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Modeling TiO_2 nanoparticle phototoxicity: The importance of chemical concentration, ultraviolet radiation intensity, and time

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ABSTRACT

As a semiconductor with wide band gap energy, TiO_2 nanoparticles (nano-TiO_2) are highly photoactive, and recent efforts have demonstrated phototoxicity of nano-TiO_2 to aquatic organisms. However, a dosimetry model for the phototoxicity of nanomaterials that incorporates both direct UV and photo-activated chemical toxicity has not yet been developed. In this study, a set of *Hyalella azteca* acute toxicity bioassays at multiple light intensities and nano-TiO_2 concentrations, and with multiple diel light cycles, was conducted to assess how existing phototoxicity models should be adapted to nano-TiO_2. These efforts demonstrated (a) adherence to the Bunsen-Roscoe law for the reciprocity of light intensity and time, (b) no evidence of damage repair during dark periods, (c) a lack of proportionality of effects to environmental nano-TiO_2 concentrations, and (d) a need to consider the joint effects of nano-TiO_2 phototoxicity and direct UV toxicity.

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1. Introduction

Nanoscale titanium dioxide (nano-TiO_2), one of the most widely used nanomaterials, has applications ranging from personal care products to solar cells (Canesi et al., 2010; Clemente et al., 2014). Because of its wide band gap energy (3.2 eV for anatase TiO_2), nano-TiO_2 can be photo-activated upon ultraviolet (UV) irradiation (wavelength < 390 nm), making nano-TiO_2 a promising photo-catalyst. Unfortunately, by generating reactive oxygen species (ROS; $OH^{\bullet}$, and $O_2^{-\bullet}$), this physicochemical property also can cause phototoxicity to a wide range of species, such as bacteria (Tong et al., 2013), marine phytoplankton (Miller et al., 2012), water column freshwater species (Bar-Ilan et al., 2012; Ma et al., 2013, 2012a, b), and benthic organisms (Li et al., 2014a, b).

Despite recent interest in the phototoxicity of nano-TiO_2, investigations have been lacking in phototoxicity dosimetry, especially regarding the combined effects of UV intensity (I), nano-TiO_2 concentration (C), and exposure time (t). Dosimetry models have been published for the phototoxicity of polyaromatic hydrocarbons (PAHs) (Oris et al., 1984; Oris and DIesy, 1986; Ankley et al., 1995, 1997). These models were founded on the well-known Bunsen-Roscoe photochemical law, which states that the concentration (P) of a photochemical reaction product is proportional to the product of light intensity and time, if there are no disturbing side reactions (Bunsen and Roscoe, 1857), and on the simple extension of this law that P is also proportional to chemical concentration (i.e., $P \propto C \cdot I \cdot t$). These models were further premised on cellular damage (D) accumulating in proportion to P until this damage reaches a toxic level. For $D \propto C \cdot I \cdot t$, a toxic effect would be associated with a constant value for $C \cdot I \cdot t$, resulting in reciprocal relationships for time-to-effect versus C·I and effect concentrations versus I·t. Although various factors such as the toxicokinetics of chemical accumulation and repair of the damage can cause deviations from strict reciprocity, a considerable degree of such reciprocity has been demonstrated for the phototoxicity of PAHs (Oris et al., 1984; Oris and DIesy, 1986; Ankley et al., 1995, 1997).

The issue here is to what degree phototoxicity of nano-TiO_2 follows similar relationships and what might be responsible for any deviations. Of particular concern for nano-TiO_2 is the proportionality of damage to the environmental concentration of the chemical. For chemicals such as PAHs that accumulate within cells and thus are in close proximity to the biochemical targets of the

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products of photo-activation, cellular damage can be reasonably expected to be proportional to chemical accumulation, which in turn can be related to environmental concentrations via simple toxicokinetic relationships. In contrast, for nano-TiO_2, consideration also must be given to material coating an organism or ingested into its gastrointestinal (GI) tract and not further absorbed, such accumulation being more physically separated from cellular receptors and not necessarily proportional to environmental concentrations. Another concern is the direct damage caused by UV light independent of the products of nano-TiO_2 photoactivation, which was not considered in the models for PAH photoactivated toxicity cited above.

In this study, we investigated phototoxicity of nano-TiO_2 to *Hyalella azteca* in acute (48 h) assays to test whether the reciprocal relationships of C, I, and t used in previous models of phototoxicity are applicable and to determine whether direct UV effects are of sufficient importance to be included in models for this toxicity. This work was not intended to fully develop a model with regulatory applications, but rather to establish certain features such a model should have. *H. azteca* was selected as the test organism because ecotoxicological studies of nanomaterials in aquatic systems have been conducted mainly on water column species, while limited studies have addressed its significance to aquatic benthic organisms, whose habitat is the ultimate repository for nanomaterials (Galloway et al., 2010; Gottschalk et al., 2009; Li et al., 2014a; Pang et al., 2012). *Hyalella azteca* has been recommended by the United States Environmental Protection Agency (USEPA) for measuring the toxicity of conventional contaminants in sediment (USEPA, 2000). Previous work in our lab confirmed that *H. azteca* is an appropriate organism for addressing the risk of photoactive nanomaterials associated with sediments (Li et al., 2014a, b).

2. Materials and methods

2.1. Study design

Two experiments were performed to investigate the relationship of toxic effects to UV intensity, nano-TiO_2 concentration, and exposure time. In one experiment, a factorial design with seven nano-TiO_2 concentrations (0–144 μg/cm^2 substrate) and eight UV intensities (0–9.4 W/m^2) was used, each treatment having duplicate test vessels containing 8 organisms each. The vessels were exposed for two 4-h illuminated periods in a solar simulator chamber, each followed by 20 h of dark, with mortality being monitored at the end of each dark period. The effects of time were addressed in this manner, rather than using a more natural photoperiod, so that the mortality attributed to each illuminated period would include any delays in death and that any deviations in the reciprocity of UV intensity and time due to damage repair during the dark periods would be more evident.

In the other experiment, mortality from UV exposure alone was investigated to more fully characterize its dosimetry and better evaluate its importance to the joint effects of UV and nano-TiO_2 exposure. Ten UV intensities ranging from 0 to 54 W/m^2 were used, each treatment having triplicate test vessels containing 8 organisms each. As in the first experiment, exposures consisted of two 4-h illuminated periods, each followed by 20 h of dark, but mortality was only determined at the end of the experiment.

2.2. Test water and chemical

Test organism culture and all bioassays were conducted in Lake Superior water (St. Louis County, MN, USA) modified by the addition of 16.6 mg/L NaCl to improve *H. azteca* health. Conductivity, pH, and dissolved oxygen in all experimental treatments were in the range of 7–9 mS/m, 8.0–8.2, and 8–10 mg/L, respectively.

A 500 mg/L nano-TiO_2 stock suspension was prepared from Aeroxide TiO_2 P25 (Evonik Degussa Corporation, NJ) by sonication in modified Lake Superior Water (MLSW) for 1 h in a bath-type sonicator (Fisherbrand, 35 kHz frequency; Fisher Scientific, Pittsburgh, PA, USA). Detailed characterizations of this nano-TiO_2 can be found in our previous study (Li et al., 2014a, c). Briefly, nano-TiO_2 in the present study had an average primary particle size of 25.1 ± 8.2 nm (transmission electron microscope, mean ± SD, n = 100), a Brunauer–Emmett–Teller (BET) surface area of 51.1 m^2/g, and a crystalline structure of 86% anatase and 14% rutile. Working suspensions were also made in MLSW and sonicated for 20 min before the initiation of bioassays.

2.3. Experimental organism

Hyalella azteca was cultured as described in our previous study (Li et al., 2014a). Briefly, *Hyalella azteca* adults were maintained in MLSW in static 5.5 gallon aquariums. Neonates 0–1 d old were collected and added to 2 L beakers of MLSW. After 7–8 days, the juveniles were collected for the toxicity tests. The culture was maintained at 23 ± 1 °C and fed daily a 1:1:1 mixture of yeast:-Ceropyl:Tetramin (YCT) and *Pseudokirchneriella subcapitata*. Photoperiod was maintained at 16 h light/8 h dark with an illumination of 1280 lux.

2.4. Bioassay system and procedures

The bioassay system consisted of a solar simulator (Q-Sun 3000 Xenon Test Chamber; Q-Lab) with a 69 × 40 cm recirculating, temperature-controlled water bath (23 ± 1 °C) and three Xenon lamps that reproduced the full spectrum of solar radiation from 280 to 800 nm. The reproduction of the solar radiation spectrum was confirmed in our previous study by comparing spectra between sunlight and simulated solar radiation (Ma et al., 2012a). Test organisms were exposed in 50 mL beakers containing 8 organisms, 0.5 mL (depth < 1 mm) of sand substrate (425 μm particle size, Unimin Corporation, New Canaan, CT, USA), and 30 mL of test solution. Such small beakers were necessitated by the size limitations of the solar simulator, but provided adequate area and volume for these small test organisms.

The working nano-TiO_2 suspension was diluted to 10–60 mg/L with MLSW in the test beakers and allowed to settle for 3 h before introduction of the test organisms. Our previous studies indicated that >80% of this nano-TiO_2 settled to the substrate within this timeframe (Li et al., 2014a, b, c). Because this experiment involved exposing an epibenthic organism to nano-TiO_2 on the substrate surface, the concentration metric used here is the mass of nano-TiO_2 per area of substrate, which ranged from 24 to 144 μg/cm^2. For the modeling issues of concern here, more details regarding the nano-TiO_2 exposure in the test organisms' microenvironment under these heterogeneous conditions need not be specified; rather, it suffices that the concentration metric used should be approximately proportional to these actual exposure conditions.

Organisms were fed 2 h before the initiation of bioassays and no food was added during the tests. Daily 4-h UV exposures were applied and mortalities were recorded at 24 h and 48 h. Different UV intensities were achieved by placing various neutral-density and stainless steel screen filters over test chambers. UV intensities were measured at the surface of the water bath with a photodiode array spectrometer (model S2000; Ocean Optics, Dunedin, FL, USA).

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