ULTRAFINE PARTICLES

MEASUREMENT METHODOLOGIES AND ATMOSPHERIC DATA

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AQMD Meeting:
ULTRAFINE PARTICLES
The Science, Technology, and Policy Issues,
April 30, 2006
Summary:

- Why Are We Interested in Ultrafine PM

- Technologies for measuring their physical, chemical and toxicological properties

- What do we know (or do not) about their sources, and formation mechanisms in urban areas

- What do we know about the impact of new technologies in improving air quality
Why Are We Interested in Atmospheric Ultrafine PM

![Graph showing the distribution of fine, coarse, and ultrafine particles by diameter. The graph plots the number and volume of particles per unit volume as a function of diameter (micrometers). It highlights different modes and submodes, such as Nucleation Mode, Aitken Mode, Accumulation Mode, Condensation Submode, Droplet Submode, and Coarse Mode.]
Ultrafine particles have a much higher deposition fraction in the lower lung than accumulation mode PM.
Overview of our Work
Air Pollution, Particulate Matter and Health Effects

- 9 million drivers daily
- 500,000 diesel trucks
- 5th busiest airport in world
- biggest US harbor
• **Continuous Monitors** for:
  - Particle Size Distribution
  - Mass and Surface Area
  - Chemical Composition

• **Time Integrated Monitors** for:
  - Size Distribution
  - Mass
  - Chemical Composition

• **Particle Concentrator Technologies** for High Volume Collection for Toxicological In Vitro and In Vivo Studies

• **Personal Ultrafine** Particle Samplers
Condensation Particle Counter (TSI 3022)
Number Concentration Measurements
Scanning Mobility Particle Sizer (TSI 3936)

Smaller particles

Larger particles

CPC

**Cutpoint**

- Stage 2: 0.18 µm
- Stage 3: 0.10 µm
- Stage 4: 0.056 µm
- Stage 5: 0.032 µm
- Stage 6: 0.018 µm
- Stage 7: 0.010 µm
Electrical Low Pressure Impactor (Dekati Instruments)
Figure 1. RSMSIII design for the Pittsburgh and Baltimore Supersites.
Concentration Enrichment To Increase Sampling Efficiency of Ultrafine PM Samplers

Figure 1. USC Ultrafine Concentrator/Nano-MOUDI System

Ambient Air

Saturator With Immersion Heater @ 35°C

Cooler @ -8°C

Virtual Impactor

Diffusion Drier

MOUDI

Nano-MOUDI

Low Pressure Vacuum Pump
Averaged ambient and concentrated outdoor aerosol size distributions at USC. major flow = 30 lpm, minor flow: 1 lpm)

Median (nm): 52.4
Mean (nm) : 69.9
GSD : 2.2
Total Conc. (p/cm³)
8,689

Median (nm): 53.7
Mean (nm) : 67.2
GSD : 1.95
Total Conc. (p/cm³)
249,659

Geller et al, J Aerosol Science, 2005
Ambient and Concentration Enriched PM Size Distribution. Total flow=600 LPM; Minor Flow: 30 LPM

Concentrator – BioSampler Tandem

Grown Particles

220 LPM

Major flow

5 LPM

concentrated ambient particles

flow out

SKC Biosampler

Ultra pure Distilled Deionized Water

Particle Concentrator for Collection of Particles for in vitro tests
Near Continuous Ultrafine Mass Concentration Monitor
(Chakrabarti et al., *Aerosol Science and Technology*, 2002)

16.7 lpm

0.15 µm Impactor

BAM Monitor

![Graph showing collection efficiency vs. particle size](image-url)
Figure 2. BAM vs. MOUDI Ultrafine PM concentration

\[ y = 0.97x + 0.60 \]

\[ R^2 = 0.92 \]
Fractal-like combustion particles have a high surface area, hence electrical mobility, but a low density.
\[ \rho_e = \frac{1}{\chi} \frac{d_{ve}^2 C_{ve}}{d_{me}^2 C_{me}} \rho_{true} \]

**FIGURE 1.** Schematic diagram of DMA-APM set-up

where \( \rho_e \) is the effective density, \( \chi \) is dynamic shape factor, \( d_{ve} \) is the volume equivalent diameter, \( d_{me} \) is the mobility equivalent diameter, \( C \) is the Cunningham correction factor, and \( \rho_{true} \) is the bulk density of the material (McMurry et al., 2002).
Figure 7. Effective density variation with respect to particle mobility diameter at I-710. Data labels indicate percentage of number concentration measured for each particle size with respective effective density.
Table 4. Summary of average effective densities of different field locations and their fractal dimensions

<table>
<thead>
<tr>
<th>Mobility diameter (d_m, nm)</th>
<th>USC</th>
<th>710-freeway</th>
<th>110-freeway</th>
<th>Riverside</th>
<th>Coast</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.14 ± 0.1</td>
<td>1.13 ± 0.10</td>
<td>1.45 ± 0.12</td>
<td>1.40 ± 0.10</td>
<td>1.19 ± 0.10</td>
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<tr>
<td>118</td>
<td>1.12 ± 0.14</td>
<td>1.00 ± 0.12</td>
<td>1.17 ± 0.02</td>
<td>1.40 ± 0.06</td>
<td>1.14 ± 0.23</td>
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<tr>
<td>146</td>
<td>1.21 ± 0.08</td>
<td>0.94 ± 0.16</td>
<td>NA</td>
<td>1.29 ± 0.06</td>
<td>0.99 ± 0.10</td>
</tr>
<tr>
<td>202</td>
<td>1.14 ± 0.24</td>
<td>0.78 ± 0.26</td>
<td>0.99 ± 0.09</td>
<td>1.06 ± 0.09</td>
<td>1.06 ± 0.20</td>
</tr>
<tr>
<td>322</td>
<td>0.86 ± 0.11</td>
<td>0.49 ± 0.07</td>
<td>0.59 ± 0.27</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>414</td>
<td>0.73 ± 0.10</td>
<td>0.31 ± 0.02</td>
<td>0.58 ± 0.06</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

Fractal Dimension

| USC   | 2.79 ± 0.15 | 2.41 ± 0.22 | 2.54 ± 0.28 | 2.83 ± 0.06 | 2.92 ± 0.15 |
Measurement of Total Nanoparticle Surface Area Deposited in the Lung

TSI Diffusion Charger

Number of Charges per particle:

\[ N \sim d_p^{1.26} \]
Indoor data indicating effect of cooking
The ratio of the surface area monitor / total particle counts can also be used to provide very rapid estimate of the average particle size:

\[ D_p \sim (\text{NSAM} / \text{CPC})^{(1/1.26)} \]
High-Volume, Very Low Pressure Drop Impactor for Separation of Coarse-Fine-Ultrafine PM

High Volume Low Pressure Drop PM Collector

- Collects 500 LPM of Coarse, Fine and Ultrafine PM under a very low pressure drop

- Light weight, low powered and portable

- Allows high volume collection of size fractionated PM for chemical composition as well as in vitro toxicology studies

Figure 4. Evaluation of the USC High Volume Low Cutpoint Impactor with an Uncoated Quartz Substrate and Different Types of Test Aerosols

- Indoor Air
- Ammonium Nitrate
- Ammonium Sulfate
Ultrafine Organics – Vehicular Emissions

Sum of three predominant hopanes: 17a(H),21b(H)-hopane, 17a(H),21b(H)-29-norhopane, 22,29,30-trisnorneohopane

- Higher at USC (downtown) than Riverside (inland)
- Enriched in ultrafine mode at both locations
Personal Cascade Impactor

• Time integrated samples in 5 size ranges (2.5 - 10; 1-2.5; 0.5 –1.0; 0.2 - 0.5; and < 0.2 μm)

• Currently testing for combined ICP/MS and GC/MS on a single substrate, will provide enough data for source apportionment of personal exposure to PM of different sizes

Contribution of a Source with a Known Tracer, I, to personal exposures in the size range j

(j : <0.2, 0.2 - 0.5, 0.5 -1.0, 1 - 2.5, 2.5 - 10 µm)

\[ C_{ij} = \left[ \frac{X_{\text{pers, IJ}}}{X_{\text{outdoor, IJ}}} \right] \times PM_{\text{pers, IJ}} \]

- Amount of tracer I in size range J on personal sample
- Amount of tracer I in size range J on outdoor sample
- Amount of PM mass measured in size range J on personal sample
Average PM Species Measured in Children in 4 Sites of Long Beach - winter
Source and Receptor Areas in the Los Angeles Basin

A map showing the source and receptor areas in the Los Angeles Basin. The sources include Atascadero, Lompoc, Riverside, and USC D, while the receptors are at Boyles Height and Riverside. The map also highlights Upland and ML.
Figure 5. Monthly average PM chemical composition in the ultrafine mode.
The temperature data for Mira Loma was not available. The data plotted above was taken from the nearest available site Riverside firestation (around 10 kms east of Mira Loma).
Relative Particle Number, Mass, Black Carbon, CO Concentration, Vs. Downwind Distance from Freeway, but not by the same degree (Zhu et al., JAWMA 52:1032-1042, 2002)
Figure 3. Correlation between traffic density and measured total particle number concentration, corrected for wind velocity at 30 m downwind from the freeway.
Significant changes occur in size distribution of PM with distance from roadway.

Generally, number concentration decreases and particle size increases with distance (Zhu et al., 2002b)

I-710 (mostly diesel)
The decrease is more pronounced for the smallest particles.

**Figure 5.** Normalized particle number concentration for different size ranges as a function of distance to the 710 freeway.

EC concentrations are much higher in the diesel traffic freeway.
Major differences in PN between day vs. evening in winter suggest condensation or semi-volatile species as a major aerosol formation mechanism.

Kuhn et al., 2005, Atmos. Environ.
The Issue of PM Volatility and Why it is Important

• Exposure and Health Implications

• Exposure and dose of semi-volatile species may differ according to whether they are in the gas or particle phases.

• The semi-volatile component of these particles may likely be present in its gaseous phase or associated with smaller sizes in indoor environments.

• Finally, given that the majority of people’s exposure during commute will be dominated to these particles, it would be useful to know whether the non-volatile or semi-volatile material is more toxic.
Impacts on Effective Control Strategies

- Impact on new emissions control technologies that better protect the public health.

- This is because particle traps remove non-volatile soot particles but not always the precursors of the smaller semi-volatile particles.

- Also, the reduction of the larger, non-volatile particles from the exhaust may increase the formation-emission of the smaller, semi-volatile PM.

- Our recent studies at the Caldecott tunnel showed that while PM mass emitted by LDV and HDV decreased by 50-70% over the past 7 yrs in California, particle numbers increased by 2-3 fold. See:

  - *Geller, M.D., Sardar, S., Fine, P.M. and Sioutas, C. “Measurements of Particle Number and Mass Concentrations in a Roadway Tunnel Environment”. Environmental Science and Technology, in press*
PM$_{2.5}$ emissions have declined by 37% (LDV) and 60% (HDV) since 1997.

PN emissions have increased

- Factor of 5.4 for LDV
- Factor of 1.3 for HDV
- Generally low to moderate correlations between PN and gaseous co-pollutants as well as PM10
- Hourly associations > 24 hr associations
- (Sardar et al, JAWMA, 2004)
- Glendora and Upland are only 6 km apart
- Influence of morning traffic in Upland decreases Pearson coefficient, $r$, between PN in the two sites

Spatial Inhomogeneity of Ultrafine PM

Data in Glendora and Upland, 2002

a) No lag time
b) One hour lag time
c) Two hour lag time
d) Three hour lag time.

Dashed lines indicate the ideal 1:1 relationship
Freeways are not the only source of ultrafine particles!
CARB Study; Westerdahl et al., 2005
LAX Study Area

Sites
A—Upwind   B—500 Meters Downwind of North Runway   C—Downwind of Taxiway
D—Downwind of South Runway   E—800 Meters Downwind of South Runway
Particle Number Distribution

- Take off
- Taxiway
- 710 Freeway
- Landings (500m)
- Coastal Air

Diameter (nm)

Dn/dlogDp

1.0E+08
1.0E+07
1.0E+06
1.0E+05
1.0E+04
1.0E+03
1.0E+02
100
10
1
Particle Counts Near LAX and On Area Freeways

Counts/cm³

Location

Upwind Site A
Downwind Site B
Taxiway Area
Site C
Terminal
Freeway 105
Freeway 710
Figure 4. Diurnal trends of size-segregated particle number, O₃ and NOₓ at USC during (a) Dec 2002–Jan 2003 and (b) Sep 2003.

Figure 6. Diurnal trends of size-segregated particle number, O₃ and NOₓ at Riverside during (a) Nov 2002 and (b) Mar–Apr 2002.

Photochemical Secondary Formation of Ultrafine PM in LA

Sardar et al., ES&T, 2005
TABLE 4. Size Fractionated PN vs Gas Pollutants — Pearson Correlation Coefficients (r) at Source and Receptor Sites

<table>
<thead>
<tr>
<th>size range (nm)</th>
<th>CO</th>
<th>NOx</th>
<th>O3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fall Long Beach</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–32</td>
<td>-0.26</td>
<td>-0.03</td>
<td>0.26</td>
</tr>
<tr>
<td>32–56</td>
<td>0.20</td>
<td>0.31</td>
<td>-0.15</td>
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<tr>
<td>56–100</td>
<td>0.49</td>
<td>0.52</td>
<td>-0.38</td>
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<tr>
<td>100–180</td>
<td>0.66</td>
<td>0.66</td>
<td>-0.50</td>
</tr>
<tr>
<td>180–320</td>
<td>0.68</td>
<td>0.70</td>
<td>-0.47</td>
</tr>
<tr>
<td>320–1000</td>
<td>0.48</td>
<td>0.56</td>
<td>-0.30</td>
</tr>
<tr>
<td>Winter USC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–32</td>
<td>0.09</td>
<td>0.23</td>
<td>-0.03</td>
</tr>
<tr>
<td>32–56</td>
<td>0.38</td>
<td>0.54</td>
<td>-0.10</td>
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<tr>
<td>56–100</td>
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<td>0.78</td>
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<td>0.75</td>
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<tr>
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<td>0.53</td>
<td>0.45</td>
<td>0.01</td>
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<tr>
<td>Summer USC</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>0–32</td>
<td>0.25</td>
<td>0.28</td>
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<td>32–56</td>
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<td>32–56</td>
<td>0.67</td>
<td>0.84</td>
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<td>0.61</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Sardar et al., ES&T, 2005

- high correlation between ultrafine PM and tracers of traffic (CO, NOx) in winter
- high correlation between ultrafine PM and O₃ in summer
Future Research in Southern California

Renewed Southern California Particle Center, funded by US EPA:

- Determine the physical and chemical properties of ultrafine PM (UFP) from real-world sources, including secondary formation, to evaluate how exposure to UFP vary with respect to:
  - location, season, and particle size,
  - assess their relative toxicity.

- Assess the contributions of these outdoor sources to indoor exposure and toxicity.

- Determine the physical, chemical and toxicological characteristics of the volatile and non-volatile UFP components that originate from mobile sources.