

## Ph.D. Defense Abstract

### Environmental Photochemistry of Aqueous Buckminsterfullerene ( $C_{60}$ ) Clusters

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Because large scale application of buckminsterfullerene  $C_{60}$  in commercial products has nearly come to realization, it is anticipated that significant quantities of  $C_{60}$  will reach the natural environment over the next decades. Therefore, it is imperative to understand its persistence, fate, and potential health impacts in the environment. To address part of this knowledge gap, this study has examined a potentially significant environmental fate process - photochemical transformation of aqueous  $C_{60}$  nanoparticles ( $nC_{60}$ ). Stable  $nC_{60}$  suspensions form upon mixing  $C_{60}$  with water, and may be an important route for  $C_{60}$  to enter the environment.

In this study,  $nC_{60}$  was observed to phototransform with a half-life of approximately 1 day under continuous fall sunlight (West Lafayette, IN,  $86^{\circ}55'$  W,  $40^{\circ}26'$  N). The loss of  $C_{60}$  from the aqueous suspension occurred concurrent with the loss of the yellow-brownish color of parent  $nC_{60}$  and the decrease in the nanoparticle size. The lost  $C_{60}$  occurred with accumulation of soluble photoproducts in the aqueous phase. The phototransformation kinetics in sunlight was dependent on the cluster size, but was independent of pH (3-11), the presence of Suwannee River fulvic acid (10 mg/L), or preparation method (THF/ $nC_{60}$  versus SON/ $nC_{60}$ ).

In contrast to reports showing no  $^1O_2$  formation during short-term irradiations ( $< 2$  h) under similar conditions, the results of this study indicate that  $^1O_2$  forms upon irradiation of  $nC_{60}$  ( $> 15$  h), using furfuryl alcohol (FFA) as a reactive  $^1O_2$  scavenger. Further,  $^1O_2$  generation was more pronounced after soluble photoproducts had accumulated in solution. Removing  $O_2$  completely quenched the losses of FFA and  $C_{60}$ , indicating  $nC_{60}$  phototransformation requires  $^1O_2$  in accordance with the phototransformation mechanism reported for molecular  $C_{60}$  in organic solvents. Additional evidence for  $^1O_2$  as a reactive intermediate is that reactions in  $D_2O$  or in the presence of azide ion accelerated or slowed  $^1O_2$  formation, respectively. In summer sunlight, reaction rates indicate that  $^1O_2$  concentration occurring during photolysis of  $nC_{60}$  is approximately 1 order of magnitude higher than the average value typically found in natural waters containing an equivalent amount of natural organic carbon.

Light within the visible portion of the solar spectrum ( $\lambda \geq 400\text{nm}$ ) was shown to be sufficient for  $nC_{60}$  phototransformation and  $^1O_2$  production. Under monochromatic light

at either 366 or 435 nm, the apparent quantum yields were  $1.48 \times 10^{-5}$  and  $2.95 \times 10^{-5}$ , respectively, again indicating the visible light is sufficient for transformation.

Characterization of the photoproducts by XPS, FTIR and  $^{13}\text{C}$ -NMR methods collectively reveal the occurrence of multiple oxygen-containing functionalities on the remaining carbon molecules, with analysis by LDI-TOF mass spectrometry indicating that most of the material retains its original 60-carbon structure.