Molecular Adsorption at PM Surfaces

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RESEARCH GROUPS

- MIDDLESEX UNIVERSITY (London)
  Ron Hamilton et al

- IMPERIAL COLLEGE (London)
  Robert Maynard, Matti Jantunen, Teresa Tetley

- NEW YORK UNIVERSITY (New York)
  Morton Lippmann, George Thurston

Collaborators:

- EXPOLIS Group (Europe-wide)
- UNIVERSITY COLLEGE (London)
- UMIST (Manchester)
- BIRMINGHAM UNIVERSITY (Birmingham, UK)
- Landcare Research (New Zealand)

Currently:
- ULUDAG UNIVERSITY (Bursa, Turkey), HEI supported
Do PM Characteristics Matter?

CURRENT REGULATORY HYPOTHESIS
- All PM$_{2.5}$ mass concentration has same toxicity

ALTERNATIVE HYPOTHESES
- PM from different sources have different characteristics (composition, size, surface area, etc)
- PM with differing characteristics have different toxicities
  
  i.e. specific PM characteristics determine PM toxicity mechanism(s)
Evidence… Epidemiology

• Increased **daily mortality** associated with episodes of **PM** pollution
  (Health Effects Institute (HEI), 2000)
• 10 µg·m⁻³ increase in PM₂.⁵
  • ∼1% ↑ in **total mortality**
  
  - 3.3% ↑ in **COPD**
  - 4.0% ↑ in **pneumonia** deaths
  - 2.1% ↑ in **cardiomyopathy/ischemic** deaths

  \{ **Respiratory** \}

\{ **Cardiovascular** \}

• **Chronic health effects** also associated with ambient PM
Evidence... Toxicological

- Specific particle characteristics are associated with increased morbidity and mortality
- Implicated PM characteristics include:
  - Surface area (e.g., Oberdorster et al 1994; Seaton et al 1995; Johnson et al 2000)
  - Metals (e.g., Dreher et al 1997)
  - Oxidative stress (e.g., Seaton et al 1996; Gilmour et al 1996; Donaldson et al 1997)
  - Elemental carbon (e.g., Lovik et al 1997; Heo et al 2001)
Unique Approach

- Traditional observations
  - Change in population (epidemiology)
  - Change in organism or cell (toxicology)

*Observe change in particle characteristics*
Particle Surfaces May Be Key

- Surface is first contact with the body.
- Huge surface area for chemical delivery and biological fluid component stripping.
- Particle surfaces are known to be modified on inhalation - opsonisation.
- Molecule specific techniques now available.

What is the composition of PM$_{2.5}$ surfaces? How does this change in biological fluid?
Site(s) of First Contact

- Mouth/Nose
- Trachea
- Bronchus/bronchiole
- Alveolar sacs
  - Surfactant Lipid/Protein (lung patency)
  - Alveolar Type I Cells (oxygen exchange)
  - Alveolar Type II Cells (secrete surfactant)
  - Alveolar Macrophages (initial <local> host defense)
Current Hypothesis: Surfactant Interaction

Pollutant Particles

Lung

Surfactant adsorbs to particle surface

Increased surface tension of surfactant

Reduced Alveolar Macrophage phagocytosis

Reduced Bacteriocidal Ability

Increased Infectivity

Death
**PM$_{2.5}$ Surface Chemistry Varies**
London Study (Kendall et al 2001, 2002)

<table>
<thead>
<tr>
<th>Species</th>
<th>BE (eV)</th>
<th>% Cover</th>
<th>BE (eV)</th>
<th>% Cover</th>
<th>BE (eV)</th>
<th>% Cover</th>
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<tbody>
<tr>
<td>O</td>
<td>532.6</td>
<td></td>
<td>532.2</td>
<td></td>
<td>533.0</td>
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<tr>
<td>NO$_3^-$</td>
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<td>-</td>
<td>407.4</td>
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<tr>
<td>NH$_4^+$</td>
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<td>-</td>
<td>402.0</td>
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<td>N-C</td>
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<td>C=O/COO$^-$</td>
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<td>-</td>
<td>288.4</td>
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<td>C-(O,N)</td>
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<td>286.1</td>
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<tr>
<td>C-(C,H)</td>
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<td>199.3</td>
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<td>SO$_4^{2-}$</td>
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<td>-</td>
<td>168.9</td>
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<tr>
<td>SiO$_2$</td>
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<td>-</td>
<td>101.1</td>
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<td>102.3</td>
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PM$_{2.5}$ Surface Chemistry Varies

New York Study (Kendall et al *Inhal. Tox.* 2004)

<table>
<thead>
<tr>
<th>Species</th>
<th>C-(O,N)</th>
<th>COO</th>
<th>Total C</th>
<th>N-C</th>
<th>NO$_3^-$</th>
<th>Total N</th>
<th>S</th>
<th>Si</th>
<th>P</th>
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<tbody>
<tr>
<td>New York City - urban background ($n = 6$)</td>
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<td></td>
<td></td>
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<tr>
<td>Mean</td>
<td>19.0</td>
<td>5.7</td>
<td>82.7</td>
<td>0.5</td>
<td>0.3</td>
<td>2.2</td>
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<td>SD</td>
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<td>2.2</td>
<td>2.9</td>
<td>0.3</td>
<td>0.2</td>
<td>0.6</td>
<td>0.2</td>
<td>0.5</td>
<td>0.05</td>
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<tr>
<td>New York City - urban roadside ($n = 6$)</td>
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<td></td>
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<tr>
<td>Mean</td>
<td>19.4</td>
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<td>84.1</td>
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<td>3.1</td>
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<td>SD</td>
<td>2.1</td>
<td>1.4</td>
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<td>0.3</td>
<td>0.9</td>
<td>0.1</td>
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<td>London in cigarette smoke</td>
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<td>—</td>
<td>96.5</td>
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<td>—</td>
<td>0.5</td>
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<tr>
<td>London urban roadside</td>
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<tr>
<td>Mean</td>
<td>12.6</td>
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<td>85.3</td>
<td>1.0</td>
<td>0.7</td>
<td>3.2</td>
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<tr>
<td>Species</td>
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<td></td>
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<tr>
<td>Galway “clean” site</td>
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<td>—</td>
<td>58.6</td>
<td>—</td>
<td>—</td>
<td>0</td>
<td>—</td>
<td>0.6</td>
<td></td>
</tr>
</tbody>
</table>
Trace Elements “Removed” from Urban PM$_{2.5}$ Surfaces Kendall et al. *Inhal. Tox.* 2004

% Surface Cover

- $S$
- $\text{NH}_4^+$
- $O$
- $\text{NO}_3^{2-}$
Protein Adsorption Onto Urban PM$_{2.5}$ Surfaces Kendall et al *AJP* 2000

(a) Urban PM$_{2.5}$

(b) Immersed in saline

(c) Immersed in lung fluid
Protein Adsorption at PM Surfaces
Kendall et al *Inhal. Tox.* 2004

![Graph showing protein adsorption at PM surfaces](image)

<table>
<thead>
<tr>
<th>Location</th>
<th>N-C (%) change</th>
<th>C-(O, N) (%) change</th>
<th>NH$_4^+$ (%) change</th>
<th>NO$_3^-$ (%) change</th>
</tr>
</thead>
<tbody>
<tr>
<td>London</td>
<td>510</td>
<td>69</td>
<td>-100</td>
<td>-100</td>
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<tr>
<td>New York</td>
<td>279</td>
<td>18</td>
<td>-64</td>
<td>-59</td>
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</tbody>
</table>
PM$_{2.5}$ Morphology and Area Varies with Source: NYC URBAN
PM2.5 agglomerated in lavage PM2.5 sampled into lung fluid formed dense agglomerates >10 µm. Absent in saline.
PM$_{2.5}$ Agglomeration in Lung Fluid

Backscatter electron (SEM) images of relative abundance of agglomerates in lung fluid and saline.

Lung Fluid  Saline
Molecular attractive forces increased in lung fluid measured by AFM
Molecular adsorption of proteins and phospholipids measurable

DPPC
Molecular adsorption of proteins and phospholipids measurable
Research Conclusions

- Carbon dominates urban PM$_{2.5}$ surfaces.
- Trace species are washed from the PM surfaces in lung fluid and saline.
- Protein depositing to PM$_{2.5}$ surfaces from lung fluid modifies particle chemistry/behaviour.
- AFM may determine interactive forces between PM and other substances, in liquids.
- Molecular adsorption of specific proteins and phospholipids detectable.
Current Hypothesis: PM adsorbs surfactant in a PM area/composition dependent manner
LOCATION: Uludag University, Bursa