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Review

# Behavior and characterization of titanium dioxide and silver nanoparticles in soils

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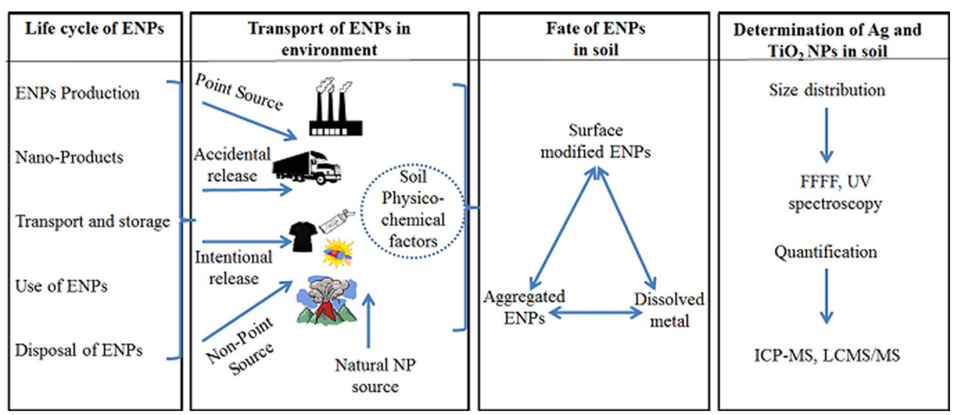
## HIGHLIGHTS

- Humic acids modify coating affecting mobility of nano Ag and $TiO_2$.
- Bio-availability and toxicity are also affected by coatings.
- Increase mobility increases risk of negative effects.
- Interaction ENPs-environment need to be addressed in a conservative way.

## GRAPHICAL ABSTRACT

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## ABSTRACT

The presence and transport of emerging Engineered Nano Particles (ENPs) in the environment is driven by combination of multiple factors comprising their size, charge and aggregation/agglomeration rate along with interactions with different soil types. Due to the complexity of the soil, it is difficult to associate an exact concentration with the possible transport pathways, interactions and transformation mechanisms. Major uncertainties arise with the increased number of extraction and filtration steps required for determining the exact toxicity doses of ENPs. Due to these issues, $TiO_2$ and Ag behavior, characterization, transport, and environmental effects in soils are still not clear. In soils, $TiO_2$ and Ag have been mainly reported to be present in the surroundings of point sources and are driven by their aggregation/agglomeration rate in combination with different soil types. $TiO_2$ and Ag are mainly transported by interstitial water depending on their zeta-potential in the local soil. Along the transport route, $TiO_2$ and Ag undergo alteration in dissolution, corrosion, redox reaction and coatings with the soil matrix. Their mobility is better across mineral soil in comparison to soil rich in organic colloids. The bioavailability gets modified and, in consequence, they are retained until complete degradation of the organic matrix. Depending on the soil matrix composition in terms of water content, minerals, and biological structure, the current most used methods for $TiO_2$ and Ag characterization are FFFF and UV spectroscopy coupled with

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ICP-MS and LCMS/MS. The increased flux of $TiO_2$ and Ag across soil is significant in understanding/accessing the viable threats, in particular their release affects the natural ecosystem.



**Contents**



## 1. Introduction

Particle sizes with at least two dimensions between 1 and 100 nm are defined as nanoparticles and are commercially used across several industrial processes (Cumberland and Lead, 2009; Klaine et al., 2008). Over the last 30 years, nanotechnology has engineered many structures (Bartlomiejczyk et al., 2013), with 1750 types in 2012 compared to 212 types in 2006 (Peyrot et al., 2014). Market potential of engineered nanoparticles (ENPs) is doubling every three years, for instance Ag NPs (antibacterial) market will rise from 0.79 billion in 2014 reaching $2.54 billion by 2022 (Grand View Research, 2015). In contrast, $TiO_2$ annual production is around 6 million tons (Jovanović and Guzmán, 2014), being already a billion dollars market with a price of approx. 2000$ per ton (ICI, 2015). The term of ENPs usage throughout the study is in with respect to $TiO_2$ and Ag nanoparticles. The number of nano based products will reach an estimated $3 trillion market by 2020. Their properties, size, surface area, zeta potential, and quantum effects can be tailored to adjust to special needs enabling dual-use technology applications, such as nanoelectronics, -coatings, -optics, -sensors, -monitors, -textiles and nanoweapons (Anne and Kirsten, 2014). ENPs are frequently used in electronic devices, cosmetics, environmental remediation, energy and textile industry (Bindhu and Umadevi, 2015; Peyrot et al., 2014). The possibility of feature engineering has shown a great potential with increased interest in medicine and health-related areas, such as cancer treatment and targeted drug delivery systems due to their antibacterial and antiviral properties (Cumberland and Lead, 2009). ENPs have become a general-purpose technology, expected to increase with innovation and commercialization to generate economic value. However, there is a need to create social and environment value for the society (Roco et al., 2011).

During production, at the time of land application for biosolids wastewater treatment, accidental spills or applications of nano-pesticides, ENPs find their way into the soil environment Fig. 1 (Cornelis et al., 2013). Most studies related to transport of ENPs have been performed using well-defined lab conditions, although their relevance with transport of ENPs in the natural soil environment is questionable. Only few studies have examined ENPs transport in natural soils and no systematic research of the effect of soil properties and its microbial community was conducted (Cornelis et al., 2013; Sagee et al., 2012).

Depending on exposure modeling, soil is the major sink for most of the ENPs released into the environment and their concentrations were higher in comparison to water or air (Dale et al., 2015; Suresh et al., 2013). Since the fate and transport of ENPs in the environment also involves interactions with soil microbial systems, it is widely recognized that nanomaterial-microbial interactions may also impact human health (Suresh et al., 2013).

ENPs have been examined for their potential toxicity (Table 1), associated environmental risk and consequently considered as emerging pollutants (Cañas et al., 2011; Chai et al., 2015; Choi and Hu, 2008; Throbäck et al., 2007). Understanding ENPs behavior requires better elucidation of environmental and human health risks for establishing tailored regulatory guidelines (Peyrot et al., 2014). The recent studies for hazard assessment of ENPs on different food-chain level organisms, such as bacteria, algae, fish, crustaceans and nematodes indicated that metal ENPs (such as Ag, $TiO_2$, ZnO and Cu) are toxic at environmentally relevant concentrations (Cupi et al., 2015; Holden et al., 2014).

ENPs are often used for their powerful antimicrobial and antiviral properties and have adverse effects on the survival, reproduction and mobility functions of soil organisms (Cornelis et al., 2013), depending upon the ENPs dose, size, shape and reaction with the soil environment (Cumberland and Lead, 2009). ENPs colloidal stability dominates their toxicity and is affected by many factors, such as capping agent, background electrolyte composition, environmental pH and ionic strength (Cornelis et al., 2013; Sohn et al., 2015). The behavior of ENPs across soil environment also varies with different forms of ENPs, which results in bio-availability, chemical changes and possible transformations in the soil environment (Cornelis et al., 2013).

In this study the emphases on the most commonly used nanoparticles, $TiO_2$ and Ag as examples, considering their transport into the soil, their influence on soil quality and effect on soil organisms. Information related to its characterization and development of these ENPs for their release into the environment is also discussed.

## 2. Presence of engineered nanoparticles

$TiO_2$-NPs used as white pigment in body tattoos date from ancient times (Sciau, 2012). There are many natural NPs originating from