UNIVERSITY OF CALIFORNIA

UC CEIN Center for Environmental Implications of Nanotechnology

# Long term colloidal stability and metal leachate of CNTs in natural waters

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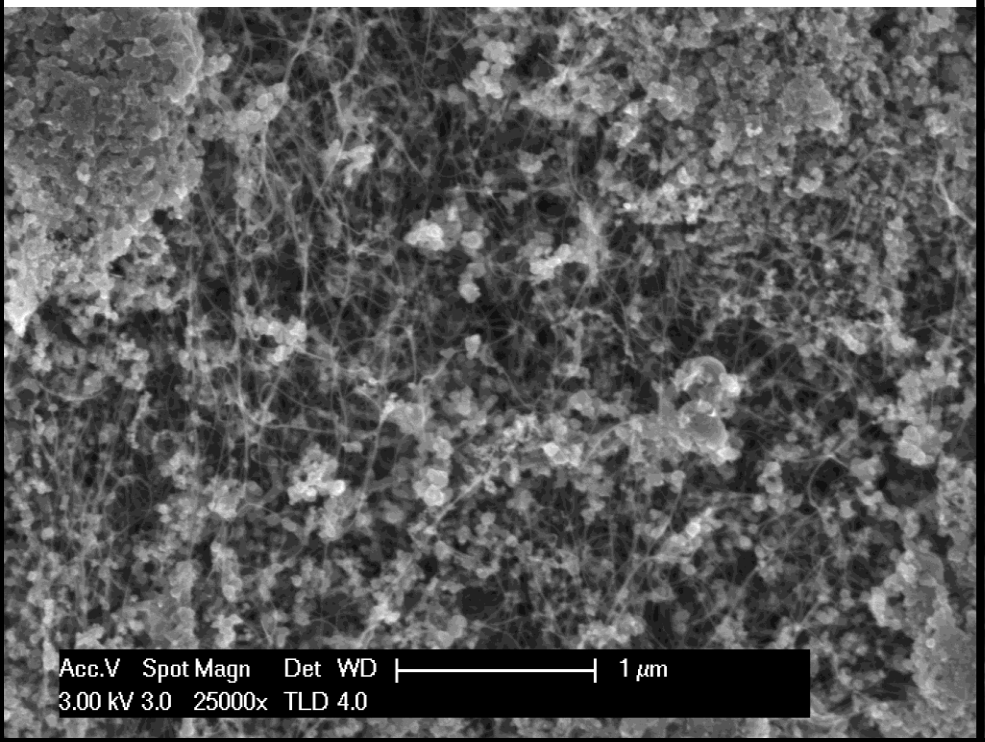
# Single-walled carbon nanotubes (SWCNTs) are…

- Rolled-up graphene sheets that are 0.5 – 1.5 nm in diameter and 0.4 – 2 µm long
- Applied in energy storage, microelectronics, composite materials, drug delivery etc
- Production rate >3,000 metric tons/yr as at 2011

Saleh et al. *Environ. Sci. Technol.*, **2008**, *42* (21): 7963–7969
FutureMarkets 2012

# Examples

| Hipco Raw (HR) | Hipco Purified (HP) |
| --- | --- |
|  |  |

# Research questions

1. How do unfunctionalized SWCNTs partition in when introduced into natural waters?
2. And how does temperature variation affect the stability of SWCNT in natural waters?
3. What fraction of metal impurities in SWCNT may leach out when exposed to natural waters?

1.

How do unfunctionalized SWCNTs partition in when introduced into natural waters?

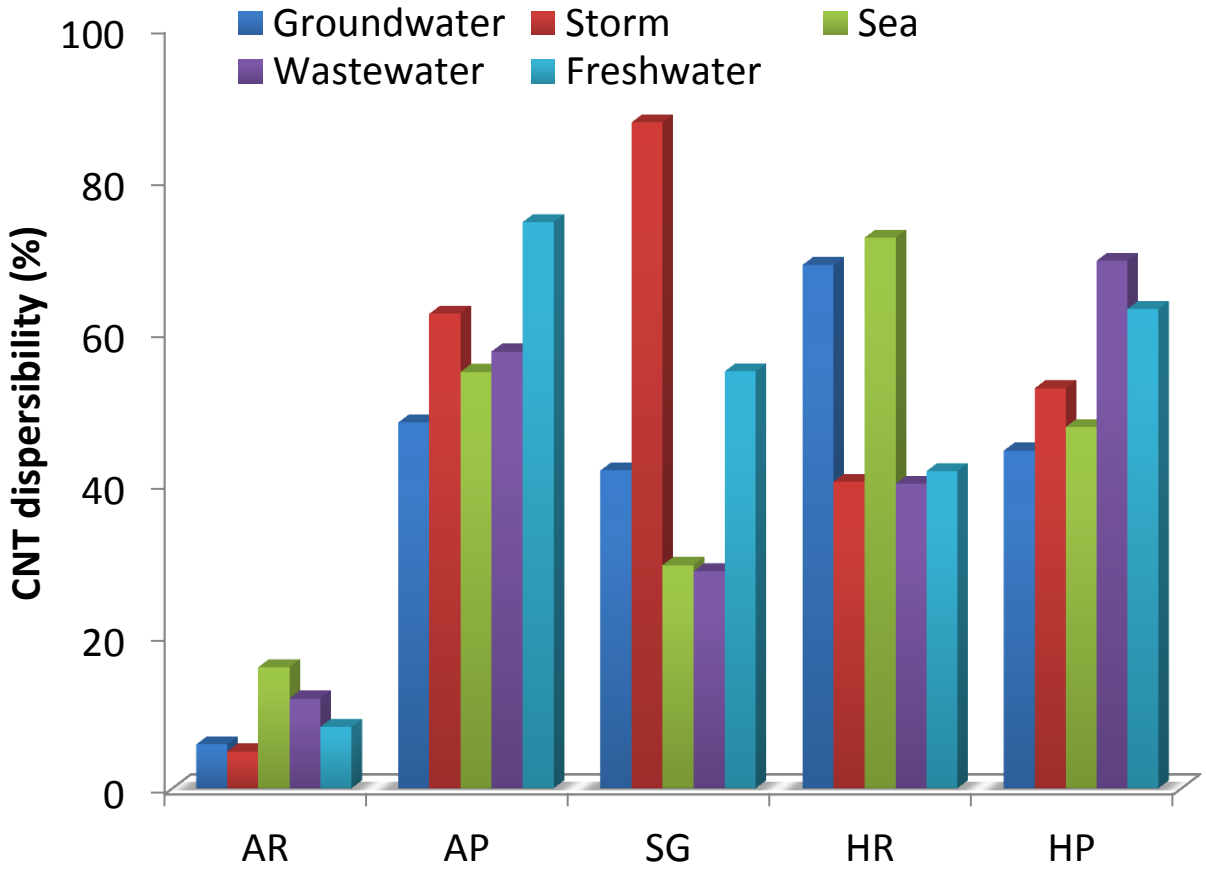
# Commercial SWCNTs

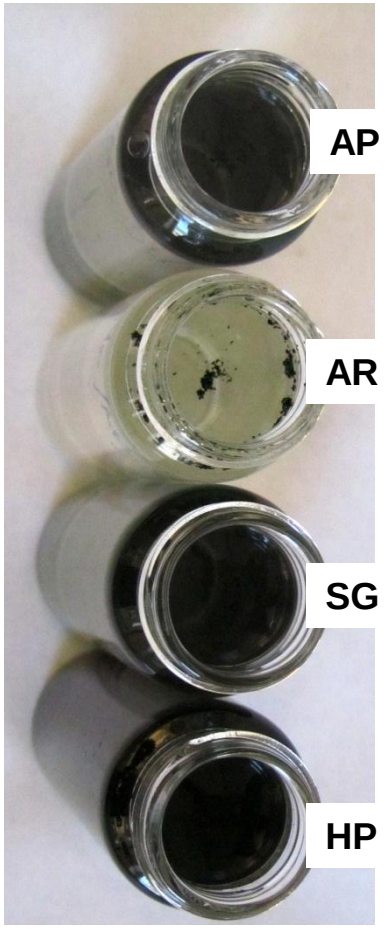
| Source | As Prepared (R) | Purified (P) |
|---|---|---|
| SweNT (CoMoCat) | | SG65 |
| NanoIntegris (HiPco) | HR | HP |
| Carbon Solutions (P2) | AR | AP |

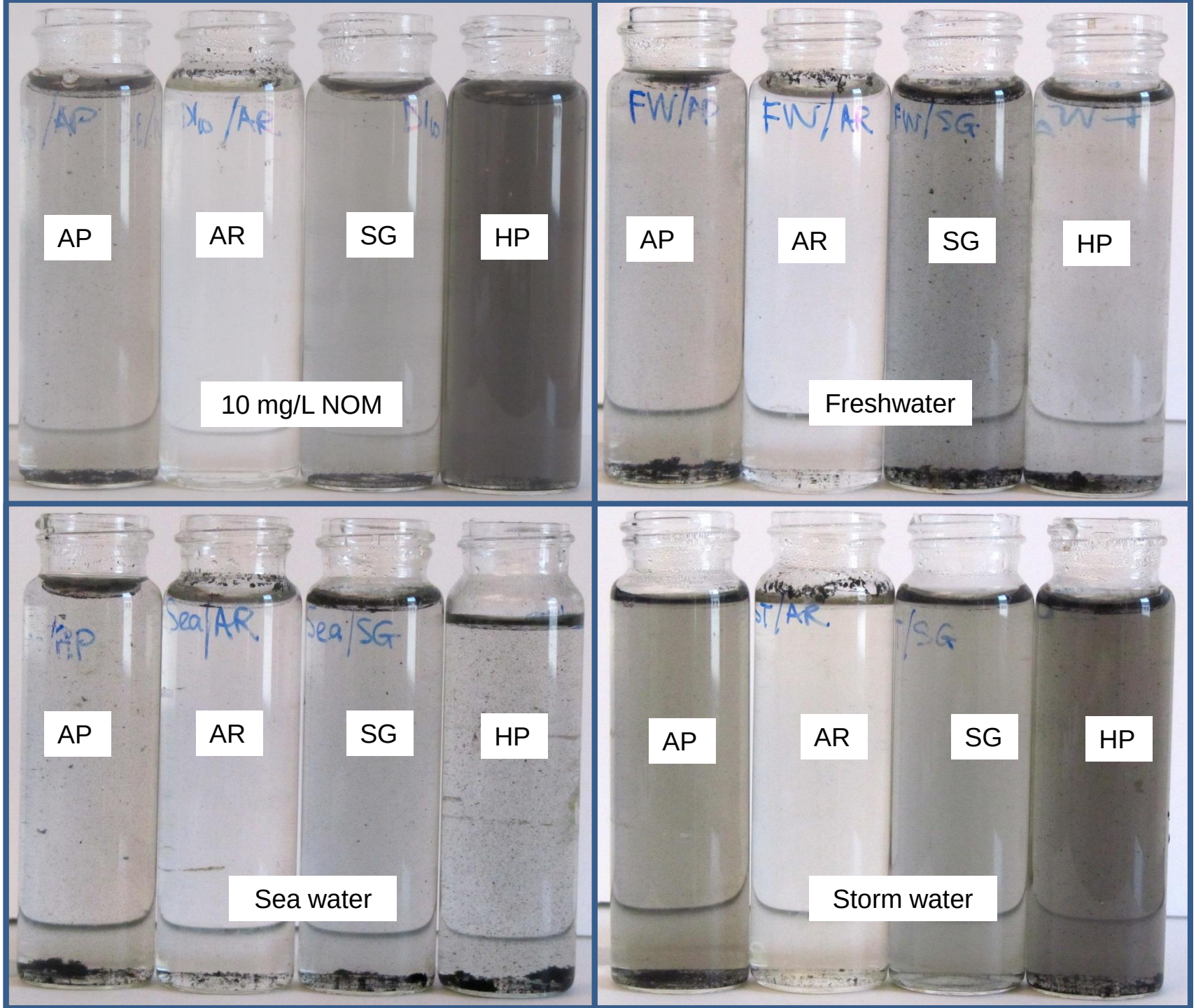
# Water characterization

| Media | pH | ZP (mV) | Conductivity (µS) | Redox (mV) | $UV_{254}$ |
|---|---|---|---|---|---|
| DI (DI) | 7.1 | -2.0 | 14.9 | 96.8 | 0 |
| DI + 10.0 mg/L NOM (DI+10) | 7.1 | -16.5 | 29.2 | 196.8 | 0.082 |
| Mineral water + 0.1 mg/L NOM (MW+0.1) | 7.8 | -4.3 | 87.4 | 159.6 | 0.002 |
| Mineral water + 1.0 mg/L NOM (MW+1.0) | 7.3 | -6.4 | 92.3 | 188.8 | 0.012 |
| Storm water (ST) | 7.7 | -5.5 | 285.0 | 166.5 | 0.242 |
| Groundwater (GW) | 7.5 | -2.5 | 1021.0 | 137.4 | 0.002 |
| Groundwater + 1.0 mg/L NOM (GW+1.0) | 6.8 | -10.0 | 1055.0 | 159.4 | 0.009 |
| Wastewater (WW) | 7.6 | 4.9 | 2430.0 | 123.8 | 0.098 |
| Sea water (Sea) | 7.3 | 39.6 | 33700.0 | 141.6 | 0.002 |

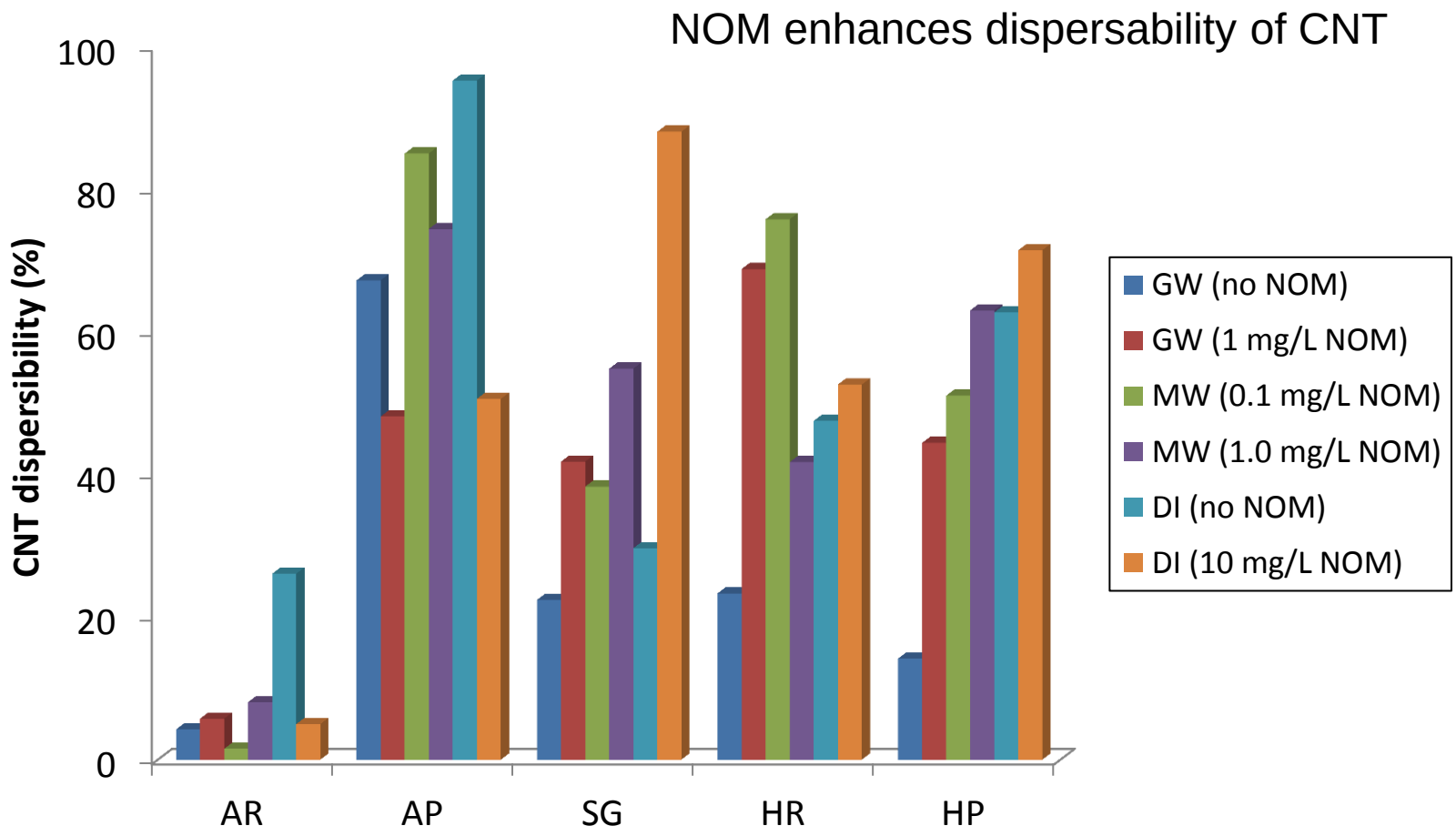
# "Dispersability"



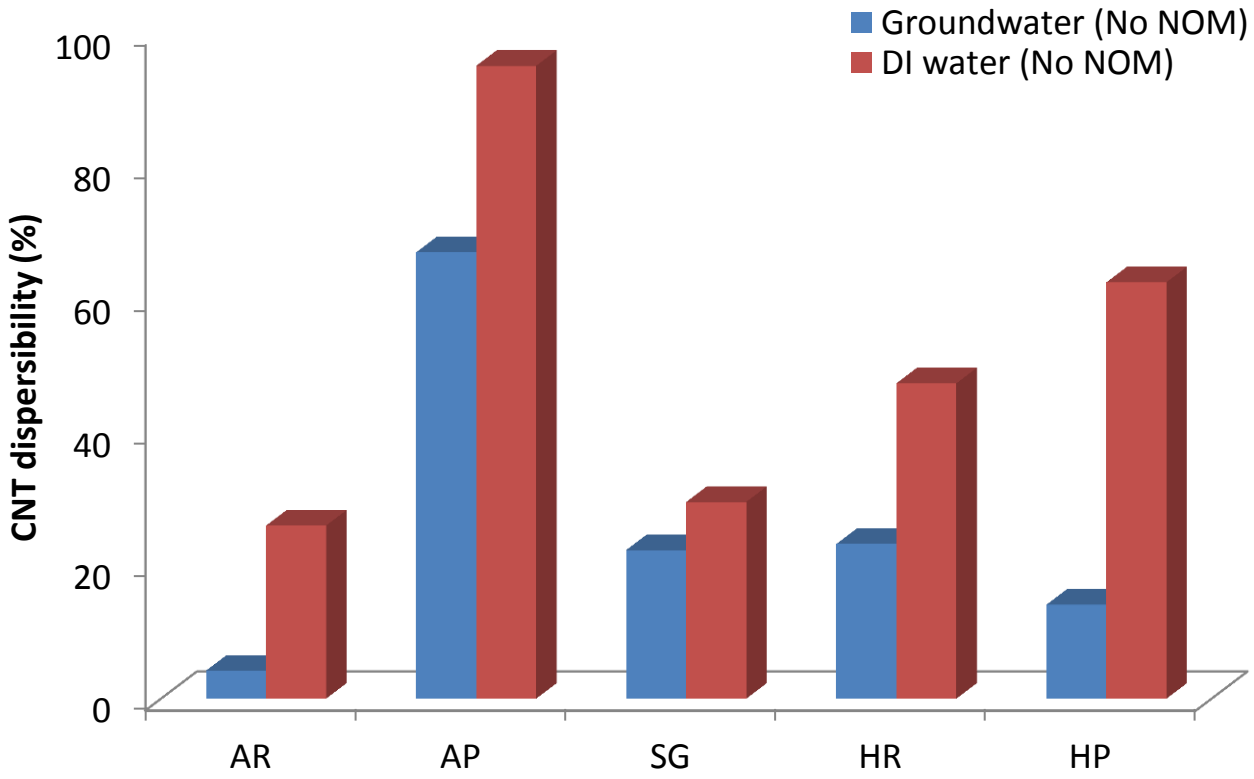




AP
AR
SG
HP
10 mg/L NOM
AP
AR
SG
HP
Freshwater
AP
AR
SG
HP
Sea water
AP
AR
SG
HP
Storm water

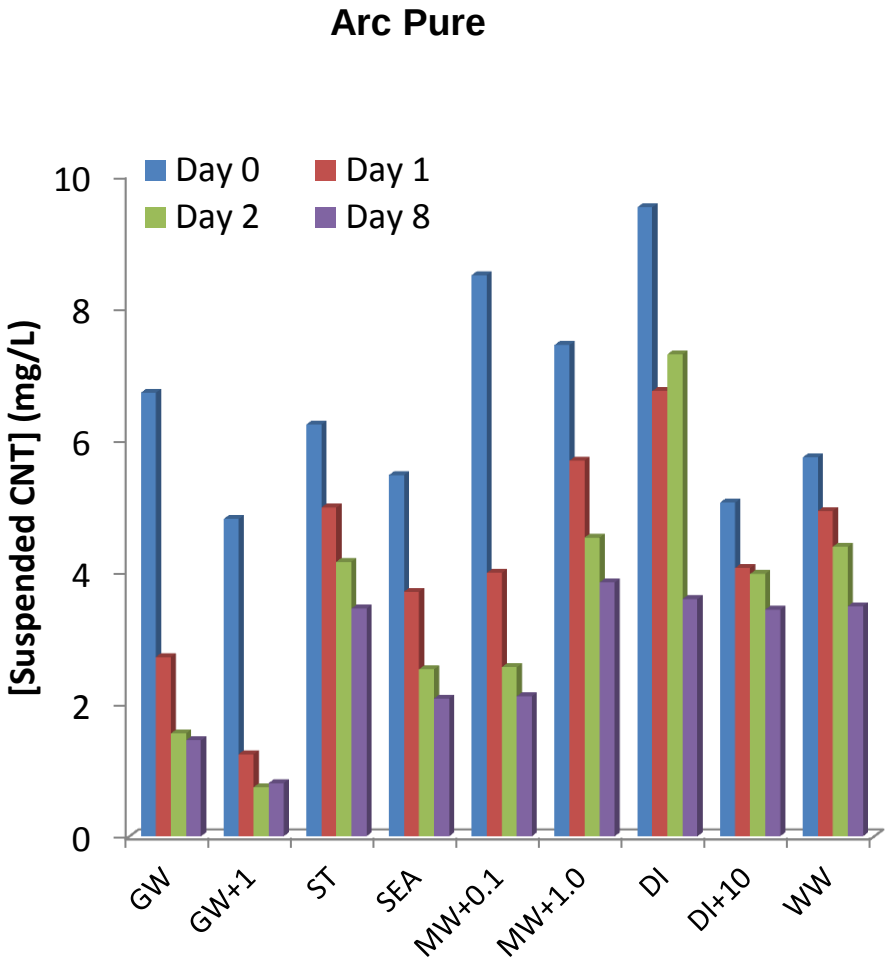
# "Dispersability"

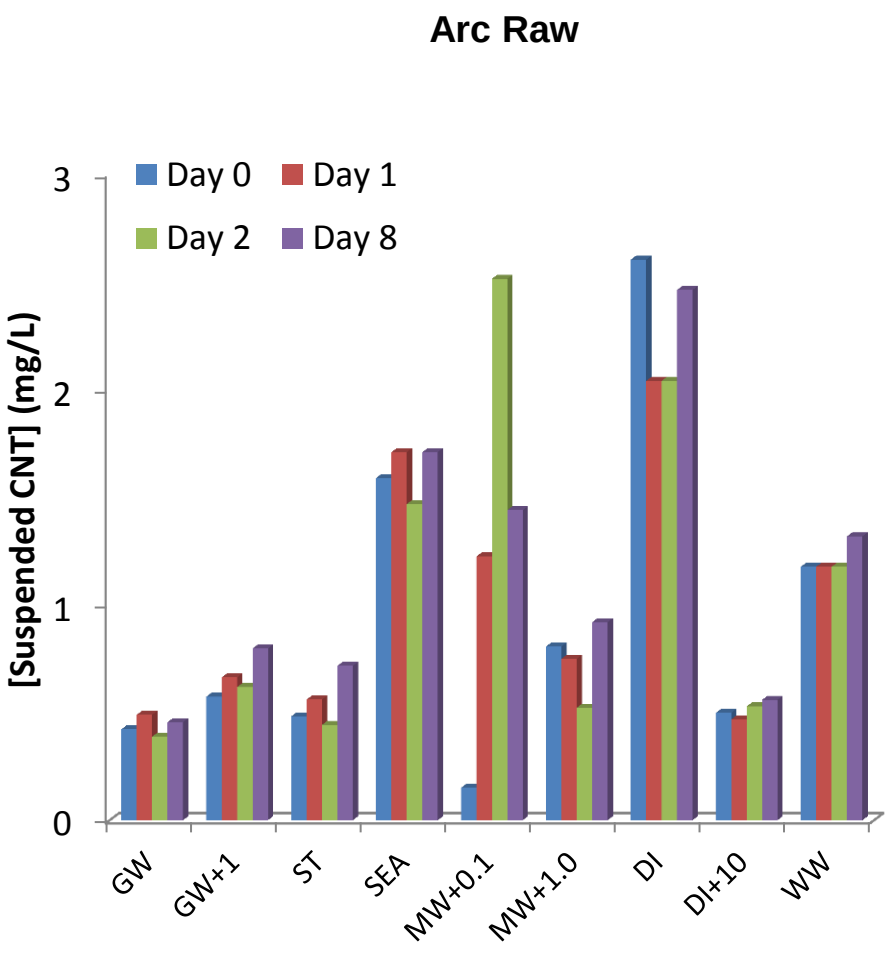


# "Dispersability"

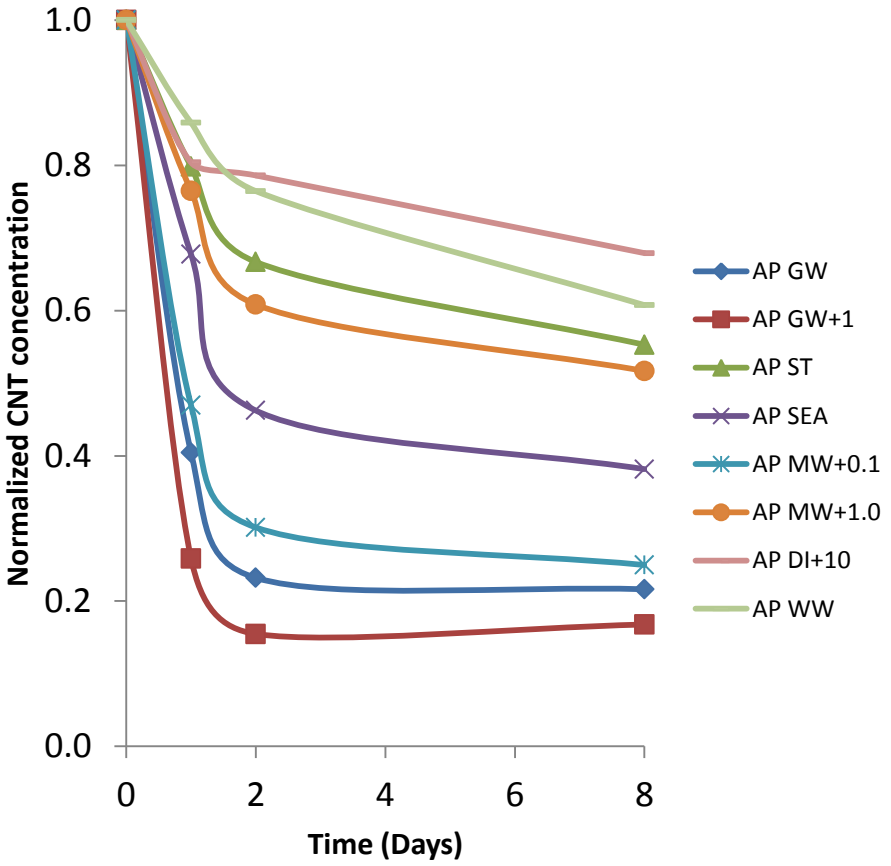


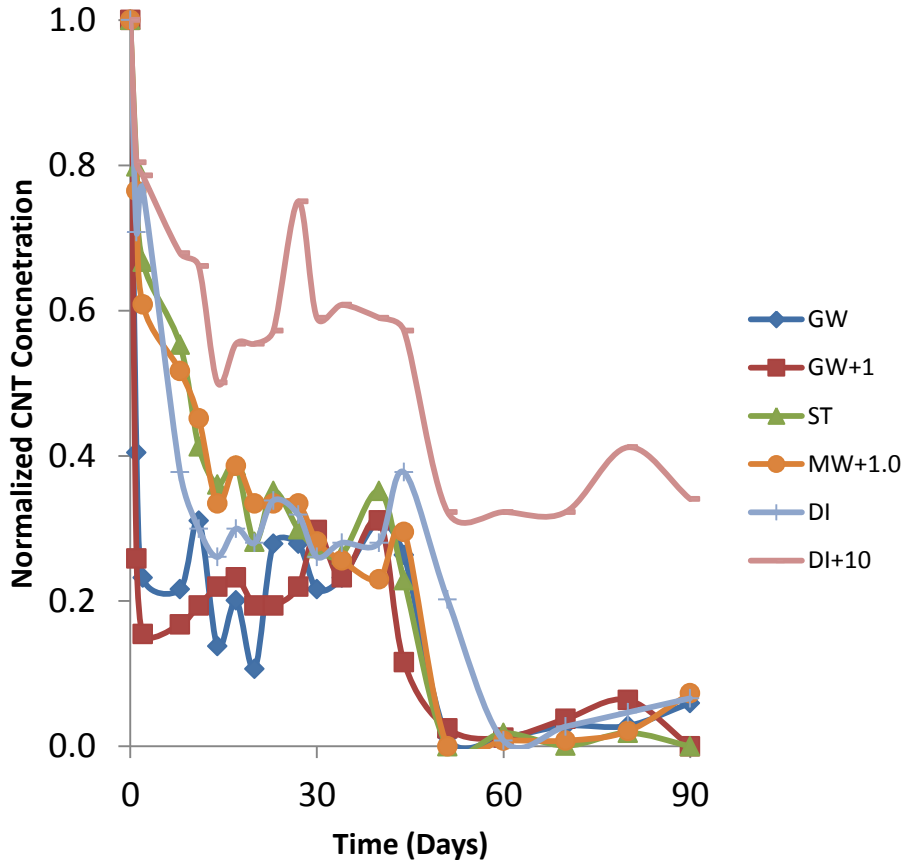
# Stability


Arc Pure
Day 0
Day 1
Day 2
Day 8
[Suspended CNT] (mg/L)
10
8
6
4
2
0
GW
GW+1
ST
SEA
MW+0.1
MW+1.0
DI
DI+10
WW


Arc Raw
Day 0
Day 1
Day 2
Day 8
[Suspended CNT] (mg/L)
3
2
1
0
GW
GW+1
ST
SEA
MW+0.1
MW+1.0
DI
DI+10
WW

# Stability


1.0
0.8
0.6
0.4
0.2
0.0
Normalized CNT concentration
0
2
4
6
8
Time (Days)
AP GW
AP GW+1
AP ST
AP SEA
AP MW+0.1
AP MW+1.0
AP DI+10
AP WW


1.0
0.8
0.6
0.4
0.2
0.0
Normalized CNT Concnetration
0
30
60
90
Time (Days)
GW
GW+1
ST
MW+1.0
DI
DI+10

2.

How does temperature variation affect the stability of SWCNT in natural waters?



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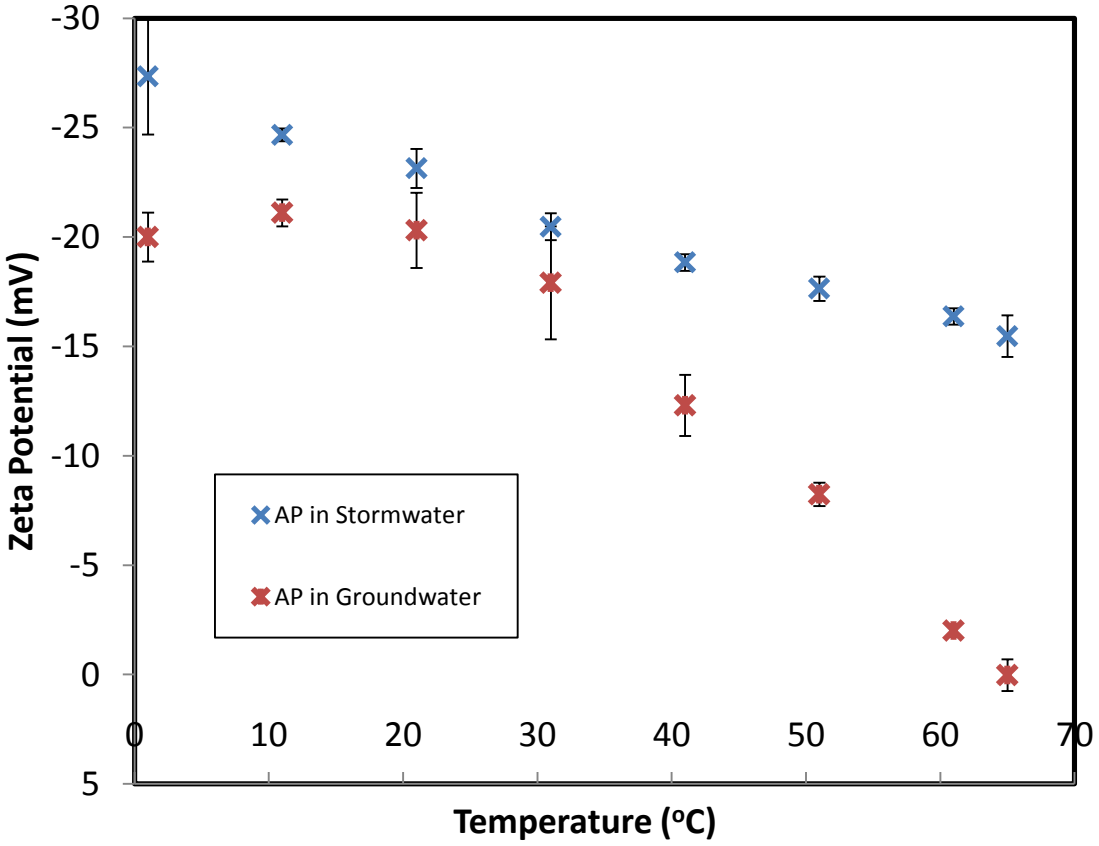
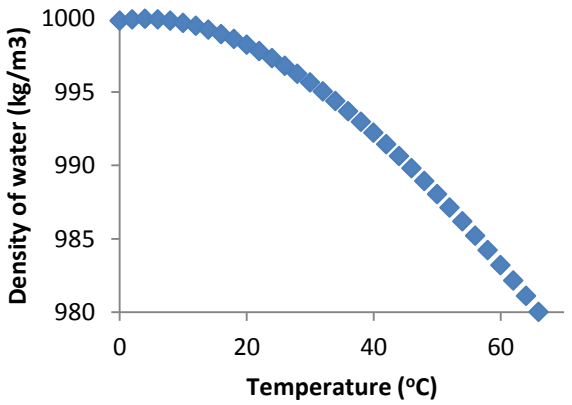
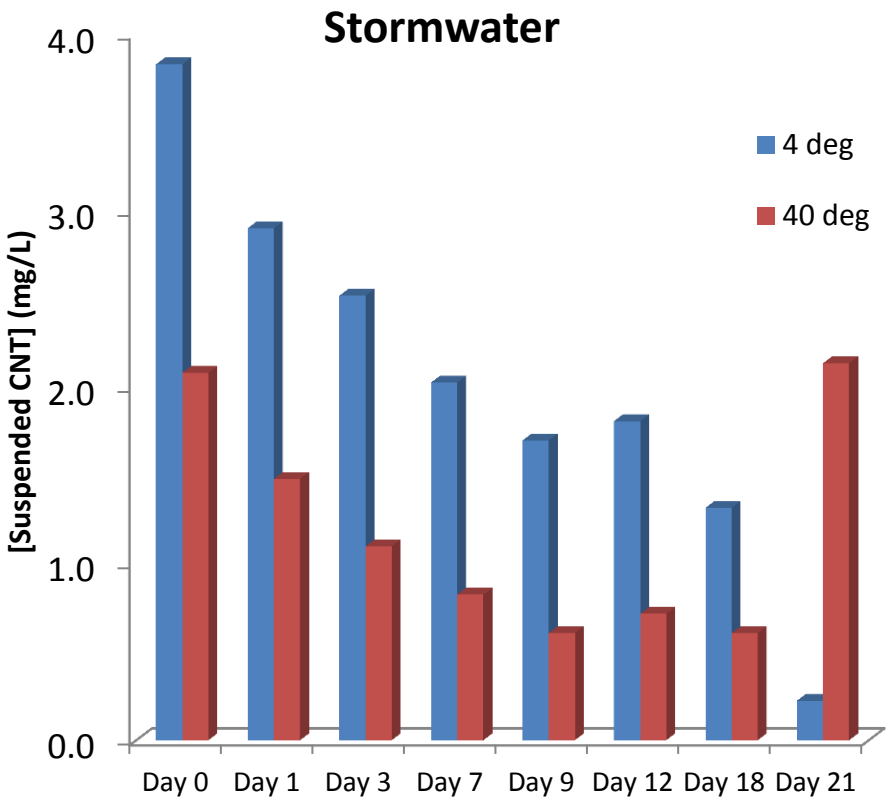
# Effect of Temperature Change

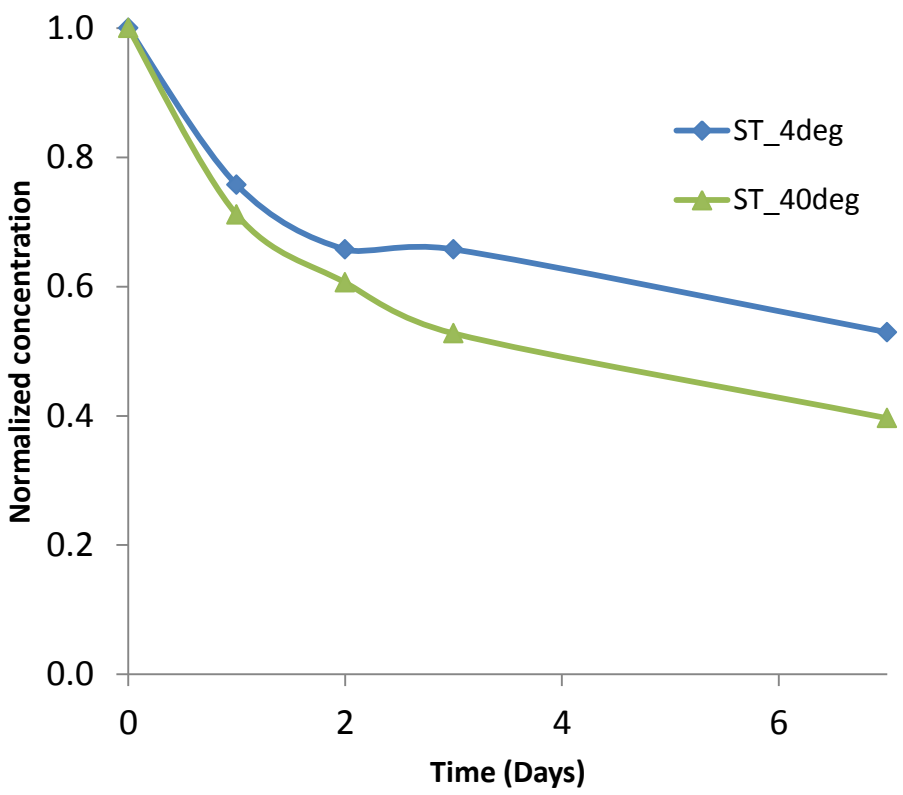



- Change in kinetic energy of NPs
- Change in surface charge (zeta potential)
- Change in density (slight)



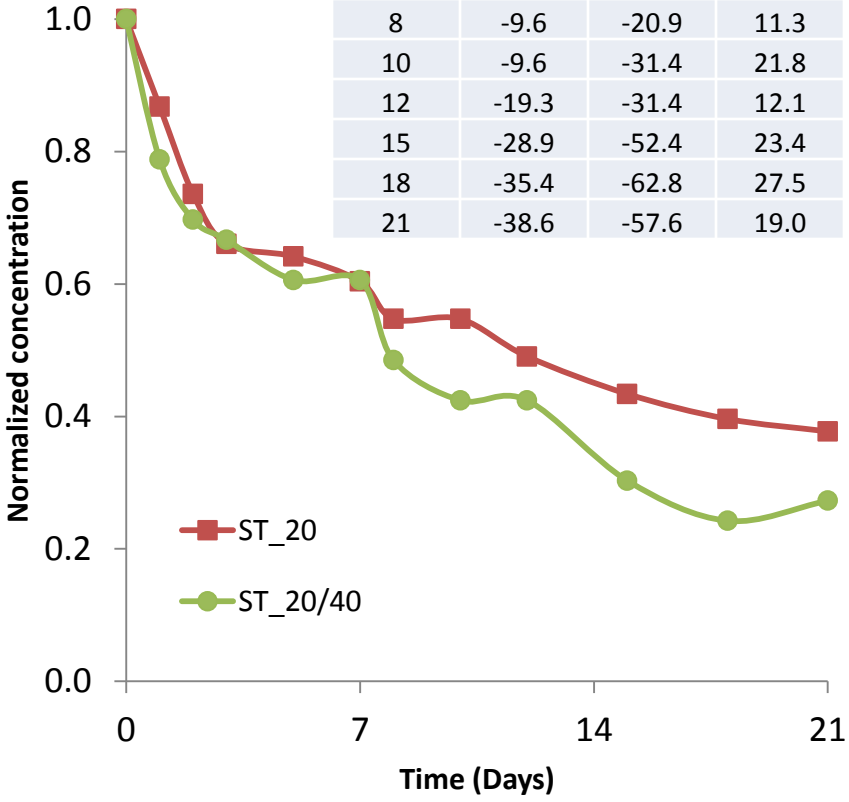
# AP in 4°C and 40°C



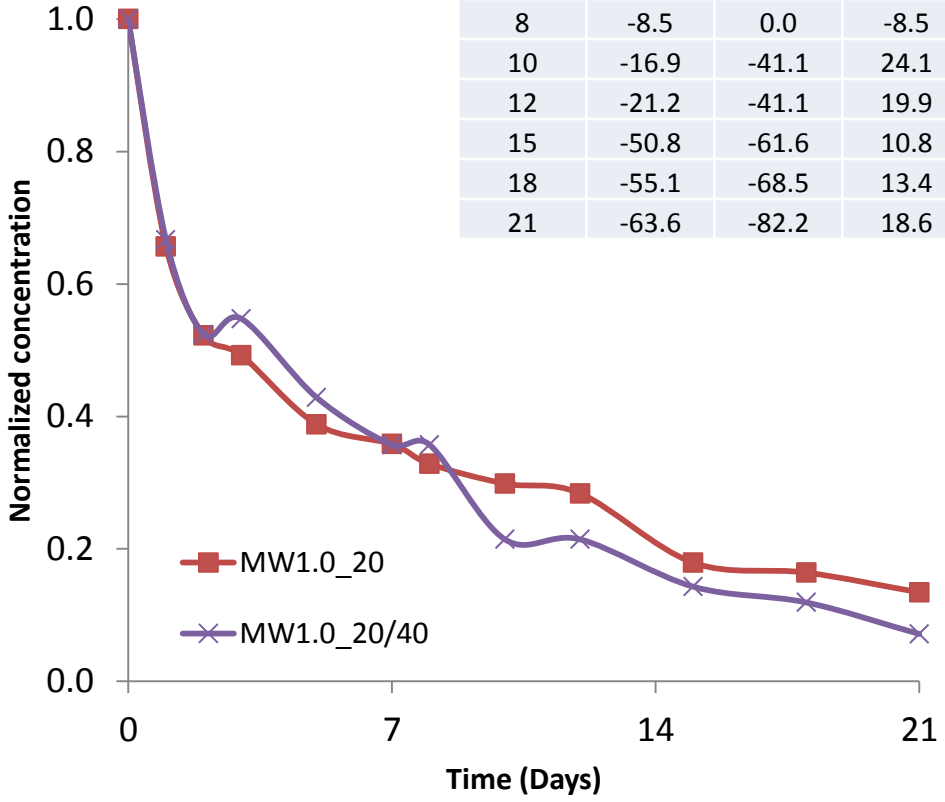



# 20°C to 40°C

| Condition | 20 | 20/40 | |
|---|---|---|---|
| Day | % Reduction | | Diff |
| 8 | -9.6 | -20.9 | 11.3 |
| 10 | -9.6 | -31.4 | 21.8 |
| 12 | -19.3 | -31.4 | 12.1 |
| 15 | -28.9 | -52.4 | 23.4 |
| 18 | -35.4 | -62.8 | 27.5 |
| 21 | -38.6 | -57.6 | 19.0 |




| Condition | 20 | 20/40 | |
|---|---|---|---|
| Day | % Reduction | | Diff |
| 8 | -8.5 | 0.0 | -8.5 |
| 10 | -16.9 | -41.1 | 24.1 |
| 12 | -21.2 | -41.1 | 19.9 |
| 15 | -50.8 | -61.6 | 10.8 |
| 18 | -55.1 | -68.5 | 13.4 |
| 21 | -63.6 | -82.2 | 18.6 |



3.

What fraction of metal impurities in SWCNT may leach out when exposed to natural waters?



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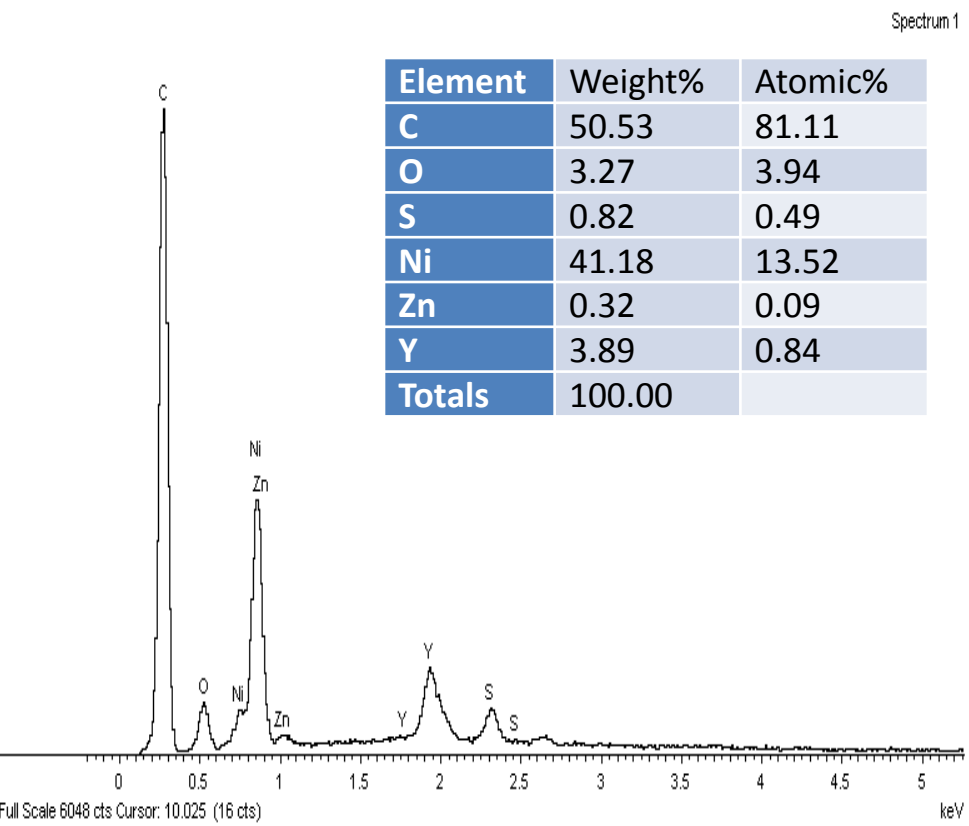
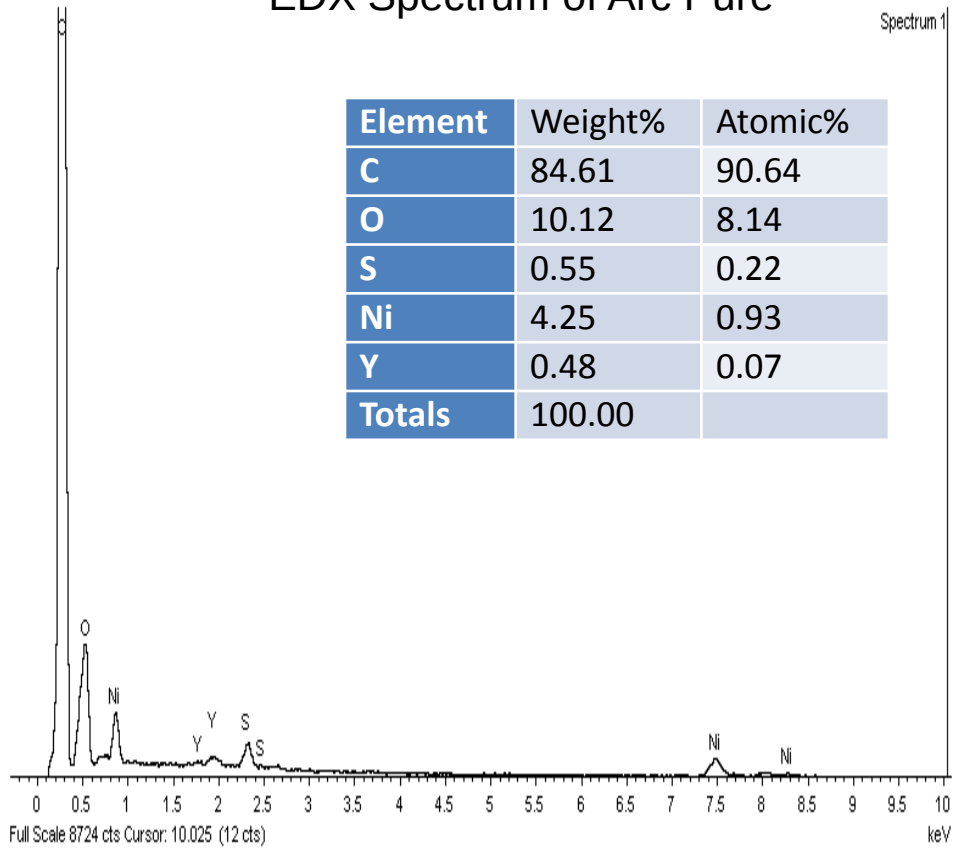
# Metal content of SWCNTs

EDX Spectrum of Arc Raw



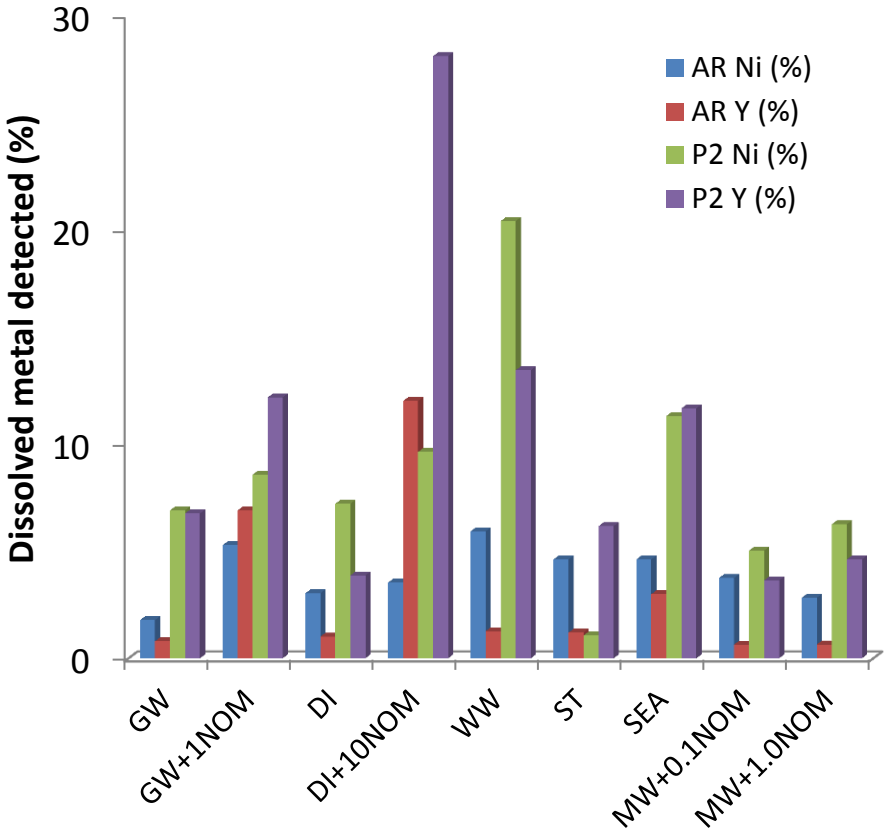

| Element | Weight% | Atomic% |
|---|---|---|
| C | 50.53 | 81.11 |
| O | 3.27 | 3.94 |
| S | 0.82 | 0.49 |
| Ni | 41.18 | 13.52 |
| Zn | 0.32 | 0.09 |
| Y | 3.89 | 0.84 |
| Totals | 100.00 | |

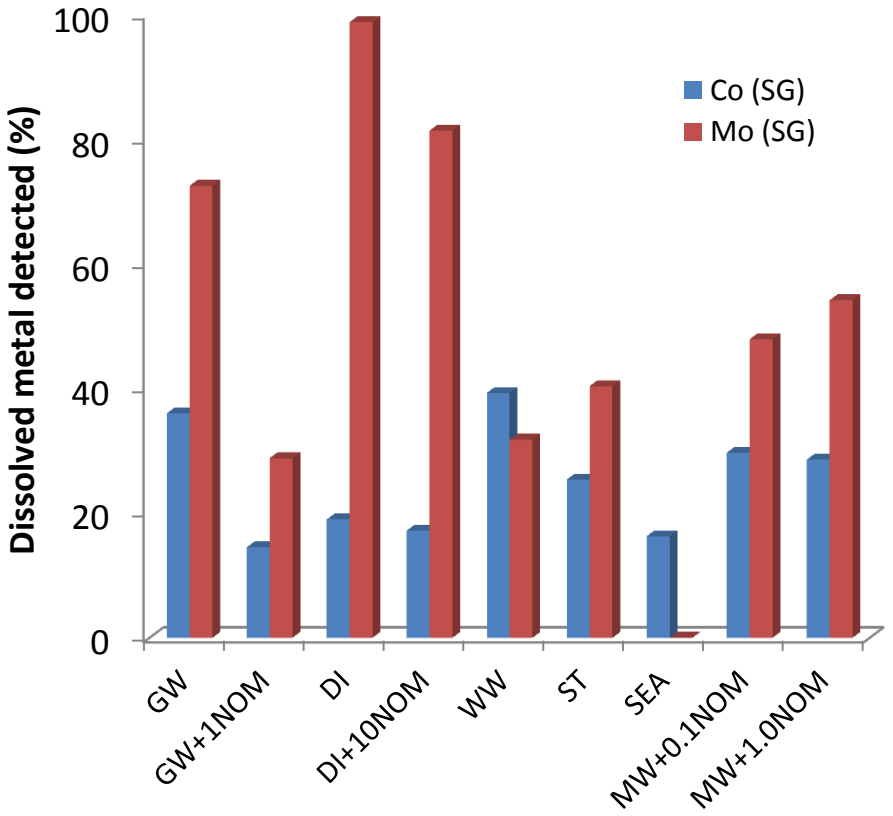
EDX Spectrum of Arc Pure




| Element | Weight% | Atomic% |
|---|---|---|
| C | 84.61 | 90.64 |
| O | 10.12 | 8.14 |
| S | 0.55 | 0.22 |
| Ni | 4.25 | 0.93 |
| Y | 0.48 | 0.07 |
| Totals | 100.00 | |

# Dissolved metal from CNT



# Environmental Implications

- Potential exposure of biota at water surface
- The stability/sedimentation of SWCNTs compares with other NPs
- Suspension of CNT in sea water is enhanced by water density and turbulence
- Metal leaching from CNT is enhanced in the natural water systems by NOM and turbulence

# Acknowledgement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  - Brittany Hall
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