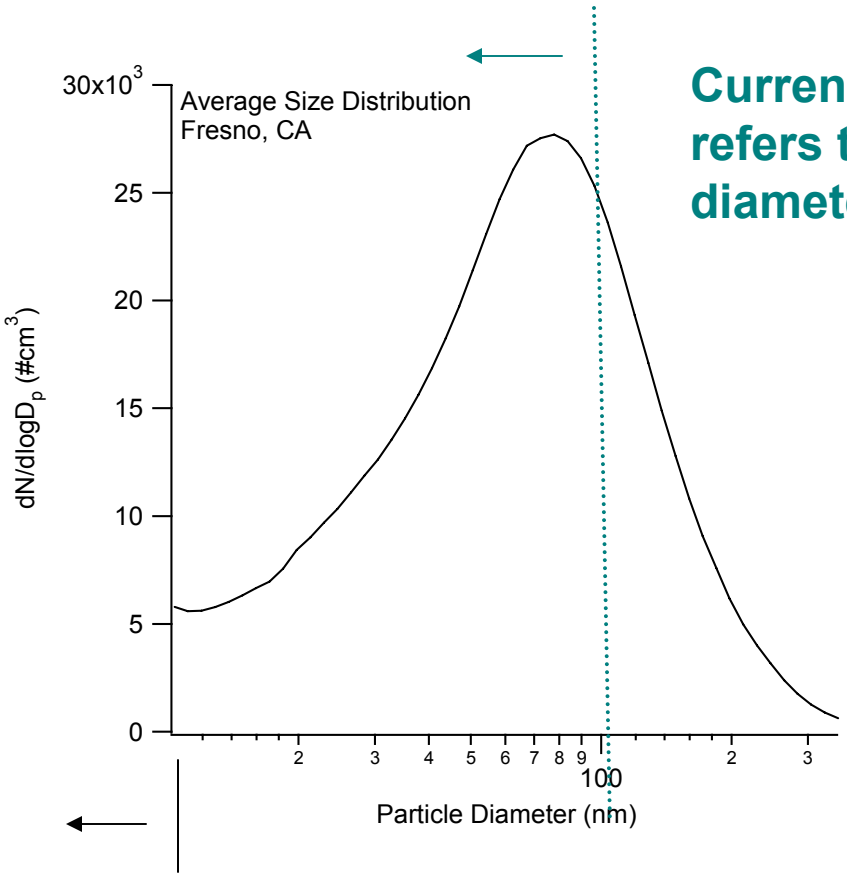
A Low-Cost Ultrafine Particle Concentration Monitor

ICAT Project 04-03

Susanne Hering
Aerosol Dynamics Inc.

What is meant by ultrafine particles?



Current usage: "Ultrafine" refers to particles <100nm diameter

Formerly, "ultrafine" meant <10nm
("ultrafine" condensation particle counters detect particles <5 nm)

Why are Ultrafine Particles Important?

- Associated with adverse health effects
- Indicator of combustion sources
- Very abundant in urban atmospheres

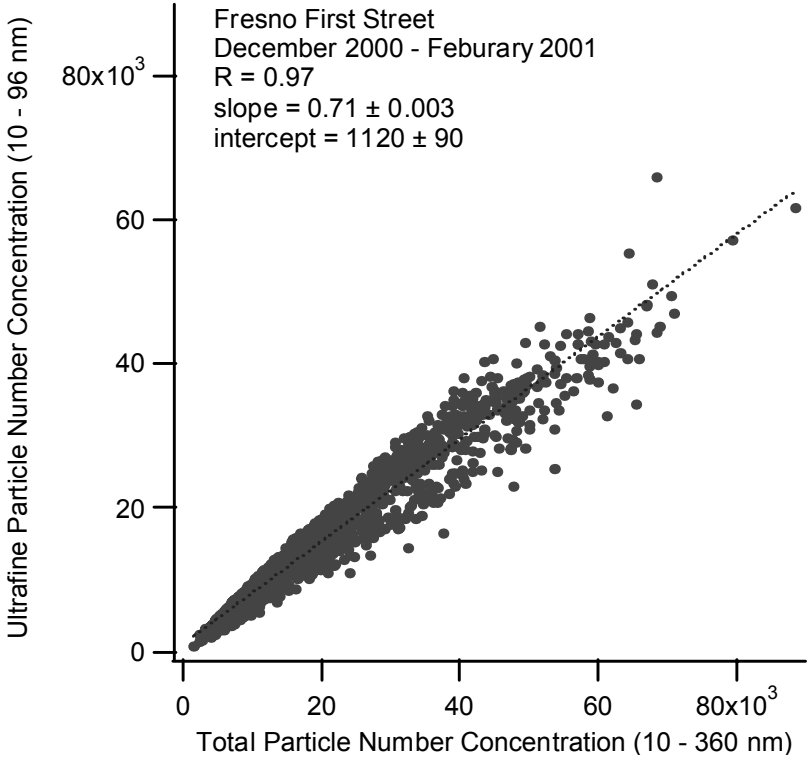
Why an micro-environmental “ultrafine” monitor?

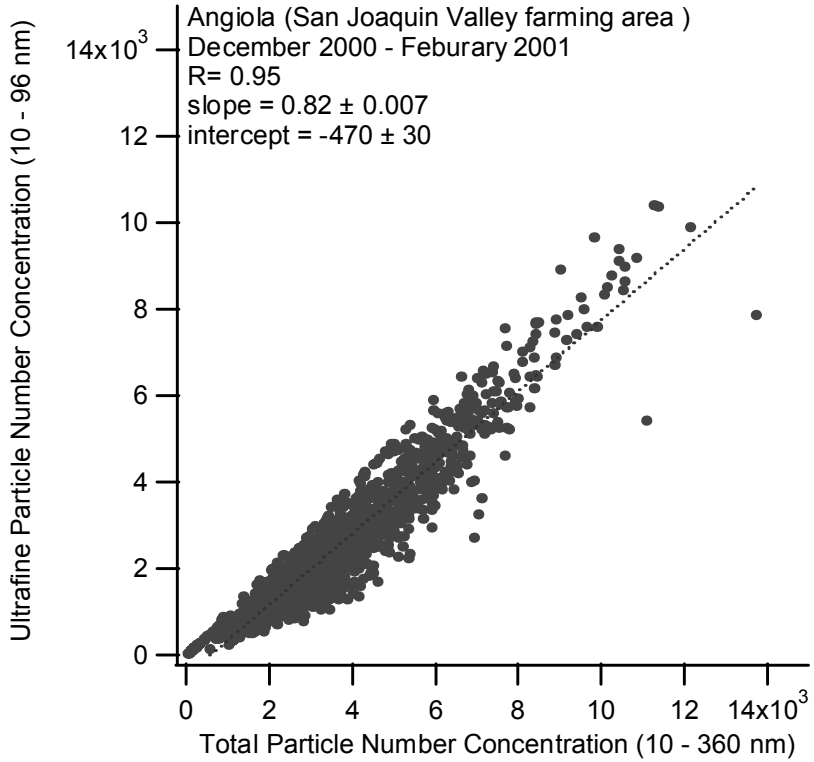
- Concentrations in occupied spaces are not well known.
- Levels are influenced by indoor and outdoor sources, as well as building ventilation and proximity to roadways.
- People spend the majority of their time indoors

What characterizes Ultrafine Particles?

- Large number concentrations
- Small mass concentration
- Often combustion / traffic related
- Also from particle nucleation events (gas to particle conversion)

Ultrafine Particles Dominate Particle Number Concentrations

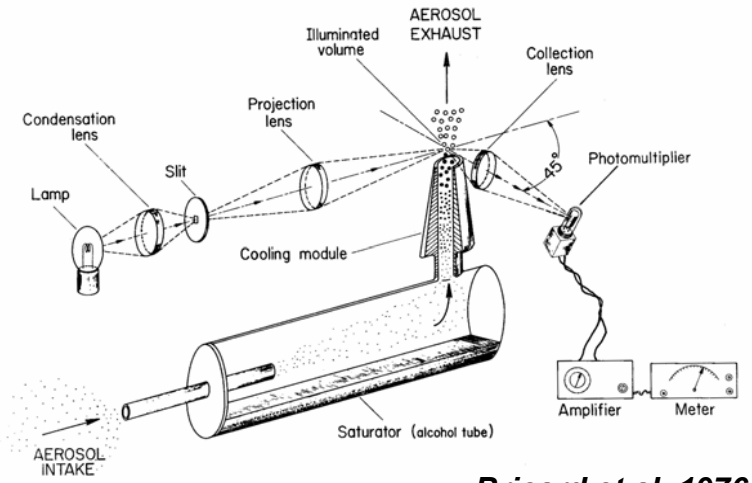




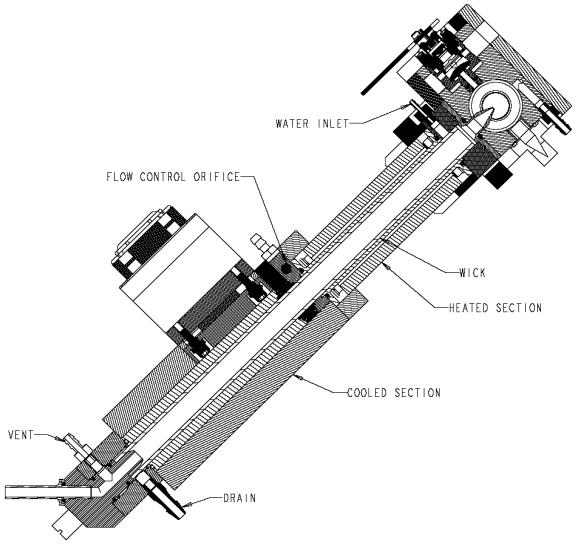
Rural and Urban Sites : Similar Relationship between Ultrafine Particle Number Concentrations and Total Particle Number Concentrations

Simplest Indicator for Ultrafine Particles:

Particle <u>Number</u> Concentration



Bricard et al, 1976



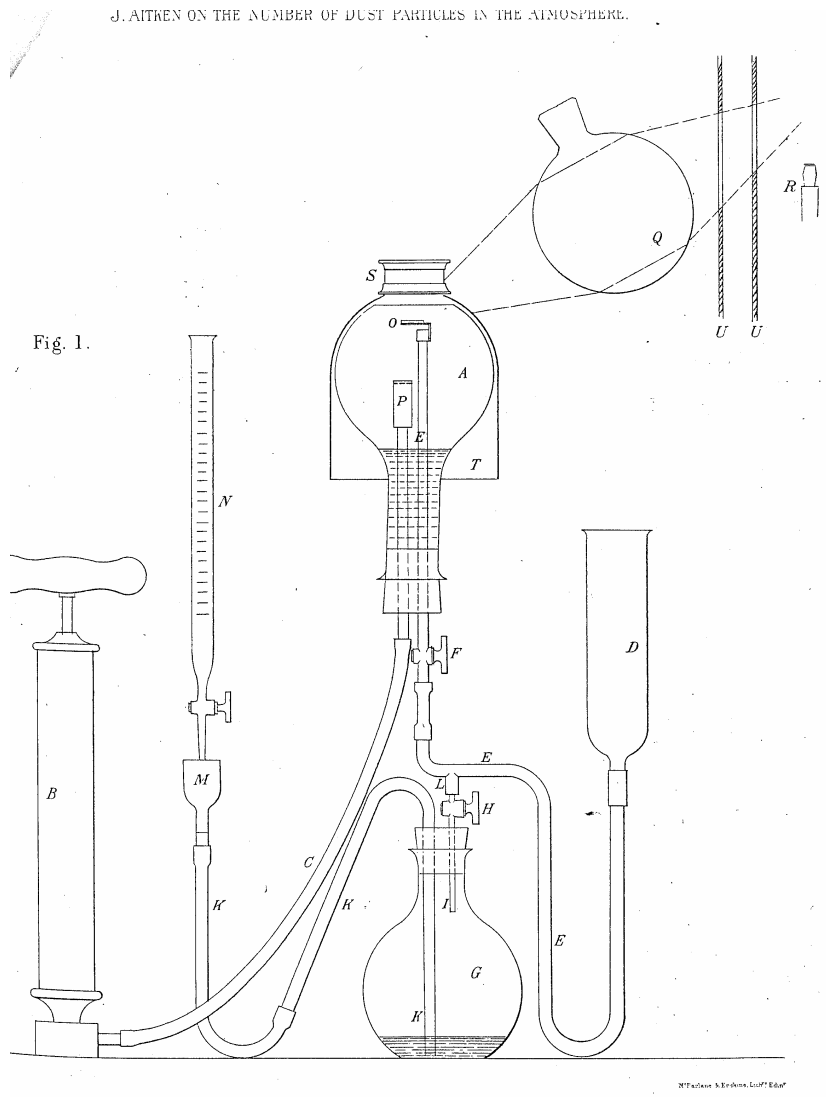
Hering et al, 2005

Historic Perspectives: Number Concentration Measurements Date from 1889

John Aitken,

"On the Number of Dust Particles in the Atmosphere",

Transactions of the Royal Society of Edinburgh, 1889



What Aitken Observed:

Number of Dust Particles in Air.

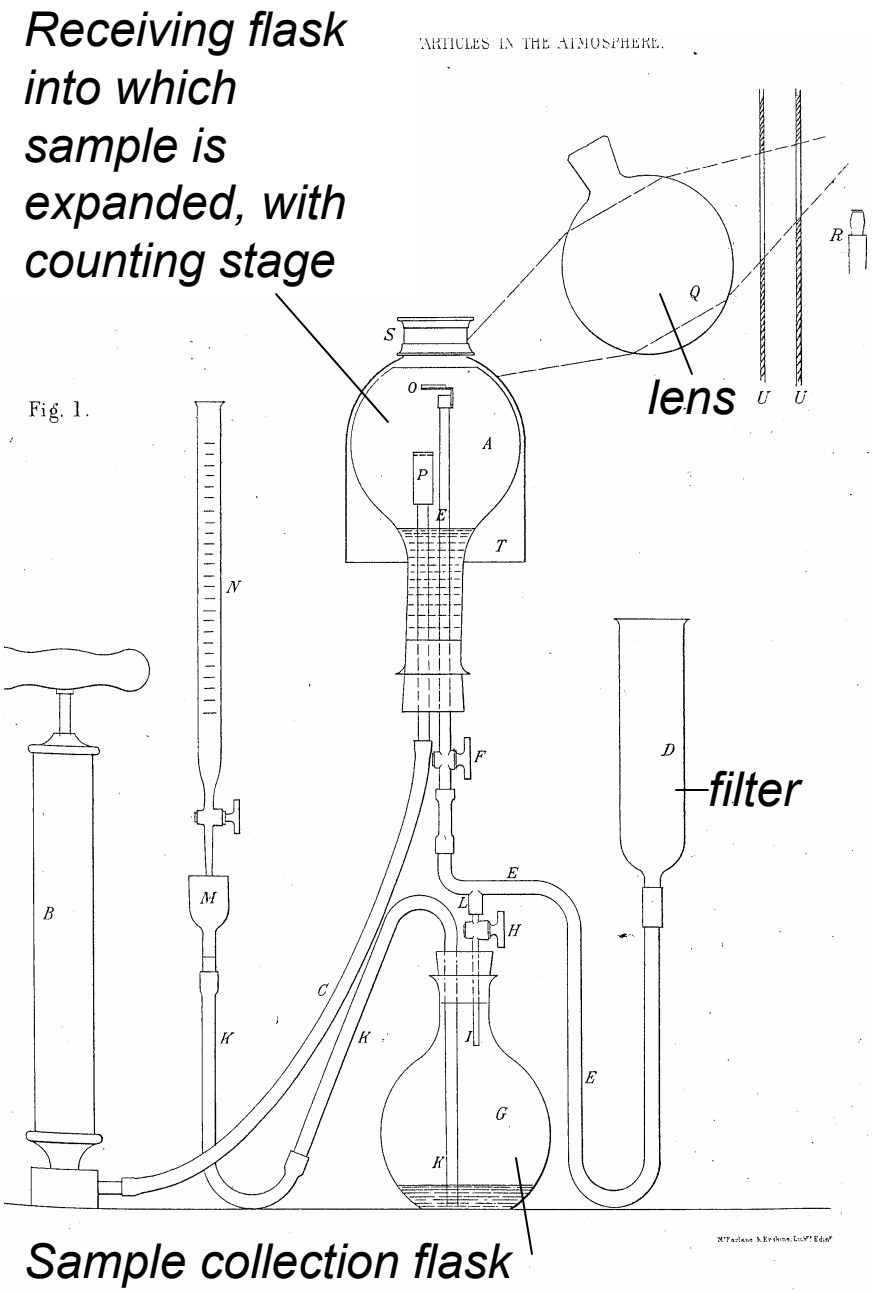
Source of Air.	Number per c.c.	Number per c. in.
Outside (Raining), . .	32,000	521,000
Outside (Fair), . . .	130,000	119,000
Room, ...	1,860,000	30,318,000
Room near ceiling, . .	5,420,000	88,346,000
Bunsen flame, . . .	30,000,000	489,000,000

"The reason of the greater number of particles in the room than that found outside was due to the particles produced by the two gas flames burning in the room at the time."

How Aitken's Instrument Worked

- **Humidified air sample**
- **Expanded adiabatically**
- **Droplets formed around particles, which then settled**
- **Counted manually**
- **Repeated with dilution**

Approach used today similar- enlarge particles through condensation to enable them to be counted.

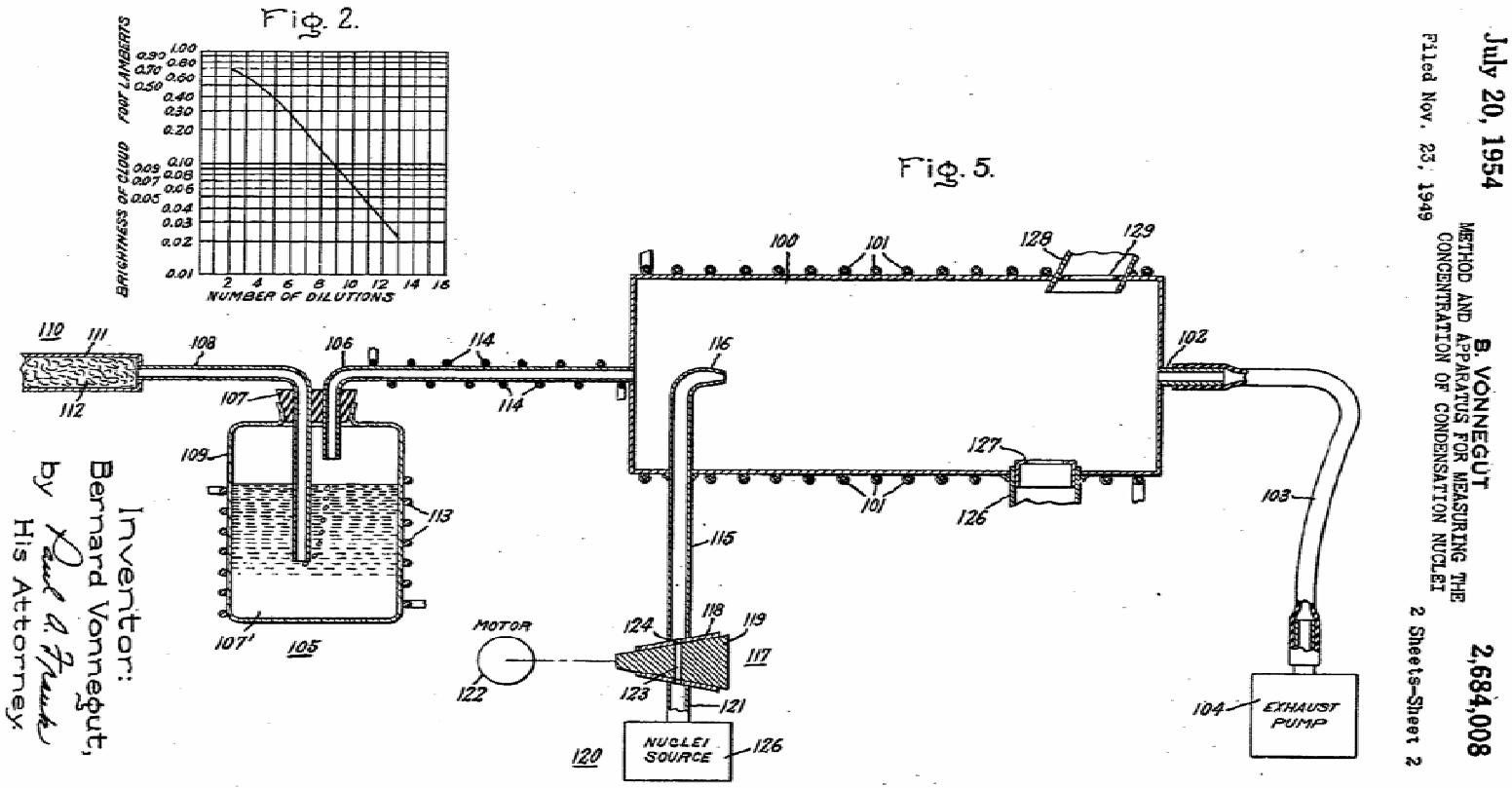


Key: Vapor supersaturation required to activate particle growth

Early instruments all used adiabatic expansion of saturated air mass

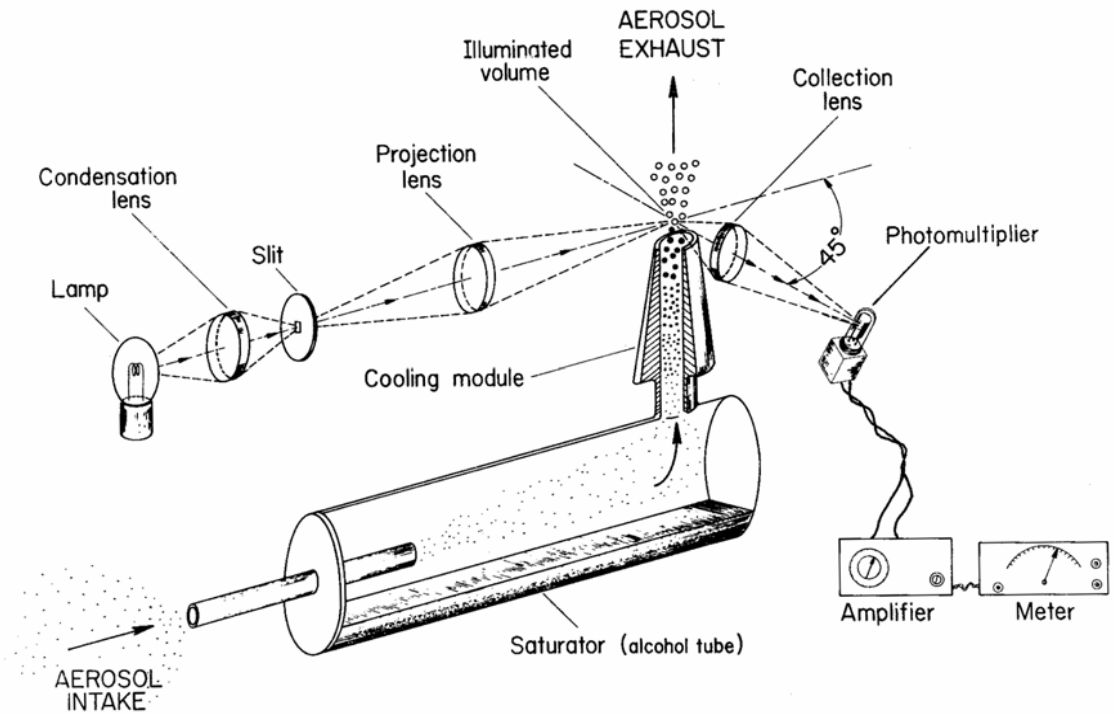
- **1912: Wilson Cloud Chamber**
  - **1929: Nobel Prize for particle physics**
  - **Determined precise expansion ratios for avoiding homogeneous and ion-induced nucleation of particles**
- **1930s: Scholz: Automated expansion for particle counting**
- **1950s: Vonnegut: Automated counting by recognizing particles grow to uniform size.**

1950s: Vonnegut, Automated Counting



Automated, but not continuous
(condensing vapor: water)

1970s: Thermally Diffusive Condensation Particle Counter (CPC)



Bricard et al, 1976

Automated & Continuous

(condensing vapor: butanol or other alcohol)

Widely used, many models

Suitable as detector for sizing instruments

Can you have a Continuous, Automated Particle Counter without Butanol?

- **Challenge**: too small for direct optical detection
- **Approach:** Create region of supersaturation to activate particle growth => form droplets
- **Why Supersaturation?** Equilibrium vapor pressure over a droplet is greater than over a flat surface due to free energy associated with surface (surface tension)
- Kelvin Relation:

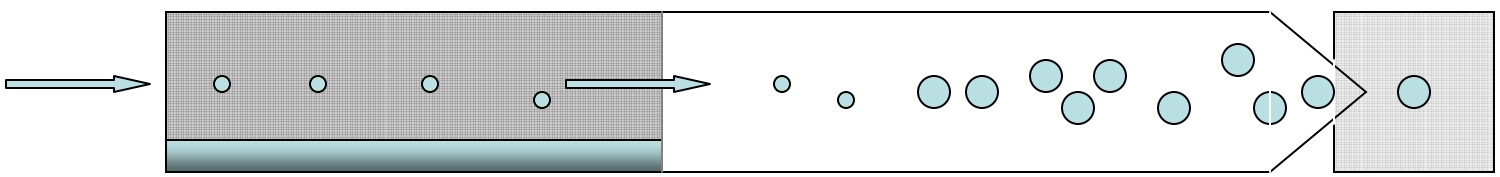
$$P_{droplet} = P_{flat\ surface} \exp(2 \sigma v / kT\rho R)$$

Surface tension

Particle radius

Thermally Diffusive CPCs: Operational Principle

- Saturate flow with vapor
- Flow into cold-walled tube
- Vapor condenses on particles
- Requires slowly diffusing vapor (e.g. butanol)



Saturator, 35°C Condenser, 10°C Optics Head

Thermal Diffusivity,
air = 0.215 cm^2/s

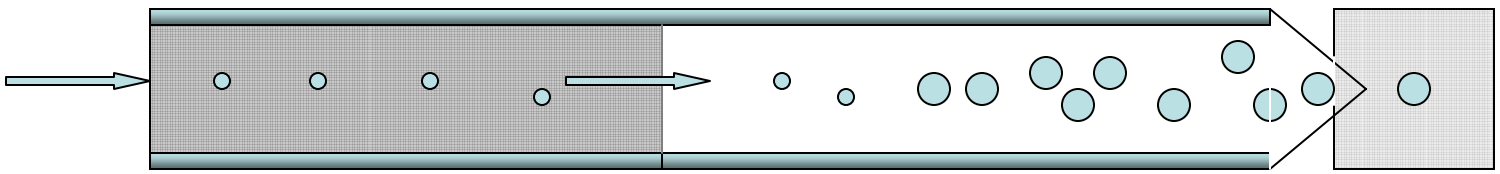
Mass Diffusivity,
butanol = 0.081 cm^2/s

Note: diffusivity of water = 0.265 cm^2/s > air

Does not work well with water

2003: Water Condensation Particle Counter (WCPC)

- Cold flow enters warm wet-walled tube
- Water vapor diffuses more quickly than flow warms
- Supersaturation, particle activation and growth occurs inside of a warm, wet walled tube.



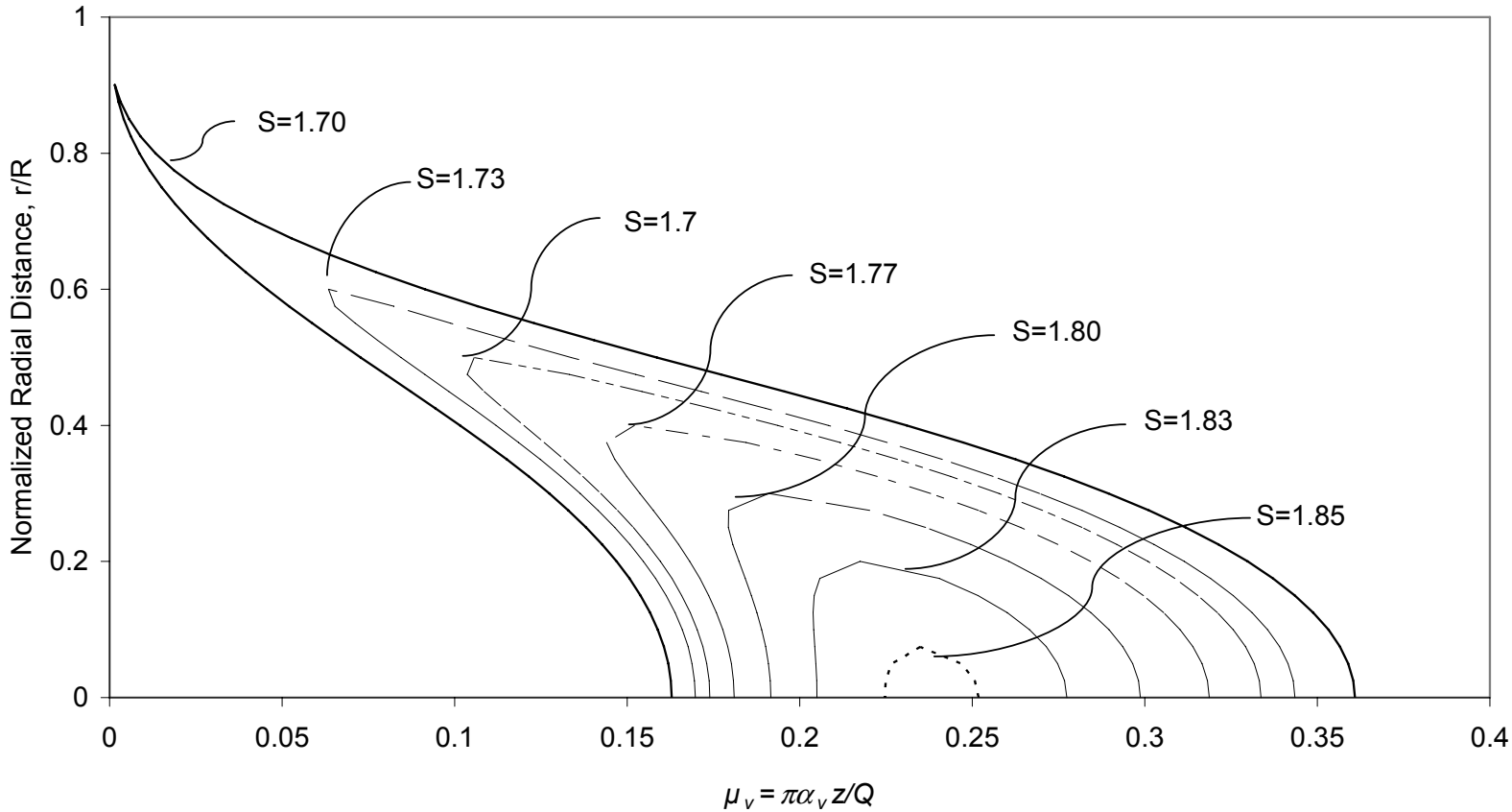
Optics Head

2003 WCPC (~5 nm) :	Saturator, 20C	Condenser, 60C
2004: Nano-WCPC (~2.5 nm)	Saturator, 12C	Condenser, 75C

Thermal Diffusivity, air = 0.215 cm^2/s

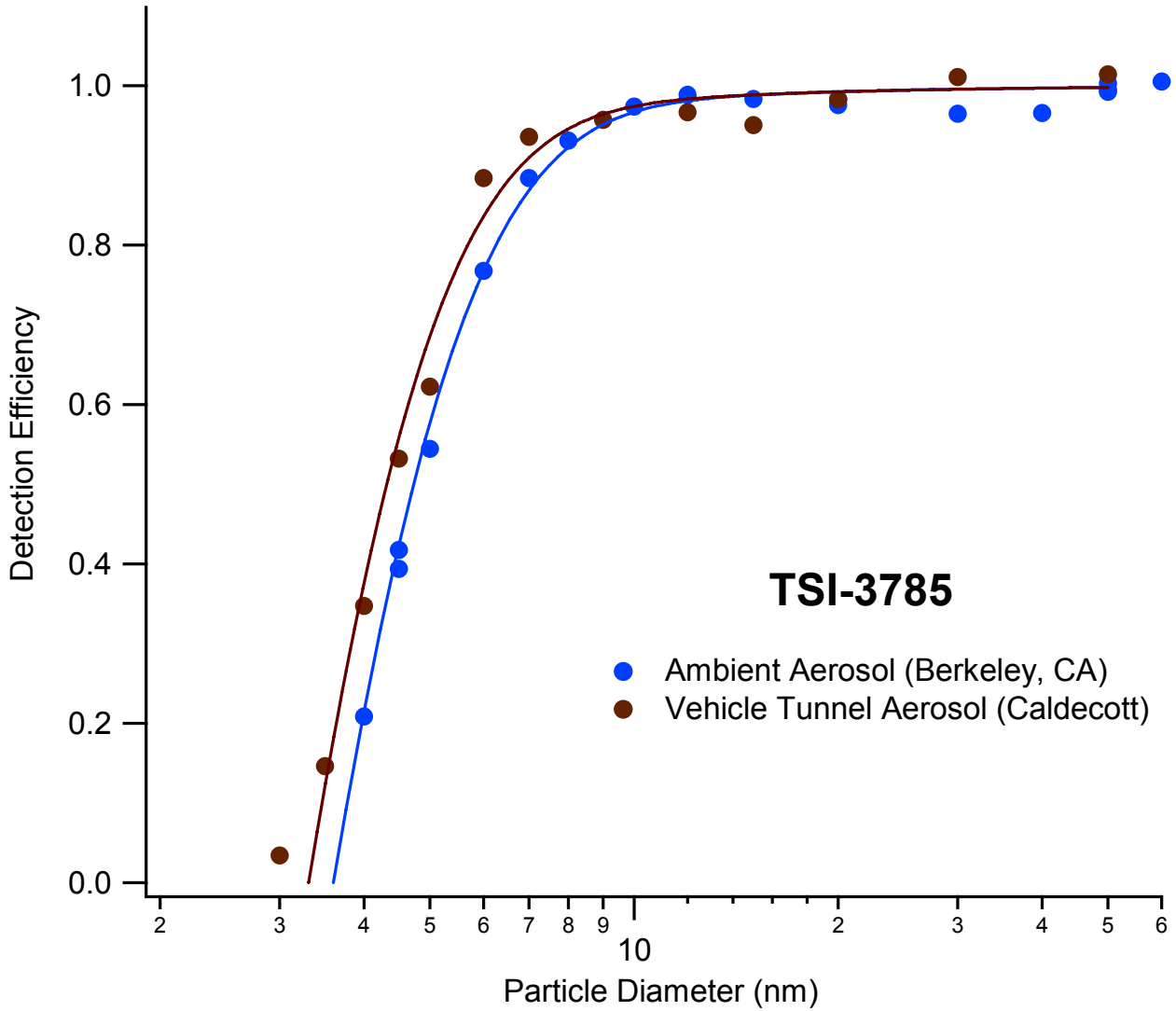
Mass Diffusivity, water = 0.265 cm^2/s

Calculated Supersaturation Profiles within the Ultrafine Water – CPC



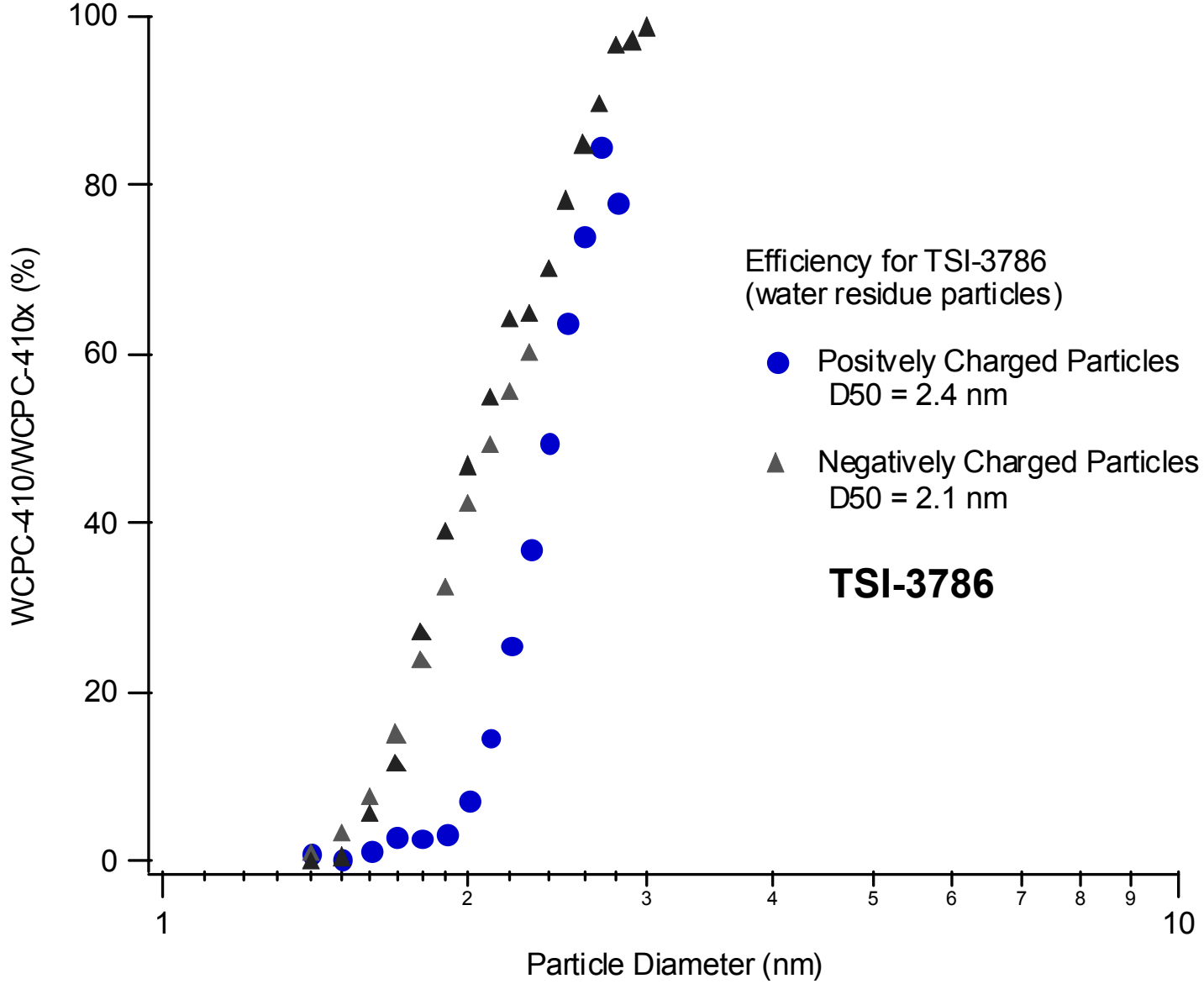
α_v = *vapor mass diffusivity*
z = *axial distance*
Q = *volumetric flow rate*

Response of the 'Standard' WCPC to Ambient Aerosols & Vehicle Emissions



Tunnel Measurements with Antonio Miguel, Arantza Eiguren-Fernandez, UCLA

Calibration of the "Ultrafine" (<10nm) WCPC Water Residue Particles



2005: Micro-Environmental WCPC

Size: 7” x 7” x 5”

Weight: 5 lb

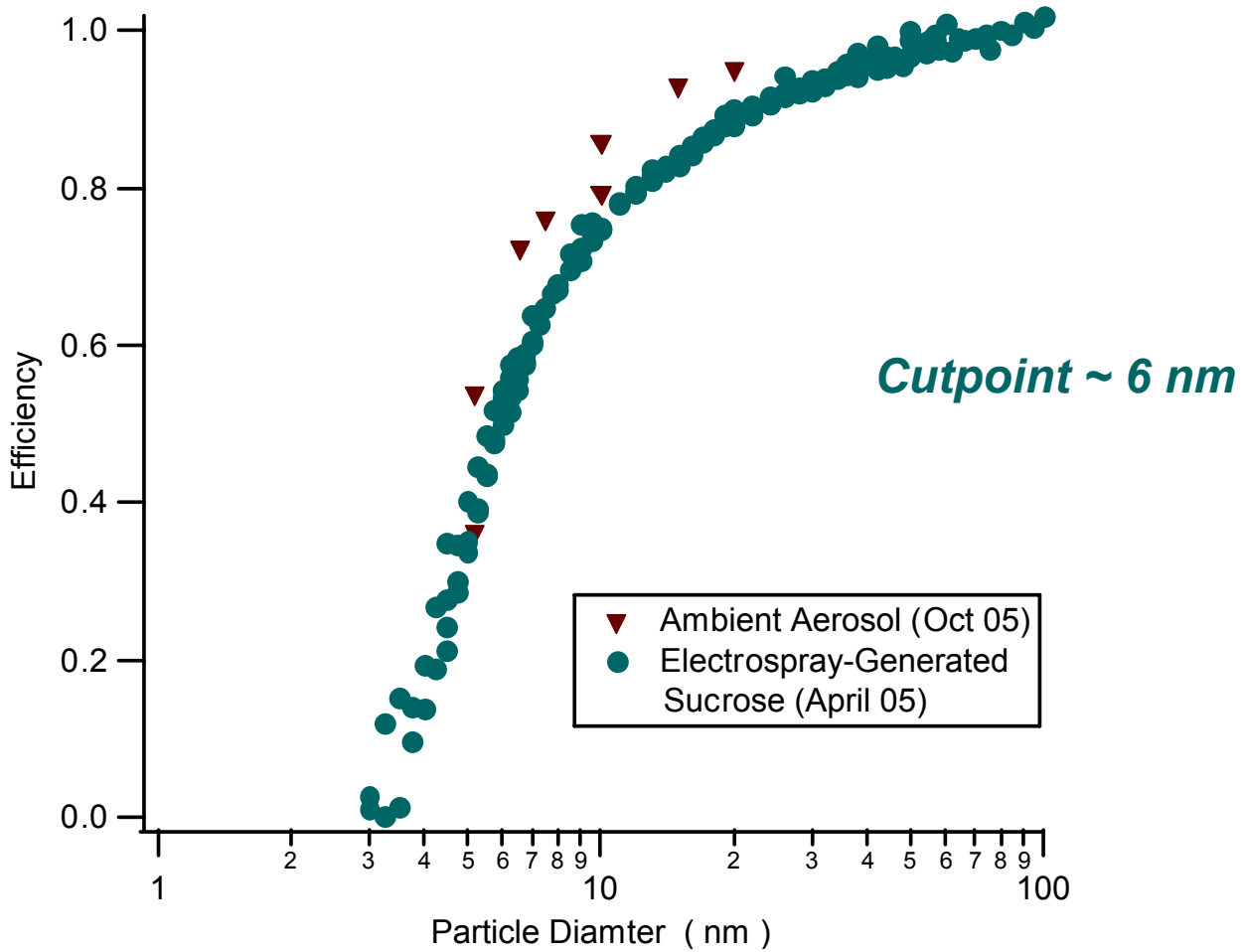
Power 12 V, 30 Watts

Features:

- internal data logging
- one week unattended
- up to 10^6 particles/cm^3
- in single count mode

Response to Near-Monodisperse Aerosols

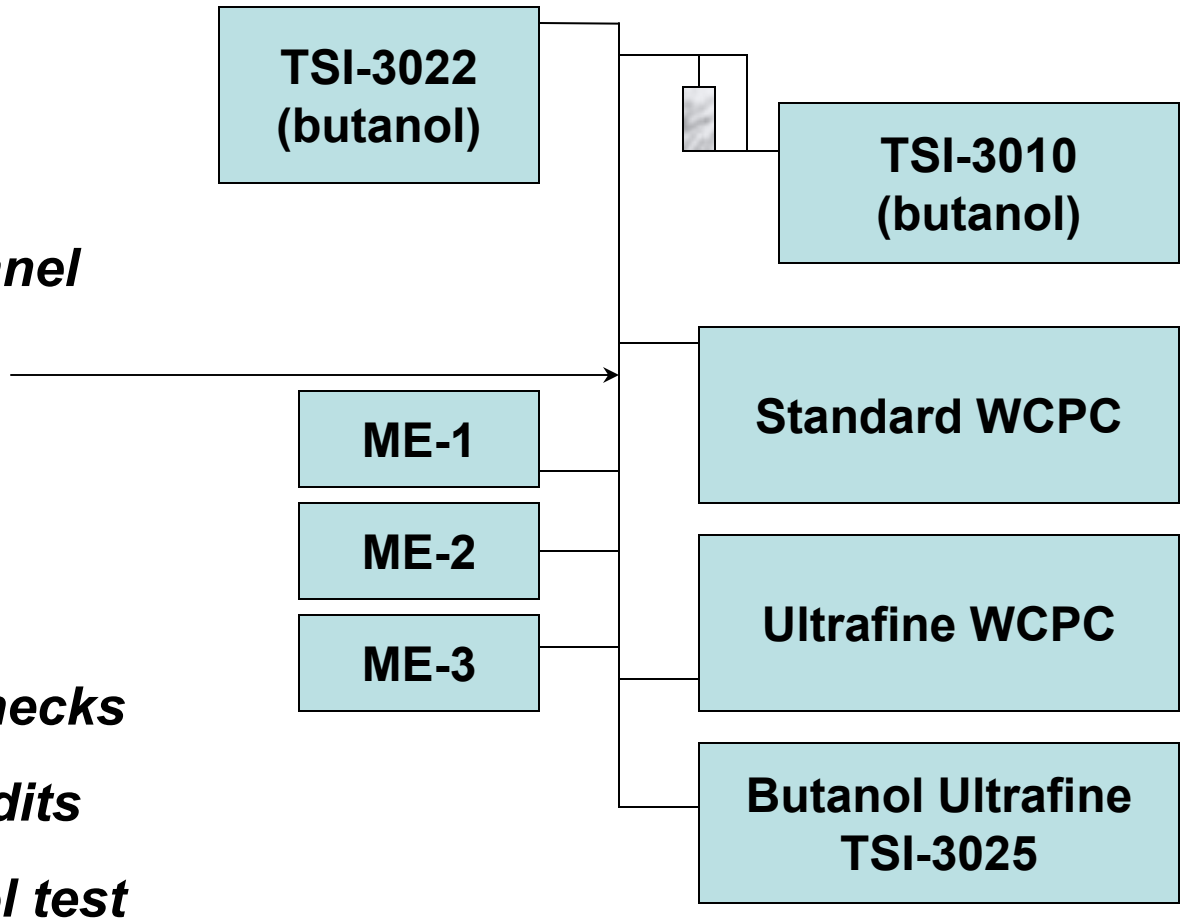
ME Prototype



How does the ME-WCPC compare to more traditional instruments under field conditions?

CPC Array:

Riverside
Berkeley
Office
Home
Freeway Tunnel



QA:

filter zero checks

flow rate audits

DMA aerosol test

Field Comparisons Among CPCs

WCPC

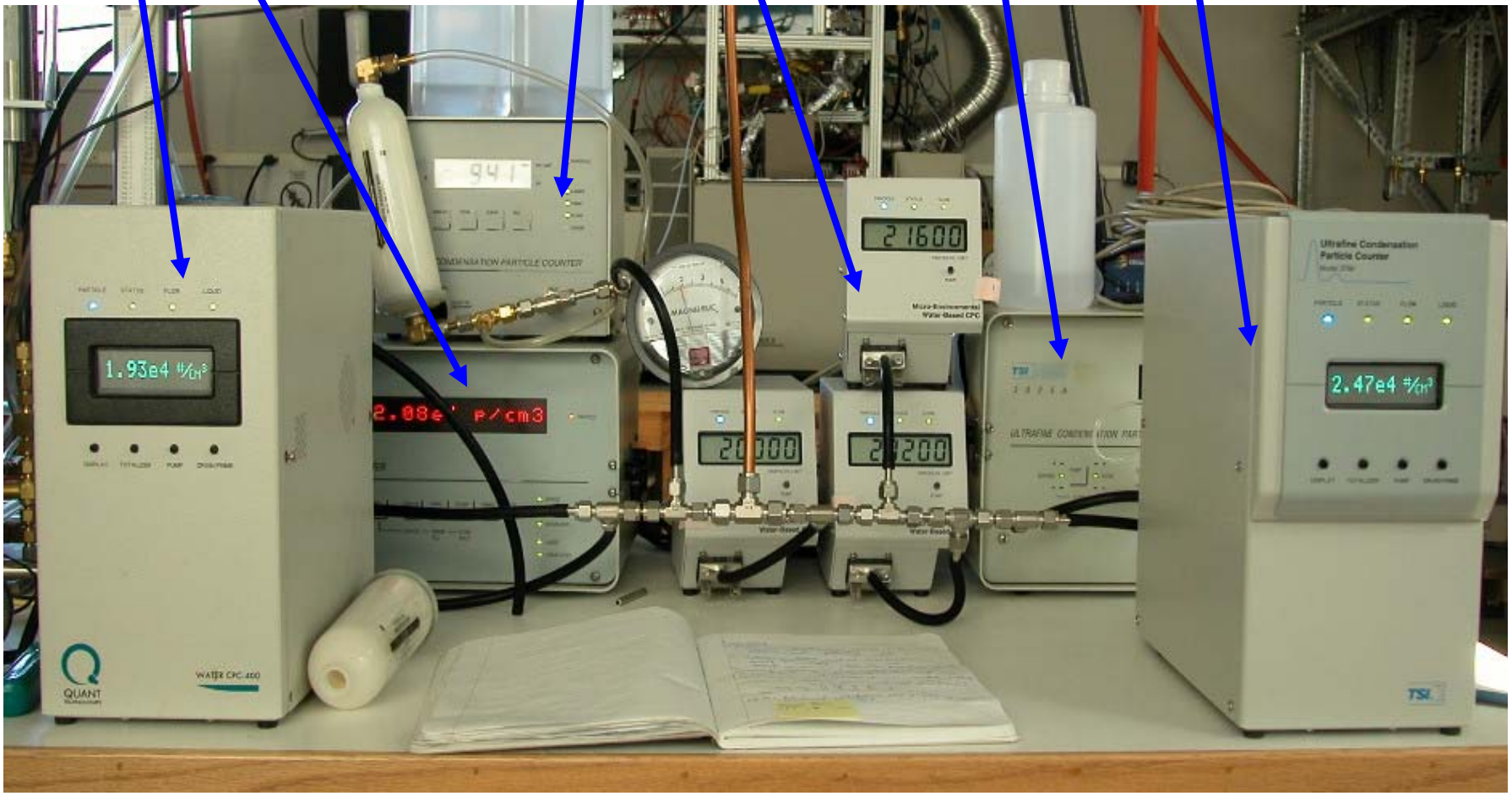
Butanol 3010 CPC

Butanol 3022 CPC

ME-WCPC

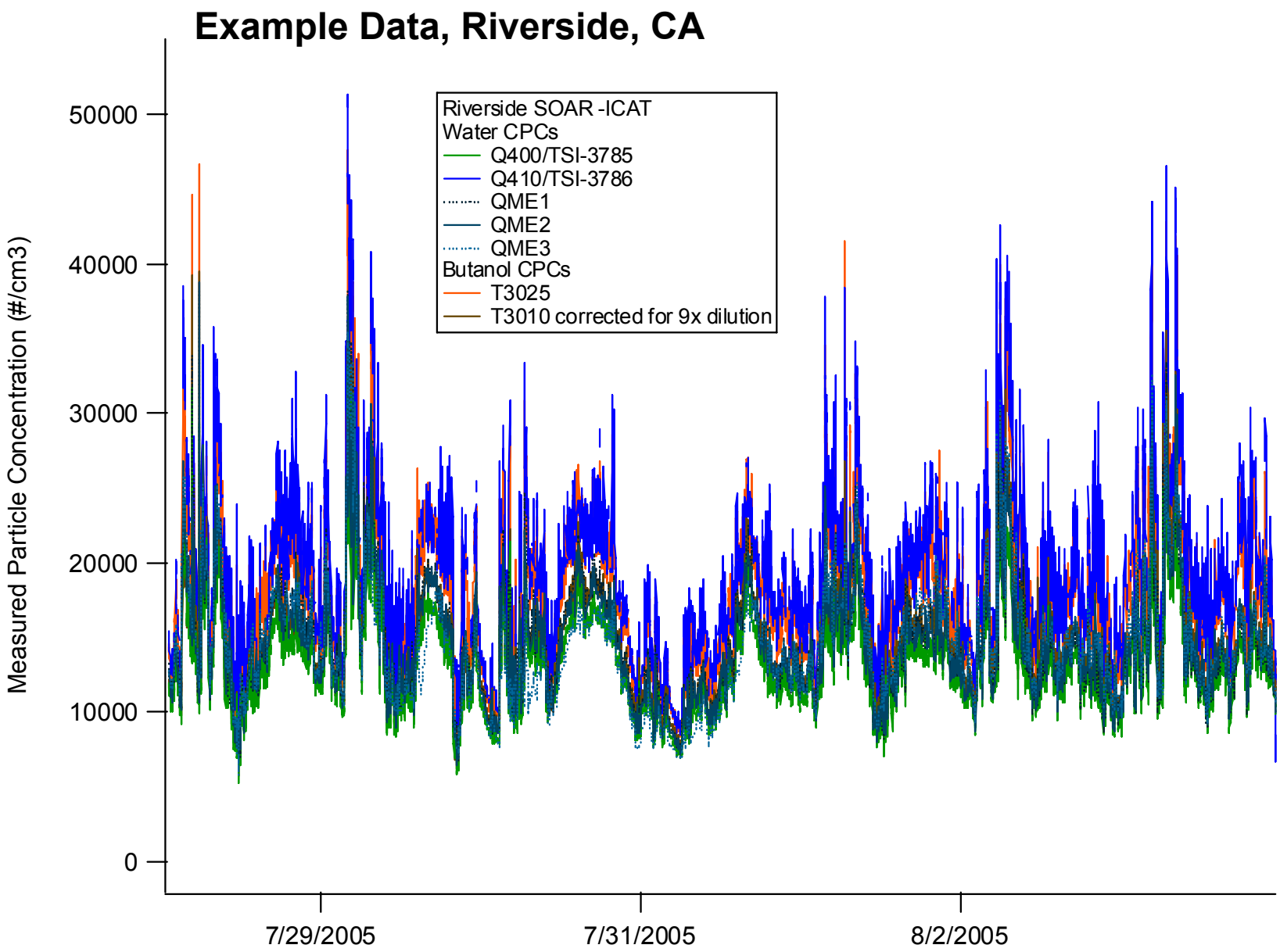
Butanol Ultrafine 3025

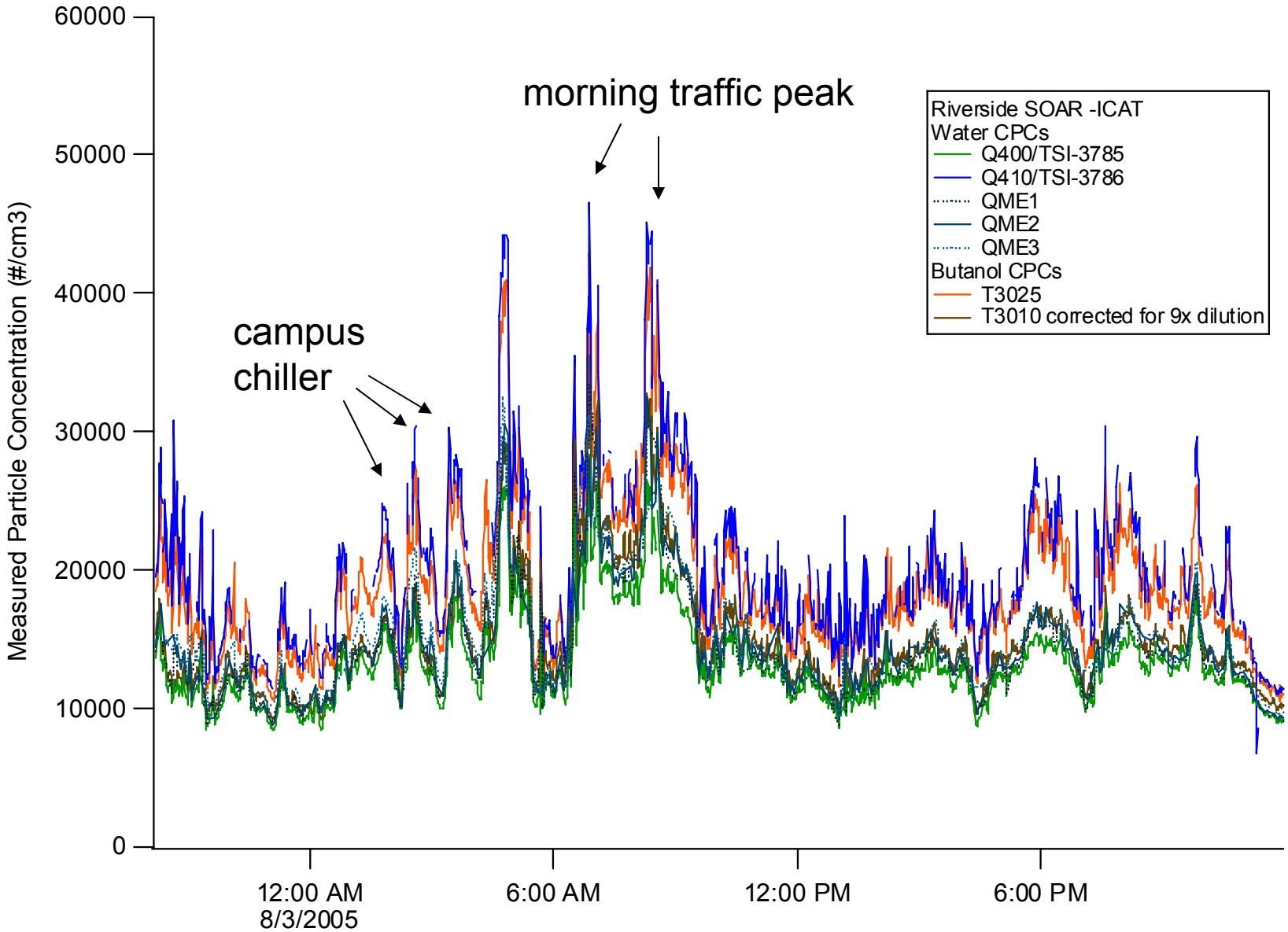
Ultrafine Water CPC



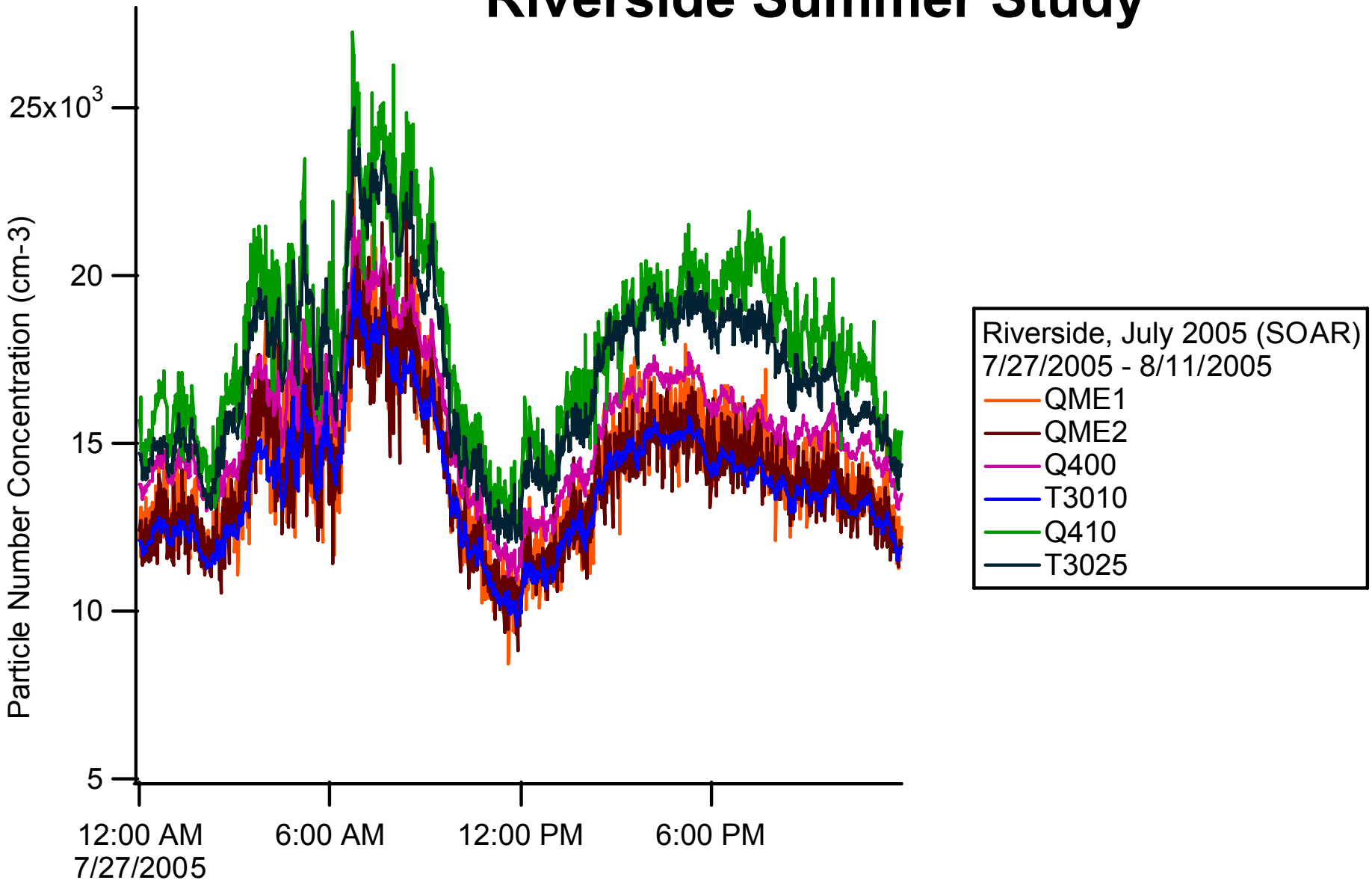
Field Comparisons

CPC	Flow (L/min)	Lower Dp (nm)	Max Concentration (single count mode)
MicroEnvironmental (ME) WCPC	0.1	~6	500,000 / cm^3
Standard WCPC	1.0	5	30,000 / cm^3
Ultrafine WCPC	0.3	2.5	100,000 / cm^3
Butanol 3010	1.0	10	10,000 / cm^3
Butanol 3025 Ultrafine	0.03	3	100,000 / cm^3
Butanol 3022	0.3	7	1,000,000 / cm^3

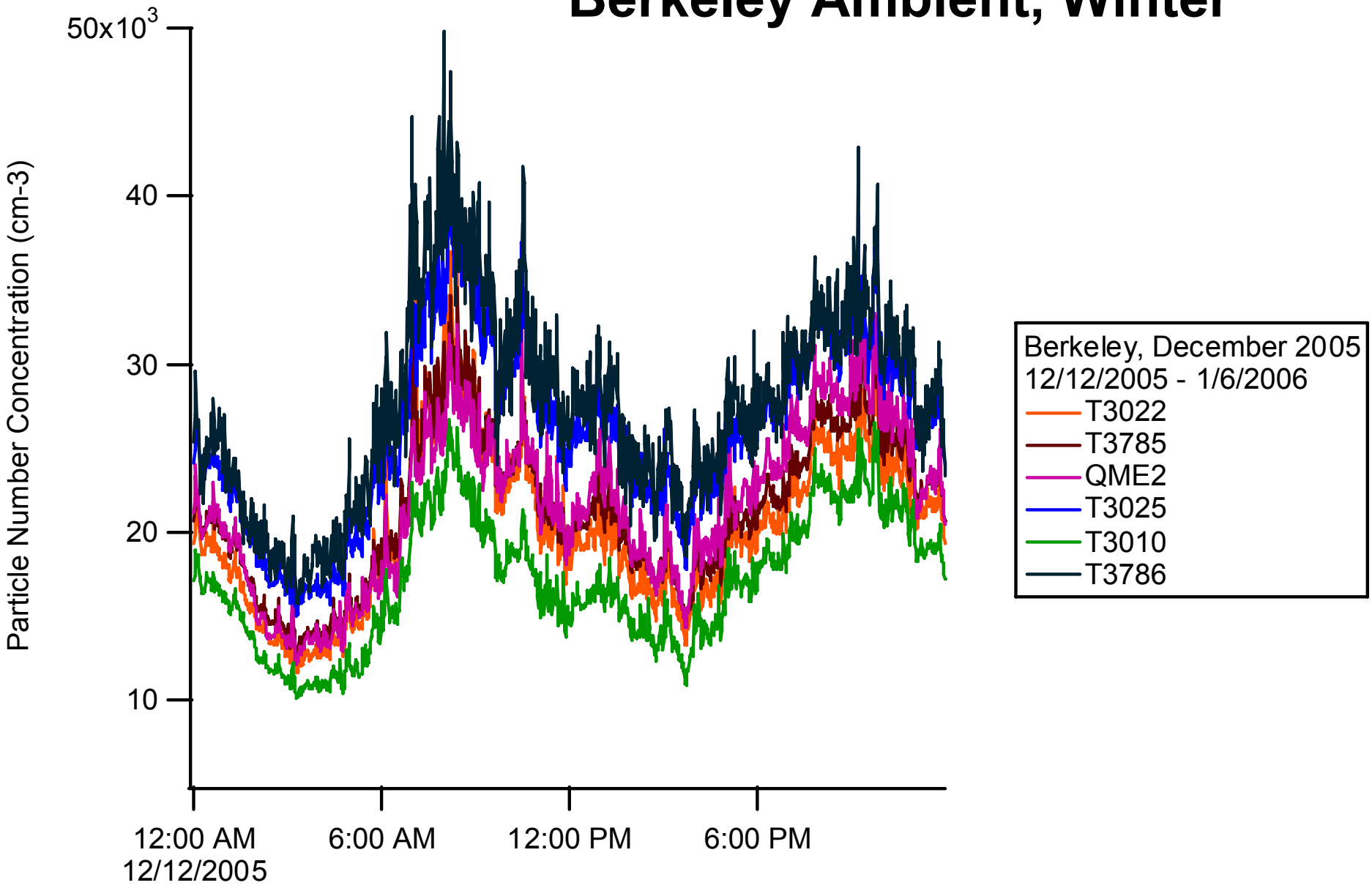

Example Data, Riverside, CA
Measured Particle Concentration (#/cm3)
50000
40000
30000
20000
10000
0
7/29/2005
7/31/2005
8/2/2005
Riverside SOAR -ICAT
Water CPCs
Q400/TSI-3785
Q410/TSI-3786
QME1
QME2
QME3
Butanol CPCs
T3025
T3010 corrected for 9x dilution


60000
50000
40000
30000
20000
10000
0
Measured Particle Concentration (#/cm3)
morning traffic peak
campus
chiller
Riverside SOAR -ICAT
Water CPCs
Q400/TSI-3785
Q410/TSI-3786
QME1
QME2
QME3
Butanol CPCs
T3025
T3010 corrected for 9x dilution
12:00 AM
8/3/2005
6:00 AM
12:00 PM
6:00 PM

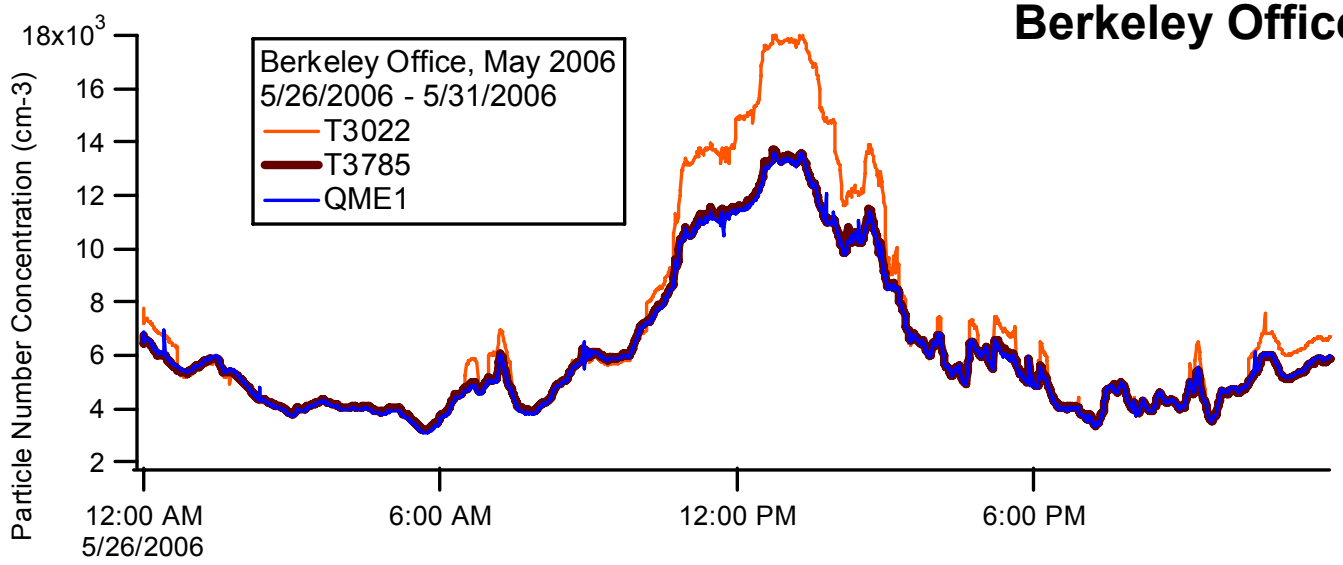
Average by Time of Day
Riverside Summer Study



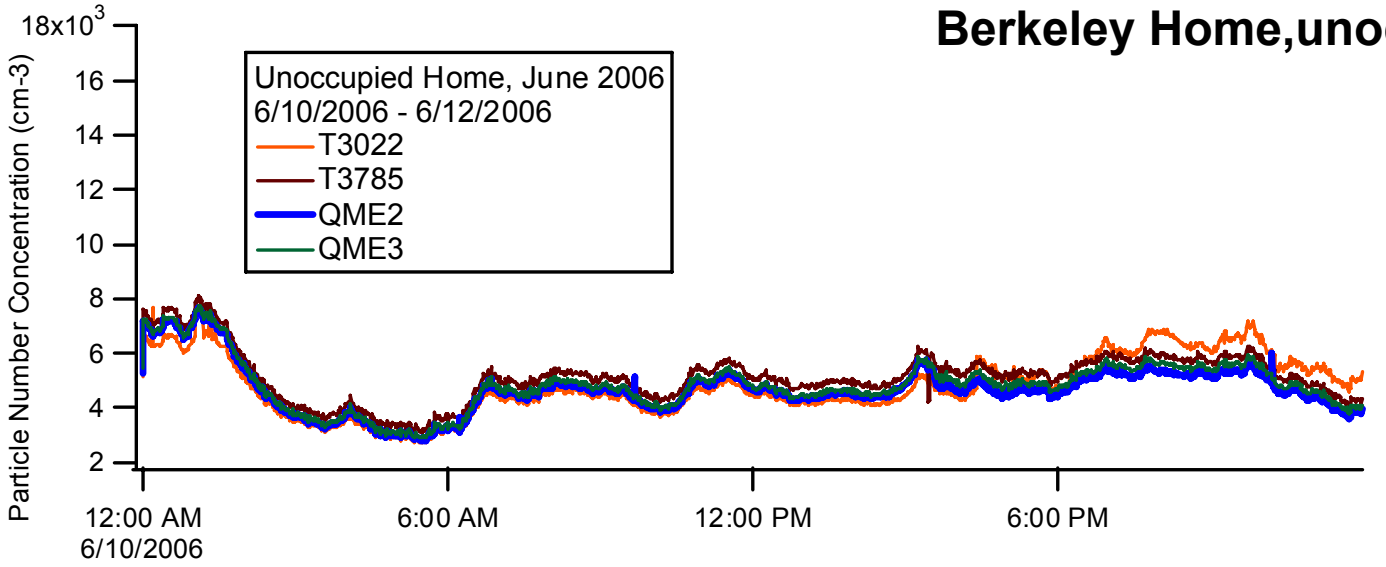
Average by Time of Day
Berkeley Ambient, Winter



Average by Time of Day
Berkeley Office

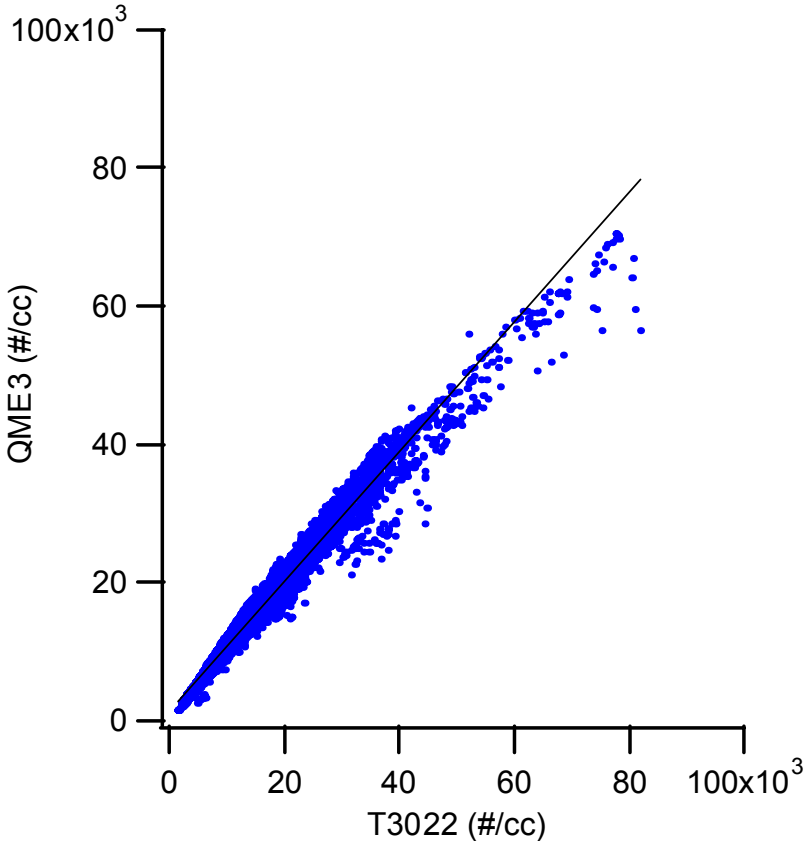


Average by Time of Day
Berkeley Home,unoccupied

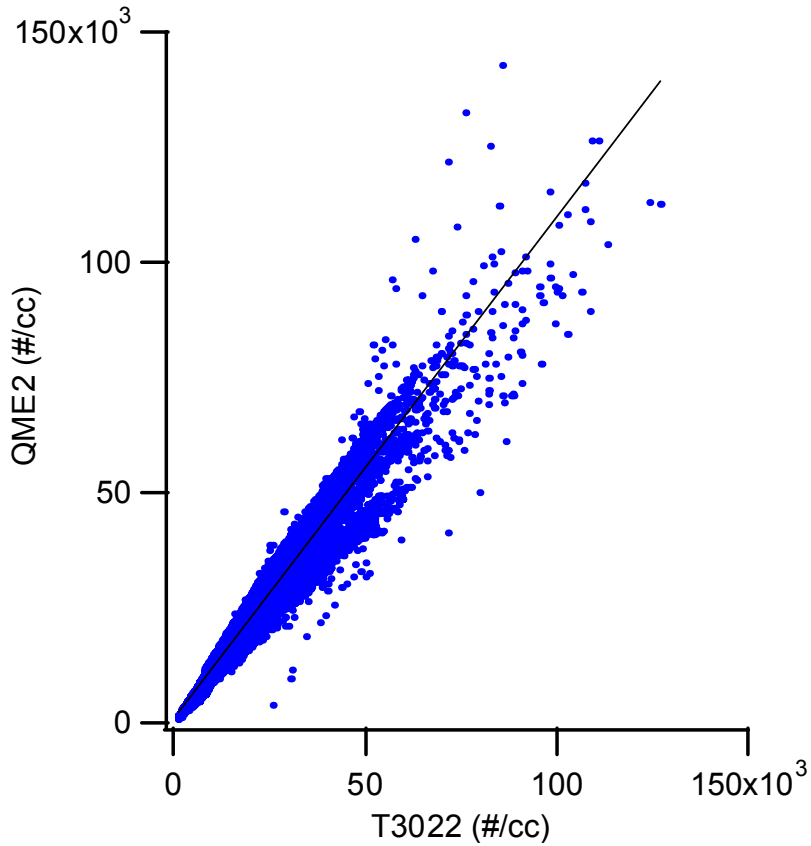


Comparison to the 'Photometric' Butanol CPC

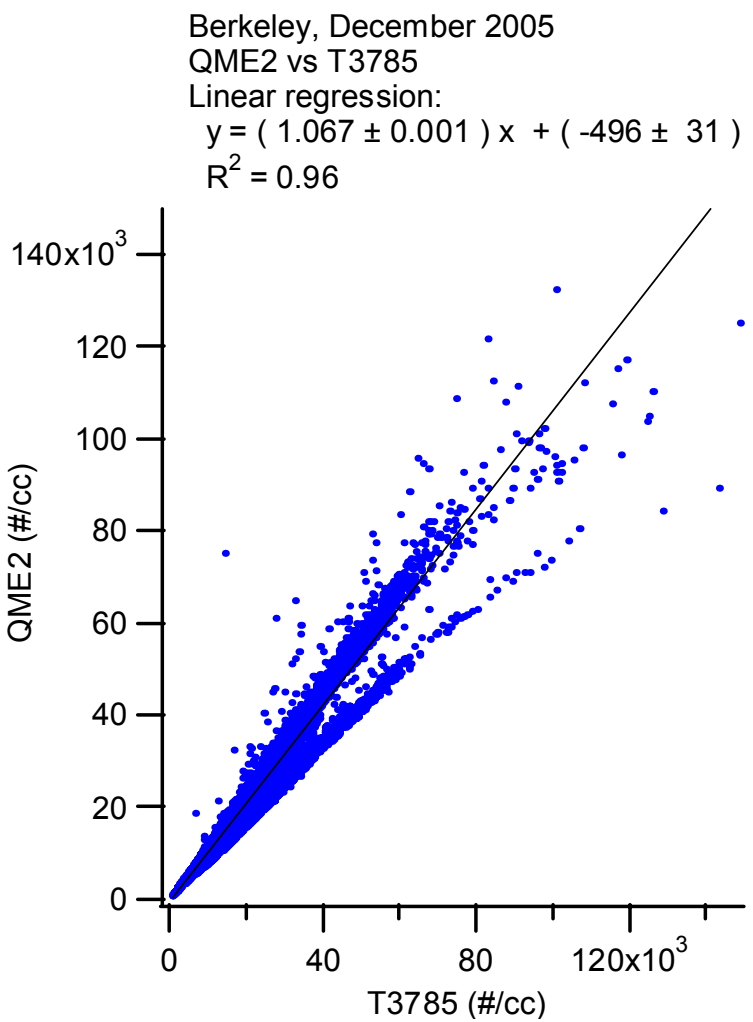
Riverside, Winter 2005
QME3 vs T3022
Linear regression:
$y = (0.942 \pm 0.001) x + (1308 \pm 17)$
$R^2 = 0.97$

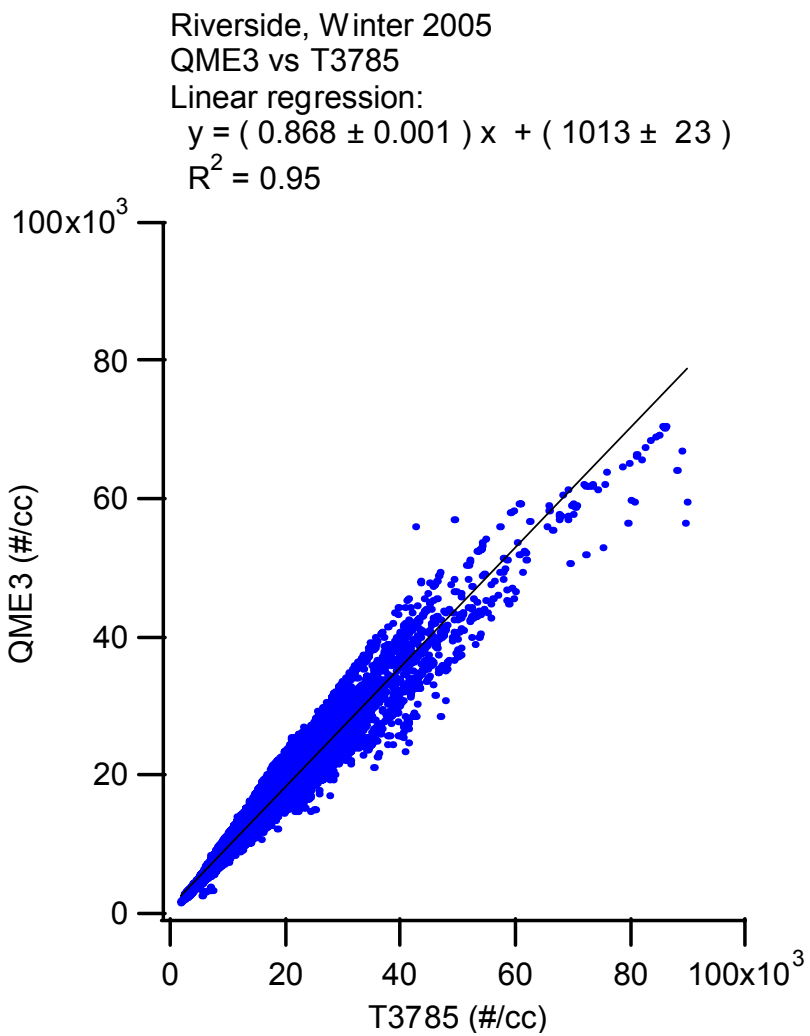


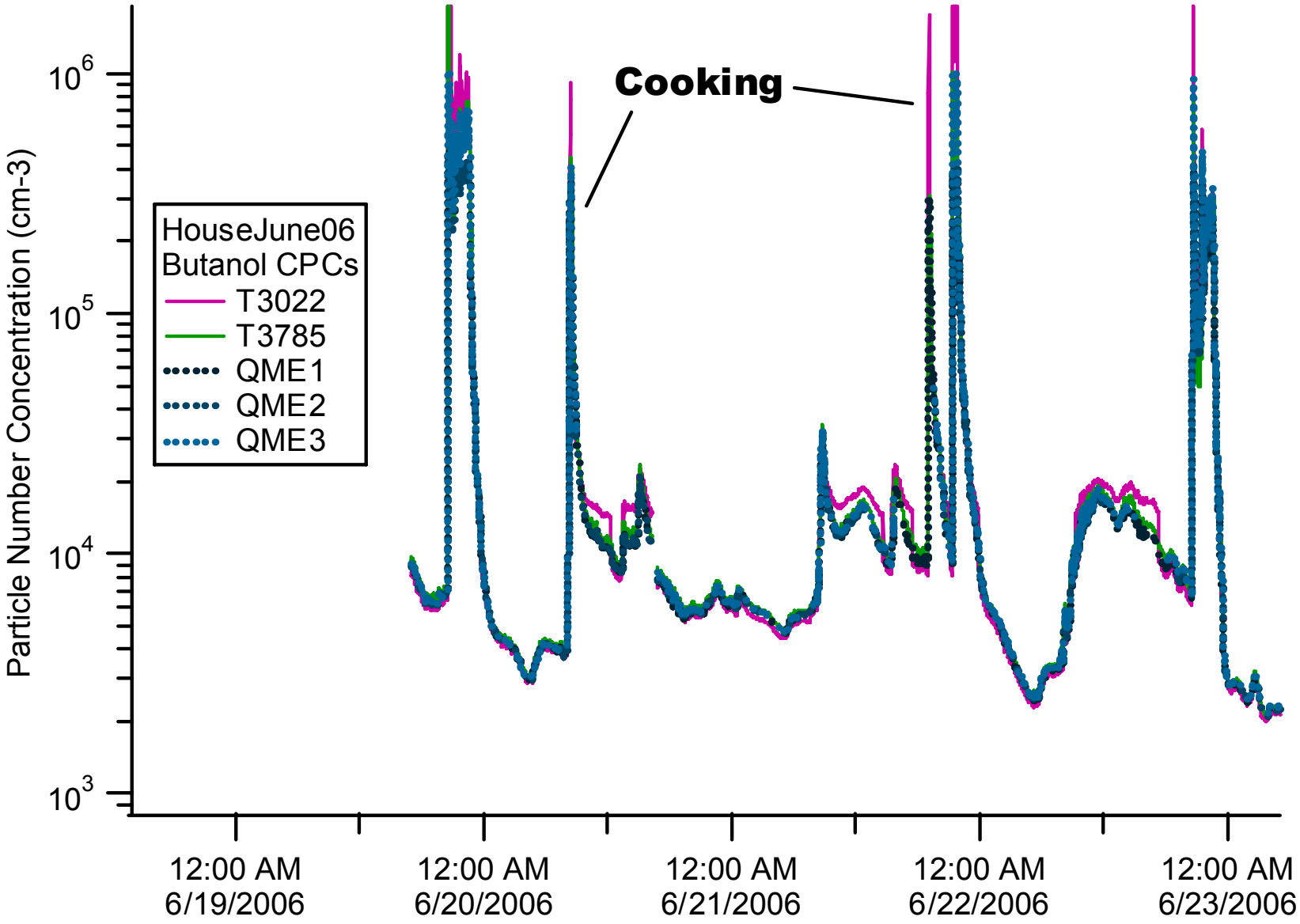
Berkeley, December 2005
QME2 vs T3022
Linear regression:
$y = (1.088 \pm 0.002) x + (1058 \pm 35)$
$R^2 = 0.94$



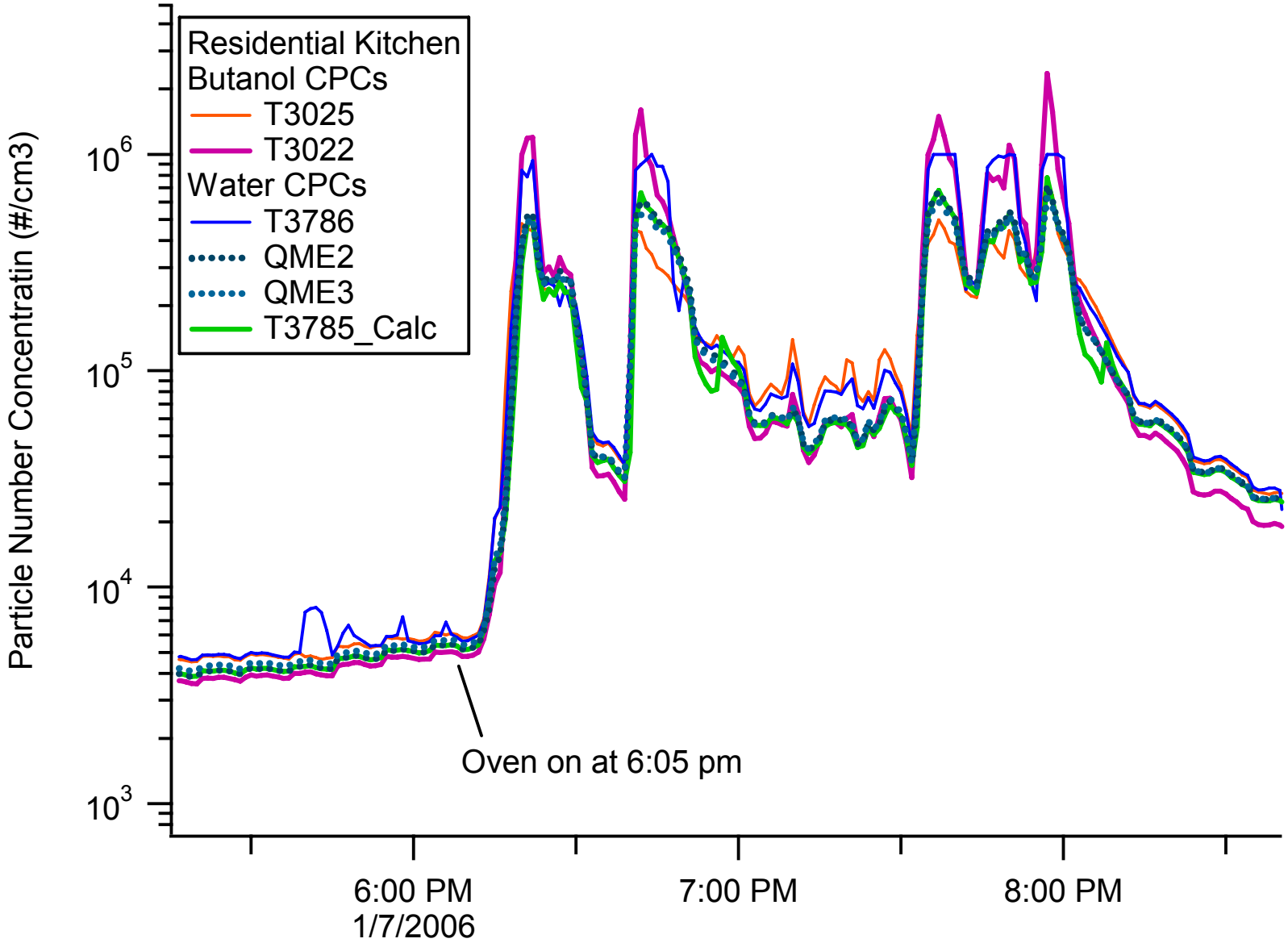
Comparison to the Standard WCPC





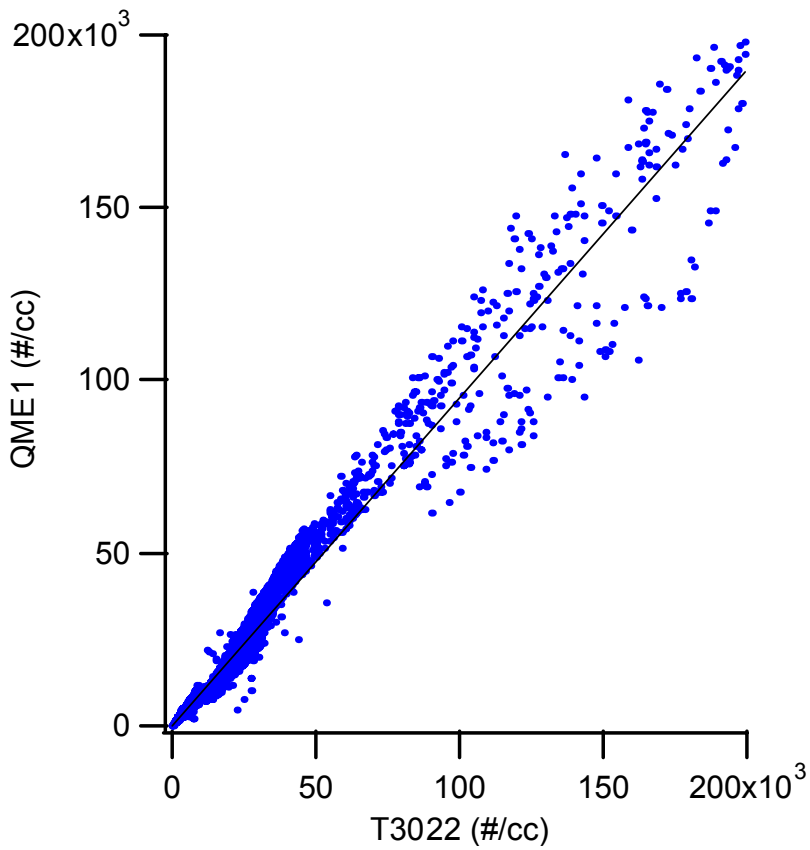

Cooking
HouseJune06
Butanol CPCs
T3022
T3785
QME1
QME2
QME3
Particle Number Concentration (cm-3)
10^6
10^5
10^4
10^3
12:00 AM 6/19/2006
12:00 AM 6/20/2006
12:00 AM 6/21/2006
12:00 AM 6/22/2006
12:00 AM 6/23/2006

ME-WCPC Measurements in a Residential Kitchen

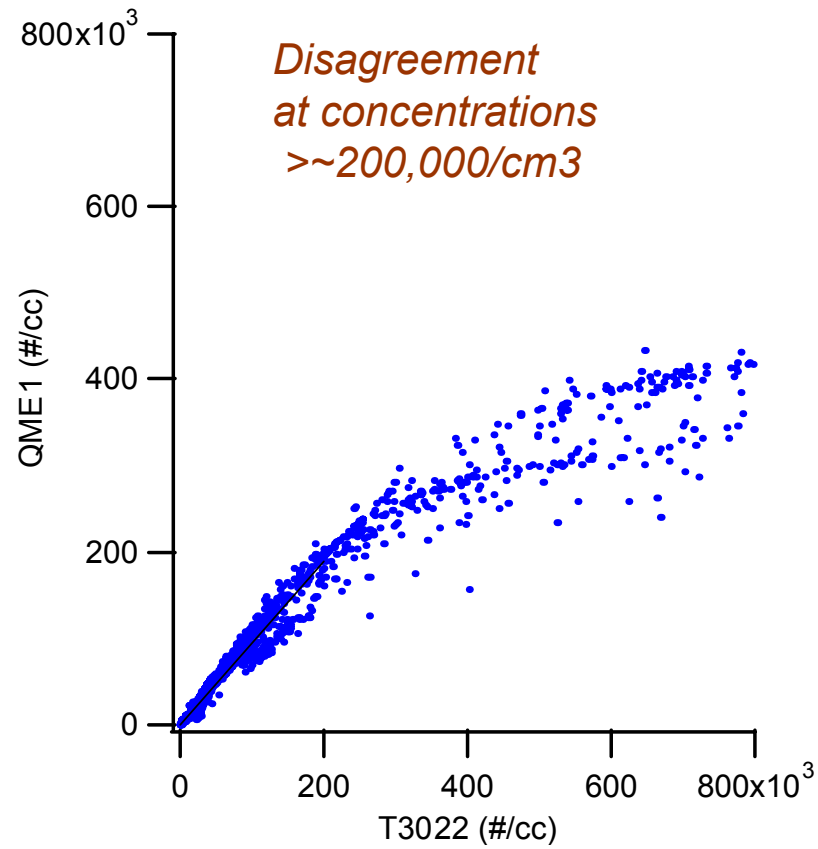


Comparison to the 'Photometric' Butanol CPC

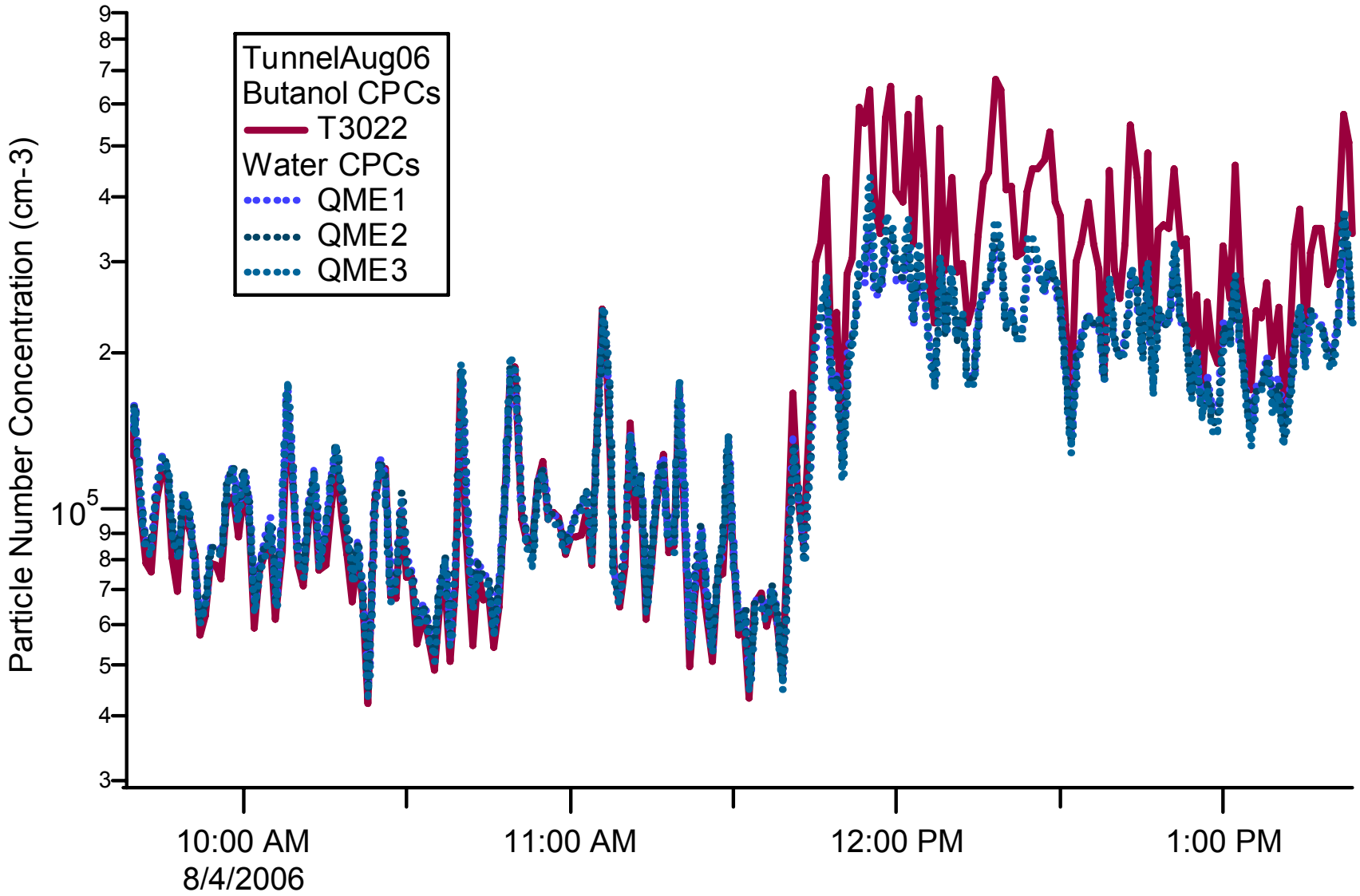
Indoors, June 2006
QME1 vs T3022
Linear regression:
$y = (0.948 \pm 0.001) x + (89 \pm 13)$
$R^2 = 0.97$



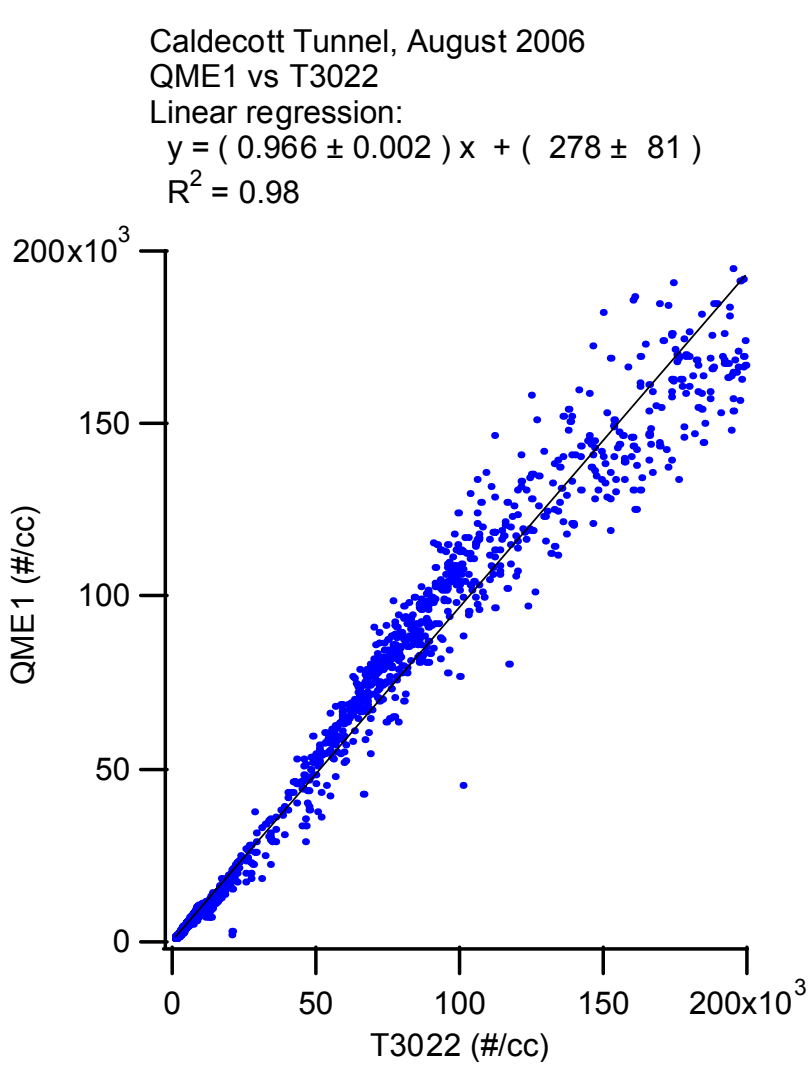
Indoors, June 2006
QME1 vs T3022
including high concentrations

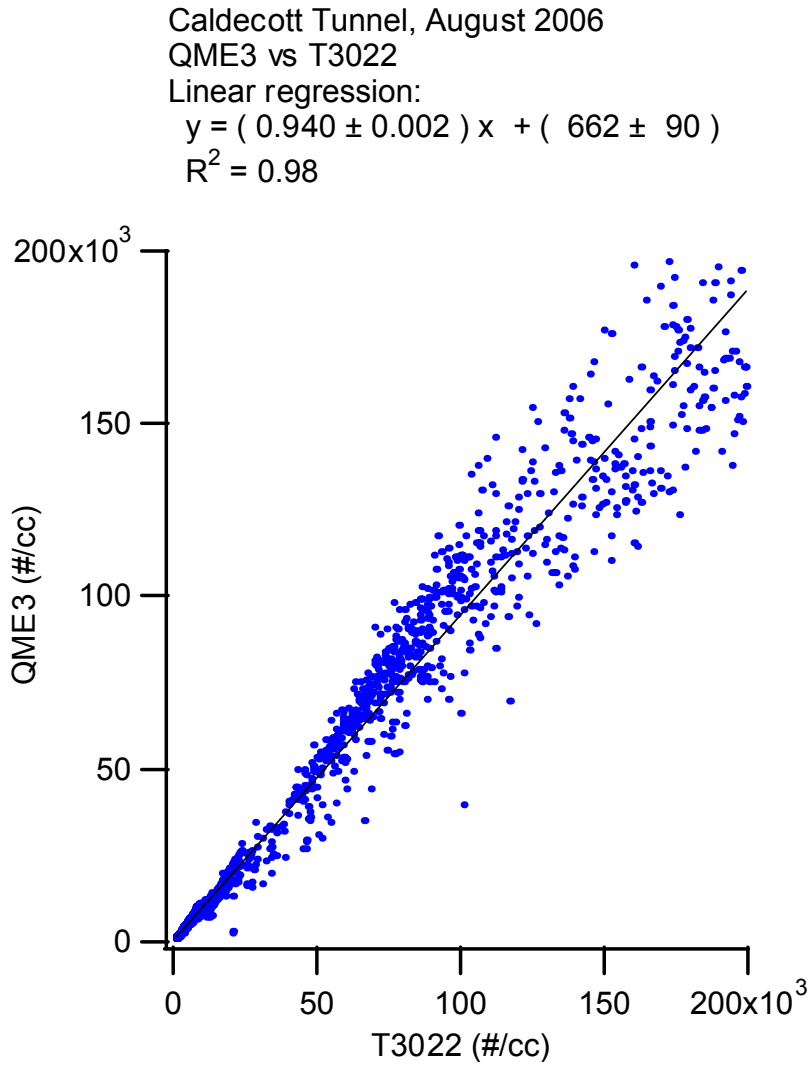


Caldecott Tunnel (Interstate 24)

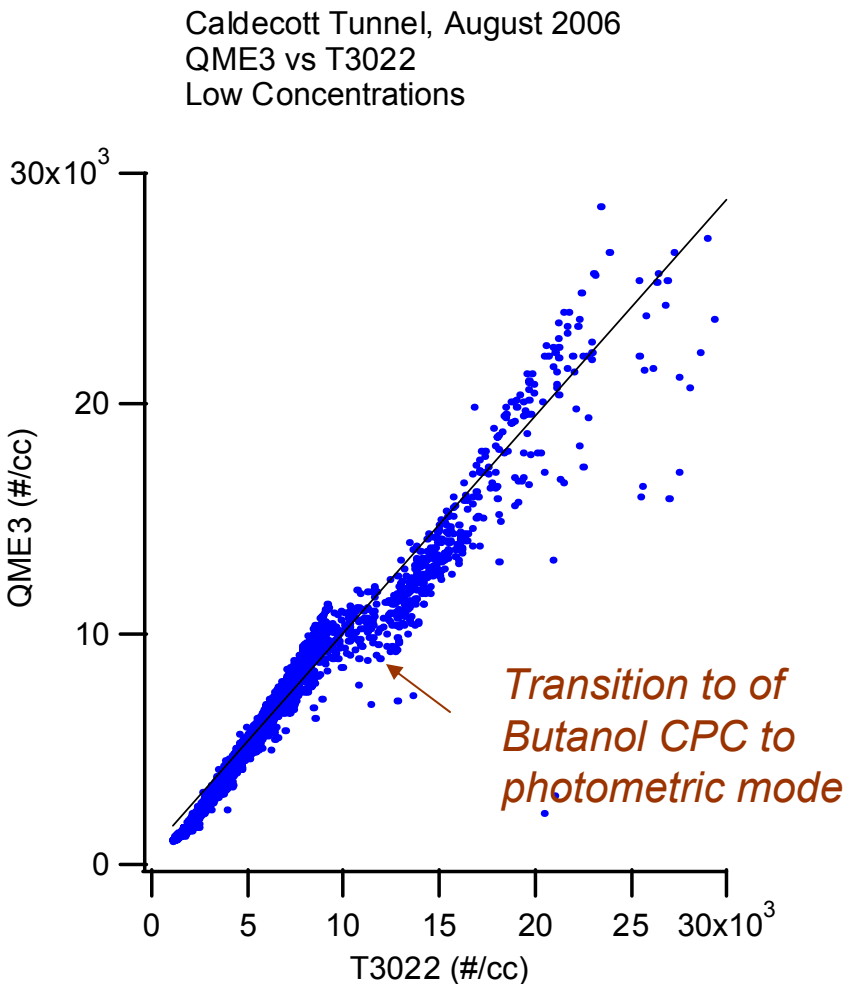


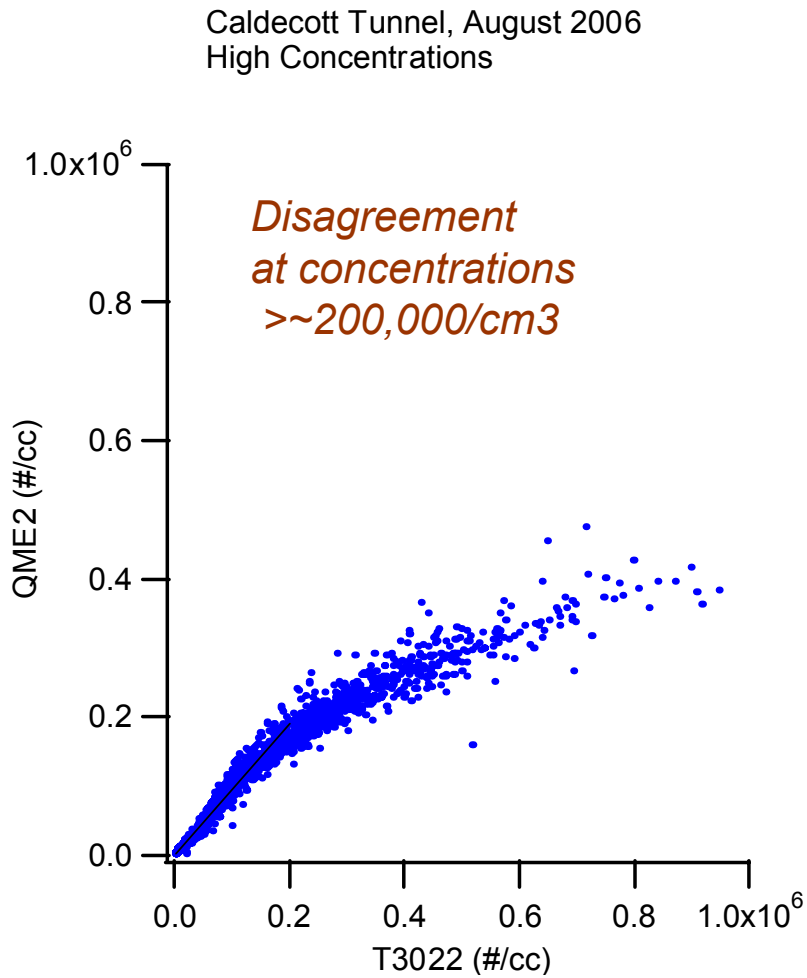
Comparison to the 'Photometric' Butanol CPC



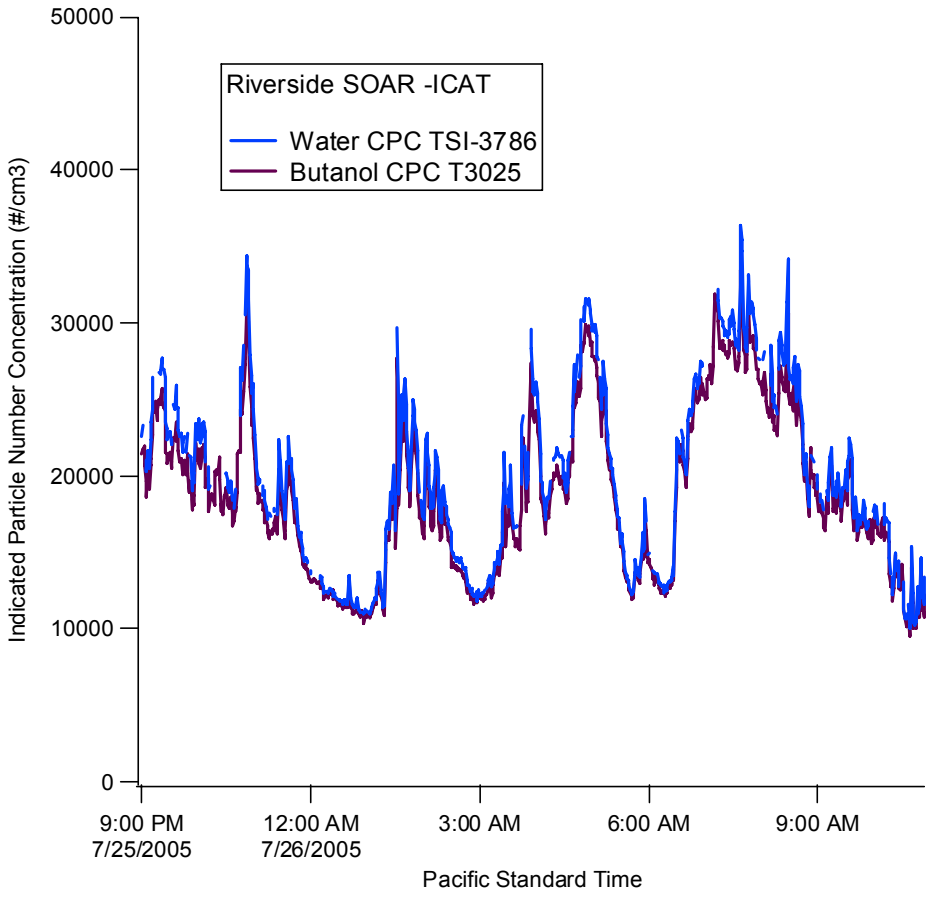


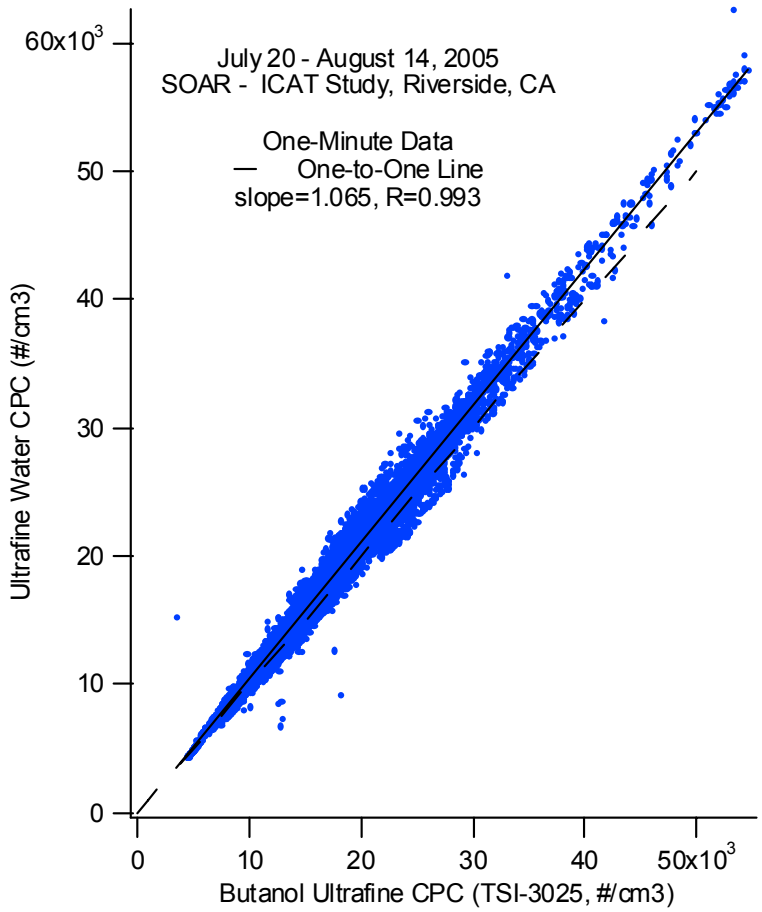
Comparison to the 'Photometric' Butanol CPC





Added Bonus: Field Comparisons of Ultrafine WCPC – 3786 & Butanol UCPC - 3025





Summary of Field Comparisons

Micro-Environmental Water Condensation Particle Counter

- **Collocated ME units:**
  - **R^2>0.97 slope : 0.9 - 1.1**

- **Comparison to "Photometric" Butanol CPC (TSI 3022) (for concentrations below ~150000cm^{-3})**
  - **R^2>0.94**
  - **slope: 0.90-1.08 with one at 0.77**

- **Comparison to Standard WCPC (3785)**
  - **R^2>0.93 slope: 0.87-1.10**

Advantages of WCPC

- No toxicity issues
- Lower cost of operation
- Comparable performance to Butanol Instruments below 150,000 to 200,000 particles/cm^3
- No loss of performance due to water uptake by wick
- Simplicity (one-piece saturator and growth tube)

Disadvantages

- Wet storage can lead to mold growth, poor flow stability
- (?) Efficiency more dependent on particle chemistry

Acknowledgements

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