

St. Louis - Midwest Fine Particulate Matter Supersite

ASSISTANCE AGREEMENT QUARTERLY REPORT for the reporting period July 13, 2002 through October 12, 2002

January 6, 2003

St. Louis - Midwest Particulate Matter (PM) Supersite Monitoring Program EPA Assistance ID No. R-82805901-0

Work Progress and Status

1. ***Routine Data Collection.*** As described in the previous Quarterly Report, core site (East St. Louis, IL) measurements under this cooperative agreement ceased on May 31, 2002. A majority of the measurement matrix has been sustained, however, under a separate cooperative agreement managed through USEPA Region VII (Michael Davis, Project Officer). The movable platform was deployed under this cooperative agreement for two weeks in August at the rural Park Hills, MO, satellite location. Subsequently, it was moved to rural northeast Kansas for two six-week intensive monitoring periods (August-September and November-December). These measurements are being conducted with the Sac & Fox Nation of Missouri in Reserve, KS, and are funded by CENRAP through the cooperative agreement with USEPA Region VII.
2. ***Site Visits.*** J. Guilliford (Administrator, EPA Region VII), A. Spratlin (Director of the Air, RCRA, and Toxics Division, USEPA Region VII), and S. Mahfood (Director, Missouri Department of Natural Resources) toured the St. Louis - Midwest Supersite on August 26, 2002.
3. ***Retrospective Analysis for Speciated Organics and Time-Resolved Metals.*** The St. Louis - Midwest Supersite measurement strategy includes daily 24-hour integrated sample collection for speciated organics analysis (GC-MS) and sustained operation of the University of Maryland High Frequency Aerosol Slurry Sampler (HFASS) for metals characterization at one-hour average time resolution. Funds were programmed to analyze about 100 days of samples for both the organics and the metals. The selection of days for such analyses is based on a two-tiered approach. Twenty-one days were targeted for analysis which represent a relatively broad spectrum of meteorological conditions and dynamic range for the aerosol bulk composition (June 22-28, 2001; November 7-13, 2001; March 19-25, 2002). We will subsequently select the remaining days to support source apportionment studies and also the ongoing modeling efforts of LADCO/Environ (see Planned Activities for the Forthcoming Quarter).
4. ***HSPH Exposure and Health Effects Panel Study.*** H. Suh and co-workers from the Harvard School of Public Health (HSPH) completed the field component of their exposure and health effects panel study "Traffic Related Particles and Cardiovascular Health in St. Louis, MO". This study tracked air quality and health indicators before, during, and after field trips from

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the subjects' residences in suburban St. Louis to the downtown area. The HSPH team is currently validating the aerosol- and gas-measurement data and is processing health measurements data which included blood pressure, blood oxygen saturation, exhaled nitric oxide, EKG, and blood samples. Routine monitoring data from the St. Louis - Midwest Supersite will be used to determine the extent to which the measurements at the fixed Supersite location represent exposures as measured by instruments deployed on the bus transporting the panel subjects, and to provide a more-detailed physical and chemical characterization of the St. Louis aerosol on days when the panel study measurements were conducted.

5. *SLU-SPH Epidemiology Study*. D. Sterling and coworkers at the St. Louis University School of Public Health (SLU-SPH) have been funded by EPRI to conducted an epidemiological study "Relationship of Cardiac and Upper Respiratory Illnesses Reported at Emergency Departments and Air Pollution in the St. Louis Metropolitan Area". This study builds upon the ongoing ARIES program in Atlanta. Additional details will be provided in a forthcoming quarterly report.

Personnel

No changes during this quarter.

Expenditures

There are no adjustments to the project budget.

Quality Assurance

The St. Louis - Midwest Supersite has elected to perform data validation - and to populate the database developed for this project by DRI - by measurement for the entire year rather than by quarter. While this has caused some delay in the initial submission to the NARSTO data archive, the data streams - when submitted - will be complete for the entire two month study period. To date we have completed data validation for: the suite of meteorological parameters; daily 24-hour integrated PM-1 mass (by SCC), PM-2.5 mass (by Harvard Impactor), and PM-10 mass (by Harvard Impactor); semicontinuous PM-2.5 nitrate by R&P 8400N (data collected for January-May 2002 only); and PM-2.5 elemental and organic carbon by the Sunset OCEC field instrument.

Results

In lieu of a detailed narrative on recent results, we have appended materials from two presentations delivered at the AAAR Annual Meeting (October 2002, Charlotte, NC).

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1. *Validation of a Semicontinuous ECOC Instrument (Park, et al.)*. These slides detail our efforts to validate the Sunset ECOC semicontinuous field instrument. [We regret the file translation into Acrobat adversely affected the text formatting.]
2. *Measurement of St. Louis Aerosol Size Distribution: Observation of Particle Events (Shi, et al.)*. These slides summarize the preliminary analysis of particle size distribution measurements conducted by University of Minnesota. Note that the terminology "traffic events" is too restrictive; while these event do indeed track with NO_x and CO, the particles might rise from other local/metropolitan scale sources and not necessarily motor vehicles.

Planned Activities for the Forthcoming Quarter

Twelfth quarter activities will focus on data validation for the full first year of semicontinuous and integrated sampling, and populating the database developed by DRI to support submissions to both the NARSTO data archive and Supersites programwide relational database. Activities will also focus on retrospective analyses of HFASS samples for hourly-average metals (University of Maryland) and high-volume filter samples for 24-hour average organics speciation (University of Wisconsin).

LADCO has initiated a PM modeling effort to support air quality planning efforts by its member states. This work, in part contracted to Environ, includes a detailed comparison of the modeling results to measurements at the Pittsburgh and St. Louis - Midwest Supersites. The PIs from these respective Supersites have been participating in monthly conference calls, and Turner will be participating in a LADCO-hosted modeling review meeting slated for November 2002.

The St. Louis - Midwest Supersite will convene its third data analysis meeting on October 22, 2002. A copy of the agenda is attached.

Publications and Presentations

A project overview briefing was presented at the 27th Annual Conference of the National Association of Environmental Professionals, Detroit, MI, June 26, 2002. The St. Louis - Midwest Supersite consortium delivered five (5) presentations at the Annual Meeting of the American Association for Aerosol Research (AAAR), October 2002, Charlotte, NC.

One paper has been accepted for presentation at the A&WMA Symposium on Air Quality Measurement Methods and Technology (November 2002, San Francisco, CA). One papert has been accepted for presentation at the 2003 Annual Meeting of the Air & Waste Management Association. Ten (10) abstracts have been submitted for the 2003 AAAR PM Meeting (Particulate Matter: Atmospheric Sciences, Exposure and the Fourth Colloquium on PM and Human Health).

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Quarterly Report Summary

See Attached

St. Louis - Midwest Supersite Consortium Workshop
Tuesday, October 22, 2002
St. Louis, MO
STRAW MAN AGENDA - 10/16/02 REVISED DRAFT

Tuesday, October 22

8:00 AM - 8:15 AM	greetings; coffee, juice, rolls
8:15 AM - 9:15 AM	Washington U: workshop charge, status of data integration, overview of data quality, climatological highlights
9:15 AM - 10:00 AM	U Minnesota: update on analysis of aerosol physical properties
10:00 AM - 10:15 AM	Break
10:15 AM - 11:00 AM	U Wisconsin: evaluation of continuous carbon measurements, plans for detailed organics analysis and semi-continuous Hg monitoring
11:00 AM - 11:45 AM	U Maryland: assessment of blank determinations, initial retrospective analyses
11:45 AM - 12:30 PM	lunch (provided) in meeting room
12:30 PM - 1:45 PM	* HSPH: update on "bus study" (30 min) * SLU: epi study plans and data needs (15 min) * Additional discussion of integration with exposure and health effects studies (30 min)
1:45 PM - 2:30 PM	DRI: database plans and issues
2:30 PM - 2:45 PM	Break
2:45 PM - 3:15 PM	survey data analysis plans and schedules of individual groups
3:15 PM - 3:45 PM	identify standard analyses useful to multiple groups
3:45 PM - 5:30 PM	negotiate data analysis and reporting responsibilities and timelines (including abstracts for PM2003 meeting); chart specific tasks and interactions
5:30 PM	Adjourn Workshop



Validation of a Semi-Continuous EC OC Instrument

Min-Suk Bae, Jeff DeMinter, Jamie Schauer
University of Wisconsin-Madison

Jay Turner
Washington University

David Smith, Bob Cary
Sunset Laboratory

Motivation

- Scientific and regulatory communities seek real time instruments for particulate matter chemistry
 - Quantitatively compare to traditional off line measurements
 - Sampling and Analysis
 - Minimum of hourly resolution (= 1 Hour)
- ECOC measurements unique challenges
 - Split between organic carbon (OC) and elemental carbon (EC) is operationally defined
 - Sorption artifacts during sample collection are not completely understood
- NIOSH 5040 ECOC method is being used for EPA Chemical Speciation Network

ECOC Measurements at the St. Louis Midwest Supersite

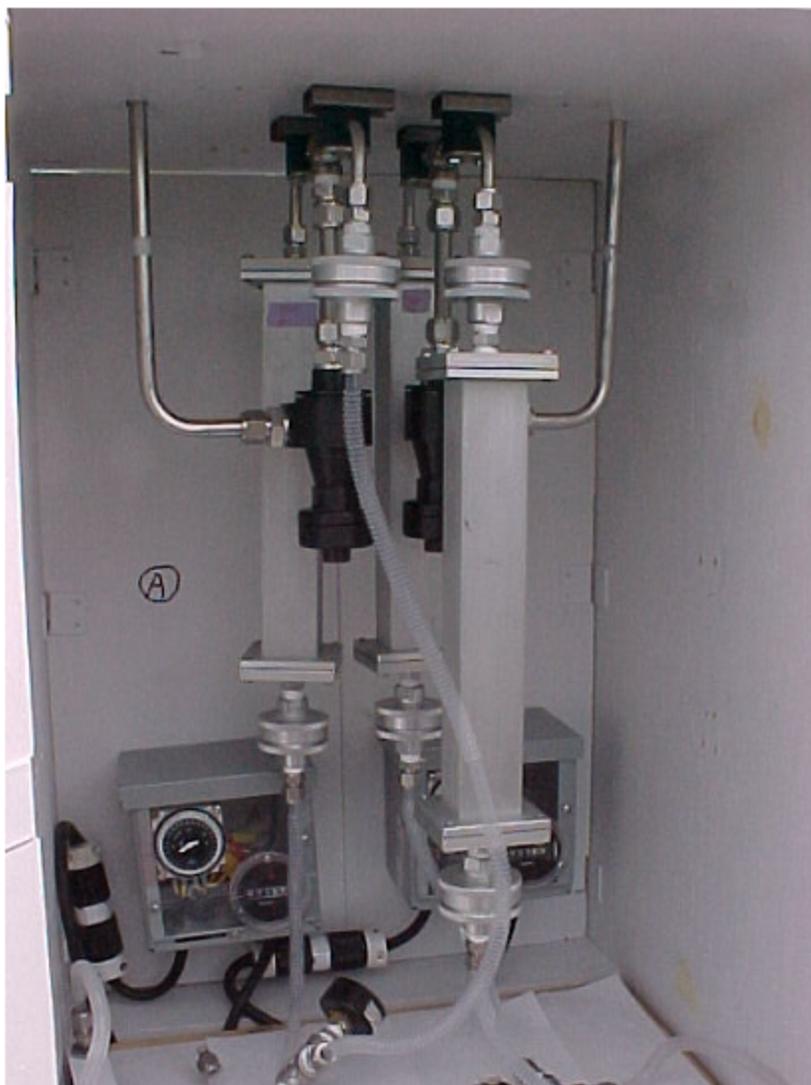
- Located East St. Louis, Illinois
 - 2.3 miles east of downtown St. Louis, MO
 - Residential neighborhood in industrial corridor
- Samples collection May 2001 through April 2003
- Co-located with a broad range of integrated and semi-continuous aerosols measurements
- Integrated with health studies
- ECOC measurements
 - Employing NIOSH 5040 based method

ECOC Measurements at the St. Louis Midwest Supersite

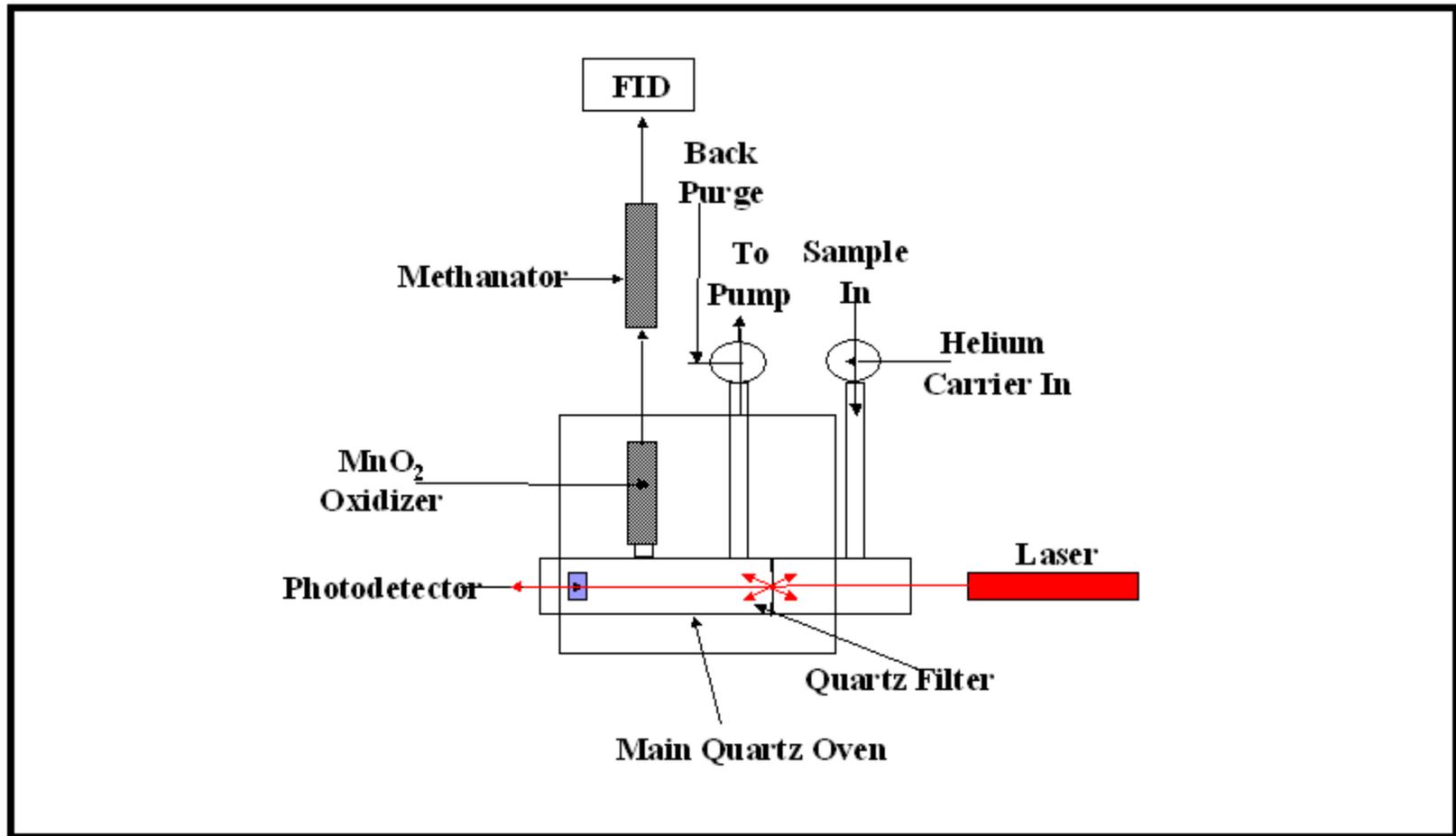
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ECOC Measurements

- **Integrated Aerosol Sample Collection**
 - Denuded PM_{2.5} - Daily
 - Organics denuder - Carbon paper
 - Off line ECOC analysis
 - 24 Hour Average
 - Undenuded ECOC – Every other day
 - Denuder Efficiency – Every other day
- **Two Semi-Continuous ECOC Analyzers**
 - Use same denuder as integrated sampler
 - Alternating sample collection
 - One hour sample collection
 - 20 minute analysis
 - Continuous 24 hour sample collection



Simplified block diagram for the Sunset Laboratory Semi-continuous E COC Field Analyzer



EC/OC Analysis Methods

Sample ID: STL_Inst2_Monona 5/29/2001 1

FID: FID:OK FID2:OK DL= 10

Split time Used = 445 seconds

Volatile area= 37710.0

Pyrolyzed area= 7650.0

Elemental area= 11390.0

Calibration area= 159350.0

Organic C = 7.06 \pm 0.55 ug/sq cm

Carbonate C = 0.00 \pm ug/sq cm

Elemental C = 1.09 \pm 0.25 ug/sq cm

Total C = 8.15 \pm 0.71 ug/sq cm

FID2 Calibration area= 38841.0

Sample Volume = 1461.86

Manually Integrated Area =

Manual peak:

start =

0

Integrate

end =

744

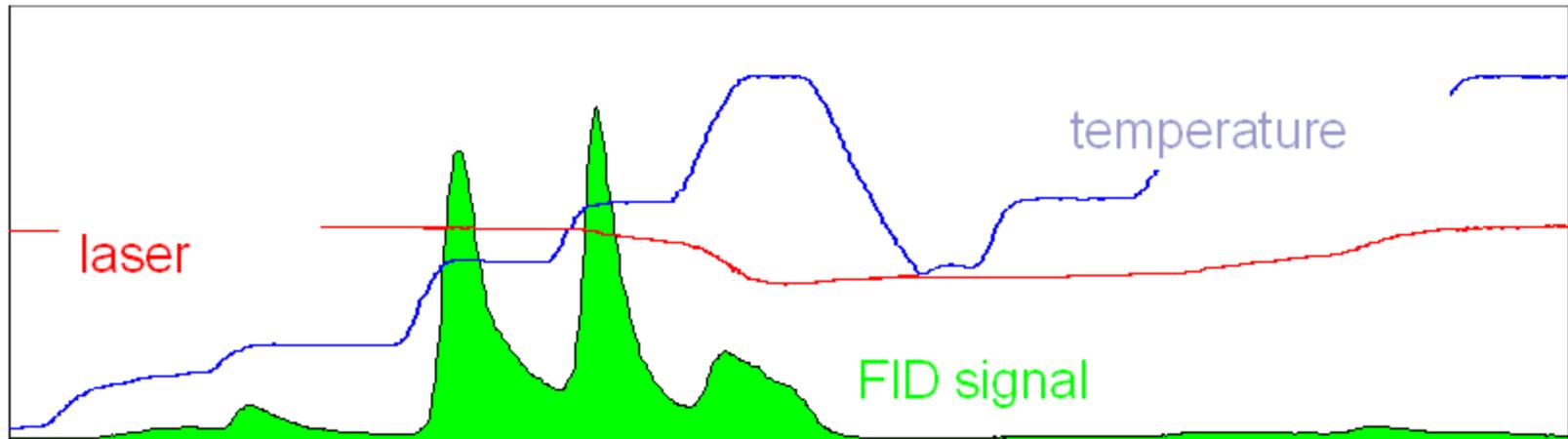
FID1

FID2

Temperature

Laser Transmittance

Absorbance 0-6

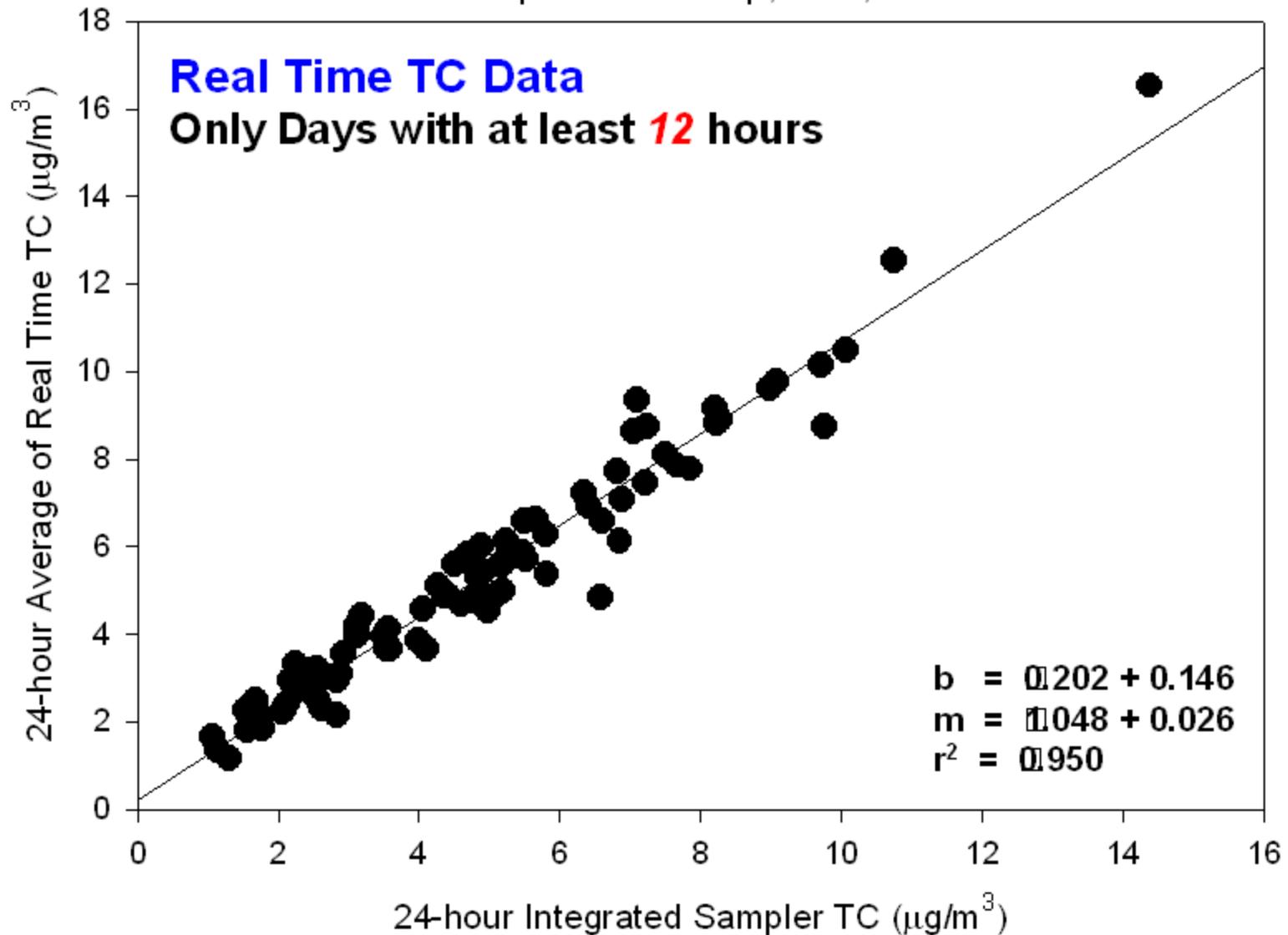


UC/EC Analysis Program (c) Sunset Laboratory, Inc.

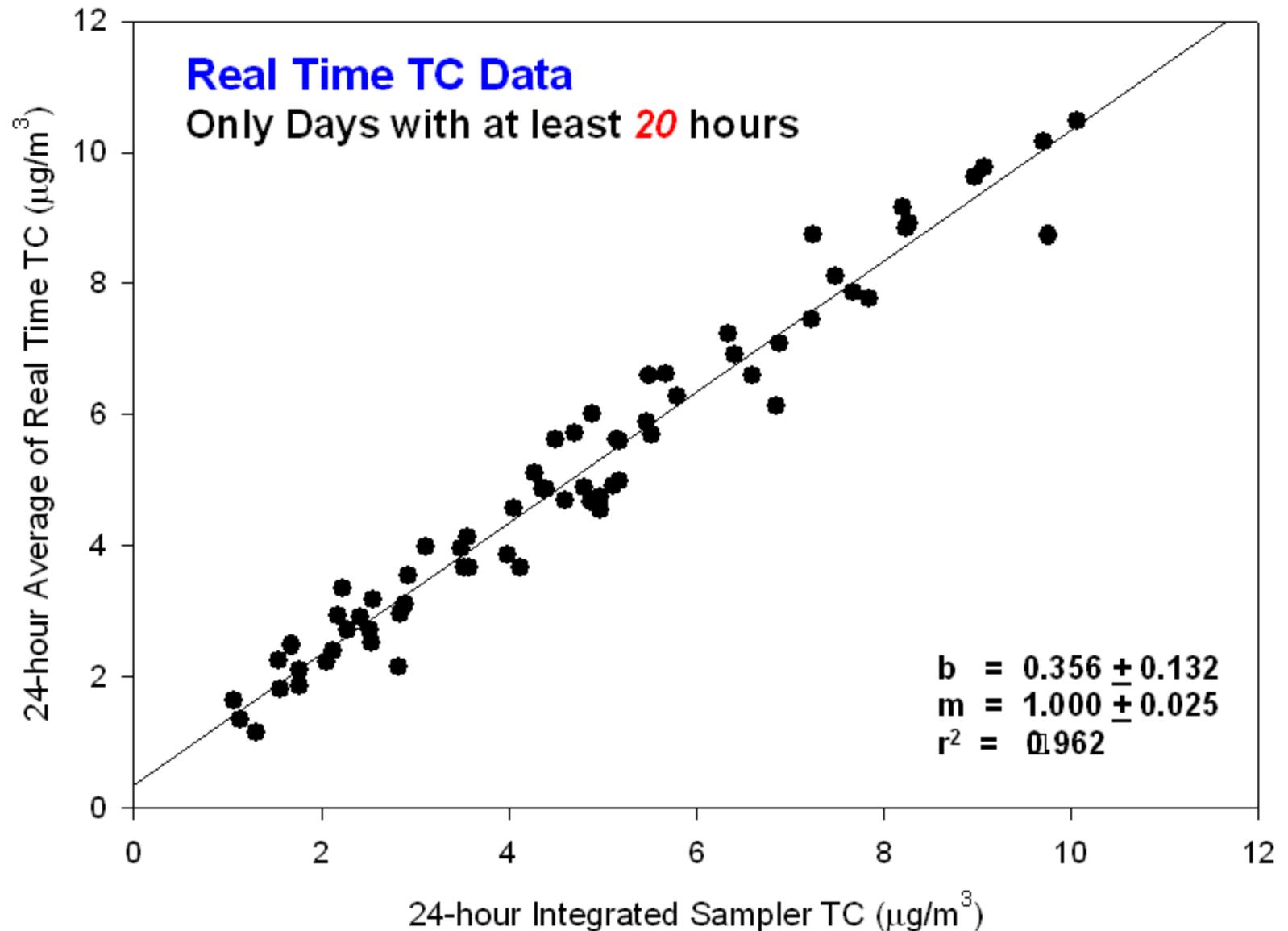
helium

2% oxygen

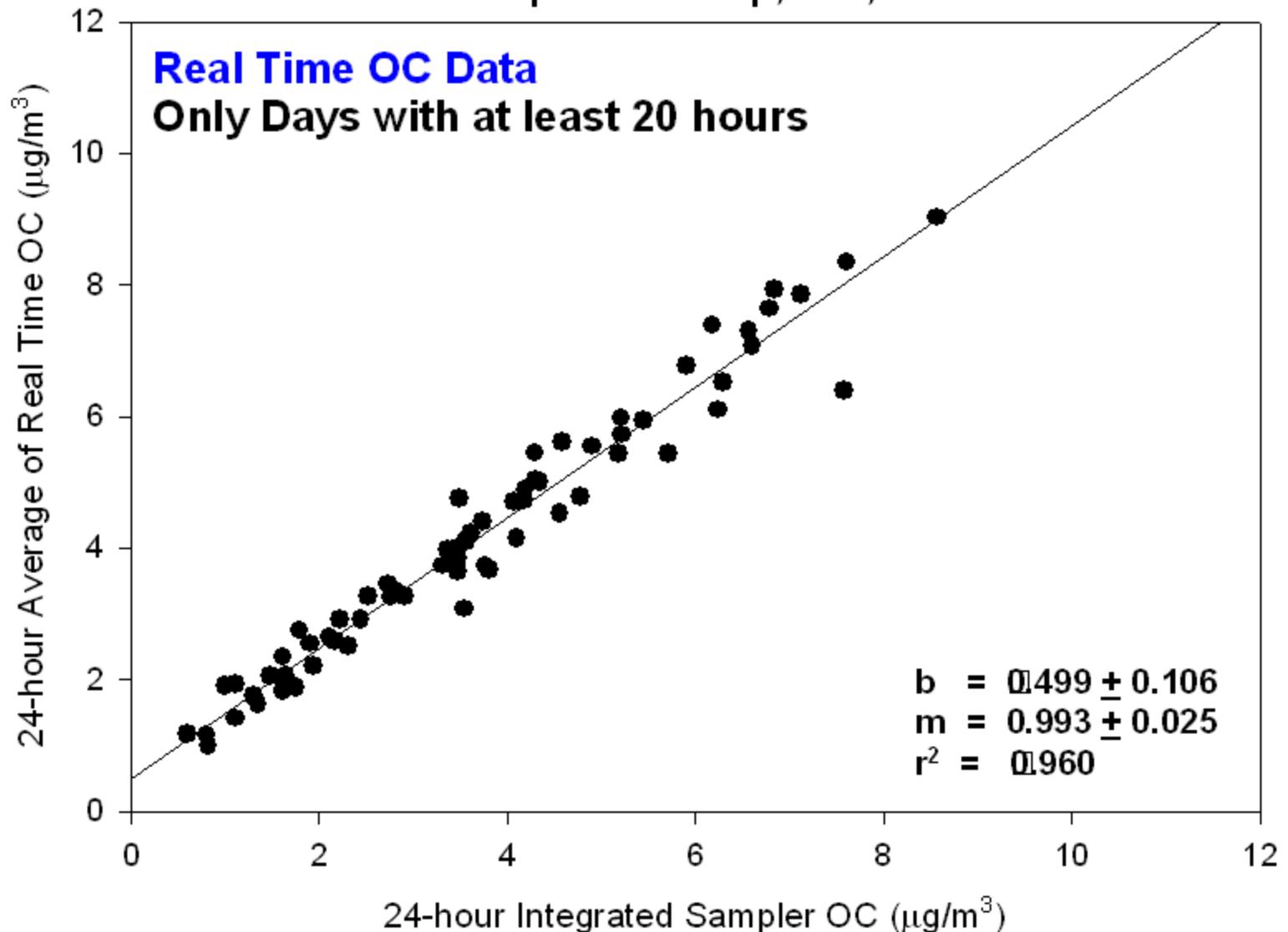
Comparison of Real Time and Integrated Fine Particle TC
St.Louis Supersite - Sep, Oct, Nov - 2001



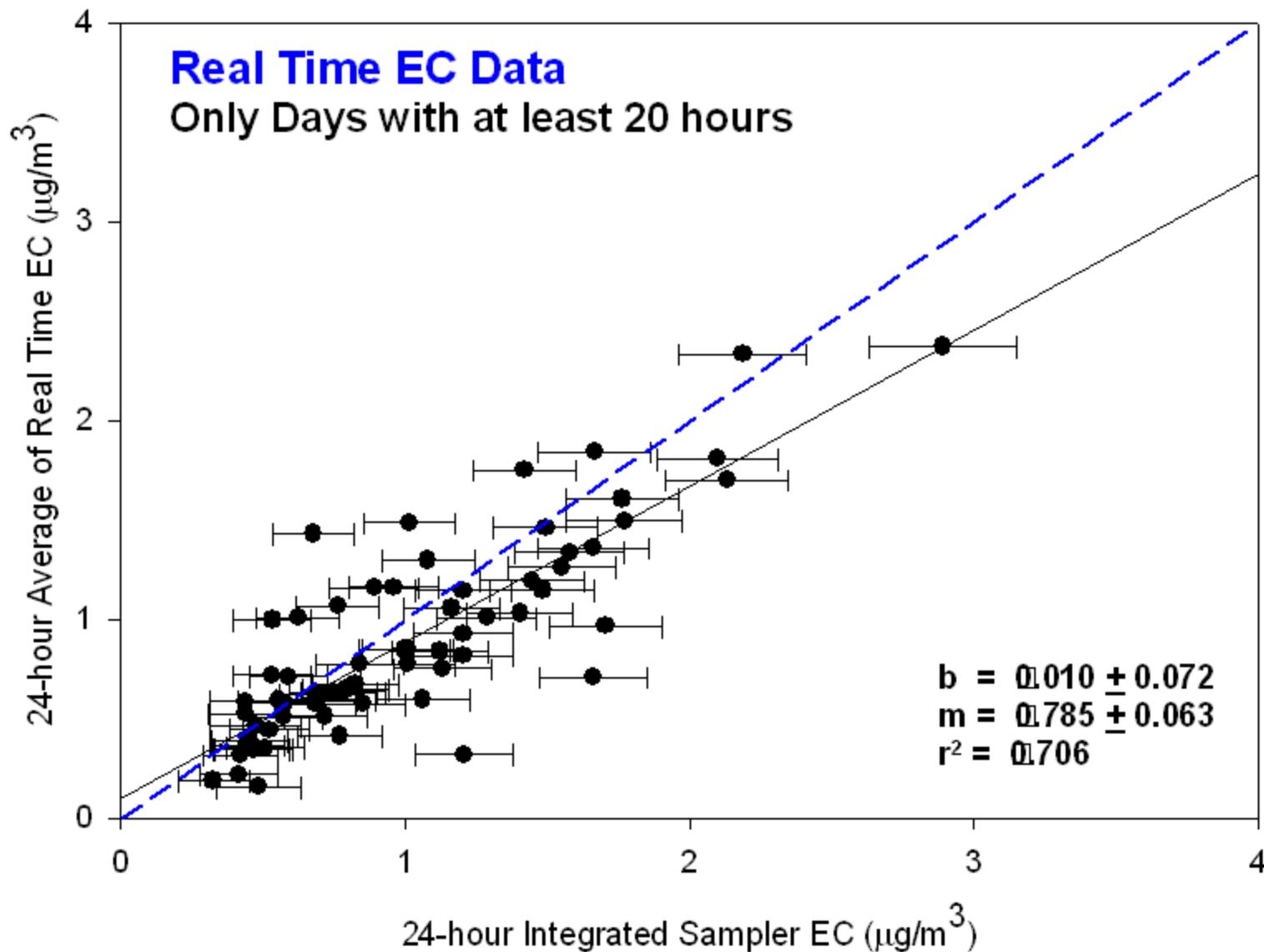
Comparison of Real Time and Integrated Fine Particle TC
St.Louis Supersite - Sep, Oct, Nov - 2001



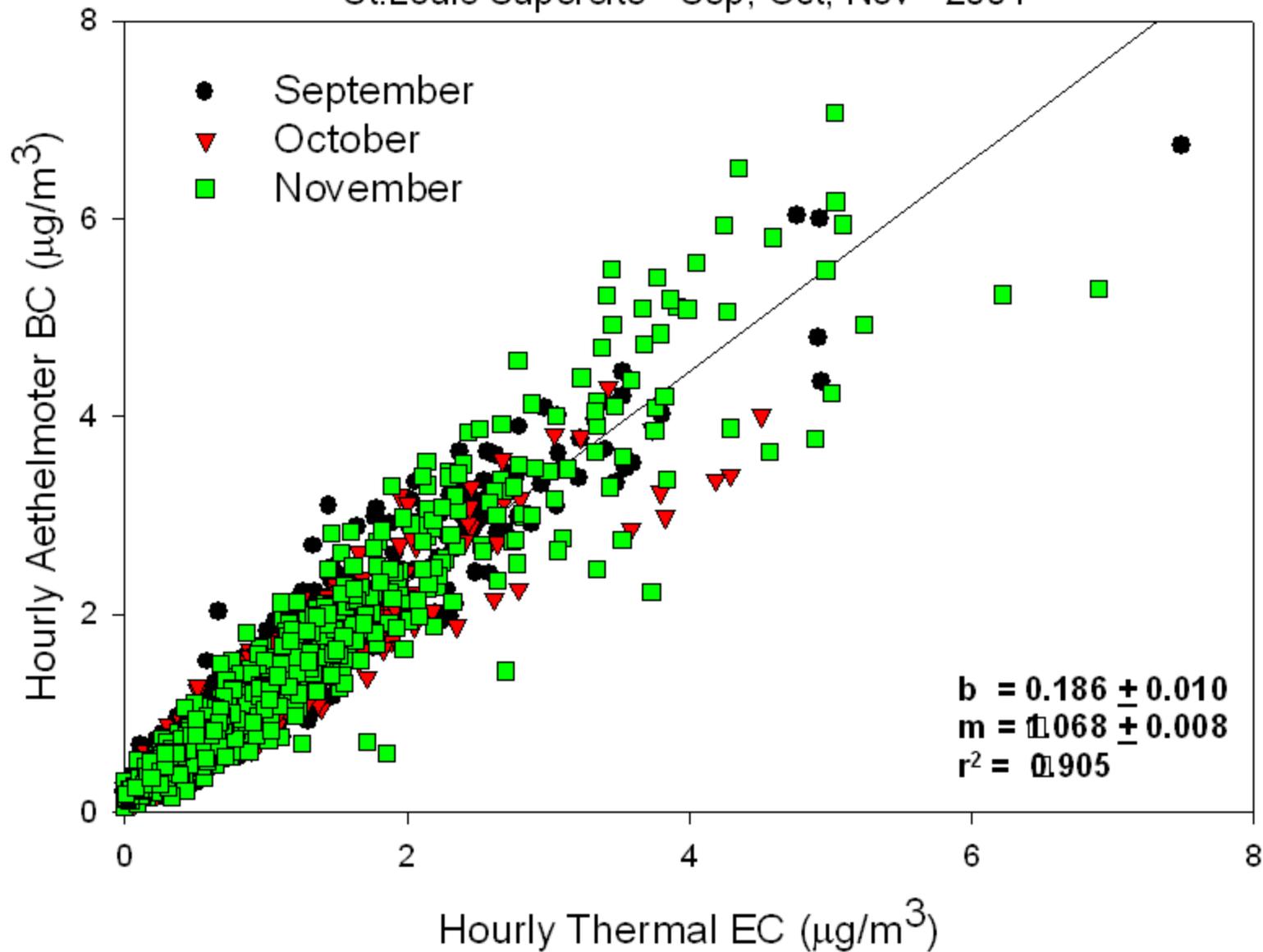
Comparison of Real Time and Integrated Fine Particle OC St.Louis Supersite - Sep, Oct, Nov - 2001



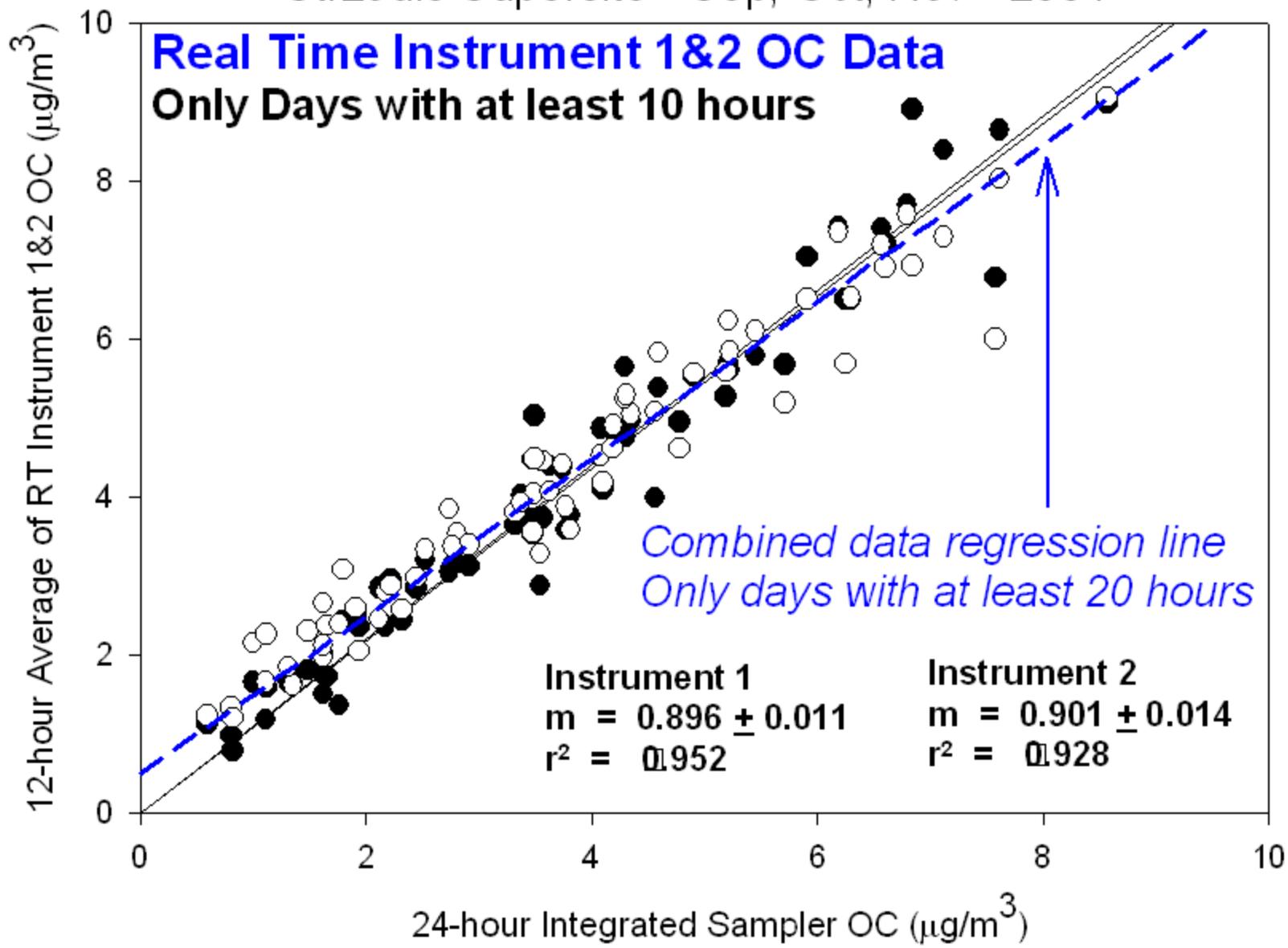
Comparison of Real Time and Integrated Fine Particle EC
St.Louis Supersite - Sep, Oct, Nov - 2001



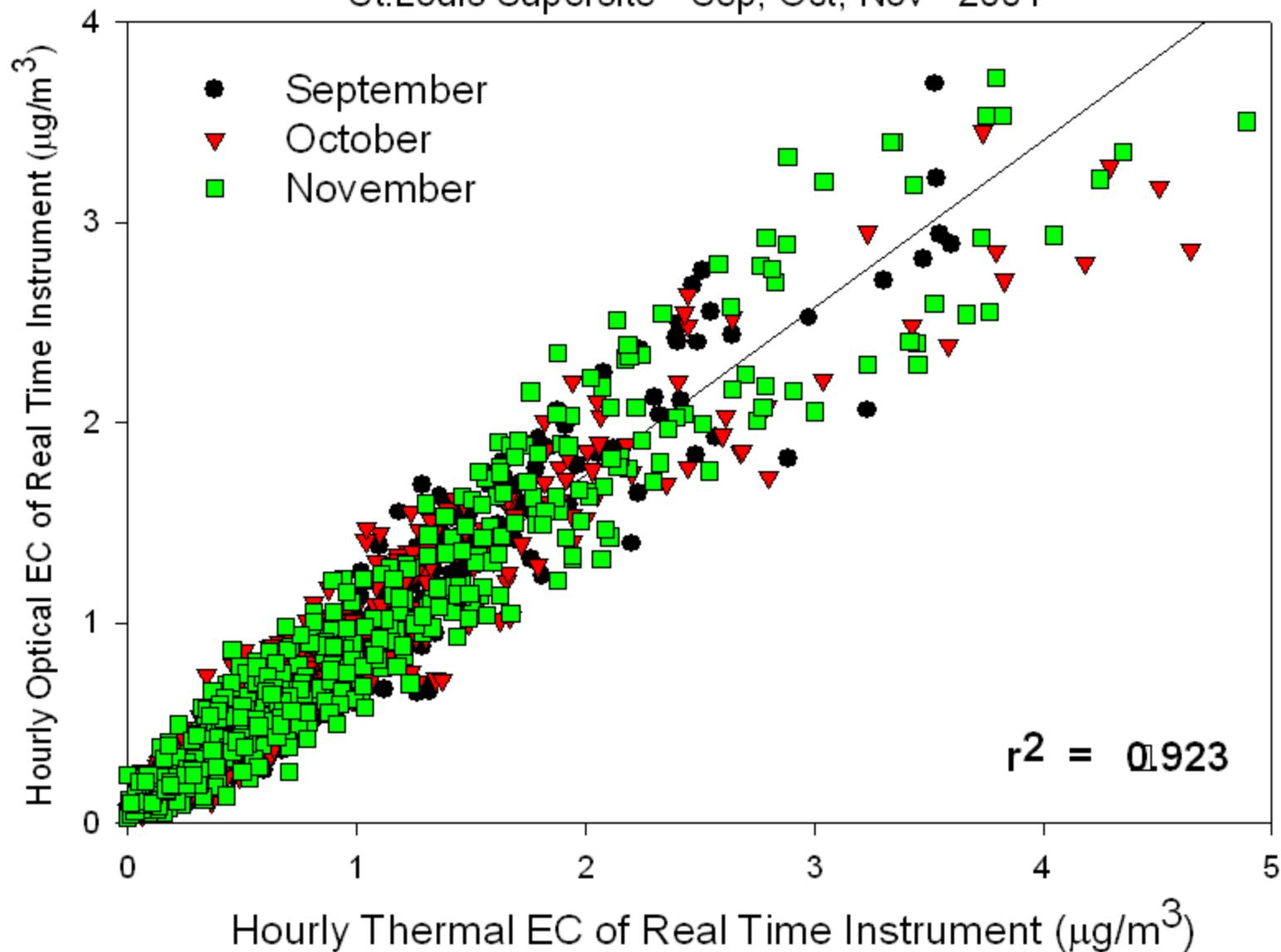
Comparison of hourly Thermal EC and Aethalometer BC
St.Louis Supersite - Sep, Oct, Nov - 2001



Comparison of Real Time Instrument 1&2
and Integrated Fine Particle OC
St.Louis Supersite - Sep, Oct, Nov - 2001



Comparison of hourly Thermal and Optical BC
St.Louis Supersite - Sep, Oct, Nov - 2001



Conclusion

- Continuously operated Semi-Continuous In-Situ EC/OC analyzers were operated at the St. Louis Supersite that parallel the NIOSH 5040 ECOC method
- TC and OC show excellent agreement with the co-located filter based measurement
- At low EC concentrations observed at the St. Louis Supersite, there exists significant uncertainties in both Integrated and Semi-Continuous ECOC measurements, but they show good correlation.
- Under condition of St. Louis Supersite, the operation of ECOC in-situ that measured every other hour shows good agreement with Continuous measurement
- The semi-continuous ECOC analyzer can be used to make optical BC measurements that agree well with an aethalometer

Measurement of St. Louis Aerosol Size Distribution: Observation of Particle Events

Qian Shi, Hiromu Sakurai,
and Peter H. McMurry

Department of Mechanical Engineering
University of Minnesota

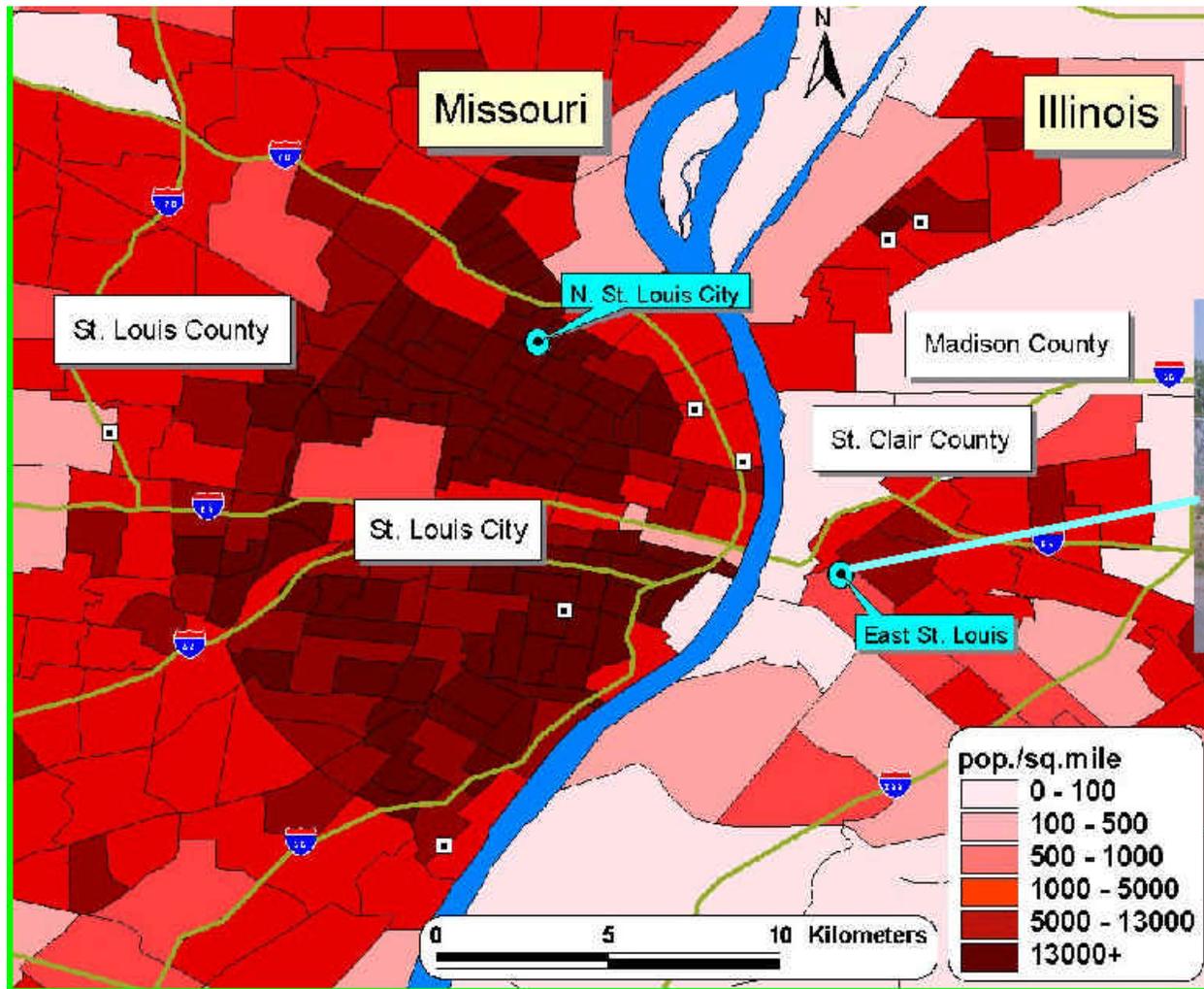


Outline

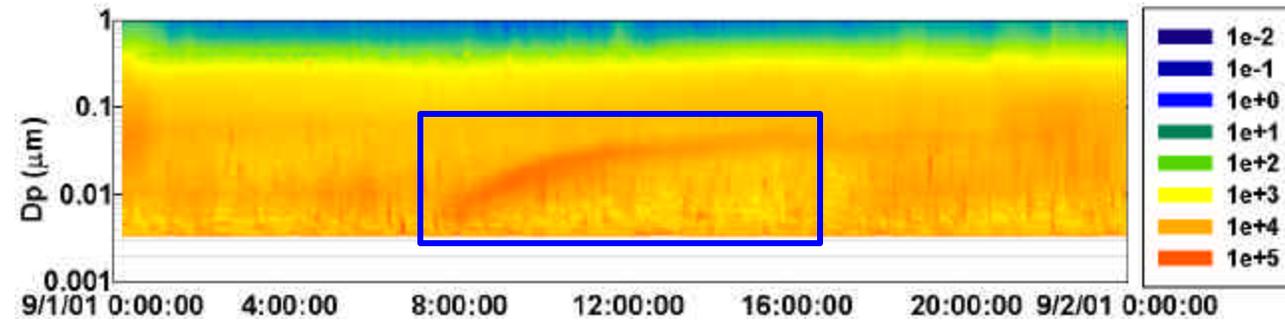
- Introduction: St. Louis Midwest Supersite
- Particle Size Distribution (PSD) instrumentation
 - Nano-SMPS (0.003-0.04 μm)
 - Reg-SMPS (0.03-0.4 μm)
 - LasairOPC (0.1-2 μm)
 - ClimetOPC (0.3-10 μm)
- Observations of particle events: 4/1/01-4/30/02
- Conclusions



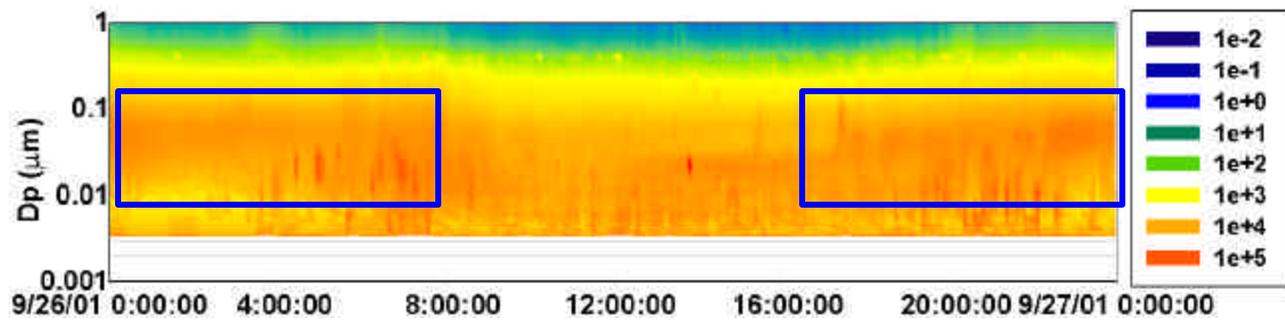
Sites in the City of St. Louis, MI



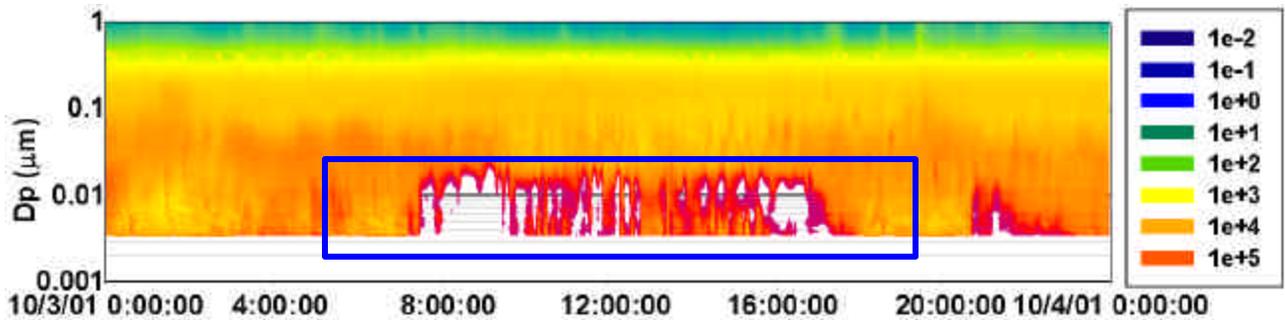
Ultrafine Particle Events Observed in St. Louis



Regional
Nucleation
Event



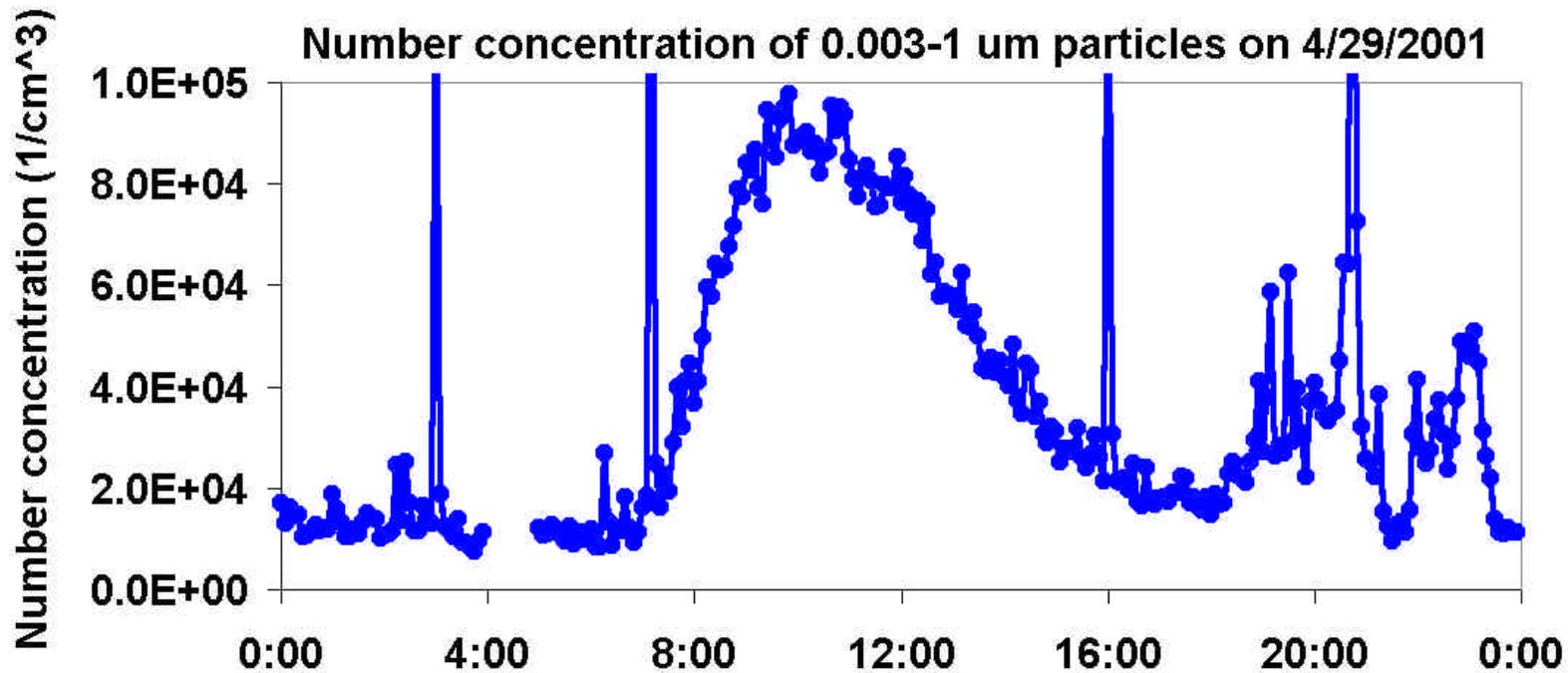
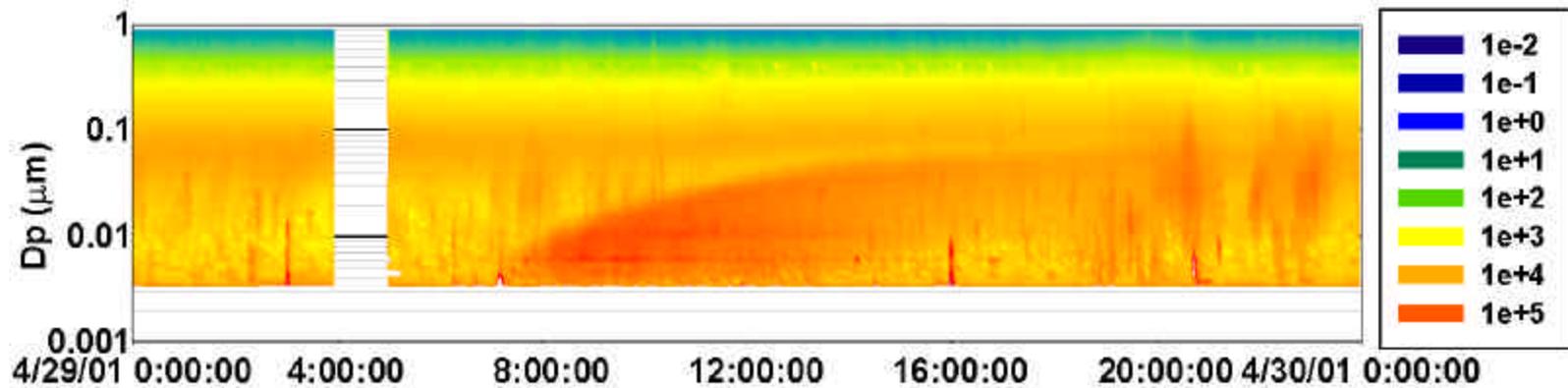
Traffic
Event



"3-30 nm"
Event

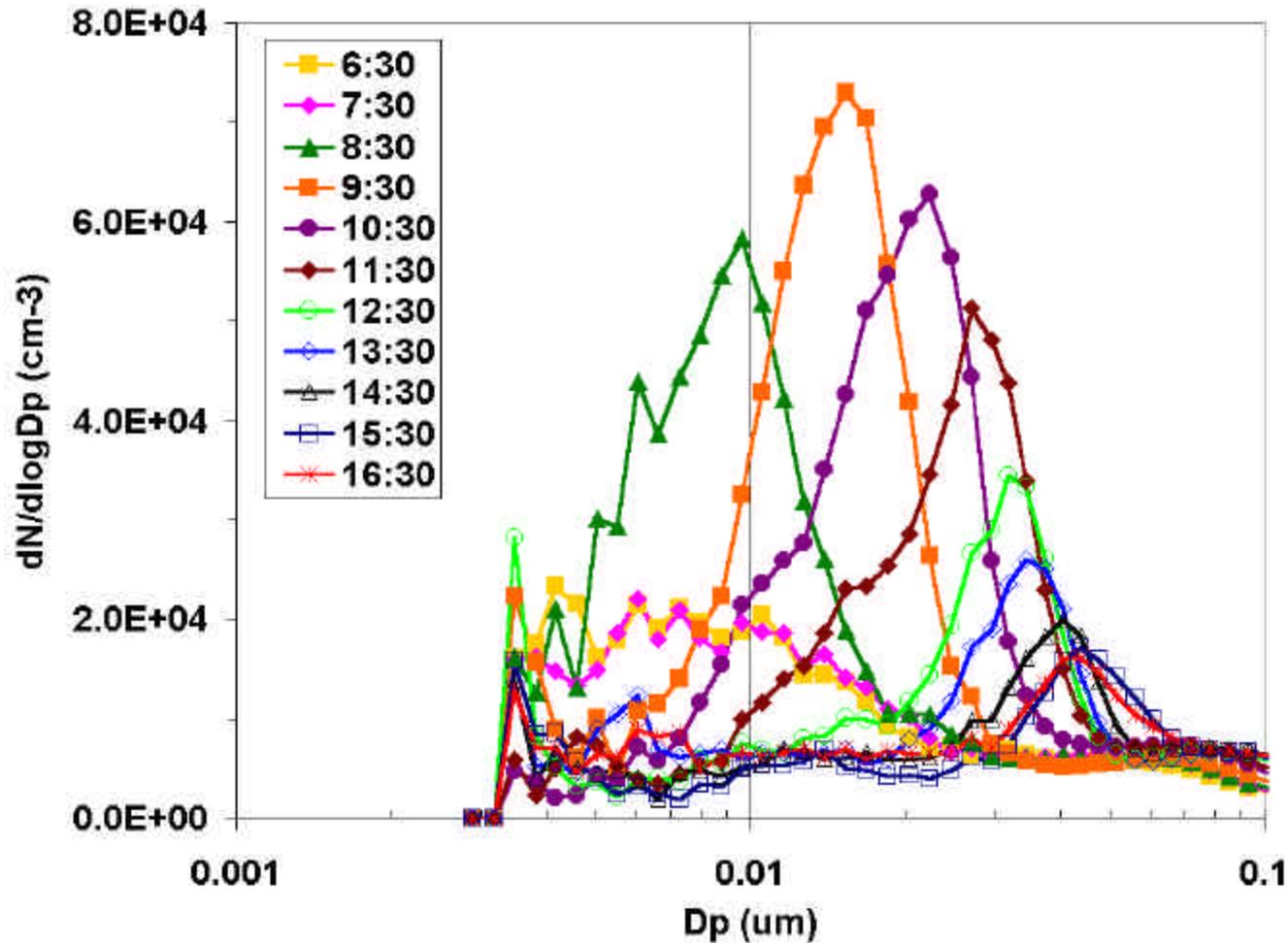


Nucleation and growth (April 29, 2001)

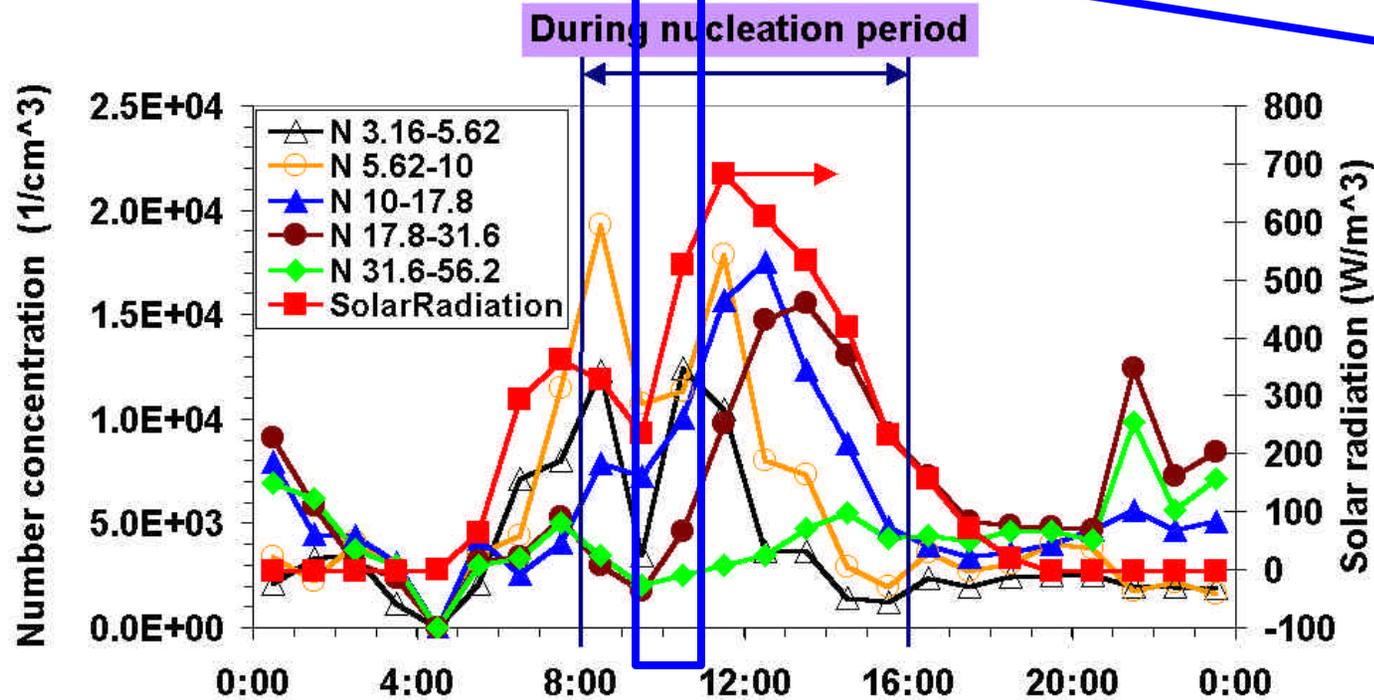
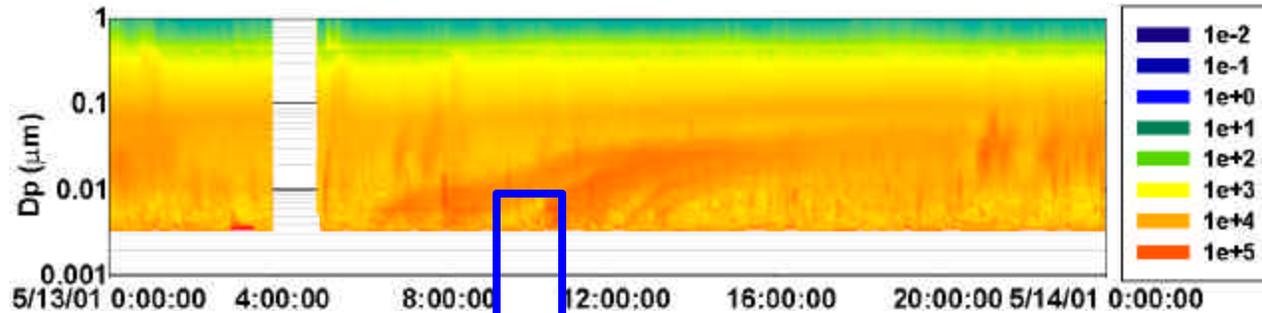


Nucleation event (September 1, 2001)

Size distributions before and during a nucleation period



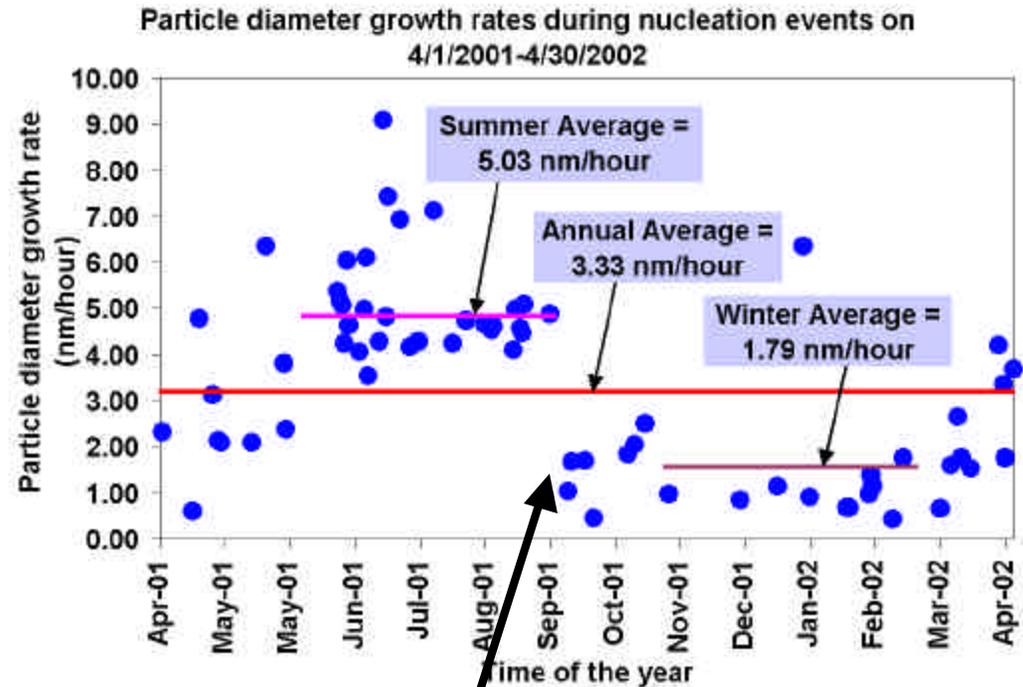
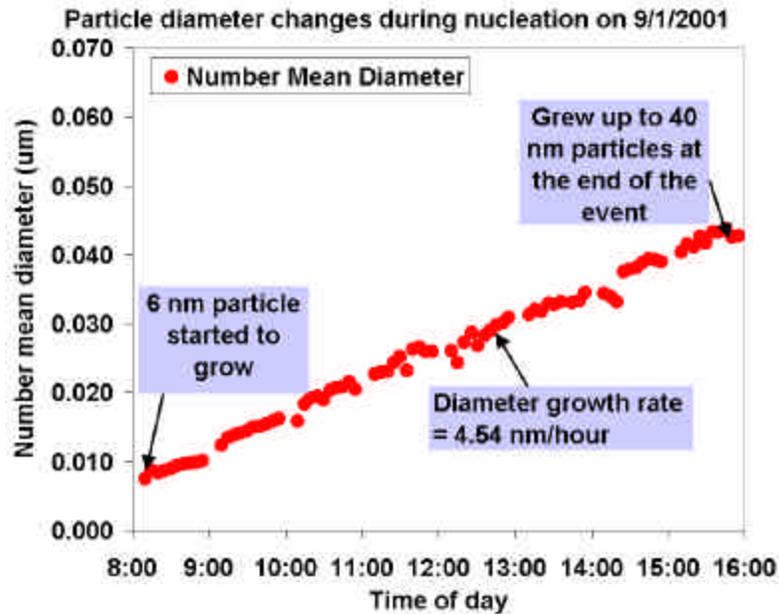
Nucleation event (May 13, 2001)



Particle production does not only occur in a simple burst in the morning?



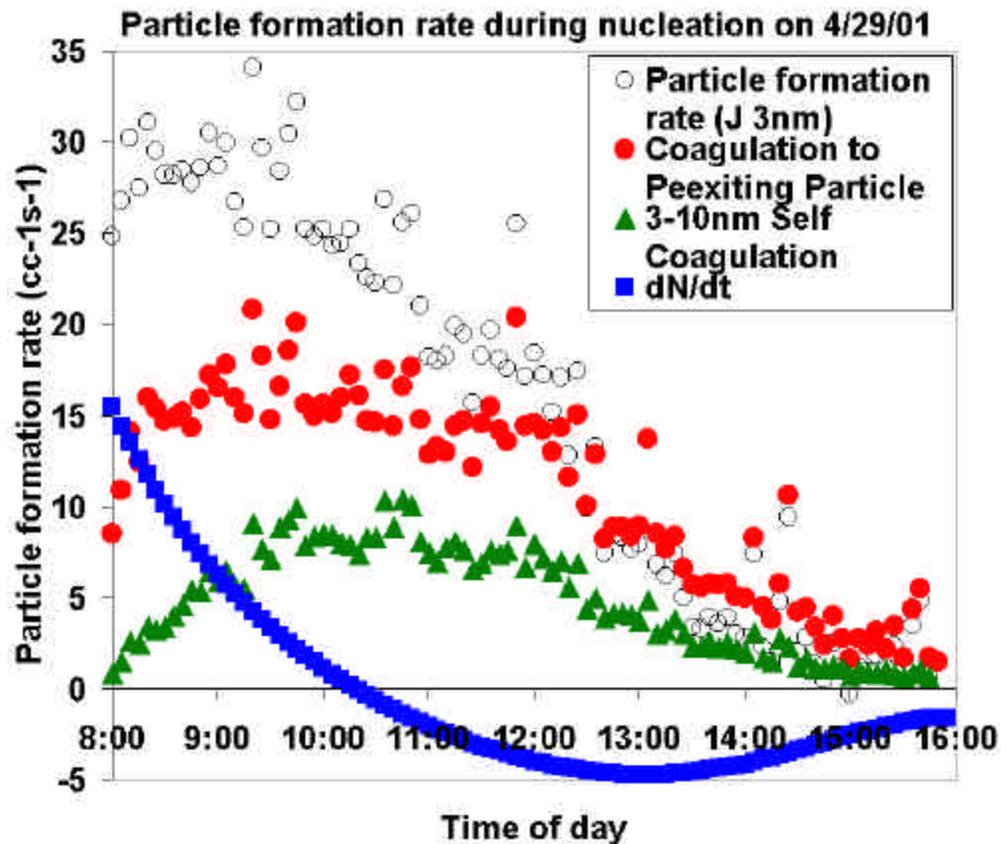
Diameter growth rate during nucleation



Particles tend to grow faster in summer month?



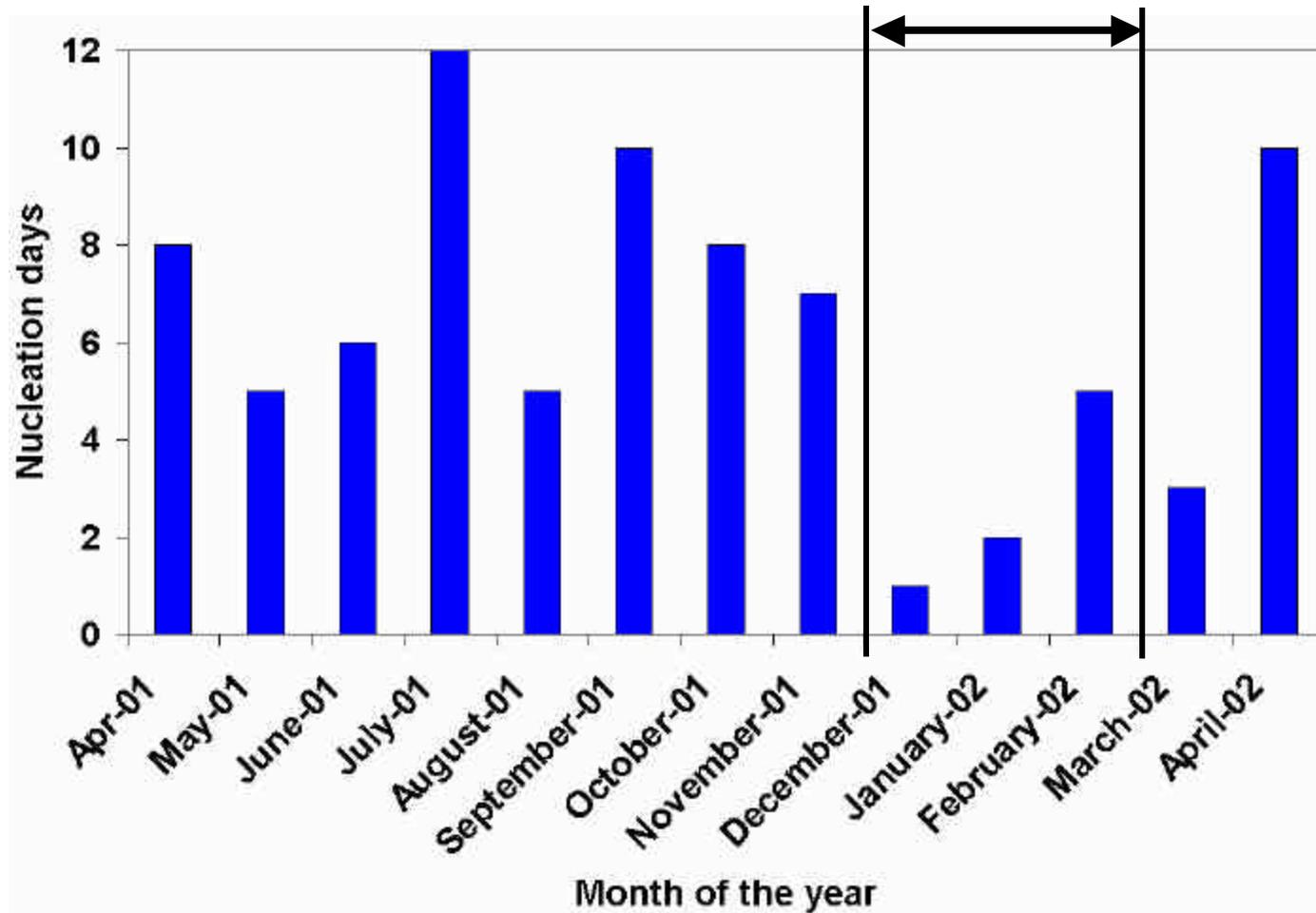
Particle formation rate during nucleation



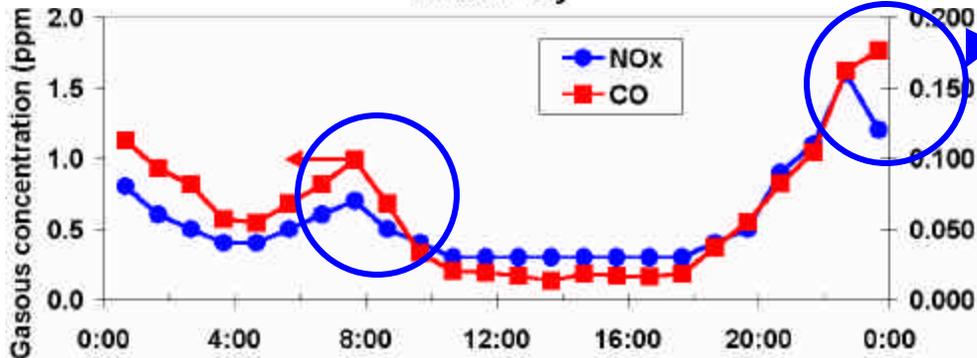
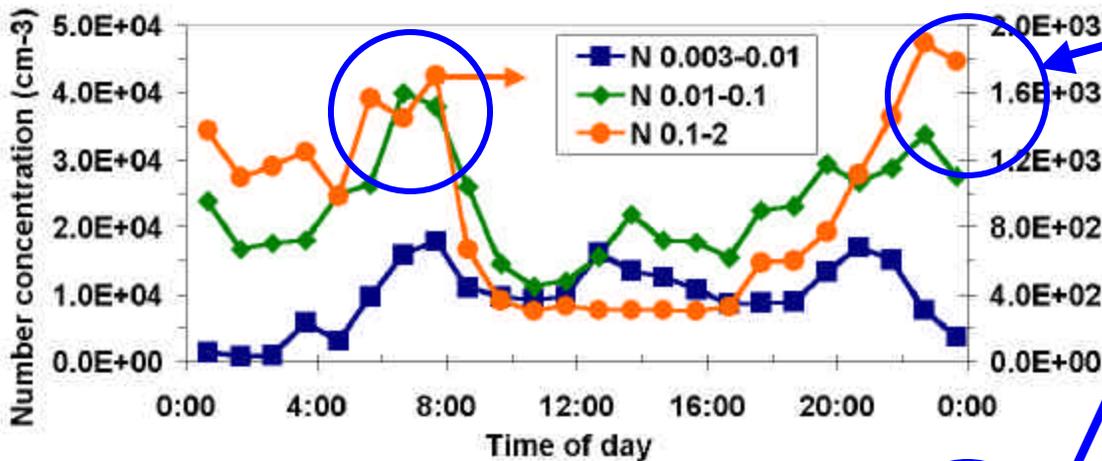
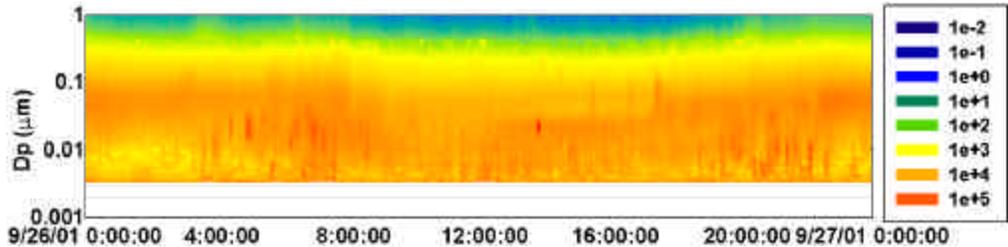
$$J_{3nm} = \left(\frac{dN}{dt} \right)_{Observed} + \left(\frac{dN}{dt} \right)_{Inter\ modal\ Coagulation} + \left(\frac{dN}{dt} \right)_{Intro\ modal\ Coagulation}$$

Seasonal trend of nucleation events

Less nucleations occurred in winter months



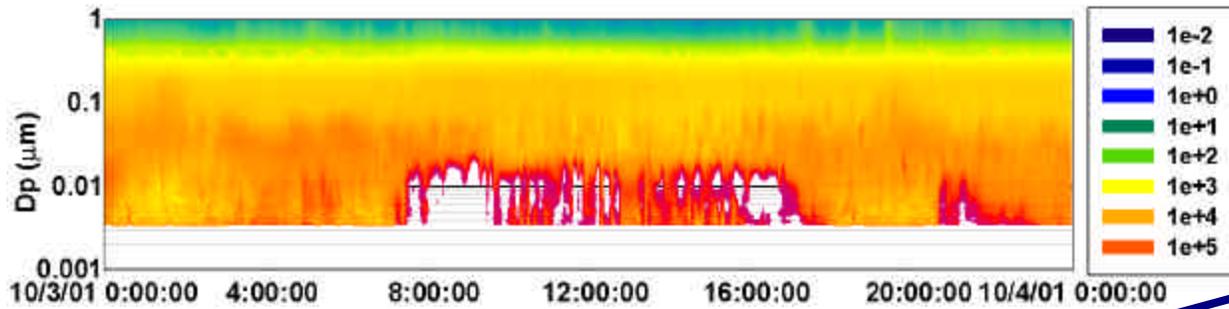
Traffic event (September 26, 2001)



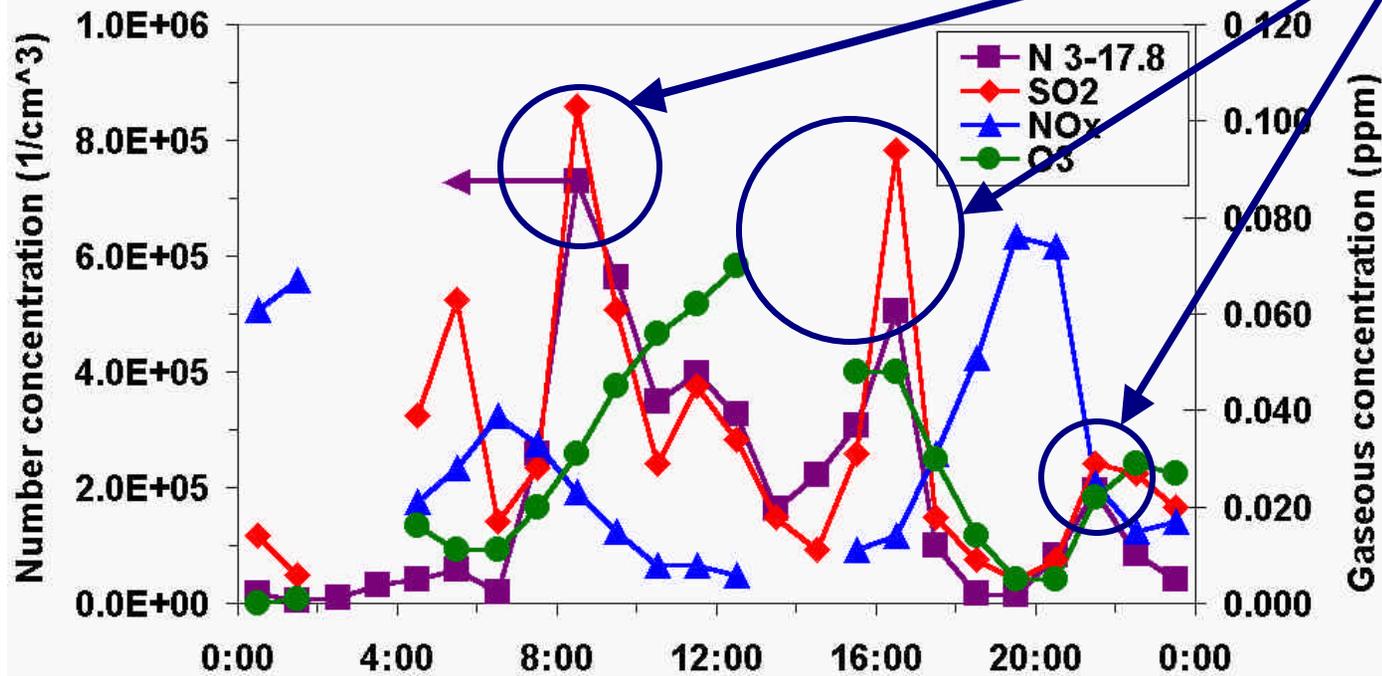
The elevation on particle number concentration is positively correlated with high concentrations of NO_x and CO



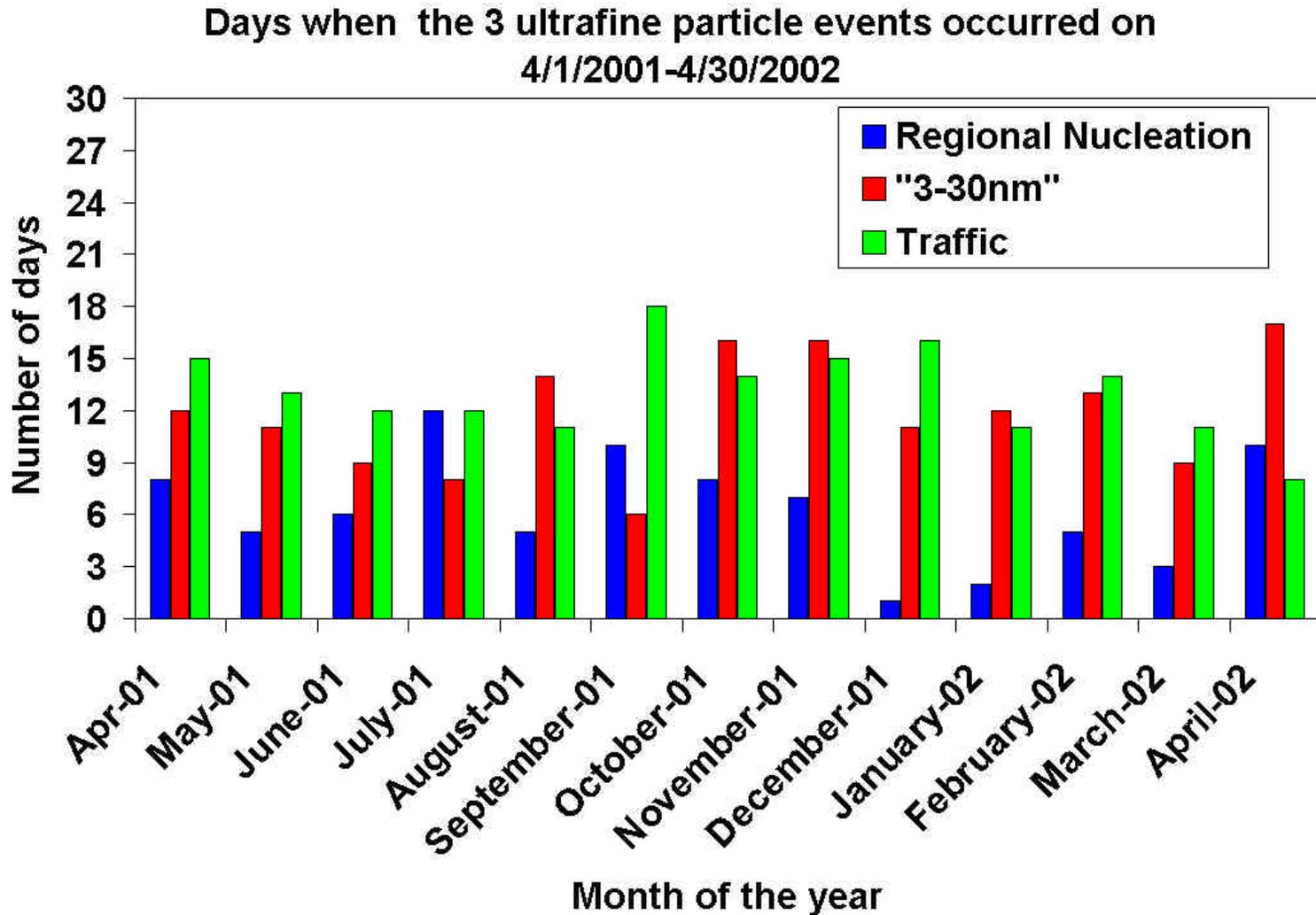
"3-30 nm" event (October 3, 2001)



The burst is highly correlated with very high concentration of SO₂



Summary chart on the 3 ultrafine particle events



Conclusions

- During the period of 4/1/2001-4/30-2002, we occasionally observed three types of “ultrafine particle” (sub-100 nm) events.
- On about 85 days in each season we observed clear evidence for nucleation and subsequent growth (usually from 3 nm to 40 nm). These events occur more often in spring, summer and autumn.
- We also observed that concentrations of 10-100 nm particles were often correlated with NO_x and CO, and reached peak levels early in the morning (about 7 a.m.) or around 11 p.m. These events occurred on at least 10 days per month. We think they resulted from the traffic-generated particles.
- We observed very high number concentrations of particles in the 3-30 nm diameter range on 10 or more days per month, but without growth afterwards (“3-30 nm Event”)

