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Influence of soil type on TiO_2 nanoparticle fate in an agro-ecosystem

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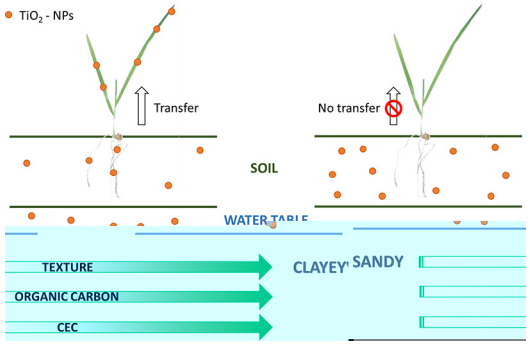
HIGHLIGHTS

- Sewage sludge spreading represents a major exposure pathway for food crops.
- Knowledge about the influence of soil characteristic on NP fate is very scarce.
- High organic matter and clay contents decrease NP mobility and bioavailability.
- Transfer of TiO_2-NPs to wheat leaves in typical agricultural soils is very low.
- The presence of TiO_2-NPs in soil did not affect plant development.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanoparticles (NPs) and in particular TiO_2-NPs are increasingly included in commercial goods leading to their accumulation in sewage sludge which is spread on agricultural soils as fertilizers in many countries. Crop plants are thus a very likely point of entry for NPs in the food chain up to humans. So far, soil influence on NP fate has been under-investigated. In this article, we studied the partitioning of TiO_2-NPs between soil and soil leachate, their uptake and biotransformation in wheat seedlings and their impact on plant development after exposure on 4 different types of soil with different characteristics: soil texture (from sandy to clayey), soil pH, cationic exchange capacity, organic matter content. Results suggest that a NP contamination occurring on agricultural soils will mainly lead to NP accumulation in soil (increase of Ti concentration up to 302% in sand) but to low to negligible transfer to soil leachate and plant shoot. In our experimental conditions, no sign of acute phytotoxicity has been detected (growth, biomass, chlorophyll content). Clay content above 6% together with organic matter content above 1.5% lead to translocation factor from soil to plant leaves below 2.5% (*i.e.* below 13 mg Ti·kg^{-1} dry leaves). Taken together, our results suggest low risk of crop contamination in an agro-ecosystem.

1. Introduction

For more than a decade, nanotechnologies have attracted the interest of industrials and scientists throughout the world. The manipulation of matter at the nanometer scale opens up new possibilities in many different fields, such as industry, medicine and sustainable development. Nanotechnologies imply the use of a huge amount of nanoparticles

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(NPs), *i.e.* particles with at least one dimension below 100 nm. The new properties exhibited by NPs are also a source of questions about a potentially different behavior and toxicity.

The number of commercial goods available on the market and (officially) containing NPs has increased from 54 in 2005 to 2850 in 2016 in all fields of everyday life (cosmetics, food containers, sporting goods, personal care, medicine, construction, agriculture) (*The Project on Emerging Nanotechnologies*, 2015; http://nanodb.dk/en/analysis/consumer-products/, n.d.). TiO_2-NPs are one of the most used NPs, appearing in about 25% of the products according to nano-databases (*The Project on Emerging Nanotechnologies*, 2015; http://nanodb.dk/en/analysis/consumer-products/, n.d.). One can estimate a yearly production of TiO_2-NPs comprised between 1000 and 10,000 tons (Piccinno et al., 2012). Under their nanometric form, they are mainly used for their photocatalytic properties for instance in construction materials (self-cleaning materials) or for their UV-adsorbing properties in cosmetics (sunscreens) (Piccinno et al., 2012). Besides, they can be found in small proportions in food additives (Jovanovic, 2015; Weir et al., 2012).

This expansion of the use of TiO_2-NPs is inevitably leading to an increased dissemination in the environment. The release may be accidental, during the production or transport of NPs, or chronic, during the life cycle of products containing NPs. It has been shown that, TiO_2-NPs contained in certain textiles and paints are detached from their matrix during laundry or weathering and finally end up in wastewater treatment plants (Windler et al., 2012; Mackevica and Foss Hansen, 2016; Zhang et al., 2015; Mitrano et al., 2015) and in particular in sewage sludge, where they can reach a concentration of 2 $g \cdot kg^{-1}$ (Sun et al., 2016). Moreover, the spreading of sewage sludge as soil fertilizer is a common practice in agriculture with quantities reaching 3 tons (dry weight)/ha/year and is regulated for instance in the US, in Australia and in Europe for sludge heavy metal content but nothing about NPs (Gottschalk et al., 2009; Kim et al., 2012; Gottschalk et al., 2013; Sharma et al., 2017). This leads to the dissemination of TiO_2-NPs in agricultural soils. In addition, the expected environmental concentrations could be much higher locally with the intentional introduction of NPs in the environment. For instance, thanks to their unique UV properties, TiO_2-NPs are used for purification purposes in both soil and water (Zimbone et al., 2017; Bessa da Silva et al., 2016; Wu et al., 2016; Sanz Lobón et al., 2017). Another critical case is the use of nanopesticides (Bergeson, 2010; Sastry et al., 2010). Indeed, TiO_2-NPs are used in crop protection products for some years in order to optimize the product efficiency and then to eventually reduce the amount of inputs into the environment (sustainable development). The introduction of these products on the market is also expected to increase in the coming years (Khot et al., 2012; Ghormade et al., 2011; Gogos et al., 2012; Nair et al., 2010).

Until very recently, most of the NP risk assessment studies have been carried out on a single organism in simplified conditions (hydroponics), exposed to high concentrations of NPs during short time, simulating acute contaminations (Cox et al., 2016; Laxma Reddy et al., 2016). Over the last years, studies related to the fate of NPs in the environment evidenced a trend towards more realistic exposure scenario: soil exposure, longer exposure period and lower NP concentrations (Cox et al., 2016; Laxma Reddy et al., 2016).

Studying the fate of TiO_2-NPs in soil is challenging. Indeed, soil is a very complex matrix. Moreover, the contribution of TiO_2 engineered nanomaterials is challenging to measure in the soil because of the high geogenic Ti background (≈0.6% of the terrestrial crust). Accordingly, to date, only modeling studies can help approximate the amount of engineered TiO_2-NPs that is ending up in the environment. The last article estimation forecasts the presence of 61 mg of $TiO_2 \cdot kg^{-1}$ of soil amended with sewage sludge (Sun et al., 2016), making agricultural soil the main sink for nanomaterials in the environment and crop plants a privileged point of entry for NPs in the food chain up to humans.

Currently, knowledge about the interactions of NPs with soil is very limited. Once NPs reach the soil, they can be either physically retained or chemically adsorbed onto the surface of soil particles (Laxma Reddy et al., 2016). These interactions could mitigate NP phytotoxicity and bioavailability (Laxma Reddy et al., 2016), meaning that a same contamination could lead to very distinct consequences according to soil type. The literature published on plants exposed in soils suggested a very limited transfer of NPs to aerial parts. For a better risk assessment, it is thus of primary importance to understand how soil characteristics control NP fate in a crop system. For this purpose we exposed wheat, a widely grown crop over the world, to TiO_2-NPs (0, 100, 500 $mg \cdot kg^{-1}$) in 4 different types of soil already containing geogenic Ti at different concentrations. Ti quantification in soil, soil leachates and wheat leaves was assessed. Ti distribution in roots and leaves and speciation in leaves were also determined using large scale research facilities. Finally NP phytotoxicity was evaluated through plant development parameters: height, fresh and dry weights and chlorophyll content.

2. Material and methods

2.1. Experimental set-up

TiO_2-NPs with a nominal diameter of 25 nm and a crystalline phase mainly anatase (89%) were used (see Fig. S1 for more details).

A sand and 3 agricultural soils provided by Lufa Speyer (Germany) were chosen with different characteristics (Table 1): texture ranging from sand to clayey loam, organic carbon content from 0 to 2.09%, cation exchange capacity (CEC) from 0 to 10 meq/100 g and pH from 5.1 to 7.2.

Exposure concentrations of TiO_2-NPs represented a realistic condition (100 $mg \cdot kg^{-1}$) and a higher and plausible concentration after several years of sewage sludge spreading (500 $mg \cdot kg^{-1}$). TiO_2-NP suspensions (100 or 500 $mg \cdot L^{-1}$ and ultrapure water as control) were mixed with soil with a ratio of 1:1 (w:w) for 12 h on a shaker (200 rpm) in containers wrapped with aluminum foil. This mixing strategy was chosen to ensure the most homogeneous matrix as possible for plant exposure. After this step, the mixture was poured in a folded standard filter paper (Fisherbrand, Dia/Size 330 mm) and separated in soil leachates and soil (after 8 h of settling). After weighting, soil leachates were evaporated and prepared for Ti quantification to determine the Ti mobility.

6 individual replicates for each type of soils (Jovanovic, 2015) and each level of contamination (Piccinno et al., 2012) were set-up with each a wheat seed (*Triticum aestivum* L., cv. Courtaud). All experiments

Table 1
Soil characteristics (soil provided by Lufa Speyer - Germany: silty sand: soil 2.1, loamy sand: soil 2.2, clayey loam: soil 6S). Characteristics were provided by the supplier. For leachates, different lowercase letters indicate significant differences ($p < 0.05$) among all treatments.

	Sand	Silty sand	Loamy sand	Clayey loam
Particle size (%)				
<0.002 mm	0.0 ± 0.0	2.9 ± 0.8	6.4 ± 0.9	41.7 ± 1.3
0.002–0.05 mm	0.0 ± 0.0	9.1 ± 1.4	11.6 ± 0.7	36.1 ± 2.2
0.05–2 mm	100.0 ± 0.0	88.0 ± 1.0	82.0 ± 0.7	22.2 ± 1.5
Water holding capacity				
g/100 g	25.3 ± 2.8	31.8 ± 3.0	46.5 ± 6.0	39.6 ± 5.0
Weight per volume				
g/1000 mL	1756 ± 6	1430 ± 57	1220 ± 78	1330 ± 96
Organic carbon				
%	0.0 ± 0.0	0.74 ± 0.14	2.09 ± 0.40	1.69 ± 0.17
pH value				
0.01 M $CaCl_2$	6.3 ± 0.0	5.1 ± 0.5	5.5 ± 0.1	7.2 ± 0.1
Cation exchange capacity				
Meq/100 g	<2	4.0 ± 1.0	10.0 ± 0.5	22.0 ± 6.0
Leachates				
mL	10.6 ± 0.1^{c}	9.1 ± 0.2^{bc}	8.0 ± 0.3^{ab}	6.3 ± 0.6^{a}