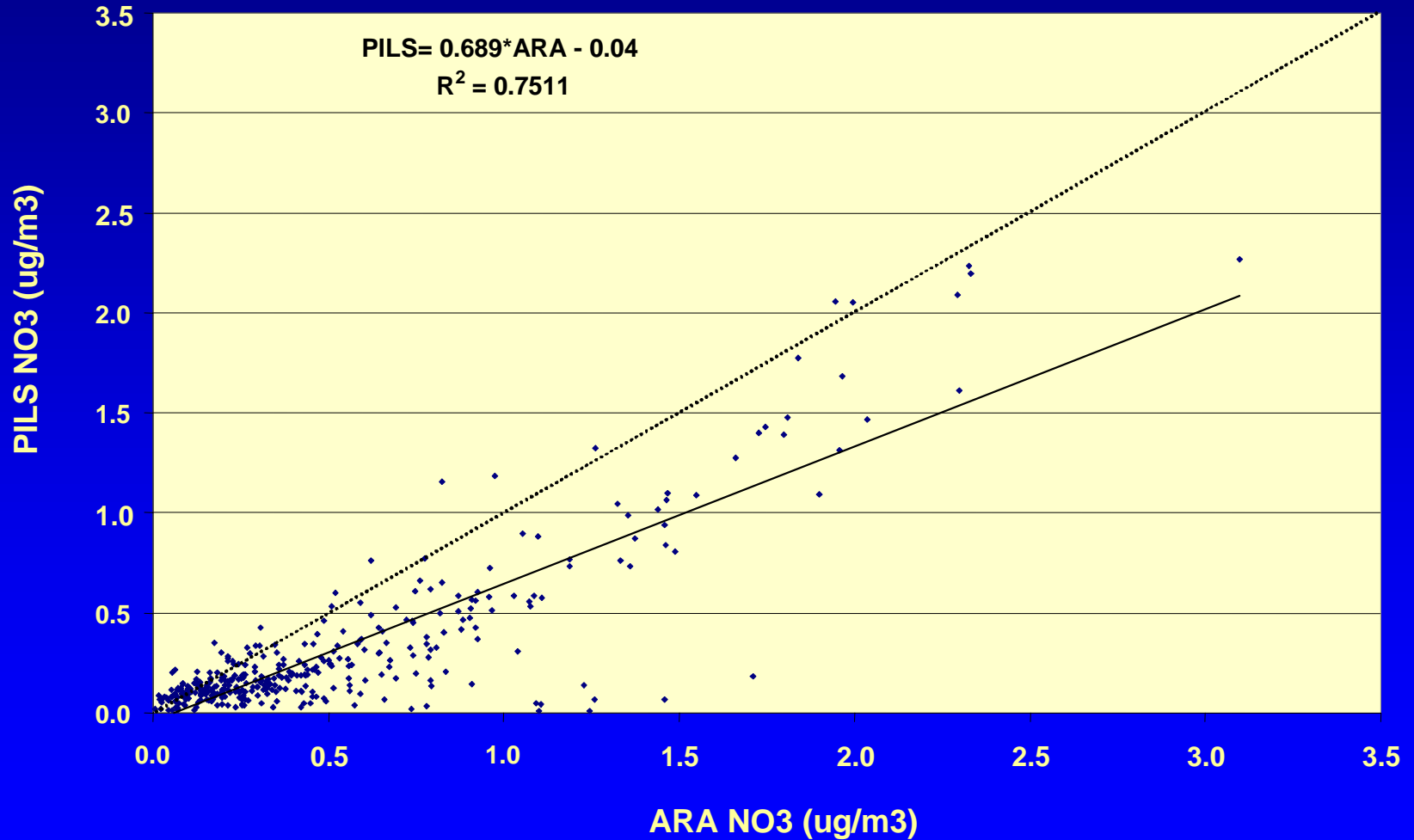
Time Series of Hourly NO_3^-



Diurnal Pattern for NO₃⁻



Scattergram of Hourly NO_3^-



Continuous vs. Filter Summary

24-Hr Averages

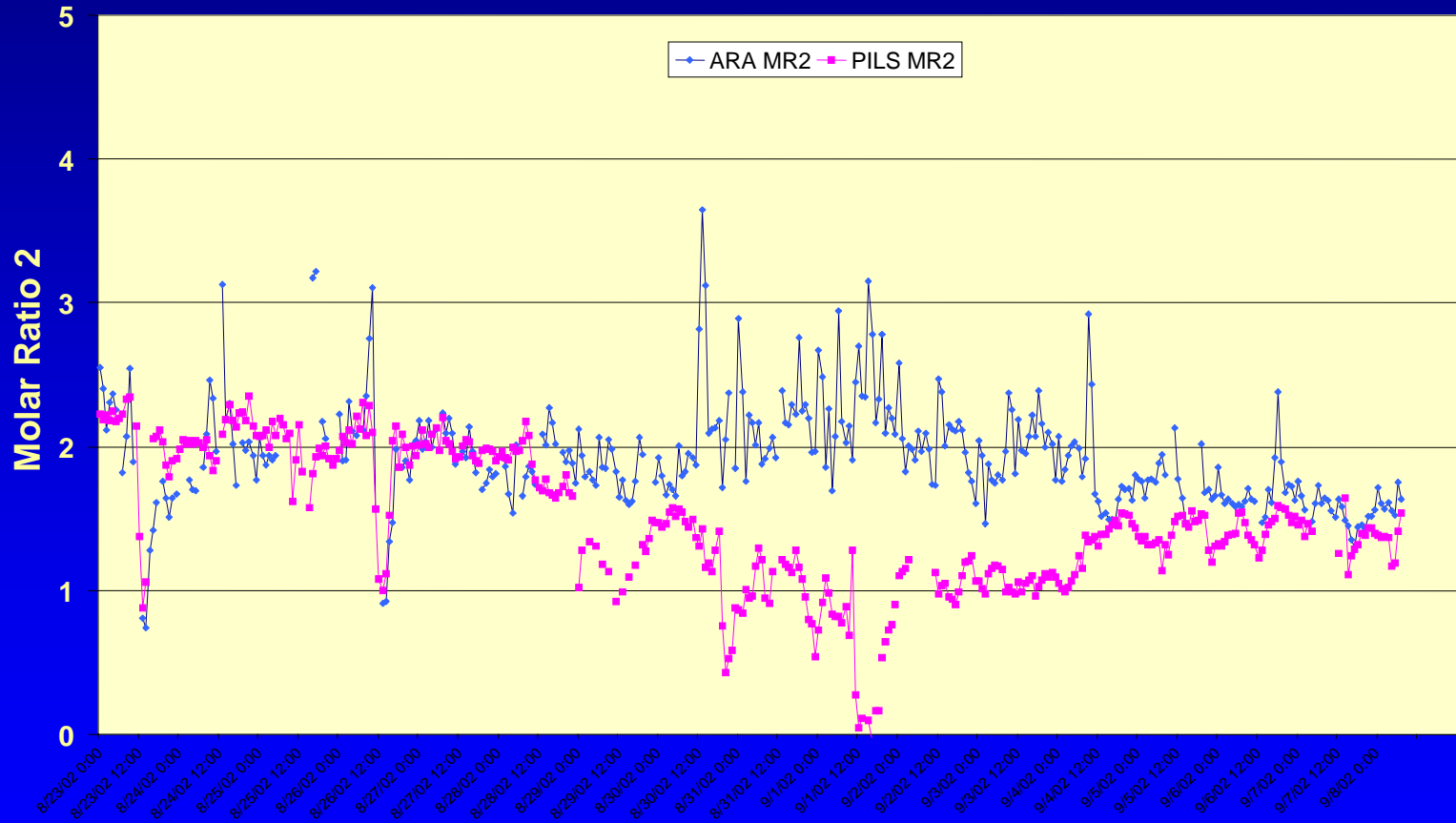
	Filter	PILS			
	Mean	Mean	%E	MAE	MAPE
SO4 (30)	5.59	5.26	-5.8	0.51	9.9
NH4 (19)	1.89	1.70	-10.2	0.29	12.6
NO3 (23)	0.45	0.33	-26.8	0.15	27.7

	Filter	ARA			
	Mean	Mean	%E	MAE	MAPE
SO4 (36)	5.82	6.10	4.8	0.43	8.5
NH4 (32)	2.15	2.10	-2.1	0.20	9.6
NO3 (35)	0.45	0.54	22.0	0.13	34.5

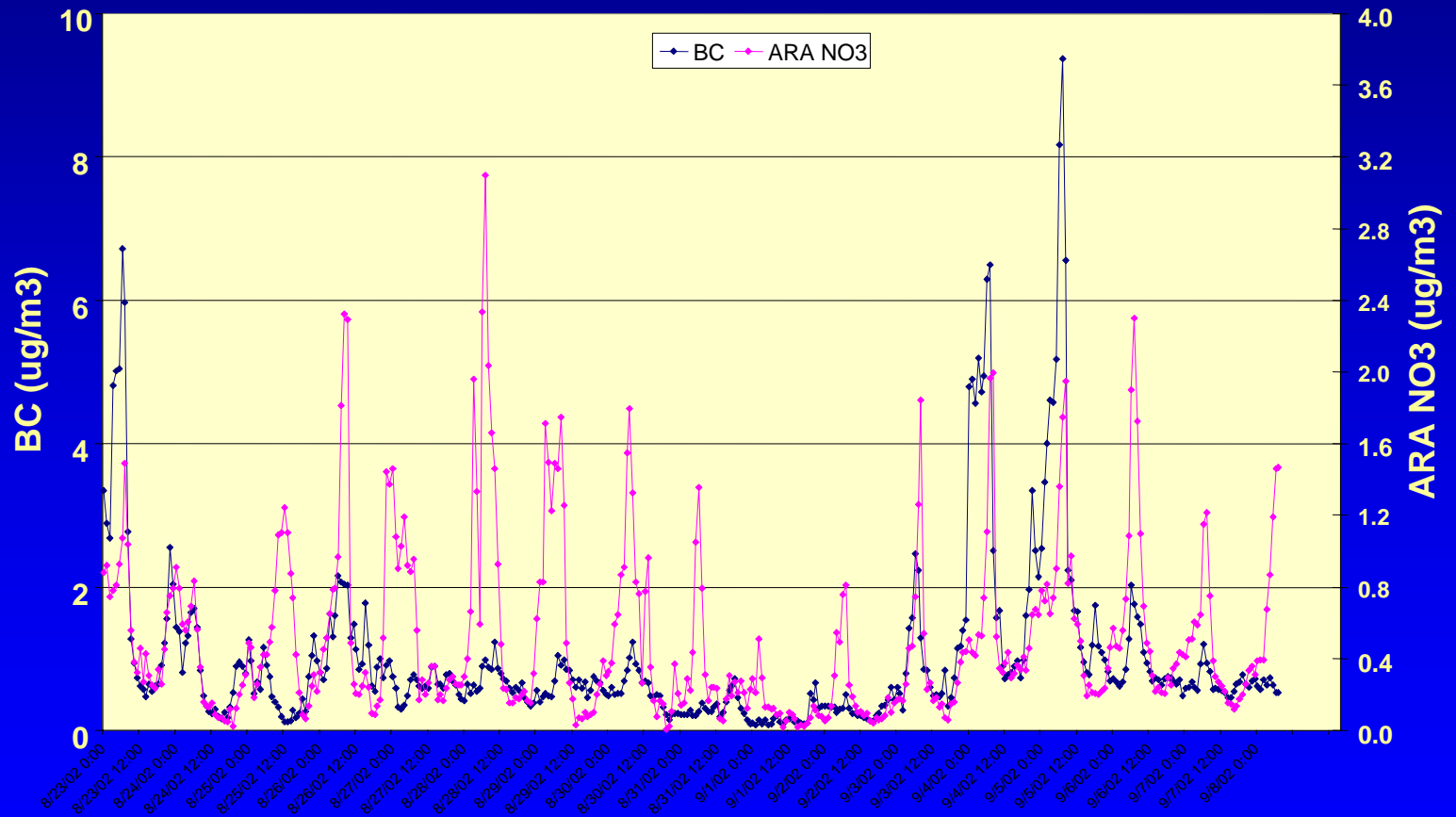
MAE = median abs. error; MAPE = median abs. % error

Sulfate Composition

$x\text{sNH}_4^+:\text{SO}_4^{2-}$ (molar)



Time Series of BC and ARA NO₃⁻



Conclusions

- Sulfate shows good overall agreement (+/- 10-15%) with 24-filter samples and between analyzers.
- Ammonium shows sporadic agreement, but also significant disagreement, at times.
- Differences in ammonium can imply large differences in relative neutralization of sulfate ($\text{NH}_4^+:\text{SO}_4^{2-}$ molar ratios)
- Nitrate shows serious disagreement, but agrees more or less on timing of peaks (a.m.). Data suggest ARA measurement could include other particulate-nitrogen species (e.g., NO_x on soot).