Ultrafine Particles

Ultrafine Particles

Smaller than 0.1 um [100 nm]

Nanoparticles

Smaller than 0.01 um [10nm]

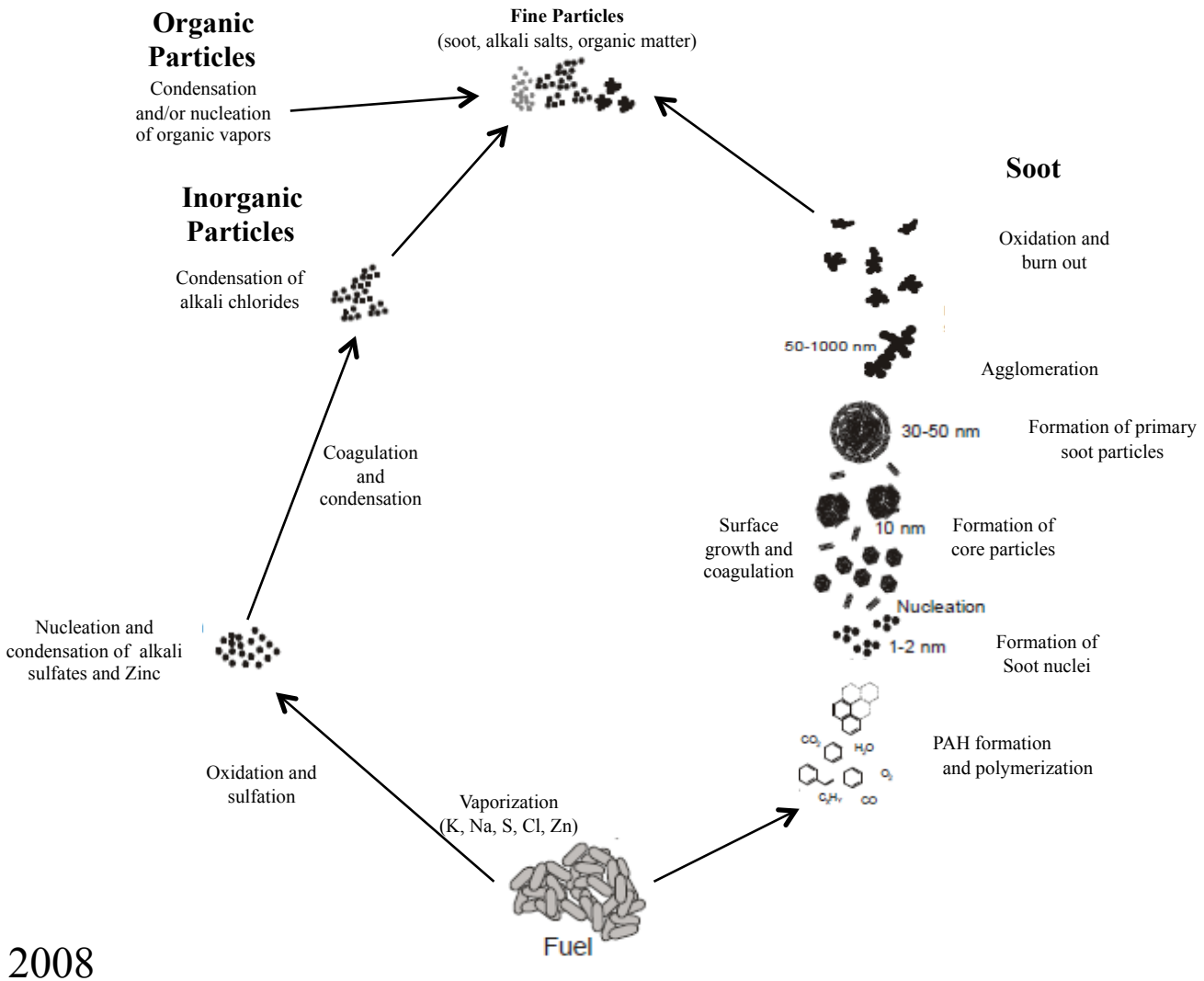
Formation

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.

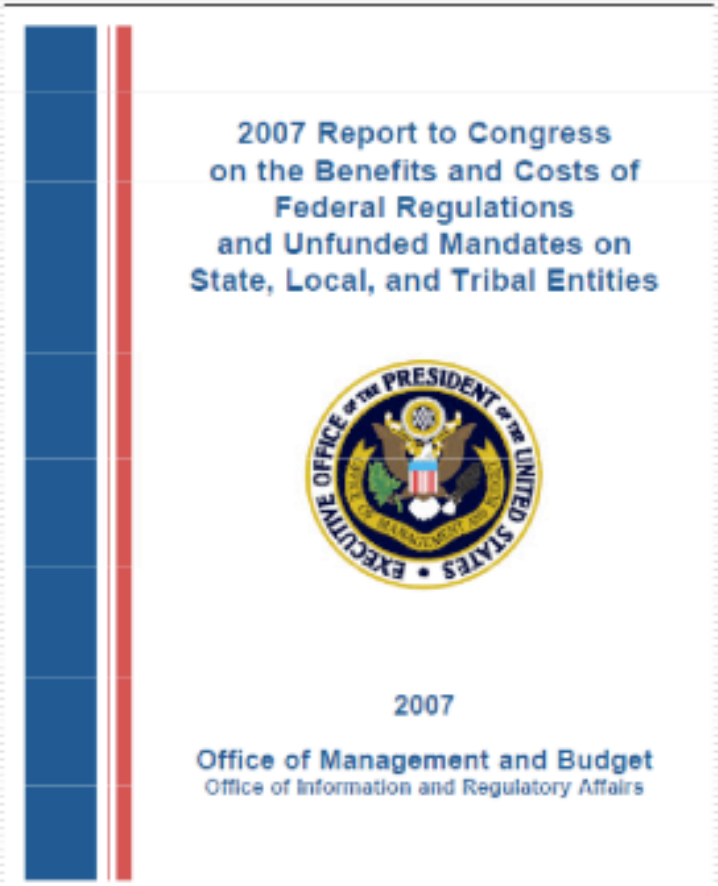
Lighty, JS, et. al., Combustion Aerosols: Factors Governing Their Size and Composition, J Air Waste Management, 50:1565.

Fine Particle Formation



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

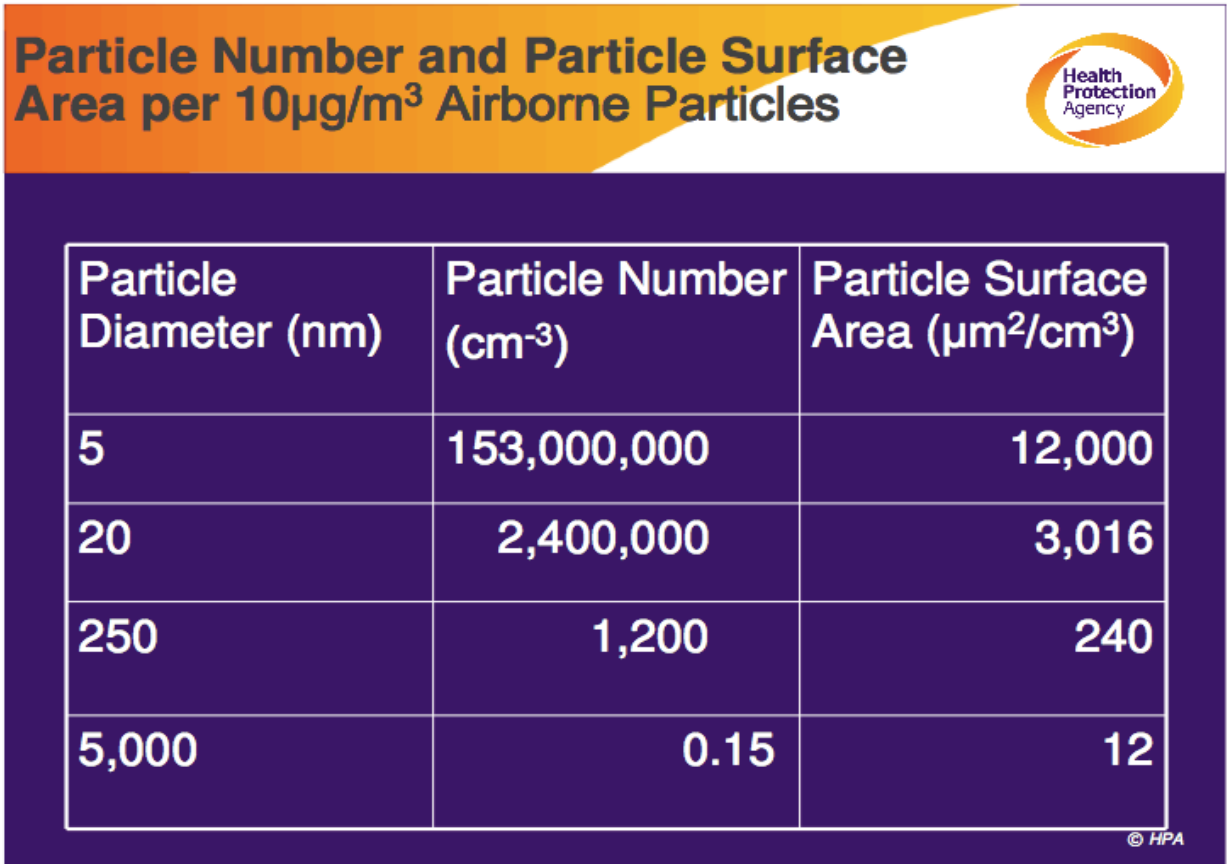
Health Effects

- 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
  - Geophys Res Lett. 26:2403, 1999; Abdul-Khalek, I, et.al. The Influence of Dilutional Conditions on Particle Size Measurement, Society of Automotive Engineers 1999-01-0142.
- Compliance monitoring such as 2-4 hr steady state stack tests of a boiler cannot measure the transients.
  - Lighty, JS, et. al., Combustion Aerosols: Factors Governing Their Size and Composition, J Air Waste Management, 50:1565
- A major question for biomass combustion is that a decrease in mass emissions is accompanied by an increase in the numbers of smaller particles.
  - Lighty, JS, et. al., Combustion Aerosols: Factors Governing Their Size and Composition, J Air Waste Management, 50:1565

Particle Number and Particle Surface



Particle Number and Particle Surface Area per 10µg/m³ Airborne Particles

Health Protection Agency

Particle Diameter (nm)	Particle Number (cm^{-3})	Particle Surface Area ($\mu m^2/cm^3$)
5	153,000,000	12,000
20	2,400,000	3,016
250	1,200	240
5,000	0.15	12

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.

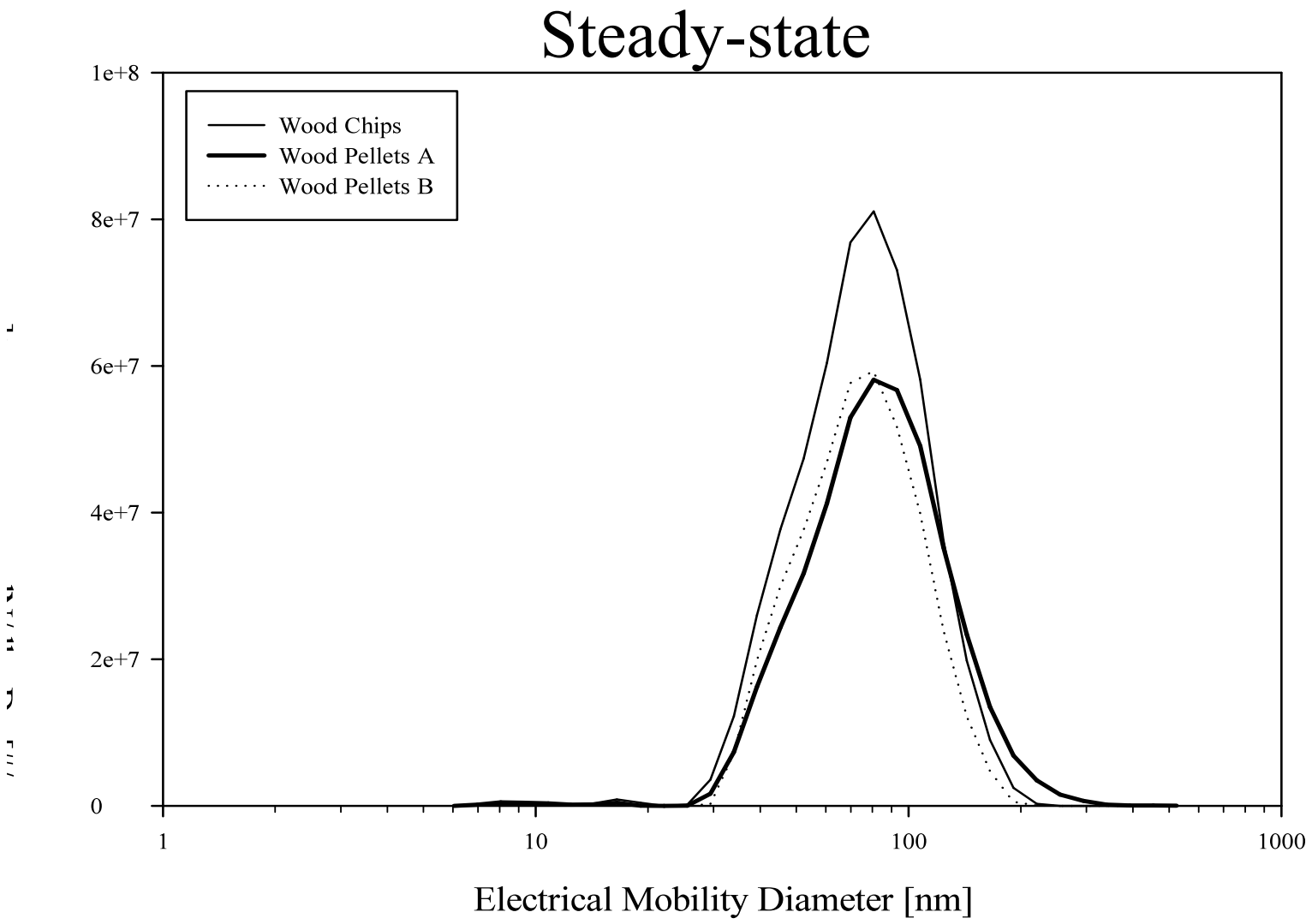
Lighty, JS, et. al., Combustion Aerosols: Factors Governing Their Size and Composition, J Air Waste Management, 50:1565, Morawska, et.al.,

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
  - Hoffman, W, Modeling inhaled particle deposition in the human lung, J Aerosol Science, 42:693, 2011.

Ultrafine Particle Number Size Distribution

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



Ultrafine Particle Number Size Distribution

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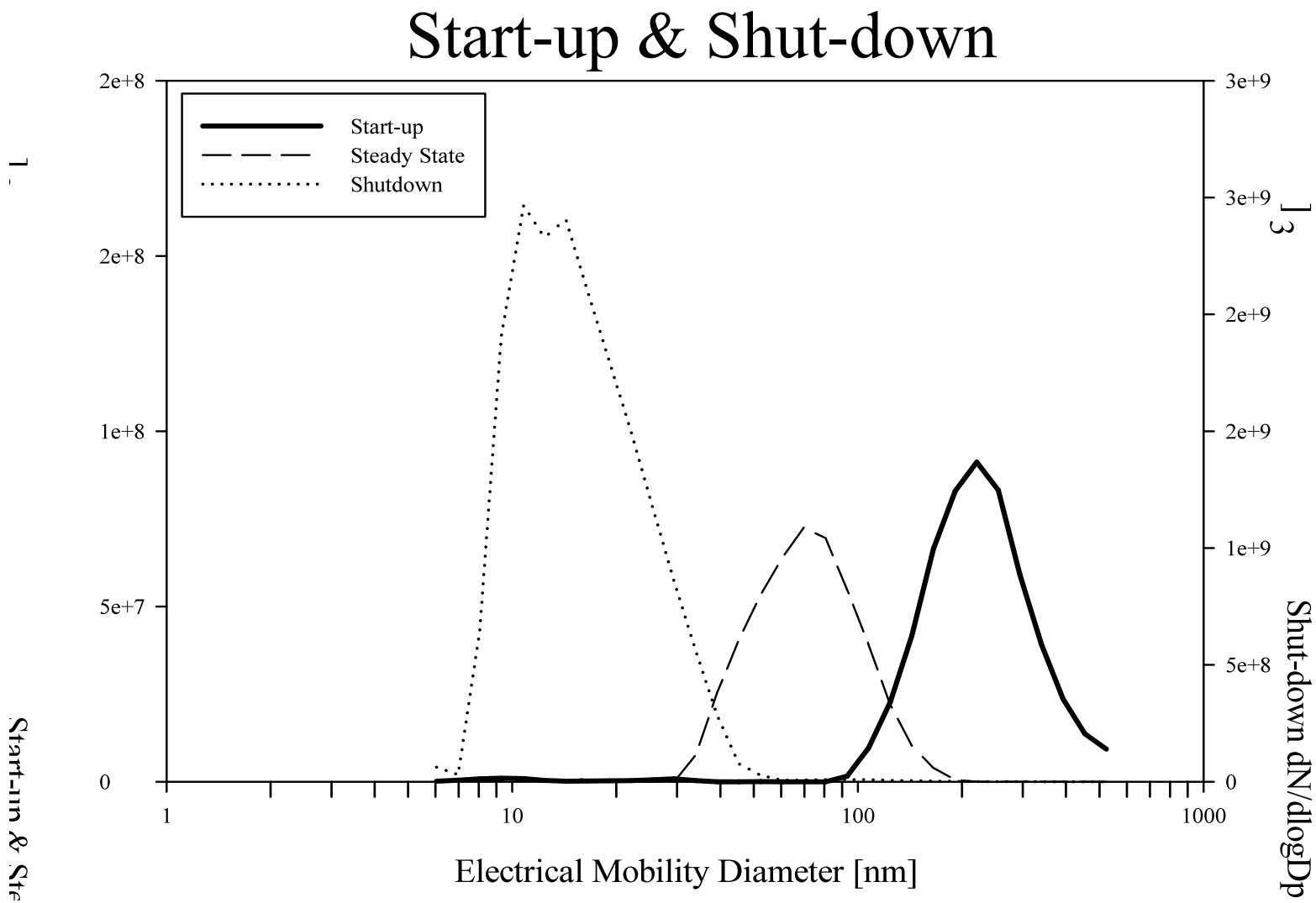
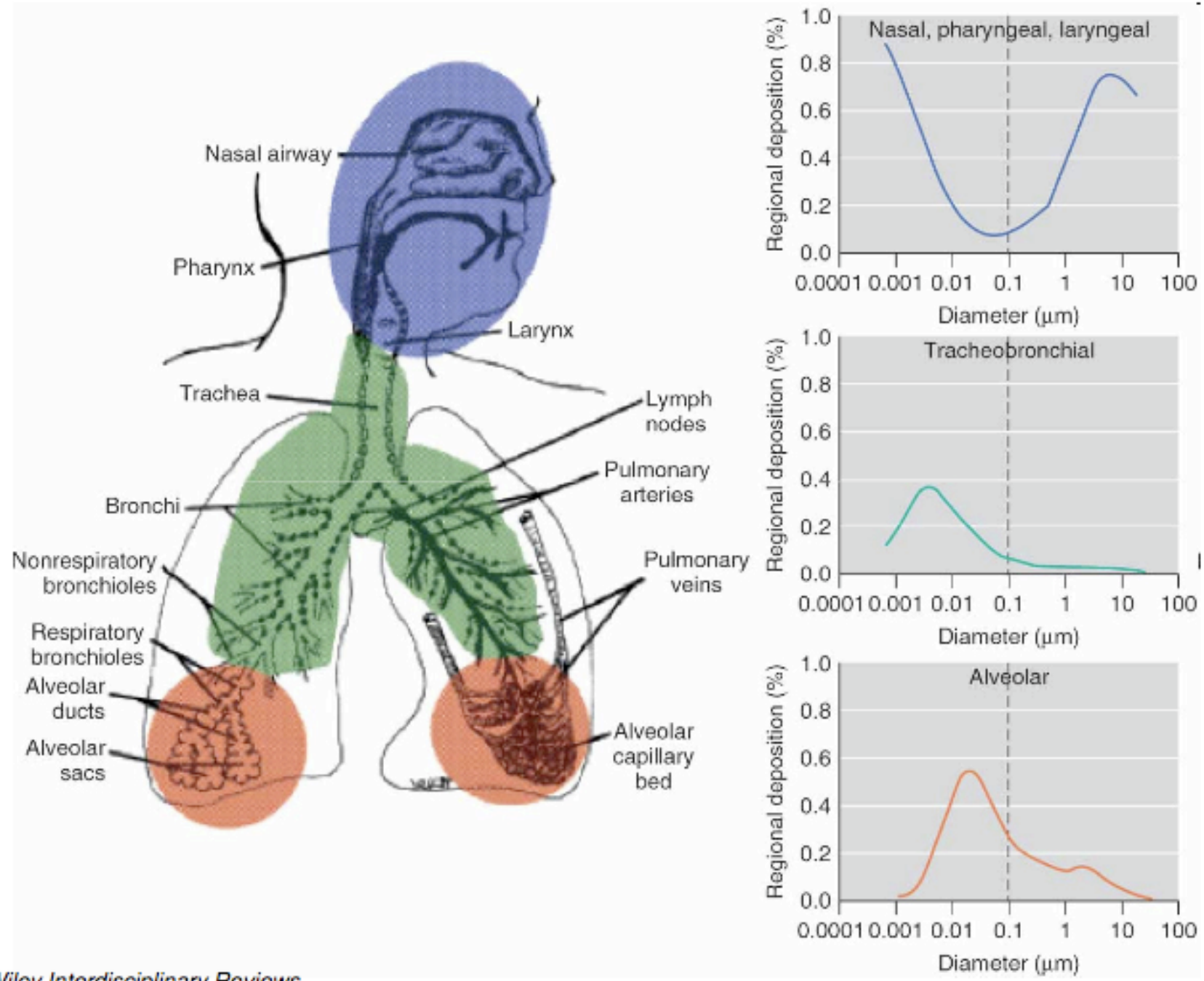


Multiplication factor

- 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 particles/day



Wiley Interdisciplinary Reviews

Fine Particle Deposition in Human Respiratory Tract

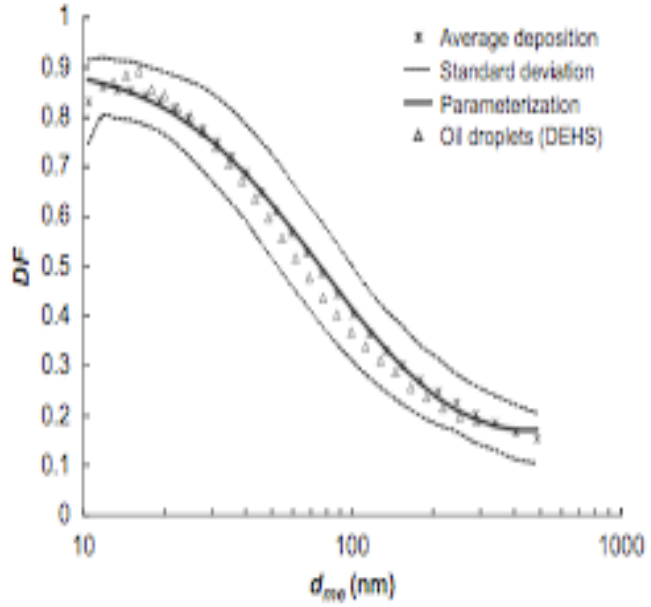
- The total amount of particles deposited in the respiratory tract is of interest rather than the deposited fraction.
  - Varying with exposure time, breathing volume some individuals receive a substantially higher dose than others
    - Londahl, J, et.al., Deposition of biomass combustion aerosol particles in the human respiratory tract, Inhalation Toxicology, 20:923, 2008.
- Increased alveolar deposition at rest and primarily less than 0.5 um.
    - Broday, D, Deposition of fractal-like soot aggregates in the respiratory tract, J Aerosol Sci 42:372, 2011.

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.
  - Lighty, JS, et. al., Combustion Aerosols: Factors Governing Their Size and Composition, J Air Waste Management, 50:1565.
- 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.
  - Lennon, S, et.al. Experiments on Particle Deposition in the Human Resp Tract, J Aerosol Sci, 28:464, 1998; Lighty, JS, et. al., Combustion Aerosols: Factors Governing Their Size and Composition, J Air Waste Management, 50:1565.

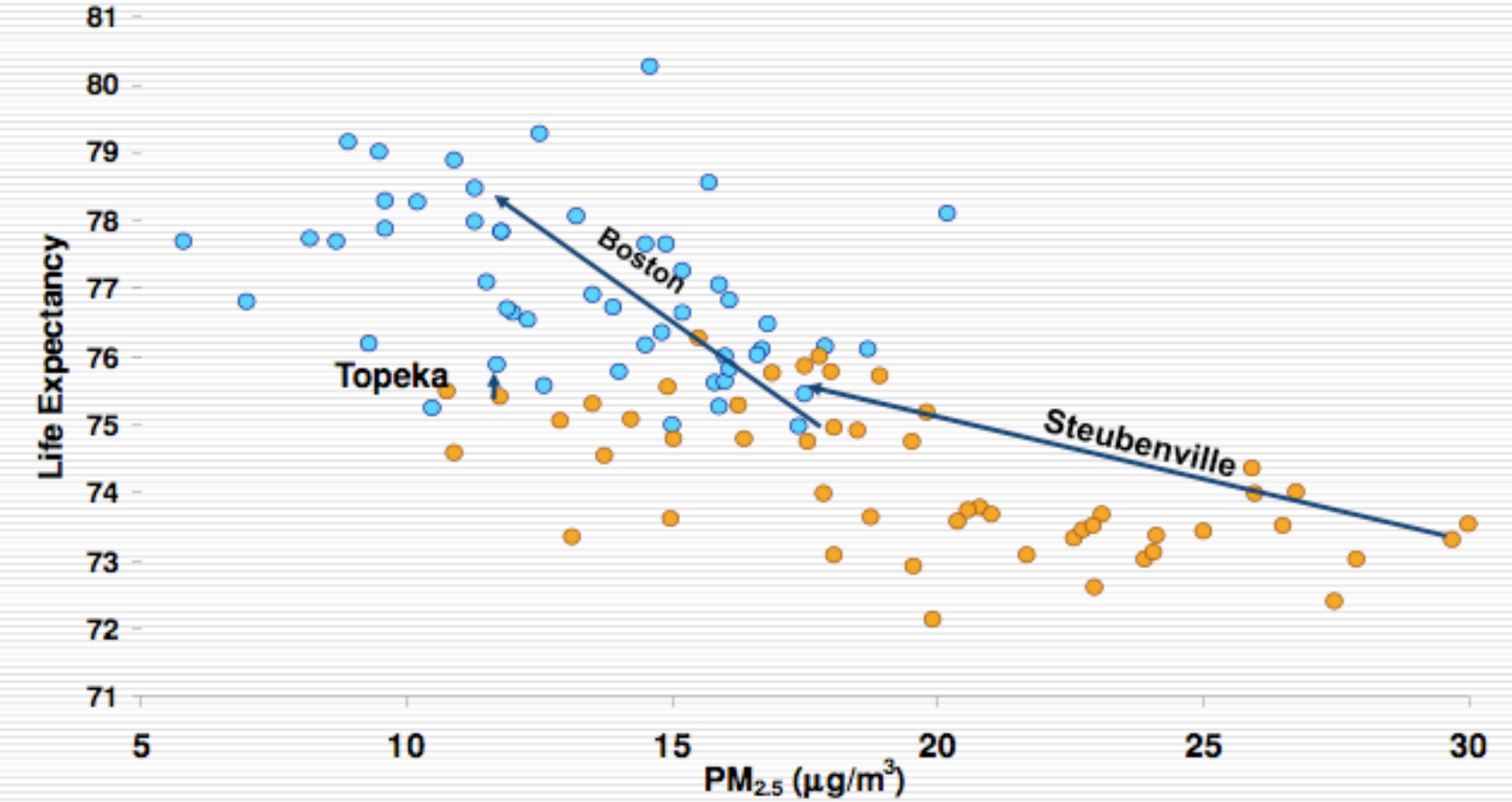
Lung deposition

- 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



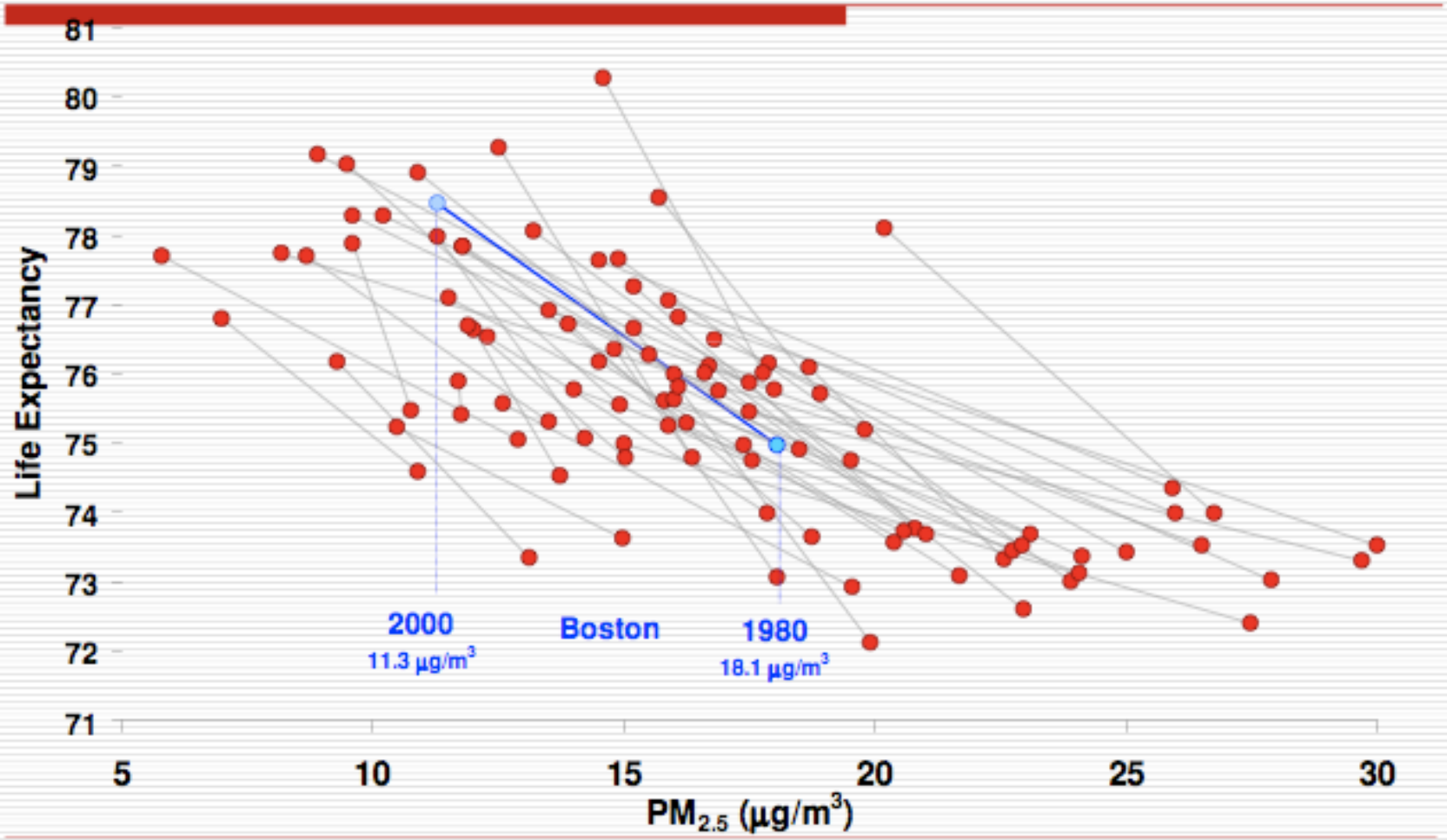
Rissler, J, et. al. Lung deposition of particulate matter. J Aerosol Science 48:18-33, 2012

Life Expectancy vs $PM_{2.5}$ 1980-2000



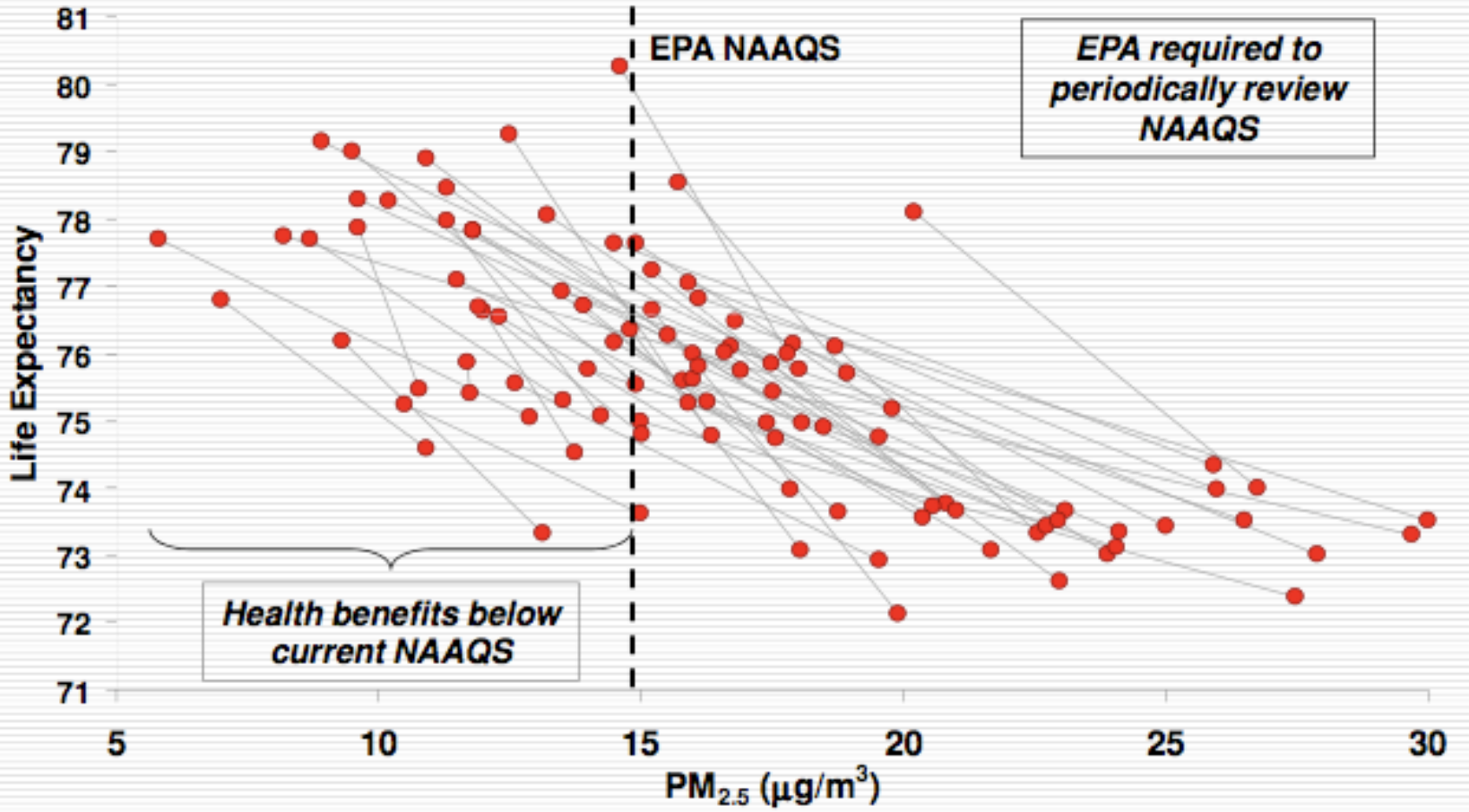
Pope, Ezzati, Dockery. NEJM 2009; 360:376

Life Expectancy vs $PM_{2.5}$ 1980-2000



Pope, Ezzati, Dockery (NEJM 2009)

Life Expectancy vs $PM_{2.5}$ 1980-2000



Pope, Ezzati, Dockery (NEJM 2009)

Influence of Particle Size on Particle Number and Surface Area for a Given Particle Mass

PARTICLE DIAMETER	RELATIVE NUMBER OF PARTICLES	RELATIVE SURFACE AREA
10 µm	1	1
1 µm	10^3	10^2
0.1 µm	10^6	10^4
0.01 µm	10^9	10^6

Particle characteristics

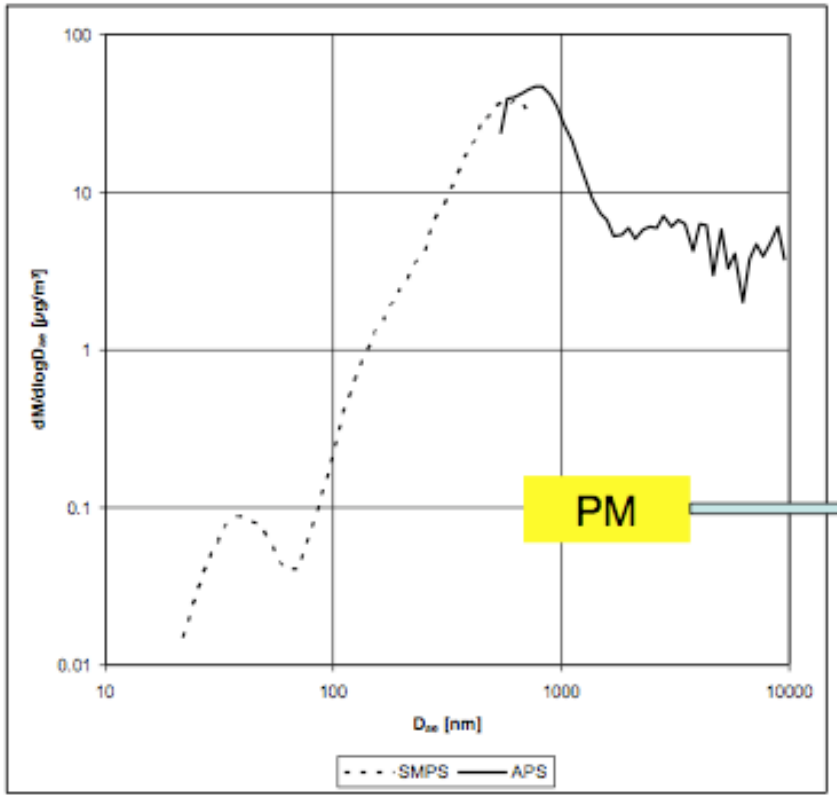
Particle Number, Surface Area and Mass

Measuring:

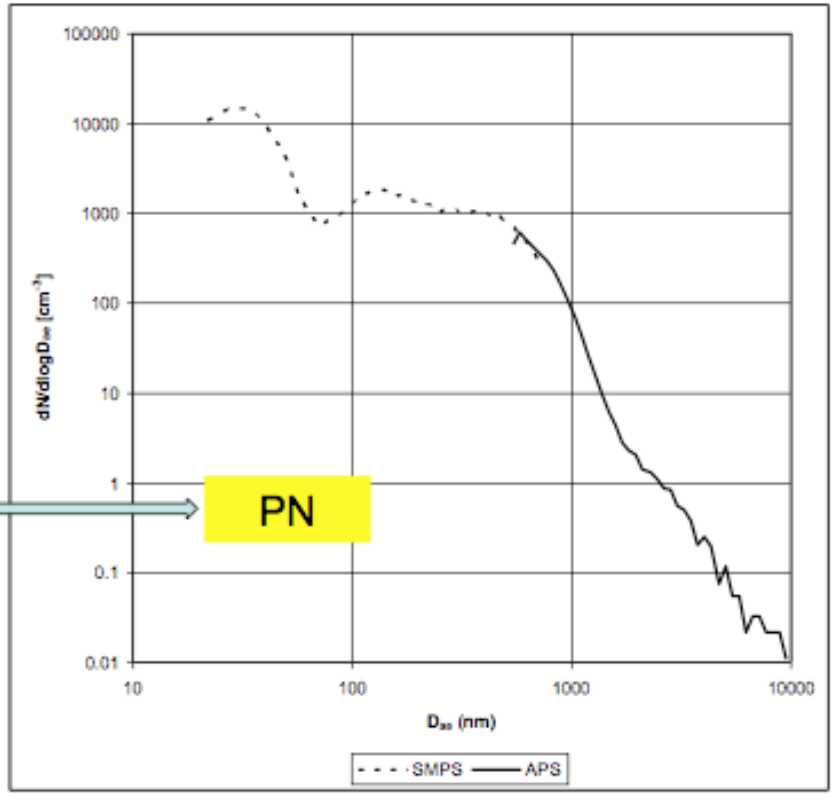
- **Particle number reflects particles < 100 nanometres primarily**
- **Particle surface area reflects mainly particles of 50-1000 nm**
- **Particle mass reflects particles of > 100 nanometres (usually to 2.5 µm or 10 µm)**

Measure number not mass

- While "traditional" PM measurements put the weight on large particles, PN measurements shift this weight to ultrafine particles (or nanoparticles).



PM → PN



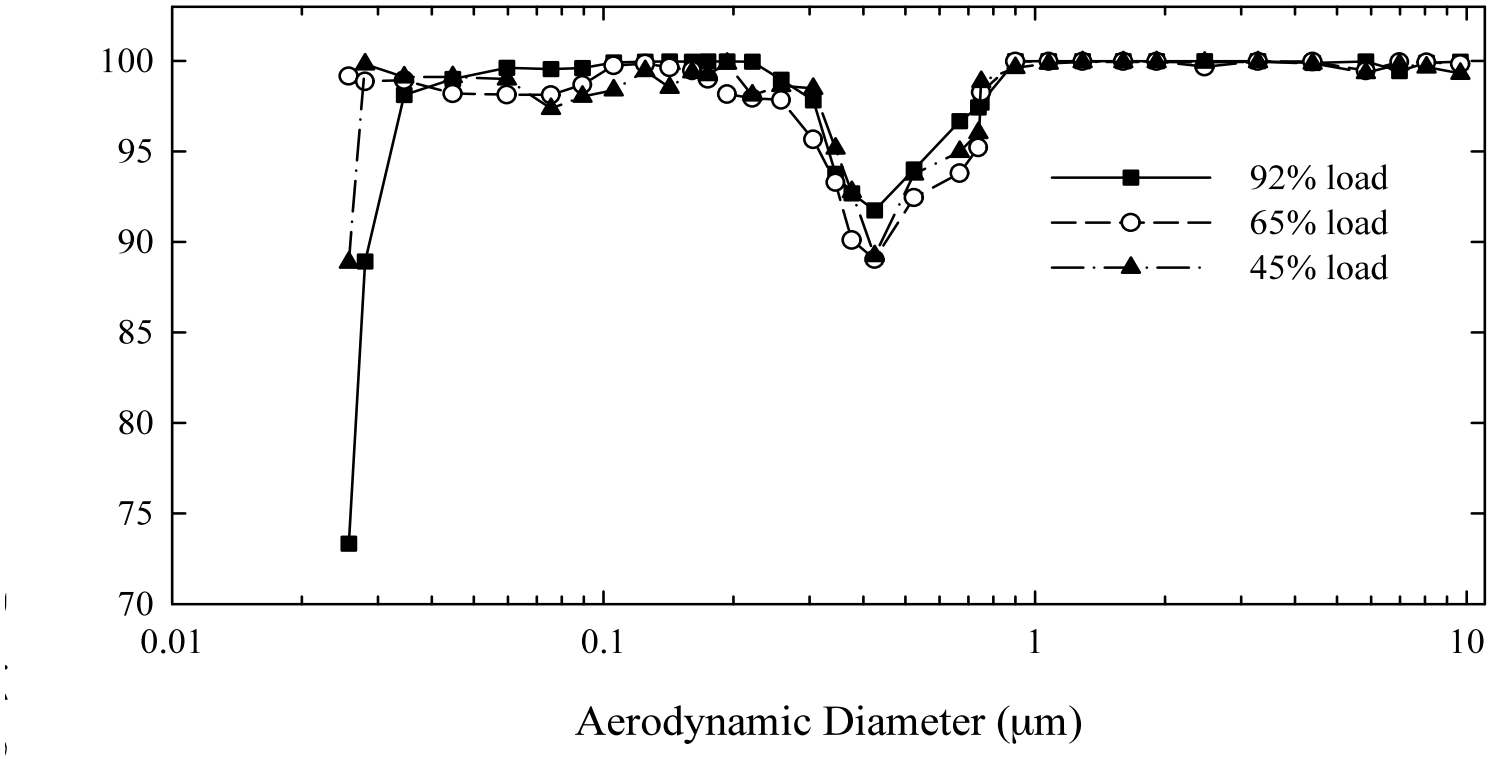
http://www.npl.co.uk/upload/pdf/20100608_mansa_horn.pdf

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 [< 1.0um or 100nm] while in coal combustion the coarse fraction dominates particle mass.
  - Lillieblad, L, et.al., Boiler Operation Influence on the emissions of biomass fired boilers, Energy and Fuels [American Chemical Society], 18:410, 2004.

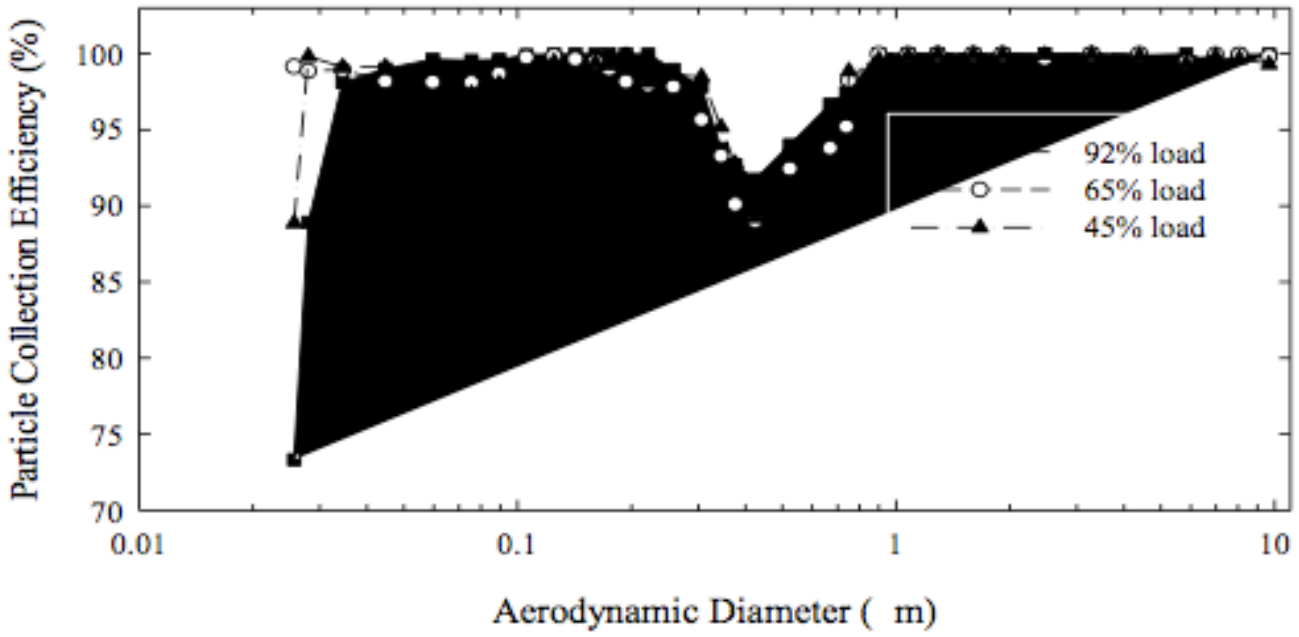
ESP Collection Efficiency

http://www.sustainableproduction.org/downloads/PHopke_7Nov2011.pdf



Collection efficiency of the ESP over the full range of measured particle size ($0.01 < d_a < 10$ μm) 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%.
  - Mohr, M.; et.al. Aerosol Sci. Technol 1996, 24, 191-204. Yla¨ talo, S. I., et.al. AerosolSci.Technol. 1998, 29, 17- 30. McCain, J. D., et.al. J.AirPollut.Control Assoc. 1976, 25, 117-121
- 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.
  - Strand M, et.al. Ash Penetration through an ESP, Energy & Fuels 16:1499, 2002
- 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.
  - Rissler, J Experimental deposition of particulates in the respiratory tract, J of Aerosol Sci, 48:18-33, 2012.
- 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.
  - Lighty, JS, et. al., Combustion Aerosols: Factors Governing Their Size and Composition, J Air Waste Management, 50:1565.

Fine particle numbers

- The average fine particle number concentration was 4.4-5.5 × 100,000,000 particles cm-3. Coarse particle concentration was 3.6-10.5 X 10 3/cm3– a difference of 10000 fold.
  - Strand M, et.al. Ash Penetration through an ESP, Energy & Fuels 16:1499, 2002
- The total concentration of emitted particles [CFB] was 5.7-6.3 x 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 um.
  - Pagels, J, et.al. J of Aerosol Science 34:1043, 2003., Hasler, P, Biomass for Energy and Industry European Conference, 1998.

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.***[1] 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

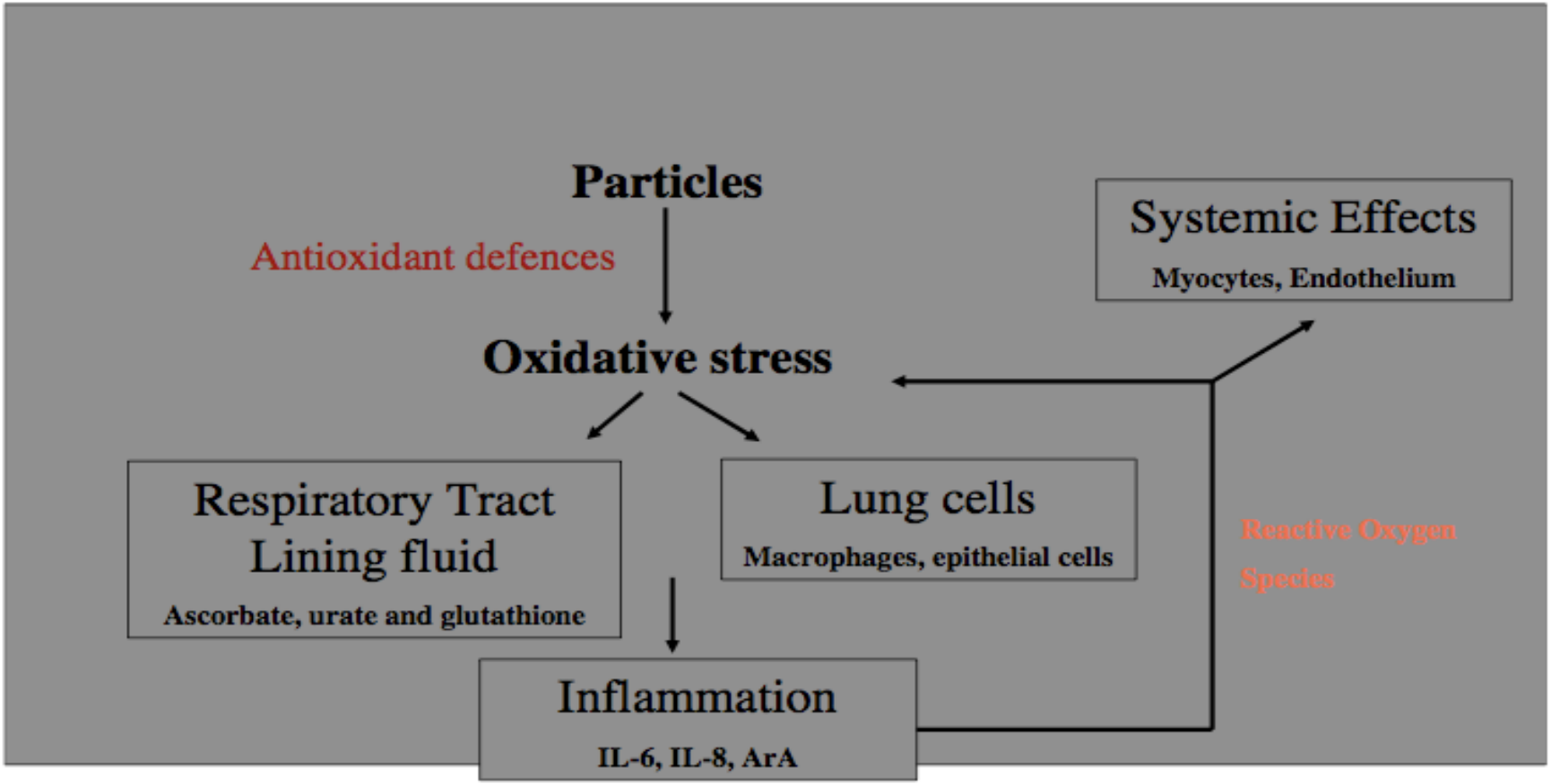
DANGER

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



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
  - September 2012 http://www.ehjournal.net/content/pdf/1476-069X-11-40.pdf
  - http://ehp03.niehs.nih.gov/article/fetchArticle.action?articleURI=info%3Adoi%2F10.1289%2Fehp.117-a505a
- Increased incidence of asthma by 300%
  - California Childrens Health Study--Künzli et al., Amer J Public Health 93:1494 2003, McConnell, et.al., Lancet 359:386, 2001.
- Decreased lung function by 20% [similar to tobacco exposure]
  - Gauderman, et. al. Amer J of Resp and Crit Care Med, 166:76, 2002

Future danger

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

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

- "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.