

ABSTRACT

Chen, Chia-Ying. Ph.D., Purdue University, December 2010. Sorption and Photochemistry of Manufactured Carbon Nanomaterials in the Aquatic Environment. Major Professor: Chad T. Jafvert.

With the growing use of carbon-based manufactured nanoparticles, including buckminsterfullerene and single-walled carbon nanotubes (SWNTs), it is likely that they will enter the environment through use, disposal, and spills; however, their environmental fate and subsequent effects on ecosystems have not been extensively studied. One of the key knowledge gaps in understanding their effects on the environment is the lack of quantitative data on their transformations in the natural environment, which is crucial for lifecycle analysis. To this end, this study has examined two potentially important environmental fate processes - sorption and photoreactivity - of these nanomaterials. Although C_{60} is extremely hydrophobic, molecular C_{60} does exist in water, and it is through this dissolved concentration or activity that its environmental distribution will be regulated (i.e., thermodynamically controlled), including its self-association to form clusters or nanoparticles. The distribution of C_{60} between soil and mixtures of ethanol (EOH) and water were measured at ethanol mole fractions ranging from $X_{EOH} = 1.0$ to 0.4 for two soils. By measuring K_p at $X_{EOH} = 1.0$ for a series of soils that ranged in organic carbon and clay mineral content, possible mineral contribution to the overall partition process was found for some of the soils. After correcting for any mineral contribution to sorption, the organic carbon normalized partition coefficient, K_{oc} , at each value of X_{EOH} was calculated from the measured K_p values. Through a classical thermodynamic relationship, the K_{oc} values determined at $X_{EOH} = 1.0$ to 0.4 were extrapolated to estimate the pure water (i.e., $X_{EOH} = 0$) K_{oc} value of $10^{7.1}$ (L/kg). Accounting for dissolved organic matter (DOM) in any natural water-soil mixtures may lower this estimate by over a factor of 2, placing this estimate in good agreement with C_{60} 's octanol-water partition coefficient, K_{ow} ($= 10^{6.7}$). Also, the photoreactivity of single-walled carbon nanotubes (SWNTs) that (i) have been functionalized via acid oxidation to contain carboxylic acid groups, (ii) further functionalized via esterification with polyethylene oxide groups, or (iii) are unmodified (i.e., unfunctionalized) was examined. Aqueous colloidal dispersions of both types of functionalized nanotubes generated reactive oxygen species (ROS) including singlet oxygen (1O_2), superoxide anion (O_2^-), and hydroxyl radicals ($\cdot OH$) in light within the solar spectrum ($\lambda = 300$ to 410 nm) under aerobic conditions. Defects in the fullerene surface caused by functionalization, as well as differences in amorphous carbon and metal impurity content within the different SWNT preparations, may facilitate ROS production. Experiments suggest that the metal impurities may especially contribute to $\cdot OH$ generation. It appears that the functionalized nanotubes can act as the electron donors directly (resulting in a change in their properties) or can shuttle electrons from other electron donors to form these reactive oxygen species. Addition of NADH as an electron donor to colloidal dispersions of carboxylated SWNTs resulted in O_2^- generation in the absence of light, suggesting dark reaction electron transfer as a potential mechanism of toxicity.