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Critical Review

POTENTIAL SCENARIOS FOR NANOMATERIAL RELEASE AND SUBSEQUENT ALTERATION IN THE ENVIRONMENT

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Abstract—The risks associated with exposure to engineered nanomaterials (ENM) will be determined in part by the processes that control their environmental fate and transformation. These processes act not only on ENM that might be released directly into the environment, but more importantly also on ENM in consumer products and those that have been released from the product. The environmental fate and transformation are likely to differ significantly for each of these cases. The ENM released from actual direct use or from nanomaterial-containing products are much more relevant for ecotoxicological studies and risk assessment than pristine ENM. Released ENM may have a greater or lesser environmental impact than the starting materials, depending on the transformation reactions and the material. Almost nothing is known about the environmental behavior and the effects of released and transformed ENM, although these are the materials that are actually present in the environment. Further research is needed to determine whether the release and transformation processes result in a similar or more diverse set of ENM and ultimately how this affects environmental behavior. This article addresses these questions, using four hypothetical case studies that cover a wide range of ENM, their direct use or product applications, and their likely fate in the environment. Furthermore, a more definitive classification scheme for ENM should be adopted that reflects their surface condition, which is a result of both industrial and environmental processes acting on the ENM. The authors conclude that it is not possible to assess the risks associated with the use of ENM by investigating only the pristine form of the ENM, without considering alterations and transformation processes. Environ. Toxicol. Chem. 2012;31:50–59. © 2011 SETAC

Keywords—Nanomaterials-containing products Nanoparticles Environmental transformation Fate Transport Risk assessment

INTRODUCTION

The risks associated with exposure to engineered nanomaterials (ENM) will be determined in part by the environmental processes that control fate, transport, and transformation. These processes will determine exposure levels and toxicity of ENM [1–4]. The specific processes that must be considered are not unique to nanomaterials, but the responses of ENM to these processes are likely to differ considerably from those of chemical contaminants historically considered in risk assessments. In most cases, ENM will enter the environment contained in products and will be released from these products during their life cycle through product use, disposal, or weathering [5]. Fate and transport processes will act on the product matrix as well as on the ENM contained within it, both prior to and after release from the matrix. Furthermore, the ENM will subsequently change in form and chemistry. It is less likely that ENM will occur in the environment in their as-manufactured form. This fact raises the question of whether the study of unaltered ENM, the form generally used in environmental, health, and safety (EHS) investigations, can provide an adequate evaluation of the risk of ENM use.

Fate and transport processes that can act on nanomaterials in products, and after their release, include photochemical transformation, oxidation and reduction, dissolution, precipitation, adsorption, desorption, combustion, biotransformation, and abrasion, among other biogeochemically driven processes [3,6,7]. In addition, ENM are also affected by agglomeration or aggregation and settling [8]. The nature of the ENM surface will control aggregation, because all forms of ENM (pristine and altered) are subject to these processes. We will not, however, consider them in this discussion. Hypothetical case studies will be used to illustrate how fate and transport processes are likely to act on ENM as they exist in currently available products. The examples include titanium dioxide in sunscreen and paint, nanoscale silver in textiles, composite structures containing carbon nanotubes, and cerium oxide in the fuel combusted in diesel engines. These products and materials were selected for hypothetical case studies because they differ in fundamental properties or behaviors critical for assessing the risks of exposure to nanomaterials. These include their solubility (insoluble

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TiO_2 vs soluble nano-Ag), redox activity (unreactive TiO_2 vs reactive cerium oxide), and product use pathways to the environment.

CATEGORIZING NANOPARTICLES

The vast body of experimental work with ENM has been conducted with what we term pristine ENM, the as-manufactured form. However, for the purpose of building a risk assessment methodology for products containing ENM, a framework that includes additional categories of ENM should be implemented to reflect the diversity of potential ENM bulk and surface properties (Fig. 1). In addition to pristine ENM (P-ENM), ENM embedded in products should be classified as product-modified ENM (PM-ENM). Engineered nanomaterials acted upon by environmental processes while still associated with the product are considered product-weathered ENM (PW-ENM). Finally, after ENM are released from the product and are acted on by environmental processes, they can be classified as environmentally transformed ENM (ET-ENM). Future laboratory research should strive to obtain data on all four forms of ENM.

Pristine ENM having a wide range of surface coatings have been evaluated for toxicity and stability [9,10]. In most cases, P-ENM are industrially modified to form the PM-ENM that are embedded in final products. The modifications to P-ENM allow them to be homogeneously dispersed or incorporated into the matrix or at the surface of the final product [11]. In many cases, this involves modifying the hydrophilic–hydrophobic properties for the use of P-ENM in organic solvents, modifying surface charge for use with aqueous solvents, or a variety of alterations to manipulate surface reactivity. In the case of incorporating ENM into a material, the matrix can be the following: a solid, such as nano-TiO_2 in self-cleaning cement; membranes incorporating nano-SiO_2 or nano-Ag; carbon nanotube-reinforced composites; nano-Ag in textiles; or a liquid, such as TiO_2 in cosmetics and paints or CeOx in fuels. For example, the nano-TiO_2 particles incorporated into sunscreens are generally covered by an AlOOH or an SiO_2 layer to prevent any reactive oxygen species (ROS) production, and a second hydrophobic layer can be added to allow homogeneous dispersion in the cream (Fig. 2).

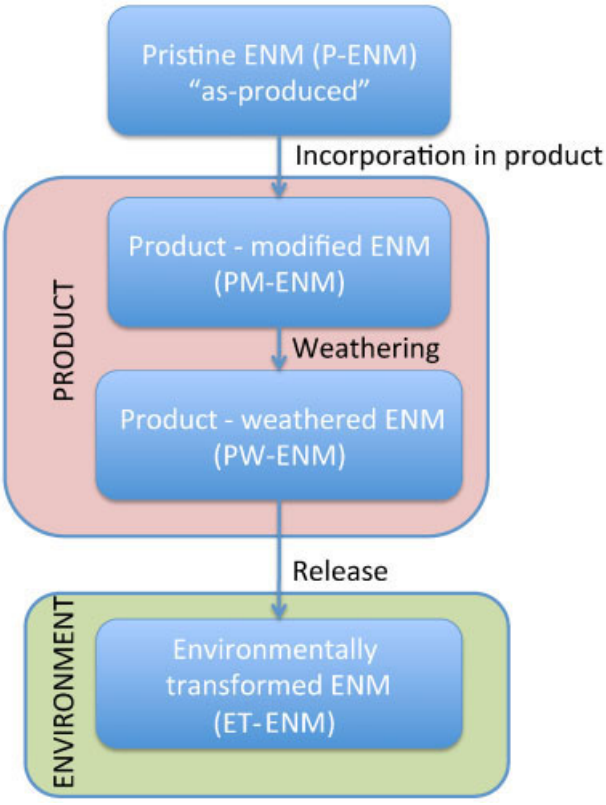

Fig. 1. Categorization of engineered nanomaterials (ENM) into pristine ENM (P-ENM; as produced), product modified ENM (PM-ENM; as incorporated into product), weathering and altered EMN (PW-ENM; in product and during release), and environmentally transformed ENM (ET-ENM). [Color figure can be seen in the online version of this article, available at wileyonlinelibrary.com]

Adding a structured nanolayer at the surface of a commercial product can require different modifications or processes. For example, with self-cleaning glass, the nano-TiO_2 layer is deposited at a high temperature on the glass surface while being formed [12]. In other cases, the nanoparticles are less strongly bound to the material, such as incorporating silver into textiles [13]. It becomes clear that the physical, chemical, and biological properties of the nanomaterials-containing products (PM-ENM) differ from those of the P-ENM from which they are made.

A key issue is whether the PW-ENM released during the weathering of products containing nanomaterials have an increased or decreased reactivity or toxicity relative to the pristine and modified materials. The research challenge is to determine whether altering commercial nanomaterial products will release PW-ENM with high reactivity or whether the weathering of the product will lead to a certain kind of passivation through surface amorphization, adsorption, surface redox evolution, or other mechanisms. Below, some case examples illustrate the fate processes that occur as a result of releases during product weathering. Of course, when PW-ENM are released from the product, they will undergo further transformations in the environment, resulting in ET-ENM formation.

FATE AND TRANSFORMATION PROCESSES

Several important alteration and transformation processes can act on the products and ENM. In many cases, these processes act on all four types of ENM defined previously, although the rates and products of reaction may differ for each ENM type. For this reason, in most of the following discussion, we use the generic ENM designation, unless reference is made to the specific ENM type for clarity. The alteration and transformation processes can be combined into what we term fate processes, which can occur during use and after products or ENM enter the environment. These fate processes have been incorporated into the hypothetical case studies presented here, in which each process has been labeled numerically. In the following discussion, these numbers are shown in parentheses.

In photochemical transformation (process 1), incident light may penetrate the product and reach photoreactive ENM, inducing excitation ENM [14,15] and generation of free radicals [16] or by direct interaction with other components of the product [17]. The extent to which this process will influence the creation of PW-ENM (or possibly ET-ENM) is related to the incident light wavelength, the capacity of the light to penetrate the product and the outer layers of the ENM (for example, aggregated or surface-coated particles may have lower light penetration efficiency), and the capacity of the photosensitive portion of the ENM to be excited or photodegraded. Photochemical transformations occur at fast rates after the incident light has reached the target, and the rate-determining step is the

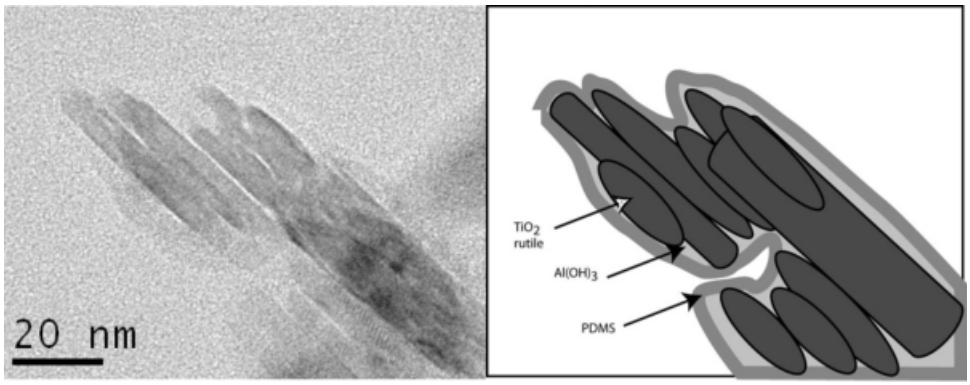

Fig. 2. (**Left**) Transmission electron microscopy image of nano-TiO_2 material used in sunscreen. (**Right**) Schematic view of the nanocomposite formulation consisting of a TiO_2 core and Al(OOH) and polydimethylsiloxane layers.

mass transfer from the surface of the material to the external media. Photochemical processes may also alter the interaction of ENM with environmental components (for example, photoactivation of TiO_2 may alter its binding to dissolved organic matter) [18].

Materials in a given oxidation state are susceptible to oxidation (process 2) or reduction (process 3) if the reaction is thermodynamically favorable [19]. In general, redox potentials are used to estimate the susceptibility of a compound to undergo these processes [20]. Redox reactions are highly influenced by a variety of environmental conditions, including the presence of reducing or oxidizing agents that can accelerate the rates of reaction, the pH of the media that determines the favorability of the reaction, the presence of the necessary reactants that will determine whether the redox reaction can take place, and the presence of adsorbed substances or stabilizers on the surface of the ENM that will reduce the rates of transformation [21]. For the present discussion, it was decided to separate oxidation from reduction, because different components of a composite nanomaterial, once released into the environment, may undergo different redox pathways.

Dissolution (process 4a) refers specifically to the release of individual ions or molecules that are soluble in water [4,22–24]. The dissolution process can involve reaction of the surface molecules and ultimate release of the ionic form [21] or direct dissolution of the constituent materials, followed by a diffusional transport of the dissolved compounds [25]. Precipitation (process 4b) refers to the formation of a new solid material after the dissolution and transport of ionic species and reaction or deposition of these dissolved species with the available ligands or suspended material that are present in natural waters [26,27]. These two processes are regulated by the solubility product (K_{sp}), which determines the equilibrium among the ionic species in the solution. These constants are dependent on the ionic strength (activity coefficients corrections), ligand availability (such as for metal complex species formation), pH, and temperature of the surrounding media [19]. The presence of adsorbed substances may decrease or increase the dissolution rates by protecting the surface from the media or by the removal of surface atoms in processes of adsorption or desorption, respectively [25]. Thermodynamic calculations can be used to predict the stable phases under certain environmental conditions; however, slow kinetics and diffusion rates may retard the attainment of the final product [28–30].

Adsorption (process 5a) is the process by which substances attach to the surface of solids by means of Van der Waals attractions (physisorption), electrostatic interactions (ion exchange), or chemical bonding (chemisorption), as discussed by Dabrowski [31], Rabe et al. [32], and Pan and Xing [33]. In physisorption, the adsorbate is weakly and nonspecifically bound to the surface of the ENM. For ion exchange and chemisorption, either a charged interaction or chemical bonding to specific available surface sites is involved. Adsorption of substances may have two opposing effects on the stabilization of the particles. If surface coverage is partial, then the dispersion may be destabilized, and aggregation occurs by a bridging effect between the free surface and the nonadsorbed functional groups of the adsorbate, especially in the case of large molecules such as polymers or humic substances. If, however, the surface of the particles is totally covered, the dispersion may be stabilized, which will reduce the aggregation induced by both electrochemical and steric interactions [34]. Electrostatic modifications of colloidal stability can also occur after chemisorption of small inorganic or organic molecules [35]. Furthermore, the particle may adsorb contaminants or small biological entities and act as a vector for their transport in the environment [36–40]. Sorption processes may be particularly important with respect to changing the surface characteristics of the PM-ENM to that of the PW-ENM and ET-ENM.

A large quantity of literature is available on the influence of organic matter coatings on the behavior of ENM in natural systems, which directly affects the colloidal stability of ET-ENM in suspension [8]. Because natural organic matter (NOM) is a ubiquitous constituent of natural waters, these changes in the surface properties of PW-ENM and ET-ENM by NOM should be significant, for example, because they affect agglomeration of particles [1,41,42].

Desorption (process 5b) of chemisorbed species will occur if the equilibrium with the media is altered by lowering the chemical potential (for example, concentration) of the adsorbed substance in the surrounding media. Modifing the aqueous ionic composition alone may be sufficient for desorption of nonspecific physisorbed species [31]. In certain cases, another substance with greater affinity for the surface sites of the adsorbent may interact with the surface and promote desorption of the originally adsorbed substances, followed by adsorption of the new substance. Moreover, the particle itself may undergo deposition (different from sedimentation) onto a collector and experience immobilization when attached to the external surface [1]. Desorption processes will strongly affect the coatings of the PM-ENM, especially if only weakly bound to the surface.

Combustion (process 6) is the process of reactions with air at an elevated temperature and generally implies oxidation of the elemental components of the ENM or even phase transformation

[43]. If the former occurs, then it is a special case of oxidation (process 2) facilitated by heat. This process will occur mainly when products containing PM-ENM are incinerated, an exception being cerium oxide in fuels. The presence of other oxidized constituents such as byproducts of the combustion processes may lead to adsorption of foreign substances to the PW-ENM.

Biotransformation or biodegradation (process 7) may induce transformation of the ENM [44] or their alteration products [45]. Biologically mediated transformation may include all of the previously described processes, with the exception of combustion. The rates and relative importance of each process is a result of conditions in the biological compartments, such as processes after ingestion by multicellular animals [46] or enzymatic reactions mediated by microorganisms [47]. One of the physical processes that will influence the final destination of the PM-ENM is abrasion (process 8) or mechanical erosion. Abrasion is the process by which physical forces, such as turbulent fluid regimes or strong collision of solid materials, induce the breakdown of the original material and may lead to the release of PW-ENM- or PW-ENM-containing particles in different shapes and sizes [48–52]. Shear stress estimations may indicate the final shape and size of the PW-ENM after undergoing abrasion processes. Processes such as oxidation may be facilitated by the mechanical energy introduced by abrasion.

RELEASE AND ALTERATION OF ENM

The scientific consensus is that producing, using, and disposing of ENMs leads to environmental releases of nanoparticles [5,53,54]. However, very little actual data from real-world conditions are available on the emissions of PW-ENM from products and releases into the environment. This is caused primarily by a lack of techniques and instrumentation capable of detecting and quantifying both ENM emissions and the resultant environmental concentrations.

Initial measurements show evidence for the release of PM-ENM and PW-ENM from consumer products. Kaegi et al. [51] presented direct evidence of the environmental release of nano-TiO_2 by leaching from painted house facades under the influence of sun and rain. The same authors recently showed evidence that Ag is released from nano-Ag-containing paints [50]. Several studies have investigated release from consumer products during use. Examples include changes in Ag speciation in textiles [55] and release from textiles into water [56,57], washing liquid [13], sweat [58], and washing machines [59]. Also, different studies have been published on abrasion of particles from coatings [48,49,60] or textiles [61]. One major conclusion of all these studies is that the vast majority of the released particles are large agglomerates containing PM-ENM and PW-ENM, but also that single, dispersed PW-ENM can be found. As shown in Figure 3, with two examples of released particles, it is obvious that for both Ag released from paints and ZnO released from coatings, the released PW-ENM are still embedded in the matrix, so the environmental behavior of PW-ENM is still determined to a large extent by the properties of the matrix. This is, of course, however, product specific. In other cases PM-ENM and PW-ENM may not be bound strongly to the matrix.

A handful of modeling studies have tried to quantify PW-ENM release to the environment. Some studies evaluated release to the environment from a restricted set of PM-ENM-containing products during the consumption or use phase [62–65]. Other studies modeled release throughout the whole life cycle of PM-ENM-containing products, including ENM production and manufacturing of products, use, recycling, and disposal [66,67]. Sewage sludge, wastewater, and waste incineration of products containing PM-ENM were shown to be the major pathways through which PM-ENM enter the environment.

The original P-ENM incorporated into the products are modified during product manufacture and use and are altered and transformed after release by the environmental factors discussed above. An example of an alteration during use is the phase transformation of Ag nanoparticles caused by exposure to bleach under washing conditions [55]. After the PW-ENM reaches the environment, transformation processes can significantly change their behavior. Auffan et al. [17] and Labille et al. [68] have shown that the hydrophobic coating of a TiO_2-$Al(OH)_3$-polydimethylsiloxane nanomaterial (Fig. 2) used in sunscreen creams was desorbed and oxidized on contact with water, resulting in a stable aqueous suspension of TiO_2-$Al(OH)_3$ nanoparticles. However, because the $Al(OH)_3$ coating was not affected, the material was still not photoreactive and did not produce ROS compared with photocatalytic TiO_2.

Soluble ENM undergo dissolution reactions. For example, both thermodynamic calculations and kinetic measurements indicate that metallic Ag nanoparticles will not persist in realistic environmental compartments containing dissolved

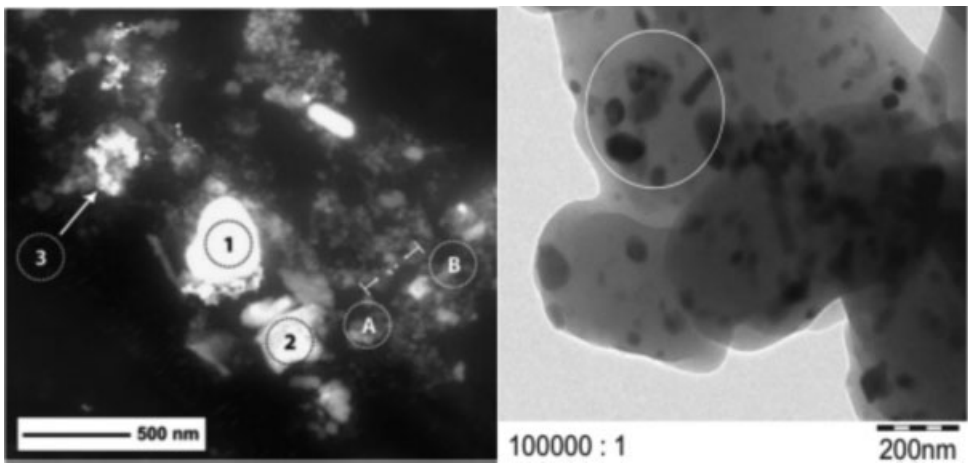

Fig. 3. Particles released from nano-Ag containing paint by natural weathering (**left**, the area labeled 3 contains the Ag nanoparticles, whereas areas 1 and 2 are TiO_2-containing particles) [50] and from a surface coating containing nano-ZnO by abrasion (**right**) [49]. Images reprinted from Kaegi et al. ([50]; ©2010) and Vorbau et al. ([49]; ©2009), respectively, with permission from Elsevier.

oxygen [21]. However, this oxidation process is slow under most environmental conditions and can require months to reach completion. Nano-Ag was recently shown to transform rapidly under anaerobic wastewater treatment conditions into insoluble silver sulfides [69]. Phenrat et al. [70] reported that partial or complete oxidation of nanometer-sized zero-valent iron under environmental conditions decreased its redox activity, agglomeration, sedimentation rate, and toxicity to mammalian cells. Also, biological modification of ENM and microbially mediated redox processes can change the fate and toxicity of ENM such as quantum dots and carbon nanotubes [25,46,71].

HYPOTHETICAL CASE STUDIES

To illustrate the major processes and pathways of ENM, we present five case studies involving hypothetical scenarios. The discussion is illustrated using figures that show the likely flow and transformation of PM-ENM, starting with the nanomaterial-containing product and ending with their distribution in environmental compartments as ET-ENM. In the first step, we illustrate the important processes and the relative rates that result in the release of the PM-ENM from the product and how they alter the form of the released PW-ENM. The released PW-ENM, and possibly the original nanomaterial-containing product, can then undergo a treatment process or can pass directly into an environmental compartment. The three most important treatment processes are waste incineration, wastewater treatment, and landfill disposal. These important chemical processes act on all ENM classes and are identified by our numbering scheme.

Case study 1: NanoTiO$_2$ in sunscreen

This case study focuses on TiO_2, an inorganic, insoluble ENM present in a dispersed form in the product [18,29]. In the dispersed form, PM-ENM can be released readily from the product through normal use and disposal. Because sunscreens are consumed during use and are lost during swimming or washed off during bathing, almost all of the original product is released either into wastewater or directly into rivers [72]. This is different from the other four case studies, in which direct release of the product does not readily occur; rather, release results from accidental spills or less likely pathways (see the discussion below for CeO_2). Figure 4a illustrates the major reactions involved in TiO_2 alteration and release and transformation. In all figures, the initial set of reactions is acting on both the PM-ENM and the matrix in which it is dispersed. Subsequent reactions are considered to be acting on the released PW-ENM. The processes that alter and transform TiO_2 are photochemistry and adsorption or desorption of coatings [17]. Incineration involving high-temperature combustion of TiO_2-containing products can result in chemical and physical sintering of the TiO_2. Within a wastewater treatment plant (WWTP), the important processes that affect TiO_2 are dissolution and precipitation, adsorption and desorption, and biotransformation

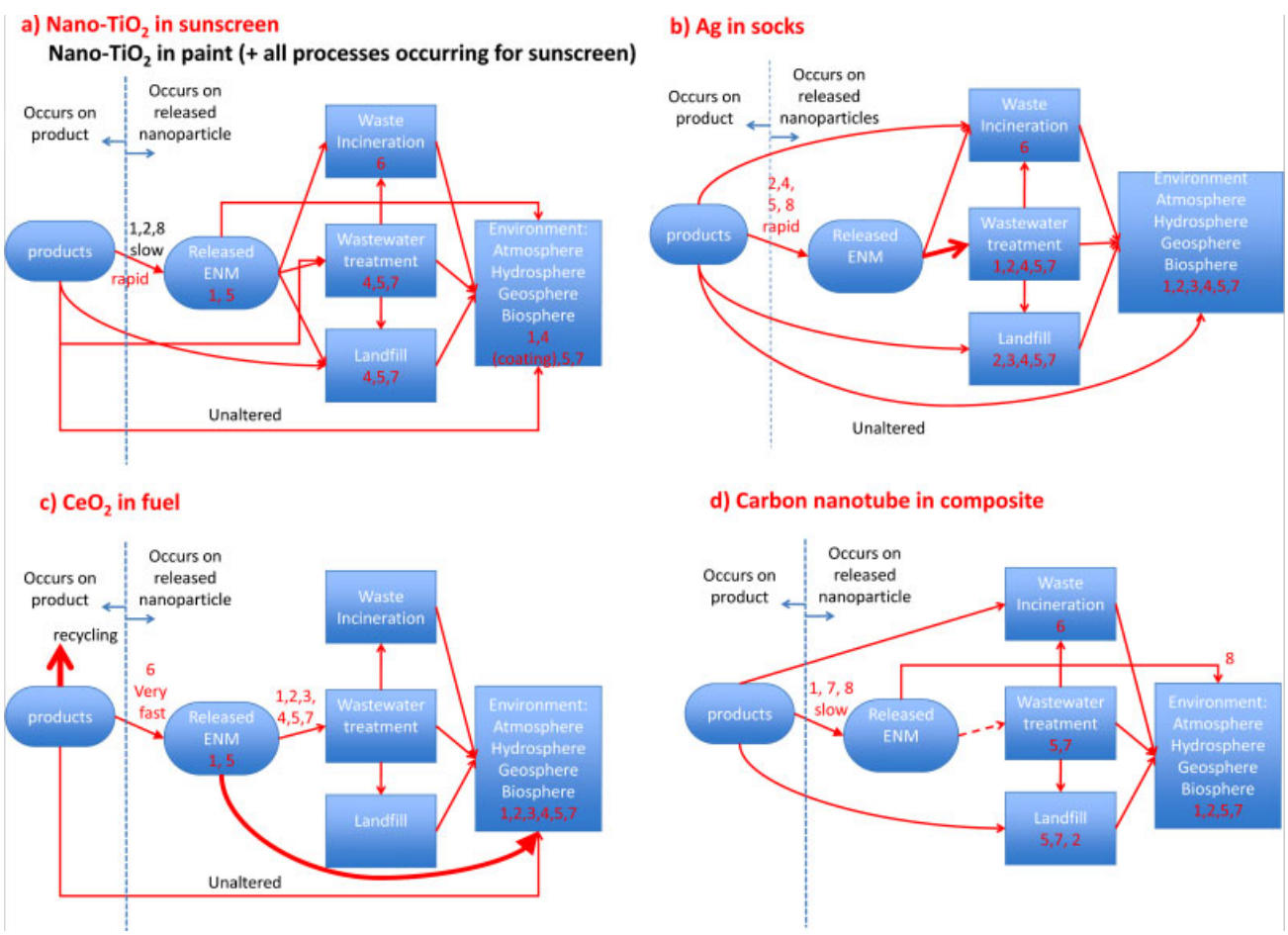

Fig. 4. (**a–d**) Material flow diagrams showing the release of engineered nanomaterials (ENM) from different products and the transformation reactions during transfer from one environmental compartment to another: TiO_2 release from sunscreen and paint, Ag release from textiles, CeO_2 release from fuels and carbon nanotubes release from composites. The numbers refer to the processes identified in the text. [Color figure can be seen in the online version of this article, available at wileyonlinelibrary.com]

[73]. With respect to dissolution, although the TiO_2 is considered insoluble [74], the PM-ENM may contain other components that are soluble. For example, T-Lite SF (a UV filter used in sunscreens) consists of a TiO_2 core, a layer of Al oxide, and a coating of polydimethylsiloxane (see Fig. 2). It has been shown that the outer layers are susceptible to degradation and desorption reactions [17,68], leading to marked changes in PW-ENM properties, such as water dispersability, making a hydrophobic material water dispersable. The same processes are expected to occur in landfills, although the rates and relative importance of the three types of reactions are likely to be different from those in a WWTP. In assigning adsorption and desorption as being important, we have not differentiated between desorption of the initial coating materials on the PM-ENM and the formation of new surface coatings of environmental surfactants, such as NOM or biomolecules on the PW-ENM and ET-ENM. For the environmental compartment, we have identified photochemical transformation of the surface as an additional process, because of the known photoreactivity of TiO_2 [18].

Case study 2: Nano-TiO_2 in paint

Our second case study also examines TiO_2, but in this case the form is that of an ENM contained within a solid matrix (Fig. 4a). In this form, PW-ENM release is likely to be a much slower process than the release from sunscreen, because the TiO_2 first must be released from a solid matrix that is intended to hold it tightly. Although it is possible that improper use and disposal of TiO_2-containing paint could lead to environmental releases, it is more likely that release will occur from painted surfaces through abrasion and photochemical and oxidation reactions that act on the paint matrix. However, direct release into water during paintbrush washing also must be considered [62]. Environmental variables such as temperature, humidity, sunlight, wind, and rain will be controlling factors [51]. The slower release rate will result in an additional alteration of the PW-ENM prior to transport because it is under the influence of weathering for a longer period. The chemical reactions leading to the transformations, fate, and effects of TiO_2 in the treatment systems (if storm water runoff is not collected separately and discharged to water bodies without treatment) and the environment are the same as for our previous case study, but they will be influenced by the type of TiO_2 that is used (photoreactive or photostable).

Case study 3: Nano-Ag in textiles

In our third case study, we examine nano-Ag in textiles. Surface-functionalized nano-Ag materials are currently used in many consumer products as an odor-destroying, infection-fighting additive, including use in slippers, socks, underwear, and shoe liners [27]. The potential exists for nano-Ag to be released from textile products into the aquatic environment. Recent studies have shown that nano-Ag is released in significant quantities into distilled water [56,57] or washing liquid [13] by laundering textiles. According to modeled environmental concentrations, nano-Ag transported to WWTPs by release from textiles will be primarily incorporated into biosolids [67,75], but when treatment of wastewater is inadequate, the potential exists for the release of nano-Ag into receiving waters at concentrations that may pose a hazard to aquatic organisms [75]. Therefore, releases into the environment are also likely to occur in agricultural fields as a result of the use of biosolids for soil amendment and in receiving waters downstream of discharges of municipal wastewater (Fig. 4b).

However, recent studies that have assessed the fate of nano-Ag under conditions typical for washing of textiles (agitation, detergents, bleaching) have shown that nano-Ag undergoes considerable alteration. Dissolution of nano-Ag to dissolved Ag^+ is now widely recognized as a significant fate process in natural waters [76]. However, Impellitteri et al. [55] reported that >50% of the nano-Ag released from socks during washing with detergents was converted to AgCl, which is relatively insoluble in water. Geranio et al. [13] observed that little dissolution of Ag occurred under the high-pH conditions typical of textile washing and that most of the nano-Ag was released in a particle size fraction >450 nm as a result of mechanical stress from the washing action. Once released into the aquatic environment, the transformation and toxicity of nano-Ag or dissolved species appear to be tightly linked to physicochemical parameters, including the concentrations and types of dissolved organic matter, pH and ionic strength, redox environment, and presence of inorganic ligands [2,77]. Thus, as illustrated in Figure 4, the primary fate processes that affect the distribution of nano-Ag from textiles in the environment are abrasion (process 8), oxidation (process 2), dissolution and precipitation (process 4), adsorption and desorption (process 5), and microbial transformation (process 7), processes that can take place during the release from washed fabrics, in the WWTP during treatment, and in the receiving environment (agricultural soils, surface waters). However, biosolids containing nano-Ag may also be deposited into landfills, so dissolution, partitioning, and transformation processes may govern environmental fate under this scenario. Finally, biosolids may be incinerated, resulting in emissions into the atmosphere that are controlled by combustion processes (process 6).

Case study 4: Nano-CeO_2 in fuel

This case involves the most rapid release and alteration processes among the various scenarios. First, the CeO_2 is completely dispersed in the fuel and is exposed to high temperatures just prior to its release into the environment [63]. Because most of the CeO_2 is captured by diesel filters or the catalytic converter [78], its pathway to the landfill and to recycling is more important than for the other ENM [63] (Fig. 4c). Little is known about the materials that flow through recycling and how much of this recycled material will carry CeO_2 back into the environment. Even if the nano-CeO_2 is used mainly catalytically to promote soot oxidation and degradation, no data exist on the possible Ce reduction (Ce^{4+} to Ce^{3+}) during or after the combustion process.

Case study 5: Carbon nanotubes in composites

The final case study explores multiwalled and single-walled nanotubes, hereafter referred to as CNT, which are embedded in a composite material. Carbon nanotube composite materials are used in a variety of consumer products, including tennis rackets, bicycle frames, and automobile bumpers [53,54]. The intended use and disposal of these consumer products often expose them to a variety of environmental conditions that will affect the alteration of the composite material as well as the transformation of the CNT after it is released from the composite. Figure 4d illustrates the processes and reactions involved in altering the composite material and transforming the released CNT.

The release of CNT from these products may occur over a much longer time period than our other examples of ENM products. The use of CNT in composite matrices creates a much more durable product that can withstand physical and chemical

processes [79], so this material will probably be altered at a slow rate. However, degradation processes of these materials have not been fully investigated, so altering the composite material and releasing CNT are difficult to evaluate [53]. First results indicate that CNT can be released on photochemical degradation (process 1) of CNT-containing composites [80,81]. The PM-ENM composite material will be subjected to UVA/B radiation and abrasive forces while in use that will weaken molecular bonds and release CNT over an extended period. These released CNT (PW-ENM) would make their way into waste water treatment plants or be directly deposited into environmental compartments where they would undergo transformation by photochemistry (process 1) [81], oxidation (process 2), adsorption of NOM [33] and other organic colloids [34], biotransformation (process 7), and continued abrasive forces (process 8). These transformative processes would change CNT aggregation, dispersability, and interaction with biota in the environmental compartment.

Measurements carried out at factories producing ENM indicate that worker exposure is possible, such as during the production and handling of dry powders [82–86]. However, the extent to which such worker exposure leads to ENM release to the environment is currently unknown. There is no doubt that once the ENM are released (for example, to indoor air), they are likely to enter the environment eventually.

The disposal methods illustrated in Figure 4 (incineration, WWTPs, and landfill disposal) would apply to both the CNT composite and the released CNT. Incinerating CNT composites subjects them to high temperatures that result in the airborne release of CNT. In the case of CNT, theoretically all particles should be burned and mineralized during incineration, because the temperature (about 850°C) is higher than the ignition temperature of CNT (about 600°C), and the waste is incinerated in the presence of oxygen. Disposal of CNT composites in landfills could lead to degradation or transformation of the polymers, resulting in the release of CNT.

CURRENT KNOWLEDGE GAPS

As shown in the case studies summarized above, some knowledge is available on the forms and identity of the PW-ENM that are actually released. However, the studies so far have looked at only a very small set of possible products and release scenarios (for example, textiles, outdoor paints, abrasion of coatings). The released particles were often characterized only to a limited extent, such as by transmission electron microscopy or by using a simple size fractionation. Knowledge of the size, composition, and surface characteristics of the PW-ENM and ET-ENM is therefore extremely scarce. The analytical methods to identify and especially to characterize and quantify ENM at micrograms per liter or lower concentrations in natural systems are not yet available, with the possible exception of fullerenes [87,88]. However, characterizing PW-ENM coming out of products could be addressed by using existing techniques, as described in the accompanying review on analysis of ENM [89]. Many efforts are underway to apply these techniques to ENM in environmental and biological media [90].

Almost nothing is known about the environmental transformation, behavior, and effects of PW-ENM and ET-ENM, although these are the materials actually released into the environment. This may also be a reflection of the scarce knowledge on the identity of PM-ENM used by industry and incorporated into products. Indeed, no regulation currently exists that requires manufacturers to describe and identify the types of nanoparticles used in commercial products. Research on the fate and effects of ENM has been done almost exclusively on pristine material, which is easily available from vendors or from material scientists and chemists, rather than focusing on the PM-ENM that are incorporated into manufactured material. Research must address the issue of whether the behavior and especially the effects of ENM incorporated into larger fragments of a matrix differ relative to the free ENM. Further research also must show whether the alteration and transformation processes result in a similar or more diverse set of ENM. For example, does coating of the surface by NOM override the initial coating of the material, and, thus, do ENM with different coatings behave similarly after being altered and transformed in the environment?

IMPLICATIONS

Effects assessment

The sources and fate of ENM in the environment will influence the choice of tests that are appropriate for assessing the effects of the material. For example, the case study presented above for nano-TiO_2 released into the environment as a result of sunscreens shows that an important fate process is the deposition into biosolids in WWTPs. In several parts of Europe and North America, biosolids are used widely for soil amendment to agricultural lands; therefore, nano-TiO_2 is likely to be applied to agricultural soils, where the potential exists for effects on soil organisms, including invertebrate species and micro-organisms. Thus, testing protocols are required to assess the impacts of ENM on soil organisms and communities, including the effects on nutrient cycling mediated by micro-organisms [91]. These protocols should include methods to evaluate the role of toxic responses resulting from the photoactivation of ENM. On the other hand, in some countries, such as Switzerland, incineration is the primary method of disposal for biosolids, and in this case protocols would be needed to assess the potential impacts of nano-TiO_2 released into the air and its subsequent return to the land surface via dry and wet deposition. Erosion and surface runoff may also lead to the transport of soil-bound TiO_2 to natural waters and sediments.

The transformations of ENM over short to long temporal scales introduce major challenges for assessing biological effects. As described earlier, many ENM undergo rapid transformations when released into the environment that may profoundly affect toxicity. For instance, nano-Ag may release toxic Ag^+ over time periods of hours to days, and these cations may undergo further transformation to insoluble or soluble Ag salts, with the redox conditions dictating the dominant transformation process. Similarly, alteration of nano-TiO_2 applied in paints to exterior facades may affect the structure of the material over longer temporal scales. Present methods for assessing the biological effects of ENM do not include protocols that take into account the influence of these transformations on toxicity.

Finally, effects assessment protocols should try to mimic the natural environment as much as possible to reflect the fate processes that are likely to predominate when ENM are released into the atmosphere, geosphere, or hydrosphere. For example, high hardness in water is likely to promote precipitation of ENM into sediments, whereas high NOM conditions in water will promote dispersion of ENM in the water column. Therefore, protocols must be developed that clearly define the conditions of the test medium and account for the types of exposures that could occur under a variety of exposure scenarios.

Table 1. Advantages and disadvantages of the use of pristine versus altered engineered nanomaterials (ENM) for environmental risk assessment of ENM

Pristine (standard) material	Industrially modified or environmentally altered material
Nonrealistic exposure	Environmentally relevant exposure
Good to obtain mechanistic effects and identification of the active fraction of the final altered material	Final exposure a distribution of different ENM depending on the extent to which the pristine nanoparticle was modified or environmental alteration took place
Material easy to obtain	Modified materials difficult to separate from matrix compounds and obtain in pure form
High exposure concentrations of pure material possible	Low exposure concentrations, the ENM often making up only a small portion of the released material
Environmentally altered or transformed products not considered	Alteration and transformation products may be more or less toxic than parent material

In addition, effects tests that are conducted in artificial media, such as algal growth media, might not accurately reflect the exposure scenarios that will be observed in the natural environment (see Handy et al. [89] in this issue).

Exposure assessment

As discussed, ENM are subject to a range of fate processes that can influence their distribution within the hydrosphere, geosphere, and atmosphere. To assess exposure, analytical methods will be required to detect ENM in a range of environmental media, in some cases including complex matrices, such as biosolids and biological tissues (see Unrine et al. [92] in this issue). In cases in which ENM are composed of elements that are relatively rare within environmental matrices (such as Ag, Ce, and Se), developing analytical methods will be less problematic. In cases in which the ENM are composed of common elements (such as Ti, Si, Al, and C), however, it will be more difficult to develop analytical methods capable of detecting the low concentrations of these materials in nanoform relative to background levels. In addition, analytical methods are required to evaluate the levels of transformation products present in environmental matrices. In some cases, these analytical techniques are already available using methods and instrumentation available for studies of metal speciation (for example, analysis of Ag_2S by electrochemical techniques), but, in other cases, novel analytical methods will have to be developed (for example, analysis of hydroxylated transformation products of CNT).

Finally, methods are required to analyze ENM in biological tissues to assess potential bioaccumulation or biomagnification. As discussed above, technical challenges are associated with many of the currently available analytical techniques, but some recent developments, such as microscopy of tissues or of whole organisms using Raman spectroscopic techniques or X-ray microspectroscopy, show potential for quantifying the degree of bioaccumulation of ENM. The fate of ENM may also provide some clues of the dominant bioaccumulation pathways in the environment. For example, deposition of ENM to sediments in aquatic environments may result in high exposures of benthic invertebrates, including deposit and filter feeders, such as bivalves [93]. Conversely, in the case of ENM applied to soils in biosolids, soil invertebrates, such as earthworms, may be subject to the highest degree of exposure. Micro-organisms in soils and sediments may also be vulnerable to effects from exposure to ENM [94]. Therefore, the fate and transformation processes will provide information on organisms appropriate for evaluating the potential for bioaccumulation.

Risk assessment

The fate and transformation processes that affect ENM introduce many uncertainties into ecological risk assessments (Table 1). One of the key issues facing regulators and industry will be whether the risk assessment should target the specific formulation of the PM-ENM and not just the pristine material. The fate of a PM-ENM, including the transformations and the partitioning into environmental compartments, may vary with the matrix the manufacturer uses to protect or modify its surface properties. For example, polymer coatings such as polyvinylpyrrolidone may be more stable than coatings prepared from biomolecules such as citrate, leading to differences in the temporal scales for ENM alteration. Impurities or artifacts introduced during the manufacturing process may also influence the fate of the ENM or may enhance toxicity. This situation is analogous to risk assessments for pesticides, which currently target only the active ingredient and not the commercial formulation. In the case of PM-ENM, it is critical that the commercial product the manufacturer develops be subject to an ecological risk assessment. It is necessary to incorporate material testing protocols that simulate processes such as abrasion and alteration processes into tests to predict the fate of PW-ENM. It is not clear whether separate risk assessments are required for different ENM that differ only in particle size. This should be an area for further study that will be critical for developing appropriate risk assessment procedures. However, these issues are not restricted to ENM because many chemicals undergo modification and alteration reactions during incorporation into products or release from them (for example, release of metals in dissolved or particulate form). The proper balance between adding detail and simplifying fate processes depends on the question to be answered.

Finally, it may be necessary to develop ecological risk assessment procedures that take into account formation of ET-ENM over the short to long term. This is analogous to assessments for nonylphenol ethoxylate surfactants, which were judged to pose only a low-level hazard to the environment, but are now known to be microbially transformed under aerobic conditions into the estrogenic compound nonylphenol. It is entirely possible that some ET-ENM pose a greater risk to the environment than the original manufactured material, or vice versa, similar to the case of some conventional chemicals, for which also the degradation products may be more harmful than the parent compounds. Therefore, it is advisable to develop risk assessment protocols that will protect the public and the environment from this eventuality.

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