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Titanium dioxide nanoparticle exposure reduces algal biomass and alters algal assemblage composition in wastewater effluent-dominated stream mesocosms

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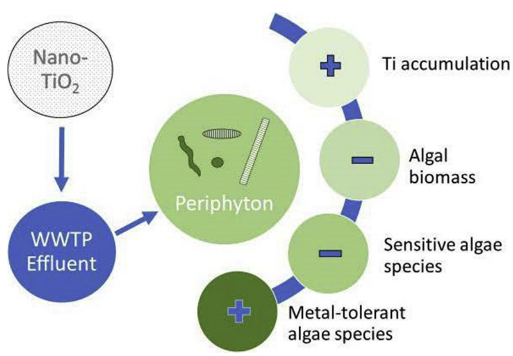
HIGHLIGHTS

- TiO_2NP are under consideration for treating pharmaceuticals in wastewater.
- Outdoor stream mesocosms using effluent as sourcewater were dosed with TiO_2NP.
- There was significant periphyton Ti accumulation in the high concentration group.
- Periphyton biomass declined and algal assemblage structure was altered.
- Significant ecological impacts could result from using TiO_2NP to treat wastewater.

GRAPHICAL ABSTRACT



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ABSTRACT

A 5-week mesocosm experiment was conducted to investigate the toxicity of titanium dioxide nanoparticles (TiO_2NPs) to periphytic algae in an environmentally-realistic scenario. We used outdoor experimental streams to simulate the characteristics of central Texas streams receiving large discharges of wastewater treatment plant effluent during prolonged periods of drought. The streams were continually dosed and maintained at two concentrations. The first represents an environmentally relevant concentration of 0.05 mg L^{-1} (low concentration). The second treatment of 5 mg L^{-1} (high concentration) was selected to represent a scenario where TiO_2NPs are used for photocatalytic degradation of pharmaceuticals in wastewater. Algal cell density, chlorophyll-*a*, ash-free dry mass, algal assemblage composition, and Ti accumulation were determined for the periphyton in the riffle sections of each stream. The high concentration treatment of TiO_2NPs significantly decreased algal cell density, ash-free dry mass, and chlorophyll-*a*, and altered algal assemblage composition. Decreased abundance of three typically pollution-sensitive taxa and increased abundance of two genera associated with heavy metal sorption and organic pollution significantly contributed to algal assemblage composition changes in response to TiO_2NPs. Benefits of the use of TiO_2NPs in wastewater treatment plants will need to be carefully weighed against the demonstrated ability of these NPs to cause large changes in periphyton that would likely

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propagate significant effects throughout the stream ecosystem, even in the absence of direct toxicity to higher trophic level organisms.

1. Introduction

Laboratory studies have extensively explored the effects of titanium dioxide nanoparticles (TiO_2NPs) on aquatic organisms (Aruoja et al., 2009; Binh et al., 2016; Hall et al., 2009; Kulacki et al., 2012), but have fallen short in addressing the associated behavior and toxicity in natural waters under field conditions. TiO_2 was approved as a food additive by the Food and Drug Administration (FDA) in 1996, and is used widely in food and pharmaceutical and personal care products, in medical devices, and in paints and coatings (Shah et al., 2017; Weir et al., 2012). Currently, data on the presence and use of TiO_2NP in food and pharmaceuticals and personal care products is scarce because production volume can be considered proprietary and companies are not yet required to report information on nanomaterial production (Hendren et al., 2011). TiO_2NPs are widely used in the medical field for devices, implants, dressings, and targeted cancer treatment, as well as electronics and computers (Nowack and Bucheli, 2007). Bulk elemental Ti is practically nontoxic on its own and is actually used in commercial fertilizers to stimulate higher crop productions (Lyu et al., 2017), while bulk TiO_2 can exert some toxicity. However, in comparative studies conducted with bulk TiO_2 and TiO_2NPs, the TiO_2NPs demonstrate higher toxicity (Aruoja et al., 2009; Sendra et al., 2017). TiO_2NPs exhibit negligible release of the most common ion Ti^{4+} (Dalai et al., 2012), and toxicity studies conducted with Ti^{4+} have found that it is minimally toxic (Puleo and Huh, 1995) at concentrations realistically expected to be found in association with elemental Ti. However, nano-TiO_2 has been demonstrated as toxic to algae, fish, daphnids, and bacteria in several studies (Aruoja et al., 2009; Binh et al., 2016; Hall et al., 2009; Kulacki et al., 2012), which indicates that the nanoparticles are largely responsible for toxicity.

The lack of public information regarding TiO_2NP use in pharmaceuticals and person care products, paints, coatings, medical devices, etc. hinders accurate estimates of the amount of TiO_2NP being released into natural waters. While TiO_2NPs once represented a very small fraction of the total amount of titanium dioxide produced (~3% in 2009), one of the more recent predictions available suggests that industries will have largely converted to using TiO_2NP by 2025 (Robichaud et al., 2009). Recent estimates of the lower and upper bounds of production in the United States for TiO_2NPs were 7800 and 38,000 tons per year, respectively (Hendren et al., 2011). For the year 2012, the most recent date that production data could be obtained, Keller et al. (2013) estimated a worldwide production volume of 88,000 metric tons per year.

TiO_2NPs are photoactivated by, and absorb UV light, making them an ideal coating in outdoor applications. The characteristically high surface area-to-volume ratio inherent to nanoparticles serves to reinforce the innate nature of titanium dioxide photocatalytic activity and UV absorption at wavelengths ranging from 345 to 388 nm (Shao and Schlossman, 1999). However, their increased use in outdoor applications translates to an increased probability of particle release to the environment. The photocatalytic properties that make TiO_2NPs especially suited for outdoor use also render them phototoxic, and in part determine the degree of toxicity of TiO_2NPs to aquatic biota because higher toxicity is observed when TiO_2NPs are photoactivated (Clemente et al., 2012).

Stream periphyton is likely the first aquatic community to exhibit a response to effluent and contaminant releases (Sabater et al., 2007). Periphyton is a complex benthic assemblage of algae, bacteria, microfauna, and fungi, protected by a mucopolysaccharide matrix (Sabater et al., 2007), serving as the base of the food web in stream ecosystems that do not receive substantial inputs of allochthonous materials (Wetzel, 2011). Stream periphyton has been shown to be sensitive to the concentrations of contaminants, dissolved organic matter, and nutrients, making it a useful bioindicator of anthropogenic disturbances such as habitat degradation or localized contaminant release (Sabater et al., 2007). While periphyton can mediate the impacts of anthropogenic nutrients and contaminant stressors via sequestration from the water column (Hill et al., 2010), this accumulation of contaminants has an environmental cost because periphyton can become a concentrated repository and source of contaminants in freshwater ecosystems (Hill et al., 1996; Hill et al., 2010).

Generally, TiO_2NP toxicity to periphytic algae occurs as a function of nanoparticle surface area and size, with smaller particle sizes corresponding to more toxic effects (Hartmann et al., 2010; Hund-Rinke and Simon, 2006; Navarro et al., 2008). TiO_2NP-mediated impacts on algal cells in natural waters are likely a result of the release of reactive oxygen species (ROS) and/or TiO_2NP aggregate-mediated shading (Navarro et al., 2008; Wang et al., 2016). Both ROS toxicity and shading can result in inhibition, but this usually requires adsorption of the particles onto the surface of algal cells. In the case of shading effects, nanoparticle aggregates may attach to and/or entrap algal cells, which can reduce available light needed for photosynthesis and restrict numerous other cellular functions (Aruoja et al., 2009; Li et al., 2015; Navarro et al., 2008). Experiments designed to account for effects of light attenuation by nanoparticles have demonstrated that the presence of a layer of TiO_2NP aggregates in direct contact with algal cells can also cause decreases in growth independent of a shading effect (Aruoja et al., 2009; Hund-Rinke and Simon, 2006). Particles in direct contact with algal cells may increase cell membrane permeability and enter the cytoplasm (Dalai et al., 2013; Li et al., 2015). Subsequent membrane and cell wall damage can occur if UV light is present, due to the production of ROS (Li et al., 2015; Wang et al., 2016) that occurs when TiO_2NPs undergo UV-induced photoexcitation (Dalai et al., 2013). This ROS production can lead to oxidative stress and can damage DNA, proteins, and cell membranes (Dalai et al., 2013).

Few outdoor large scale mesocosm studies have been conducted to date that incorporate periphyton as the matrix of interest to study algal toxicity. Periphyton represents one of the most important communities in terms of algal biomass in streams and rivers, and is a food source to a wide range of biota (Lamberti, 1996). Therefore, periphyton is an important biological matrix to include when studying TiO_2NP toxicity in natural systems. Laboratory studies have provided a solid basis for an understanding of the concentrations of TiO_2NPs and some of the associated mechanisms that cause toxicity to algae. However, field experiments are crucial to our understanding of the effects of TiO_2NPs in natural conditions, in that environmental complexity can be represented and the research conducted at environmentally relevant spatial and temporal scales (Joern and Hoagland, 1996; Schindler, 1998). One of the major goals of the work presented was to build on the foundation of laboratory studies that have been conducted, and add environmental complexity to aid in our understanding of how real-world exposures may adversely affect freshwater ecosystems.

To investigate environmentally realistic exposures of TiO_2NPs to periphytic algae, we conducted a 5-week outdoor press-dose mesocosm study using experimental streams with municipal wastewater effluent as source water to mimic the worst-case scenario in southwestern United States streams during drought conditions when effluent may comprise most, if not all of the stream flow, and to represent a scenario in which TiO_2NPs have the greatest risk of impacting stream ecosystems.