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
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

<table>
<thead>
<tr>
<th>Source</th>
<th>As Prepared (R)</th>
<th>Purified (P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SweNT (CoMoCat)</td>
<td></td>
<td>SG65</td>
</tr>
<tr>
<td>NanoIntegris (HiPco)</td>
<td>HR</td>
<td>HP</td>
</tr>
<tr>
<td>Carbon Solutions (P2)</td>
<td>AR</td>
<td>AP</td>
</tr>
</tbody>
</table>
# Water characterization

<table>
<thead>
<tr>
<th>Media</th>
<th>pH</th>
<th>ZP (mV)</th>
<th>Conductivity (μS)</th>
<th>Redox (mV)</th>
<th>UV&lt;sub&gt;254&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI (DI)</td>
<td>7.1</td>
<td>-2.0</td>
<td>14.9</td>
<td>96.8</td>
<td>0</td>
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<tr>
<td>DI + 10.0 mg/L NOM (DI+10)</td>
<td>7.1</td>
<td>-16.5</td>
<td>29.2</td>
<td>196.8</td>
<td>0.082</td>
</tr>
<tr>
<td>Mineral water + 0.1 mg/L NOM (MW+0.1)</td>
<td>7.8</td>
<td>-4.3</td>
<td>87.4</td>
<td>159.6</td>
<td>0.002</td>
</tr>
<tr>
<td>Mineral water + 1.0 mg/L NOM (MW+1.0)</td>
<td>7.3</td>
<td>-6.4</td>
<td>92.3</td>
<td>188.8</td>
<td>0.012</td>
</tr>
<tr>
<td>Storm water (ST)</td>
<td>7.7</td>
<td>-5.5</td>
<td>285.0</td>
<td>166.5</td>
<td>0.242</td>
</tr>
<tr>
<td>Groundwater (GW)</td>
<td>7.5</td>
<td>-2.5</td>
<td>1021.0</td>
<td>137.4</td>
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<tr>
<td>Groundwater + 1.0 mg/L NOM (GW+1.0)</td>
<td>6.8</td>
<td>-10.0</td>
<td>1055.0</td>
<td>159.4</td>
<td>0.009</td>
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<tr>
<td>Wastewater (WW)</td>
<td>7.6</td>
<td>4.9</td>
<td>2430.0</td>
<td>123.8</td>
<td>0.098</td>
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<tr>
<td>Sea water (Sea)</td>
<td>7.3</td>
<td>39.6</td>
<td>33700.0</td>
<td>141.6</td>
<td>0.002</td>
</tr>
</tbody>
</table>
"Dispersability"

- CNT dispersibility (%)
- Groundwater, Storm, Sea, Wastewater, Freshwater
- AR, AP, SG, HR, HP

Graph showing the dispersibility of CNTs in different environments.
10 mg/L NOM

Sea water
Freshwater
Sea water
Storm water
“Dispersability”

NOM enhances dispersability of CNT
“Dispersability”
Stability

**Arc Pure**

**Arc Raw**
Stability
2. How does temperature variation affect the stability of SWCNT in natural waters?
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

Stormwater

[Suspended CNT] (mg/L)

Normalized concentration

Time (Days)
20°C to 40°C

<table>
<thead>
<tr>
<th>Condition</th>
<th>20</th>
<th>20/40</th>
<th>Diff</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day</td>
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<td></td>
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<tr>
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<td>-20.9</td>
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<td>10</td>
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<td>21</td>
<td>-38.6</td>
<td>-57.6</td>
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</table>

<table>
<thead>
<tr>
<th>Condition</th>
<th>20</th>
<th>20/40</th>
<th>Diff</th>
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<tbody>
<tr>
<td>Day</td>
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<tr>
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<tr>
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<td>15</td>
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<tr>
<td>18</td>
<td>-55.1</td>
<td>-68.5</td>
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<tr>
<td>21</td>
<td>-63.6</td>
<td>-82.2</td>
<td>18.6</td>
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</table>
3. What fraction of metal impurities in SWCNT may leach out when exposed to natural waters?
Metal content of SWCNTs

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
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<tbody>
<tr>
<td>C</td>
<td>50.53</td>
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<tr>
<td>O</td>
<td>3.27</td>
<td>3.94</td>
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<tr>
<td>S</td>
<td>0.82</td>
<td>0.49</td>
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<tr>
<td>Ni</td>
<td>41.18</td>
<td>13.52</td>
</tr>
<tr>
<td>Zn</td>
<td>0.32</td>
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<tr>
<td>Y</td>
<td>3.89</td>
<td>0.84</td>
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<tr>
<td>Totals</td>
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</table>

EDX Spectrum of Arc Raw

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
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<tbody>
<tr>
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<td>84.61</td>
<td>90.64</td>
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<td>10.12</td>
<td>8.14</td>
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<tr>
<td>S</td>
<td>0.55</td>
<td>0.22</td>
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<tr>
<td>Ni</td>
<td>4.25</td>
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<tr>
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<td>0.07</td>
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<tr>
<td>Totals</td>
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</table>
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
  – Daniel Dunham