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Review

# Understanding the fate and biological effects of Ag- and $TiO_2$-nanoparticles in the environment: The quest for advanced analytics and interdisciplinary concepts

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## HIGHLIGHTS

- Mechanisms of NOM sorption to NP and their effects on aggregation are largely unknown.
- Masking, catching and dissolution processes determine nanoparticle fate & effect.
- Assessment of environmental impacts on NP fate and effects needs further studies.
- Single particle analytics enlighten nanoparticle speciation in the environment.
- Still an analytical challenge: nanoparticle characterization in complex matrices

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## ABSTRACT

Engineered inorganic nanoparticles (EINP) from consumers' products and industrial applications, especially silver and titanium dioxide nanoparticles (NP), are emitted into the aquatic and terrestrial environments in increasing amounts. However, the current knowledge on their environmental fate and biological effects is diverse and renders reliable predictions complicated. This review critically evaluates existing knowledge on colloidal aging mechanisms, biological functioning and transport of Ag NP and $TiO_2$ NP in water and soil and it discusses challenges for concepts, experimental approaches and analytical methods in order to obtain a comprehensive understanding of the processes linking NP fate and effects.

*Abbreviations:* AF4, asymmetrical flow-field flow fractionation; AAS, atomic absorption spectroscopy; AFM, atomic force microscopy; AS, activated sludge; BET, Brunauer–Emmett–Teller sorption model; CCC, critical coagulation concentration; CDI, charge determining ions; CPE, cloud point extraction; DLS, dynamic light scattering; DLVO, Derjaguin–Landau–Verwey–Overbeek theory; DNA, deoxyribonucleic acid; DOM, dissolved organic matter; EDX, energy dispersive X-ray spectroscopy; EINP, engineered inorganic nanoparticles; EPS, extracellular polymeric substances; ETP, effect-triggering pathways; EXAFS, extended X-ray absorption fine structure; FA, fulvic acid; FFF, field flow fractionation; FT-IR, Fourier-transform infrared spectroscopy; HA, humic acid; HDC, hydrodynamic chromatography; HMW, high molecular weight; ICP, inductively coupled plasma; IJP, inkjet-printing; LMW, low molecular weight; MALS, multiangle light scattering; MS, mass spectrometry; MSPE, magnetic solid phase extraction; NOM, natural organic matter; NP, nanoparticles; OES, optical emission spectroscopy; OM, organic matter; PSS, polystyrene sulfonate; PVP, polyvinylpyrrolidone; PZC, point of zero charge; ROS, reactive oxygen species; SCD, supercritical drying; SEC, size exclusion chromatography; Sed-FFF, sedimentation field flow fractionation; SEM, scanning electron microscopy; SERS, surface enhanced Raman spectroscopy; SHR, Schulze–Hardy Rule; SP, single particle; TEM, transmission electron microscopy; TOF-SIMS, time-of-flight secondary ion mass spectrometry; UC, ultracentrifugation; UF, ultrafiltration; UV, ultraviolet radiation; UV–vis, ultraviolet–visible spectroscopy; XANES, near-edge X-ray absorption fine structure; XAS, X-ray absorption spectroscopy; XRD, X-ray diffraction.

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Ag NP undergo dissolution and oxidation with $Ag_2S$ as a thermodynamically determined endpoint. Nonetheless, Ag NP also undergo colloidal transformations in the nanoparticulate state and may act as carriers for other substances. Ag NP and $TiO_2$ NP can have adverse biological effects on organisms. Whereas Ag NP reveal higher colloidal stability and mobility, the efficiency of NOM as a stabilizing agent is greater towards $TiO_2$ NP than towards Ag NP, and multivalent cations can dominate the colloidal behavior over NOM. Many of the past analytical obstacles have been overcome just recently. Single particle ICP-MS based methods in combination with field flow fractionation techniques and hydrodynamic chromatography have the potential to fill the gaps currently hampering a comprehensive understanding of fate and effects also at a low field relevant concentrations.

These analytical developments will allow for mechanistically orientated research and transfer to a larger set of EINP. This includes separating processes driven by NP specific properties and bulk chemical properties, categorization of effect-triggering pathways directing the EINP effects towards specific recipients, and identification of dominant environmental parameters triggering fate and effect of EINP in specific ecosystems (e.g. soil, lake, or riverine systems).



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## 1. Introduction

Engineered inorganic nanoparticles (EINP) are used increasingly in industrial and agricultural applications, consumer products and a variety of medical applications (Gottschalk et al., 2009; Liu and Cohen, 2014; Nowack et al., 2012). They are thus expected to enter the environment unintendedly and via various pathways, acting in an unknown manner on biota in soils and waters. A multitude of aging processes determines their fate and modifies their biological effects. Aging of EINP is regarded as an environmental process leading to EINP transformation without the complete loss of the original nanoparticle phase. It includes interactions with dissolved organic matter (DOM), multivalent cations and natural colloids as well as homo-aggregation, hetero-aggregation and chemical transformation. This results in a large heterogeneity of EINP species differing in size and shape, transport properties and biological functions.

This review will focus on $TiO_2$ nanoparticles (NP) and Ag NP with the objective of developing a basis for the understanding of metallic and oxidic EINP in more general. The use of $TiO_2$ NP and Ag NP is increasing worldwide and both Ag NP and $TiO_2$ NP are known for their potential adverse effects to organisms in the environment (Levard et al., 2012; Sharma, 2009). Applications of $TiO_2$ NP include medicine, food industry, personal care products, catalysis, water purification and inactivation of pathogens in water and numerous building materials such as roof tiles, paint, and plaster (e.g., Aitken et al., 2006; Hossain et al., 2014; Sharma, 2009). Ag NP find use as antibacterial agents in consumers' products like clothes, cosmetics products, food storage containers, household appliances, and children's toys (Nanotechnologies, 2014). The release of Ag NP into the environment by washing clothes and children's products has already been reported (Benn and Westerhoff, 2008; Geranio et al., 2009; Quadros et al., 2013).

Together with colloids from iron oxide, alumina, aluminosilicates, and cerium dioxide, $TiO_2$ NP and Ag NP belong to the best studied nanoparticles with respect to colloidal stability and environmental fate (Philippe and Schaumann, 2014b). Over the past years, knowledge on aggregation and biological effects of $TiO_2$ NP has developed significantly

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