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Review

Environmental concentrations of engineered nanomaterials: Review of modeling and analytical studies

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ABSTRACT

Scientific consensus predicts that the worldwide use of engineered nanomaterials (ENM) leads to their release into the environment. We reviewed the available literature concerning environmental concentrations of six ENMs (TiO_2, ZnO, Ag, fullerenes, CNT and CeO_2) in surface waters, wastewater treatment plant effluents, biosolids, sediments, soils and air. Presently, a dozen modeling studies provide environmental concentrations for ENM and a handful of analytical works can be used as basis for a preliminary validation. There are still major knowledge gaps (e.g. on ENM production, application and release) that affect the modeled values, but over all an agreement on the order of magnitude of the environmental concentrations can be reached. True validation of the modeled values is difficult because trace analytical methods that are specific for ENM detection and quantification are not available. The modeled and measured results are not always comparable due to the different forms and sizes of particles that these two approaches target.

1. Introduction

For engineered nanomaterial (ENM), an increasing breadth of applications has been predicted, and already observed, ensuring prosperous future developments in the field (Hu and Cui, 2012; Mangematin and Walsh, 2012; Mihranyan et al., 2012). There is also consensus that from such applications, ENMs may end up in relevant quantities in the environment (Boxall et al., 2007; Alvarez et al., 2009; Wiesner et al., 2009; Nowack et al., 2012). To evaluate the potential risks of ENMs to the environment, it is crucial to link quantities of environmental release and concentrations to possible ecotoxicological effects (Alvarez et al., 2009; Aschberger et al., 2011). On the effect side, quite a lot of research has been conducted and critically reviewed in many papers (Baun et al., 2008; Handy et al., 2008a, 2008b; Klaine et al., 2008; Kahru and Dubourguier, 2010; Peralta-Videa et al., 2011; Handy et al., 2012; Klaine et al., 2012). In contrast, for the exposure and concentration assessment part, we are still faced with a lack of quantitative knowledge and appropriate methods for detecting, characterizing and quantifying ENM in complex natural media (Hassellöv and Kaegi, 2009; Mitrano et al., 2012; von der Kammer et al., 2012). However, some analytical evidence on ENM release into the environment has been published. The first case reported that nano-TiO_2 is emitted from paints on building facades into urban runoff (Kaegi et al., 2008). Later the same evidence was shown for Ag released from paints containing nano-Ag (Kaegi et al., 2010). ENM release was also observed during washing of textiles (Benn and Westerhoff, 2008; Geranio et al., 2009; Benn et al., 2010; Kulthong et al., 2010; Farkas et al., 2011; Lorenz et al., 2012; Windler et al., 2012) and from different abrasion processes of surface coatings (Hsu and Chein, 2007; Guiot et al., 2009; Vorbau et al., 2009).

Based on the evidence that ENM are released to the environment, several authors have made first modeling attempts to predict the environmental concentration of ENM. These efforts combine analytical techniques to get the first quantitative information on their occurrence in technical and natural systems. It is the goal of this review to collect and review, for the first time, these studies reporting modeled (predicted) or measured environmental concentrations (PEC and MEC) of ENM, to present the methods used and to evaluate the reliability of the results. It is essential for a preliminary validation of early modeling and/or analytic outputs to see how well the results match each other. The challenge in the case of ENM is that modelers and analysts come across with an enormous variation and uncertainty or distinct lack of knowledge about

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Table 1
Overview and characterization of modeling and analytical methodologies used to assess the concentrations of engineered nanomaterial (ENM) in the environment.

Studies	Modeling study	Deterministic approach (scenarios)	Stochastic approach	Analytical study	Filtration	Microscopic examination	Spectroscopic analysis	Chromatography	Regional/ national/ continental scale	Local scale	Size distribution (0–100 nm)
Mueller and Nowack, 2008	x	x							x		x
Park et al., 2008	x	x								x	x
Koelmans et al., 2009	x	x							x		x
Gottschalk et al., 2009	x		x						x		x
Tiede et al., 2010	x	x							x		x
O'Brien and Cummins, 2010b	x		x						x		x
Musee, 2010	x	x								x	x
Johnson et al., 2011a	x	x	x							x	x
Johnson et al., 2011b	x	x	x							x	x
Gottschalk et al., 2011	x		x							x	x
Hendren et al., 2013a	x		x								x
Park et al., 2008				x	x	x	x			x	x
Kiser et al., 2009				x	x	x	x			x	
Farré et al., 2010				x	x		x	x		x	
Johnson et al., 2011a				x	x		x			x	
Johnson et al., 2011b				x	x	x	x			x	
Neal et al., 2011				x	x		x			x	
Mitrano et al., 2012				x	x		x			x	
Westerhoff et al., 2011				x	x	x	x			x	
Sanchis et al., 2011				x	x		x	x	x		
Khosravi et al., 2012				x	x		x			x	x
Majedi et al., 2012				x	x	x	x			x	x

the most influential parameters: potential production, application and environmental release volumes; physicochemical contaminant properties (size distribution, agglomeration and purity state, surface reactivity etc.), background concentrations and environmental fate/behavior (geographic dispersion, degradation, transformation etc.) of these materials. Faced with such complexity, we set ourselves an additional goal to see to what degree disagreement in the results has its origin in indispensable idealizations and simplifications in the parametric and conceptual modeling framework or, rather, in the experimental and analytic design.

In this review we exhaustively cover all the studies quantifying environmental concentrations of ENM until the beginning of 2013. Purely methodological discussions or qualitative results were not considered. Individually predicted concentrations for a few ENM (Al_2O_3, Au, SiO_2, organo-silica, latex, hydroxyapatite) from a single source (Boxall et al., 2007) were also not reviewed since a comparison to other results would have been impossible. A summary of the methodologies, environmental compartments and materials used is given in Table 1.

2. Modeling studies

Modeling ENM in the environment began with Boxall et al. (2007), who presented the first quantitative approach for assessing ENM release and concentrations for environmental media. It is the merit of these authors to provide the theoretical basis on ENM release quantification that opened (to varying extents) the field for several subsequent modeling studies discussed in the following passages. Several algorithms were developed for calculating PECs for a series of ENM in water, biosolids and soils. Due to a virtually complete lack of empirical information at that time on ENM production and use amounts, these calculations were fully based on a hypothetical model input and were therefore not further used in our evaluation. In this case, we focused instead on their study of 2010 (Tiede et al., 2010).

Mueller and Nowack (2008) went one step further and for the first time used a material flow analysis (MFA) to replace hypothetical calculations. This approach included two emission scenarios: a contemporary one to reflect the best available knowledge (at that time) for a comprehensive spectrum of ENM release into natural compartments; and a worst-case one for a conservative estimation of such release. Using a life-cycle perspective, this MFA combined assumptions and initial empirical information on ENM production quantities, release rates and behavior in technical compartments. The environmental concentrations were calculated according to the European technical guidance assuming well-mixed and homogeneous compartments (ECB, 2003). Sedimentation and degradation processes in the aquatic environment were excluded due to a total lack of data. PECs were computed for nanosized Ag, TiO_2 and CNTs for Switzerland. The results provided in this work constitute the first peer-reviewed assessment of ENM concentrations in the environment, although environmental fate processes were covered only to a limited extent. However, they provided a starting point with which all future modeling studies can be compared.

Park et al. (2008) applied emission and atmospheric dispersion models for their work on nanosized CeO_2 emissions from its use as a diesel additive. Calculations for different emission scenarios for vehicles were performed by varying the traffic intensities, geographic locations and distances from the ENM sources (e.g. from the edge of the highway). Air concentrations were calculated for a street canyon and a highway scenario. Terrestrial PECs were modeled for soils near highways considering the ENM accumulated during a 40-year period. This work is restricted to a single application (CeO_2 use in fuels) and only considers one possible transfer of CeO_2 into soils, e.g. neglecting transfer via wastewater and sludge application. However, it is able to provide a worst-case evaluation of a use with significant potential for environmental release and assuming some worst-case events, e.g. all diesel cars use CeO_2 and the particle filter does not trap the particles in the exhaust. Ulrich