Toxicity of Metal Oxide Nanoparticles in a Marine Phytoplankton – Zooplankton Food Chain

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Abstract

Metal oxide nanoparticles are increasingly utilized and are therefore commonly discharged into aquatic environments, increasing exposure and potentially impacting aquatic organisms. Metal oxides have been shown to negatively affect several species of marine phytoplankton; however, uncertainties exist about whether the toxic effects observed are due to nanoparticulate metal oxides or dissolved metals liberated from the nanoparticles. Additionally, the uptake and accumulation pattern of metals in marine phytoplankton, after exposure to nano-metal oxides as compared to dissolved metals, is to a large extent unknown. This information is needed to provide information about the mode of toxicity to phytoplankton and to understand potential routes of exposure to higher trophic levels dependent on phytoplankton as primary producers. To compare the interactions of different forms of metals with phytoplankton cells, the diatom *Thalassiosira weissflogii* was exposed to ZnO, AgO, and CuO nanoparticles as well as $ZnCl_2$, AgCl, and $CuCl_2$ for 7 d. Growth, metal accumulation, and metal distribution within the algal cells were measured to elucidate differences in toxicity and bioavailability between the different forms of metals. Additionally, the authors tested whether feeding on ZnO-exposed phytoplankton could cause toxic effects in a widespread and ecologically important marine grazer, the copepod *Acartia tonsa*. *T. weissflogii* cultured with ZnO were continuously fed to *A. tonsa* for 7 d, and reproduction and survival were quantified. Concentration-dependent metal accumulation and reduced population growth were observed in *T. weissflogii* exposed to nano-metal oxides as well as dissolved metals, with more significant effects observed after exposure to dissolved metal exposure. *T. weissflogii* exposed to metal oxides had proportionally higher metal concentrations in the cell wall fraction, whereas algae exposed to dissolved metals had higher proportions of metal in the organelle and endoplasmic reticulum fractions. Feeding on ZnO-exposed diatoms led to a decrease in copepod survival and reproduction. The EC20s corresponding to the dissolved zinc concentration in the *T. weissflogii* exposure media were 112 mg/L (13 mg/g dry wt) and 143 mg/L (16 mg/g dry wt) for copepod survival and reproduction, respectively. Unlike past dietary studies with dissolved metals which reported reproduction as the most sensitive endpoint, this dietary study with nanoparticles demonstrated copepod survival as the most sensitive endpoint tested. The differences observed could have been a consequence of the metal distribution within the phytoplankton diet (i.e. higher percentage of metal accumulated in the cell wall). These results provide evidence of trophic transfer of metal contaminants associated with metal oxide nanomaterials within a marine plankton community, leading to a reduction in individual demographic performance of an important coastal marine grazer.