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# The role of pesticides in aggregation of TiO<sub>2</sub> nanoparticles in aquatic environments

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## ABSTRACT

The fate and behavior of engineered nanoparticles (NPs) released in aquatic environments will be influenced by the water chemistry, as well as the pesticide load due to the potential for NP interaction with anthropogenic organic molecules (AOMs). As such, surface charge and aggregation of pure hydrophilic 100 % rutile and pure hydrophilic 100 % anatase titanium dioxide nanoparticles (TiO<sub>2</sub> NPs, 5–30 nm) were evaluated in a modeled water solution in the presence of three common AOMs, glyphosate, aminomethylphosphonic acid (AMPA), and 2,4-D. The surface charge and size distribution were assessed over time as a function of various factors including surface chemistry of the NPs and AOMs, presence of mono- and bi-valent cations, pH, and ionic strength of the aqueous solution. The presence of AOMs (5 µg/L) affected TiO<sub>2</sub> NP (5 mg/L) homoaggregation in solutions (IS = 10<sup>-3</sup> M - 10<sup>-2</sup> M)

with pH values below the NP point of zero charge (PZC) for the anatase NPs (pH=6.5) and with pH values above the NP PZC for the rutile NPs (pH=4.5). No changes in NP aggregation were observed in very low (IS=10<sup>-4</sup>M) or very high (IS= 10<sup>-1</sup>M) ionic strength solutions. Passing through the PZC resulted in irreversible aggregation of the NPs, even in the presence of AOMs. The presence of the pesticides also caused a significant modification of the NP surface charge (zeta potential) over a large range of salt concentrations (IS=10<sup>-4</sup>M - 10<sup>-1</sup>M). Compared to mono-valent cations, bi-valent cations (Ca<sup>2+</sup>) favored NP aggregation and an increase in zeta potential. Finally, these results demonstrated that, among the studied AOMs, glyphosate (with 4 pKa-s from 0.8 to 11) affects NP aggregation/stabilization in a wide range of physicochemical conditions. Overall, these results will aid in the evaluation of potential environmental risks posed by engineered NPs in the aquatic environments exposed to pesticide load.