Photocatalytic Effects of TiO_2 Nanoparticles: Is there an Impact on the Ecotoxicity of PAHs?

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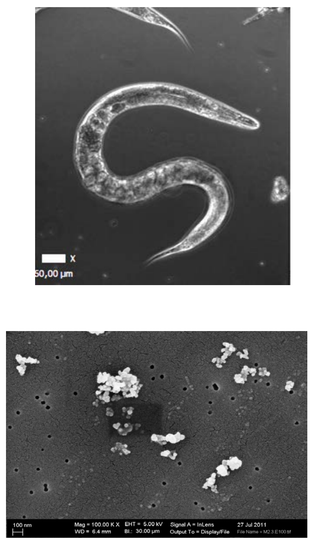
Background

- Titanium dioxide nanoparticles (TiO_2 NPs) are used in a variety of consumer products and expected to increasingly enter the aquatic environment [1].
- TiO_2 NPs catalyze the degradation of PAHs under UV irradiation. They are currently being considered for use in the remediation of PAH-polluted soils and wastewaters [2], although little is known about the effects of potential products of this photo modification process to the aquatic environment.
- Photo oxidation of PAHs can alter bioavailability (water solubility) and intrinsic toxicity of contaminants.

Materials and methods



Bioassay: ISO 10872:2010 - Chronic test of *C. elegans* (Nematoda), endpoints: reproduction, fertility and growth

Test material:

- TiO_2 NPs P 25 Aeroxide (Degussa AG) (primary particle size 21 nm; 75% anatase, 25% rutile)

  Dispersion: in ultrapure water using magnetic stirring and ultrasonic bath
- Phenanthrene, solvent DMSO

Particle characterization:

- Dynamic Light Scattering (DLS) and Zeta-Potential
- Scanning Electron Microscopy (SEM).

Main objectives: **1) Assess the solar irradiation-mediated ecotoxicological effects of TiO_2 NPs on *Caenorhabditis elegans***
2) Investigate the impact of TiO_2 NPs on the toxicity of phenanthrene

Results

Effects of solar radiation on TiO_2 toxicity

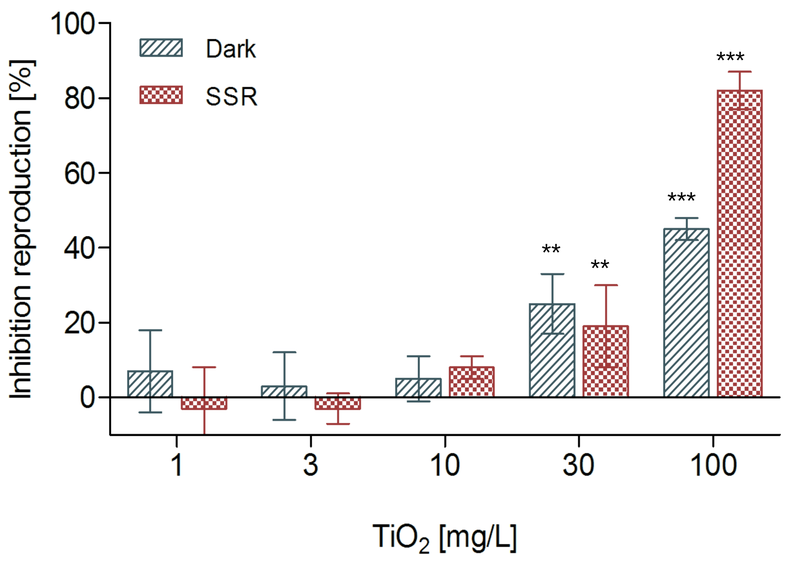


*Fig. 1: Inhibition of reproduction of C.elegans exposed to TiO_2 with and without SSR [mean inhibition and SD in %, n=4]; p-Values **<0.01 *** < 0,001 (One-Way ANOVA* at α = 0.05, post test Dunett*).*
SSR: 30 min irradiation ,4 h after start of the test, 231 W/m² at 300-800 nm.

- TiO_2 NPs significantly inhibit the reproduction of *C.elegans* (LOEC 10 mg/L to 30 mg/L)
- 30 min simulated solar radiation (SSR) increases the toxicity by a factor of approx. 2 (EC50 of 53 mg/L (SSR))

Effects solar radiation on phenanthrene toxicity

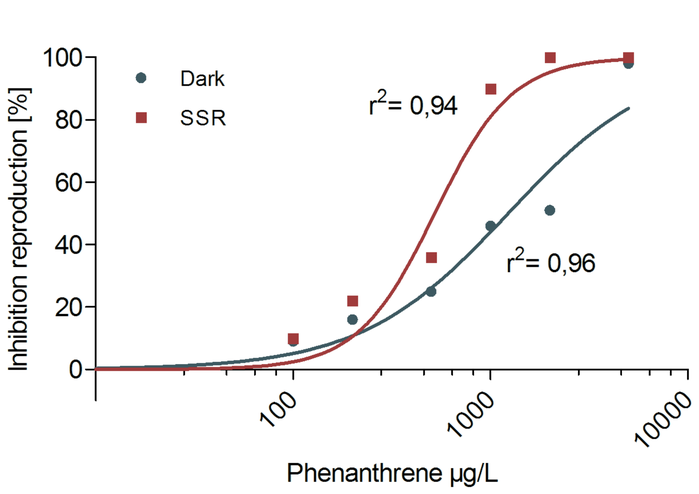


Fig. 2: Inhibition of reproduction of C.elegans exposed to phenanthrene with and without SSR [mean inhibition, n=4]; nonlinear fit of log (x). SSR: 30 min irradiation ,4 h after start of the test, 231 W/m² at 300-800 nm.

SSR increases the toxicity of phenanthrene by a factor of approx. 2. [EC50 of 1230 µg/L (no-SSR) and 522 µg/L (SSR)].

Effects of solar radiation and TiO_2 on toxicity of phenanthrene (combined exposure)

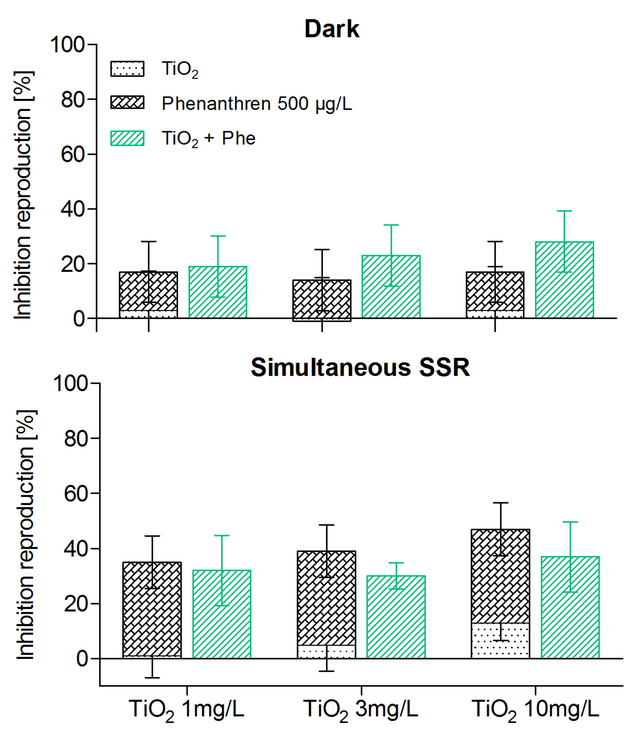


Fig. 3: Inhibition of reproduction of C.elegans exposed to phenanthrene and TiO_2 [mean inhibition and SD in %, n=4]. Grey bars: added single substance effects; green bars: effects of combined exposure. SSR: 30 min irradiation, 4 h after test start, 231 W/m² at 300-800 nm.

Dark: TiO_2 NPs increase the toxicity of phenanthrene slightly, effects are not significant.

SSR: Simultaneous irradiation of *C.elegans* exposed to TiO_2 and phenanthrene decreases toxicity slightly, effects are not significant.

Conclusions

- ❖ **Reproduction of *C.elegans* is significantly inhibited by exposure to TiO_2 NPs at concentrations of 10 mg/L and higher**
- ❖ **Simulated solar radiation increases the inhibition by a factor of approx. 2**
- ❖ **Phenanthrene toxicity is not significantly affected by simultaneous exposure to TiO_2 or TiO_2 and SSR**
- ❖ **Agglomeration and sedimentation of the particles is observed in the test system**
- ❖ **Agglomerated particles are bioavailable for *C.elegans* and ingested into the intestinal tract**

Ingestion of TiO_2 particles

Agglomerated TiO_2 particles are taken up into the worm intestinal tract within 96 h exposure to TiO_2 (Fig. 4 A and B).

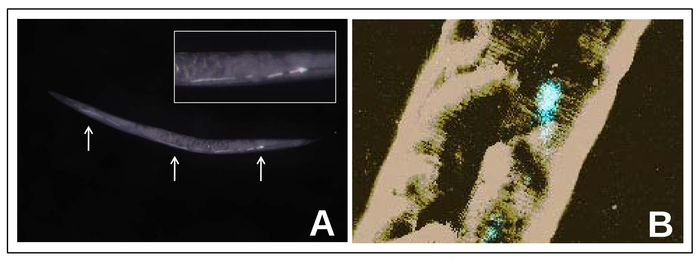


Fig. 4 C.elegans exposed to 20mg/L TiO_2 for 96 h;
A)Stereomicroscope images
B) EDX mapping of Titanium with 20 keV

Agglomeration of NPs

Dynamic Light Scattering

- Mean particle size and SD increase with increasing particle concentrations (253 nm +/-79 to 718 nm +/-145)
- Addition of the test media M9 leads to further agglomeration, particle sizes increase by a factor of 1.15 to 1.92
- Particle sizes do not significantly change during the exposure period of 96 h (Fig. 5)

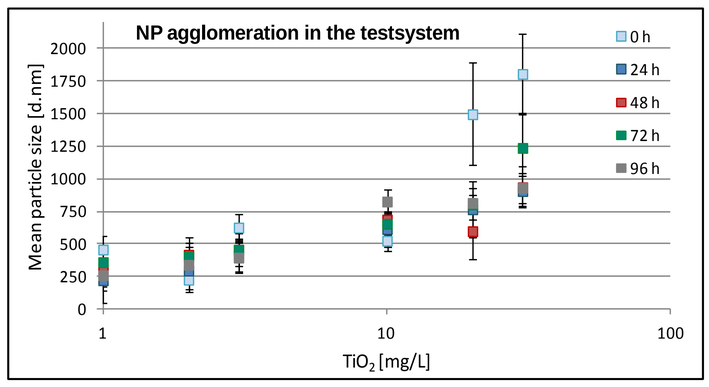


Fig. 5: DLS measures of TiO_2 dispersions introduced into the test media M9 after 0, 24, 48, 72 and 96 h. Average Intensity Mean values of particle diameter (10 repeated measures) and SD.

Scanning electron microscopy

Compared to DLS data:

- Particle sizes are of the same magnitude (453 nm +/- 58 nm for H_2O suspensions; 413 nm +/- 77 nm for suspensions added to M9)
- Particle sizes do not increase with increasing concentrations
- Addition of M9 media has no impact on particle sizes

Acknowledgements

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Reference

[1] Gottschalk, F.et al., 2009. Modeled Environmental Concentrations of Engineered Nanomaterials (TiO2, ZnO, Ag, CNT, Fullerenes) for Different Regions. *Environmental Science & Technology*, 43(24), 9216-9222.

[2] Dong et al. 2010. Photocatalytic degradation of phenanthrene and pyrene on soil surfaces in the presence of nanometer rutile TiO2 under UV-irradiation. *Chemical Engineering Journal* ,158(3):378-383.