

CHEMICAL AND PHYSICAL SOIL PROPERTIES INFLUENCING TiO₂ NANOPARTICLES AVAILABILITY IN TERRESTRIAL ECOSYSTEMS

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ABSTRACT

Nanotechnology is a new and fast emerging field that involves the design, production and use of structures at the nanoscale. Despite the widespread application of nanotechnology in agricultural, environmental and industrial sectors, a growing concern is coming to light in the recent years about the effects of nanoproducts within different environmental compartments and their likely impacts on human health. Precautionary measures are warranted until possible risks have been elucidated, hence the fate and behavior of nanoparticles in soils and groundwater must be investigated. Using three different Italian soils, we conducted a preliminary investigation of TiO₂ nanoparticles (TiO₂-NPs) behavior in soil suspensions. Aliquots of TiO₂-NPs suspensions with and without soil were periodically collected after their preparation, and monitored for aggregate size distribution and Ti concentration. Experimental results suggest that soil properties affect the behavior of TiO₂-NPs, in particular the dissolved organic matter as well as the ionic strength seem to be the main influencing factors.

Key Words : Soil properties, Soil suspensions, TiO₂ nanoparticles, Aggregate stability in soil Solution, Nanotechnology

INTRODUCTION

Nanotechnology materials are defined as structures with at least one dimension in the approximate range of 1-100 nanometers. Due to their small size, nanoscale materials have novel characteristics including extraordinary strength, high chemical reactivity, electrical conductivity and stability. The increased reactivity of nanomaterials with respect to the corresponding conventional forms must be attributed to the much higher surface area per unit mass and to the quantum effects¹.

The growing use of engineered nanoparticles in numerous industrial applications and consumer products makes risk assessments for human health and the environment necessary. For example, the identification of factors that influence the behavior

of nanomaterials in the environment and especially in soil, is decisive in evaluating health and safety issue². The environmental fate and transport of manufactured nanomaterials and their impacts on air, water and soil ecosystems are of growing concern, even though fundamental properties influencing the fate of nanomaterials in the environmental compartments are not well understood as a result of their extreme diversity and complexity³. One of the challenges for the risk associated with the release of nanomaterials is how their properties change once they interact with the environment⁴. Particle size, size distribution, shape, surface and core chemistry, agglomeration state, crystallinity, redox potential, purity, catalytic activity, surface charge and porosity are all important in understanding nanomaterials behavior⁵. Within the soil compartment, the nanoparticle characteristics are

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affected by soil properties, such as pH, Eh, organic matter content.

Metal oxide nanoparticles are receiving increasing attention for a large variety of applications. Manufactured TiO₂-NPs are a good example of a nanomaterial that has been accepted as having many properties useful for a wide range of applications, from 'self-cleaning' surfaces to cosmetics⁶. Nanoscale TiO₂ is produced and applied in the greatest quantities amongst nanomaterials⁷. Several studies have been published on the ecotoxicological effects of nanoscale TiO₂, therefore it is essential to understand the behavior of TiO₂-NPs in the environment in order to assess possible routes of exposure to humans and ecosystem⁸.

This study aims to provide the baseline information on the processes and phenomena involved in the potential soils' contamination with 'nanowaste'. Thus, to better understand the transport through soils of TiO₂-NPs, laboratory batch experiments were performed using TiO₂-NPs suspended with three different types of Italian soils.

MATERIAL AND METHODS

Soil samples were collected in different areas of Tuscan (Italy) at the top-layer (0-20 cm) and sieved through a 2 mm sieve after air-dried. The basic properties that can influence the behavior of nanoparticles, i.e. texture, organic carbon content, cation exchange capacity, pH and electrical conductivity were determined on this soil fraction according to standard procedures reported in Methods of Soil Analysis⁹. In short, soil pH was determined using a glass electrode in a soil/water ratio of 1:2.5, cation exchange capacity (CEC) using barium chloride (pH 8.1), organic matter (OM) by dichromate oxidation and texture by the pipette method.

TiO₂-NPs used for the batch experiments were purchased from Sigma-Aldrich (USA). The average particle size of 25 nm, anatase crystal phase purity of 99,7% and specific surface area 200-220 m²/g were provided by the manufacturer. For each soil, suspensions were prepared by shaking both TiO₂-NPs and soil with milli-Q water (ratio 1:25:500, respectively) and soil with milli-Q water (ratio 1:20, respectively). After 24h shaking mixtures were transferred into 1L columns and allowed to settle undisturbed for 9 days. Aliquots

of all suspensions were taken into the first centimeters of the columns in periods of 0, 3, 6 and 9 days, and analyzed for titanium concentration and aggregate size distribution. Analysis of titanium were performed after a completely dried suspension aliquots and digestion in H₂SO₄/NH₄SO₄ solution using an ICP-OES (Liberty Axial, Varian). The aggregate size distribution was determined using a laser particle analyzer (Mastersizer 2000, Malvern).

RESULTS AND DISCUSSION

The main properties of sampled soils are listed in **Table 1** where the content of OM and the particle size distribution (texture) highlight their particular characteristics. For example, soil III, the poorest in clay and OM content, presents a predictable lowest capacity of cationic exchange, and its higher electrical conductivity indicates an elevated ionic strength of the medium. On the contrary, the higher content of clay and OM in soil II is consistent with its higher CEC.

Table 1 : Selected and representative characteristics of sampled soils

Soil properties	Soil I	Soil II	Soil III
pH (H ₂ O)	8.0	6.1	8.8
CEC (cmol ⁽⁺⁾ kg ⁻¹)	41.6	52.1	14.4
Sand (%)	23.9	37.7	90.3
Silt (%)	33.3	27.9	6.6
Clay (%)	42.8	34.3	3.1
OM (%)	0.86	9.50	0.15
EC (mS.cm ⁻¹)	134	438	728

Table 2 shows the concentration of Ti in the different aliquots of soil suspensions at the different sampling times. The concentration of Ti-NPs suspended without soil showed an abrupt decrease at the beginning of observation and after 3 days 2.1% of the initial Ti concentration remained permanently suspended in milli-Q water. Lower initial Ti concentration in the aliquots of soil suspended only with milli-Q water (titanium naturally present in soils) showed a similar decay but a constant concentration was found after day 6. At this time Ti concentrations were 0,27%, 3,7% and 2,7% of the initial value for soils I, II and III, respectively. Soil I + TiO₂-NPs showed Ti

Table 2 : Concentration of Ti (mg.L⁻¹) in the different aliquots of soil suspensions sampled at 0, 3, 6 and 9 days after suspensions preparations with the different soils (I, II and III) and manufactured TiO₂ nanoparticles (TiO₂-NPs)

[Ti] (mg L ⁻¹)		Time (d)			
		0	3	6	9
	TiO ₂ -NPs	1073	23	23	23
	soil I	113	0.82	0.30	0.30
	I + TiO ₂ -NPs	1284	0.61	0.24	0.24
	soil II	70	2.9	2.6	2.6
	II+TiO ₂ -NPs	1290	78	15	15
	soil III	48	2.8	1.3	1.3
	III + TiO ₂ -NPs	1225	1.1	0.60	0.60

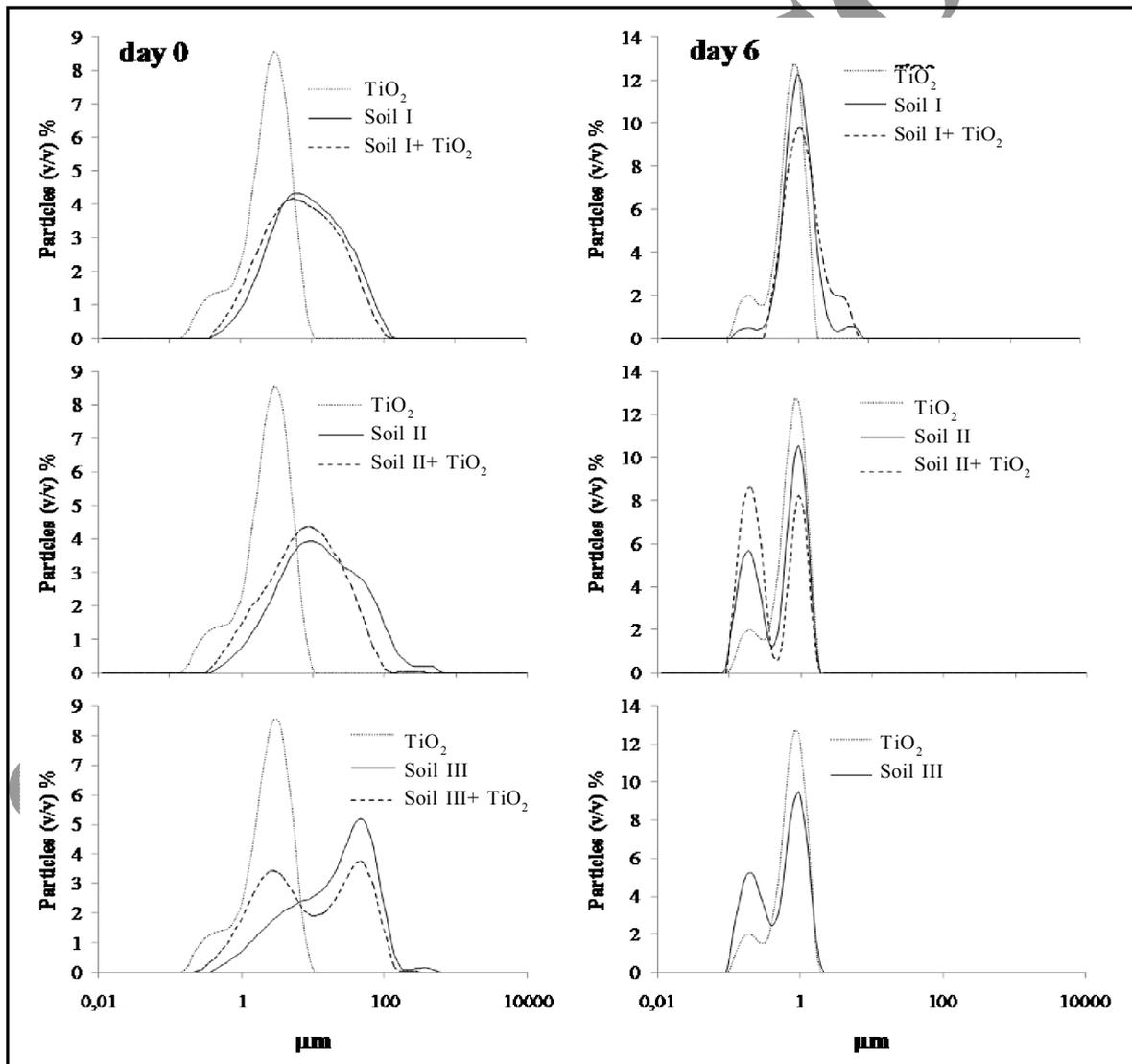


Fig. 1 : Size distribution of aliquots of suspended particles sampled after 0 and 6 days settling

concentrations similar to soil I alone at days 3 to 9. In soil II + TiO₂-NPs the Ti concentration was significantly higher than in soil II alone at all sampling times. Soil III + TiO₂-NPs showed Ti concentration lower than soil III alone since day 3. This behavior could be justified by the relative higher OM content, and probably the dissolved organic matter contributed to the stabilization of the aggregates of TiO₂-NPs in suspension. The molecules of organic matter solubilized in milli-Q water can act as a kind of surfactant reducing the collision and agglomeration between nanoparticles, thus giving a sterically stabilized system. This finding is consistent with the mechanism of stabilization of colloidal particles by steric interaction that was showed to be valid in case of natural organic matter (10, 11, 12). In soil III the higher settling of TiO₂-NPs could be attributed to a higher ionic strength and pH of the medium. Some authors (3, 10) reported an aggregation of nanoparticles due to the high ionic strength that compressed the diffuse double layer, causing the fast settling of NPs.

Fig. 1 shows the aggregate size distribution of aliquots sampled at time 0 and 6. At the beginning of the experiment (day 0) size distribution showed the formation of micron-sized aggregates of TiO₂-NPs in milli-Q (between 0.15 and 10 mm with a peak at 2.7 mm), while all soils suspended in water showed size distribution consistent with their textural classification. Suspensions of TiO₂-NPs and soils gave distributions where the contribution of the two components were recognizable, particularly in the case of soil III (sandy soil). From day 6 TiO₂-NPs in milli-Q water showed a decrease of size distributions giving a stable bimodal distribution. All soils and their mixture with TiO₂-NPs showed a size distribution similar to that of TiO₂-NPs alone with a peak around 0.2 and 1.0 mm, suggesting that TiO₂-NPs were still present as aggregates when suspended with soils. The visual examination of suspensions showed a reduction of quantity of suspended soil colloids and TiO₂-NPs with time, particularly in soils I and III. In the light of experimental results and visual observations we could suppose a higher adsorption effect in the particles of clayey soil (soil I) and higher TiO₂-NPs aggregation in sandy soil (soil III) resulting in higher sedimentation.

Contrarily, soil II rich in organic matter maintained nanoparticles of manufactured TiO₂ in suspended stable aggregates.

CONCLUSION

The present study provides evidence that the soil properties affect the behavior of TiO₂-NPs, that are specially influenced by the OM content and ionic strength. Dissolved organic matter (soil II) induces higher presence of TiO₂-NPs in soil suspensions, thus suggesting a possible transport through the circulating soil solution. The higher ionic strength (soil III) and the higher clay content (soil I) can induce higher/faster settling and lower presence of TiO₂-NPs in soil solution.

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REFERENCES

1. Edinburgh Napier University, Engineered Nanoparticles: Review of Health and Environmental Safety (ENHRES), <http://nmi.jrc.ec.europa.eu/project/ENHRES.htm>, (2009).
2. Scheringer M., Environmental risks of nanomaterials, *Nat. Nanotechnol.*, **3** (6), 322-323, (2008).
3. Klaine S.J., Alvarez P.J.J., Batley G.E., Fernandes T.F., Handy R.D., Lyon D.Y., Mahendra S., McLaughlin M.J., and Lead J.R., Nanomaterials in the environment: Behavior, Fate, Bioavailability and Effects, *Environ. Toxicol. Chem.*, **27** (9), 1825-1851, (2008).
4. Royal Society and The Royal Academy of Engineering, Nanoscience and nanotechnologies: Opportunities and uncertainties, Royal Society Policy Document 19/04. Final Report. London, UK, (2004).
5. Darlington T.K., Neigh A.M., Specer M.T., Nguyen O.T. and Oldenburg S.J., Nanoparticle characteristics affecting environmental fate and

- transport through soil, *Environ. Toxicol. Chem.*, **28** (6), 1191-1199, (2009).
6. Woodrow Wilson internet database - <http://www.nanotechproject.org/inventories/consumer>.
 7. Aitken R.J., Chaudhry, M.Q. Boxall, A.B.A. and Hull M., Manufacture and use of nanomaterials: current status in the UK and global trends, *Occupat. Med.-Oxford*, **56** (5), 300-306, (2006).
 8. Kaegi R., Ulrich A., Sinnet B., Vonbank R., Wichser A., Zuleeg S, Simmler H., Brunner S., Vonmont H., Burkhardt M., and Boller M., Synthetic TiO₂ nanoparticle emission from exterior facades into the aquatic environment, *Environ. Pollut.*, **156** (2), 233-239, (2008).
 9. SSSA Book Series, Sparks D.L. (Ed.), in: Methods in Soil Analysis, Part 3: Chemical Methods, Soil Science Society of America, Inc., Madison USA, (1996).
 10. Tandros T.F., Colloidal Stability: the role of surface forces - Part 1, Willey-VCH Verlag GmbH & Co KGaA, Weinheim, (2007).
 11. Hyung H., Fortner J.D., Hughes J.B., and Kim. J-H., Natural organic matter stabilizes carbon nanotubes in the aqueous phase, *Environ. Sci. Technol.*, **41** (1), 179-184 (2007).
 12. Giasuddin A.B.M., Kanel S.R., and Choi. H., Adsorption of humic acid onto nanoscale zerovalent iron and its effect on arsenic removal, *Environ. Sci. Technol.*, **41** (6), 2022-2027, (2007).

