Nanoscale Interactions between Engineered Nanomaterials and Black Carbon (Biochar) in Soil

Grant # USDA NSE 2012-67021-19300

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Project Objectives- An understanding of the interactions between engineered nanomaterials (NMs) and soil constituents, and a comprehension of how these interactions may affect biological uptake and toxicity is currently lacking. Black carbon (BC) is a natural constituent of soils due to fire history, and can be present at up to several percent by weight through the emerging practice of applying manufactured charcoal (biochar) to improve soil fertility. The structure of BC is nanoporous and hydrophobic, properties that may favor its heteroaggregation with engineered NMs. However, published reports on BC-NM interactions are completely absent. We have selected four NMs likely to be found in agricultural soils: zero-valent silver (n-Ag^0), cerium oxide (n-CeO_2), multiwalled carbon nanotubes (MWCNTs, ^{14}C-labelled), and n-C60 fullerene. The objectives are:

1. Quantify and characterize the binding and binding reversibility of NMs to macroscopic BC particles in aqueous suspensions as a function of solution composition and BC surface and pore characteristics (including the effects of weathering) with the goal of establishing a mechanistic model for these interactions. This objective will include a determination of the effect of BC addition on the retention of NMs in soil columns.
2. Determine the impact of BC nanostructure and weathering on the biological effects and accumulation of engineered nanomaterials in soil-based plant and earthworm bioassays. The effect of biochar on plant/worm biomass, transpiration, photosynthetic potential, reactive oxygen species production, and particle accumulation will be determined. An essential goal of this objective is to determine the correlation between bioavailability and physical availability as assessed in Objective 1.

The results will serve agriculture by providing a mechanistic foundation for the fate and bioavailability of NMs in soil that will aid in the development of accurate nanotoxicity risk assessments.

Approach and Progress- The materials have been prepared and characterized, and experiments to fulfill objectives 1 and 2 are underway. Biochars were produced from pecan shells at heat treatment temperatures (HTT) of 300, 350, 400, 500, 600, and 700 °C for 2 h. Both CO_2 surface area and porosity in the micropore region increased with HTT (129 → 542 m^2/g and 0.051 → 0.15 cm^3/g, respectively). However, the N_2 B.ET. surface area (<3 m^2/g) was not a useful parameter due to diffusion-limited adsorption of N_2 at 77 K. The pH of the product increased with increasing HTT.

Commercial n-CeO_2 (<25 nm) was obtained from Aldrich. In addition, n-CeO_2 was synthesized by two methods: 1) a room temperature method using $Ce(SO_4)_2$ and NH_3 solution with stirring for 2h (expected size <10 nm); and 2) a hydrothermal crystallization method by Masui et al. (2002) starting with $CeCl_4$ and citric acid plus NH_3, and heating to 80 °C for 24 h (expected size <10 nm). The X-ray diffraction spectra and TEM images of the commercial and two synthesized cerias are consistent with their expected particle size. The zeta potential curve for 100 mg/L in 10 m*M* NaCl indicates nanoparticle suspension stability at pH 3–5 and at pH

≥10. As expected, nanoparticles suspended in sodium citrate are more stable at a wider pH range than suspensions in sodium chloride. The Z-average size of 0.2 μm-filtered Aldrich ceria suspension in citrate was monomodal, independent of time (up to 5 d) and ranged from ~180 at pH 4 to ~190 at pH 7 to ~140 at pH 10.

A filtered suspension of 100 mg L^{-1} Aldrich ceria in 0.5 m*M* sodium citrate tribasic at pH 7.6 ±0.1 was mixed with different amounts of the 500 °C biochar at 20 °C for 2 days. After settling, ICP-MS analysis of the liquid phase showed ~14– 23% more elemental Ce than blanks. This indicates, first, that heteroaggregation of n-CeO_2 with this biochar seems unimportant, and second, that biochar may actually promote dispersion of ceria. Our working hypothesis is that dispersion is promoted by the soluble organic matter associated with the biochar.

The effect of biochar amendment to soil at 0, 0.5, and 5% on the toxicity and accumulation of n-CeO_2 (Aldrich, 0-2000 μg/g) by soybean and zucchini was determined. After one month of exposure, biomass (tissues and total), pigment production (chlorophyll A, chlorophyll B, and cartenoids), and Ce content of the tissues as determined by ICP-MS was measured as a function of treatmentAnalysis from the zucchini exposure is currently underway. For soybean, there were minimal effects of biochar presence on Ce uptake or plant biomass; in several instances, the trend was for decreased uptake with char presence, but there were no effects of statistical significance. Perhaps the most interesting finding was a significant decrease in pigment content/production in soybean upon ceria exposure, regardless of char presence. This is particularly interesting given the lack of biomass effects.

Water-dispersed n-C_{60} was prepared by stirring bulk fullerene in water for several weeks in the dark or by sonicating a fullerene-containing toluene layer in a large volume of water. Concentrated and more regularly shaped n-C_{60} could be prepared by adding naturally occurring surfactants. Dispersed n-C_{60} was recovered in the aqueous phase by adding salt and extracting with toluene, and its concentration was determined by liquid chromatography. After 3 days of mixing in water, n-C_{60} was found to be strongly attached to biochar, and could not be removed even with (65 ^{o}C) toluene. Smaller n-C_{60} fractions were especially tightly bound, suggesting penetration into the pore structure. Biochars made at higher HTT were most effective. These experiments indicated that (i) porosity, (ii) DOC, and (iii) density of biochar controlled the ability of biochar to take up stir-dispersed nC_{60}. Interestingly, biochars made at low temperature decreased the size of water soluble n-C_{60} by releasing soluble organic matter accompanying the biochar. Fluorescence analysis of biochar water extracts indicated carboxyl-rich dissolved organic matter that maximized for the 500 °C biochar.

Collaborations-

- Prof. Dr. Andreas Schäffer, Institute for Environmental Research (Biology V), Aachen University, Aachen, Germany.

Notable Discoveries-

- n-CeO_2 in the presence of citrate does not adhere appreciably to biochar.
- n-CeO_2 dispersion in aqueous citrate is enhanced by biochar.
- Biochar added to soil has little effect on Ce uptake and translocation by soybean.
- Ceria added to soil growing soybean decreases pigment content or production.
- Fullerenes strongly attach to biochar, possibly by pore penetration.
- Biochars made at low temperature decreased the size of water soluble n-C_{60}, likely by releasing soluble organic matter.