Ultrafine Particles

Ultrafine Particles
   Smaller than 0.1 um [100 nm]

Nanoparticles
   Smaller than 0.01 um [10nm]

Formation
The finest particles are produced by gas to particle conversions and form the nuclei or nanoparticles. Larger supermicron particles are produced from inorganic material as is referred to as ash PM. Submicrometer particles dominate the number count of particles emitted by combustion.

Fine Particle Formation

Organic Particles
Condensation and/or nucleation of organic vapors

Inorganic Particles
Condensation of alkali chlorides

Nucleation and condensation of alkali sulfates and Zinc

Oxidation and sulfation (K, Na, S, Cl, Zn)

Vaporization

Coagulation and condensation

Surface growth and coagulation

Formation of primary soot particles

Formation of core particles

Formation of Soot nuclei

PAH formation and polymerization

Oxidation and burn out

Agglomeration

Soot

Fine Particles (soot, alkali salts, organic matter)

Fuel

Tissari et al. 2008
Benefits and Costs of Federal Regulations in US

- Largest estimated benefits of ALL Federal Regulations attributable to the reduction in public exposure to a single air pollutant: *fine particulate matter*.

- Clean Air Fine Particulate Implementation
  - Benefits ($ Millions/year)
    - $19,000 to $167,000
  - Costs ($ Millions/year)
    - $7,000
Regulations Are Ineffective

- Regulations and Permits set thresholds/permits to pollute at total mass/year
- The risk, however, is determined by the number of particles not the mass
  - Biomass combustion produces a higher number of particles emitted than any other fuel, including coal as currently permitted
The Lessons

• Total number matters more than mass of PM emitted
• Until the permitting process sets limits based on number of particles emitted the population will continue to be at increased risk
Health Effects

• Changes in particulate levels in air pollution over the last two decades account for as much as 17% of the change in life expectancy over this period.
  – Barath, S, et.al., Particle and Fibre Toxicology 7:19, 2010; Pope, CA, et.al., Fine particulate air pollution and life expectancy in the United States, NEJM 360:376, 2009.
Measurement results

• Mass measurements do not correlate with the toxicologic mechanisms

• Dilutional mechanisms effect number counting and are not standardized

• Compliance monitoring such as 2-4 hr steady state stack tests of a boiler cannot measure the transients.

• A major question for biomass combustion is that a decrease in mass emissions is accompanied by an increase in the numbers of smaller particles.
Particle Number and Particle Surface Area per 10μg/m³ Airborne Particles

<table>
<thead>
<tr>
<th>Particle Diameter (nm)</th>
<th>Particle Number (cm⁻³)</th>
<th>Particle Surface Area (μm²/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>153,000,000</td>
<td>12,000</td>
</tr>
<tr>
<td>20</td>
<td>2,400,000</td>
<td>3,016</td>
</tr>
<tr>
<td>250</td>
<td>1,200</td>
<td>240</td>
</tr>
<tr>
<td>5,000</td>
<td>0.15</td>
<td>12</td>
</tr>
</tbody>
</table>

http://www.npl.co.uk/upload/pdf/20100608_mansa_maynard_3.pdf
Particle number compared to the size

- Said another way, one particle at 5 um diameter weighs the same as 1,200,000 particles at 0.1 um.

Lighty, JS, et. al., Combustion Aerosols: Factors Governing Their Size and Composition, J Air Waste Management, 50:1565, Morawska, et.al.,
Exposure to Ultrafine Particles

• Ultrafine particles [<0.1 um] are ubiquitous in both indoor and outdoor environments, and present in very low concentrations in mass, they constitute a major portion of PM in number and surface area.
  – Kim, CS & Jaques, PA, Total lung deposition of ultrafine particles in elderly subjects during controlled breathing, Inhalation Toxicology 17:387, 2005. Authors are scientists at the National Health and Environmental Effects research Laboratory, USEPA
Ultrafine Particle Number Size Distribution

http://www.uvm.edu/~cfcm/symposium/PDFs/Chandrasekaran.pdf

Steady-state
Ultrafine Particle Number Size Distribution

Start-up & Shut-down

Electrical Mobility Diameter [nm]
Multiplication factor

- Numbers presented above are per cubic cm.
  - Chandrasekaran above was 1,000,000,000/cm³ for a very small boiler
- To determine per cubic meter of air multiply by 100X100X100
  - 1,000,000,000,000,000 particles/m³
- Typical 50 MW biomass combustion plant has a stack flow of 13-15 m³/sec
  - 13,000,000,000,000,000 particles/sec
  - 11,232,000,000,000,000,000,000,000 particles/day
Fine Particle Deposition in Human Respiratory Tract

• The total amount of particles deposited in the respiratory tract is of interest rather than the deposited fraction.
  – Varying with exposure time, breathing volume some individuals receive a substantially higher dose than others

• Increased alveolar deposition at rest and primarily less than 0.5 um.
Lung deposition

• Fewer than 1 in 1000 alveoli has a coarse particle deposited per day, but a typical alveolus may be exposed to several hundred ultrafine particles per day.

• Most of the PM 10 mass is deposited in the nose and throat, while 60% of the inhaled PM 0.1 is deposited in the lung, with actual size-dependent deposition varying with age, health, tidal volume, and degree of oral vs. nasal breathing.
Lung deposition

- Notice the fraction of deposition for smallest particles
  - Also there is no effect of the particles agglomeration state on the particle size-dependent deposition fraction

Life Expectancy vs PM\textsubscript{2.5} 1980-2000

Pope, Ezzati, Dockery. NEJM 2009; 360:376
Life Expectancy vs PM$_{2.5}$
1980-2000

Pope, Ezzati, Dockery (NEJM 2009)
Life Expectancy vs PM$_{2.5}$
1980-2000

EPA required to periodically review NAAQS

Health benefits below current NAAQS

Pope, Ezzati, Dockery (NEJM 2009)
Influence of Particle Size on Particle Number and Surface Area for a Given Particle Mass

<table>
<thead>
<tr>
<th>PARTICLE DIAMETER</th>
<th>RELATIVE NUMBER OF PARTICLES</th>
<th>RELATIVE SURFACE AREA</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 µm</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1 µm</td>
<td>$10^3$</td>
<td>$10^2$</td>
</tr>
<tr>
<td>0.1 µm</td>
<td>$10^6$</td>
<td>$10^4$</td>
</tr>
<tr>
<td>0.01 µm</td>
<td>$10^9$</td>
<td>$10^6$</td>
</tr>
</tbody>
</table>
Particle characteristics

Particle Number, Surface Area and Mass

Measuring:

- Particle number reflects particles < 100 nanometres primarily
- Particle surface area reflects mainly particles of 50-1000 nm
- Particle mass reflects particles of > 100 nanometres (usually to 2.5 μm or 10 μm)
While “traditional” PM measurements put the weight on large particles, PN measurements shift this weight to ultrafine particles (or nanoparticles).

Measure number not mass

http://www.npl.co.uk/upload/pdf/20100608_mansa_horn.pdf
Particle number increases with increasing boiler load

• The total particle number concentration increased and the particle size decreased as the boiler load increased.
  – Combustion of forest residues results in a larger fine particle fraction

• The major portion of the particle mass in biomass combustion is in the submicrometer range [\(<1.0\,\mu\text{m or } 100\text{nm}\)] while in coal combustion the coarse fraction dominates particle mass.
Collection efficiency of the ESP over the full range of measured particle size ($0.01 < d_a < 10 \mu m$) at different boiler loads.
Electrostatic Precipitator feasibility

(Laing et al, 2010)
ESP Efficiency

- However, field measurements have shown that there is a “penetration window” in the sub-micrometer size range where the collection efficiency can be as low as 70-80%.
- Very low collection efficiency of about 0.5 in the 0.3-0.6 um size range. At <0.8 um the ESP showed an efficiency of 82.6% when used with a condenser and 95.6% at 0.8 um<d<6 um. The flue gas condenser had no effect on fine particle concentration.
- The vast majority of particles deposited in the respiratory tract are deposited in the pulmonary region, with measurements showing more deposition during diesel idling that running, contrary to the model.
- The result is the removal efficiency of particles from air is least efficient in a size range from 0.1-1.0 um. Particles in the 0.1-0.3 um range have the highest penetration through APCD, so the 0.1-1.0 um particles form a larger fraction of the total mass distribution leaving the APCD than they do in the uncontrolled emissions.
Fine particle numbers

• The average fine particle number concentration was $4.4-5.5 \times 100,000,000$ particles cm$^{-3}$. Coarse particle concentration was $3.6-10.5 \times 10^3$ cm$^{-3}$—a difference of 10000 fold.
• The total concentration of emitted particles [CFB] was $5.7-6.3 \times 100,000,000$ at 50% and 100% load with a size range of 15-200nm.
  – Rissler, J, et. al., Hygroscopic behavior of aerosols emitted from biomass fired grate boilers, Aerosol Sci and Technol 33:919, 2005
• A dominating fine mode [PM1 > 90% of PM 10] by mass, with more than 80% of the particles having a diameter <$1.0$ nm.
Particle numbers with ESP

- 11,232,000,000,000,000,000 particles per day
- ESP Efficiency of 90% which is too high
  - 1,123,200,000,000,000,000 particles per day with ESP
DANGER

• The latest draft of the US EPA Air Quality Criteria for Particulate Matter has confirmed the presence of an apparent linear dose-response relationship between PM and adverse events. 
  http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=58003 and multiple other references

• Data from all North American studies demonstrate that this curve is **without a discernible threshold below which PM concentrations pose no health risk to the general population.**
  http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=58003,
  http://circ.ahajournals.org/cgi/content/full/109/21/2655
Underestimated Risk

• It is the opinion of the writing group that the overall evidence is consistent with a causal relationship between PM$_{2.5}$ exposure and cardiovascular morbidity and mortality. *This body of evidence has grown and has been strengthened substantially since publication of the first AHA scientific statement.* At present, no credible alternative explanation exists. These conclusions of our independent review are broadly similar to those found in the EPA’s Integrated Science Assessment for Particulate Matter final report (http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=216546). P 117
DANGER

The current permitting process is inadequate

- The most dangerous particulates [those less than 2.5 microns in size] are not specifically regulated or accounted for in the permitting process—so permits are not “protective of human health”.

- “Although the dangers to 1 individual at any single time point may be small, the public health burden derived from this ubiquitous risk is enormous. Short-term increases in PM$_{2.5}$ levels lead to the early mortality of tens of thousands of individuals per year in the United States alone.”

http://circ.ahajournals.org/cgi/content/full/109/21/2655 p 116.
The Oxidative Stress Hypothesis

Particles
Antioxidant defences
Oxidative stress

Respiratory Tract Lining fluid
Ascorbate, urate and glutathione

Lung cells
Macrophages, epithelial cells

Inflammation
IL-6, IL-8, ArA

Systemic Effects
Myocytes, Endothelium

Reactive Oxygen Species

Kelly FJ, Occupational Environmental Health 60: 612-616; 2003
Toxicologic mechanisms of ultrafine particles

• Oxidative potential is one mechanism by which ultrafine particles exert their effect. Others include:
  – Toxic heavy metals associated with the particles
  – Surface area of the particle

• These mechanisms are dependent on
  – Small size allowing the particles to penetrate cell membranes [including the placenta and blood-brain barrier] and intercellular spaces
  – Easy access to systemic circulation by high potential to deposit in the alveolar region in direct proximity to the vascular system
Examples of direct health effects

• Lower birth weight and increased incidence of premature delivery
  – http://ehp03.niehs.nih.gov/article/fetchArticle.action?articleURI=info%3Adoi%2F10.1289%2Fehp.117-a505a

• Increased incidence of asthma by 300%

• Decreased lung function by 20% [similar to tobacco exposure]
Future danger

• The regulatory timetable is driving the need for parallel advances in both health and engineering related research.

• “There is no network of ultrafine particle samplers.. and no consideration of a distinct PM standard for ultrafine particles.
  – P 104-105 of new proposed PM 2.5 regulations [EPA-HQ-OAR-2007-0492; FRL 9682-9; http://www.epa.gov/pm/2012/proposal.pdf]

• There is sufficient data, especially for children and the elderly to move forward to set acceptable thresholds — by number -- for ultrafine and nano PM emissions, especially given the history of the just released PM 2.5 revision which has been in process since 1997.