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

Transformation of NanoMaterials in the *Environment*

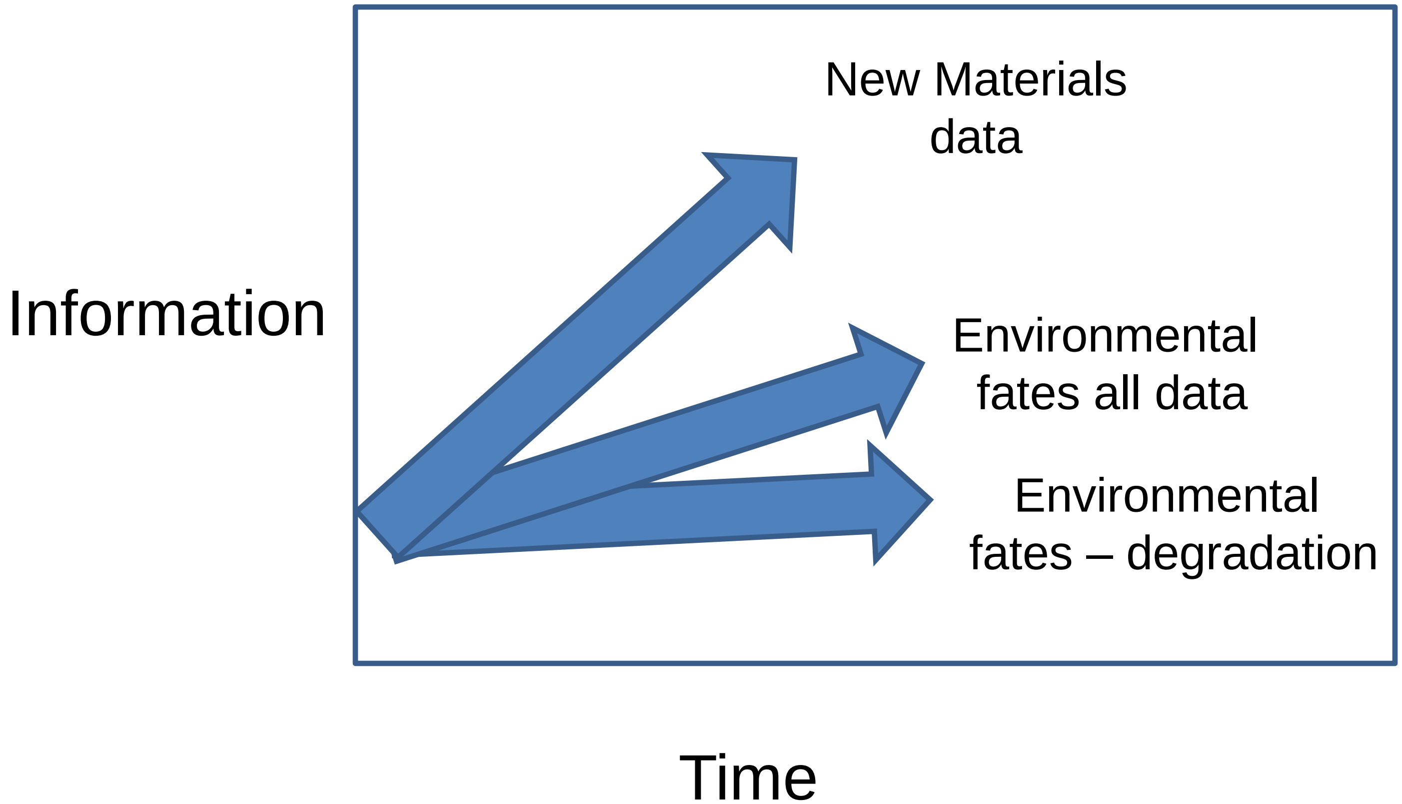
Panel 7

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)

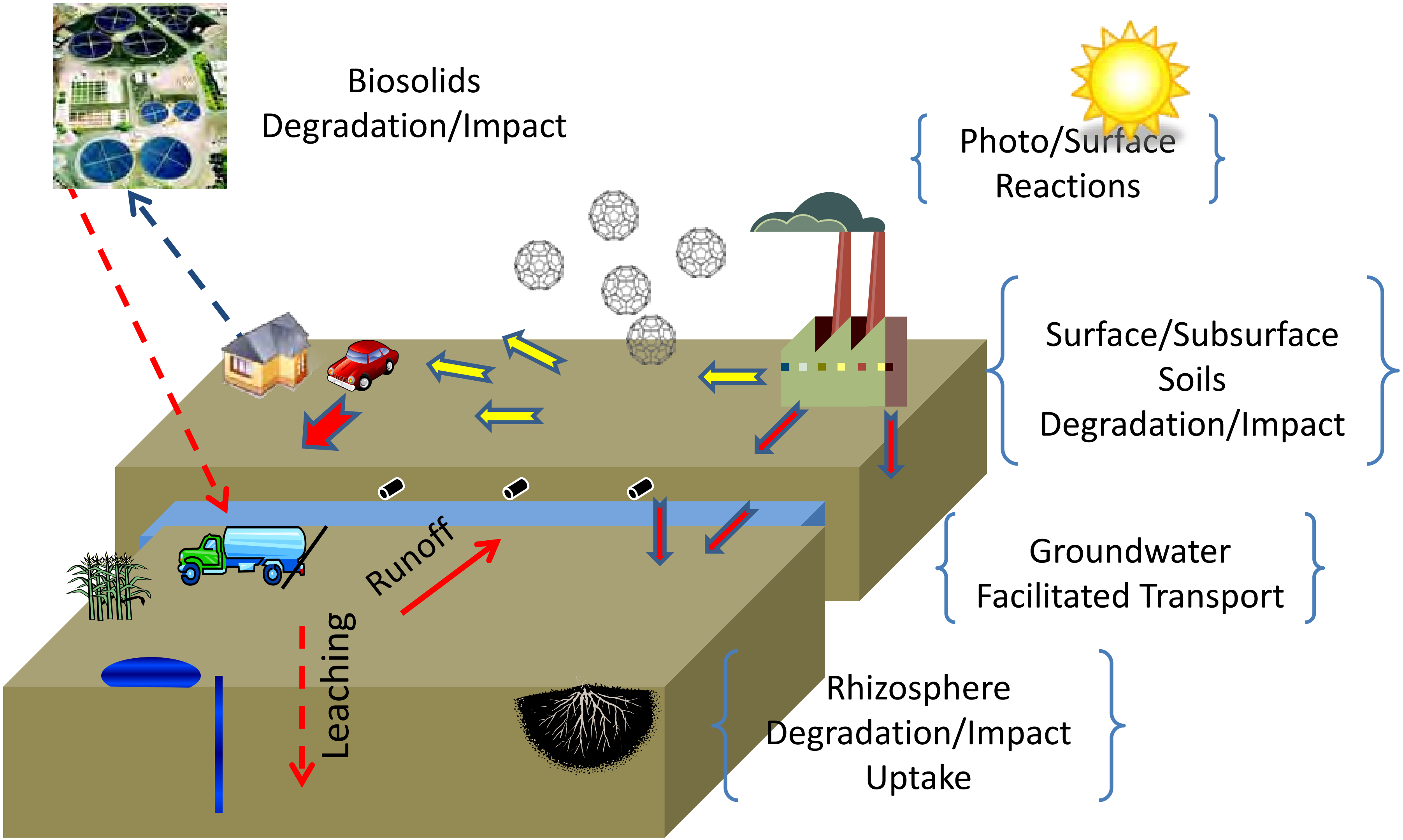


M.R. Wiesner, G.V. Lowry, P. Alvarez, D. Dionysiou and P. Biswas. 2006. Assessing the risks of manufactured nanomaterials Environ. Sci. Technol 4336-4345

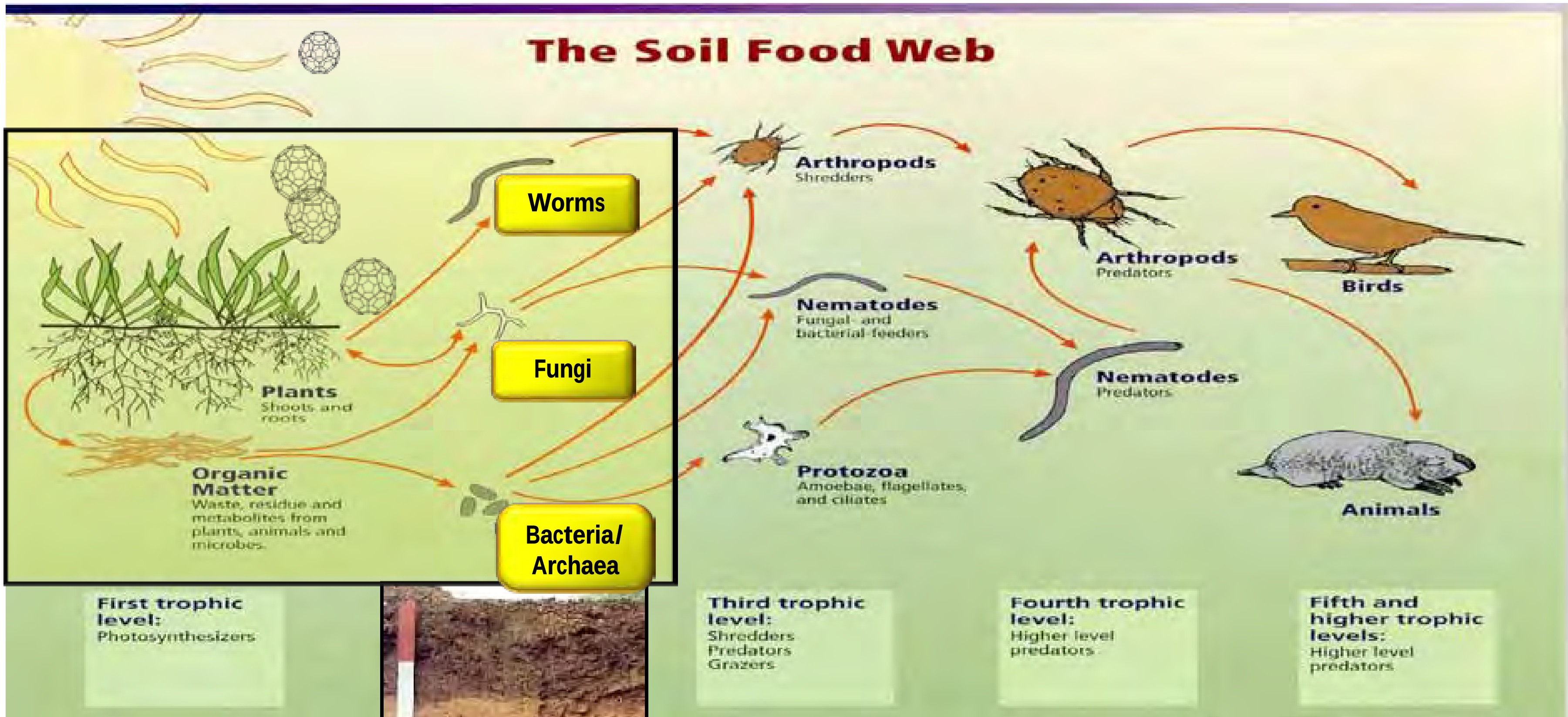
Editorial, Nature Nanotechnology 4, 533 (2009)

D. E. Meyer, M.A Curran and M. A. Gonzalez 2009. An Examination of Existing Data for the Industrial Manufacture and Use of Nanocomponents and Their Role in the Life Cycle Impact of Nanoproducts *Environ. Sci. Technol.*, 43:1256–1263

Areas of Concern

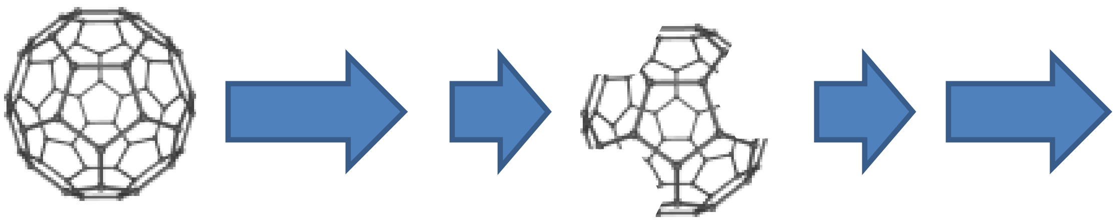


What are the impacts NP on the soil food web?



http://www.blm.gov/nstc/soil/bacteria/index.html

What roles will the environment play in removing theses materials?



CO_2

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)
under Award EEC-0404006
& 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

Compound	Log K_{ow}
Napthalene	3.36
Anthracene	4.54
Chrysene	5.86
Perylene	6.12
Hexachlorobiphenyl	6.30
p,p'-DDT	6.36
C_{60}	6.67

Kulkarni, P., and Jafvert, C. T. "Solubility of C_{60} in Solvent Mixtures", *Environ. Sci. Technol*. **2008**, 42, 845-851.
Jafvert, C. T., and Kulkarni, P., "Buckminsterfullerene's (C_{60}) Octanol Water Partition Coefficient (K_{ow}) and Hypothetical Aqueous Solubility", *Environ. Sci. Technol*. **2008**, 42, 5945-5950.

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

High Retention on Soil Surfaces

Chen, C. Y., Jafvert, C. T., "Sorption of Buckminsterfullerene (C_{60}) to Saturated Soil", *Environ. Sci. Technol*. **2009**, 43:7410-7415.

Solar Degradation

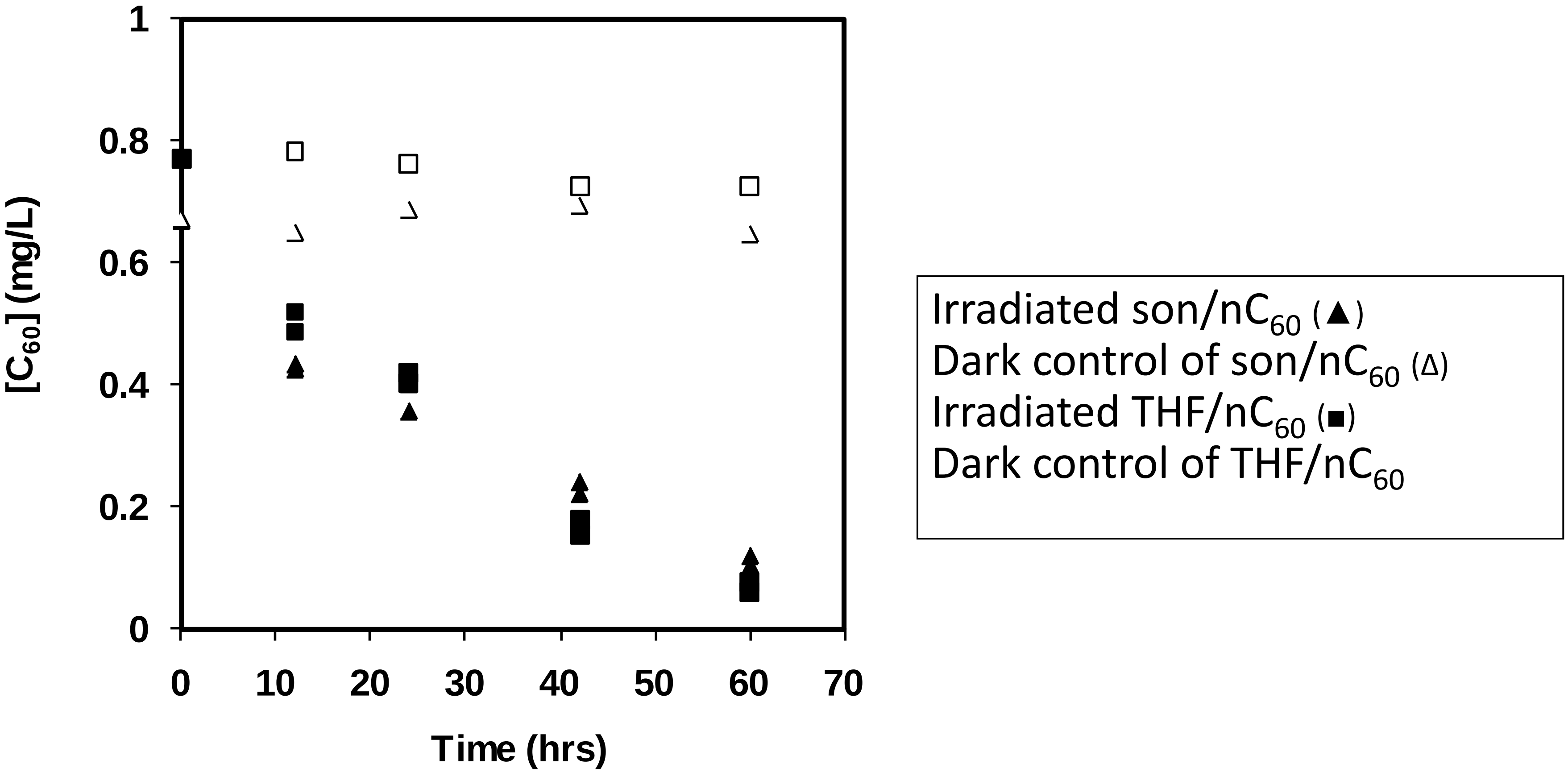
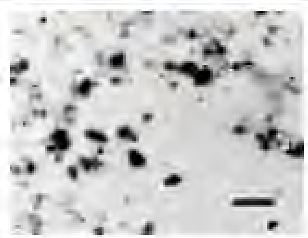
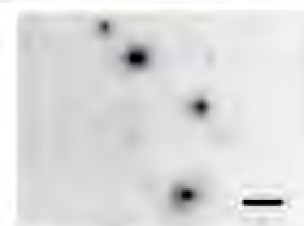


Photo-transformation of THF/nC_{60} and son/nC_{60}
under the mid-latitude solar exposure, May 13, 2008-June 6, 2008.
Conditions: pH = 7, ionic strength = 19 mM.

Irradiation of nC_{60} in light (l = 350 nm)

Irradiation time (day)	0	10	30	65
$[nC_{60}]$ (mg/L)	65	19.5	2.6	0.47
Color				
TEM image*				
Mean diameter** (nm)	500	320	250	160

Scale bars represent 1000 nm.

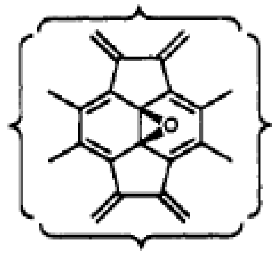
**Hydrodynamic diameter by DLS.

Photochemistry of C_{60} in Organic Solvents (Potential Aqueous Reactions of nC_{60})

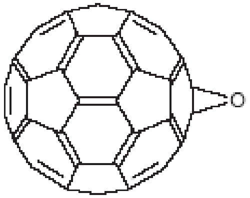
$$C_{60} \xrightarrow{h\nu} {}^1C_{60} \xrightarrow{ISC} {}^3C_{60} \xrightarrow{k_q(O_2)} C_{60} + {}^1O_2$$

Arbogast et al., 1991

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



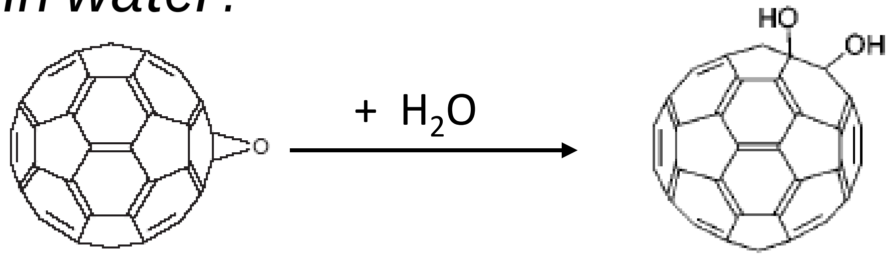
Juha et al., 1994

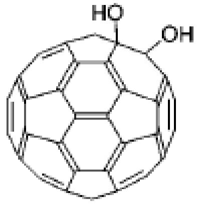


$+ {}^1O_2 \xrightarrow{h\nu}$ Further oxidation and fragmentation

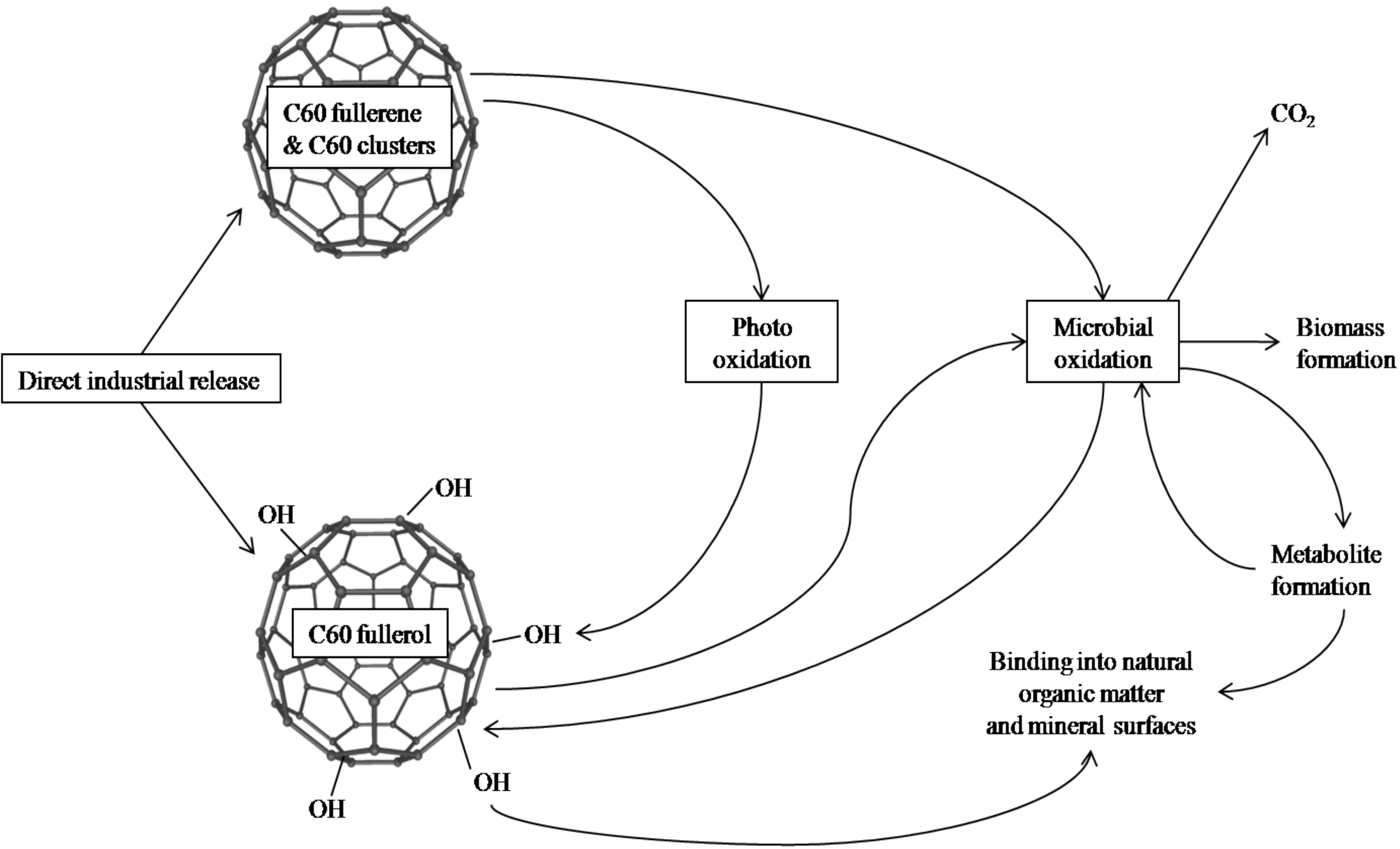
Taylor et al., 1991

In water?

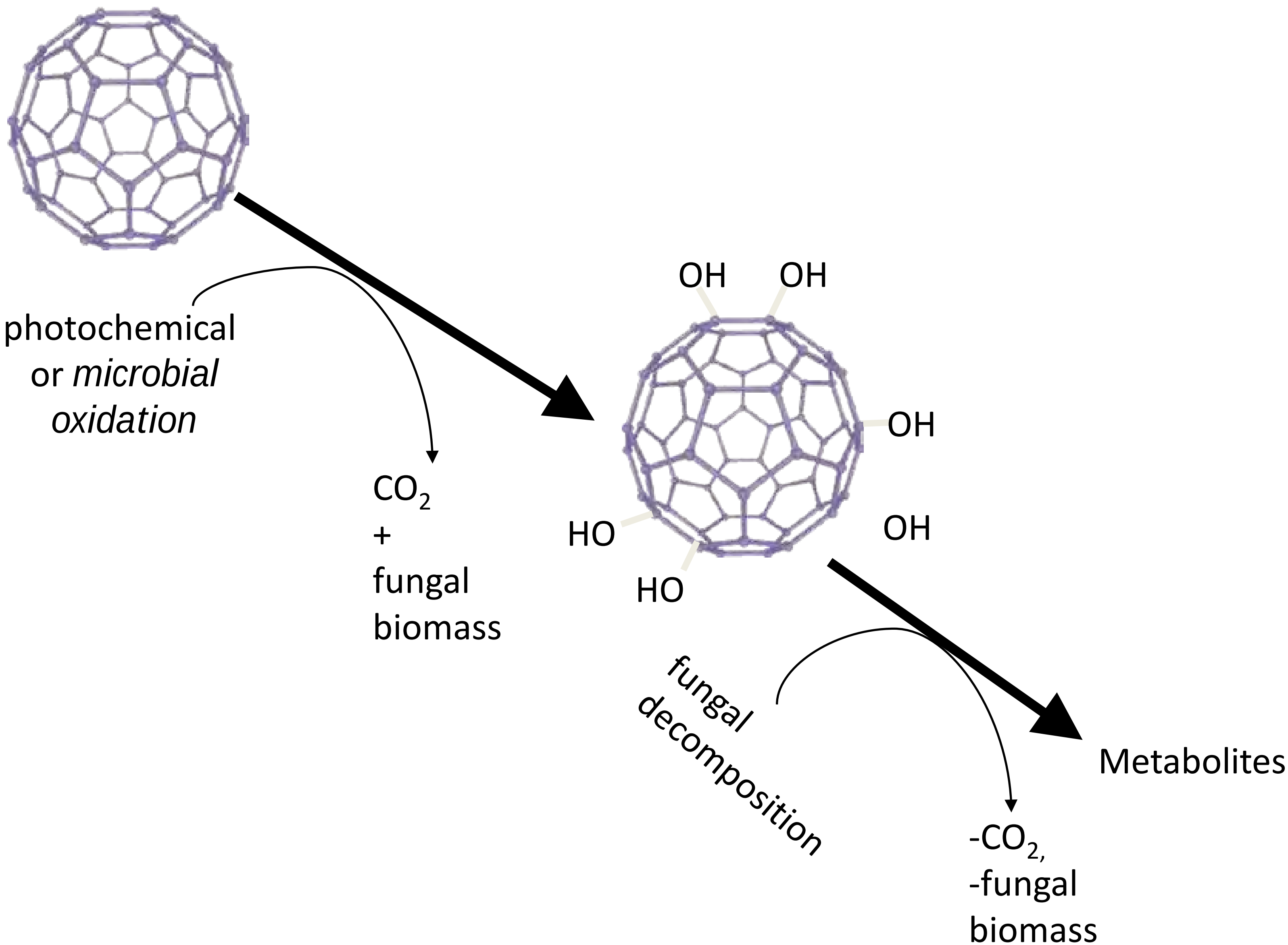


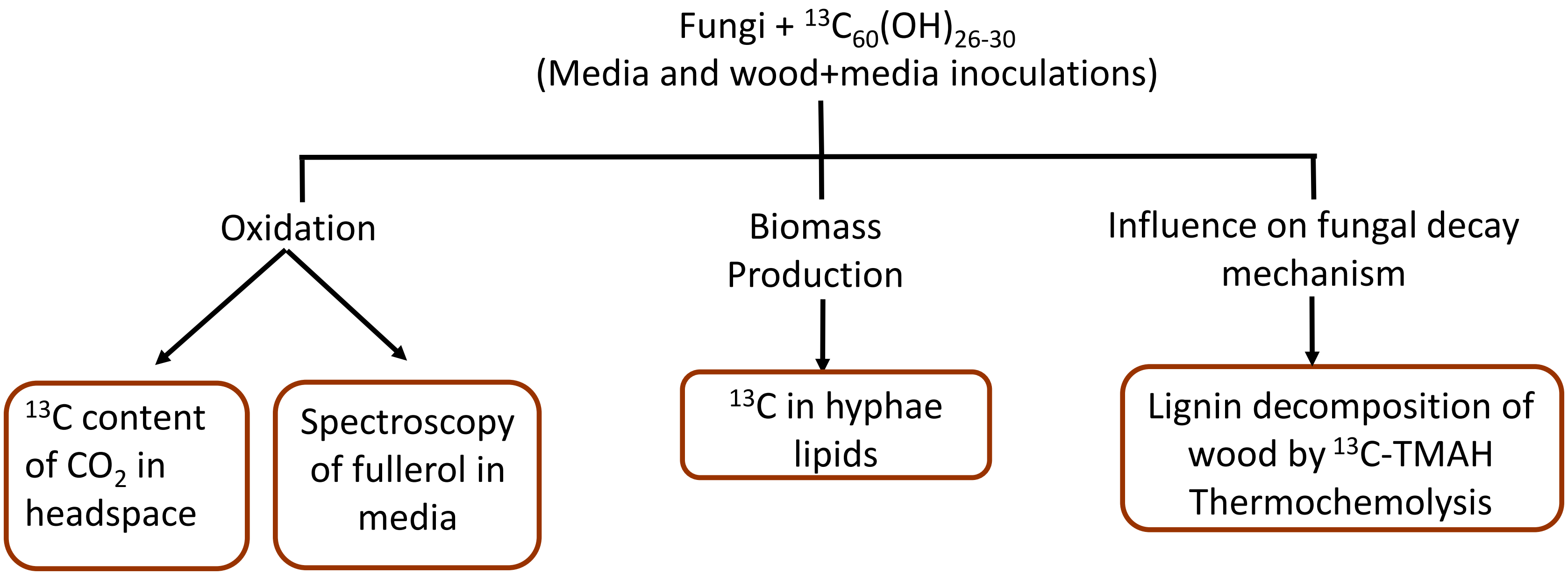


$+ {}^1O_2 \longrightarrow$ Further oxidation and fragmentation


C60 fullerene
& C60 clusters
Direct industrial release
Photo
oxidation
Microbial
oxidation
CO_2
Biomass
formation
Metabolite
formation
OH
OH
C60 fullerol
OH
OH
OH
Binding into natural
organic matter
and mineral surfaces

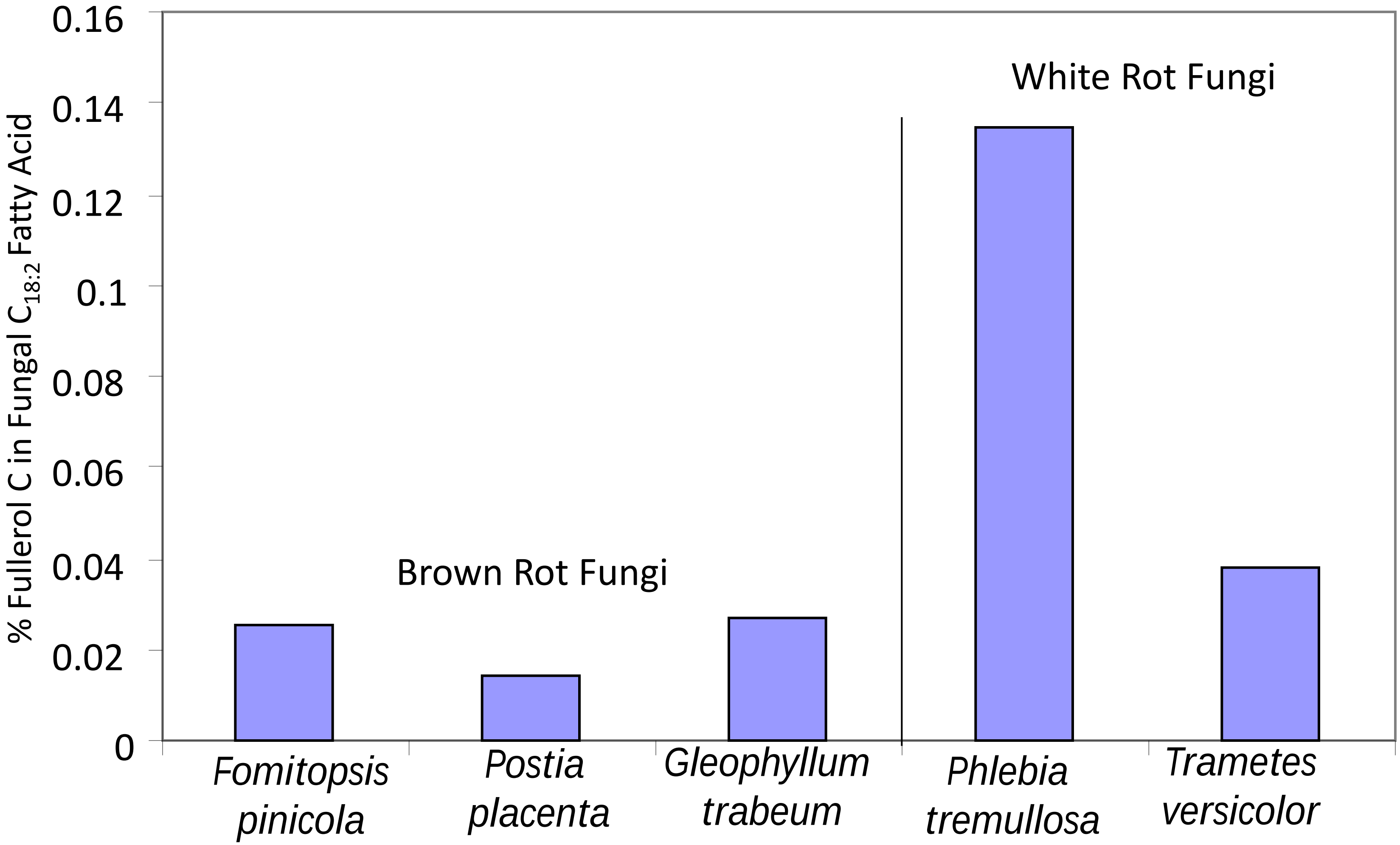
Fungal Transformation of C60





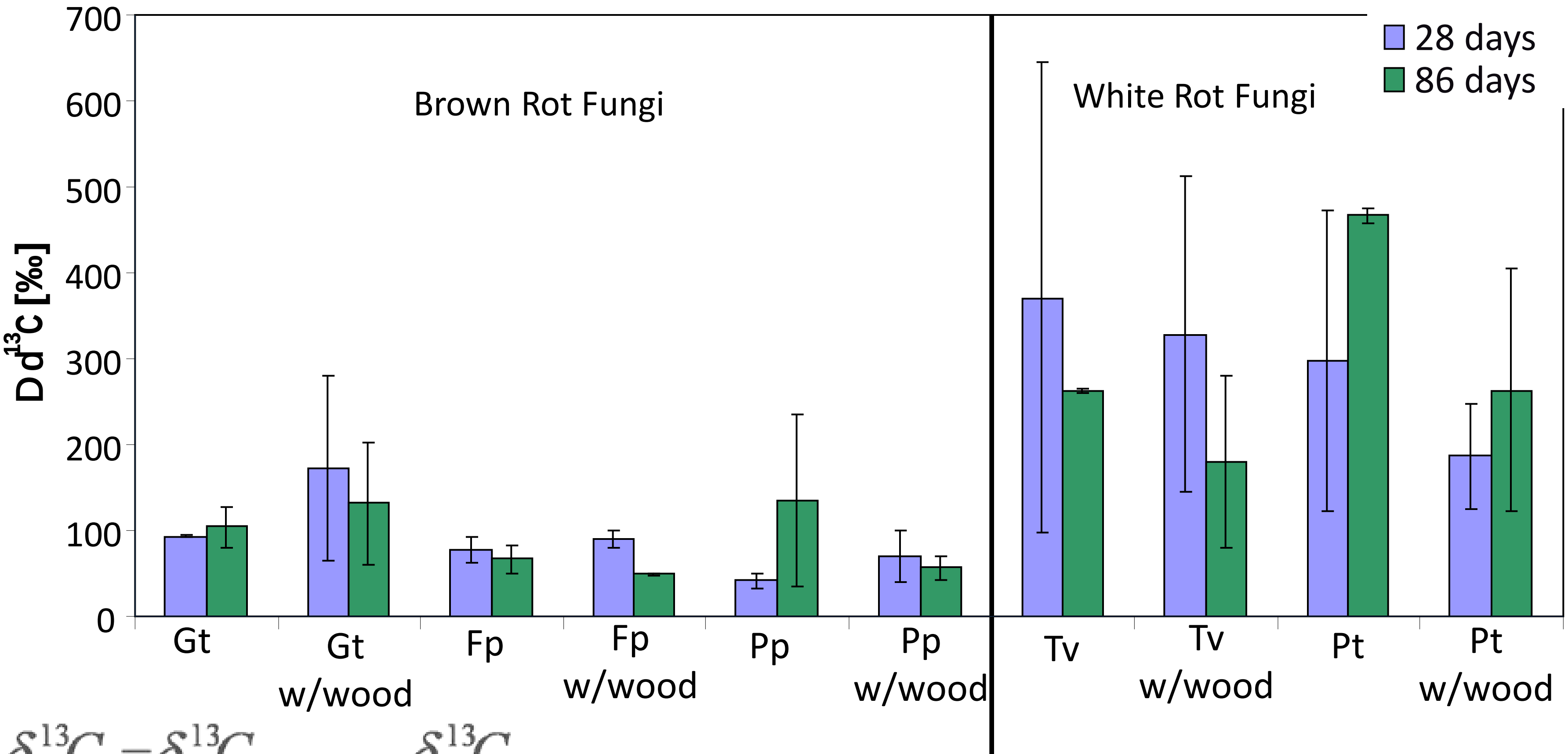
K. Schreiner, T. Filley, B. Beitler-Bowen, R. Blanchette, R. Bolskar, W. C. Hockaday, C. A. Masiello, and J. W. Raebiger (2009). "White rot basidiomycete mediated decomposition of C_{60} fullerol." *Environmental Science and Technology*, **43**(9), 3162-3168.

16 weeks decay



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}C of head space is showing some utilization

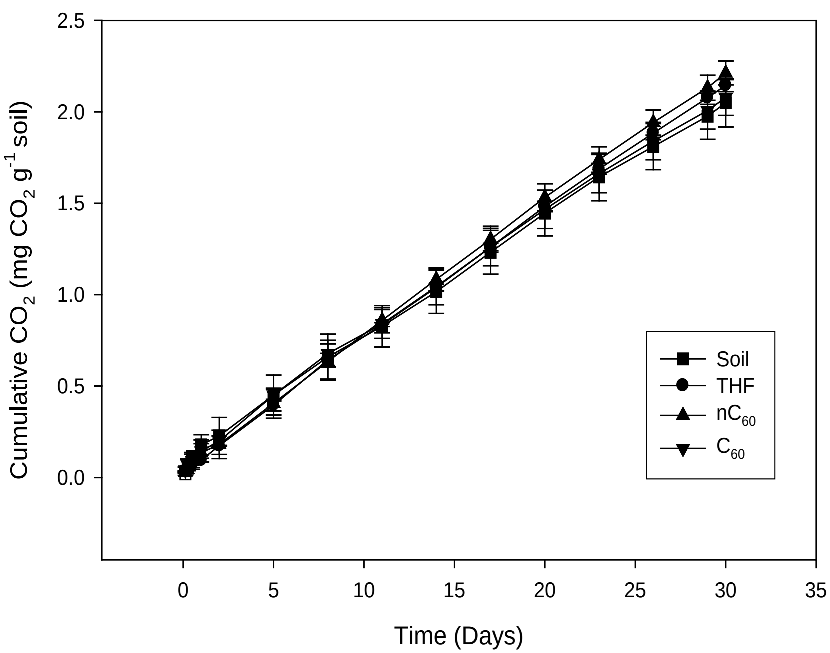


$$\Delta\delta^{13}C = \delta^{13}C_{labeled} - \delta^{13}C_{unlabeled}$$

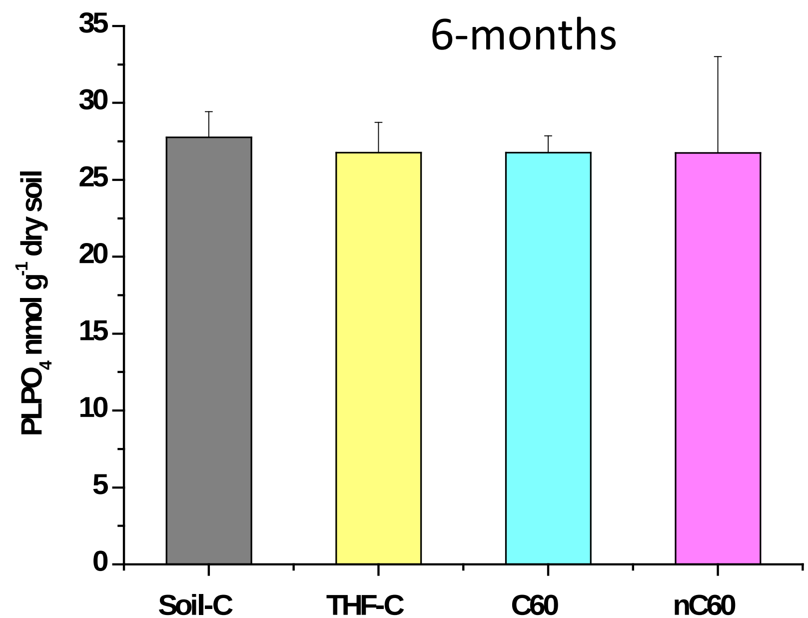
$$\delta^{13}C\ [\text{‰}] = \left(\frac{R_{CO_2}}{R_{PDB}} - 1\right) * 1000 \quad R = \frac{^{13}C}{^{12}C}$$

C60 and nC60 had little impact on soil functions

Soil Respiration



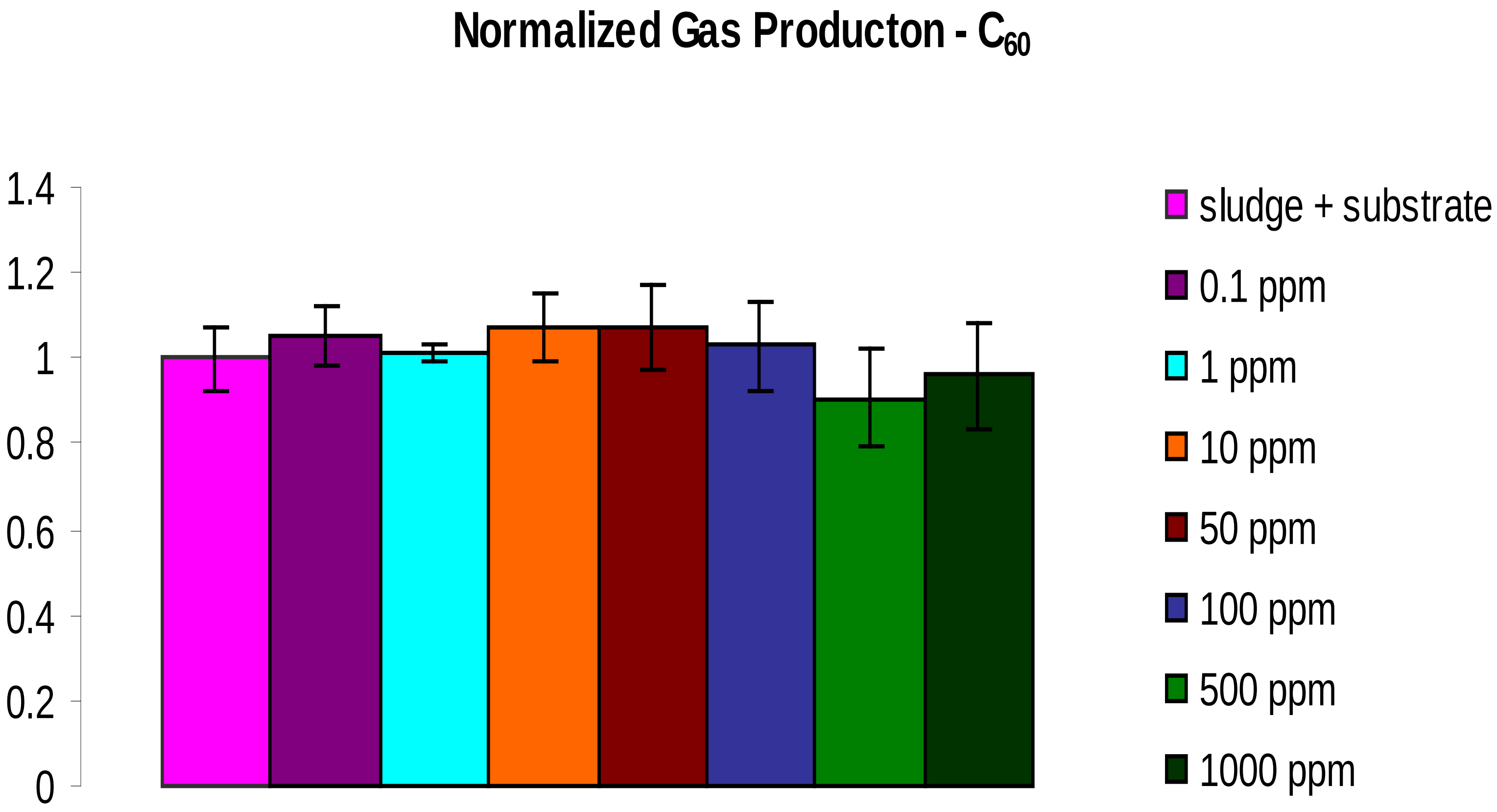
Biomass Size



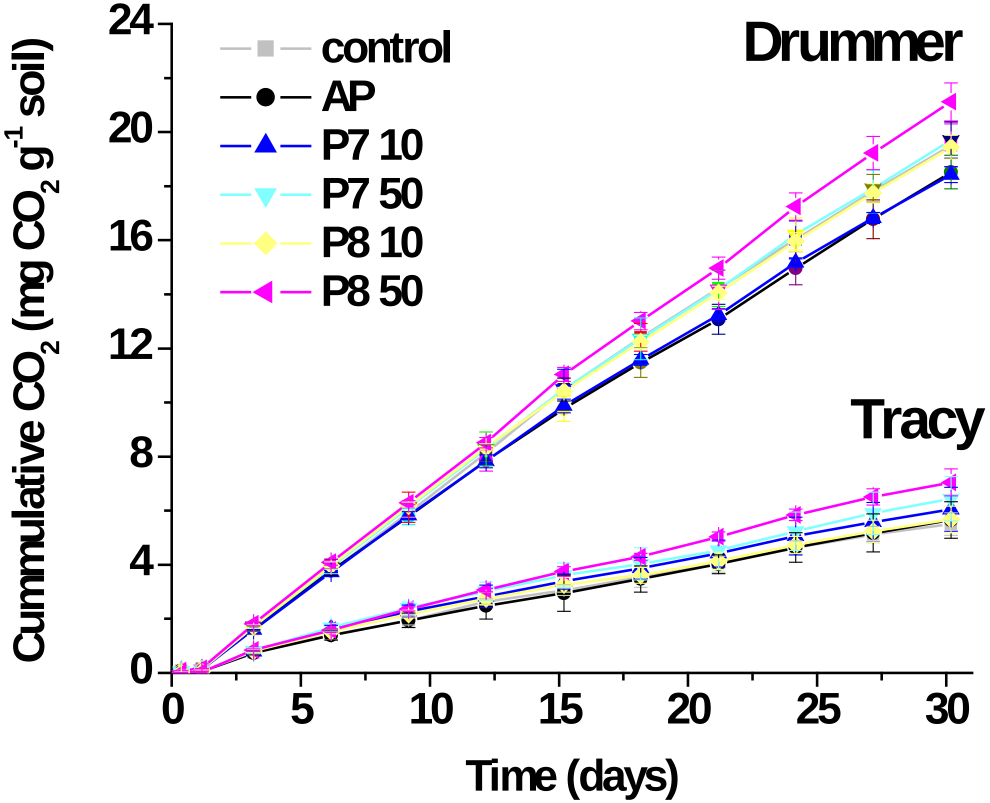
nC_{60} 1 ppm / C_{60} 1000 ppm – Drummer Soil

Tong, Z., M. Bischoff, L. F. Nies, B. Applegate, and R. F. Turco 2007. Impact of Fullerene (C_{60}) on a soil microbial community. Environmental Sciences and Technology 41:2985-2991

Anaerobic Systems & C60

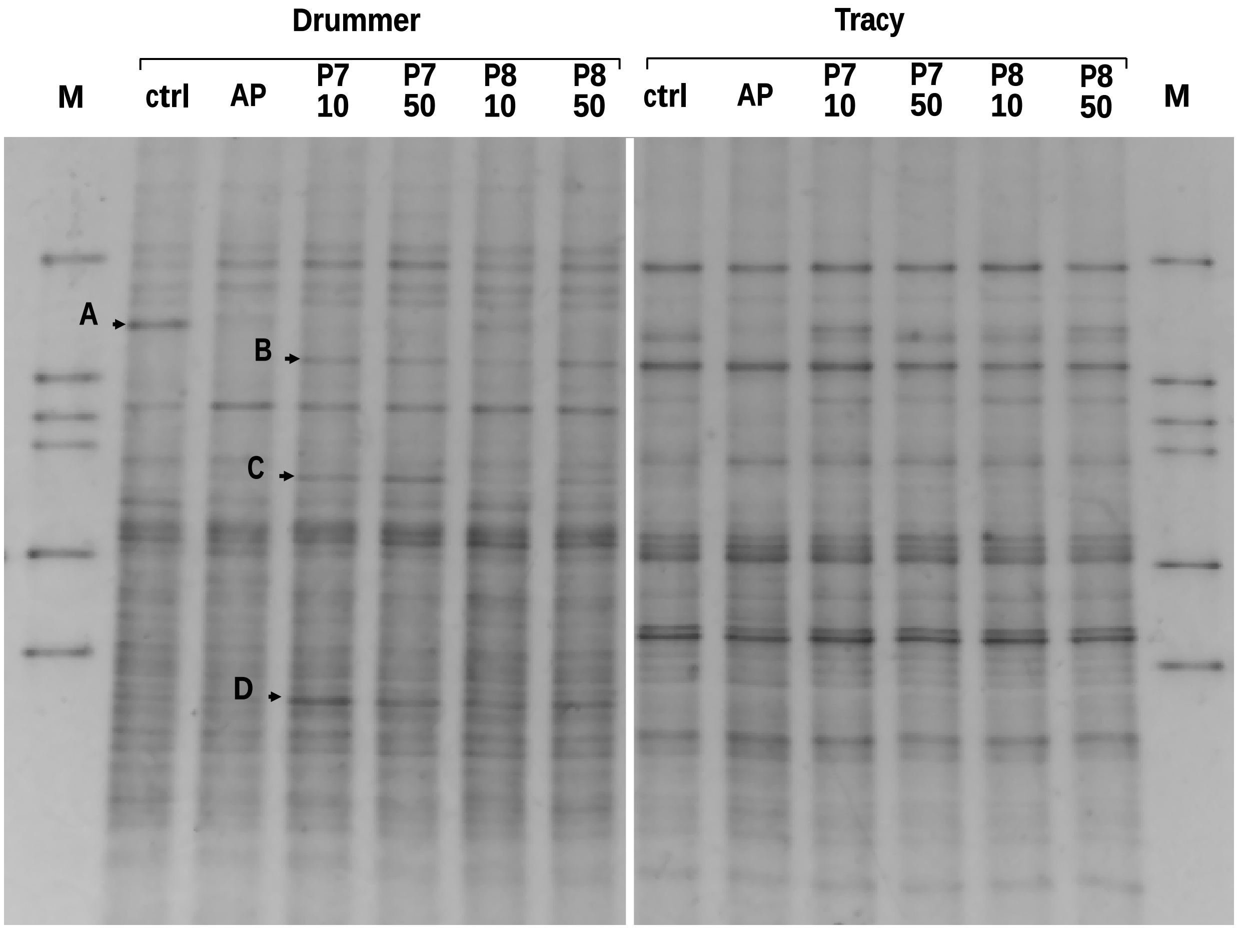


Basal Respiration - SWCT

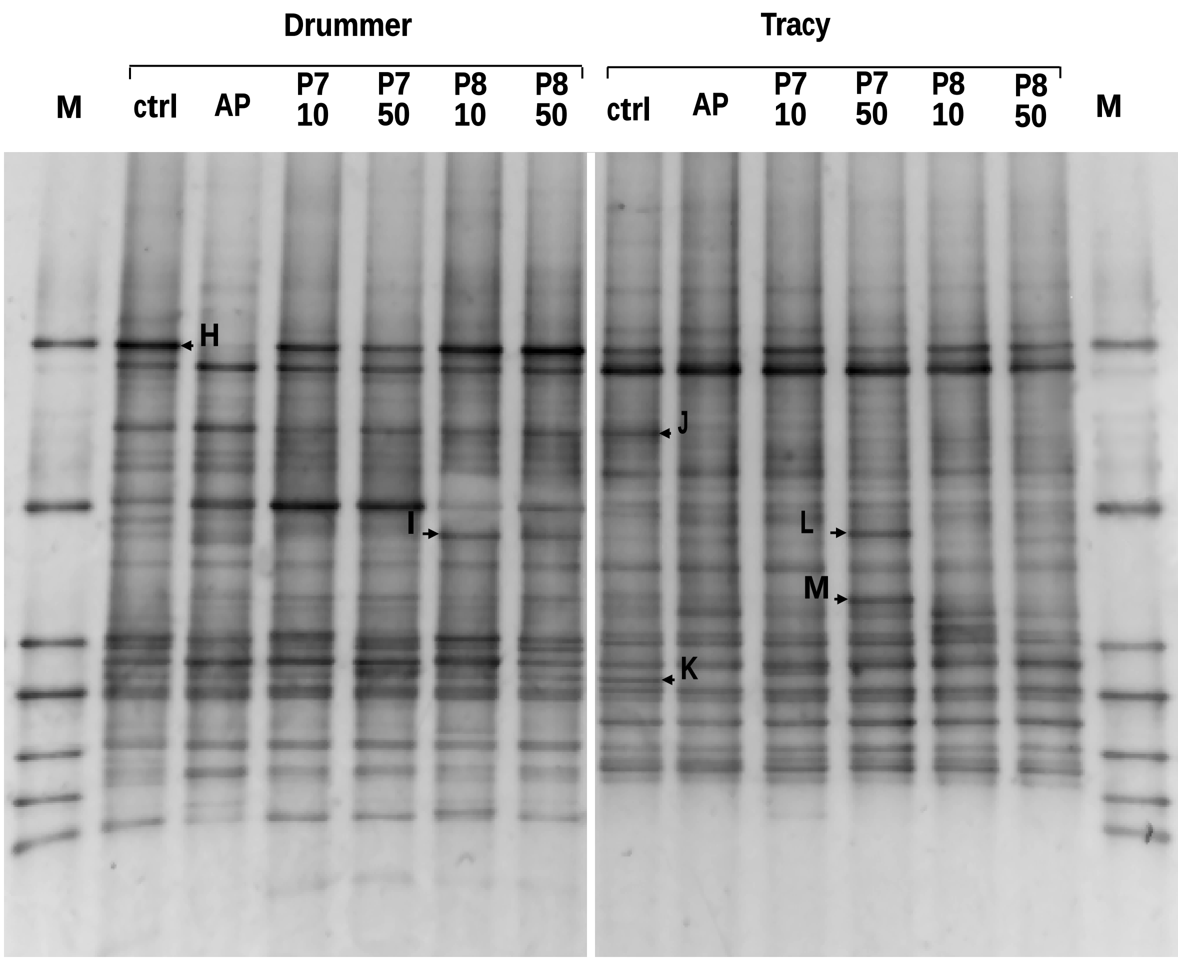


- control ----- soil control
- AP------ as-produced SWNTs
- P7 10 --- P7-SWNTs at 10 μg g^{-1} soil
- P7 50 --- P7-SWNTs at 50 μg g-1 soil
- P8 10 --- P8-SWNTs at 10 μg g-1 soil
- P8 50 --- P8-SWNTs at 50 μg g-1 soil

16S rDNA-DGGE Profiles

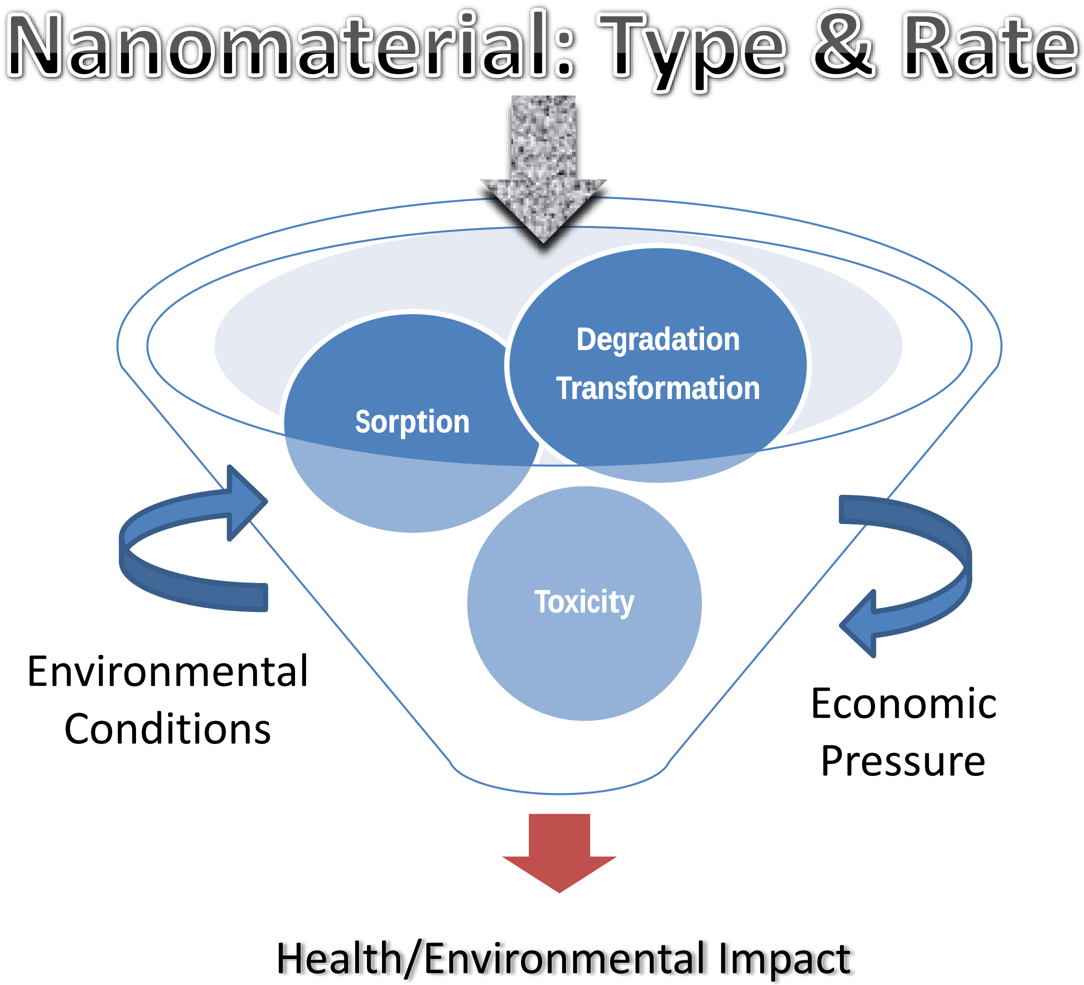


18S rDNA-DGGE Profiles



Conclusion

- Work on surface alteration of nanomatierals 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



The Environmental Caldron