



A framework to measure the availability of engineered nanoparticles in soils: Trends in soil tests and analytical tools



S.M. Rodrigues ^{a,*}, T. Trindade ^b, A.C. Duarte ^a, E. Pereira ^a, G.F. Koopmans ^c, P.F.A.M. Römkens ^d

^a Centre for Environmental and Marine Studies (CESAM), Department of Chemistry, Universidade de Aveiro, 3810-193 Aveiro, Portugal

^b Centre for Research in Ceramics and Composite Materials (CICECO), Department of Chemistry, Universidade de Aveiro, 3810-193 Aveiro, Portugal

^c Department of Soil Quality, Wageningen University and Research Centre, PO Box 47, Wageningen, 6700 AA, Netherlands

^d Alterra, Wageningen University and Research Centre, PO Box 47, Wageningen, 6700 AA, Netherlands

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ABSTRACT

In this study, the reactions of engineered nanoparticles (ENPs) in soils, with respect to their nanospecific properties, and observed effects of key soil properties (e.g. pH, ionic strength and natural colloids) on their stability in pore water are discussed. Key processes include aggregation and dissolution of ENPs, straining of ENPs in the solid matrix, stabilization of ENPs in pore water due to binding of molecules from dissolved organic matter (DOM) and inorganic colloids and the effect of artificial coatings. In view of these processes, this study provides guidance in the development of a framework to measure available and total soil contents of ENPs, via a set of extraction methods and advanced analytical tools. Particularly, the lack of effective extraction methods is thoroughly discussed regarding the identification of most relevant research gaps preventing an effective assessment of the availability, mobility and risks of exposure of sensitive receptors to ENPs in soils.

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* Corresponding author. Tel.: +351234370721; Fax: +351234370084.

E-mail address: smorais@ua.pt (S.M. Rodrigues).

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1. Introduction

The estimated global market for nanomaterials increased from \$125 million in 2000 to \$12.7 billion in 2008, and it is expected to reach \$30 billion by 2020 [1]. In 2011, the number of consumer products containing engineered nanoparticles (ENPs) exceeded 1300 [2].

The structure and composition of ENPs vary widely according to their application, and includes organic (e.g. fullerenes and carbon nanotubes) as well as inorganic materials [3]. Examples of common inorganic ENPs are metals (e.g. Ag, Au and Fe), oxides (e.g. TiO₂, ZnO, CeO₂ and SiO₂) and quantum dots (CdSe) [3]. This study will focus on inorganic ENPs, particularly metal-based ones.

There is a general agreement that the increased production of ENPs results in their increased release into the environment [4]. In 2010, Keller et al. [4] estimated that, between 9% and 37% of the ENPs (per mass of material produced) were emitted directly to air, water and soils and the remaining 63–91% was disposed in landfills. Emissions to soils result mostly from application of biosolids to land (as ENPs tend to accumulate in sludge from waste water treatment plants) [4–9].

Given the increasing production volumes and release into the environment, new regulatory needs related to the assessment of the environmental impact of ENP-containing products are expected to emerge in several countries. Among other aspects, the regulation of ENPs requires a comprehensive understanding of their complex environmental behaviour and their role in both aquatic and terrestrial systems.

Because of a lack of effective methods to identify and characterize ENPs in a complex matrix such as soil, monitoring studies on the presence of ENPs in terrestrial systems are much sparser than those related to aquatic environments [8]. In the absence of monitoring data on the quantities of ENPs in the soil, simulation studies to estimate levels of ENPs in soil were performed, which indicate concentrations of Ti, Ag and Zn related to emission of ENPs in soils of 10⁻⁸–10 mg kg⁻¹ for nano-TiO₂; 10⁻⁸–10⁻¹ mg kg⁻¹ for nano-Ag and 10⁻³–10⁰ mg kg⁻¹ for nano-ZnO [9]. Despite this large range, predicted soil concentrations for ENPs are well below common background levels of most respective metal counterparts in soil, which range from 0.02% to 2.4% (mean 0.33%) for Ti; <0.01–5 mg kg⁻¹ for Ag (mean <0.1 mg kg⁻¹) and 10–300 mg kg⁻¹ for Zn (mean 50 mg kg⁻¹) [10]. The low absolute added levels from ENPs for these metals compromise our ability to quantify ENPs in soil and evaluate them without altering their integrity. This helps us answer questions such as whether ENPs are actually emitted to the soil environment and if so, do they remain in the (soil)system as integral ENPs?

Furthermore, risks of exposure of sensitive receptors to ENPs in soils and their transport to other environmental compartments (e.g. groundwater) are not much related to their presence, but highly depend on their availability and, particularly, their tendency to be transferred into soil pore water [11]. For the detection of metallic contaminants, the availability of ENPs has long been acknowledged as crucial for risk assessment and various soil tests, including soil chemical extractions with weak extractants such as NaNO₃, NH₄NO₃, Ca(NO₃)₂ or CaCl₂ [12]. The various metals present in soils

are known to influence soil properties including pH, solid organic matter, dissolved organic matter (DOM), clay content and metal oxides [13,14].

However, recent studies on metal-based ENPs in controlled terrestrial settings suggest that the availability of ENPs in soils is determined by not only soil properties, but also specific surface and size-related properties of ENPs [8,15–19]. Thus, availability of ENPs most likely cannot be fully explained based on common soil–solution partition processes as is the case for ionic metals in soil. Understanding the physico-chemical transformation processes of ENPs in soils and their interactions with a range of soil organic and inorganic components that determine the availability of ENPs in porous media, transport to water systems and plant uptake are crucial [2,17,20–22].

The main objective of this study is to present an overview of the main mechanisms and processes determining the availability of ENPs in soils and to provide guidance in the development of a framework on the measurement of available and total soil contents of ENPs, via a set of appropriate extraction methods and advanced analytical tools. Particularly, methods for pore water collection and soil extraction are thoroughly discussed to identify the most relevant research gaps in the development an effective assessment of the availability, mobility and risks of exposure of ENPs to soils.

2. Overview of ENPs' surface characteristics relevant for soil availability studies

Several studies on the synthesis and characterization of metal-based ENPs can be found in the literature [20,21,23]. However, only the aspects pertaining to the surface chemistry and artificial coatings of ENPs, which determine their behaviour in natural systems, are discussed in this study.

Auffan et al. [21] suggest that the increased surface charge of ENPs with decreasing particle size (particularly <20 nm) is related to not only their high surface area associated with the small size, but also changes in the surface structure leading to the appearance of additional adsorption sites towards the decrease of the surface energy and stabilization. In natural soil systems, these additional adsorption sites can increase the binding capacity of ENPs to soil components.

Together with increased reactivity, metal-based ENPs are prone to more dissolution processes in soil [24]. For example, ZnO ENPs are expected to dissolve faster than non-nano ZnO particles [25]. In order to increase stability, artificial surface functionalization and coating agents are often introduced during the production of ENPs. These coating agents increase electrostatic and/or steric repulsions between individual particles that overcome van der Waals attractive forces, prevent ENP aggregation and enhance ENP stability in suspension [23,24]. Electrostatic stabilization is achieved by increasing the magnitude of negative surface charge amplifying repulsive interactions between ENPs (e.g. using citrate), whereas steric stabilization arises from the presence of a stabilizing agent (e.g. a polymer) attached to the surface of ENPs, forming a 'brush-like' layer, which resists aggregation sterically [24]. In addition to steric stabilization, polymers with charged groups (e.g.

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