

# Environmental Fate of Carbon Nanotubes

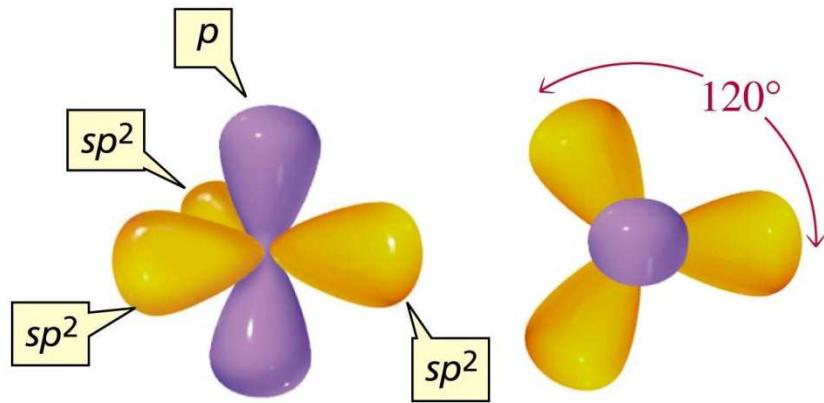
**Dr. Elijah J. Petersen**

**Biosystems and Biomaterials Division**

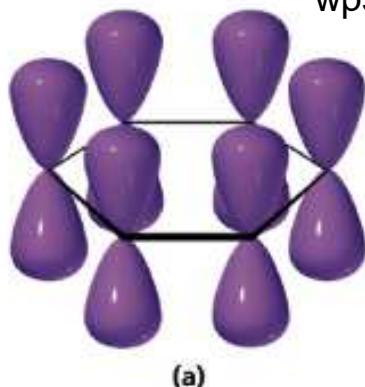
**National Institute of Standards and Technology (NIST)**

**Presented 8/12/2013 at the University of Jyväskylä**

# Carbon Nanotubes



side view

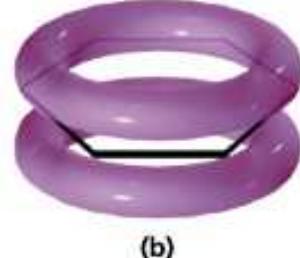


Benzene

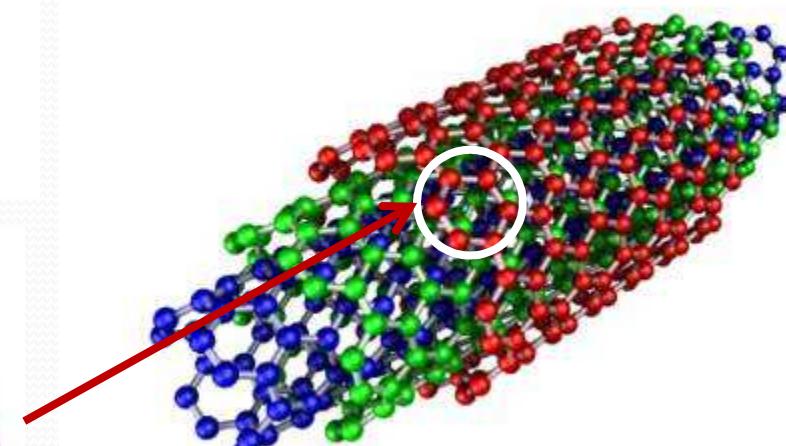
[teenbiotechchallenge.ucdavis.edu/](http://teenbiotechchallenge.ucdavis.edu/)

top view

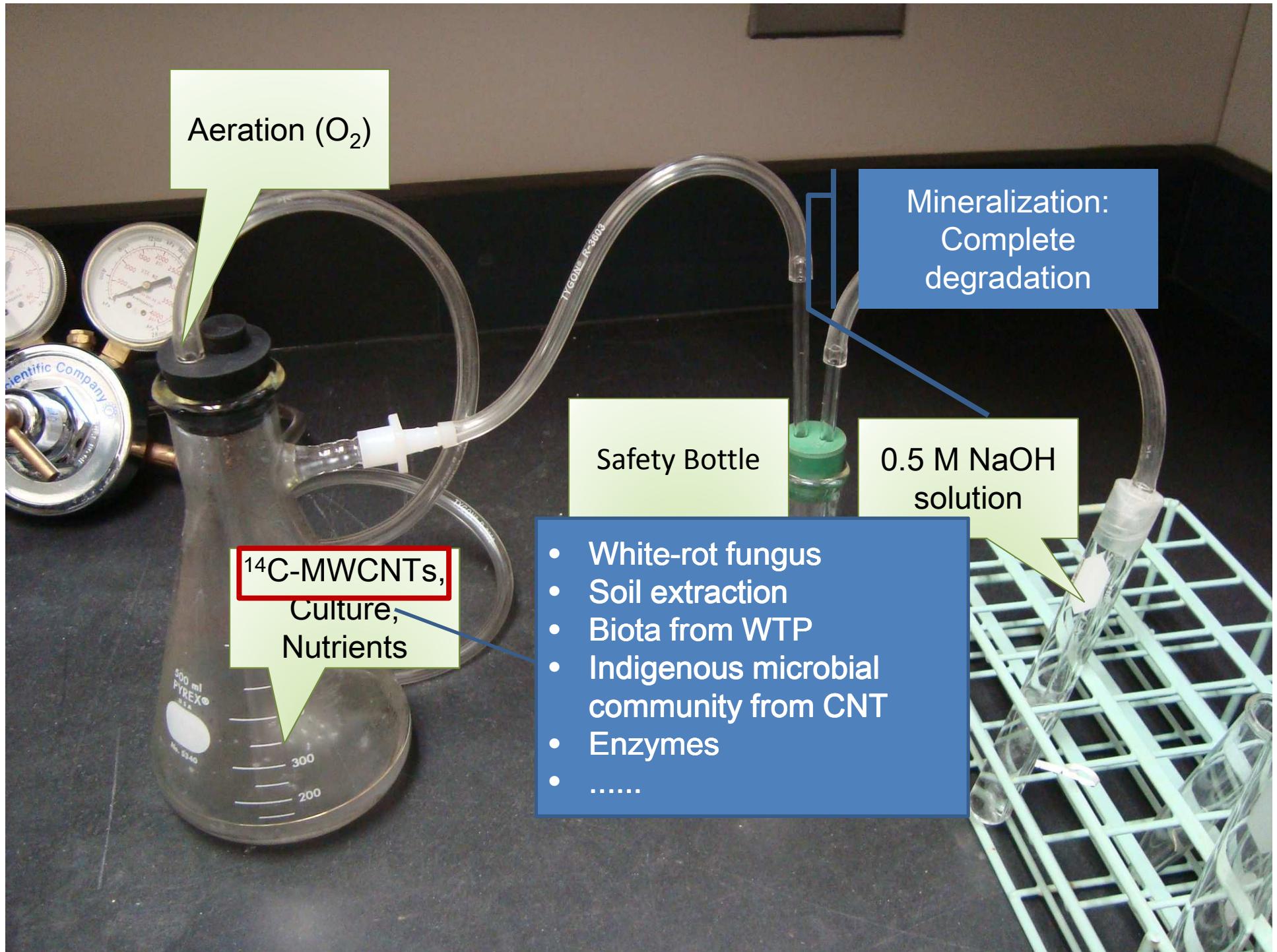
$sp^2$  orbital  
[wps.prenhall.com](http://wps.prenhall.com)



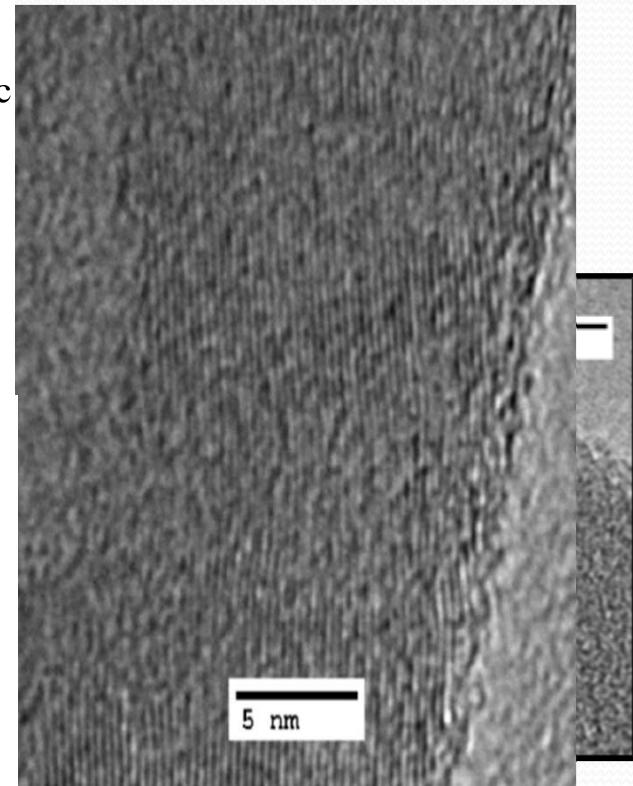
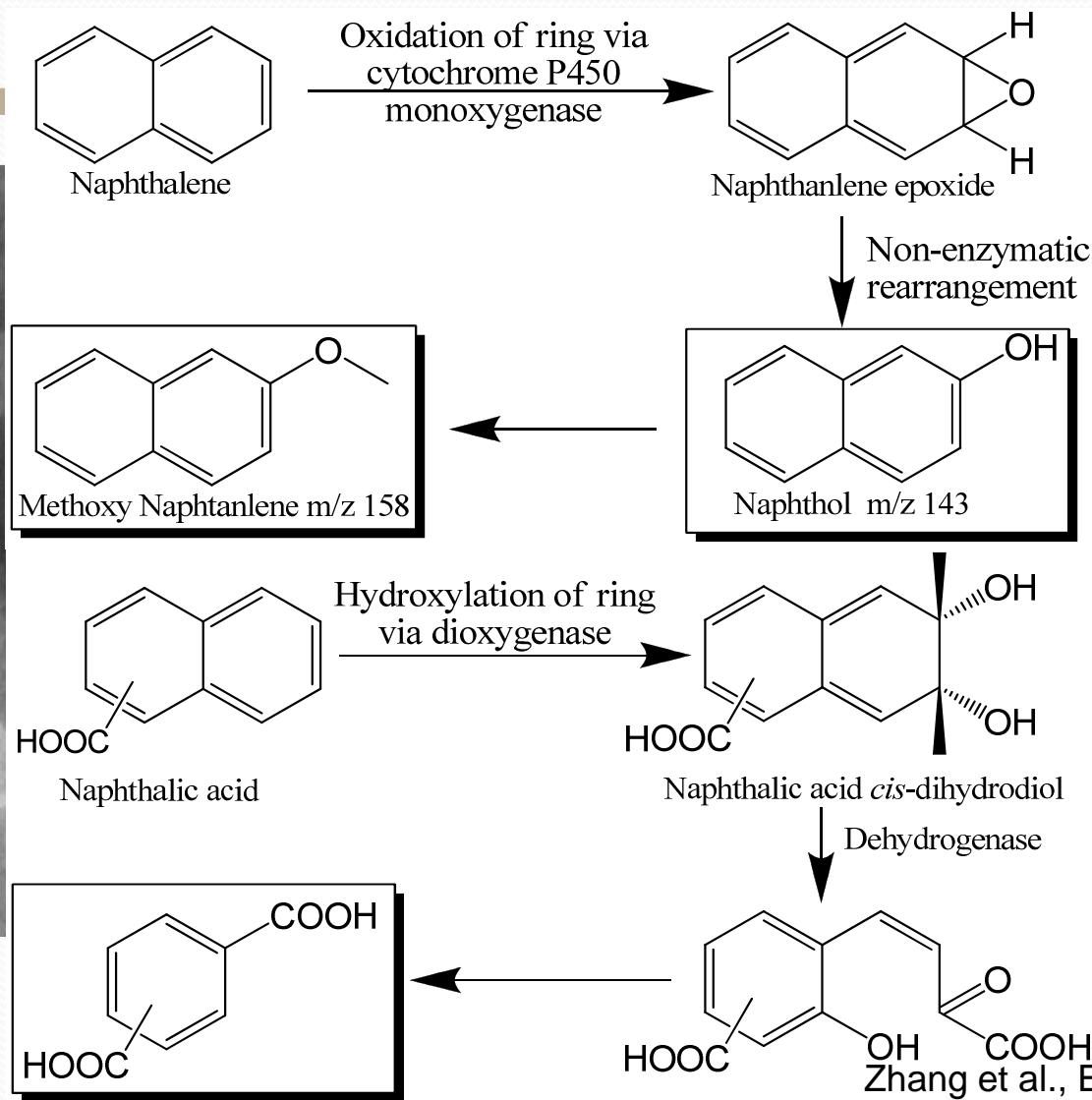
- Aromatic rings
- Inert
- → Persistent



MWCNT  
[wapedia.com](http://wapedia.com)

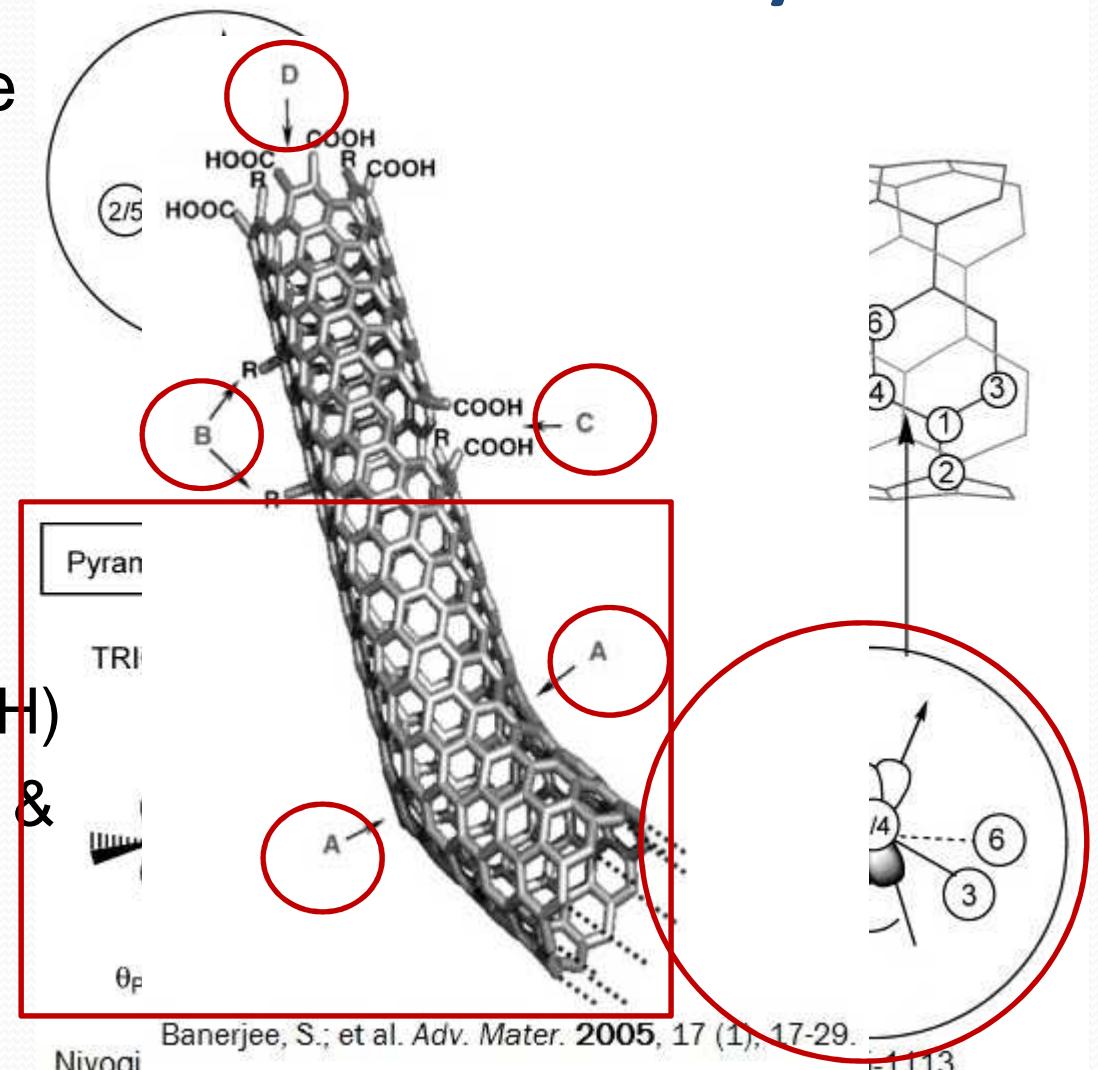


# Degradation Pathway



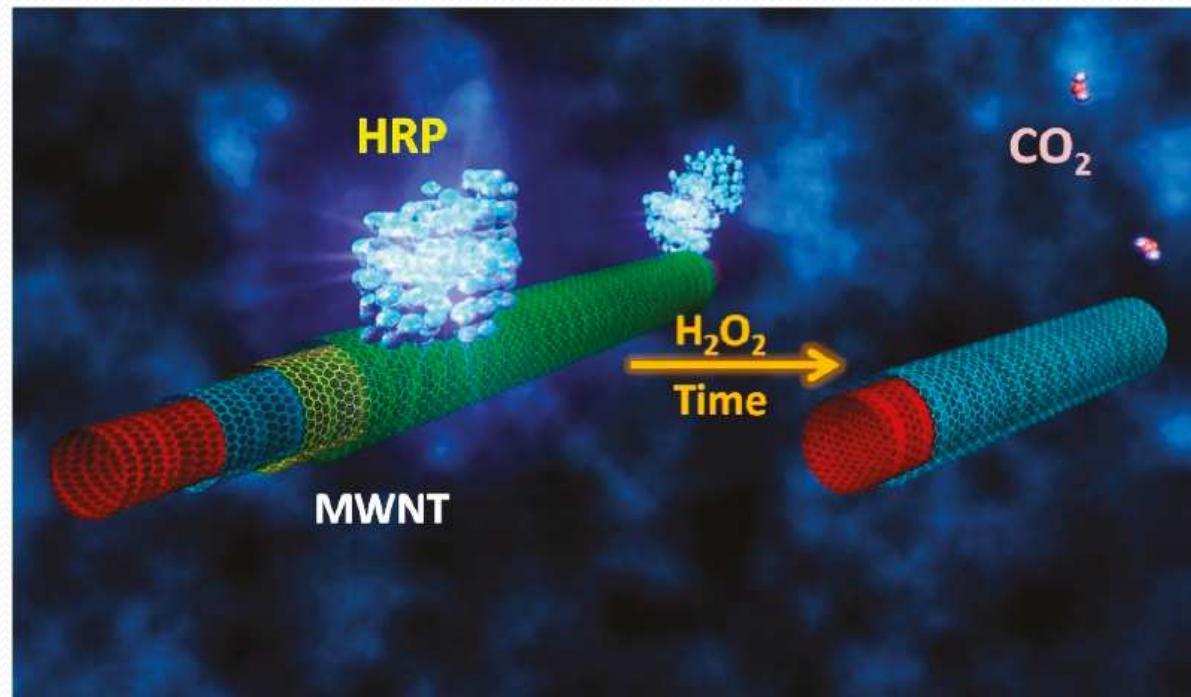
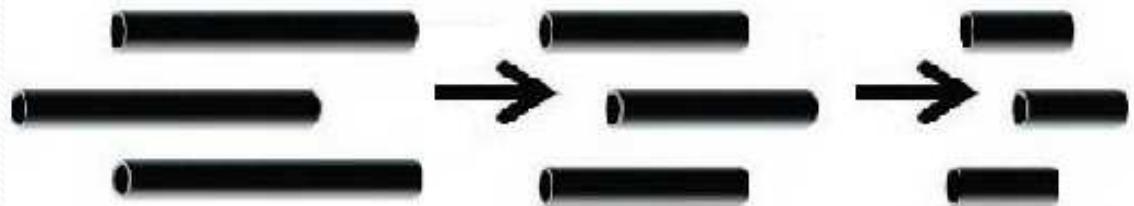
# Carbon Nanotube Reactivity

- Backbone: Curvature
  - Pyramidalization
  - Misalignment
- Structural Defects
  - A. Pentagons or Heptagons
  - B.  $sp^3$ -hybridized defects ( $R = H$  or  $OH$ )
  - C. Functional Groups & Holes
  - D. Open Ends

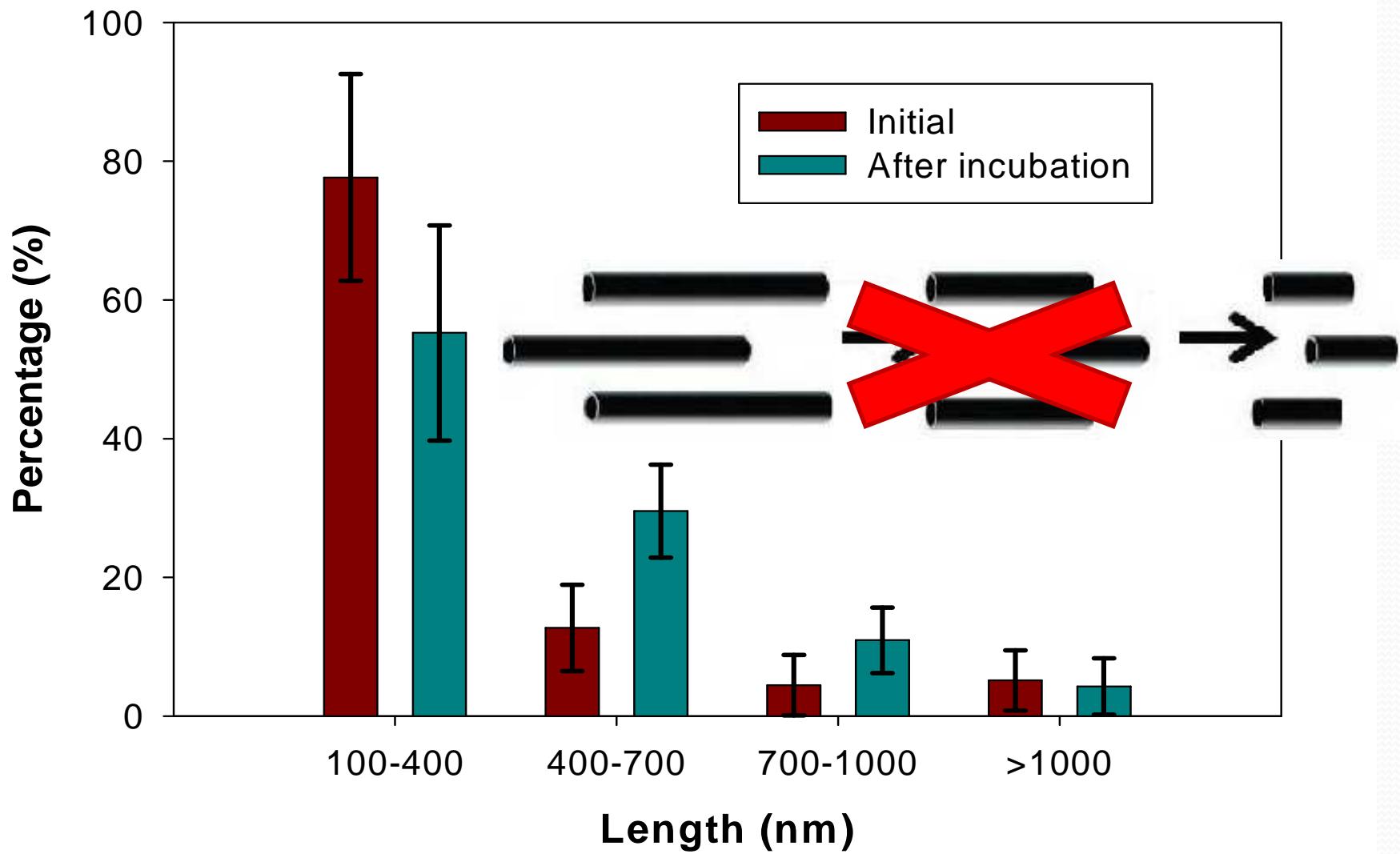


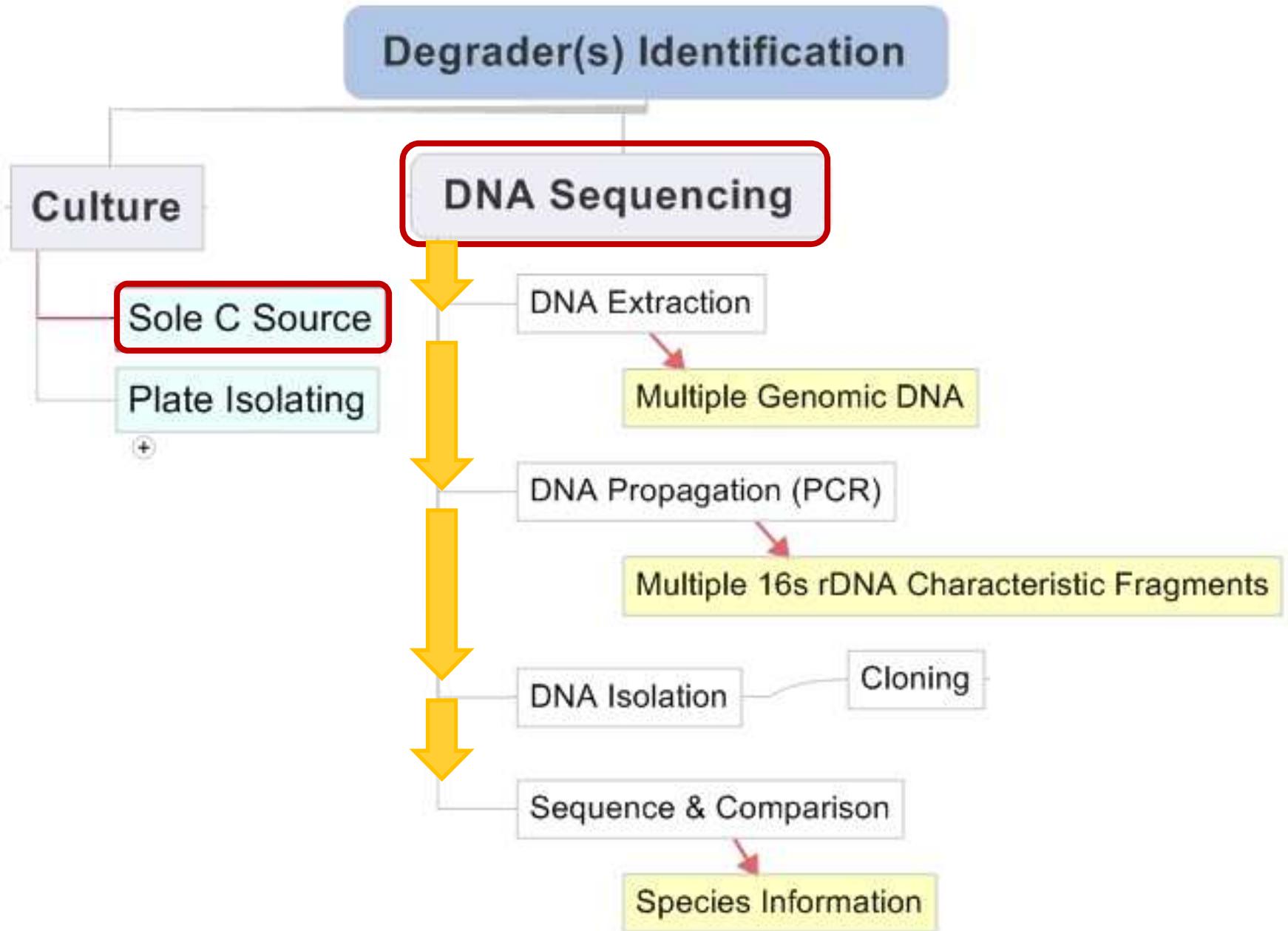
# Chop, peel, or both?

- Chop:
  - Shortening length
- Peel: Decreasing diameter



# Individual length: SEM images





# Sequence Results

## Proteobacteria

Beta Proteobacteria

burkholderiales

Burkholderiaceae

① Burkholderia

Comamonadaceae

② Delftia

Gamma Proteobacteria

Xanthomonadales

Xanthomonadaceae

③ Stenotrophomonas

Soil rhizospheres  
Groundwater  
Surface water

Gram-negative

Aerobic

Degrad Aromatic  
Compounds

Individual/Consortium  
Co-metabolic Systems

# Degraders identification



*Stenotrophomonas  
maltophilia*

Rod-shaped

Enzymes Degrading PAH

Phenol Monooxygenase

Catechol 1,2-dioxygenase

Oval-shaped

Enzymes Degrading PAH

Toluene 3-monooxygenase

Catachol 2,3-dioxygenase

Other degraders?

*Delftia acidovorans*

Rod-shaped

Enzymes degrading PAH

1,2-dioxygenase

4-hydroxybenzoate 3-monooxygenase

# Outline



**0. Background**



**1. Biotransformation**



**2. Phase distribution**



**3. Accumulation & toxicity**

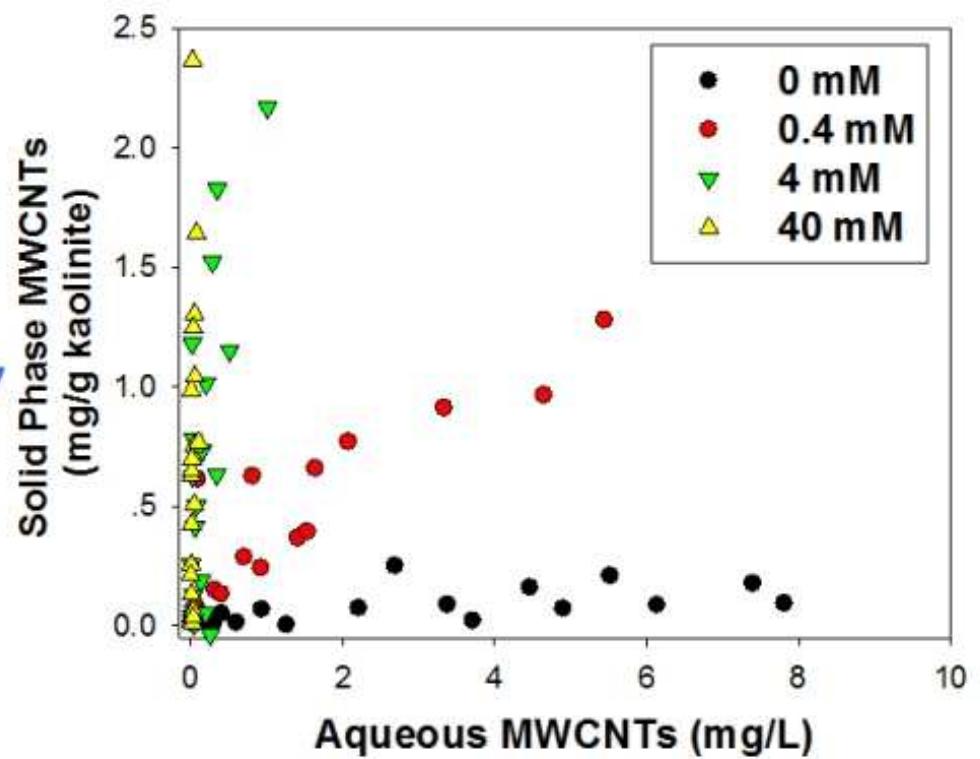
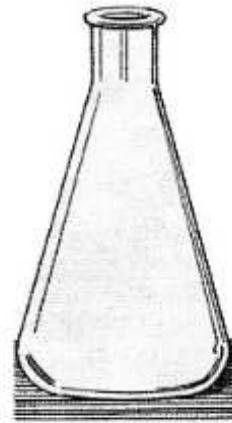
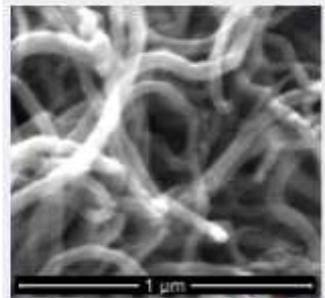


**4. Conclusions & acknowledgement**

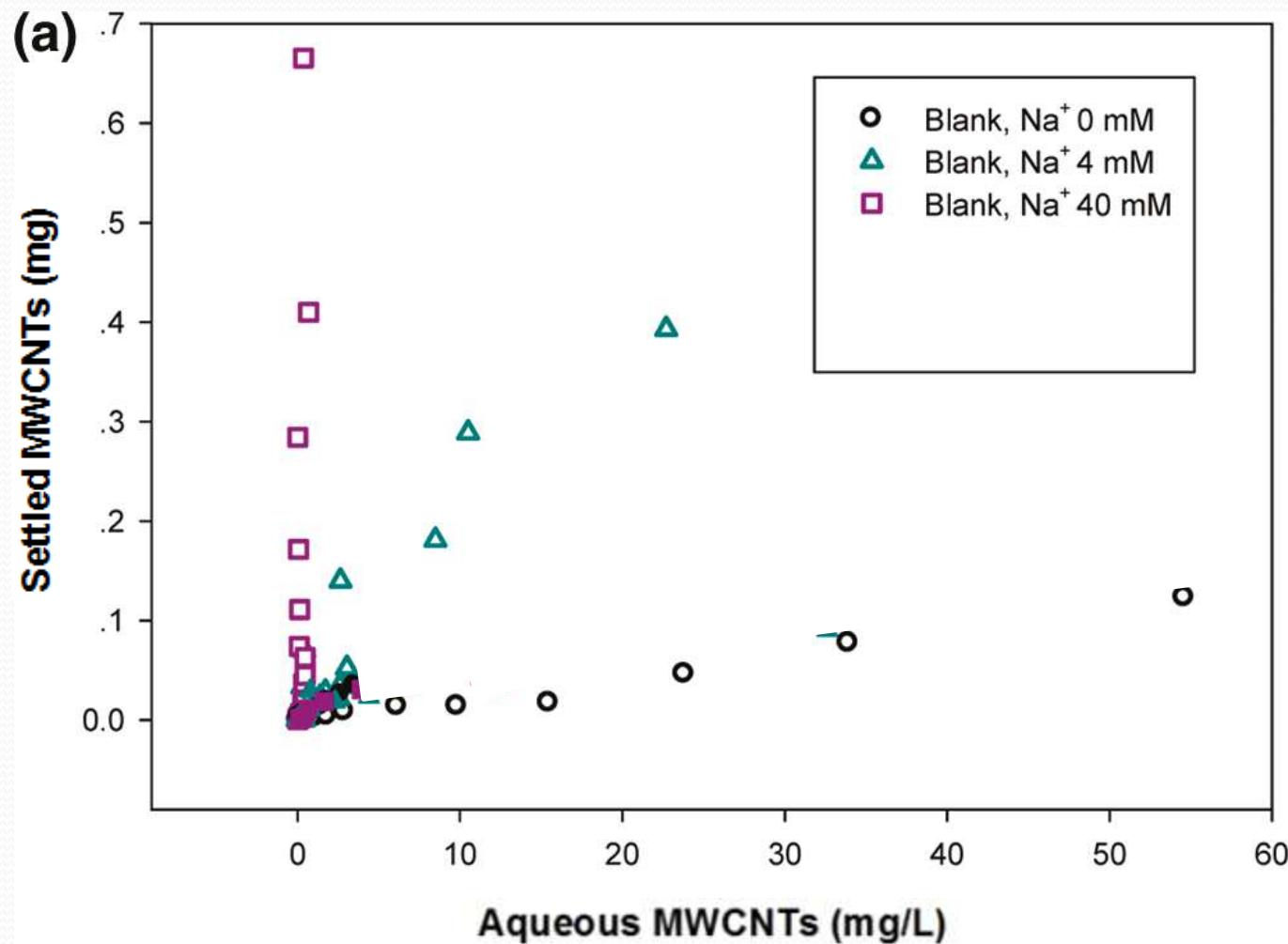
# Phase Distribution

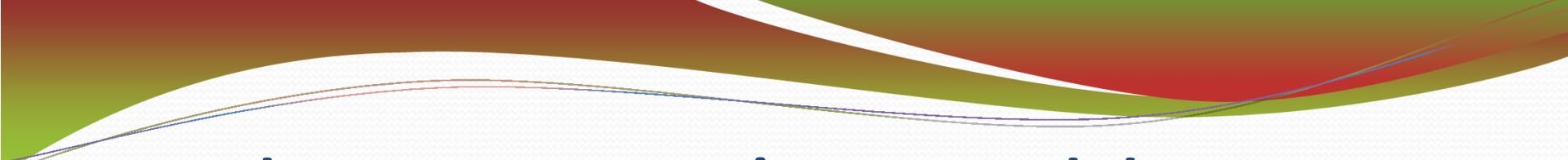
multiwall carbon  
nanotubes

soil minerals



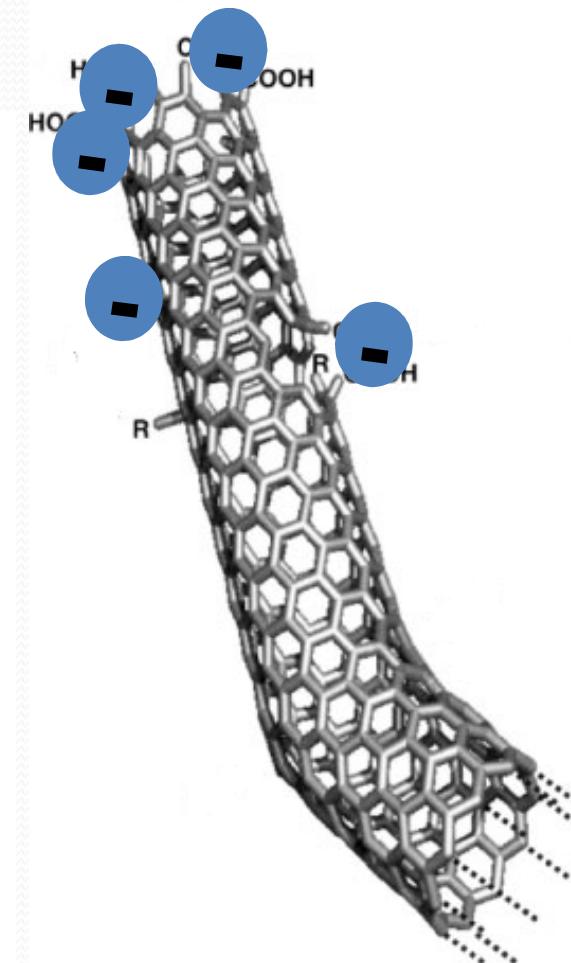
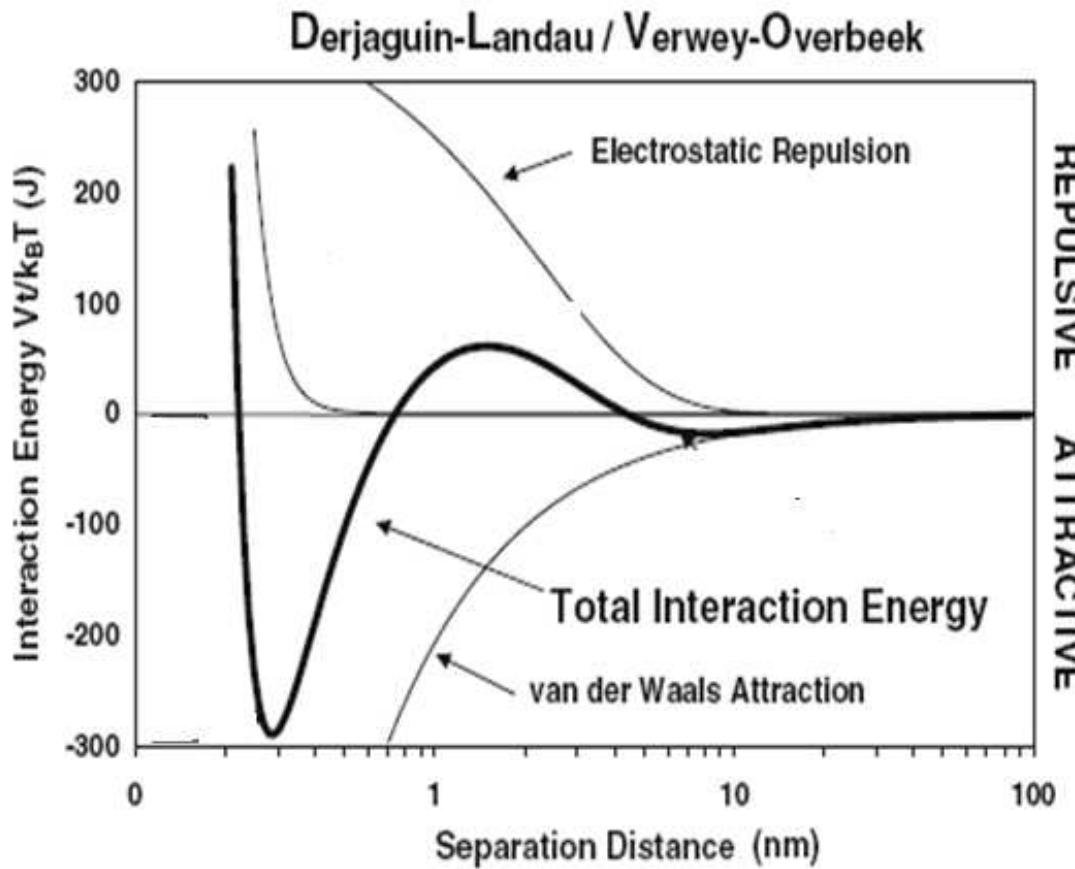
# Governing Process: Settling

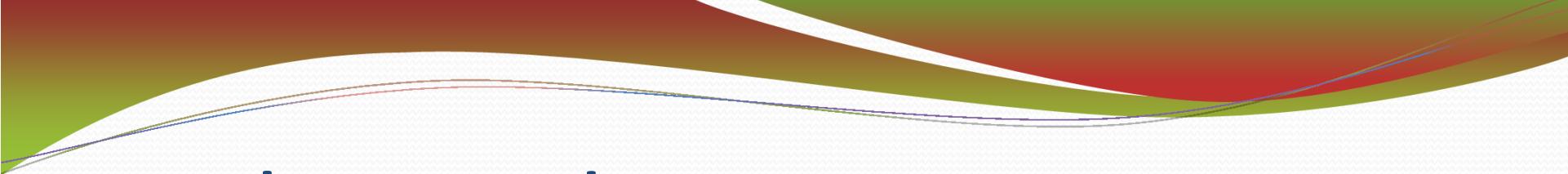




# Settle or not, it's a problem...

- Surface functional groups





# Settling and Sorption

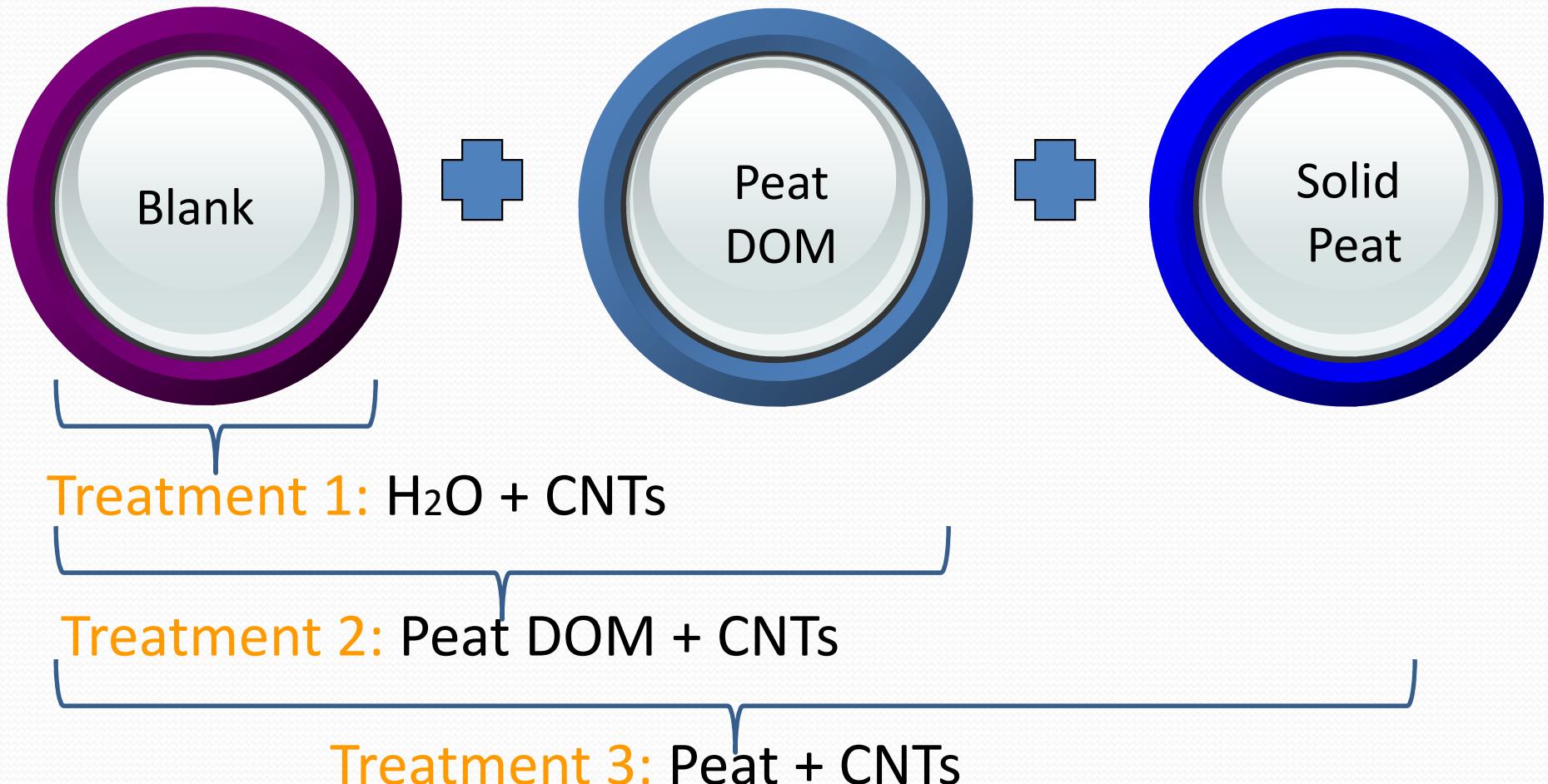
## Aqueous conditions

- Ionic strength
- pH
- Dissolved organic matters (DOM)

## Soil/Sediment

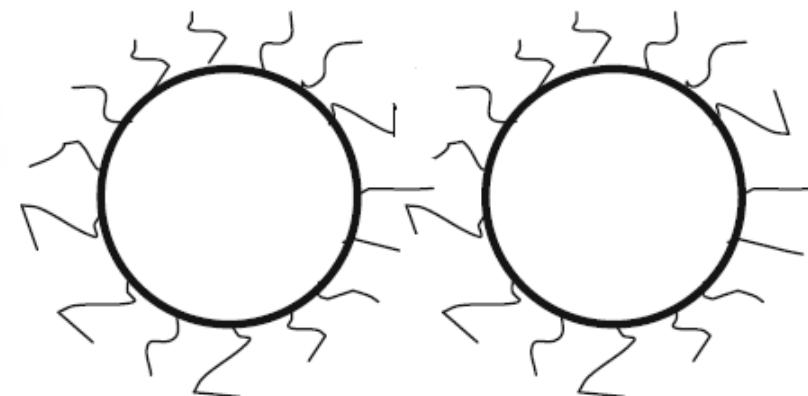
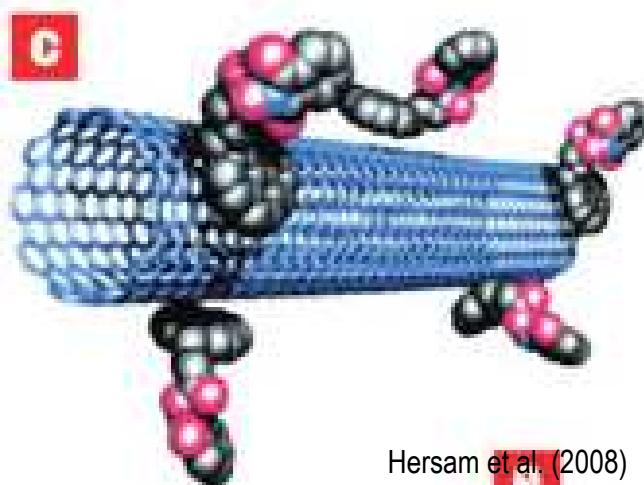
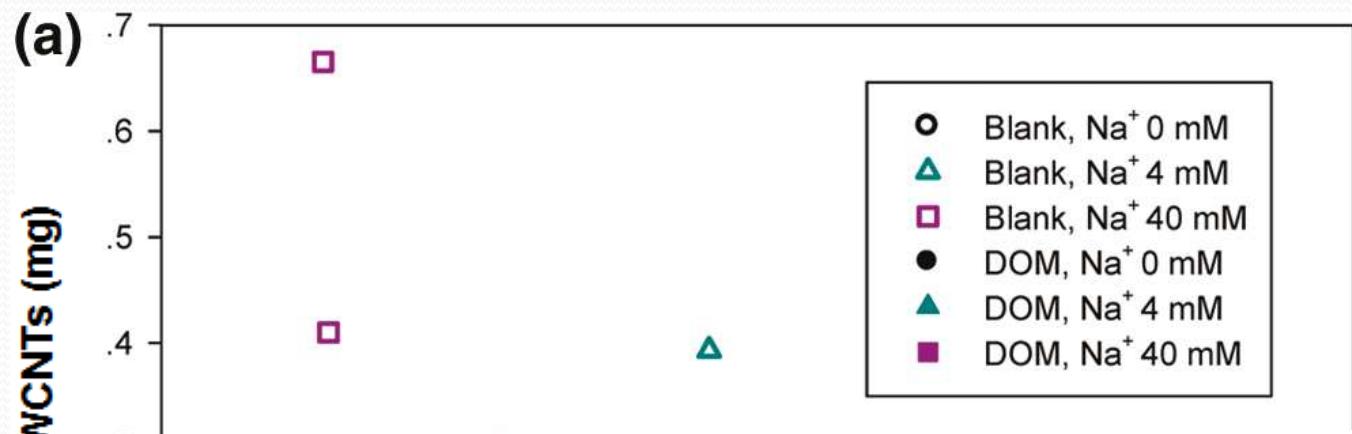
- Soil organic matters (SOM)
  - Peat
  - Shale

# Three Treatments



# Settling: Effect of DOM

- DOM help disperse MWCNTs



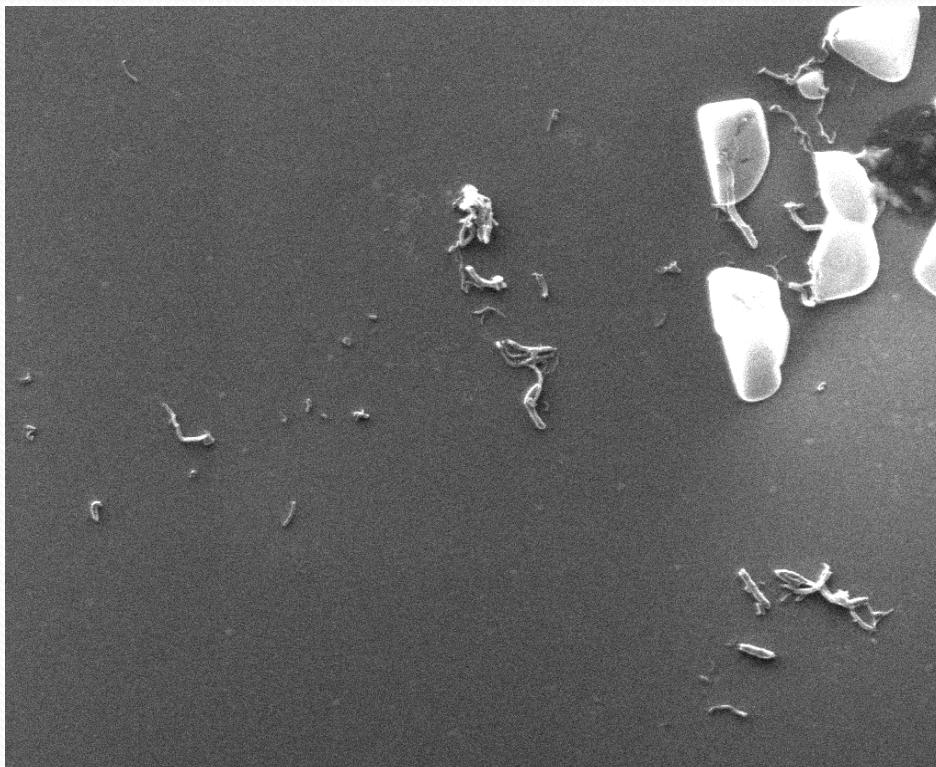
Hersam et al. (2008)

Aqueous MWCNTs (mg/L)

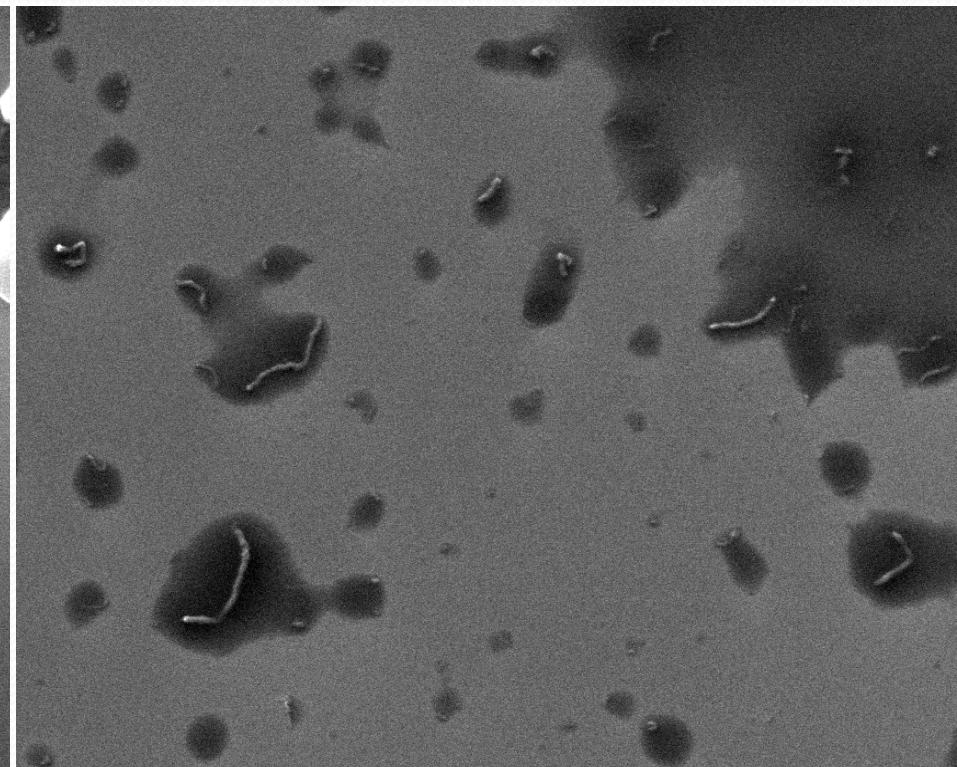
# SEM Images after Treatments

Counterion ( $\text{Na}^+$ ) treatment

DOM treatment

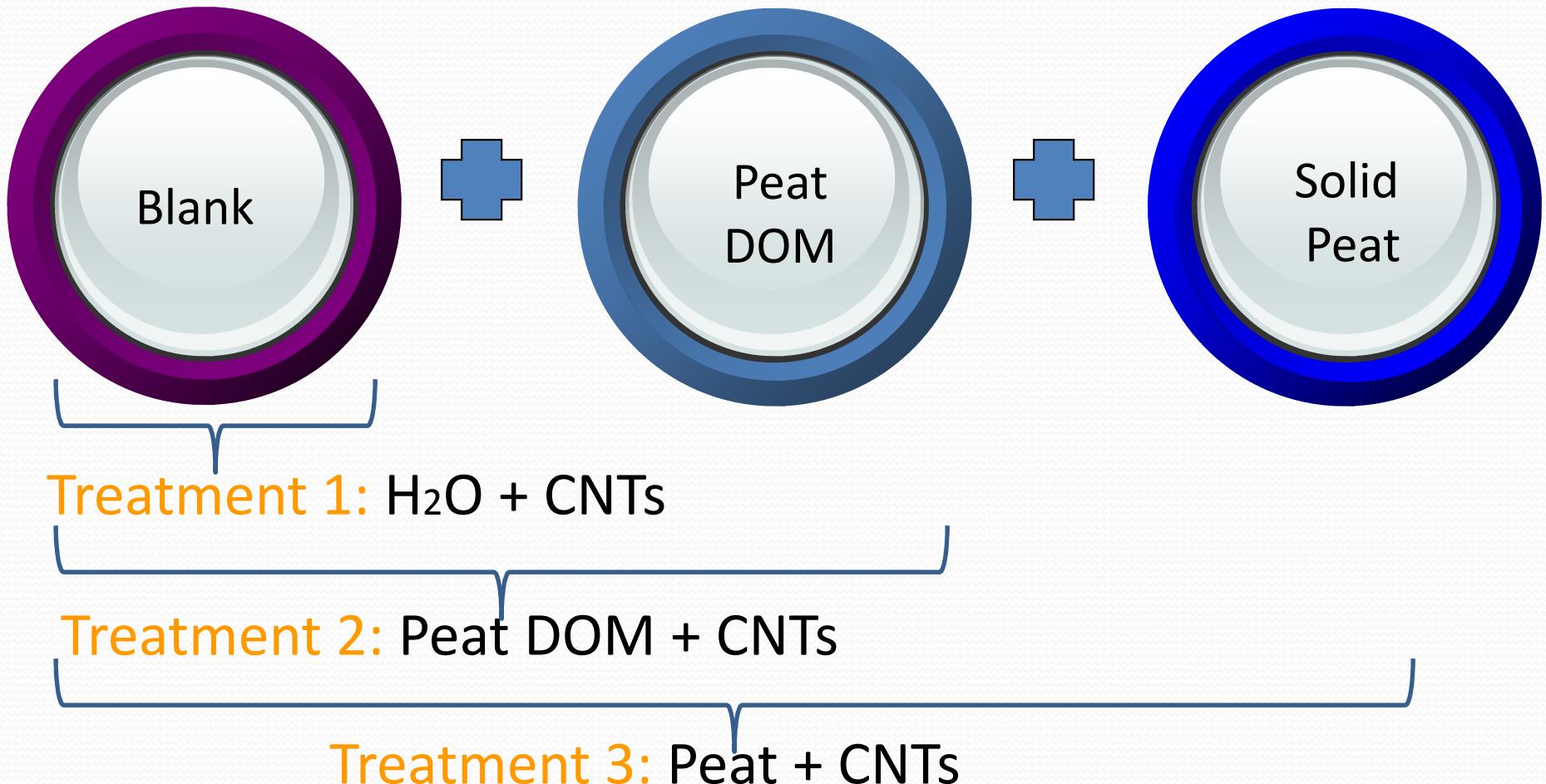


8/10/2009 | HV | mag □ | WD | 3 μm | Quanta FEG  
3:20:17 PM | 20.00 kV | 40 000 x | 9.0 mm

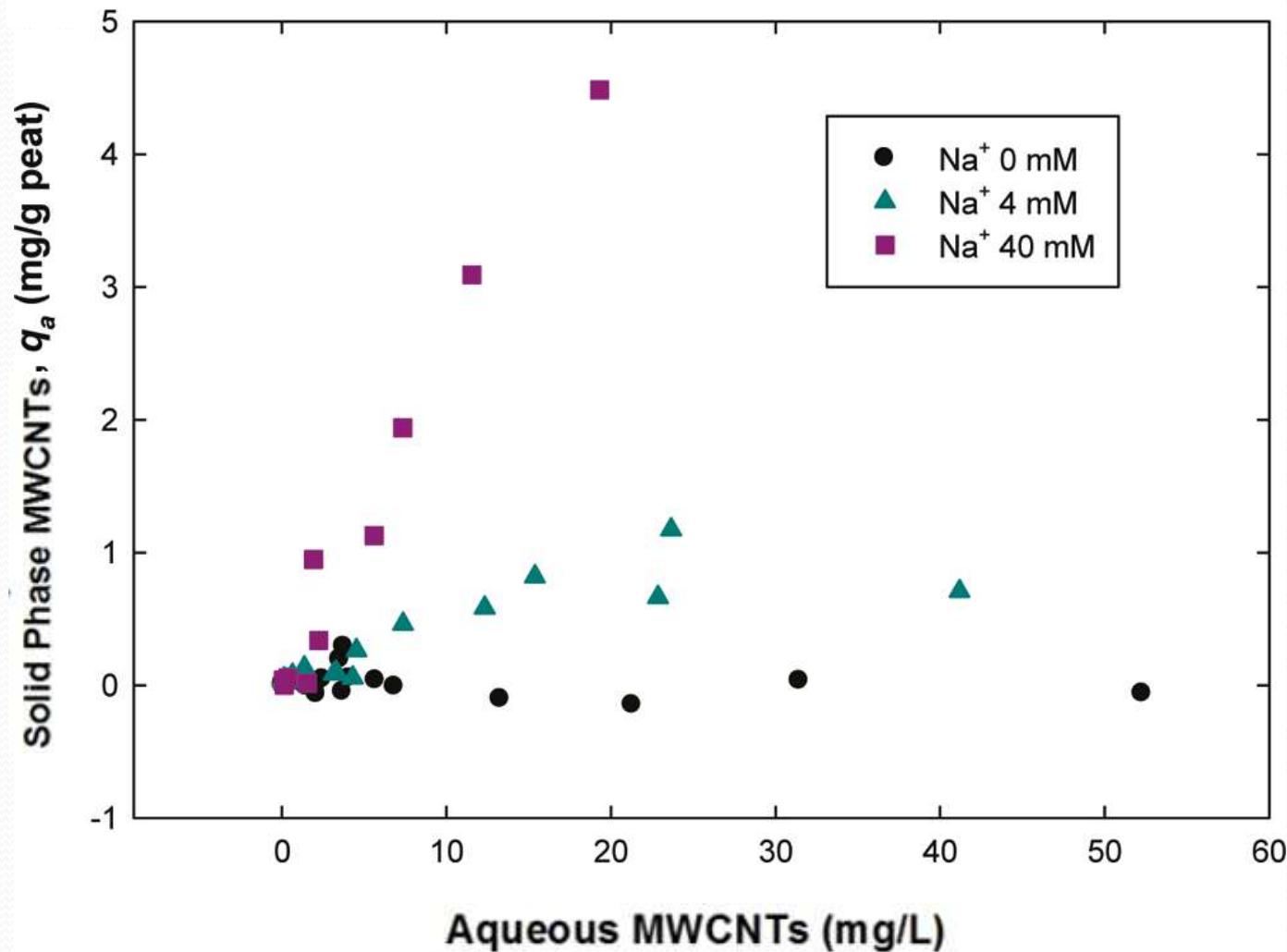


10/2/2009 | HV | mag □ | WD | 5 μm | Quanta FEG  
7:05:53 PM | 30.00 kV | 20 000 x | 11.6 mm

# Three Treatments



# Solid Peat Sorb MWCNTs



# Environmental Conditions

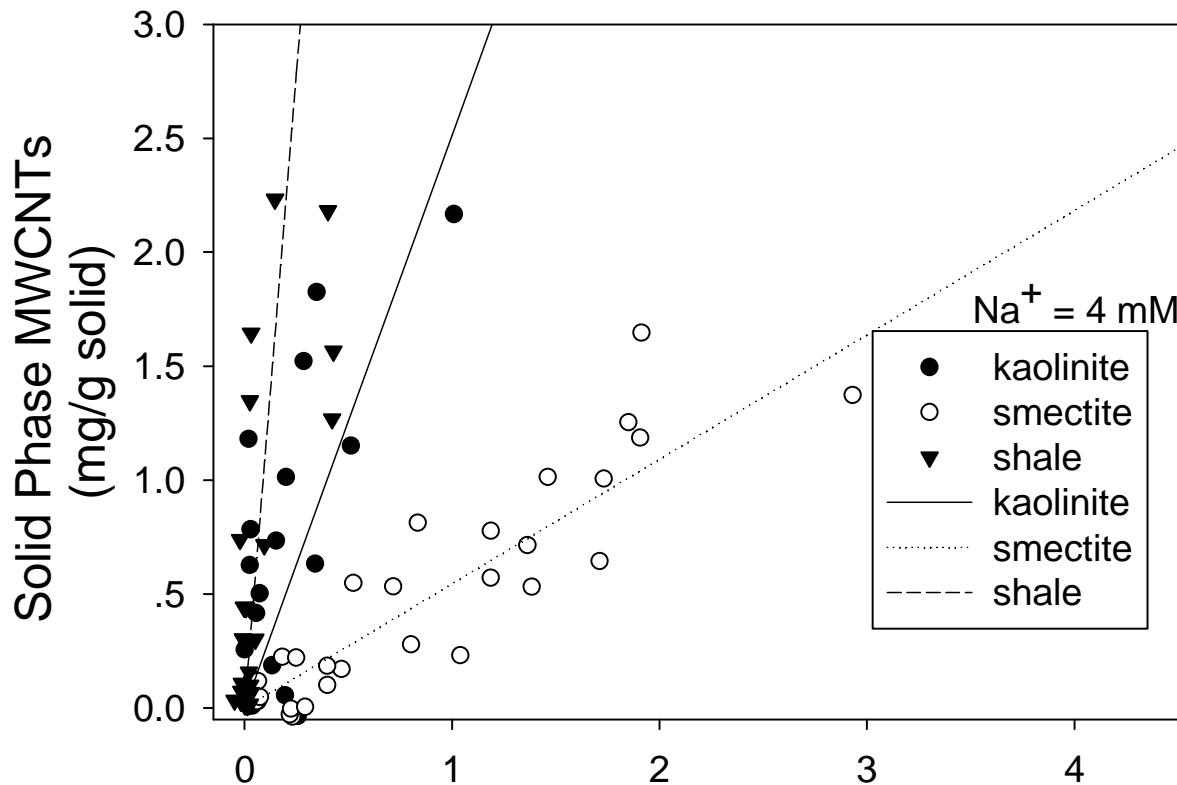
## Aqueous

- Ionic strength
- pH
- Dissolved organic matters (DOM)

## Soil/Sediment

- Soil organic matters (SOM)
  - Peat
  - Shale
- Clay minerals
  - Kaolinite (1:1)
  - Smectite (2:1)

# Phase Distribution: Clay & Shale



- Electrostatic interaction
- Insoluble SOM → strong sorption

**Table 3**  
Electrophoretic mobility values of clay particles and MWCNTs ( $\mu\text{m cm/Vs}$ ).

Zhang et al., Environ. Poll. 2013, 181, pages 335-339

Sodium conc. (mM)	Kaolinite	Smectite	Shale	MWCNTs
0	-2.17 (0.03)*	-2.78 (0.29)	-3.18 (0.57)	-1.51 (0.02)
0.4	-1.32 (0.02)	-2.14 (0.06)	-3.60 (0.73)	-1.10 (0.08)
4	-0.52 (0.02)	-1.18 (0.01)	-3.69 (0.61)	-0.95 (0.14)
40	0.01 (0.37)	-0.65 (0.08)	-3.11 (1.29)	-0.94 (0.06)

# Extended-DLVO Modeling

