



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 (TiO₂, ZnO, Ag, fullerenes, CNT and CeO₂) 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.

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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 Dubourgier, 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-TiO₂ 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

included and thus the results theoretically provide a lower estimate of the concentration range.

O'Brien and Cummins (2010a) included calculations for pharmaceutical and metal removal efficiencies in WWTP in their aquatic exposure assessment in addition to calculations for pathogen removal during drinking water treatment. The latter estimates were based on available information for known representative contaminants commonly found in Irish water supplies. Average ENM removal efficiencies of 59.8% and 70.2% were assumed for WWTPs and a removal rate between 0% and 96.95% seen for Irish drinking water facilities. The ENM contents and release amounts from relevant products and processes used (such as market penetration of nanomaterial containing products) were computed by probability distributions, as described in detail elsewhere (O'Brien and Cummins, 2010b). A few further release scenarios were considered, e.g. emissions from paints and coatings directly into surface water or via runoff as a result of material abrasion/degradation, release from plastics and packaging due to water contact/abrasion or direct emissions of fuel additives to WWTPs, such as during maintenance of filters. The market penetration for Ireland (5% of the products in a product group contain ENM) and release coefficients for ENM products were modeled with a standard deviation of 20% to account for uncertainty and variation. Surface water PECs were presented for nanosized TiO₂, Ag and CeO₂. Similar to other modeling studies, these authors also used a combination of a contemporary assessment parameters (e.g. on removal) and scenario building (e.g. when assuming a certain market penetration for nano-products). However, only some product categories were considered and no comprehensive assessment was targeted.

Another study (Musee, 2010) used a deterministic and scenario based MFA to calculate ENM emissions from cosmetic products into the water and terrestrial environments by focusing geographically on Johannesburg Metropolitan City (JHB) (South Africa). The MFA included material transmission via untreated and treated streams from WWTPs, deposition of biosolids on soils, landfilling of biosolids and landfill leachate. Low and high WWTP removal efficiency was combined with three different ENM release assumptions (minimum, probable, and maximum) computed based on ENM production taken from others (Mueller and Nowack, 2008) and adapted based on gross domestic product (GDP) information and wastewater generation per capita for JHB City. PECs (nano-Ag, nano-TiO₂) originating from cosmetic products were produced for surface water, biosolids and soils treated with such biosolids. This study therefore investigated only a very small group of products and can thus provide only a lower estimate of the targeted ENM.

Gottschalk et al. (2011) combined PMFA (Gottschalk et al., 2010a) and graph theory (Ort et al., 2009) to model first aquatic PECs for ENM at higher spatial and temporal resolutions (nanosized TiO₂, Ag, ZnO). Values for the Swiss stream network were modeled by spreading the total ENM release computed at the regional level (Gottschalk et al., 2009) over the network based on the distribution of the relevant population. The spatially dependent variation was achieved by linking diffusive ENM discharge with local dilution (stream flow data). The temporal variation was considered by integrating into the modeling flow measurement data collected over a 20-year time period. Two scenarios accounted for the whole possible spectrum of variability and uncertainty of ENM fate in the river water: a conservative one, assuming no ENM degradation/deposition, and an optimistic scenario considering rapid and complete ENM removal from the river water.

Johnson et al. (2011b) estimated sunscreen TiO₂-PECs for soils by basing their PEC modeling on their own measured concentrations in biosolids (see corresponding part in the section analytic studies). Those measured values were related to the proportion of Ti present as nano-TiO₂ (derived from market information) and data of

recommended sludge applications to soils. Surface water PECs were then modeled based on commercial information on the consumption of Ti products by the relevant population and data on dilution in the Thames and Anglian rivers in Southern England. For this purpose a GIS-based water-quality model (Williams et al., 2009) was employed. However, because only a single use source (TiO₂ in sunscreen) was considered, the PECs provided in this work can only serve as an indicative lower estimate of total nano-TiO₂ in the environment.

For their models of silver ENM, Johnson et al. (2011a) used their own effluent monitoring results as a basis (see again corresponding part in the section analytic studies). The results were converted into a typical per capita effluent load in order to model river concentrations on the basis of different dilution conditions (mean and 90% quantiles). A combination of water-quality and hydrological models (Williams et al., 2009) was applied for computing PECs in English and Welsh rivers based on mean per capita loads derived from normal distributed load quantities. Similar to Gottschalk et al. (2011), this model based work provided by local estimates of nano-Ag concentrations and thus included additional complexity compared to the regional modeling performed in preceding studies. Unfortunately, in this report an explicit insight on how agglomeration and sedimentation of the silver nanoparticles in river water are treated by these models is not given.

Arvidsson et al. (2012) proposed a particle flow analysis approach (PFA) to assess anthropogenic ENM release into the environment. In this modeling study, particle number was calculated instead of mass. Release from the use phase to the environment was considered and release scenarios were produced based on several factors including: predictions for the technology diffusion, per capita consumption of nano-products, product lifetime and ENM concentrations. Case studies were conducted for nano-TiO₂ in sunscreen, self-cleaning cement and paints (Arvidsson et al., 2012) in addition to nano-Ag in textiles, wound dressings and electronic circuitry (Arvidsson et al., 2011a). Unfortunately, PECs were not presented and for our evaluation of published environmental concentrations these studies are therefore only of limited value. The studies only concluded that currently, most nano-TiO₂ release results from sunscreen use. Furthermore, nano-Ag release may increase significantly, especially from electronic circuitry and textiles while less pronounced release from wound dressings is expected due to lower consumption volumes. These authors (Arvidsson et al., 2011b) also used colloid theory (Smoluchowski, 1917; Friedlander, 1977) for describing nano-TiO₂ agglomeration, settling, sedimentation and reactions with natural organic matter (NOM) and natural colloids once released into in surface water. From such kinetic modeling they claimed that the first three of the above-mentioned parameters (shear flows, settling, and sedimentation) were less influential on the model output than the discharge (inflow rate) of ENM to surface water and the collision efficiency on NOM and natural colloids. Recently, it was shown that at environmentally relevant concentrations of nano-TiO₂, hetero-agglomeration between nanoparticles and suspended particulate matter is much more important than homo-agglomeration between the nanoparticles (Praetorius et al. (2012)). Apart from that, the Swedish work does not aim to present environmental concentrations, but limits itself to discussing general aspects of the feasibility of such modeling and the sensitivity of the model output on the mentioned main input parameters.

The modeling studies presented so far revealed that significant amounts of ENM enter the waste stream and therefore waste incineration plants and landfills. Mueller et al. (2013) aimed to model the flows of ENM during waste incineration and landfilling in greater depth by including a more detailed description of the different processes and considering ENM-specific transformation

reactions. Four substances were modeled: nano-TiO₂, nano-ZnO, nano-Ag and carbon nanotube (CNT). The modeling showed that the major ENM flows go from the waste incineration plant to the landfill as bottom ash. The results show that waste incineration can have a strong influence on some ENM (e.g. combustion of CNT, dissolution of ZnO in acid washing) but that the majority of the ENM-mass is still expected to end up in landfills.

Fig. 1 categorizes the different modeling approaches discussed in this section according to the complexity of the model and the year published. The complexity increases from studies targeting only single uses of a selected ENM over scenario-based models to approaches that aim to model all relevant flows of a specific ENM and/or including the use of mechanistic modeling of ENM fate and behavior. Models exhibiting the highest level of complexity provide concentration estimates at a local level rather than just providing regional estimates based on well-mixed compartments. Fig. 1 also shows the relationships between the models (i.e. interconnectedness), as some models rely on results from previously published

work as input parameters or use the same methodology. In these instances, results are therefore not completely independent from each other. This especially applies to models using some of the results from the Mueller and Nowack (2008) study as input values. This work has influenced several subsequent models from the same research group (Gottschalk et al., 2009, 2010b, 2011; Mueller et al., 2013) or groups from other institutions (Koelmans et al., 2009; Musee, 2010).

Hendren et al. (2013a) recently published modeled concentrations for four types of nano-Ag with varying surface chemistries (non-coated/functionalized, polyvinylpyrrolidone-, citrate- and gum Arabic-coated) in sewage treatment plant (STP) effluents and sludge. Inspired by parsimony calculation approaches, these authors presented a streamlined model that gauges the nano-Ag input into STP influents directly from U.S. production quantities (neglecting imports and exports) of the target silver and daily water usage per capita. This nano-Ag input was then fed into mass balance calculations around the ENM fate and behavior in the STP reactors. Heteroagglomeration and biouptake, the major factors influencing such balance, were quantified for different plant operating conditions (e.g. influent flow, solids residence time and plant design parameters) and used to derive the nano-Ag partition to either the STP effluent suspension or the STP sludge. MC simulations were run in Crystal Ball[®] in order to account for the uncertainty of ENM mass input and aggregate fraction of the proposed subsystem.

3. Analytical studies

The following section contains in chronological order a critical evaluation of currently available analytical studies that targeted environmental concentrations of ENM.

Park et al. (2008) assessed nano-CeO₂ air contamination using archived PM10 filter data from monitoring sites in both the city centers of London and Newcastle, UK. Background CeO₂ concentrations were evaluated before nanoparticulate CeO₂ was used as fuel additive. The concentrations after the introduction of this diesel additive in the PM10 samples were determined after acid extraction of the filtered PM based on an ICP-AES (inductively coupled plasma atomic emission spectroscopy) method. The nanosized fraction of CeO₂ was estimated by calculating the difference between samples taken prior to and after use of nano-CeO₂ as diesel additive. The results are therefore not based on any nano-specific analysis and simply report an increase in total Ce-concentration. Regardless, this may still serve as starting point to evaluate the possible contribution of nano-CeO₂ in soils.

Kiser et al. (2009) quantified Ti (<700 nm) at wastewater reclamation sites in municipal facilities in Arizona, Colorado, California, Maryland, Iowa, and New York (USA). The collected solid phases were acidified (HNO₃/H₂SO₄ digestion method) to measure total ionic concentration. Digested samples were analyzed by ICP-OES (inductively coupled plasma optical emission spectroscopy). A scanning electron microscopy/electron dispersive X-ray microanalysis (SEM/EDX) was performed for visualizing and characterizing the Ti in solids. MECs for effluents and settled solids from these wastewater treatment sites were produced. The results are not nano-specific as all Ti smaller 700 nm was quantified, but these results can serve to define the upper limit on possible nano-TiO₂ concentrations.

Farré et al. (2010) developed a method for analyzing fullerenes in natural samples. After the ultrasonic extraction of ENM adsorbed on suspended solids in wastewater, the authors coupled liquid chromatography to a hybrid triple quadrupole linear ion trap mass spectrometry to perform the trace quantification of C₇₀ and N-methylfulleropyrrolidine C₆₀. MECs for WWTP effluents in Catalonia (Spain). This work is the first to quantitatively present trace

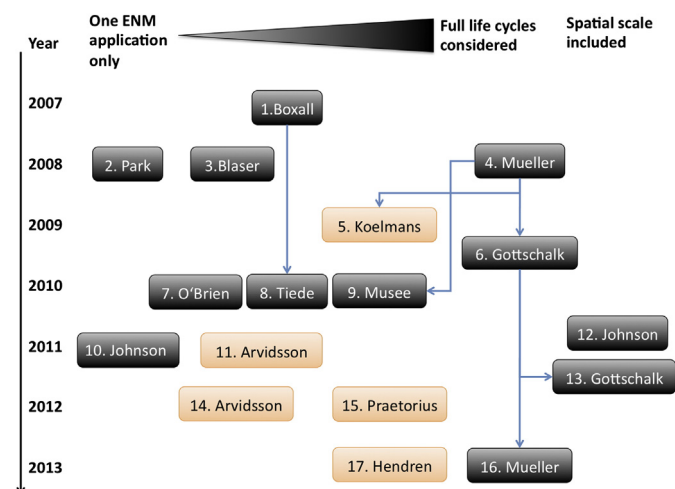


Fig. 1. Categorization of modeling approaches used to assess environmental exposure to engineered nanomaterial (ENM). Orange boxes indicate models that incorporate a mechanistic description of ENM behavior, e.g. agglomeration or sedimentation. 1) Algorithms for single hypothetical ENM applications and release estimations (e.g. cosmetics) (Boxall et al., 2007); 2. Diesel fuel ENM application and release scenario study (Park et al., 2008); 3. Modeling of the contribution of nano-functionalized plastics and textiles on the total Rhine river (silver) exposure (Blaser et al., 2008); 4. First life cycle based ENM flow model covering a comprehensive ENM application field based on a current and a high release scenario for different environmental compartments (Mueller and Nowack, 2008); 5. First mechanistic modeling (for manufactured carbon-based nanoparticles) of sedimentation fluxes including agglomeration and burial in deeper sediment layers (Koelmans et al., 2009); 6. Fully stochastic/probabilistic life cycle based ENM flow model for a comprehensive inventory of ENM applications and all environmental compartments (Gottschalk et al., 2009; Gottschalk et al., 2010a; Gottschalk et al., 2010b); 7. Study on ENM discharge (via sewage treatment) to surface water from a few nano-applications (UV protective additives in paints, antimicrobial additives in food packaging) (O'Brien and Cummins, 2010a); 8. Simple predictive algorithms on release of ENM to raw and treated drinking water (Tiede et al., 2010); 9. ENM release (into waters and soils) scenarios from the use of ENM in cosmetics (Musee, 2010); 10. ENM study on removal rates for sewage treatment and ENM use in sunscreens (Johnson et al., 2011b); 11. Study of colloid chemistry kinetics for describing nanoparticle agglomeration and sedimentation (Arvidsson et al., 2011a; Arvidsson et al., 2011b); 12. Combined measurement and modeling exercise on release of ENM from sewage treatment (Johnson et al., 2011b); 13. Stochastic/probabilistic modeling of local ENM concentrations in Swiss rivers by varying ENM release and natural dilution for different geographical and hydrological conditions (Gottschalk et al., 2011); 14. Particle number instead of mass is discussed for material flow modeling (Arvidsson et al., 2012); 15. Modeling and analysis of heteroagglomeration between ENM and suspended particulate matter in river water (Praetorius et al., 2012); 16. Predictive simulation of ENM flows during waste incineration and landfilling based on available knowledge (Mueller et al., 2013); 17. Modeling of nano-Ag flows during wastewater treatment (Hendren et al., 2013a). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

concentrations of an ENM in the environment, however, the method is not able to distinguish between natural and engineered fullerenes.

Neal et al. (2011) analyzed Ti concentrations in river water in Mid Wales and northwest England. Using 0.45 μm cellulose nitrate filters, special efforts were made to minimize sampling artifacts by filtering aliquots of water several times and by frequently changing filters. MECs were provided for river water that drains from natural, industrial and agricultural land types. The measured values include the nano-TiO₂ fraction, but also larger colloids, and therefore also provide an upper limit for nano-TiO₂ concentrations.

Johnson et al. (2011b) measured Ti in wastewater after filtration of the samples through a 0.45 μm cellulose nitrate membrane. The sludge samples were filtered through 0.2 μm filters. MECs were produced for the WWTP effluent and sludge from an activated sludge plant in the UK serving about 200,000 people. Again, the measured values also include the larger fraction of colloids and provide another estimation of an upper limit for nano-TiO₂ concentrations.

Another monitoring study (Johnson et al., 2011a) aimed to measure particulate/colloidal silver (including the nanosized material) in the influents and effluents of English WWTPs. For removing the large particulate fraction, 0.45 μm cellulose nitrate filter membranes were used. The filtrates were passed over a 1 kDa \approx 0.02 μm cross flow ultrafiltration membrane retaining the 0.02–0.45 μm colloidal fraction. The colloidal sample was digested with dilute HNO₃ and the total Ag concentration measured by ICP-MS. MECs from WWTPs across northern, central and southern England were presented. As with the Ti studies, again the values are not nano-specific but rather can be used to define an upper limit for nano-Ag concentrations.

Westerhoff et al. (2011) studied the presence and morphology of nano-TiO_x in WWTP effluents. First, the authors isolated the colloidal material by means of rota-evaporation, dialysis and lyophilization. High resolution transmission electron microscopy and energy dispersive X-ray analysis were then used to verify the presence of TiO₂ particles between 4 and 30 nm in size in these effluents. MECs (TiO_x) for wastewater effluents could be derived from selected municipal facilities in southern and central Arizona (USA). Whereas with the electron microscopy analysis it was possible to specifically detect nanoparticulate TiO₂, the total Ti analysis targeted all Ti in the 0.9 μm filtered sample, therefore including a large fraction of particles in the non-nano range.

Sanchis et al. (2011) presented the first atmospheric MECs for fullerenes. These authors used filters (<0.7 μm) to collect aerosol-bound fullerenes. Mediterranean Sea samples were taken in the spring of 2010 and 2012 (Castro-Jimenez et al., 2010; Berrojalbiz et al., 2011). Those samples were analyzed by means of a method coupling liquid chromatography to mass spectrometry (LCMS). Isotope dilution using labeled C₆₀ as surrogate internal standard was conducted for the quantification purposes.

Mitrano et al. (2012) showed that single-particle ICP-MS may be used for detecting and quantifying individual silver and other metal or metal oxide particles in real WWTP effluents with low ENM concentrations and complex matrices. MECs were presented in this study for effluents of WWTPs in Boulder, Colorado (USA). However, water samples were not filtered at nanosized dimensions and thus also particulate Ag larger than 100 nm was included in the analysis.

Khosravi et al. (2012) also presented ICP-MS data on Ti in wastewaters and sewage sludges, providing further estimates on nano-TiO₂ in these matrices. The water samples were filtered with 0.22 μm , a much lower pore size than in many other studies using filtration to remove larger particles.

Majedi et al. (2012) optimized cloud point extraction to separate the nanoparticulate fraction from water samples and applied the

method to waste water effluents. The subsequent nanoparticle identification was done by combining transmission electron microscopy with energy dispersive X-ray and UV–visible spectroscopy. A 0.05 $\mu\text{g/L}$ detection limit was achieved for ZnO nanoparticles and recoveries of spiked nano-ZnO in the range from 80 to 110%.

4. Modeled and measured ENM concentrations

Measured environmental concentrations (MEC) referring in part and to varying extents to nanosized TiO₂, ZnO, Ag, fullerenes, CNTs and CeO₂ could be obtained from different sources. PECs could be obtained from 11 modeling studies and MECs from 11 analytical studies. Nano-TiO₂ has been examined in 12 cases, nano-Ag in 9 studies, Fullerenes and CeO₂ four times each, and three analyses of CNT and nano-ZnO. PEC and MEC values are available for surface water, wastewater treatment plant effluents, biosolids, sediments, soils and air. While incomplete, this data collection extends a preliminary assessment of nanosized TiO₂, Ag, ZnO, CNT and fullerenes in surface water and STP effluents/sludge (Gottschalk and Nowack, 2012). The results are shown in Figs. 2–7.

4.1. Surface water

Nano-TiO₂: The integral view provided by Fig. 2 shows some statistical spread, as the highest and lowest concentrations vary approximately by a factor of 10⁴. Considering the model at high temporal and geographical resolution (Gottschalk et al., 2011) as

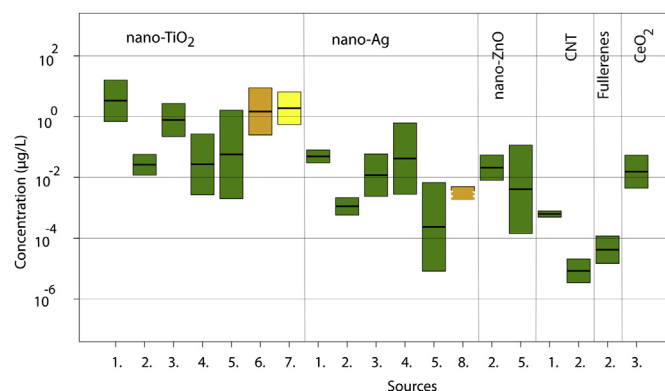


Fig. 2. Modeled and analytical concentrations of engineered nanomaterials (ENM) in surface waters. The green boxes show the range (and the arithmetic mean on the log scale) of modeled results. Yellow boxes measured concentrations and the orange boxes combine measurements and modeling. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) Sources: 1. Predicted environmental concentrations (PEC) for a current and high exposure scenario at regional level (Switzerland) covering diffusive ENM emissions from a comprehensive spectrum of ENM applications (Mueller and Nowack, 2008); 2. PECs (15–85% quantiles range of modeled probability distributions) at regional level (Europe) reflecting diffusive ENM emissions from a comprehensive spectrum of ENM applications (Gottschalk et al., 2009); 3. Range of minimal and maximal values of 90% confidence intervals for mean PECs modeled at regional level (Ireland) covering selected applications (O'Brien and Cummins, 2010a); 4. Range of local PECs (Johannesburg Metropolitan City, South Africa) for a minimum and maximum ENM release scenarios from cosmetic products via WWTPs and a dilution factor of 1 (Musée, 2010); 5. PECs at local resolution for river water (Switzerland) based on a conservative scenario without any ENM degradation/deposition and an optimistic one assuming rapid ENM removal (Gottschalk et al., 2011); 6. PECs of sunscreen ENM TiO₂ for river water of the Thames and Anglian regions in Southern England and different water flow conditions (Johnson et al., 2011b); 7. Measured environmental concentrations (MEC) (filtered Ti < 0.45 μm) for river water that drains different land types (urban, industrial, rural agricultural land) (UK) (Neal et al., 2011); 8. PECs in the Trent and the Thames basins derived from long term average water flows and two scenarios for the ENM removal efficiency in WWTPs (Johnson et al., 2011a).

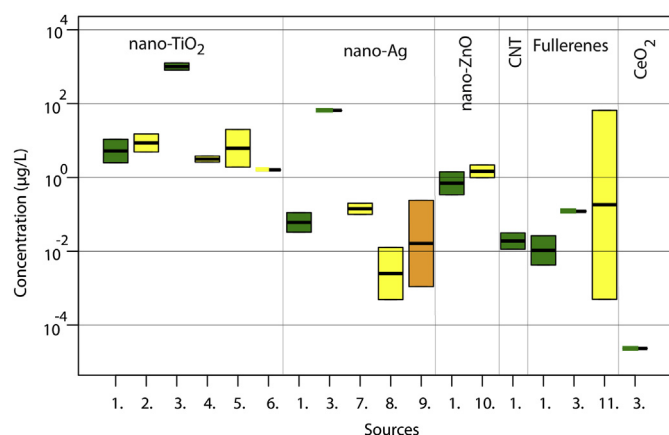


Fig. 3. Modeled and analytical concentrations of engineered nanomaterials (ENM) in waste water treatment plant effluents. The green boxes show the range (and the arithmetic mean on the log scale) of modeled results, the yellow boxes measured equivalents and the orange box combines measurements and modeling. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) Sources: 1. Predicted environmental concentrations (PEC) (15–85% quantiles range of modeled probability distributions) at regional level (Europe) reflecting diffusive ENM emissions from a comprehensive spectrum of ENM applications (Gottschalk et al., 2009); 2. Measured environmental concentrations (MEC) from selected US WWTPs (filtered Ti < 0.7 µm) (Kiser et al., 2009); 3. PECs at regional resolution (UK) for a comprehensive application scenario (all products) and ENM (nano-TiO₂) application in sunscreens (Tiede et al., 2010); 4. MECs for sunscreen Ti (<0.45 µm) from an activated sludge plant in the UK (Johnson et al., 2011b); 5. MECs (TiO_x) from selected US WWTPs (Westerhoff et al., 2011); 6. MECs (mean value) for nanoparticulate TiO₂ from the Saskatoon WWTP, Saskatchewan (Canada) (Khosravi et al., 2012); 7. MECs in waste-water effluent samples in Boulder Colorado (USA) (Mitrano et al., 2012); 8. MECs for northern, central and southern England (Johnson et al., 2011a); 9. PECs (5–95% quantiles range of modeled probability distributions) at regional level (USA) (Hendren et al., 2013a); 10. MECs for a local effluent canal in Singapore (Majedi et al., 2012); 11. MECs for effluents in Catalonia (Spain) including C₆₀ and C₇₀ Fullerene as well as N-Methylfulleropyrrolidine (C₆₀) (Farré et al., 2010).

the most updated, the nano-TiO₂ concentrations in rivers range from 3 ng L⁻¹–1.6 µg L⁻¹. This range completely includes other modeled concentration ranges (Gottschalk et al., 2009; Musee, 2010). Initial analytic efforts (Neal et al., 2011) and a combination of measurements and modeling (Johnson et al., 2011b) have roughly confirmed these modeled results (Gottschalk et al., 2009; Musee, 2010; O'Brien and Cummins, 2010a; Gottschalk et al., 2011). The measurements reveal slightly higher concentrations, which may reflect the wider material size spectrum considered (e.g. smaller than 0.45 or 0.7 µm) compared to the modeled nanoparticulate range (<0.1 µm). For Swiss rivers (Gottschalk et al., 2011), variation of the geographic location caused differences in the concentrations up to a factor of 400 (Q15%–Q85%). Likewise, temporal variation due to changes in water levels showed differences up to a factor 10 (same quantiles). A similar influence on the concentrations was attributed to the equivalent uncertainties used in that study to predict ENM discharge into Swiss river water.

For nano-Ag, a more pronounced spread between the highest and lowest PEC values is observed with approximately a factor of 10⁵ difference. This difference most likely only reflects the fact that initial estimates of nano-Ag production (Mueller and Nowack, 2008) were much higher than more recent estimates (Hendren et al., 2011). The stochastic results at the European (Gottschalk et al., 2009) and local level for a Swiss river system (Gottschalk et al., 2011) are fully consistent with predictions of the measurement and modeling exercise for the Trent and the Thames basins in the UK (Johnson et al., 2011a). Although these nanosized Ag mass balance calculations seem reasonable, they did not consider transformation of metallic Ag into mineral forms with sulfide or chloride. Kim et al. (2010) showed that during the wastewater

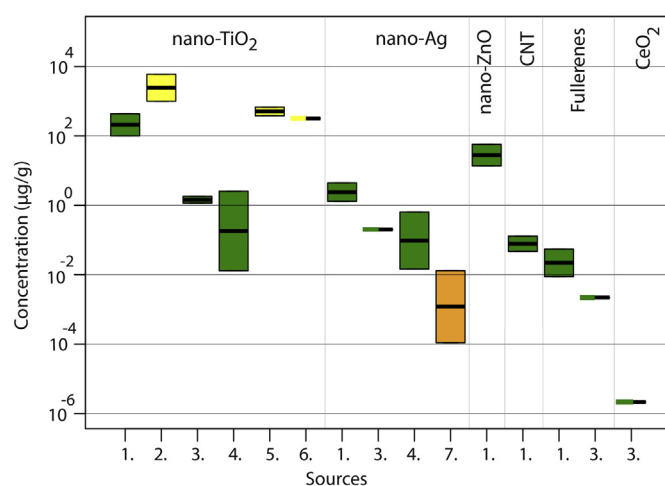


Fig. 4. Modeled and analytical concentrations of engineered nanomaterials (ENM) in biosolids. The green boxes show the range (and the arithmetic mean on the log scale) of modeled results, the yellow boxes measured equivalents and the orange box combines measurements and modeling. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) Sources: 1. Predicted environmental concentrations (PEC) (15–85% quantiles range of modeled probability distributions) at regional level (Europe) reflecting diffusive ENM emissions from a comprehensive spectrum of ENM applications (Gottschalk et al., 2009); 2. Measured environmental concentrations (MEC) (filtered Ti < 0.7 µm) from selected US WWTPs (Kiser et al., 2009); 3. PECs at regional resolution (UK) for a comprehensive application scenario (all products) and ENM (nano-TiO₂) application in sunscreens (Tiede et al., 2010) (we derived the PEC range based on a sewage sludge bulk density of 2075 kg m⁻³ (Dogru et al., 2002)); 4. Range of local PECs (Johannesburg Metropolitan City, South Africa) for a minimum and maximum ENM release scenarios from cosmetic products via WWTPs (Musee, 2010); 5. MECs for sunscreen Ti (<0.45 µm) from a UK activated sludge plant (Johnson et al., 2011b); 6. MECs (mean value) for nanoparticulate TiO₂ from the Saskatoon WWTP, Saskatchewan (Canada) (Khosravi et al., 2012); 7. PECs (5–95% quantiles range of modeled probability distributions) at regional level (USA) (Hendren et al., 2013a).

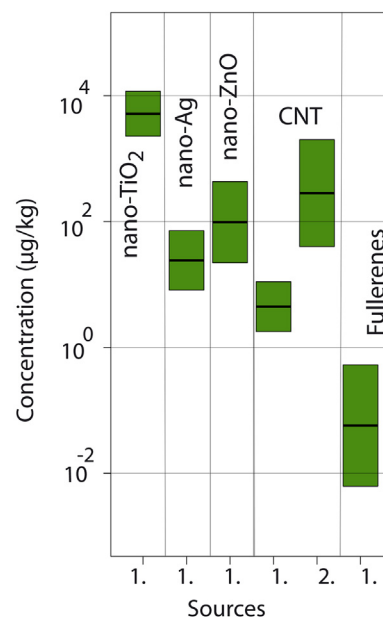


Fig. 5. Modeled concentrations of engineered nanomaterials (ENM) in sediments. The boxes show the range (and the arithmetic mean on the log scale) of modeled results. Sources: 1. Predicted environmental concentrations (PEC) (15–85% quantiles range of modeled probability distributions) at regional level (Europe) reflecting diffusive ENM emissions from a comprehensive spectrum of ENM applications (Gottschalk et al., 2009); 2. PEC range for shallow lakes (high sedimentation fluxes) and large lakes with low sedimentation fluxes (Koelmans et al., 2009).

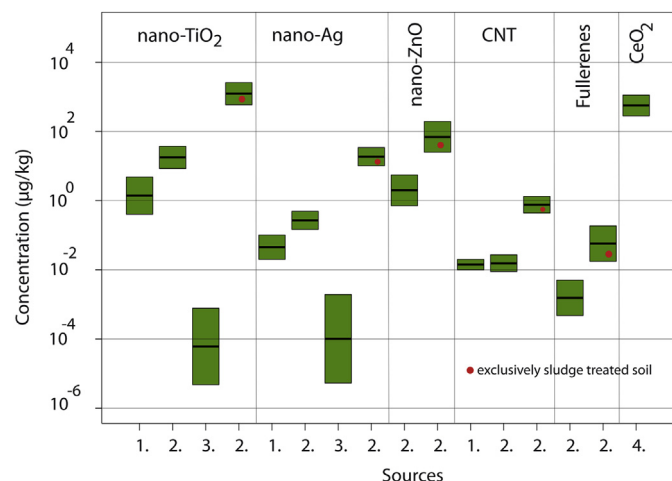


Fig. 6. Modeled concentrations of engineered nanomaterials (ENM) in **soils and soils treated with biosolids**. The boxes show the range (and the arithmetic mean on the log scale) of modeled results. Sources: 1. Predicted environmental concentrations (PEC) for a current and high exposure scenario at regional level (Switzerland) covering diffusive ENM emissions from a comprehensive spectrum of ENM applications (Mueller and Nowack, 2008); 2. PECs (15–85% quantiles range of modeled probability distributions) at regional level (Europe) reflecting diffusive ENM emissions from a comprehensive spectrum of ENM applications (Gottschalk et al., 2009); 3. Range of local PECs (Johannesburg Metropolitan City, South Africa) for a minimum and maximum ENM release scenarios from cosmetic products via WWTPs (Musee, 2010); 4. PECs for soils near highways considering the ENM accumulated during a 40-year period (Park et al., 2008).

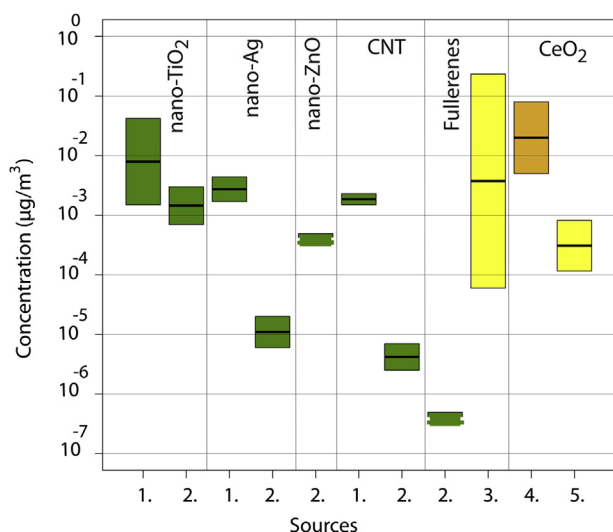


Fig. 7. Modeled and analytical concentrations of engineered nanomaterials (ENM) in the **atmosphere**. The green boxes show the range (and the arithmetic mean on the log scale) of modeled results, the yellow boxes measured equivalents, and the orange box combines measurements and modeling. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) Sources: 1. Predicted environmental concentrations (PEC) for a current and high exposure scenario at regional level (Switzerland) covering diffusive ENM emissions from a comprehensive spectrum of ENM applications (Mueller and Nowack, 2008); 2. PECs (15–85% quantiles range of modeled probability distributions) at regional level (Europe) reflecting diffusive ENM emissions from a comprehensive spectrum of ENM applications (Gottschalk et al., 2009); 3. Measured environmental concentrations (MEC) for the Mediterranean Sea atmosphere (Sanchis et al., 2011); 4. PECs in different areas of street canyons (Park et al., 2008); 5. MECs of a Newcastle city center monitoring site after the introduction of the nanoparticulate (CeO₂) diesel fuel additive (Park et al., 2008).

treatment process, most silver (independent of its initial form) is transformed into the mineral α -Ag₂S. This result was confirmed (Kaegi et al., 2011) by means of X-ray absorption spectroscopy (XAS) measurements. Thus, the concentrations of non-transformed nanosized metallic Ag could be even smaller, as the latest results would suggest. The current question, therefore, is what the fate of such α -Ag₂S is in natural media and whether particle transformation will continue: either back to the initial Ag material or into other forms of Ag (Nowack, 2010). Hoque et al. (2012) explicitly stated that their detected nano-Ag could represent insoluble silver forms such as Ag₂S or AgCl, or nano-sized Ag-containing organic colloids rather than pure ENM.

In the case of nano-ZnO, only two studies have reported concentrations in aqueous systems. Consistency was found between these probabilistic approaches (Gottschalk et al., 2009, 2011), which were based on the same total amount of ENM released. The latter fully quantifies the natural variability of the predicted concentrations. This variability combines factors such as different geographical release conditions with varying water levels in time and space (dilution).

4.2. Effluents from waste water treatment plants (WWTP)

The modeled values shown in Fig. 3 for WWTP effluents are much closer together than the surface water results. In most cases, measurements have confirmed the modeled results. A high consistency was observed for nano-TiO₂; several studies suggest concentrations of about 5 µg L⁻¹. If ignoring one single high value outlier, the upper and lower bounds of five different studies (1 model, 4 measurements) only vary approx. by a factor of 10. Similar agreement was observed for the nano-Ag results, however in a less pronounced manner. If again the one high-concentration outlier is neglected, the extremes of three other studies (Gottschalk et al., 2009; Mitrano et al., 2012; Johnson et al., 2011a) vary by a factor of 400 and converge on average values of about 100 ng L⁻¹. The recently published values (Hendren et al., 2013a) confirm such averages by enclosing, fairly accurately, all the ranges of the three previously mentioned works. However, as illustrated by the river water, for the purposes of risk assessment such concentrations have to be used while considering that the majority of the silver is present in wastewater is as α -Ag₂S (Kaegi et al., 2011).

Only one study for each nano-ZnO, CNTs and nano-CeO₂, has reported their respective concentrations, which therefore makes a comparison to other results not possible.

However, the measured values in these systems can be compared to the predicted values from the models. The nano-ZnO concentration measured by (Majedi et al. (2012) compared very well with the predicted concentrations. They found a concentration of 1.58 ± 0.59 µg/L of nano-ZnO particles in their effluent water sample. Some consistency was also seen for average fullerene values, which range from a few ng L⁻¹ to about 100 ng L⁻¹. However, the measurements (Farré et al., 2010) of different fullerenes (C₆₀ and C₇₀ and N-methylfulleropyrrolidine C₆₀) provide results that vary between 22 Spanish WWTPs by a factor 1.3×10^5 . Concentrations from 0.5 ng L⁻¹ up to 67 µg L⁻¹ were detected in wastewater effluents. The highest values were found in industrialized/highly populated/high traffic areas, e.g. near the Barcelona airport. One critical point when comparing the modeled PECs with such MECs is that measurements did not distinguish among the sources of the material detected. In contrast, models provide concentrations for ENM from specific sources such as synthesized fullerene used in new products (cosmetics, pharmaceuticals, polymer additives etc.), whereas measurements include fullerene material from natural as well as industrial or traffic exhaust fumes.

4.3. Biosolids

Considering all the nano-TiO₂ results (Fig. 4), the extreme values vary by a factor 4×10^5 . The filtrations that considered material up to 0.7 μm size (Kiser et al., 2009) went far beyond the nanosized fraction. Thus, in these sludge samples total Ti was measured rather than nano-Ti. Annually millions of tonnes of bulk TiO₂ are produced worldwide for a wide range of applications (EPA, 2010; USGS, 2012). If only a small fraction of such bulk material goes into wastewater, this could lead to significant aquatic Ti concentrations. This makes it clear that the modeled values for nanosized TiO₂ must be significantly lower than the measured total concentrations. Nevertheless, due to its extreme brightness and resistance to discoloration most (90%) (TZMI, 2009) bulk TiO₂ is used as white pigment. As shown by others (Weir et al., 2012) a part of such pigment material is in the nanosized fraction. These authors concluded that pigment TiO₂ may represent an important source for nanosized TiO₂ ending up in the aquatic and other environments. The outliers on the lower end of the spectrum in one case (Musee, 2010; Tiede et al., 2010) only reflect single ENM applications (nanomaterial embedded in cosmetics).

At first glance and when ignoring newest low PEC results (Hendren et al., 2013a), there is quite a good agreement between the nano-Ag concentrations in biosolids. The extreme values of three studies only vary approx. by a factor of 300 and agree on average concentrations around $1 \mu\text{g g}^{-1}$. However, the newest PECs (Hendren et al., 2013a) are – when comparing their averages to earlier U.S. modal values (Gottschalk et al., 2009) – about 450 times lower. As shown by Hendren et al. (2013a, Appendices), whose model was fed with nano-Ag discharge into STP treatment, a difference of a factor of 10 has to be attributed to such discharge. Therefore, the remaining difference occurs from varying the ratios of the mass of nano-Ag associated with biosolids to the concentration of such Ag materials reaching the STP effluent. Hendren et al. used experimentally determined partitioning constants (K_d) whereas Gottschalk et al. (2009), used a transfer factor from a model waste water treatment plant. This obviously means that for further modeling of sludge concentrations, such partitioning has to be adapted based on new experimental evidence and that currently there is an urgent need for such experimental evidence to be confirmed. Furthermore, as described for risk estimations of nano-Ag in water above, we have to identify the form of the target material, in some cases distinguish between multiple Ag containing complexes, in addition to quantifying the total concentration sludge organisms are exposed to.

Similar to the case of nano-TiO₂, the only results for nano-ZnO suggest concentrations in $\mu\text{g g}^{-1}$ range. Due to a lack of estimates, no further analysis can be done for CNT. For fullerenes a few ng g^{-1} are predicted. For CeO₂ the single available study showed concentrations that did not exceed the pg g^{-1} range.

4.4. Sediments

The only comparative evaluation in sediments (Fig. 5) can be done for CNT. For all other materials only one study (Gottschalk et al., 2009) provided quantitative results whose strengths and limitations have been discussed in detail elsewhere (Gottschalk et al., 2010b). However, recent measurements (Luo et al., 2011) of micro-sized Ti particles (0.1–0.7 μm) were two orders of magnitude higher than the European modeled results (Gottschalk et al., 2009) for nanosized particles. The Chinese MECs seem plausible since their higher Ti values represent a broader material size range than nanosized Ti and were (as the authors underline) exactly in the

range of the concentrations ($1\text{--}6 \mu\text{g g}^{-1}$) in biosolids measured in Arizona (USA) for similar particles ($<0.7 \mu\text{m}$) (Kiser et al., 2009). Pure nanosized ($<0.1 \mu\text{m}$) material concentrations are necessarily lower than measurements that include a material size fraction that is three times more broad (up to 3 μm). Furthermore, such measurements did not quantify only synthesized Ti material, but also considered naturally occurring Ti. From a geographical evaluation of the ENM release, the authors concluded that the difference in sediments with high concentrations compared to those with low values would come directly from anthropogenic Ti discharge (direct sewage input, WWTPs' effluent, and surface runoff). In this way, an average of $2.74 \mu\text{g mg}^{-1}$ could be attributed to anthropogenic Ti sources. This value is still about 500 times higher than the average modeled results. The remaining difference could reflect one of the main limitations of the modeled values. Namely, in the sediment modeling, the stochastic simulations (Gottschalk et al., 2009) only provide the ENM amount deposited in 2008. Assuming a zero nano-TiO₂ concentration in 2000, the annual accumulation of ENM was scaled according to the world wide market evolution of nanoproducts from the years 2001–2012. However, these estimations of the increase in nano market share are very insecure (unreliable), and thus assumptions on annual accumulations are not build on a solid foundation. Thus, these reported results should be considered preliminary and further efforts to better quantify (expected) concentrations in sediments is urgently needed.

In the case of CNTs the mean values of two studies (Gottschalk et al., 2009; Koelmans et al., 2009) varied approx. by a factor 160. This reflects well the fact that the first mechanistic work (Koelmans et al., 2009) based their sediment model on much higher (approx. up to a factor 230) ENM discharge quantities (Mueller and Nowack, 2008) than the ones modeled in the probabilistic study (Gottschalk et al., 2009). However, aside from this caveat, we note a high agreement between these two sediment studies.

4.5. Soils

Evaluation of the modeled soil concentrations (Fig. 6) is difficult since the different models do not necessarily consider the same ENM sources, environmental release routes, or release periods. In addition, measurements for natural (background) soil samples are not available. The scenario based MFA (Mueller and Nowack, 2008) shows lower concentrations by being limited to dry and wet aerial deposition of ENM on soils. Subsequent studies distinguished between generic soil concentrations and reflect direct ENM release via consumption of ENM products, aerial ENM deposition and the specific concentrations in soils treated with biosolids (Gottschalk et al., 2009). Furthermore, these later results consider time dependent ENM accumulation in soils from 2001 to 2012, whereas the first values only reflect a single years' deposition of ENM. The local scenarios that only consider ENM (nano-TiO₂, nano-Ag) from cosmetics, release via agricultural biosolids application and/or leachate from waste landfills (Musee, 2010) are much smaller (up to a factor 3×10^6) than the sludge treated soil concentrations (Gottschalk et al., 2009). However, this might be explained by South African specific market penetration values for ENM cosmetics and biosolids application rates. For CNTs, a very good agreement at low concentration levels was seen between the Swiss models (Mueller and Nowack, 2008; Gottschalk et al., 2009). Even in soils treated with biosolids the concentrations mostly do not reach $\mu\text{g kg}^{-1}$ dimensions.

In the case of CeO₂, we are confronted with a very conservative assessment since the only source (Park et al., 2008) assumes the CeO₂ from diesel additives accumulates over a 40-year period along a high traffic highway.

4.6. Atmosphere

For nanosized TiO₂, Ag and CNT modeled results for atmospheric concentrations from two sources are available (Mueller and Nowack, 2008; Gottschalk et al., 2009). Differences of about a factor 10 for nano-TiO₂, 230 for nano-Ag and 400 for CNTs can be seen between these two approaches. Such variance mainly reflects differences in approaches to model the residence time of ENM and varying ENM production amounts. A residence time of 10 days was modeled in 2009 (Gottschalk et al., 2009) based on the knowledge available for ultrafine particles (Anastasio and Martin, 2001). Under these conditions, approximately 1/36th of the constant ENM input was assumed to remain permanently in the atmosphere. The previous study from this group (Mueller and Nowack, 2008) modeled permanent air persistence of ENM without specifying a particular residence time. No differences were seen in regards to the ENM release modeling (at very low percentages) via flue gas cleaning, from the usage of products or via waste incineration processes.

Measured aerial concentrations carried out for fullerenes bound to aerosols (Sanchis et al., 2011) can be compared to the modeled values of (Gottschalk et al. 2009). The highest measurements are about $5 \cdot 10^5$ times higher than the highest modeled values. However, the spread (by an approx. factor of $4 \cdot 10^3$) in the measured data is remarkable. While the model only considers the release of a generic, synthesized fullerenes, in the measured values both the engineered and naturally occurring fullerene are captured. The four target functionalized engineered fullerene types (N-methylfulleropyrrolidine C₆₀, pyrrolidine tris-acid ethyl ester, [6,6]-phenyl C₆₁ butyric acid methyl ester and [6,6]-thienyl C₆₁ butyric acid methyl ester) were not detected at all in the analytical work. The authors concluded that the C₆₀ and C₇₀ fullerenes found in the samples originated as byproducts from combustion processes. Natural formation of fullerenes has been observed in other instances (Heymann et al., 2003) and so this conclusion is plausible. A back trajectory analysis showed that higher concentrations were associated with air that had been circulating over areas with high industrial activity. Air that had moved over the open sea (i.e. far from the coast) showed the lowest concentrations of fullerenes. In the open Mediterranean air C₇₀ is the prevalent fullerene whereas this was C₆₀ the in wastewater (Farré et al., 2010). Therefore, as underlined by Sanchis et al. (2011), cities only appear to contribute to C₆₀ exposure and the C₇₀ sources are from industrial processes. In addition, these authors concluded the variance in the C₇₀/C₆₀ ratio signified multiple sources contributed to the observed fullerene concentration. Due to the current very thin empirical evidence, however, the scenario of a single and dominant combustion source could not be excluded.

CeO₂ studies provide measured or modeled results that vary at their extremes approximately by a factor of 700. However, all predicted concentrations were higher than the measured values. It cannot be excluded that either a wider particulate filter application is the cause or that today's vehicles are possibly filtering more of the Cerium than expected. Park et al. (2008) supports this hypothesis by suggesting a lower exposure than presumed due to optimized engines and/or fuels.

5. Critical evaluation of available data

5.1. Challenges of modeling work

The comparison of the modeled concentrations using various approaches and the measurements using different analytical procedures and techniques has shown that, within a certain range, we already have some understanding of the expected environmental

concentrations of ENM. These predicted concentrations, although validated only to a very minor extent, provide very useful and urgently needed data for the environmental risk assessment of ENM (REACH, 2010; Aschberger et al., 2011).

The reviewed ENM concentrations have mostly been quantified in terms of mass per volume or mass per mass of the target environmental compartments. The critical point is that pure mass based models and analytics will not be sufficient for risk estimation purposes as long as the material size, shape, surface chemistry etc. are not provided. These facets of ENM are shown to represent the essential ecotoxicological drivers (Handy et al., 2012) and therefore should (be attempted to) be included in future iterations of models. Especially for describing the ENM interaction with the natural and technical environment, mass based units could be supplemented by indications of the material size, surface area etc. Such adaptations of the models should not be too difficult if specific characteristics of ENM found in the environment are well characterized: e.g. in aggregated or agglomerated form, ENM bound to the surface of other bulk solids. For metal nanomaterials, pertinent information could include, for example, transformations of nano-Ag with sulfide, chloride or other ligands. A first attempt to include changes in particle size distributions in environmental fate modeling of ENM has been published (Praetorius et al., 2012). Bayesian methods have already been used to assess size changes, collision rate, surface interaction, coating, zeta potential/surface charge, attachment efficiency etc. (Money et al., 2012).

Due to a lack of empirical data, presently none of the used multimedia models have considered the environmental fate and behavior based on a mechanistic description or processes (Hendren et al., 2013b). To date, only pure mass transfers between natural and/or technical compartments has been considered. This shows some limitations when reflecting on particle transfer and degradation, dissolution, complexation etc. The processes influencing the environmental concentrations of ENM such as dissolution, phase transformation, aging or agglomeration are currently beyond the reaches of what can be derived from literature sources or what can presently be elucidated analytically (Neal et al., 2011). For aquatic concentrations, more attention should be paid to the major influential parameters such as the water sediment partitioning and kinetics of resuspension, agglomeration, advective flow transfer and burial (Quik et al., 2011; Praetorius et al., 2012). For terrestrial environments no measured/experimental concentrations have been reported so far. Analytical results have only been available from two studies and two materials (fullerenes and CeO₂) for atmospheric exposure. Crucial aerodynamic parameters (diffusion (Brownian motion), agglomeration behavior, deposition of ENM aerosols) have at best been examined so far for occupational areas (Aitken et al., 2004). How the interactions between ENM and with living organisms (microorganisms, plants, animals) in environmental media could influence the entire food chain must also be investigated. Here, the biota may play a critical role for environmental concentrations of such internalized nanomaterials, but this has yet to be investigated in detail (Judy et al., 2012).

The major source of modeling errors seems to lie in uncertain ENM production and emission rates from products as well as ENM product's market penetration. Researchers still find it very difficult to quantify the amounts of ENM produced and contained, used and consumed in products (Gottschalk and Nowack, 2011; Hendren et al., 2011; Piccinno et al., 2012). However, because the different modeling studies used different estimates for production or use, the modeling results presented in this work contain this uncertainty to some extent by following different approaches to obtain the production volume and thus finally the environmental concentrations. The way to bridge the gap in our knowledge on

production and use of ENM has been summarized several times (Boxall et al., 2007; Tiede et al., 2010; Gottschalk and Nowack, 2011; Clark et al., 2012): i) Report amounts of production of ENM and of ENM-products sold in a particular region; ii) establish an inventory of ENM products by indicating the ENM concentrations and specific properties (size distribution, possible functionalization, shape etc.); iii) produce experimental/analytical data on the main emission sources, pathways, amounts and forms.

5.2. Analytical/experimental work and its comparison to and use for modeling studies

Some filtration, microscopic, spectroscopic, chromatographic and other techniques have been combined to detect and quantify the ENM under laboratory conditions. Unfortunately, these specialized methods are not yet applicable for real time sampling under natural conditions including long term monitoring. When such techniques become available, it will dramatically increase the reliability of the quantitative nature of the knowledge for environmental exposure (von der Kammer et al., 2012). Therefore, to ensure we do not compound pronounced uncertainties in concentration (and risk) assessments – and to calibrate/restructure the available models – we have to very critically evaluate the sparse measurements that are currently available.

The modeled and measured concentrations are difficult to compare due to the different underlying assumptions in the models or the different measurement techniques. The issues complicating the comparisons between modeled and measured concentrations are in the following discussed with the help of Fig. 8.

The modeling predictions of ENM have in most cases targeted the primary particles and did not distinguish between single and agglomerated particles. This is true even if the agglomerates were much larger than 100 nm. The modeling studies differ in the way they incorporate agglomeration. Some models do not consider this process and assume (due to a lack of quantitative mechanistic models) that ENM do not change their form and agglomeration state in technical or environmental systems. In contrast, other models include agglomeration and subsequent sedimentation in a simplistic way by estimating a transfer factor. Nevertheless, quite a few studies have shown that agglomeration is an extremely important parameter affecting the fate and behavior of ENM in the environment, e.g. for nano-TiO₂ (Auffan et al., 2010; Labille et al., 2010; Ottofuelling et al., 2011) or nano-ZnO (Scheckel et al.,

2010). The modeled concentrations in most cases comprise of all agglomeration states of a given ENM irrespective of the actual size of the agglomerates. This could potentially be an important omission or over simplification. We would therefore expect that modeled concentrations of ENM are higher than measured ENM concentrations, especially if the analytical procedure involved a size fractionation step.

A critical review (Isaacson et al., 2009) of the quantitative analysis of ENM showed that under natural conditions only a small part of ENM can persist in the environment. Transformation reactions rapidly change the initial form the ENM, which can be very pronounced as exemplified by the case of nano-Ag (Kim et al., 2010; Scheckel et al., 2010; Kaegi et al., 2011; Levard et al., 2012). Therefore, the modeled results possibly overestimate the environmental concentrations of nanomaterials remaining in their initial forms. Dissolution and phase transformations have been considered by some models, but only to a limited extent. So far the modeled nano-Ag concentrations do not consider the almost complete transformation of nano-Ag into Ag-sulfides during wastewater treatment. In particular this is a process that completely eliminates the initial particles and forms new, different nanoparticles. However, it has also been shown that similar particles can be formed when dissolved Ag is added to the wastewater, making the task of determining nano-specific transformations even more complex.

ENM only constitute a portion of the nanomaterials existing on earth. Conventional materials produced in high production volumes such as pigment TiO₂ may contain a nanosized fraction. Weir et al. (2012) have reported, for instance, that in a food grade pigment TiO₂ 36% of the particles had a size of less than 100 nm. These so-called ‘bulk-derived nanomaterials’ have already been detected in the environment: Kaegi et al. (2008) have found nanosized TiO₂ in runoff originating from painted facades that only contained pigment-TiO₂. Farré et al. (2010) underline that nanoparticles can also be produced as a result of natural phenomena such as e.g. volcanic eruptions and forest fires as well as by different industrial processes. These particles too can be released into the environment (Nowack and Bucheli, 2007; Adlakha-Hutcheon et al., 2009; Farré et al., 2010). For instance, soot, as part of the Black Carbon continuum, is formed by incomplete combustion of fossil fuels and vegetation. Its particle size in the nanometer to micrometer range falls partially within the nanomaterial domain (Nowack and Bucheli, 2007). Several hydrophobic fullerenes occur in soot (Howard et al., 1991; Richter et al., 1997; Ozawa et al., 1999; Isaacson et al., 2009). The fullerenes detected by Farré et al. (2010), for example, are probably mostly from combustion processes. In addition NM can be formed from a variety of different materials by abrasion processes, even if the materials do not contain any ENM (Vorbau et al., 2009; Gohler et al., 2010). Moreover, several studies (Akaighe et al., 2011; Glover et al., 2011; Maurer et al., 2012; Yin et al., 2012) have reported that metallic silver nanoparticles can be generated via reduction of silver ions (Ag⁺) derived from sources such as silver wire and jewelry in contact with water or in the presence of organic matter. These results suggest there is some potential for direct formation of nanosilver under natural conditions, implying that not all nanosilver in waters is of anthropogenic origin (Akaighe et al., 2011).

As shown in Fig. 8, measurements of NM in natural samples detect five different types of NM: ENM, bulk-derived NM, abrasion-produced NM, combustion-generated NM and natural NM. Current models for ENM exclusively model the engineered portion of the total nanosized fraction and therefore we expect that measurements of the nanosized fraction will always be higher than model predictions. However, the measurements could also be smaller than the modeled values because most analytical methods involve

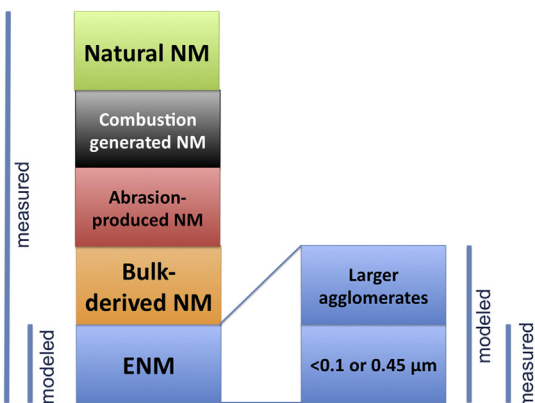


Fig. 8. Spectrum of modeled and measured environmental concentrations of nanomaterials. In addition to engineered nanomaterials (ENM) measurements refer also to bulk-derived NM (nanosized-fraction of pigments), combustion-generated NM and natural NM. The ENM-fraction consists of agglomerates in the nano-range (that are measured by the analytical methods) and larger agglomerates (that are not detected).

a size-fractionation and target only particles smaller than a discrete nominal cut-off (e.g. 450 or 100 nm). Because the modeling results available also consider agglomerates larger than 100 nm and thus target the complete ENM pool, measurements of only the nano-fraction may indeed be smaller than the modeled ENM concentration. Further development of analytical procedures and methods that are able to identify and quantify specifically ENM is needed in order for the models to be validated.

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