

The Influence of Natural Organic Matter on the Fate and Effects of Carbon Nanomaterials.

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A compound may be classified as nano in size if its diameter or another dimension is <100 nm (Mackay, C. et al., 2006, Lead, J. and Wilkinson, K., 2006). Many materials can be manufactured in nano sizes and have current and future commercial uses; nanoengineered titania particles for sunscreens and paints, silica nanoparticles as solid lubricants, and alumina nanoparticles in shampoos, detergents, and antiperspirants (Lecoanet, H. et al., 2004). There are already over 300 commercially available products containing some type of nanotechnology (Maynard et al. 2006), and the industry is expected to exceed \$1 trillion by 2015 (Nel et al. 2006). Despite industrial safeguards and environmental regulation, chemical contaminants from manufacturing processes are routinely deposited in aquatic ecosystems. Thus, increased manufacture and use of these materials will result in nanoparticles entering the aquatic environment.

Engineered carbon nanoparticles are inherently insoluble in aqueous systems. However, as is the case with many aquatic contaminants, the aqueous stability and bioavailability of these compounds may be influenced by the water quality of the receiving stream. Natural organic matter (NOM) exists in all surface waters and consists of complex molecules with varying molecular weight and chemical characteristics as well as both polar and apolar components. Lu and Su (2007) have shown that multiwalled nanotubes (MWNTs) will adsorb NOM from surface waters. Furthermore, Hyung et al. (2007) has demonstrated that the stability of MWNT suspensions were increased in the presence of NOM. This increased stability is likely to lead to increased exposure times for aquatic biota and, thus, increased potential for deleterious toxicological outcomes.

The goal of this study was to characterize the influence of NOM on the fate, bioavailability, and effects of MWNTs and the fullerenes C60 and C70 in aqueous medium by completing the following specific objectives: (1) characterize the behavior and stability of carbon nanomaterial suspensions as a function of NOM source and concentration; (2) characterize the acute toxicity of a stable NOM-Nanomaterial complex to the zooplankton *D. magna*; and (3) explore the NOM-Nanomaterial complex using electron microscopy techniques.

The acute toxicity of MWNTs in different NOM sources was determined using 96 hr. static toxicity tests with renewals every 24 hrs. The test designed used 3 different sources of NOM each at DOC concentrations of 15 mg/L, and one of the sources with additional concentrations of 5, 10, and 20 mg/L as DOC. Two of the NOM sources were Black and Edisto River waters that were collected from rivers in South Carolina and isolated by reverse osmosis (RO) (Sciera, K. et al., 2004). The third NOM source was Suwannee River Natural Organic Matter (SR-NOM) that was purchased from International Humic Substances Society (St. Paul, MN, USA). The acute toxicity of C60 and C70 was determined using 96 hr. static toxicity tests with renewals every 24 hrs using SR-NOM as the NOM source at concentrations of 2.5, 5, and 15 mg/L as DOC.

Multi-walled nanotubes (MWNTs) were made by Dr. A. Rao's Laboratory at Clemson University (Clemson, SC, USA) using the thermal chemical vapor deposition method catalyzed by the decomposition of a ferrocene-xylene mixture (Andrews, R., 1999). The

fullerenes C60 and C70 were purchased from SES Research (Houston, TX, USA) and are 99% pure.

In order to suspend the nanomaterials in NOM, they were first weighed on waxed weigh paper and then placed in a 100 mL glass centrifuge tube. NOM solution was added to a centrifuge tube and the solution was sonicated with a total solution volume of 100 mLs. The solutions were allowed to settle for approximately 24 hrs before the supernatant (stable solution) was removed with a glass pipette. Test concentrations of NOM-Nanomaterial were achieved by sonicating appropriate volumes of NOM-Nanomaterial supernatant stock solution in dilution water containing NOM.

The response of *D. magna* to MWNT suspended in SR-NOM was not influenced by the dissolved organic carbon (DOC) concentration. The source of NOM has a significant influence on the toxicity of MWNT to *D. magna*. This is evident when the LC50 values from the Black River, Edisto River, and Suwannee River are compared with concentrations of NOM normalized DOC concentration.

There was not a significant enough effect to *D. magna* to derive an LC50 value when exposed to C60 and C70 fullerenes. The sonication method that was used was not able to create solutions with high enough concentrations of fullerenes to derive an LC50 value. Scanning electron microscopy and transmission electron microscopy was used to visually examine NOM-Nanomaterial complexes as well as ingested NOM-Nanomaterial complex within the *D. magna* gut tract.

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