Fullerenes in the Environment: Potential Toxicity, Stability and Bioavailability

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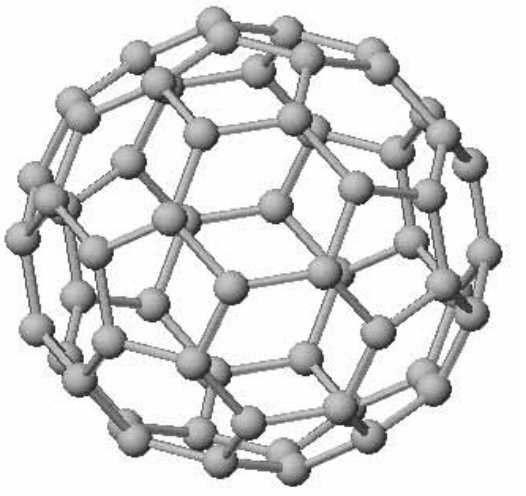
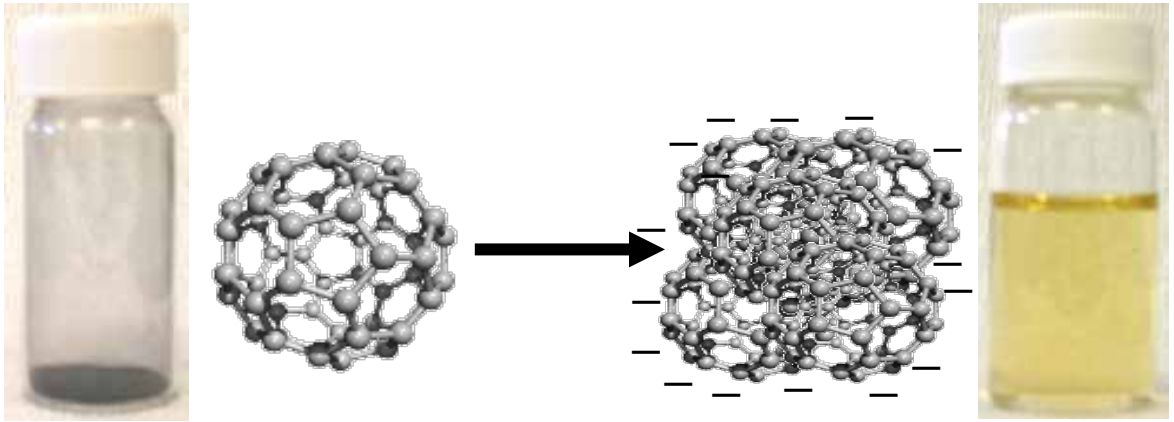
11 March 2011

C_{60} (buckminsterfullerene)

Photocatalyst
and Antioxidant
(sp2 hybridized)



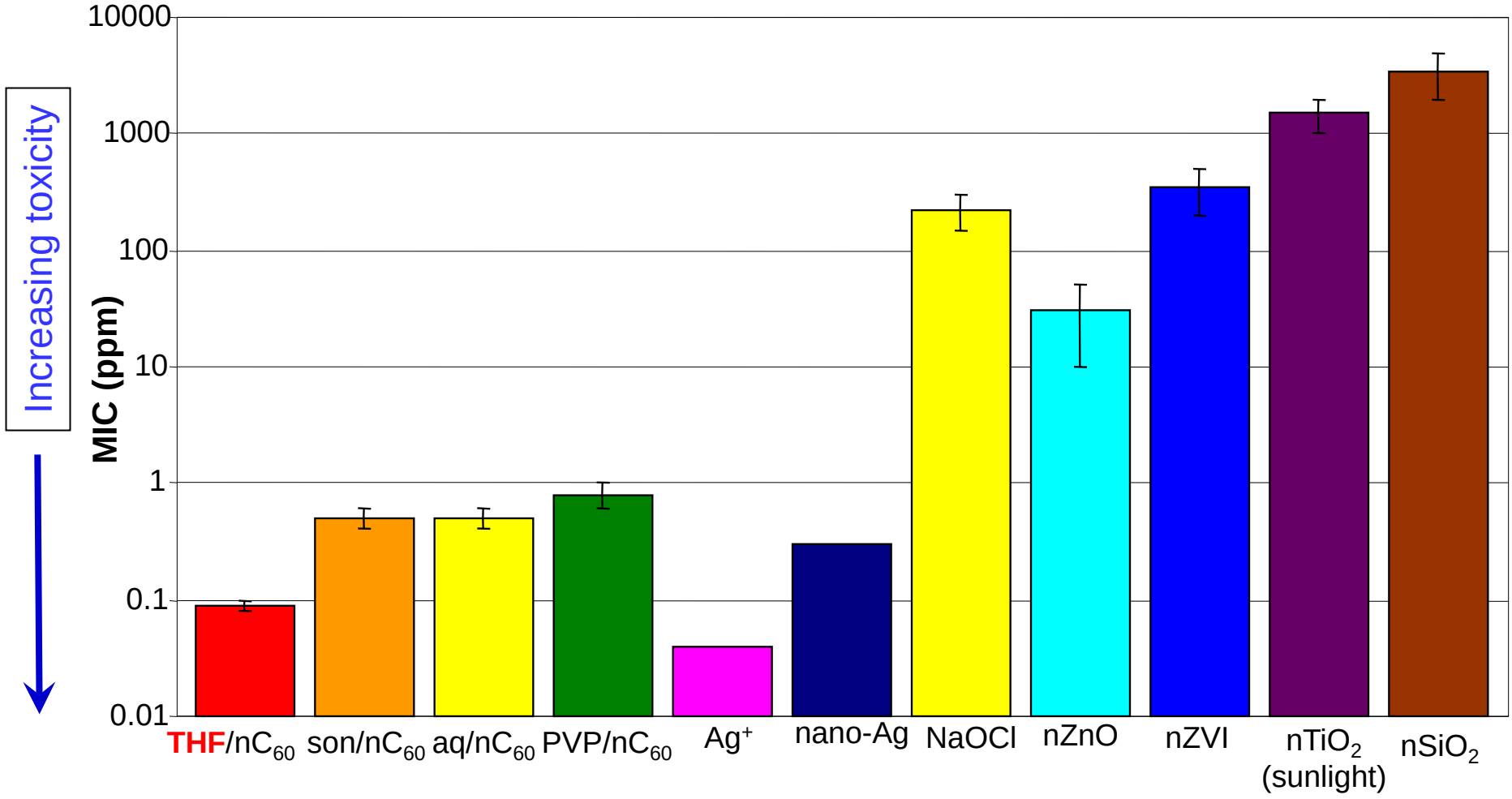
R. Buckminster Fuller (Bucky)



Solid or solution

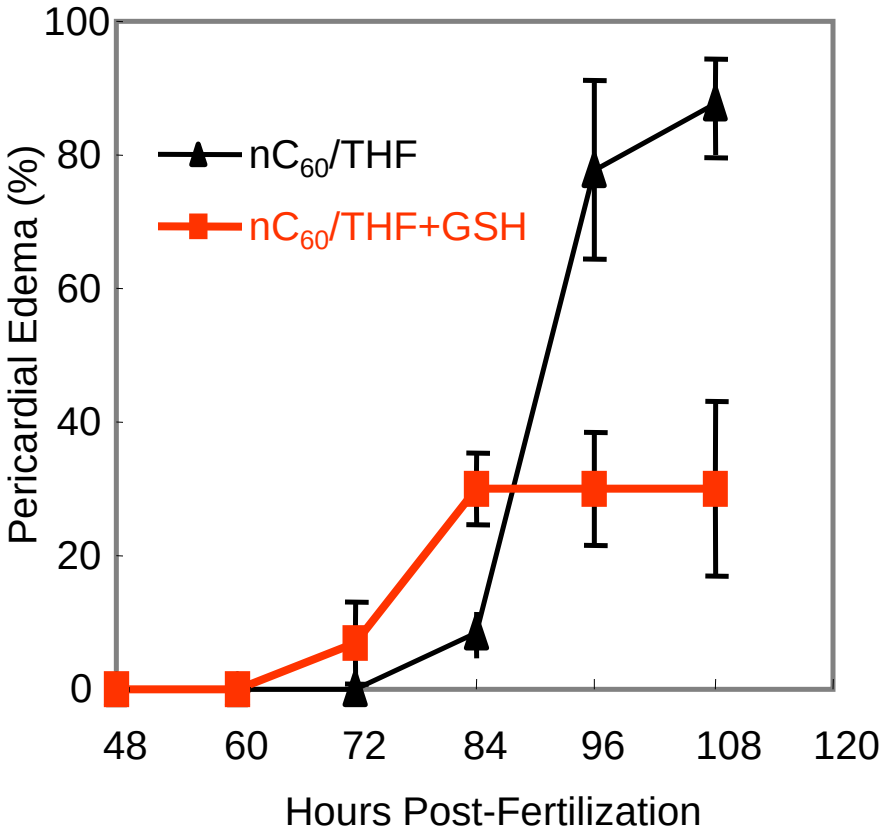
nC_{60} (20-200 nm)

nC_{60} may be more toxic to bacteria than many other common nanomaterials



Developmental toxicity of nC_{60} (Zebrafish)

Mitigation by GSH suggest that toxicity is related to oxidative stress

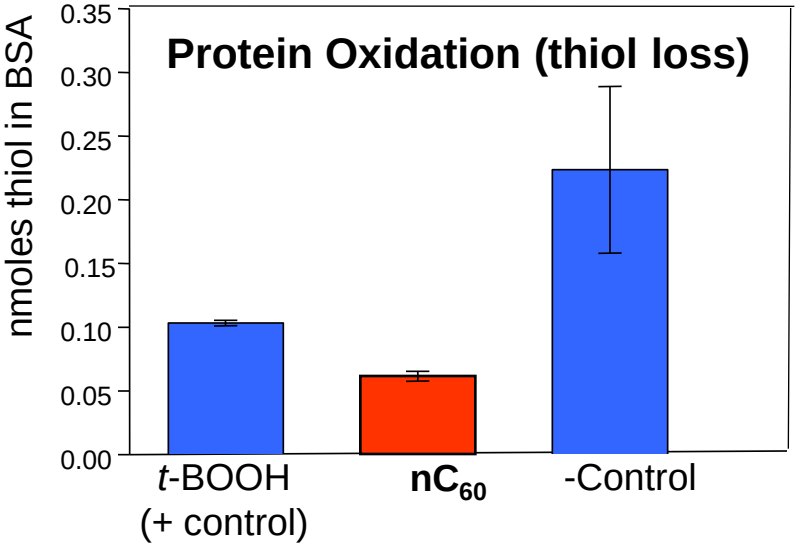


Zebrafish larva with pericardial edema due to nC_{60} exposure (1 mg/L)

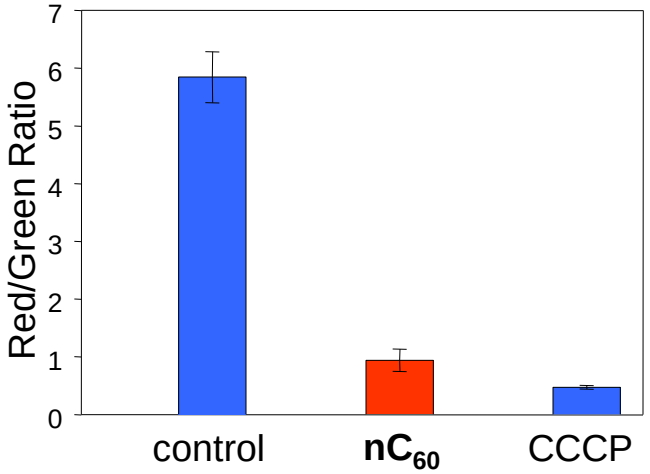
X. Zhu, Lin Zhu, Y. Li, Z. Duan, W. Chen and P.J. Alvarez* (2007). *Environ. Toxicol. Chem.* 26(5):976-979

Antibacterial Mechanism

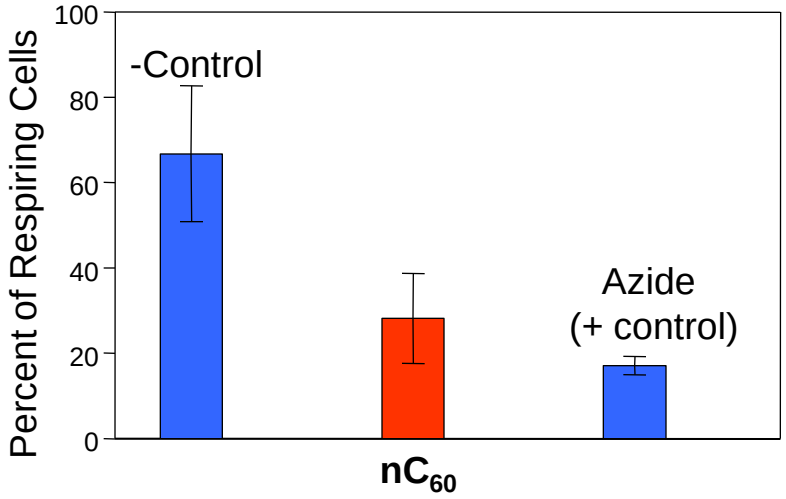
nC_{60} exerts ROS-independent oxidative stress, with evidence of protein oxidation, collapse of membrane potential, and *interruption of cellular respiration & energy transduction*



Decrease in *B. subtilis* membrane potential



Decrease in *E. coli* respiration



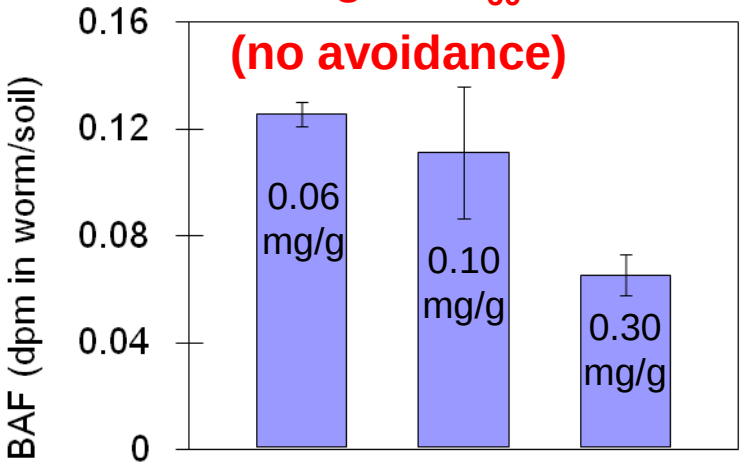
Lyon D.Y., L. Brunet, G.W. Hinkal, M.R. Wiesner, and P.J.J. Alvarez (2008). Nanoletters. 8(5**):** 1539-1543.
Lyon & Alvarez (2008). ES&T. 42:8127-8132

"Dry" $^{14}C_{60}$ Bioaccumulation in Earth Worms

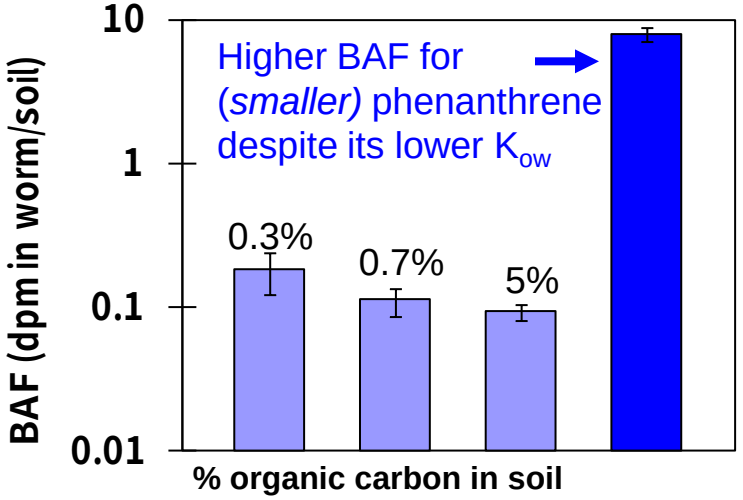
Eisenia fetida

- Epigeic worm
- Lives at or near the surface
- Consumes surface litter and soil organic matter
- Sexually mature weight 0.3-0.6 g
- Bioaccumulation factor:
  BSAF = ^{14}C in worm/^{14}C in soil

Lower BSAF at higher C_{60} concentration



Soil NOM had little effect on BSAF



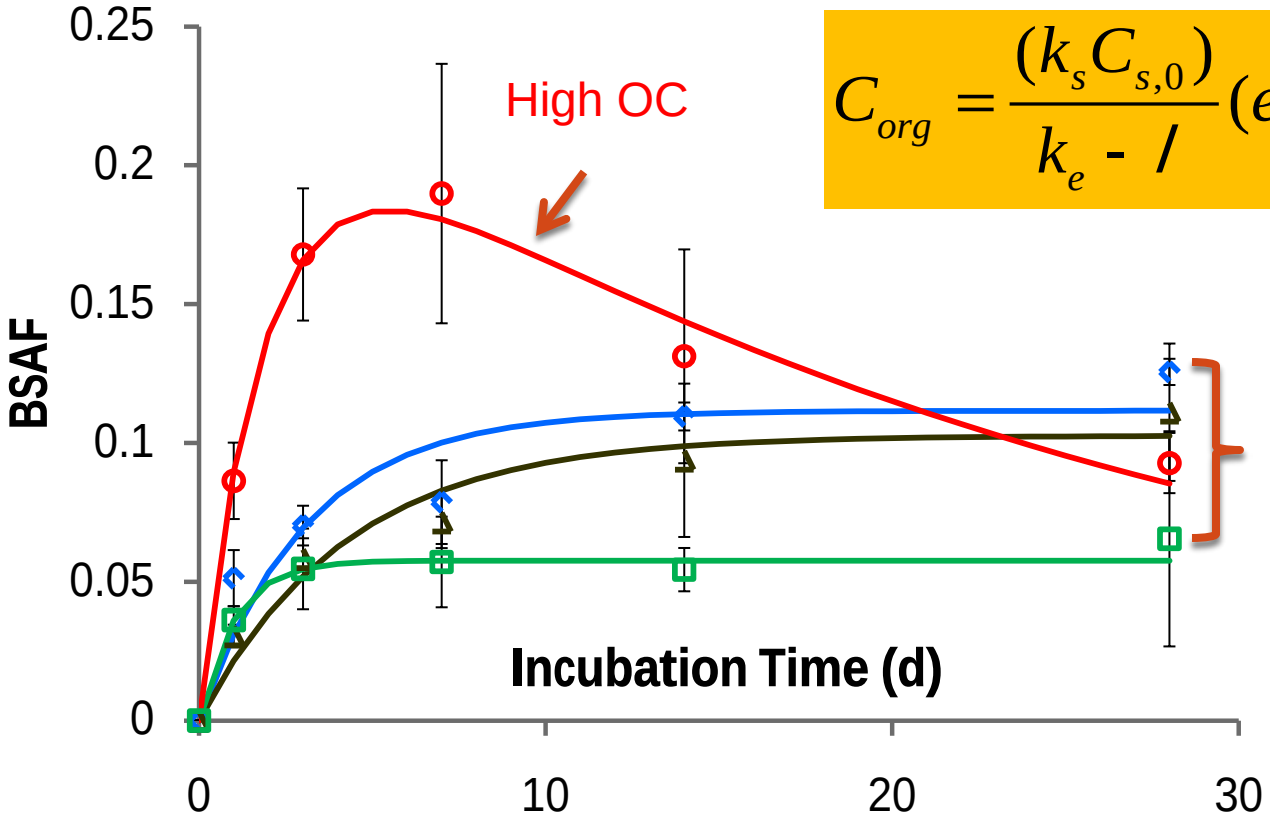
Li D., J.D. Fortner, D.R. Johnson, C. Chen, Q. Li and P.J.J. Alvarez (2010). ES&T. 44: 9170-9175

Effect of Dissolved NOM (e.g., in soil pores)

- NOM can exert a surfactant-like effect to prevent C_{60} precipitation as large (less bioavailable) aggregates.

Higher BSAF for high-OC soil initially

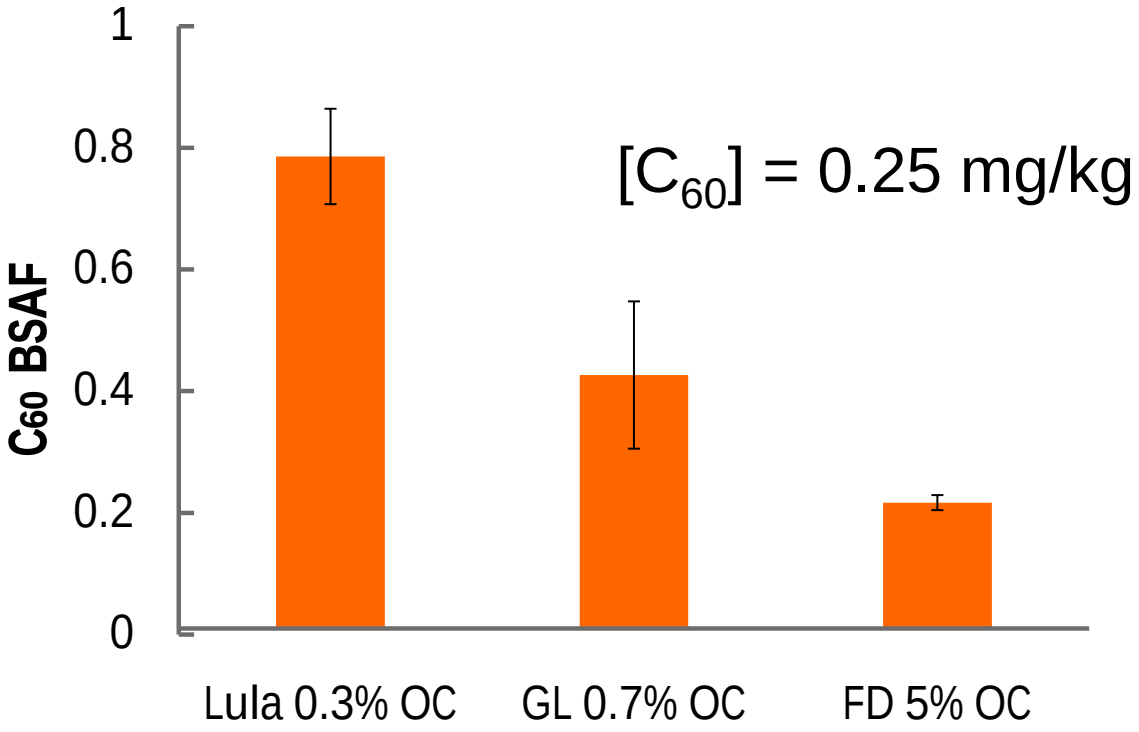
$[C_{60}]$ = 100 mg/kg



$$C_{org} = \frac{(k_s C_{s,0})}{k_e - l}(e^{-l t} - e^{-k_e t})$$

- Dissolved NOM likely increased "solubility" of C_{60} in pore water (and bioavailability), resulting the initial peak.
- Exceeded sorption capacity and soil OC did not affect final BASF

BSAF decreased at higher OC in low-dose soil (sorption capacity not exceeded)

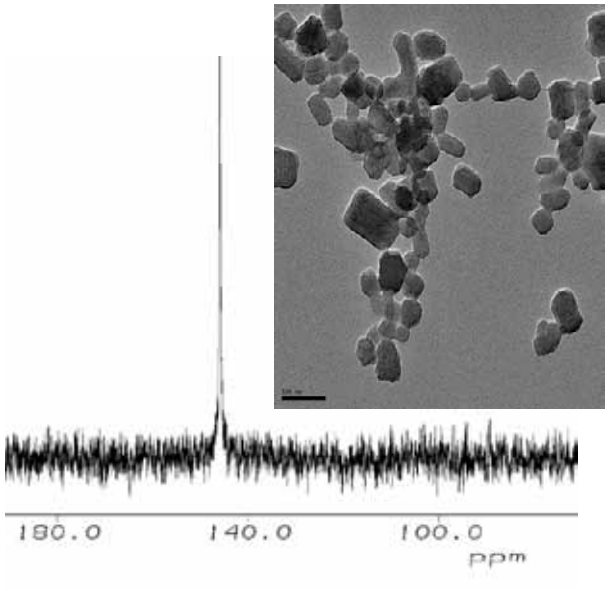


- Higher BSAF values than for high-dose soil where less bioavailable C_{60} precipitates predominated
- Greater partitioning of molecular C_{60} in soils with higher content of OC probably decreased bioavailability.

^{13}C-NMR and TEM of nC_{60} before & after ozonation

Derivatized, soluble products as $C_{60}(O)_x(OH)_y$ (y + x = ~29)

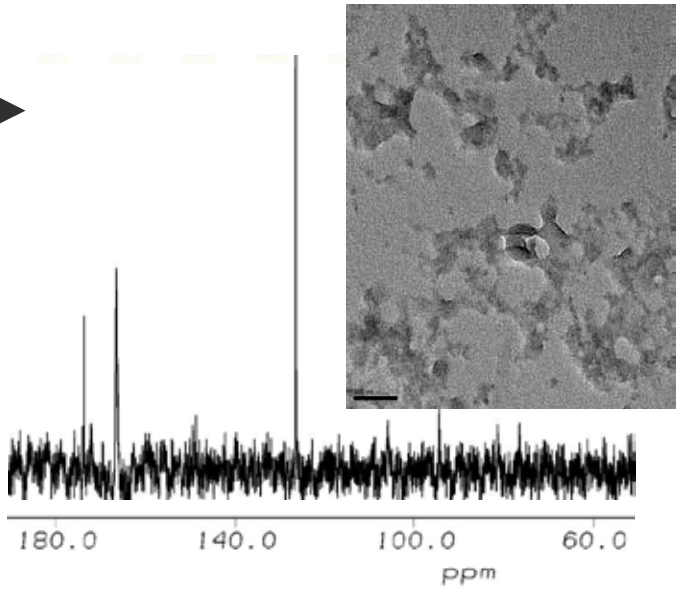
nC_{60} (aq)



O_3 (aq)

(smaller aggregates)

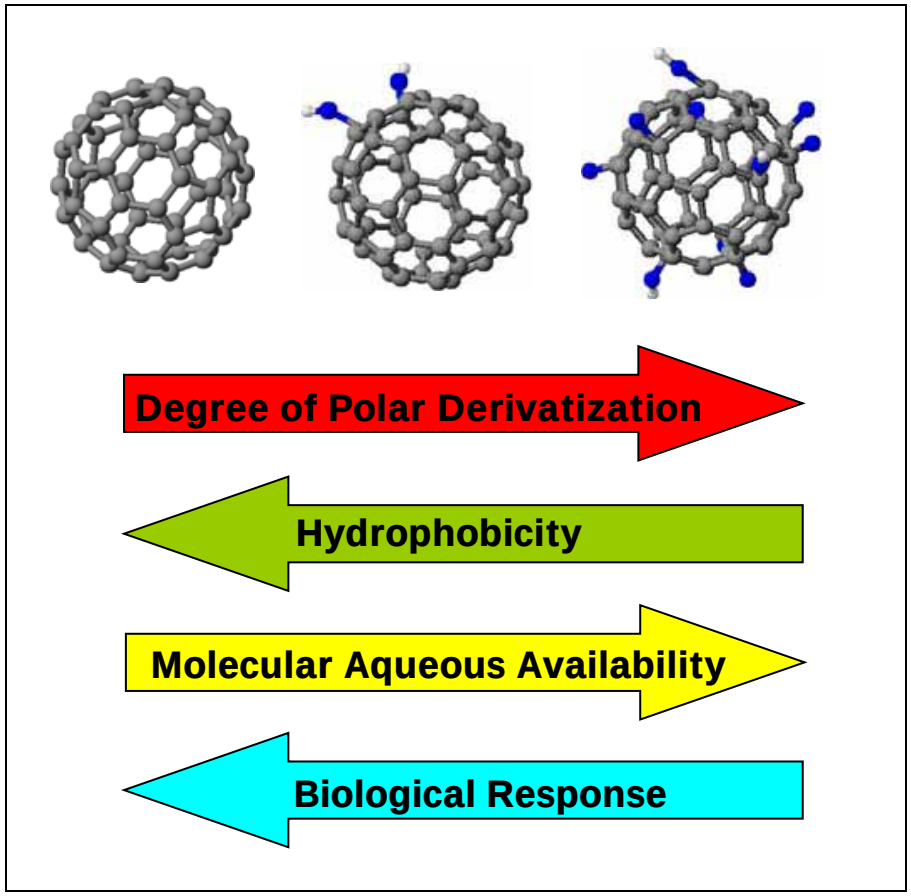
$nC_{60}(O)_x(OH)_y$



Fortner et al. *Environmental Science and Technology 2007, 41, (21)*

While nC_{60} resists attach by hydroxyl radicals and hydrides (Lee et al. 2010, ES&T, 44: 3786), it is slowly hydroxylated under light (Hou & Jafvert 2009, ES&T, 43: 5257)

Conclusion



- Similar to association with NOM, bio/photo transformation of C_{60} could significantly influence mobility (↑), bioavailability (↑), reactivity (↓) and toxicity (↓)
- Higher exposure to something less toxic? Risk?