Benthic Food Chain Studies with TiO_2 Nanoparticles

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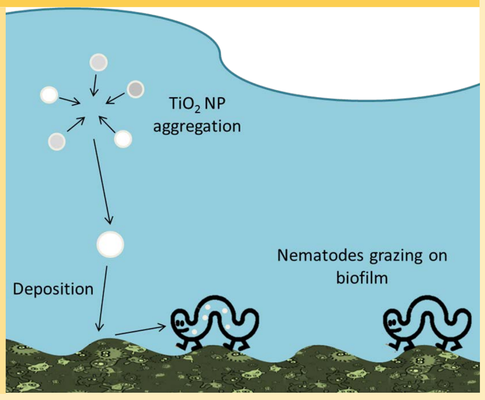
Introduction

Background

- TiO_2 nanoparticles are used in a wide array of products
- TiO_2 nanoparticles tend to aggregate and sediment in natural waters[1]
- Benthic systems are likely to be the most exposed to TiO_2 nanoparticles[1,2]
- Food chain implications of TiO_2 nanoparticle use are not known



Nanoparticle-Food Chain Theory

- Bioconcentration and biomagnification based on partitioning paradigm (thermodynamic control)
  - For biomagnification to occur the chemical activity (a):

    $a_{organism} > a_{diet}$
  - How does on apply this model to nanoparticles?
- Nanoparticles are largely controlled by kinetic processes, so the partitioning paradigm may not apply.

Materials

Types of TiO_2 Nanoparticles

Flame synthesized

- P-25 from Degussa
- TiO_2 doped with Niobium (EMPA)
- TiO_2 radio labeled with ^{48}V (HZDR)

Solution synthesized (ETH)

- Enriched in ^{50}Ti for quantification
- Particle surface chemistry readily modified with enediol functionalities[3]

Materials

Culturing *P. acumintus*

- Single nematode isolated from the Chriesbach River
- Cultured in media of protozoa pellet, wheat seed, cholesterol and hemoglobin
- Bacteria endosymbiotic to the nematode feed on media
- Nematode feeds on bacteria

Chriesbach River

pH	8.2
DOC	3.7 mg/L
Ionic Strength	8 mM
Ca^{+2}	2.6 mM
Mg^{+2}	0.6 mM
Cl^-	0.97 mM
Na^+	0.84 mM

Methods

Kinetics of TiO_2 uptake

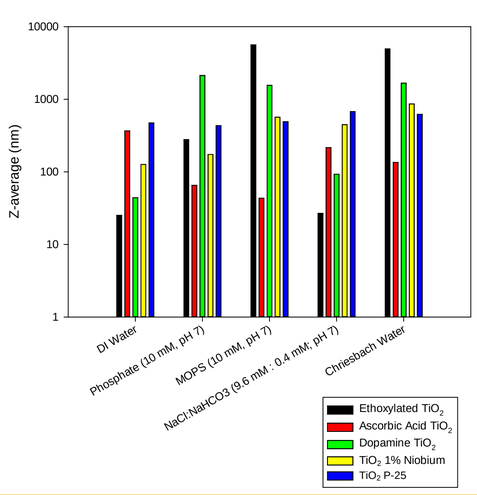
- Expose nematodes to 1 and 10 mg/L TiO_2 in Chriesbach river water
- Expose and depurate over the course of 24 hrs
- Measure TiO_2 by LSC or HF digestion followed by ICP-MS

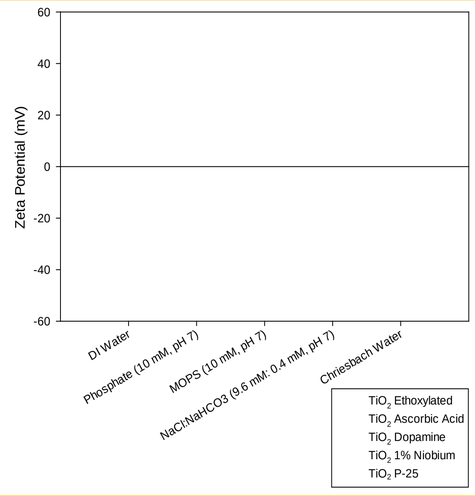
Effect of Concentration on Uptake

- Exposed to 0.01-100 mg/L Nb - TiO_2 in Chriesbach river water
- After for 48 hour exposure, nematodes washed and uptake of TiO_2 quantified
- Uptake from water and from biofilm

Characterization of TiO_2 Nanoparticles in Aqueous Matrices

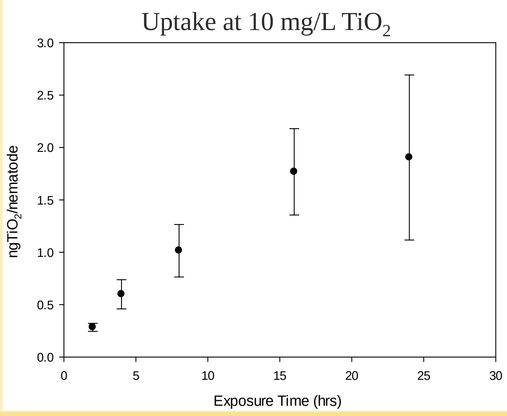
Size and Surface Charge

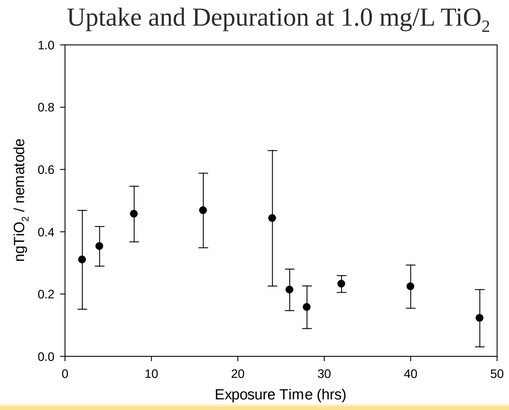




Size and charge of TiO_2 nanoparticles is highly dependent on solution and surface chemistry

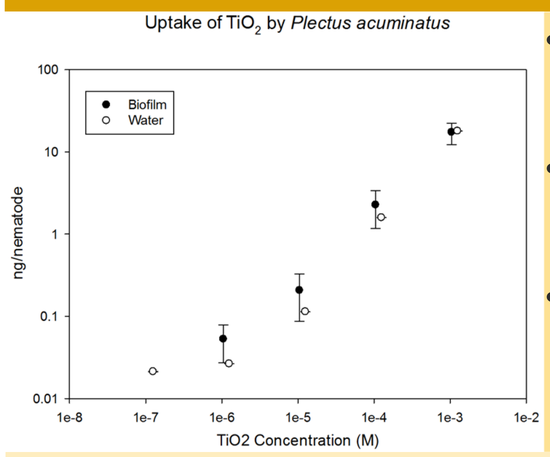
Kinetics of TiO_2 Nanoparticles Uptake and Depuration



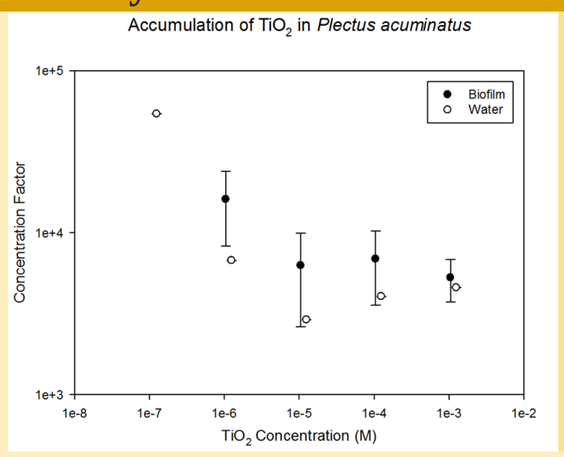


- TiO_2 uptake increases over 16 hours
- Steady state between 16 and 24 hours
- Factor of 5 decrease in uptake compared to 10 mg/L
- Fast and incomplete depuration

Uptake of TiO_2 Nanoparticles by *P. acuminatus*



- Nematodes can take up TiO_2 nanoparticles directly from the aqueous phase
- At low TiO_2 nanoparticle exposure concentrations uptake deviates from linearity
- Environmental exposures are likely to be several orders of magnitude lower, than lowest concentration tested

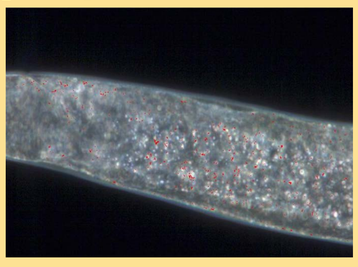


- At high TiO_2 nanoparticle exposure concentrations, the concentration factor is fairly constant
- At low TiO_2 nanoparticle exposure concentrations, the concentration factor increases
- If a thermodynamic paradigm was applicable the concentration factor would be constant across all exposure concentrations

Hyperspectral Imaging of TiO_2 Nanoparticles Uptake

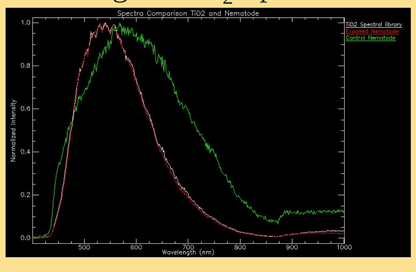
TiO_2 nanoparticles in suspension

TiO_2 nanoparticles in nematode



Control nematode

Matching of TiO_2 Spectra



Results & Discussion

- Size and charge of TiO_2 nanoparticles depend on chemistry of solution and particle surface
- All TiO_2 readily sediment from suspension in Chriesbach water
- *P. acuminatus* uptake TiO_2 increases over 16 hours, constant between 16 and 24 hours
- *P. acuminatus* readily depurate TiO_2, but depuration is incomplete
- TiO_2 nanoparticles uptake is dose dependent at higher particle concentrations, but is non-linear at lower concentrations
- The concentration factor is not constant over the exposure concentrations studied, indicating that the thermodynamic paradigm may not apply
- Uptake of TiO_2 nanoparticles is readily visualized with hyperspectral imaging

References

1) Ferry *et al* Nature Nanotechnology, **2009**, 4, 441-444
2) Keller *et al* ES & T, **2010**, 44, 1962-1967
3) Kotsokechagia *et al* Langmuir, **2008**, *24* , 6988–6997

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