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 $\mu g \cdot m^{-3}$ increase in $PM_{2.5}$
  - ~1% ↑ in total mortality

  – 3.3% ↑ in COPD
  – 4.0% ↑ in pneumonia deaths

  } **Respiratory**

  – 2.1% ↑ in cardiomyopathy/ischemic deaths

  } 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

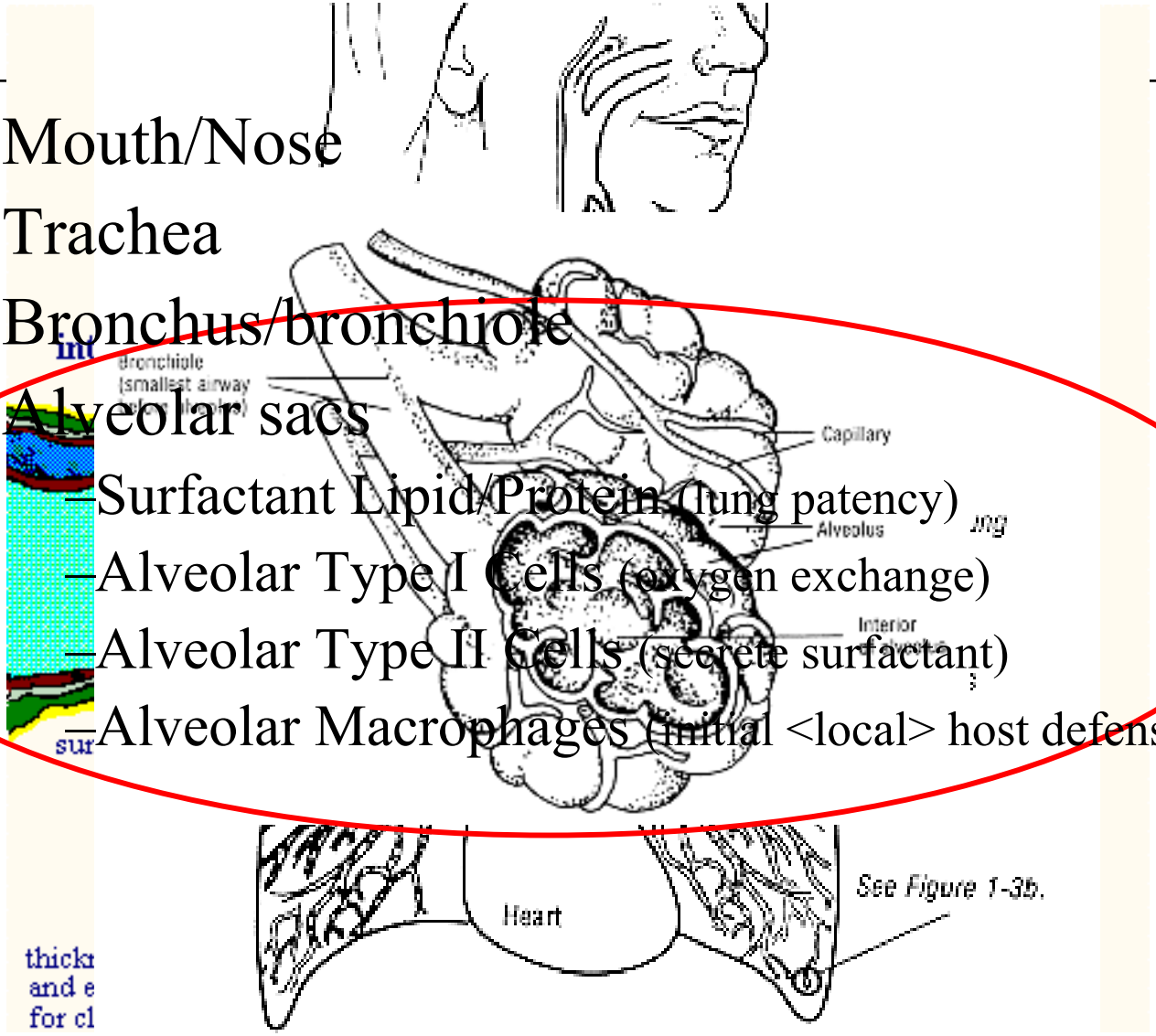
Particle Surfaces May Be Key

- 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?

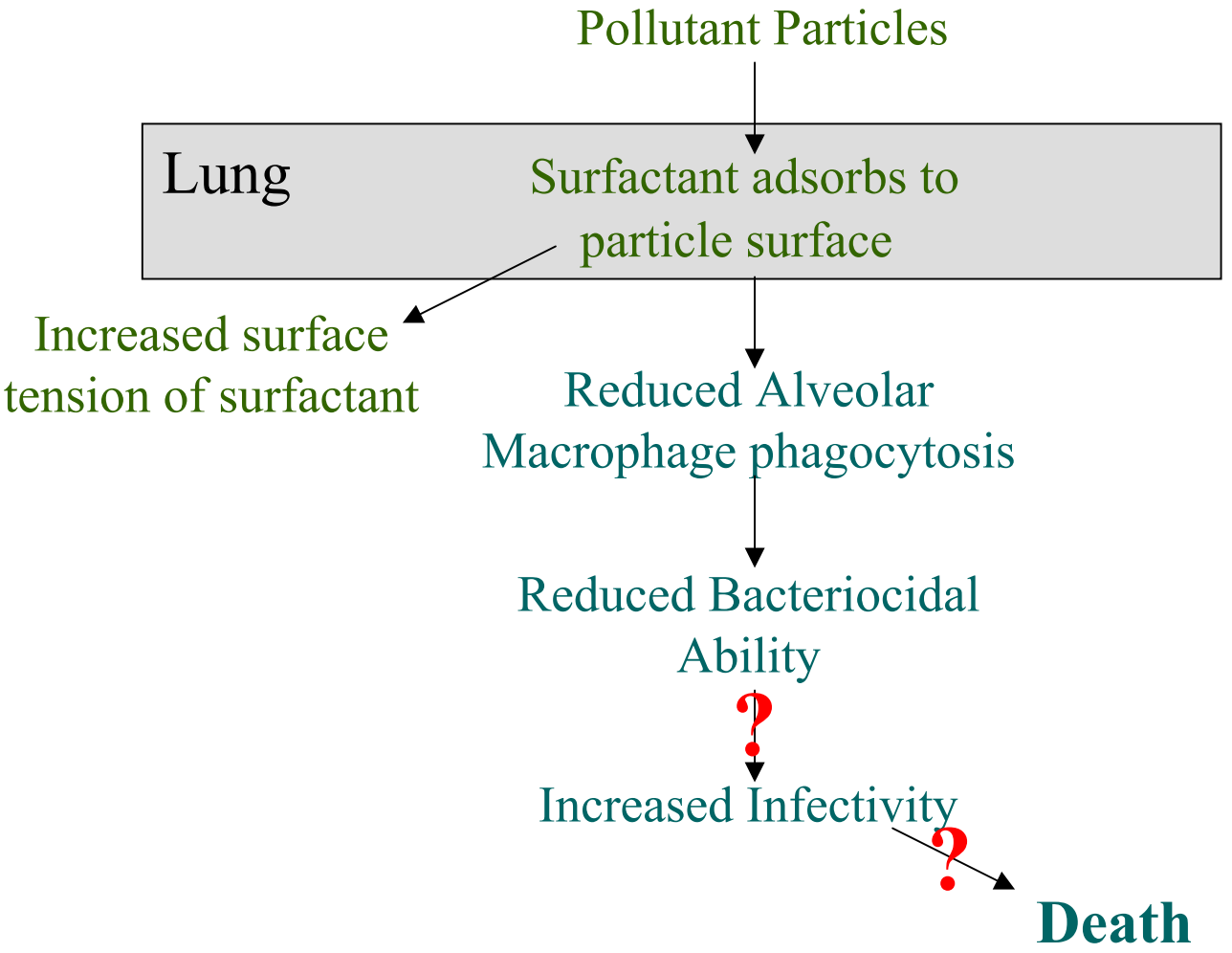
How does this change in biological fluid?

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



$PM_{2.5}$ Surface Chemistry Varies
London Study (Kendall et al 2001, 2002)

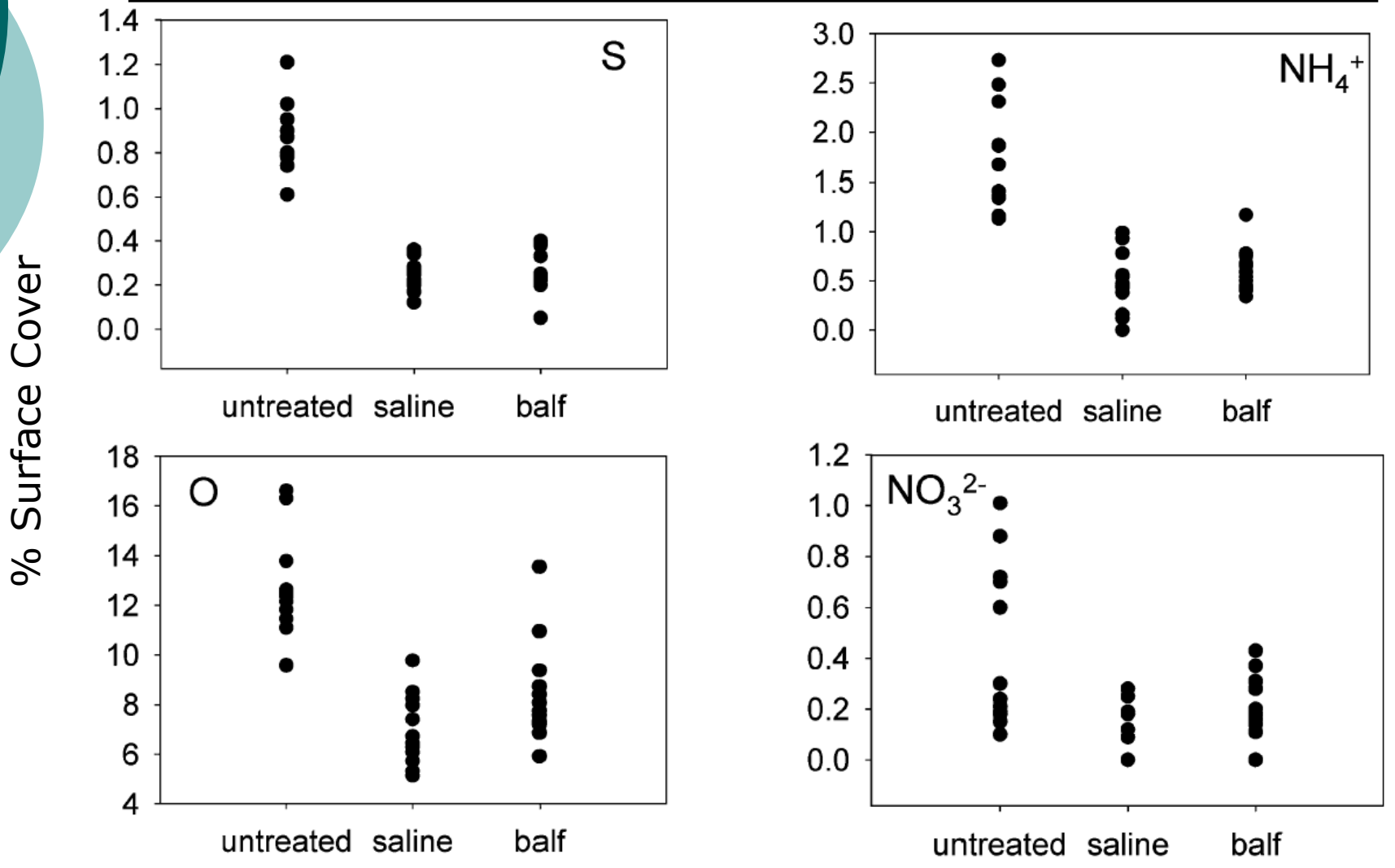
	"Clean Air" $PM_{2.5}$		Urban $PM_{2.5}$		Smoke $PM_{2.5}$	
Species	BE (eV)	% Cover	BE (eV)	% Cover	BE (eV)	% Cover
O	532.6		532.2		533.0	
NO_3^-	-	-	407.4		-	-
NH_4^+	-	-	402.0		-	-
N-C	-	-	400.0		400.0	0.5
C=O/COO$^-$	-	-	288.4		-	-
C-(O,N)	-	-	286.1		-	-
C-(C,H)	284.6		284.6		284.7	
Cl^-	199.3	11.0				
SO_4^{2-}	-	-	168.9		-	-
SiO_2	-	-	101.1		102.3	0.6

$PM_{2.5}$ Surface Chemistry Varies

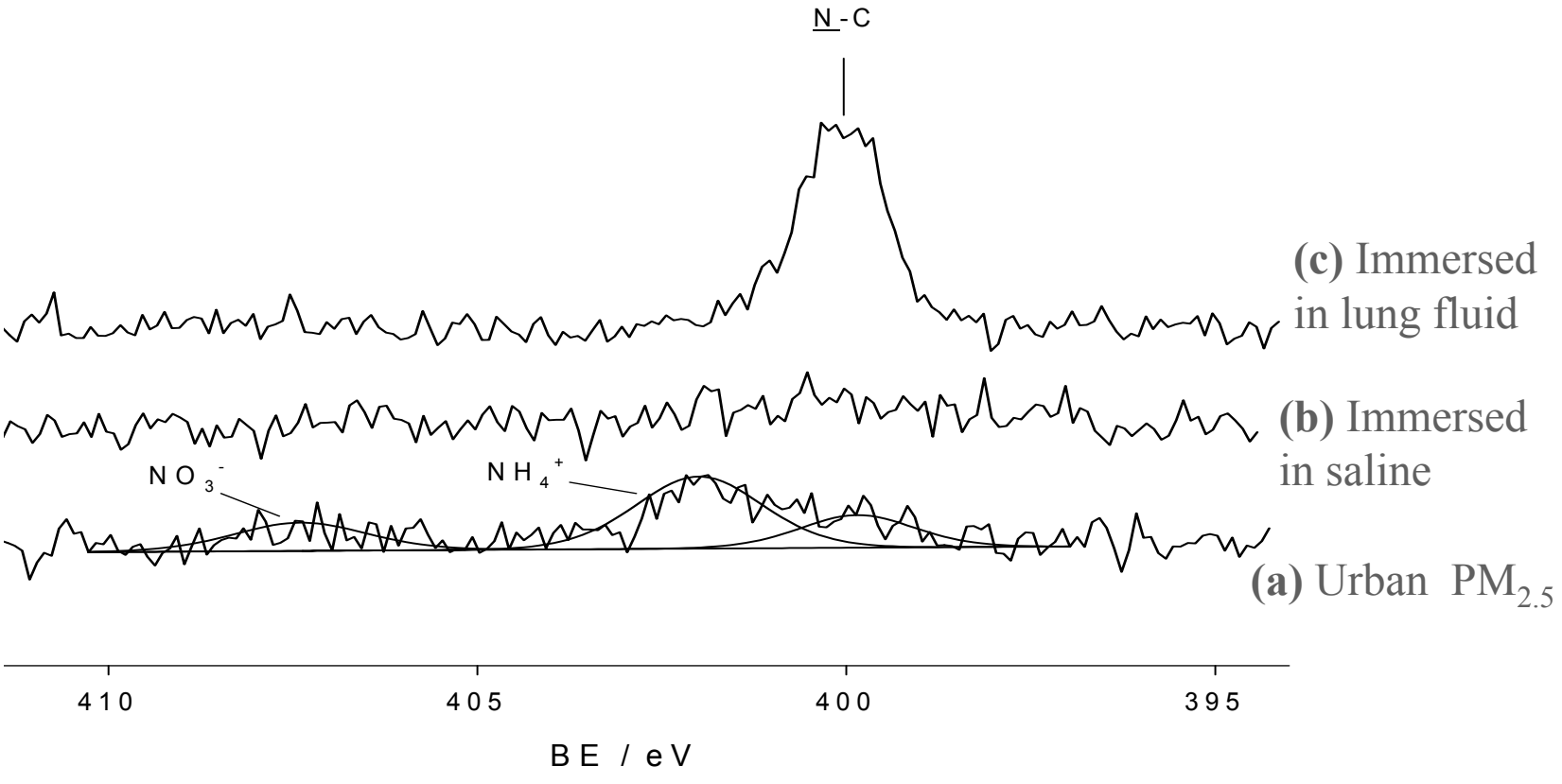
New York Study (Kendall et al *Inhal. Tox.* 2004)

ecies	C-(O,N)	COO	Total C	N-C	NO_3^{2-}	Total N	S	Si	
ew York C	n background ($n = 6$)								
Mean	19.0	5.7	82.7	0.5	0.3	2.2	0.9	0.8	0
SD	2.8	2.2	2.9	0.3	0.2	0.6	0.2	0.5	0
ew York	n roadside ($n = 6$)								
Mean	19.4	6.9	84.1	0.5	0.6	3.1	0.9	0.4	0
SD	2.1	1.4	2.6	0.2	0.3	0.9	0.1	0.1	0
ecies	C-(O,N)	C-O	Total C	N-C	NO_3^{2-}	Total N	SO_4^{2-}	Si	
ondon in	ette smoke								
Mean	—	—	96.5	0.5	—	0.5	—	—	
ondon url	ide								
Mean	12.6	6.2	85.3	1.0	0.7	3.2	0.5	0.6	
lway "cle	site								
Mean	—	—	58.6	—	—	0	—	0.6	

Trace Elements "Removed" from Urban $PM_{2.5}$ Surfaces Kendall et al *Inhal. Tox.* 2004

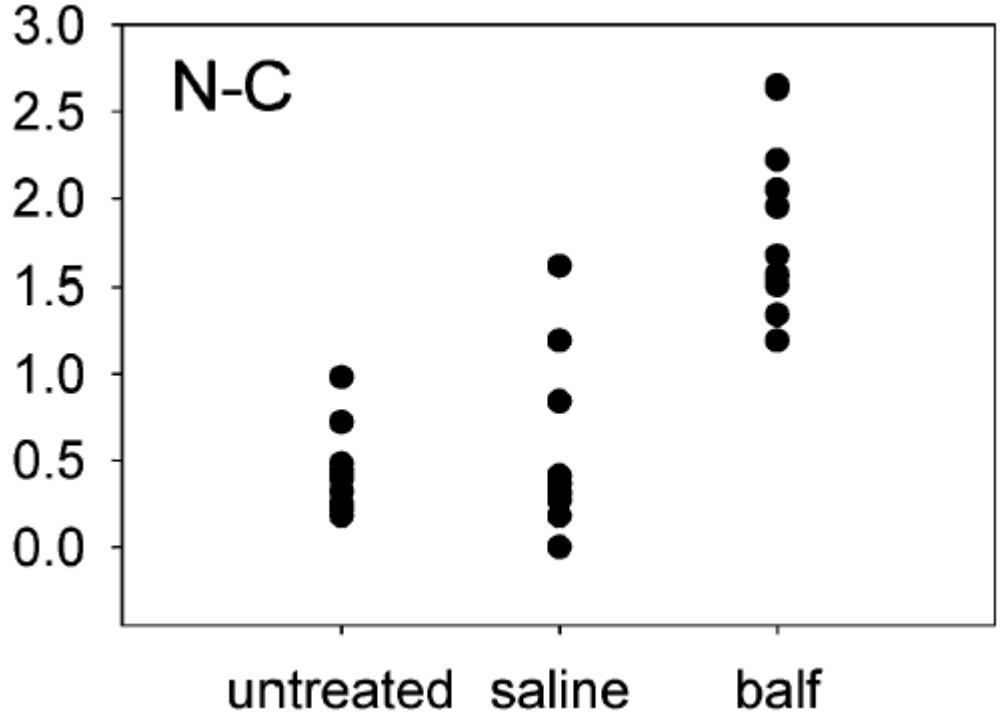


Protein Adsorption Onto Urban $PM_{2.5}$ Surfaces Kendall et al *AJP* 2000



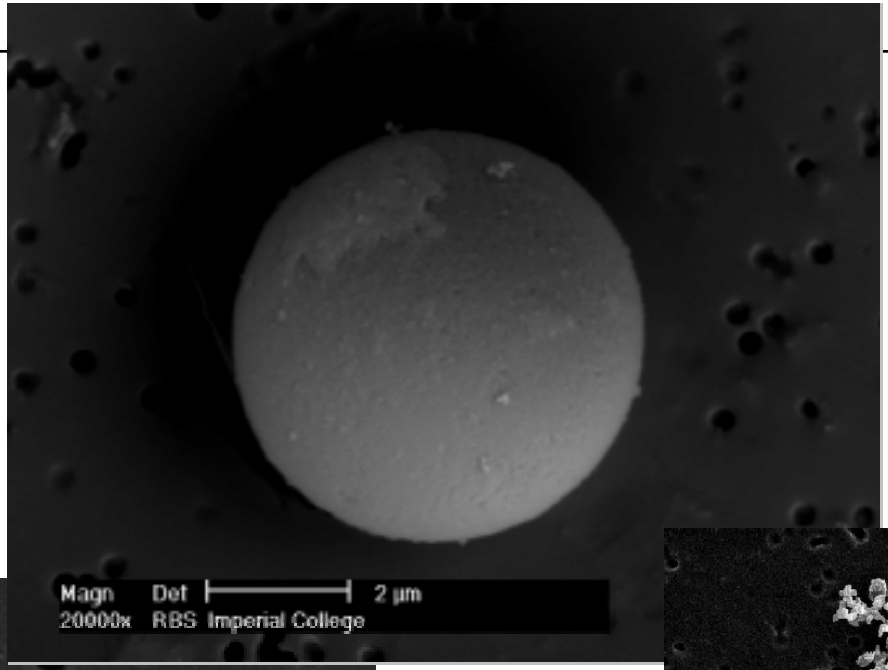
Protein Adsorption at PM Surfaces

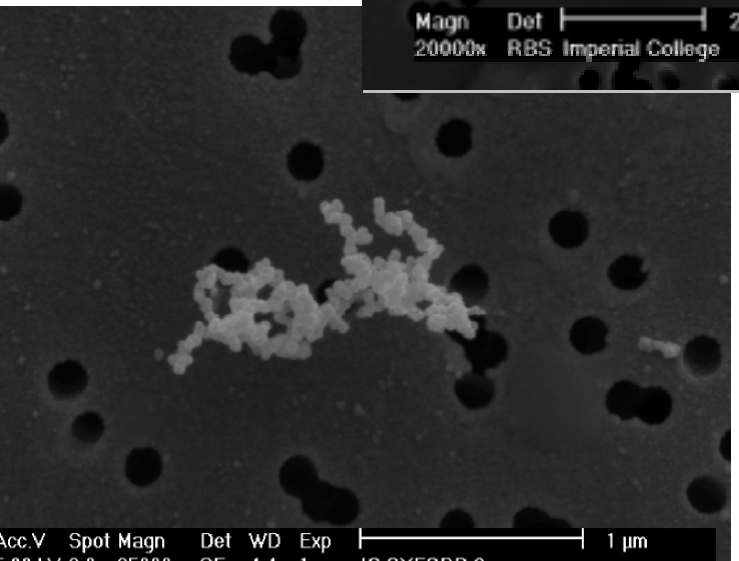
Kendall et al *Inhal. Tox.* 2004

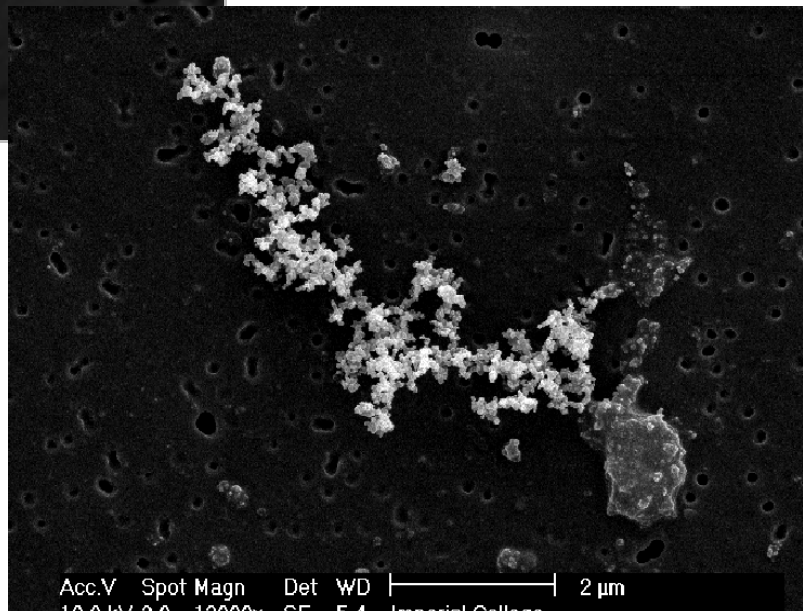


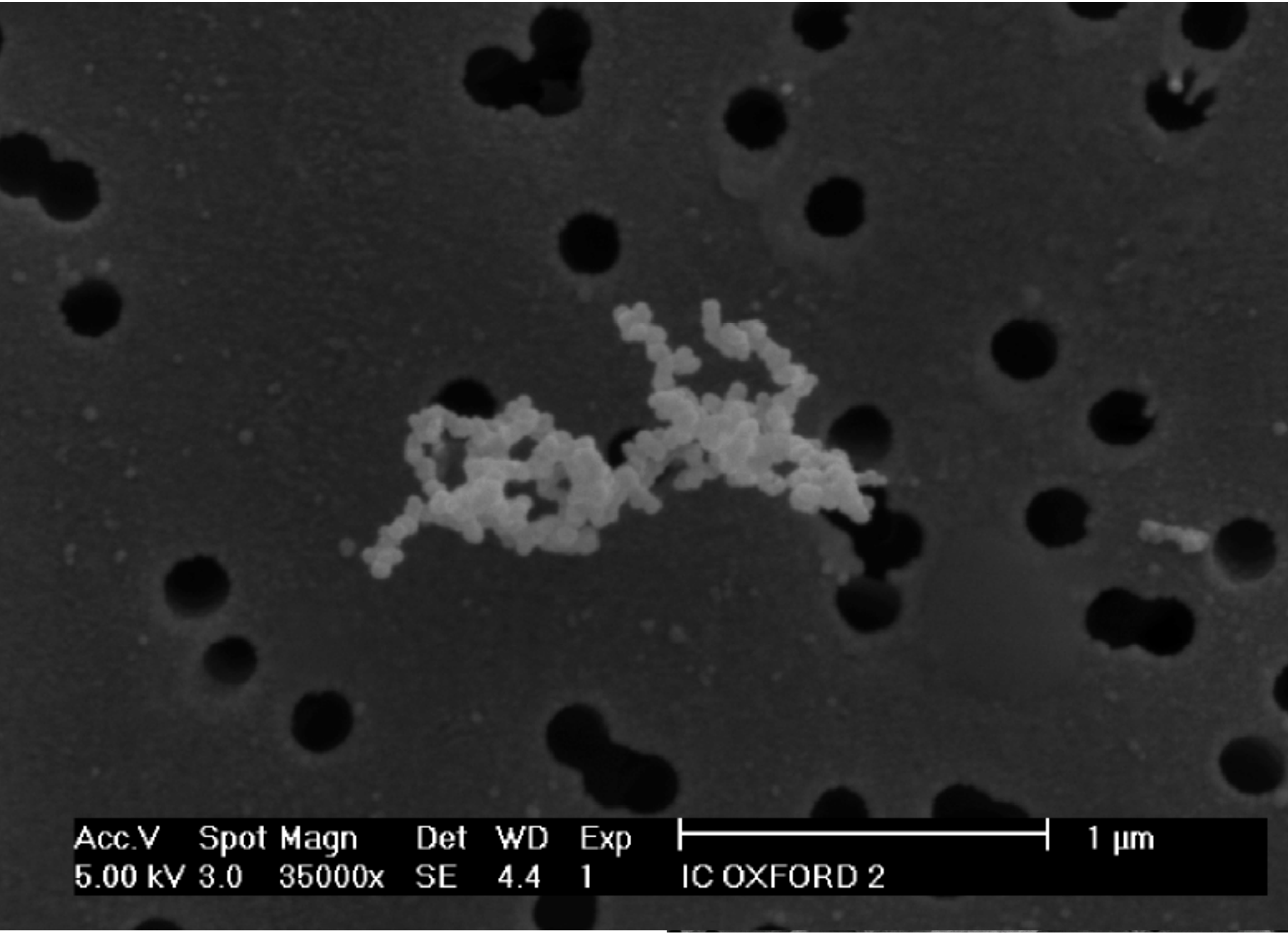
Location	N-C (% change)	C-(O, N) (% change)	NH_4^+ (% change)	NO_3^{2-} (% change)
London	510	69	−100	−100
New York	279	18	−64	−59

$PM_{2.5}$ Morphology and Area Varies with Source: NYC URBAN





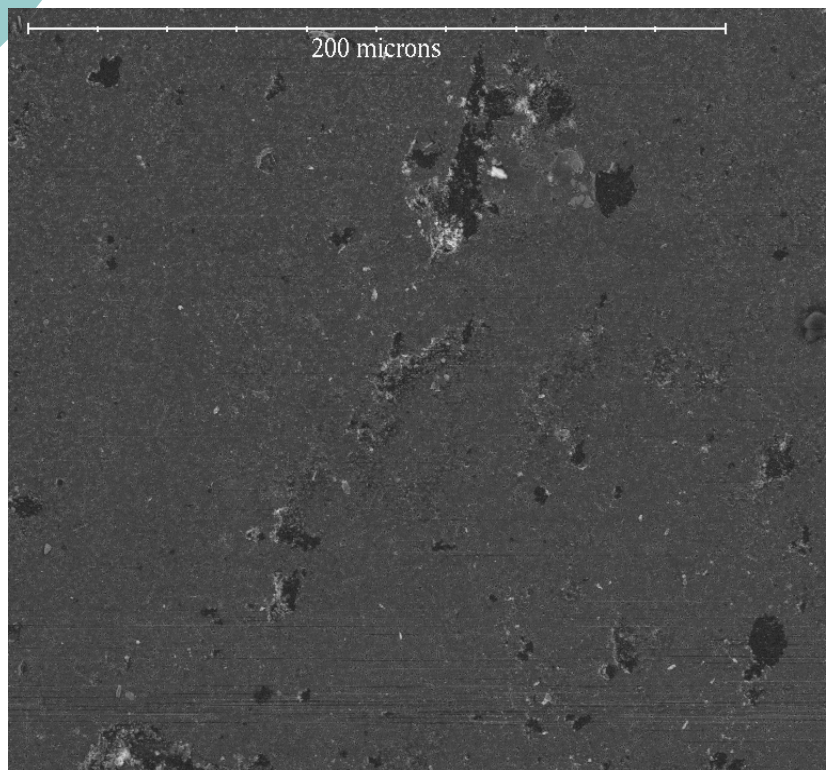



Acc.V Spot Magn Det WD Exp
5.00 kV 3.0 35000x SE 4.4 1
1 µm
IC OXFORD 2

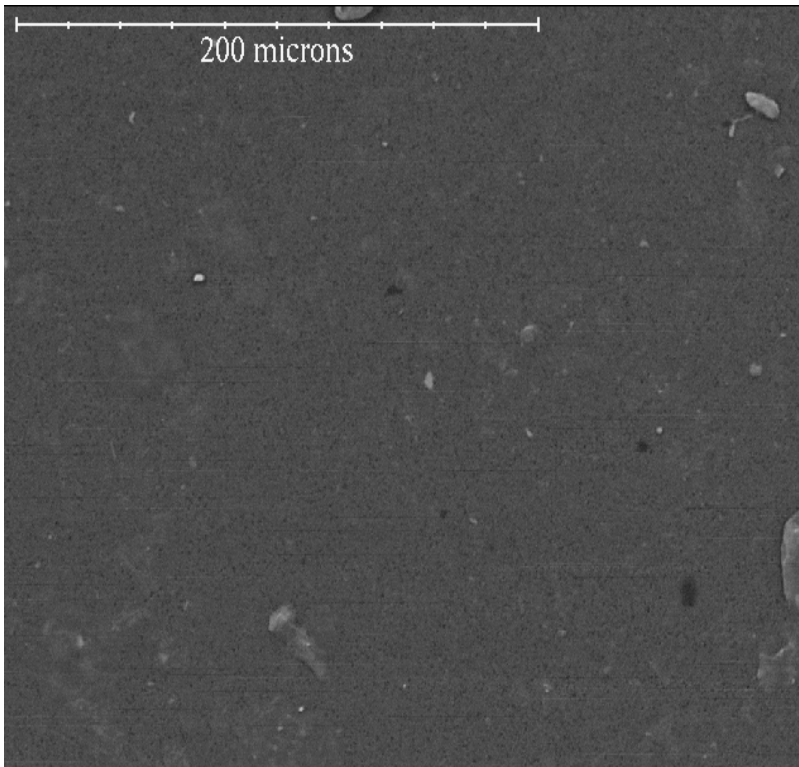
$PM_{2.5}$ Agglomeration in Lung Fluid

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

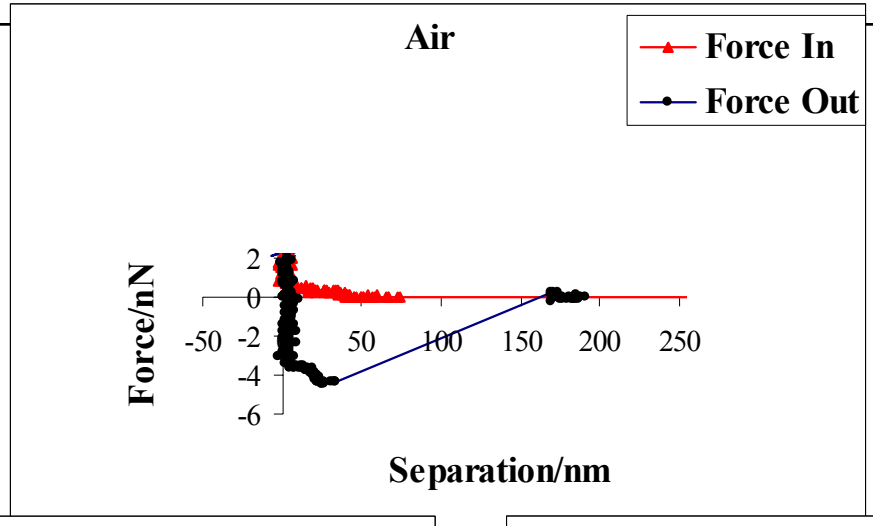
Lung Fluid

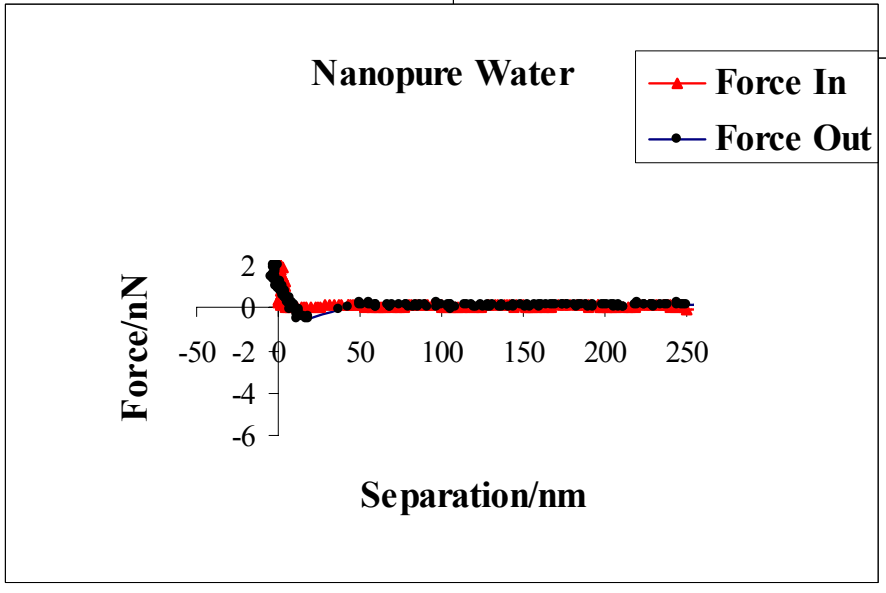


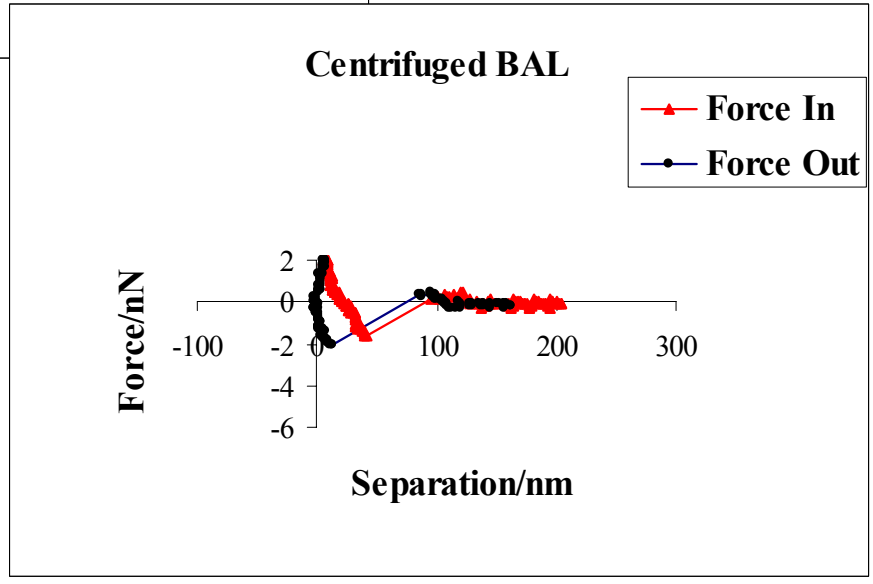
Saline



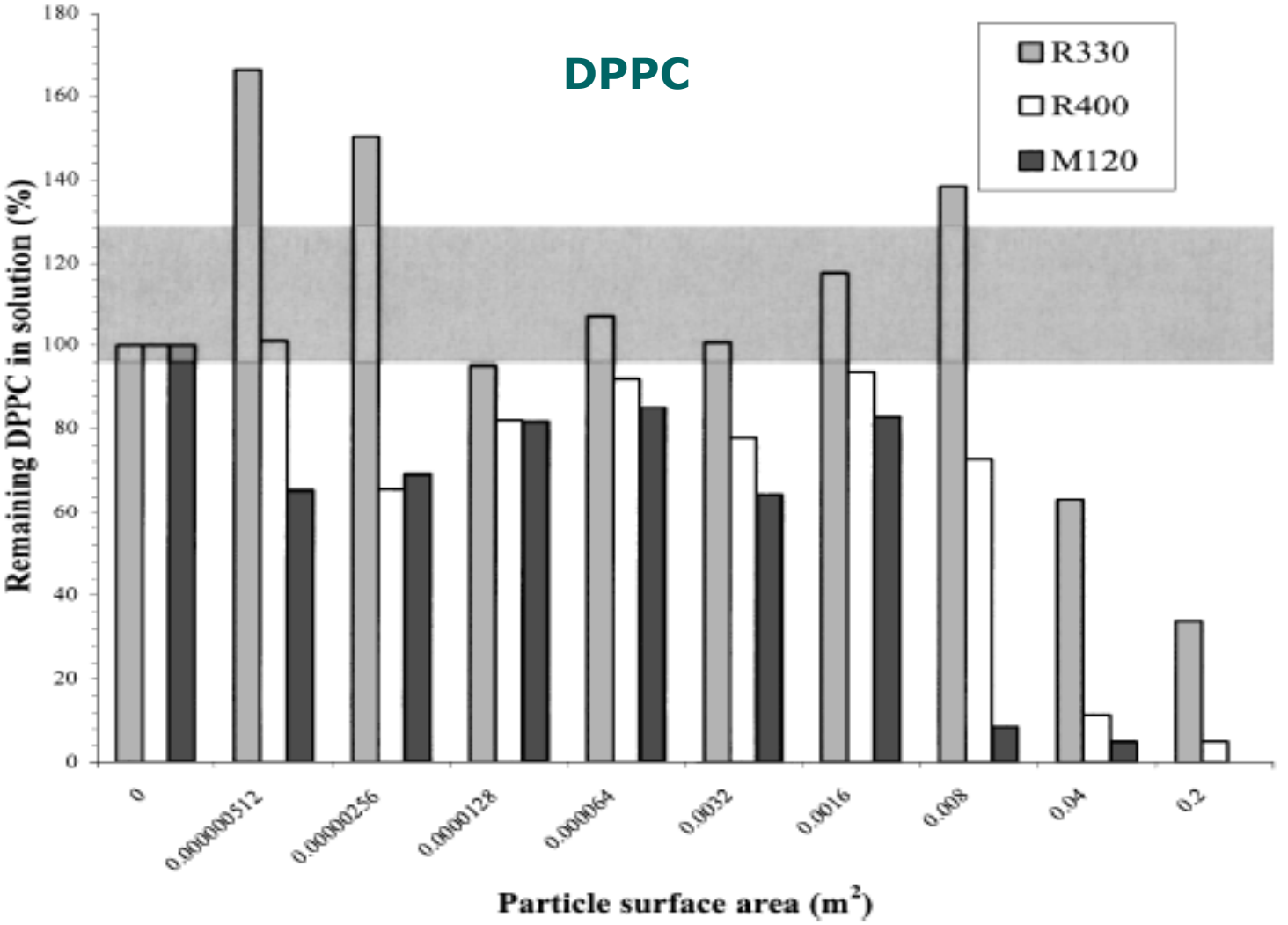
Molecular attractive forces increased in lung fluid measured by AFM



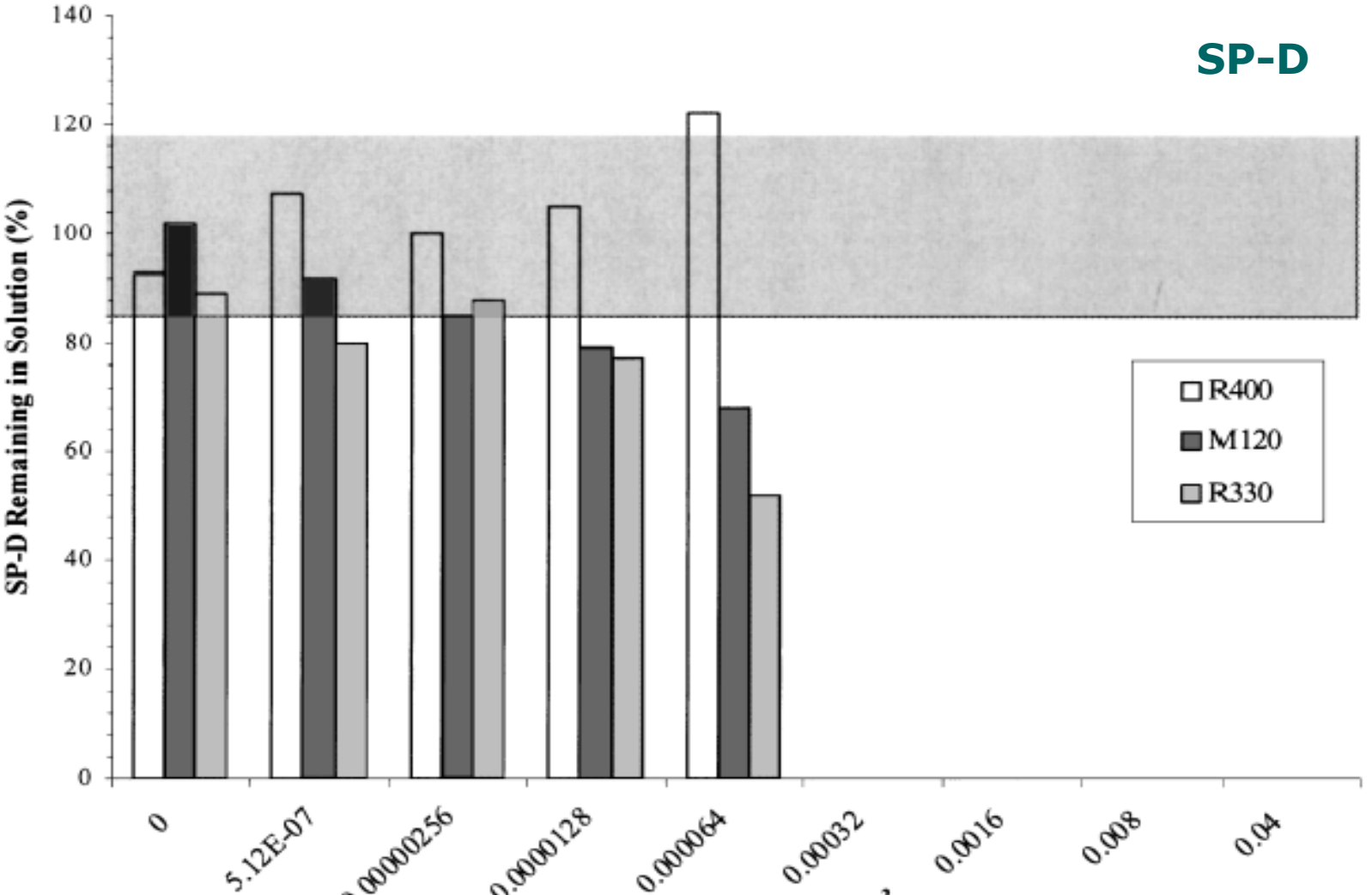




Molecular adsorption of proteins and phospholipids measurable



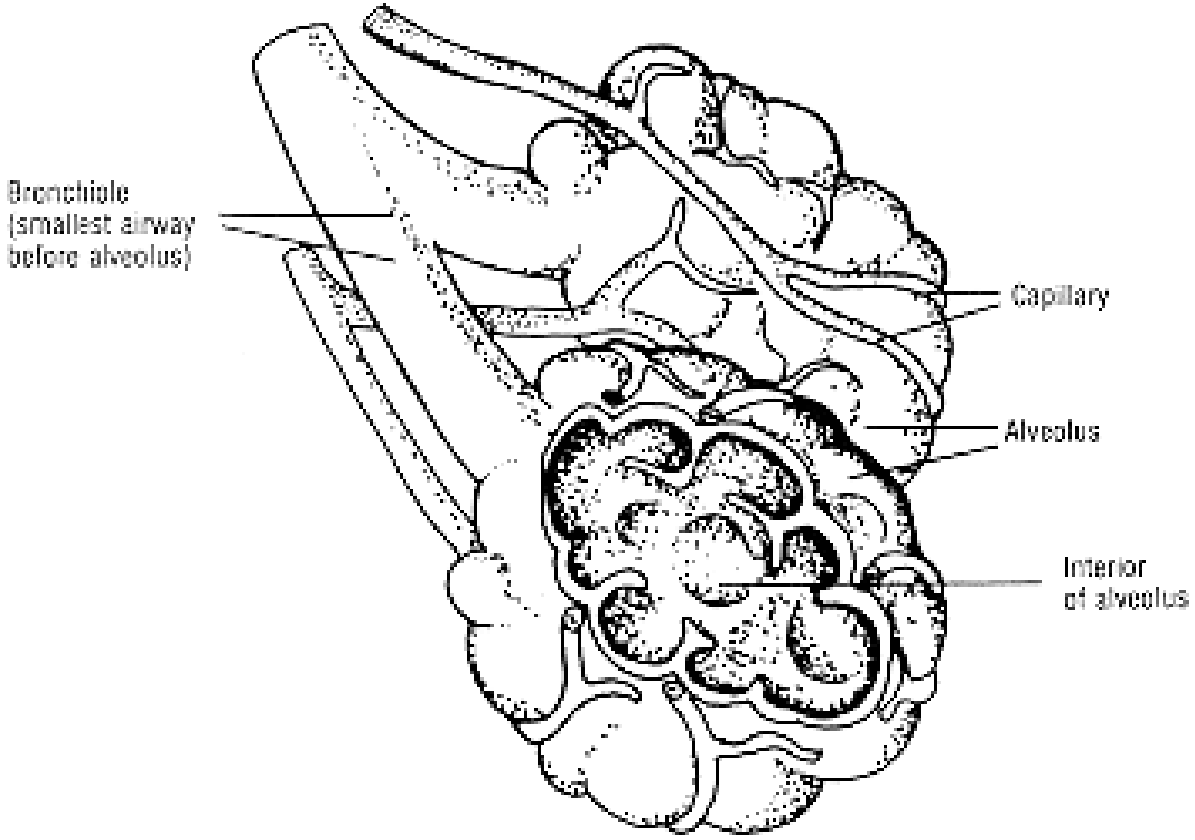
Molecular adsorption of proteins and phospholipids measurable



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