Towards an Understanding of the Environmental Destiny of Nanomaterials Released to Environment

Transformation of NanoMaterials in the *Environment*

Panel 7

Ronald Turco, Purdue University
Is it possible to keep up?

“In the case of nanotechnology, the remarkable variability of nanomaterial compositions, the new properties of these nanomaterials and the introduction of new manufacturing processes bring extra challenges to the process of adopting either mandatory or voluntary risk management approaches.”

*Essential features for proactive risk management*
Vladimir Murashov & John Howard
Nature Nanotechnology 4, 467 - 470 (2009)


Areas of Concern

- Biosolids Degradation/Impact
- Photo/Surface Reactions
- Surface/Subsurface Soils Degradation/Impact
- Groundwater Facilitated Transport
- Rhizosphere Degradation/Impact Uptake
- Runoff
- Leaching
What are the impacts NP on the soil food web?

http://www.blm.gov/nstc/soil/bacteria/index.html
What roles will the environment play in removing these materials?

- CO₂
- Microbial Biomass
- New Products
Assessing Manufactured Nanomaterials in the Environment
ANE–Purdue

Solubility and Sorption

Role of Sunlight

Response of Bacteria
Response of Eukarya (fungi)
Response of Archaea

National Science Foundation (NSF)
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& United States EPA under Award RD-83172001-0

Ron Turco, Tim Filley, Chad Jafvert, Loring Nies, Bruce Applegate, Natalie Carroll, Inez Hua, Robert Blanchette, Leila Nyberg, Zhonghua Tong, Kathryn Schreiner, Pradnya Kulkarni, Mi-Youn Ahn, Scott Shepherd, Marianne Bischoff and Benjamin Held
(Funding: NSF, EPA, Water Center, College of Ag)
Comparison to other hydrophobic compounds suggests \( C_{60} \) will be a highly retained material.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Log ( K_{ow} )</th>
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<tr>
<td>Napthalene</td>
<td>3.36</td>
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<tr>
<td>Anthracene</td>
<td>4.54</td>
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<td>Chrysene</td>
<td>5.86</td>
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<td>Perylene</td>
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<tr>
<td>Hexachlorobiphenyl</td>
<td>6.30</td>
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<td>( p,p' )-DDT</td>
<td>6.36</td>
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<tr>
<td>( C_{60} )</td>
<td>6.67</td>
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</tbody>
</table>

$K_{oc}$, was estimated to be $10^{7.1}$ L/kg C -Carbon, $10^{6.2} - 10^{7.1}$ for natural waters with NOM

*High Retention on Soil Surfaces*

Solar Degradation
Photo-transformation of THF/nC₆₀ and son/nC₆₀ under the mid-latitude solar exposure, May 13, 2008-June 6, 2008.
Conditions: pH = 7, ionic strength = 19 mM.
Irradiation of nC$_{60}$ in light ($\lambda = 350$ nm)

<table>
<thead>
<tr>
<th>Irradiation time (day)</th>
<th>0</th>
<th>10</th>
<th>30</th>
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<tr>
<td>[nC$_{60}$] (mg/L)</td>
<td>65</td>
<td>19.5</td>
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<tr>
<td>Mean diameter** (nm)</td>
<td>500</td>
<td>320</td>
<td>250</td>
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Scale bars represent 1000 nm.
**Hydrodynamic diameter by DLS.
Photochemistry of $C_{60}$ in Organic Solvents (Potential Aqueous Reactions of $nC_{60}$)

$$C_{60} \xrightarrow{h\nu} ^1C_{60} \xrightarrow{ISC} ^3C_{60} \xrightarrow{k_q(O_2)} C_{60} + ^1O_2$$

$$^3C_{60} + \frac{n}{2}^1O_2 \rightarrow C_{60}O_n$$

In water? $^1O_2 \xrightarrow{h\nu} \text{Further oxidation and fragmentation}

$^1O_2 + H_2O$ $\rightarrow \text{Further oxidation and fragmentation}$

Arbogast et al., 1991
Juha et al., 1994
Taylor et al., 1991
Fungal Transformation of C60

photochemical or microbial oxidation

CO₂ + fungal biomass

fungal decomposition

-CO₂, -fungal biomass

Metabolites
Fungi + $^{13}\text{C}_{60}$(OH)$_{26-30}$

(Media and wood+media inoculations)

Oxidation

- $^{13}\text{C}$ content of CO$_2$ in headspace
- Spectroscopy of fullerol in media

Biomass Production

- $^{13}\text{C}$ in hyphae lipids

Influence on fungal decay mechanism

- Lignin decomposition of wood by $^{13}\text{C}$-TMAH Thermochemolysis

Neither white rot nor brown rot fungi significantly incorporated fullerol carbon into biomass (although a small proportion does). This is true even as white fungi completely bleached the fullerols.
Enrichment in $^{13}\text{C}$ of head space is showing some utilization

\[
\Delta \delta^{13}\text{C} = \delta^{13}\text{C}_{\text{labeled}} - \delta^{13}\text{C}_{\text{unlabeled}}
\]

\[
\delta^{13}\text{C} \ [\%/oo] = \left( \frac{R_{\text{CO}_2}}{R_{\text{PDB}}} - 1 \right) \times 1000
\]

\[ R = \frac{^{13}\text{C}}{^{12}\text{C}} \]
C60 and nC60 had little impact on soil functions

Soil Respiration

Biomass Size

nC₆₀ 1 ppm / C₆₀ 1000 ppm – Drummer Soil

Anaerobic Systems & C60

Normalized Gas Production - C$_6$O

- sludge + substrate
- 0.1 ppm
- 1 ppm
- 10 ppm
- 50 ppm
- 100 ppm
- 500 ppm
- 1000 ppm
Basal Respiration - SWCT

Cumulative CO₂ (mg CO₂ g⁻¹ soil)

Time (days)

control
AP
P7 10
P7 50
P8 10
P8 50

control ----- soil control
AP------ as-produced SWNTs
P7 10 --- P7-SWNTs at 10 µg g⁻¹ soil
P7 50 --- P7-SWNTs at 50 µg g⁻¹ soil
P8 10 --- P8-SWNTs at 10 µg g⁻¹ soil
P8 50 --- P8-SWNTs at 50 µg g⁻¹ soil
16S rDNA-DGGE Profiles

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# 18S rDNA-DGGE Profiles

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- **H**: Indicates a specific band or feature in the Drummer profile.
- **J**: Indicates a specific band or feature in the Tracy profile.
- **I**: Indicates a specific band or feature in both profiles.
- **K**: Indicates a specific band or feature in both profiles.
Conclusion

• Work on surface alteration of nanomaterials shows changes are possible (Filley et al., & Jafvert et al.)
  – Rethinking the need for “activation”
• Early efforts have looked at the impact on soil systems and shown few effects (carbon materials)
• Need better detection methods ($^{13}$C / $^{14}$C) for tracking and metabolism studies
Nanomaterial: Type & Rate

Health/Environmental Impact

Toxicity
Degradation Transformation
Sorption

Environmental Conditions
Economic Pressure

Health/Environmental Impact

The Environmental Caldron