



## DELIVERABLE REPORT

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## Scope of the NanoMILE report on environmental transformation reactions

The NanoMILE project aims to establish a fundamental understanding of the mechanisms of manufactured nanomaterial (MNM) interactions with living systems and the environment and a wide range of target species, across the entire life cycle of MNMs. NanoMILE defines life cycle to mean the production / processing, use and disposal of MNMs, which has more recently begun to be referred to as “value chain”. A further purpose is to establish an understanding of changes in the nature of MNMs as they undergo transformations within products and biological or environmental compartments across their life cycle and, critically, to feed this information into subsequent research within the NanoMILE project to ensure that these “aged” and transformed MNMs are tested for their biological/environmental role. A major direct aim for WP3 of NanoMILE is to investigate and quantify the alteration and transformation of MNMs in products during their use and release into the environment or biota. Exposure to MNMs in occupational, consumer or environmental settings may either be to the original, parent MNMs, or to MNMs that have been incorporated into products and then subsequently released, either in their original form or in an altered form due to industrial or natural processes. To date, few studies have tried to establish what changes the MNMs undergo when they are incorporated into, and released from, products. As a result there is major uncertainty as to the state of many MNMs following their release and much of current testing which is on pristine MNMs may not be fully relevant for risk assessment purposes.

In WP3 relevant MNMs selected from the libraries of WP2 will be exposed to different processes and biophysicochemical conditions, in order to characterize the changes that occur to the MNMs. This work will further deliver altered MNMs for testing studies or provide detailed protocols on how to induce these alterations, to the other WPs addressing impacts of the MNMs.

In this report, key environmental alteration and transformation processes that affect MNMs during the different life cycle stages are reviewed. The focus is on processes that act within the product, during their release and on the released particles in various environmental compartments including wastewater treatment works, freshwaters and sediments. Fate processes that can act on MNMs in products, and after their release, will also be considered. These include photochemical transformations, oxidation and reduction, dissolution, precipitation, adsorption and desorption (of natural organics to the nanomaterials and nanomaterials onto macroscopic surfaces), combustion, biotransformation, and abrasion among other biogeochemically-relevant processes. Knowledge on this subject is very limited and papers addressing it are only now starting to be published. This literature review will strongly inform subsequent experimental approaches and experimental design within the WPs. The information derived from this review will be used in task 3.2 to identify the transformation processes that will be studied for the particle types that are being provided under WP2. The selection of MNM for aging studies will then be made in MS5 “Selection of MNMs for ageing studies with reference to needs of WPs 5-8”. Key information will additionally be transferred to WP5, which is concerned with understanding the time-resolved behavior of the MNMs in representative exposure media, to facilitate interpretation of impacts of dissolved ions and other media components on MNMs surface properties and physico-chemical behavior and binding of biomolecules.



# Using a life cycle approach to understand MNM aging and transformations during use of nano-enhanced products

## 1. Introduction: Assessing the Life Cycle Approach

The rapid advancement of nanotechnology has enormous potential for the development of new products and applications in a number of industrial and commercial sectors. Manufactured nanomaterials (MNM) may provide economical savings because less raw materials are used, functionality is increased and there may be reduced environmental pollution compared with traditional industries<sup>1, 2</sup>. However, there are concerns related to the increased use of MNMs including, 1) that applications can lead to human and environmental exposures, 2) that their new properties and high mobility may have unknown longevity and consequences in environmental and human health and 3) that there is little obligation under current legislation for manufacturers to label products as having nano-components or to assess the ecotoxicological aspects (except for materials produced in quantities > 100 tonnes, which is not the case for any MNM as of yet)<sup>3</sup>.

Coupled with the fact that the myriad of particle types and applications can lead to different physico-chemical changes over time<sup>4</sup>, this highlights major knowledge gaps in regard to the potential health and environmental effects posed by MNM<sup>5-7</sup>. In the context of assessing these potential risks, a life cycle approach (covering production, use and disposal of a chemical or product) can represent a more holistic view on the impacts of MNMs<sup>8</sup>. Some considerations of the suitability of life cycle assessment (LCA) approaches for various MNMs have been developed<sup>9-11</sup> with specific LCA analysis assessing MNM impacts either from cradle-to-gate<sup>12-14</sup> or from cradle-to-grave<sup>15-18</sup>. Many nanotechnologies are considered as an enabling technology and a single MNM type may have multiple different applications (e.g. nanosilver is used as medical coating but also in consumer products, washing machines etc.<sup>19</sup>), making one direct scenario from product use to environmental exposure impossible. Considering that life cycles of many MNMs are determined by their application within products it becomes clear that relevant exposure scenarios and particle aging/transformations of the MNMs are strongly dependent on the life cycle of the nano-enhanced products themselves.

To date, research concerning the general theme of MNM release and transformation has fallen into one of four categories: 1) transformation of an individual, specific MNM in the laboratory, 2) experimentation concerning MNM release during a given process (e.g. laundering fabrics), 3) MNM transformation in a single environment (e.g. water treatment plants), or 4) models attempting to encompass the entire life cycle from information derived through categories 1 – 3 (i.e. cradle to grave). For the latter, it is necessary to distinguish release from MNM production, MNM incorporation into products, product use, recycling and/or disposal of nano-products. Factors such as MNM production and application are important to frame the potential breadth of exposure. MNM emission models, coupled with analytical laboratory studies, can point to more specific release scenario(s) for a given MNM/product pair. While in theory these case studies should be verified in “real world” systems, in practice there are relatively few examples of pilot scale or full-scale environmental MNM releases. Indeed such efforts are hampered by the enormous difficulties of detecting MNMs in complex environmental scenarios due to strong background scattering, and of distinguishing between manufactured and ambient nanoparticles in many cases (e.g. silica, titania, carbon-based, nanoclays etc.).

Mathematical modeling has aided in the assessment of the potential fate of many common MNMs (e.g. Ag, TiO<sub>2</sub>, ZnO, CNT, etc.). Mass balance, multi-compartment models have provided increasingly comprehensive analysis to identify the key parameters of environmental release and exposure<sup>20</sup>. This life cycle approach to material flow modeling has been adopted by several groups, who propose probable release concentrations of MNMs on either regional<sup>21-23</sup> or global<sup>24</sup> scales. Production rates of MNMs have been estimated by both academic<sup>25-27</sup> and industry/market sources<sup>28, 29</sup>. However, the models that exist have several aspects of uncertainties deriving from lack of well-defined data on production volumes to physico-chemical changes in the MNM that influence fate. The most dominant parameters of the materials flow modeling approach – associated with the highest uncertainties – are the assessment of the mass of MNMs that are produced, and of the amounts that may be released during the manufacturing processes or directly from nano-products. Therefore, quantitative data on MNM emissions, both in

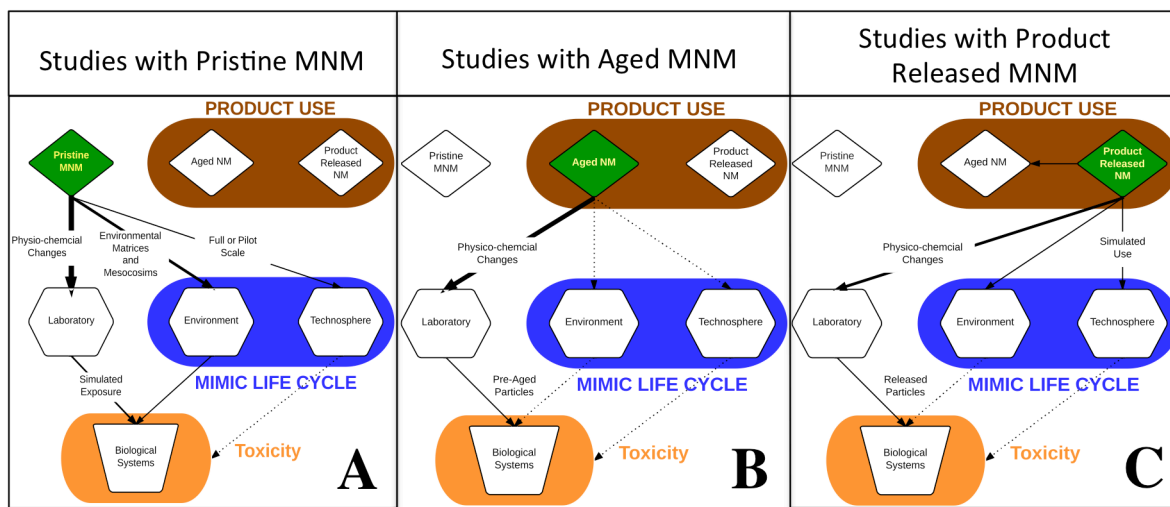


terms of total mass and relative rate, during various stages of the life cycle (manufacturing, production, use, disposal) are urgently needed. Likewise, understanding how particles age and transform would allow more precise determination of the final states and fate of MNM.

One reason why quantitative data are difficult to obtain, or that even qualitative data is difficult to estimate, is because manufacturers do not necessarily report details or quantities of specific MNMs used in products. MNM classes (such as silver, titanium dioxide, etc.) are not uniform categories of substances but rather have multi-faceted properties that can dynamically change the materials' characteristics including size, purity, crystalline form, porosity and functionality. Indeed, many of the physico-chemical properties are in fact distributions even within a single batch of a MNM, such that each individual MNM may well be unique, while current measurement techniques, particularly those in routine use, can only provide an average description (e.g. mean size and size distribution are commonly used, but other characteristics such as surface charge, porosity etc. are also distributions and not homogeneous across all particles). Additionally, MNM functionality can be modified continually, confounding prediction of how, when, and what form particles will be in when released from a given product. While the manufacturing and production portions of the product life cycle will likely be in a controlled, industrial setting, the use and disposal of nano-products in the consumer realm is decidedly less predictable and includes more variables. Experimental, laboratory release studies provide direct information aiming to measure releases of specific MNMs from various products. MNM release from textiles<sup>30-32</sup>, paints and facades<sup>33-35</sup>, sunscreens and personal care products<sup>36, 37</sup>, polymers<sup>38</sup>, food packaging<sup>35</sup> and foodstuffs<sup>39</sup> and a multitude of other products<sup>40</sup> have all been investigated. As much of MNM are destined to, at one time, flow through wastewater treatment facilities after nano-product use, the release of MNMs from these plants has also been explored<sup>41-44</sup>.

To date, the predominant focus of environmental health and safety research on MNM has lain in assessing the fate, transport and toxic properties of the pristine (i.e. as manufactured) materials, although it is increasingly understood that significant transformations occur even in the exposure media (e.g. cell culture media or OECD waters or soils) as a result of interactions with media components including salts, proteins or other available ionic species or macromolecules<sup>45, 46</sup>. Because environmental systems are dynamic and the surfaces of MNMs are highly reactive, physiochemical changes to engineered or incidental coatings and subsequent reactions in the environment will greatly complicate how the particle(s) behave. Additionally, when a nano-enhanced product is used, aging and transformations of the MNMs is likely to occur and after these materials are released from a product, it is unlikely that they will behave the same as pristine particles in the environment. Furthermore, the same particle may have different transformation by-products depending on its intended use or purpose. For example, after textile washing, Ag MNMs may alter in the tap water, in the wash water, or in the waste water treatment plant transforming the pristine particle into Ag<sup>+</sup><sup>47</sup>, AgCl<sup>48</sup>, or Ag<sub>2</sub>S<sup>49</sup>, respectively, or resulting in re-precipitation of "new" Ag nanoparticles (NPs) which may have different composition and interactions than the parent ones<sup>50, 51</sup>. Determining the transformation of MNMs is key to understanding their final fate.

This highlights the fact that, since MNMs will readily be aged/transformed during a product's life cycle, it would be prudent to also consider how these by-products differ from pristine MNMs in terms of health and safety, in addition to fate and transport. The current experimental regime in testing MNM transformations in the laboratory, technosphere (e.g. waste water treatment, waste incineration, recycling systems), biosphere, and environment is reviewed in Figure 1. Most experimental schemes focus on the use of pristine MNMs (Figure 1 A) in a variety of conditions by directly studying MNMs in a laboratory setting (thick black arrows), which can be considered mechanistic studies. Alternatively, aged particles (i.e. those that are stored or otherwise transformed by chemical or physical factors so that they no longer have the same characteristics of their pristine counterparts) or product released (i.e. particles released during product use) could provide a more realistic basis for studying MNMs in the environment. Less research has been focused on mimicking the product life cycle to understand how aged or product released particles (Figure 1 B and C) will behave in the environment or the technosphere. This is in part due to the increased analytical challenges associated with increasingly complex systems. These difficulties in analysis also lead to fewer studies that use biologically or environmentally relevant concentrations of MNMs. To date, very few publications have focused on how aged or product released MNMs will affect biological systems. Researchers need to move towards increasingly complex models of release and transformation, thereby more closely mimicking real-world conditions and thus allowing more critical (and appropriate) data to be used for modeling and/or risk assessment studies.



**Figure 1:** Current experimental regimes in testing of MNM transformations in the technosphere, biosphere, and environment. Note that most experimental schemes use pristine MNMs in a variety of exposure conditions or test MNMs in controlled laboratory experiments (panel A). Fewer attempt to characterize aged particles (panel B) or those used in products (panel C) which would give a more holistic understanding of the transformations of MNMs during product use and through the life cycle.

Understanding these transformations of pristine MNMs is essential to correctly extrapolate the fate of particles during the use and disposal phases of a nano-product's life cycle. By better understanding probable endpoints of aged materials, MNM fate can be better incorporated into the general structure of materials flow modeling and risk assessment. The interplay between particle composition, size, structure, surface modifications, surface chemistry, incorporation into the product (matrix), and use or disposal route of the product may all affect the extent and type of transformations possible. There have been several reviews in recent years concerning the release and environmental transformation of MNMs. Using hypothetical test cases, Nowack et. al examined the likely fate of a wide range of MNMs released from products<sup>4</sup>. There, the authors concluded that it is not possible to assess the environmental risks by only studying the pristine material and that alteration and transformation processes need to be considered when determining fate. Lowry et al. outlined numerous environmental transformation processes and presented the idea that while the effects measured for pristine MNMs may be representative of exposures occurring at manufacturing or processing sites, environmental exposures will consist solely of transformed MNMs and so data related to pristine MNMs may not be predictive of real-world scenarios<sup>52</sup>. Airborne nanomaterial exposure, focusing on the workplace, was reviewed by Kuhlbusch et al.<sup>53</sup>. Their underlying conclusion was that the amount of MNMs released correlated with the material itself in addition to the physical/mechanical aging process used. For example, the release of individual MNMs from the product line-up was rare, agglomerated nano-objects (>300 nm) were regularly released during handling of dry nano-powders, but processes involving high energy input (e.g. sanding, drilling) did not release MNMs from the matrix of coatings and composites. In these cases, MNMs were released while still associated with the matrix or the physical process of sanding, etc. itself created nano-sized particles of the material. Other MNM release and transformation reviews were material specific, such as the case with Ag MNMs<sup>54, 55</sup> or carbon nanotubes (CNTs)<sup>56-58</sup>.

The goal of this present review is to derive the possible transformations common MNMs may undergo during the use, aging, or disposal of nano-products based on how these products will be used by the consumer. We determined a selection of some of the most important MNM categories (Ag, TiO<sub>2</sub>, ZnO, and CNT) and uses (textiles, personal care products, etc.) based on the comprehensive probabilistic materials flow modeling analysis of Sun et al.<sup>59</sup>, and the priority MNMs determined within NanoMILE WP2 (see for example D2.2 and MS2). Information was garnered either from peer-reviewed literature or by estimating likely scenarios when experimental work was not yet available. Other MNM categories that were not reviewed by Sun et al. yet feature prominently in some applications and are NanoMILE priority MNMs, such as CeO<sub>2</sub>, are discussed in relation to appropriate products. Specific applications of MNMs were investigated, and through understanding how the MNMs will be used, predicted likely release, aging, and transformations from the pristine material are described. This will prove useful



in narrowing the number of physical experiments that need to be conducted, by helping to determine specific gaps in knowledge of the MNM transformation process, where more focused effort can be placed.

### 1.1. Definition of terms – Release and transformation

The terms release, transformation and aging in the context of nanomaterials are not per se clearly defined and thus will shortly be defined in this section.

MNM releases could occur at any point during the manufacture, use or disposal of a nano-product. A release scenario, as defined by Nowack et al.<sup>57</sup>, is the operational and/or environmental conditions of any treatment or stress of a MNM or MNM composite material during all life-cycle phases that results in the release of MNMs/composite material into indoor (e.g. workplace, dwelling) and/or environmental (e.g. air, water, soil, sediment) compartments. Included in this definition is the set of parameters controlling the type, form and magnitude of MNM release. A MNM could either undergo a transformation process while still functioning within the nano-product, after its release, or both. In this review we describe both transformations occurring within the matrix and after release.

Transformation is considered a change/alteration to either: 1) the primary particle, 2) the coating of the MNM, or 3) the conformation of a particle community (e.g. agglomerate formation or (de)agglomeration). In many instances, a particle may experience multiple transformation processes in sequence (e.g. surface oxidation followed by dissolution). General examples of chemical transformations include a change to the particle surface, change in the oxidation state, or formation of a core-shell particle by surface transformations. Physical transformation may include either a change to the aggregation or agglomeration prevention (e.g. stabilizing with natural organic matter in natural waters) or de-agglomeration of particles (e.g. surfactants dispersing agglomerates). Here, we consider the delineation between transformation and aging to be the fact that an aging process is a transformation over time. Timing is important to the transformation process: MNMs may transform before they are released from the nano-product or after. Here, we review several possible MNM transformation processes that are prevalent and pertinent to understanding environmental fate of MNMs.

### 1.2. Description of Processes (Chemical, Physical and Biologically Mediated MNM Transformations)

Environmental and biological systems are dynamic and variable; many physico-chemical changes will impact MNMs, their (incidental) surface coatings, and reactions before and after release from consumer goods. Understanding the impact of these transformations may help forecast the benefits and/or risks associated with their use. Photochemical transformations, oxidation and reduction, dissolution, sulfidation, adsorption/desorption, agglomeration, biotransformation/biodegradation, re-precipitation, macromolecule interactions, or combustion are all possible, either to the MNM core or to the coatings, at some point during the MNM life cycle. These transformations greatly impact MNM behavior. In some cases they could enhance potential toxicity if occurring within an organism/cell (e.g. Ag MNM releasing  $\text{Ag}^+$  ions) or conversely may limit the MNMs' persistence in the environment (e.g. dissolution of ZnO MNMs releasing  $\text{Zn}^{2+}$  ions, which then disperse). In other cases the transformation can decrease reactivity (e.g. adsorption of NOM onto MNM surface), and in others transform the MNM into a less hazardous form (e.g. insoluble Zn-phosphate from soluble ZnO). Here, we briefly review several chemical, physical, and biologically mediated transformations with representative examples of how this may impact MNMs during the product life cycle, as summarized in Table 1 and Figure 2.

In relation to photo-chemical transformations, MNMs may be released or transformed from the product depending on incident light wavelength, the capacity of the light to penetrate the outer layers of the coating/product, and the photosensitivity or photo-degradation potential of the MNMs in question. Light may induce excitation of the MNM<sup>60, 61</sup>, generation of free radicals<sup>62</sup> and/or changes to the MNM surface (coating)<sup>36</sup>. The rate-determining step is the mass transfer of ions from the materials surface and/or matrix to the surrounding media. Several MNMs, including  $\text{TiO}_2$  and ZnO, are specifically used for their photo-catalytic ability. Because of

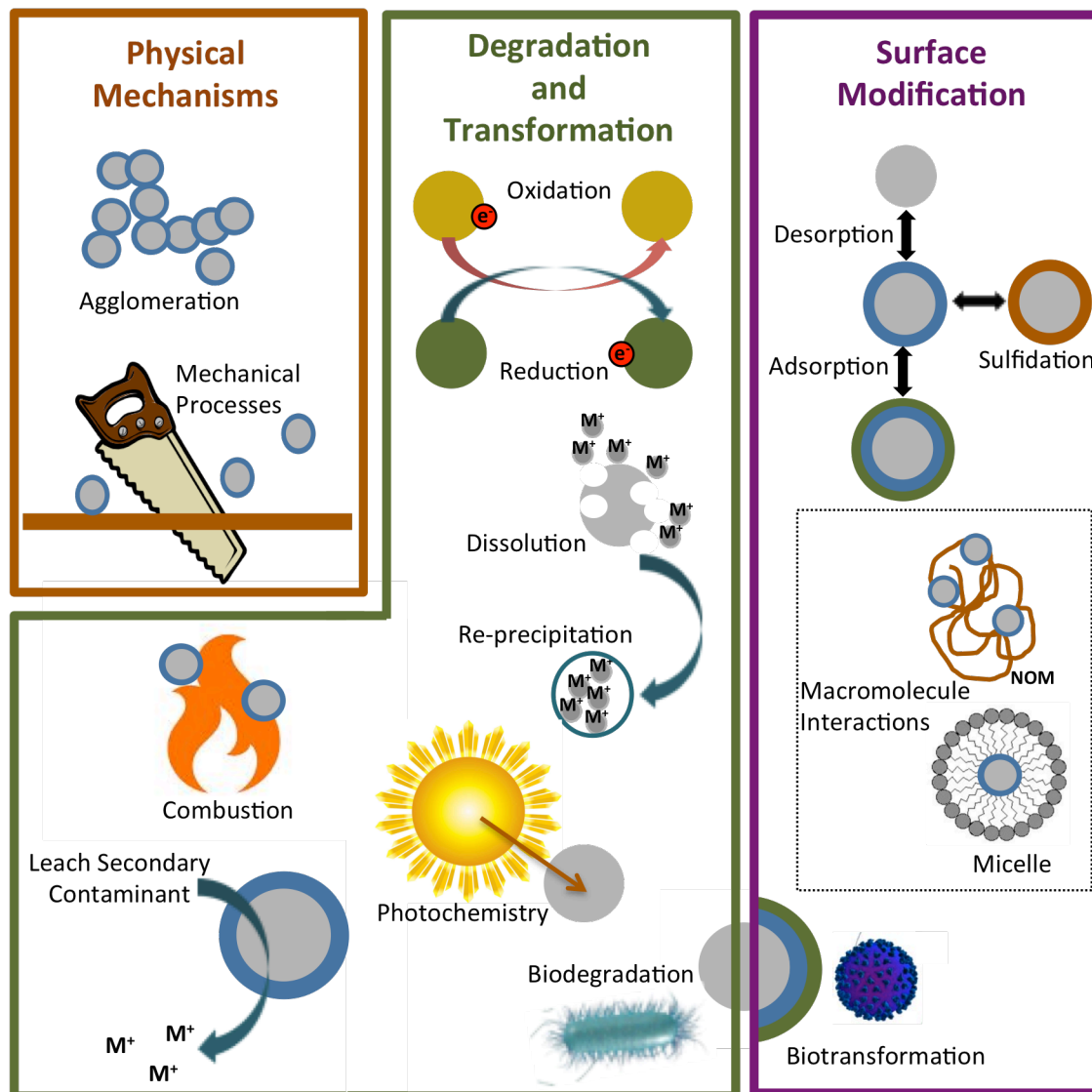




their transparency to visible light and UV absorbent qualities, these MNMs have been incorporated into a variety of commercial products from paints, to solar panels, to self-cleaning materials<sup>63</sup>. They have also been used in sunscreens for many years as a UV blocker and thus are prime examples of MNMs with potential for photo-chemical transformations.



Both oxidation and reduction are highly influenced by water chemistry and so release from nano-products may be dependent on how the product is used. Representative examples include the use of MNMs in textiles, where the material is exposed to high levels of oxidants (cleaning solutions), or in sunscreens where the MNMs may have contact with pool water containing disinfectants. In some cases, oxidation may form a relatively insoluble oxide



**Figure 2:** Key MNM transformations including degradation and chemical transformation, changes to the particle surface and physical mechanisms acting on the MNMs. Many transformations are not isolated events but rather interconnected steps in a series as an MNM ages.

surface coating on the MNM surface, which can hinder further oxidation. Alternatively, oxidation can be a prerequisite for dissolution, such as the case with Ag MNMs where the oxidation of Ag(0) to Ag(I) causes subsequent  $Ag^+$  release<sup>64</sup>. Concerning environmental systems, natural waters and aerated soils are primarily oxidizing zones whereas groundwater, wastewater and sediment could cause MNM reduction<sup>52</sup>. Cycling between different redox states could occur in more dynamic redox environments such as tidal zones or as water makes its way from a washing machine into a waste water treatment plant. Photochemistry, essentially sunlight catalyzed redox reactions, can be an important process for (degrading) MNM coatings and contributes to the persistence of some MNMs, resulting in variable toxicity. This is exemplified by the degradation of (some) Ag MNMs coatings, which induced aggregation and settling of the MNMs, thereby removing them from the water column<sup>65</sup>. Conversely, many particles are used for their photo-reactivity (e.g.  $TiO_2$ ,  $ZnO$ , CNT), which may produce reactive oxygen species (ROS), thereby increasing the potential for toxicity<sup>66</sup>.



Dissolution is the release of individual ions or molecules from MNMs that are water-soluble. One prominent example of the importance of dissolution as a transformation pathway is highlighted with Ag MNMs, where dissolution can influence MNM longevity and biological mode of action (i.e. antimicrobial properties and toxicity)<sup>67-69</sup>. Both thermodynamic calculations and kinetic measurements suggest that Ag MNMs will not persist in realistic environmental compartments containing dissolved  $O_2$ <sup>54, 70, 71</sup>. This sensitivity to oxygen results in the formation of partially oxidized Ag MNMs with chemisorbed  $Ag^+$  or soluble  $Ag^{+72, 73}$ . Dissolution has been shown to follow first-order kinetics under relatively short time periods (under 48h) at low (<1  $\mu g/L$ ) total Ag concentrations<sup>74</sup>. Preferential dissolution of smaller particle sizes has been suggested<sup>75</sup>, while others describe dissolution as nearly independent of particle size<sup>76, 77</sup>. The released  $Ag^+$  may rejoin existing MNMs, form secondary precipitates and/or solution-phase complexes with other species<sup>78, 79</sup>, including interaction with dissolved organic carbon (DOC)<sup>80-82</sup>, a process which is described below.

Another transformation possibility is adsorption of substances to the MNM surface via van der Waals attractions (physisorption), electrostatic interactions (ion exchange) or chemical bonding (chemisorption). After release from a nano-product, adsorption may have one of two opposing effects: agglomeration by bridging between the particles or full coverage of the particle surface. The latter possibility decreases the chance of further dissolution or chemical change and (generally) increases the steric stability of the MNM preventing agglomeration and/or settling. For example, several mechanisms whereby DOC may slow Ag MNM dissolution have been presented, including surface adsorption of DOC and subsequent blockage of oxidation sites<sup>83</sup>, reversible reactions of released  $Ag^+$  returning to  $Ag^0$  with humic/fulvic substances acting as reductants<sup>84</sup>, and oxidation of DOC by  $H_2O_2$ , where DOC serves as a competitive sink for oxidants near the particle surface<sup>85</sup>.

Desorption will strongly affect the coatings of product-weathered MNMs, especially if the initial capping agent was only loosely bound to the MNM surface. Additionally, chelating agents could strip the particles of their manufactured surface functionality, leaving the particle surface bare and exposed. Modifying the ionic composition of the media, or changing the equilibrium of the system, could promote desorption of MNM coatings. This lack of data regarding stability and adhesion strength of MNM coatings, and their displacement potential under environmental conditions was recognized and highlighted as a major knowledge gap by the EU-FP7 modeling project ModNanoTox (see ModNanoTox Final report and Deliverable D7.3 – Document for dissemination to the Nanosafety cluster and dissemination report).

Combustion is a chemical reaction between a fuel and an oxidant and this process can oxidize elemental components of MNM surface (coatings) and/or cause phase transformations of the MNM due to the elevated temperature. Most MNMs will undergo this process during the incineration of materials or waste, especially in the EU where waste incineration is common. The exception is  $CeO_2$  additives in fuels, where the particles would be transformed during petrol use.

Biotransformation and/or biodegradation may affect all of the previously described transformations, save combustion. Rates and relative importance of this process will depend on the MNM/microbe interaction, enzymes or ingestion. Biologically mediated transformation of both the MNM core and particle coating is possible, affecting surface charge, aggregation and reactivity. Redox reactions are important biologically, and thus production of ROS, both intracellularly and extracellularly, is possible and an important consideration. Some bacteria have even demonstrated reduction of ionic  $Ag^+$  to “produce” Ag nanoparticles<sup>85, 86</sup>. Biotransformation of many MNM surfaces have been observed, ranging from oxidation of CNTs<sup>87</sup>, to degradation of organic or polymer coatings/capping agents<sup>88</sup>, to dissolution of the particle inside plant tissue<sup>89</sup>. These changes may ultimately change the stability of the MNM and/or its toxic potential.

Many MNMs either utilize metals during catalysis as a part of production, or incorporate MNMs into a larger structure or scaffolding that is a different composition from the primary MNM material. For example, Mo, Ni, Co, Y and Fe are typically utilized for the catalytic growth of CNTs<sup>90, 91</sup>. After synthesis the product is typically cleaned to remove these impurities, but residual metal catalysts often persists<sup>92</sup>. Likewise, the synthesis of  $TiO_2$  MNMs often involves surfactants or polymers to promote crystalline formation or control morphology<sup>93, 94</sup>, resulting in impurities (e.g. Si) in commercially available particles. Leaching of a secondary contaminant, such as catalytic precursors or other impurities<sup>95, 96</sup>, will have environmental and health consequences. Therefore, assessment of transformations of the primary particle should also include consideration of release of these impurities.



Re-precipitation is the process of dissolved ions forming NPs, though notably, these would not be MNMs. The formation of these naturally occurring nano-scale materials in the environment has recently received increased attention, as many physical, chemical, and biological processes are capable of creating a range of MNMs. Besides the biologically mediated formation of Ag NPs mentioned previously, redox active NOM can drive the reduction of ionic Ag to form Ag NPs. While this process has been shown to proceed in the dark<sup>97, 98</sup>, sunlight driven reduction of Ag and Au ions to Ag and Au MNMs in natural waters was much faster<sup>99</sup>. For example, Hou et al. recently demonstrated the (simulated) sunlight driven formation and transformation of Ag nanoparticles in river water and synthetic natural water samples containing NOM and Ag ions<sup>100</sup>. Additionally, this process may happen in laundry wash water, where after Ag MNM imbedded in textiles dissolve, the ions could be precipitated from solution due to surfactants and detergents. Dissolution of ZnO MNMs and re-precipitation of Zn carbonates or phosphates in natural waters is also plausible.

In addition to the chemical transformations listed above, physical transformations of MNMs can also be considered, including forces such as abrasion and mechanical erosion. Specific to carbon nanotubes, breaking and/or shortening of the tubes may be a possibility. Other examples include polymers, which often need to undergo several finishing steps to go from mold to final product. Either high-energy mechanical processes (e.g. sanding, cutting, drilling<sup>101-103</sup>) or a gentler, long-term abrasion (e.g. product use<sup>104, 105</sup>) could result in nano-object release from the material. While some studies have investigated this aspect of physical weathering, a wider range of polymers and products needs to be tested, and detailed consideration of adhesion strength to the NM surface and hardness of the matrix is needed, before a generic conclusion can be made<sup>106</sup>.

Agglomeration is a specific physical transformation process which increases size and reduces the surface area to volume ratio and thus affects the reactivity of the MNMs. As described by Buffle et al, factors influencing agglomeration can be understood in aquatic systems by considering the roles of three types of colloids: (i) compact inorganic colloids; (ii) large, rigid biopolymers; and (iii) fulvic compounds or refractory organic matter, each having a different stabilizing/destabilizing effect<sup>107</sup>. Agglomeration can take one of two forms: homoagglomeration (interactions between MNMs) and heteroagglomeration (interaction between MNMs and other particles in the environment). Because MNMs will be in dilute concentrations in environmental systems, homoagglomeration is unlikely and heteroagglomeration will dominate. Quik et al. suggest that the main route of the removal of most MNMs from the water column is likely to be agglomeration, followed by sedimentation<sup>108</sup>. In lieu of complex experiments to understand this process, simplification of agglomeration processes through modeling may prove useful<sup>109</sup>. However, agglomeration and deposition behavior relies on a myriad of physicochemical interactions between the particles and water chemistry and challenges still remain in quantifying the transport of MNMs and nano-agglomerates<sup>110</sup>.



**Table 1:** Possible chemical, physical, and biologically mediated MNM transformations during the nano-product life cycle.

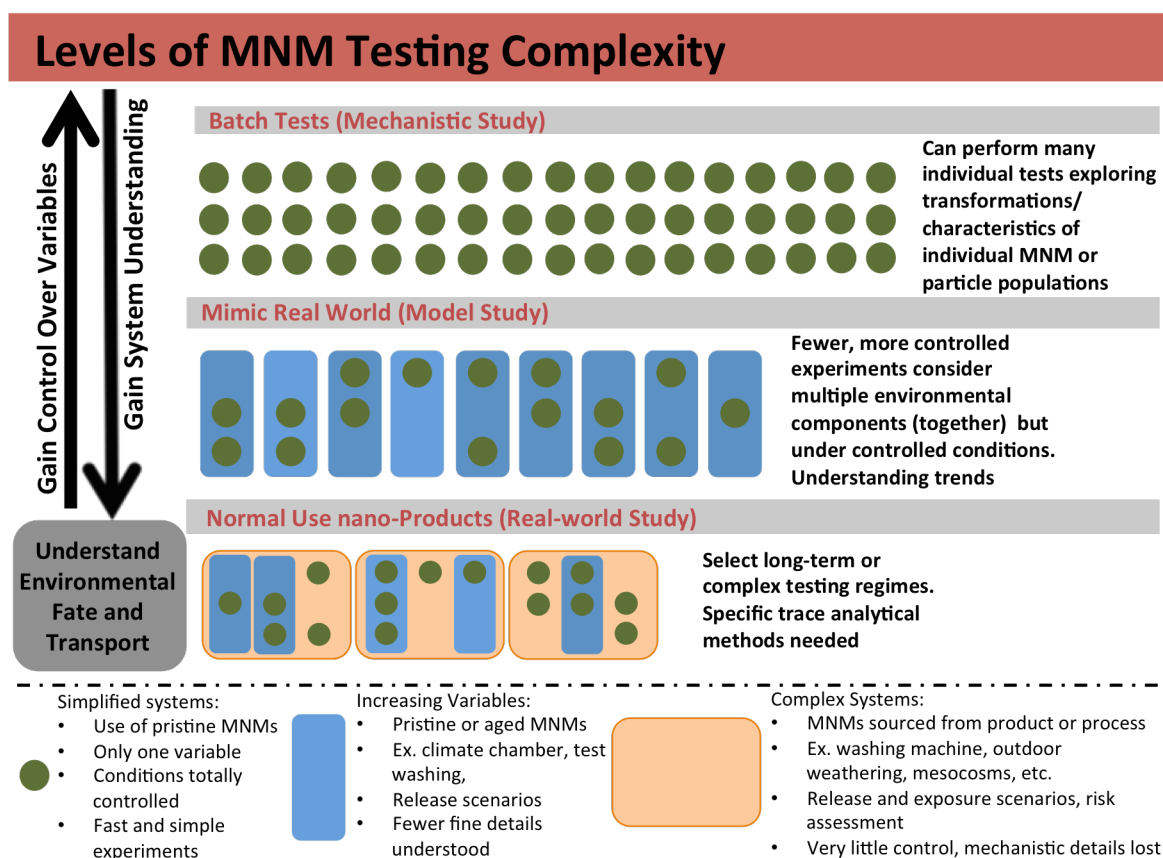
Process	Description	Governing Factors	Example(s) of Physical MNM Change	Potential Rate Determining Step(s)	Effected Particle(s)
Oxidation and Reduction	A coupled process in natural systems involving transfer of electrons	<ul style="list-style-type: none"> <li>Depending on material, can undergo oxidation, reduction, or both</li> <li>Some environmental factors increase redox potential: solution pH and chemistry</li> <li>*Natural waters and surface soils oxidizing environments while sediments and groundwater favor reduction</li> </ul>	<ul style="list-style-type: none"> <li>Alter ratio of oxidized element in sample</li> <li>Prerequisite to MNM dissolution</li> </ul>	<ul style="list-style-type: none"> <li>Concentration and composition of oxidant/reductant</li> <li>Presence or absence of oxide shell on MNM</li> </ul>	Ag, Fe, Ce
Photochemistry	Dependent on incident light wavelength, photo-catalytic ability	<ul style="list-style-type: none"> <li>* Ability of light to penetrate outer coating/layers</li> <li>Generation of ROS</li> </ul>	<ul style="list-style-type: none"> <li>Change to MNM coating</li> <li>Oxidation state</li> <li>Generation of reactive oxygen species (ROS)</li> <li>Particle persistence</li> </ul>	Mass transfer of from the materials surface and/or matrix to surrounding media	TiO <sub>2</sub> , ZnO, Ag
Dissolution	Release of individual ions or molecules that are water soluble	Particle size, capping agent, composition, and solution chemistry may all affect dissolution rates	<ul style="list-style-type: none"> <li>MNM surface properties</li> <li>Toxicity</li> <li>Particle persistence</li> </ul>	Oxidation of particle surface	Ag, ZnO
Mineralization	Example: Sulfidation Class B metals' affinity for sulfur molecules make them highly reactive with inorganic sulfur. Also formation of carbonates and phosphates possible	Particle size, capping agent, composition, and solution chemistry may all affect sulfidation rates	Formation of relatively insoluble metal-sulfide shell (and in cases interior of particle)	<ul style="list-style-type: none"> <li>Redox state</li> <li>Availability of sulfide</li> </ul>	Ag, ZnO, CuO
Absorption	Adsorption of substances to MNM surface (e.g. macromolecules, organic or inorganic ligands)	Change in MNM stability can effect surface charge, toxicity (bioavailability) and environmental fate and transport	<ul style="list-style-type: none"> <li>Agglomeration by bridging particles</li> <li>Covering particle surface increasing stability</li> <li>Coating decreasing attachment efficiency -- greater mobility in environment</li> <li>Organic ligands may affect dissolution, charge, and stability against aggregates</li> </ul>	N/A	All materials
Desorption	Loosely bound capping agents/coatings or presence of chelating agents that could leave MNM particle bare	Strongly affects the coatings of product-weathered MNM's, especially if capping agent loosely bound to MNM surface	N/A	N/A	All materials
Biotransformation/Biodegradation	Biologically mediated transformation process (all above in table)	<ul style="list-style-type: none"> <li>Intracellular and extracellular transformations</li> <li>Affect NM core and/or coatings</li> </ul>	<ul style="list-style-type: none"> <li>Redox reactions</li> <li>Change to particle stability: surface charge, aggregation state, reactivity</li> <li>Reduction of M<sup>+</sup> to form NM from solution</li> </ul>	Rates and relative importance dependent on MNM/microbe interaction, enzyme, or ingestion	Ag, FeO, CNT
Macromolecule Interactions	In living cells biomacromolecules and in the environment geomacromolecules and humic substances (e.g. NOM) can modify MNM surface	Types and amounts of biological and environmental components	<ul style="list-style-type: none"> <li>Formation of protein coronas</li> <li>Coating by biomacromolecules affect dissolution rate, ROS production and bioaccumulation (toxicity) potential</li> <li>Displacement of synthetic capping agents for humic substances</li> </ul>	N/A	All materials
Combustion	Oxidizing elemental components and phase transformation	Disposal/waste stream differences that vary by country or region	<ul style="list-style-type: none"> <li>Complete combustion of material</li> <li>Combustion only of surface coatings</li> </ul>	Temperature	CNT, ZnO, Ag (incineration) TiO <sub>2</sub> (surface) CeO <sub>2</sub> (fuels)
Leaching Secondary Contaminant	During MNM production, surfactants, polymers, etc. are added to promote crystallinity formation or control morphology which may then leach from the MNM	Impurities can change MNM surface characteristics and/or MNM functionality making prediction of fate or toxicity more difficult	<ul style="list-style-type: none"> <li>Decreased photocatalytic activity in TiO<sub>2</sub> with silica loading</li> <li>Si or P leach from TiO<sub>2</sub> similar to diffusion controlled dissolution of minerals</li> <li>Release of catalyst impurities from CNT</li> </ul>	Concentration of impurity and host matrix/structure. Varies dependant on system	All MNM complexes and CNT
Re-precipitation	Dissolved ions forming NMs dependent on solution chemistry	Water chemistry and, in some cases, strength of light	<ul style="list-style-type: none"> <li>Sunlight driven photo-reduction of Ag metal</li> <li>Formation of Zn-carbonate after ZnO dissolution</li> <li>Adsorption of M<sup>+</sup> to organic material in water</li> <li>High-energy mechanical process (e.g. sanding, cutting, etc.)</li> </ul>	Dependent on re-precipitation products	Ag, ZnO
Physical Transformations	Change due to physical force or weathering	Dependent on MNM incorporation into product that will experience physical force. Physical change to the MNM themselves or dispersion into air depending on conditions.	<ul style="list-style-type: none"> <li>Gentle, longer term abrasion (e.g. wearing fabric/textile or natural weathering)</li> <li>Breaking and/or shortening of CNT</li> </ul>	N/A	All Materials
Agglomeration	Individual particles form bound clusters	<ul style="list-style-type: none"> <li>Heteroaggregation most likely in environmental situations</li> </ul>	<ul style="list-style-type: none"> <li>Reduces surface area:volume ratio and effects reactivity</li> <li>Changes transport of MNM (sedimentation, etc.)</li> <li>Changes uptake and toxicity potential</li> </ul>	N/A	All materials

### 1.3. MNM Product Release Studies

During product use, both environmental and human activities can stress a nano-product resulting in MNM releases. Generally, use of a given product will have two areas of impact: first during consumer exposure through product interaction and, subsequently, environmental exposure with product use or disposal. Sometimes these two phases will be distinct (e.g. user exposed to Ag MNM in textile through wearing, subsequent environmental exposure after washing) and at other times they may be concurrent (e.g. user applying sunscreen and swimming in a pool).



There are different levels of complexity that MNM release and transformation studies can be performed at (see Figure 3). The simplest of these are batch tests, which typically use pristine or at least standardized test materials. These tests generally have a narrow focus that allow control over the physical and chemical conditions and are therefore suitable to investigate the mechanisms of particle transformations, aging, or release by changing one variable at a time. Because at this level tests are relatively fast and simple, many individual tests can be preformed. However, they have limited relevance to real-world systems because there, MNMs would be exposed to a more dynamic environment. The second level of complexity contains studies that mimic the real world but are performed under controlled conditions. Here, more variables are included in these model studies (e.g. climate chamber, test washing) but fewer fine details can be understood. While fewer, more complex experiments can be performed at this level, by considering multiple environmental or system components together one can understand trends and gain broader understanding of MNM behavior. At this level, some combined process could be investigated, such as aqueous suspension of MNM with UV irradiation, since multiple processes will usually act on the particles at the same time affecting the transformation by-products. Although these studies are not directly transferable to the real world they can provide a better estimate of the magnitude of MNM release or narrow the possibilities of transformation products. The highest level of complexity comes from the normal use of nano-products or long-term environmental investigations. These experiments are complex and relate to specific release and exposure scenarios where one can derive risk assessment from MNM use (e.g. household washing machine, outdoor weathering, mesocosms). In these instances, there is very little control of the experimental variables, the mechanistic details of the process are lost, but one gains system understanding. However, when data is obtained in these real-world studies it can be directly used for release and exposure scenarios. These types of studies are of the highest relevance because they include the normal use of products and would be most beneficial for modeling and/or risk assessment work in order to confirm expected or calculated MNM release and transformations. Specific trace analytical methods are needed to detect and measure MNMs under these real-world conditions, an



**Figure 3:** Levels of MNM testing complexity. Many individual tests (green circles) performed to understand mechanistic changes to individual particles. Some of these tests are preserved in model studies (blue rectangles) but some details are lost due to the increasingly complex nature of the tests. Real world studies (peach squares) retain some of the information from the two lower tiers of tests but largely gain a broader understanding of MNM fate and transport while losing control over mechanistic details.



important area of research which needs to be further developed, in tandem with health and environmental safety scenarios.

#### 1.4. Quantitative Analysis and Analytical Approaches to MNM Detection

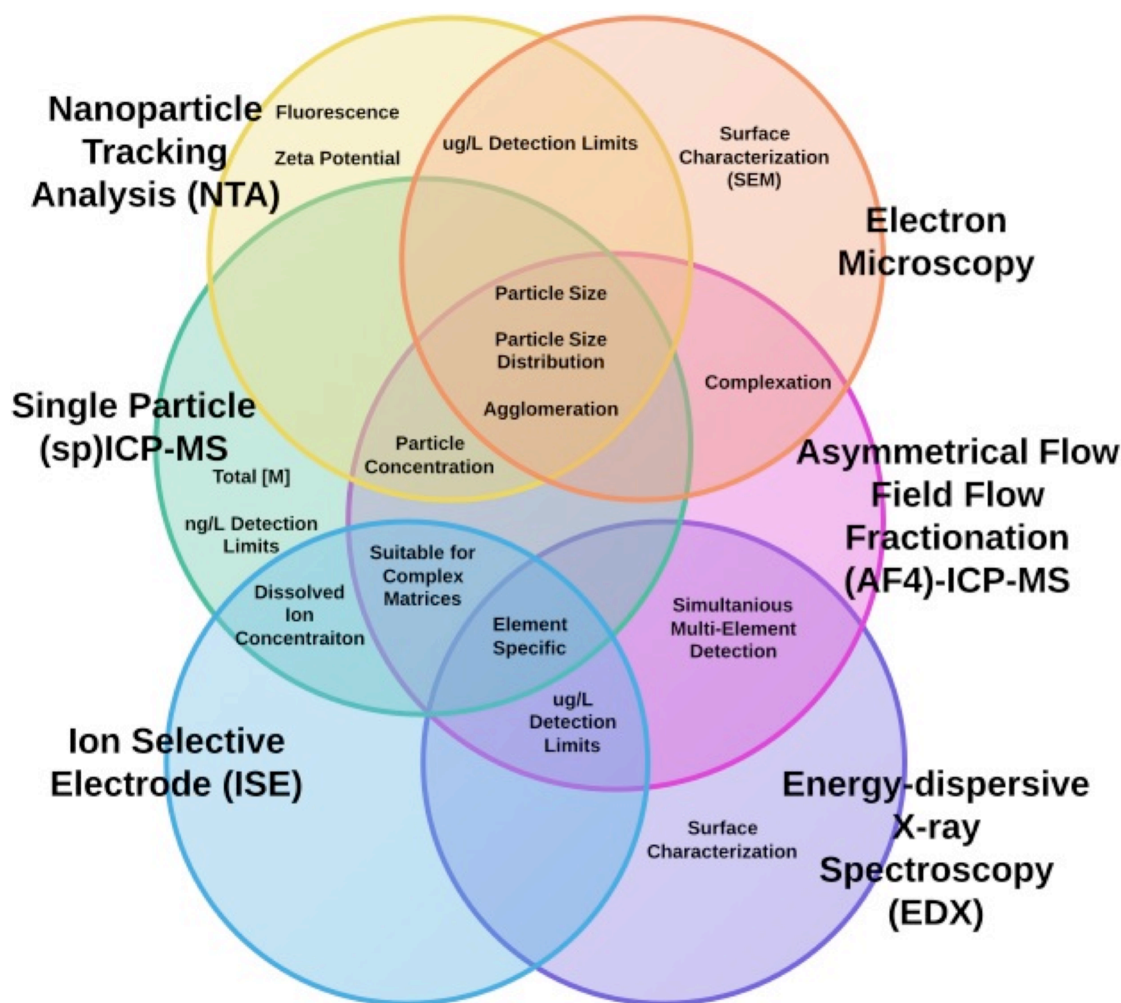
Qualitative and quantitative identification of MNMs is complex, as these materials have very low mass, can be highly dynamic in terms of particle agglomeration or reactivity, co-exist with ambient particles in the same size range (i.e. natural analogs) and also often coincide with molecules or macro sized counterparts of the same chemical composition. Furthermore, differentiation between incidental MNMs and engineered MNMs is relevant when evaluating the potential effects of the latter material. For instance, the behavior of engineered nano-TiO<sub>2</sub> in paints needs to be compared to the properties of (traditional) pigment TiO<sub>2</sub> in paints.

MNMs released from products may occur as: 1) free MNMs, 2) MNM aggregates/agglomerates, 3) particles embedded in the matrix, where the particles may or may not be released from the matrix, or 4) dissolved ions. In the simplest analytical cases, only total element concentrations are measured in the analysis and thus no “nano-specific” qualities are determined. However, ideally, there are several important characteristics that can be determined in relation both to the particle population and change(s) to individual MNMs. In many cases, non nano-specific methods are used to characterize MNM release from products, environmental, or toxicological studies, examples of which are shown below. Among the main challenges with moving towards increasingly complex experimental regimes is that in these real-world studies, researchers have very little control over conditions and specific trace analytical methods need to be developed. Previously, to perform a proactive risk analysis, the only way to obtain information on the MNMs in various environmental spheres was through models that predicted environmental concentrations. However, analytical methods are approaching an appropriate level of maturity to begin more rigorous, realistic MNM release/transformation scenarios in the lab (i.e. at an appropriate concentration and in increasingly complex matrices).

All comprehensive MNM release studies should implement multiple characterization techniques (see below), but often only a fragment of data is obtained because of difficulties with analysis. It is evident that characterization of the particles is highly relevant: especially size, surface coating, aggregation, concentration (of both NP and dissolved counterparts) and mobility within the matrix are needed as a minimum. Furthermore, MNM concentrations used in many laboratory studies are significantly higher than predicted environmental concentrations, often due to the limited sensitivity of the detection and quantification methods available, but which can lead to quite different agglomeration behavior. An issue with conducting experiments at MNM concentrations orders of magnitude higher than measured or expected environmental concentrations is that there is little known about the linear up-scaling/downscaling of MNMs' fate & behavior due to their tendency to interact with each other and with the matrix<sup>111</sup>. This hampers the ability to directly apply laboratory results to a larger scale. Fortunately, a few trace analytical methods have proven useful in model systems and are primed to be used in real-world studies.



Nanomaterial characterization is accomplished using a variety of different techniques drawn from interdisciplinary areas. Some examples of relevant techniques for real-world studies include single particle ICP-MS (spICP-MS), asymmetrical flow field flow fractionation ICP-MS (AF4-ICP-MS), nanoparticle tracking analysis (NTA), electron microscopy, ion selective electrode (ISE), energy-dispersive x-ray spectroscopy (EDX) and imaging techniques such as electron microscopy. The capabilities and highlights of these techniques are compared in Figure 4. The very low concentration detection limits make spICP-MS uniquely well suited for MNM release studies. Moreover, spICP-MS is the only method that can count, size and chemically identify MNMs in aqueous dispersions<sup>112, 113</sup>. Separation techniques, such as AF4 and hydrodynamic chromatography (HDC) have higher detection limits (in the  $\mu\text{g/L}$  vs.  $\text{ng/L}$  range), but useful information about particle size distribution, complexation and core/shell structures of specific size fractions of a sample can be obtained because of the ability to couple these instruments with ICP-MS<sup>114, 115</sup>. Sensitive X-ray based techniques can examine chemical speciation and thus MNM transformations of the primary particle surface. Visualization of the sample, either directly with electron microscopy or indirectly with NTA, is a satisfying way to observe MNM in either dried or aqueous samples, respectively. ISE is a fast and effective way to measure element specific ionic concentrations, which could be relevant when studying MNM dissolution, etc. However, it is noteworthy that this is not a very sensitive method. There are several other techniques that are often used in the study of MNMs, but they may be more suited to a laboratory setting rather than detecting particle transformations in actual environmental or biological samples. While UV/Vis or dynamic light scattering (DLS) are often used, yet we do not consider these techniques to be environmentally relevant because high MNM concentrations are required and one can not differentiate between incidental particles and MNM in the nano-range. Furthermore, these techniques are ill suited to polydisperse systems or systems containing aggregates, even in laboratory samples. Differential centrifugal sedimentation (DSC) can separate polydisperse samples, but without the capability to hyphenate to an element specific detector, the technique has less to offer in complex



**Figure 4:** Features of environmentally relevant MNM detection and characterization techniques





environmental experiments than AF4 for example. Atomic force microscopy (AFM) and Fourier transform infrared spectroscopy (FTIR) both are used to analyze the particles' surface characteristics, but this is best done with raw MNM samples and are not best suited for complex matrices. Transmission electron microscopy (TEM) is also used frequently in the study of MNMs, though the technique requires rather high particle number, is costly, samples are susceptible to change depending on TEM grid preparation and may not be best suited to environmental samples where extraneous material could obscure particle detection. While this is a brief overview of current analytical techniques, we refer to a recent review by von der Kammer et. al which delves into a number of these techniques, and others, in more detail<sup>116</sup>.

## **2. Life Cycle Approach to Estimating Likely MNM Release and Transformation from Commercial Production and Products**

Specific applications will ultimately determine the type and extent of transformations a given nano-composite may undergo. In the following sections, we evaluate more specifically the possible particle transformations based on how MNMs will be implemented into products, how those products will be used, and what use or environmental stresses the product is likely to encounter. In general terms, MNMs will be transformed over time in products by interacting with the matrix material, degradation or change to unstable coatings or other aging processes, and ultimately be released from the product as a different MNM than was manufactured<sup>117</sup>. The release of MNM may occur along any stage of a product life cycle, which will be controlled by both the product design and external impacts<sup>58</sup>. Based on these specific applications on MNMs, we were able to narrow the number of likely MNM exposures. Here we present a selection of possible transformations and aging reactions based on their typical use in consumer goods.

Applications were considered if they made up 5% or more of the market share value for nano-enhanced products containing Ag, TiO<sub>2</sub>, ZnO, or CNT, as determined by a recent life-cycle based material flow modeling study<sup>59</sup> (Figure 5). Exceptions were included where the authors felt that market presence of certain materials could increase dramatically in the coming years but did not yet comprise over 5% of current product use (e.g. Ag in paints and TiO<sub>2</sub> in food) or for selected MNMs applications not included in the materials flow modeling report (e.g. CeO<sub>2</sub> in fuels). Additionally, we acknowledge that many applications can bridge two (or more) of the market category divisions, for example edible coatings to prevent food spoilage could be included in either the "food" category or the "coatings" category. Recognizing that significant overlaps exist, we attempted to limit the analysis of transformations to only one group per product for simplicity. Therefore, transformations that are inherently applicable to multiple product categories (e.g. transformations in WWTP, re-precipitation in natural waters) will be addressed only once and referred to where appropriate.

We start with a section about transformation reactions that occur during storage and end of life treatments. These reactions are product-independent and may thus be experienced by all products.

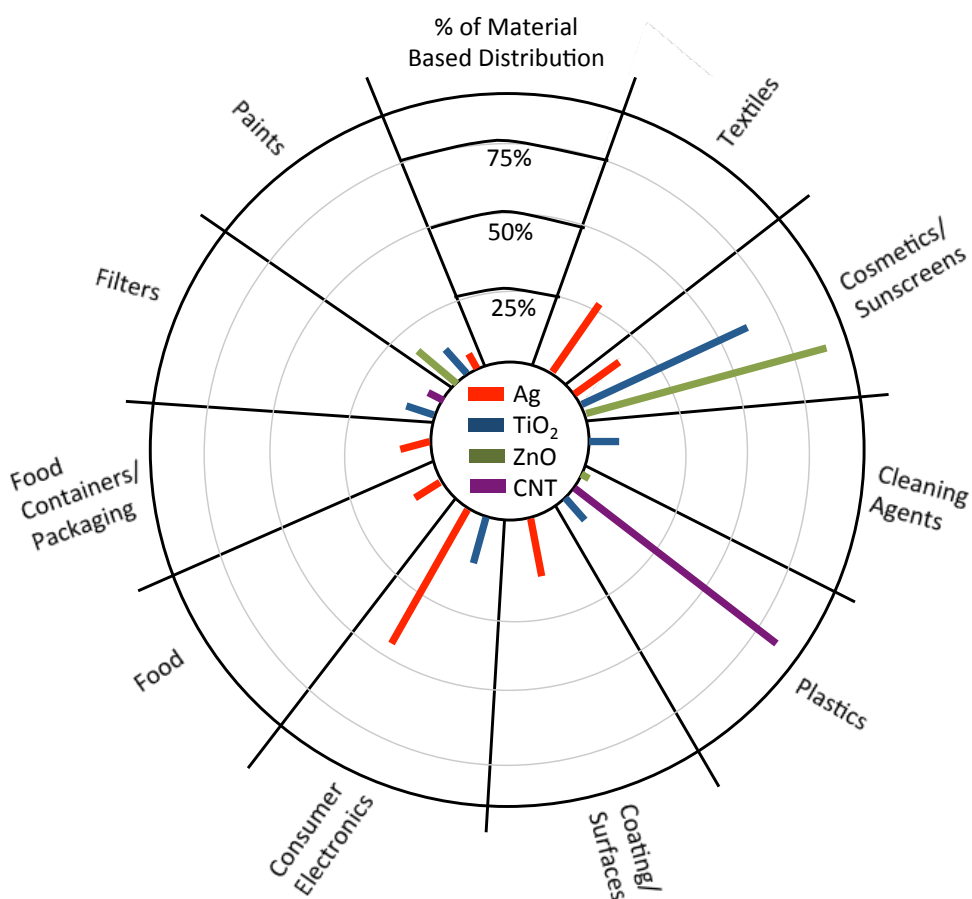
### **2.1. Product Independent Reactions**

#### **2.1.1 Product Storage (pre-use)**

MNM incorporated into products may be stored for some time exposed to the atmosphere including humidity and varying temperature. During this time changes in the crystal structure and/or the surface may occur. Structure stabilization is driven by surface energy loss. MNM have excess free energy relative to bulk material because a large fraction of their atoms are located near the surface and thus lack full coordination. Surface energy loss can be achieved by growth and/or morphology changes, as well as structural transformations with or without growth of the particle. In the study reported by Ali and Winterer<sup>118</sup>, the authors could correlate their growth observations with an improvement in the degree of crystallinity and a decrease in the defect density with time, showing that

ZnO particles tended to produce a self-healing effect, even in ambient conditions. The particle size affects phase stability when it decreases to nano size. Hence, phase reversal can occur if the stable bulk phase possesses a higher average surface energy<sup>119</sup>: wurtzite hexagonal form of ZnS is thus stabilized at small particle sizes while sphalerite is the stable form in the bulk material. In the case of  $\text{Fe}_2\text{O}_3$ , the phase transition was found to be dependent on the initial size of the particle and on its environment<sup>120</sup>, with increased rate of hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) to maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) conversion as the size decreases, supposedly related to the increased occurrence of maghemite-like defects on the smallest hematite particle surface.

A model of crystalline structure transformation was proposed by Goodell et al.<sup>121</sup>. There, the authors suggested that the permeation of water vapor through the aggregates of MNMs and bound to the surface would favor particle-particle contact and induce stabilization of a more crystalline structure. It should be noted that these crystalline re-organizations may lead to atom displacements and formation of cluster structures, as suspected in Co-rich doped Ti/Co/O nanopowder<sup>122</sup>, and/or to variation in the lattice parameter, as observed with maghemite  $\gamma\text{-Fe}_2\text{O}_3$  under varying relative water pressure.<sup>123</sup> Again, water appears to play an important role in the process of transformation by its ability to chemisorb on surfaces, organize in solid-like or liquid-like layers, react with adsorption sites, etc.



**Figure 5:** Percentage of each MNM category in various applications, based on data from Sun et al.<sup>59</sup> These materials were selected because either they are currently used in large quantities ( $\text{TiO}_2$ , ZnO), are used in a large number of products (Ag), or because a relatively large amount of information is available about their properties (CNTs).

Oxidation is a prominent aging process of MNMs generally, not only for Ag and  $\text{TiO}_2$  which are featured in the materials flow modeling. In one study where copper NP were left unattended for 6 years under ambient conditions, a thick oxide coating was formed on the particles' surface; increasing the particle size by up to 50% over the length of the experiment<sup>124</sup>. After this time period, the aged NP dissolved more readily, which gives rise to environmental and health concerns, as dissolution will not proceed identically with new and aged MNMs. However, oxidation may



affect various types of MNMs differently. When studying core/shell clusters, Yin et al.<sup>125</sup> showed that the chemical distribution between the core and the shell is the determining factor as to whether oxidation takes place. Thus, a Cu-rich core/Au-rich shell structure was found to be stable after exposure to air for 12 days, due to the protective effect of Au. Conversely, the opposite, configuration of an Au-rich core/Cu-rich shell underwent surface oxidation.

Quantum dots (QDs) were also found to undergo oxidation, even when capped with an organic ligand. In their study, Bowen et al.<sup>126</sup> aged CdSe QDs capped with TOPO in air for several weeks. SeO<sub>2</sub> was recovered after one day of exposure, which desorbed from the surface of the QD, while Cd was not oxidized because of the TOPO protection. The instability of these TOPO coated nanocrystals was confirmed by Alivisatos<sup>127</sup>, as when exposed to visible light, CdS and CdSe form SO<sub>4</sub> or SeO<sub>4</sub>, respectively, that evaporate from the surface to leave reduced Cd and a newly exposed CdS or CdSe layer. The consequence of this selective protection against oxidation is a modification of the chemical composition of the MNMs, with a decrease of the Se/Cd ratio and, eventually, the destruction of the nanocrystals by these redox cycles within a few days. The same protective effect can be deduced from aging experiments on ZnO and Fe-doped ZnO powders coated with PAA<sup>128</sup>: the PAA layer helps stabilize particle size and magnetism by acting as a barrier to diffusion.

A consequence of such oxidation processes that may be encountered is morphological changes associated with particle size evolution. Morphological changes are illustrated by Co nanoflakes used in a self-assembled multilayer Co/Sb sandwich, which were found to creep through the Sb layer to form long Co nanowires, decreasing their properties of magnetization and resistance<sup>129</sup>. In the example reported by Thurber et al.<sup>128</sup>, unprotected ZnO powders almost doubled in diameter after four years of exposure to ambient air. Surprisingly, the rate of increase was found to be higher for larger starting samples and was not assigned to sintering. Another example of particle growth can be found in the study reported by Ali and Winterer<sup>118</sup>: the growth of ZnO nanocrystals in powder form at room temperature was observed and it was found to be dependent on the water vapor partial pressure. The authors of the study propose a growth mechanism based on the chemisorption of water molecules on the surface of ZnO NPs, dissociation of the H<sub>2</sub>O molecule at surface defects, and diffusion of Zn interstitially close to the surface and through ZnO to migrate toward other particles or towards the inter-particle region to minimize the overall surface energy.

Another approach to reducing excess surface free energy is binding of any available molecules to the surface, which in many product scenarios could include polymers or other macromolecules<sup>130</sup>. Such binding can often be irreversible, as demonstrated by multiple studies of MNM interactions with proteins, whereby even when the MNM-protein complexes are placed in a large excess of buffer the proteins remain attached to the MNM surface despite being at higher concentrations there<sup>131, 132</sup>. Biomolecule binding has been shown to change the surface charge of MNMs, as reflected by dramatically altered zeta potentials, as well as the agglomeration behavior. This could be particularly relevant for MNMs utilized in food and cosmetics for example, and those in textiles.

### 2.1.2 End of Life Cycle (disposal)

At the end of life cycle, many products will be disposed of in solid waste, either as raw products transported directly to a landfill or as incineration byproducts. For the purposes of this review, deposition of MNMs in landfills is considered a final sink and so no further transformations are considered. However, we note that it is possible for further changes to the particles to occur and/or leaching of materials from the landfills may be a possibility, especially in places where waste disposal is not tightly controlled. If incinerated, residual material is either found in the bottom ash or the filter ash, where either process would burn away any organic coatings the particles initially possessed. Depending on how high the temperatures are, transformation of the crystal matrix could also be possible. This process could be analogous to the transformations observed in the annealing processes of some NP synthesis techniques. Structural transformations were found, for instance, under calcination of the anatase form of TiO<sub>2</sub><sup>133</sup>. The anatase crystalline form of TiO<sub>2</sub>, a distorted octahedral structure, is more photoactive than rutile, which looks more like slender prismatic crystals<sup>134</sup>, and that is why anatase is preferred in most composite applications. However, it is less stable and has a lower density than rutile and phase transformation of anatase to rutile occurs at approximately 600°C/700°C. Additionally, Thongsuwan et al.<sup>135</sup> found that an increase of temperature could cause aggregation of the primary TiO<sub>2</sub> particles when heating them beyond 500°C. However,



thermal stability is one of the properties of most interest in development of nano-composites and in some cases the incorporation of nano  $\text{TiO}_2$  may help preserve the integrity of the material. Indeed, Esthappen et al.<sup>136</sup> demonstrated an enhanced thermal stability when nano  $\text{TiO}_2$  was added to a polypropylene polymer. It may be noted that anatase and rutile do not possess the same surface chemistry, the hydroxyl groups on the surface of anatase being more acidic than those on rutile<sup>134</sup>. These characteristics will affect the dispersability of nano- $\text{TiO}_2$  in an aqueous medium as well as its interactions with humic substances, which in turn may influence its transfer from the source to the environment.

Acids are also used in the incineration process to clean flue and filter ash in the hope of metal recovery for elements such as Zn. For  $\text{TiO}_2$  particles, this may affect any surface coating left on  $\text{TiO}_2$  MNMs but will not dissolve the particle itself. On the other hand, ZnO would be completely dissolved under acidic conditions. We note that acid washing is not necessarily specific to the waste incineration scenario. Plastics may also be treated this way when they are being recycled, where an acid wash is used as a preparation/cleaning step to remove dirt or debris from the surface. Here,  $\text{TiO}_2$  and ZnO will behave as described above, with  $\text{TiO}_2$  being resistant to change and ZnO entirely dissolving. Other MNMs incorporated into the products, such as Ag MNM, would also likely be dissolved during this cleaning process. Additionally, any organic macromolecules or biomolecules bound to the surface could be “digested” in this step, revealing the underlying “bare” NM.

## 2.2. Textiles

Previously, the function of textiles and clothing were limited to comfort, decoration (design) and protection from inclement weather. The aim of using MNM in textiles is to produce materials with improved or novel functionalities or combination of various functionalities (i.e. multi-functional textiles). These materials may be self-cleaning, water and/or dirt repellent, antimicrobial, conductive and antistatic (wrinkle-resistant), solvent-, UV-, and abrasion resistant, have decreased flammability or increased strength and durability of dyes or colorants<sup>117, 137</sup>. Textiles using nanotechnology also provide advanced protection against extreme weather and improved comfort in terms of weight, moisture transport and permeability, plus superior tear and puncture resistance. Beyond performance clothing, textiles in the medical field have also made significant progress by incorporating nanotechnology in the area of antibacterial textiles, antimicrobial wound dressing, and anti-adhesive wound dressings.

**Table 2:** Known and probable transformations of MNMs imbedded in textiles. Specific studies cited when possible.

Transformation Process	MNM Affected	Life cycle activity	Change to Particle	Possible Implications	Representative Example(s)
Oxidation	Ag	Washing	Oxidation by $\text{O}_2$ , Dissolution,	<ul style="list-style-type: none"> <li>Increased toxicity</li> <li>Decreased effectiveness in product over time</li> </ul>	Release of $\text{Ag}^+$ in simulated washing cycle with surfactants <sup>32</sup>
	Ag	Contact with bleaching, oxidizing agents	Dissolution, phase transformation	<ul style="list-style-type: none"> <li>Dissolution</li> <li>Formation of AgCl</li> <li>Leached Ag goes to WWTP and bio solids in AgCl form</li> </ul>	Hypochlorite/detergent solution converts Ag to AgCl in presence of NaCl <sup>32, 48</sup>
	Ag	Contact with detergents/complexing agents	Ag complexation, stabilization	Formation of stable MNM suspension	N/A
	MNM Coating	Various	Destruction of coating	Change to particle stability, oxidation extent, toxicity, etc.	N/A



Dissolution	Ag	Washing	Ion formation	Increased toxicity	Wash in DI water nearly all impregnated Ag released in first few cycles <sup>30, 32, 138</sup>
	Ag	Wearing	Coating alteration	<ul style="list-style-type: none"> <li>Exposure to sweat or urine coats particles with AgCl</li> <li>pH of sweat changes [Ag] released</li> </ul>	<ul style="list-style-type: none"> <li>Cease Ag<sup>+</sup> release<sup>139, 140</sup></li> <li>Normal skin pH had lowest [Ag] release<sup>141</sup></li> </ul>
	Ag	Contact with detergents/complexing agents	Ag complexation, stabilization	Formation of stable MNM suspension	N/A
Precipitation	Ag	Washing	AgCl formation	Precipitation and/or decreased toxicity	Nature of (in)soluble Ag species varies as a function of total Ag and Cl <sup>-142</sup>
	Ag	Exposure to air	Metallic Ag particle formation	Generation of small secondary particles	Small Ag particles formed in humid conditions <sup>51</sup>
Reduction	Ag	Washing	Formation of Ag(0) from Ag <sup>+</sup>	"new" particle formation	N/A
UV Irradiation	Ag	Wearing in sun	Oxidation of particle surface	Change in reactivity	N/A
	Ag	WWTP disinfection	N/A	Attempt to purify water	No removal of Ag MNM at neutral pH <sup>143</sup>
	MNM Coating	Wearing in sun	Destruction of coating	<ul style="list-style-type: none"> <li>Change to particle stability (agglomeration and sedimentation)</li> <li>Susceptibility to oxidation and dissolution</li> </ul>	Degradation of gum arabic coating in sunlight <sup>65</sup>
Incineration	Ag	After disposal	Change in chemistry	<ul style="list-style-type: none"> <li>Reduce agglomeration of particles</li> <li>Trace amounts of Ag left in bottom ash</li> </ul>	<ul style="list-style-type: none"> <li>TEM image after textile burned in furnace<sup>141</sup></li> <li>Modeling result only<sup>144</sup></li> </ul>
Release of MNM	Ag, TiO <sub>2</sub>	Abrasion and Sweat	Release of Ag	<ul style="list-style-type: none"> <li>pH of sweat contributes to release (alkaline increased release)</li> <li>Physical stress s may mobilize more particles</li> <li>Compared to other pathways, minor exposure</li> </ul>	<ul style="list-style-type: none"> <li>Migration of textiles into artificial sweat under physical stress (particles specified)<sup>140</sup></li> <li>Chemical mobilization of Ag into sweat (form unspecified)<sup>31, 141, 145</sup></li> </ul>
	Ag	Abrasion and Sweat	Re-precipitation	<ul style="list-style-type: none"> <li>Possible formation of AgCl, stabilized as Ag-chloro-complexes</li> <li>Compared to other pathways, minor exposure</li> </ul>	<ul style="list-style-type: none"> <li>Migration of textiles into artificial sweat under physical stress<sup>140</sup></li> </ul>

Four main factors affect the quantity of NM release and subsequent transformations over the lifetime of a textile, including: 1) incorporation into the material (location, adhesion to matrix, textile composition, MNM form), 2) use of textile, 3) cleaning/washing technique and associated chemicals (e.g. bleach, detergent) and 4) disposal. The only material that currently makes up 5% or more of the total market share in any MNM category is Ag. Thus the remainder of this section is focused on Ag MNM alone, despite the current development of functional textiles for



an array of applications<sup>146</sup>. Depending on material design and external impacts to the textile, MNM may be released as single particles, agglomerates, embedded in the matrix, and/or as dissolved ions. Where the release occurs (i.e. during washing, wear, directly to the environment, or after product disposal) will also play a large role in the types of transformations Ag MNMs may undergo following release. Since textiles are an important source of Ag MNM, washing, cleaning, wearing, and disposal of these fabrics have all been studied in detail and a myriad of physico-chemical changes were observed to the particle during washing and cleaning of these nano-enhanced products (Table 2). Colloidal stability and chemical form (ionic, complexed, etc.) will govern mobility and is essential to determine bioavailability and toxicity. A relatively large fraction of Ag MNMs in textiles will likely be released into wastewater after washing and thus the transformations in treatment plants and bio-solids have also been investigated. Other sources of incidental Ag MNM release, such as release to air from abrasion, contact with skin, biological fluids (e.g. sweat, urine) or incineration were less substantial. Therefore, the most important contribution of textiles as a source of MNMs is emission to water compartments and into soils by application of bio-solids.

The washing of nano-textiles releases both dissolved and particulate silver, with some of the Ag released comprising of particles (or agglomerates) larger than 450 nm<sup>30, 32, 40</sup>. Incorporation of zerovalent silver into fabrics is common, and thus in these instances oxidation from Ag(0) to Ag(I) is a prerequisite for the appearance of Ag<sup>+</sup> in solution. The sensitivity of Ag-MNM to oxygen is well known<sup>72</sup> and the chemisorbed Ag<sup>+</sup>, either formed in air<sup>147, 148</sup>, during exposure to water<sup>71</sup>, or when in contact with detergents, can be easily released once the textile is laundered. However, the dissolution process is complex, with the extent and rate of dissolution being dependent on a multitude of factors ranging from solution chemistry to redox environment to particle specific characteristics such as capping agents and method of MNM incorporation into the fabric<sup>67</sup>. Quadros et al. assessed the potential for Ag MNM exposure to children from a blanket, plush toy, and a variety of other non-textile items<sup>139</sup>. Methods of simulated release varied to mimic product use. Fabric products released the highest quantities of silver, mostly in ionic rather than particulate form. The authors concluded that the exposure risk to children would be low, similar to results from Kulthong et al<sup>141</sup>. For example, an area of the fabric that was exposed to sweat or urine released a small amount of silver until the particles became coated in AgCl, thereafter inhibiting further ionic release. Additionally, von Goetz et al. demonstrated that dissolved Ag was released from fabrics exposed to sweat, with Ag-chloro-complexes being the major dissolved species due to the high chloride content in sweat<sup>140</sup>.

Incorporation of Ag MNM into textiles affords easy contact with air on the fabrics' surface. Under most atmospheric conditions, Ag becomes tarnished after exposure to air. Formation of Ag<sub>2</sub>S is the most common corrosion product in indoor air<sup>147</sup> while strong oxidants, such as NO<sub>x</sub> and ozone, can accelerate Ag<sub>2</sub>S formation significantly<sup>149-151</sup>. Alternatively, transformation of Ag to AgCl is usually more dominant in outdoor environments, where in these instances, environmental components including ozone, UV light and humidity can accelerate atmospheric corrosion of Ag MNM<sup>148, 152</sup>. Humidity and sweat may also promote the generation of secondary MNMs. Indeed, the generation of Ag MNMs has been observed in the vicinity of parent particles (and indeed bulk metals<sup>51</sup>) in ambient conditions with variable relative humidity<sup>51</sup>. The formation proceeds in three stages: 1) by oxidation and dissolution of Ag from the surface of the pristine particles, followed by 2) diffusion of the Ag<sup>+</sup> ions in an absorbed water layer, and finally 3) formation of a new MNM by chemical transformation and/or photoreduction. The formation of new Ag seeds should be favored by widely used capping agents or stabilizers: PVP, citrates and aminoalkylsilanes, for instance, are known to reduce Ag<sup>+</sup><sup>153</sup>. Mechanistic stress to the textile may hypothetically also release Ag MNM directly into the air, such as when wearing the textile or during the tumble drying process when laundering. Under these conditions, released MNMs are susceptible to undergo agglomeration, adsorption to other (incidental) particles, dissolution in droplets, or oxidation by atmospheric oxidants once released into the atmosphere<sup>154</sup>. Dust and lint would subsequently be collected and disposed of through the trash and eventually end up in landfills or incineration.

As previously mentioned, materials flow modeling studies suggest that the majority of the Ag MNMs released from textiles will deposit in wastewater treatment plants (WWTPs). Therefore, it is important to assess how WWTPs themselves influence the speciation of Ag. Predating the emergence of the MNM boom, Lytle investigated the speciation of Ag from various sources and suggested that in WWTPs the solubility of Ag would largely be controlled by sulfides<sup>155</sup>. More recently when collecting sewage sludge, Kim et al. found Ag<sub>2</sub>S present<sup>49</sup> which Kaegi et al. confirmed was derived from *in situ* processes from the reaction of soluble Ag or Ag MNMs with reduced S<sup>44</sup>. The resulting Ag<sub>2</sub>S was rapidly formed, which has important implications to potential particle toxicity, as sulfidation of Ag MNMs has been shown to strongly decrease the release of toxic Ag<sup>+</sup> in solution<sup>156</sup>. Two major complicating factors have the potential to influence Ag MNM sulfidation in these systems. First, particle surface





functionalization (e.g. different capping agents) may change the extent of agglomeration, dissolution and/or toxicity of Ag MNM<sup>157, 158</sup>. Second, not all Ag reaching the WWTP is in metallic form: AgCl MNMs are used in some functional textiles<sup>138</sup> and transformation of metallic Ag MNM during washing in the presence of bleach<sup>48</sup> will change particle chemistry before reaching the WWTP. In a comprehensive study, Lombi et al. found that surface functionality did not significantly influence the transformation of metallic Ag to Ag<sub>2</sub>S, and that added silver salt and AgCl MNMs were also converted to sulfide during anaerobic digestion. Levard et al questioned the stability of Ag species in sewage sludge during post-processing (namely oxidation prior to land application)<sup>54</sup> due to the transformations involving sulfide species. Lombi et al. showed that the speciation of Ag continues to be dominated by sulfides after six months of simulated stockpiling/composting<sup>159</sup> and noted that Ag sulfides are more recalcitrant to oxidation than NPs of other metals such as Cu or Zn<sup>160</sup>. The aforementioned studies agree that neither the form of Ag added (salt, Ag MNMs, AgCl NPs) nor the surface functionalization of the Ag MNMs influence the removal efficiency of Ag from the WWTP and so significant buildup of MNMs in sewage sludge is expected. Therefore, the final consideration is that traditional wastewater treatment by-products (biosolids from setting tanks, etc.) may become too concentrated with MNMs to be reapplied to land as compost or fertilizer. However, in terms of determining the safety of such a procedure, the transformed, sulfidized particles should be studied instead of pristine MNMs or intermediate by-products from washing.

Incineration of particles should also be considered. In many European countries, incineration of waste is common. In the United States, approximately 15% of the total 7 million dry tons of biosolids were incinerated in 2007<sup>161</sup>, a percentage that is likely to increase in the future because of increased interests in power generation from biosolids<sup>162</sup>. Firstly, the surface coatings of MNMs which are incinerated would be burned off and the particle surface would become oxidized. A second consideration is that Ag MNMs would not enter the incineration plant in pristine form, but rather as already transformed particles (e.g. Ag<sub>2</sub>S, etc.). Impellitteri et al. provided XAS data suggesting that significant amounts of Ag in incinerated biosolid samples (30-50%) converted back to elemental silver while the remainder was still associated with sulfate and sulfhydryl groups<sup>163</sup>. The resulting incineration ash may have several uses; one of which is for building roads. In this case, fully transformed MNMs (of various starting and ending compositions) may directly go into the environment. Conversely, in countries where landfilling is the major form of waste disposal, the fraction of Ag MNMs which still adhere to the product until disposal will have a different fate. Any remaining Ag MNMs on the textiles would likely dissolve, though for the purposes of this review, a landfill is considered a final sink and so no further transformations are considered.

## 2.3. Sunscreens, Cosmetics, Personal Care Products and Cleaning Agents

Both organic and inorganic MNMs are used in the cosmetic and sunscreen industries, but here we focus on inorganic MNMs such as TiO<sub>2</sub> and ZnO. These materials have become popular for their UV filtration and absorption properties and because they reduce the chalky appearance of traditional formulations. Various modifications to the standard TiO<sub>2</sub> or ZnO MNMs has been reported to increase the sun protection factor (SPF) even further<sup>164, 165</sup>. Many of the investigative techniques utilized for assessment of topical drug delivery systems are being used to understand how nanotech products in cosmetics affect (or penetrate) the skin. Health-wise, physico-chemical characteristics which may be important in understanding MNM safety in cosmetic products include particle morphology, size (distribution), surface chemistry, surface coating, surface charge, specific surface area, pore density, porosity, water solubility, agglomeration or aggregation, crystalline phase, crystallite size, photocatalytic activity, valance of hydrophobicity and hydrophilicity, redox potential, and the potential for free radical formation<sup>166</sup>.

**Table 3:** Possible transformations of Ag, TiO<sub>2</sub> and ZnO MNM in cosmetics. Specific studies cited when possible.

Transformation Process	MNM Affected	Life cycle activity	Change to Particle	Possible Implications	Representative Example(s)
Oxidation	Ag	Contact with fresh water	Dissolution	Increased toxicity	Increased toxicity





	TiO <sub>2</sub>	Contact with pool water	Surface Transformations	Change to particle stability	Protective coatings stripped from particles <sup>167</sup>
	MNM Coating	Various	Desorption or destruction	Change to particle stability, toxicity, etc.	Change in stability <sup>36</sup>
Dissolution	Ag	Contact with water	Ion formation	•Dissolution •Increased toxicity	Dissolution in environmentally relevant and processed waters
	ZnO	Contact with water	Ion formation	•Dissolution •Increased toxicity	Dissolution in environmental and biological media <sup>168</sup>
	ZnO	Contact with water	Re-precipitation	Precipitation with carbonate, potentially decreased toxicity	Precipitation in sea water <sup>169</sup>
	TiO <sub>2</sub>	Contact with pool water	Ion Formation		Dissolved species detected <sup>170</sup>
UV Irradiation	Ag	Use in sun	Surface Transformations	Breaking down MNM coating	Susceptibility to agglomeration or dissolution
	ZnO	Use in sun	Surface Transformations	Breaking down MNM coating	N/A
	TiO <sub>2</sub>	Use in sun	Surface Transformations	Breaking down MNM coating	• Produce reactive oxygen species (ROS) •Aggregation and settling
Micellation	ZnO	Bathing	Form stable suspensions	Surfactants cover MNM	N/A
	TiO <sub>2</sub>	Bathing	Form stable suspensions	Surfactants cover MNM	N/A

Studying possible transformation of MNMs used in sunscreens and cosmetics is of particular interest because there is a high exposure potential; both for human exposure since the products are intended to be used regularly and directly on the body, and for environmental exposure after use<sup>166, 171</sup>. TiO<sub>2</sub>, ZnO, or Ag MNMs are dispersed in products and will be readily released during product use: sunscreens and cosmetics are washed off during bathing or swimming and almost all of the original product is released either into wastewater or directly into rivers<sup>172</sup>. Estimates of MNM release from these items during use range from 75% to 95%<sup>20, 24</sup>. Initial releases will be to water, soils and larger water bodies, which are likely to be the final fate, but in some cases only after passing through WWTPs. This creates a large opportunity for many transformations of the particles (Table 3).

TiO<sub>2</sub> particles themselves are photocatalytic<sup>173, 174</sup>, but this effect is minimized through coating the particles with magnesium, silica, alumina, zirconium and/or in combination with various organic coatings to ensure their safety in lotions and to prevent the generation of reactive oxygen species<sup>175, 176</sup>. Over time, these inert coatings may break down if they are not able to withstand UV illumination or dispersion in water during its lifecycle, therefore exposing the TiO<sub>2</sub> core<sup>36</sup>. While surface transformation of the particle coating in part or in whole is likely, the particle core itself will probably remain intact. Variable efficiency of the coatings to protect particles during direct<sup>177</sup> and indirect UV exposure, in addition to modifications during different exposure scenarios, have been observed. For example, Auffan et al. noted that during the aging of TiO<sub>2</sub> MNM with two successive protective layers (one organic, one inorganic) used in cosmetics, 90% of the total Si of the organic layer was desorbed while the remaining fraction was surface oxidized<sup>36</sup>. The inorganic layer (consisting of Al(OH)<sub>3</sub>) was affected to a lower extent and continued to protect against photocatalytic superoxide formation. Degradation byproducts of the same material were tested by Labille et al under simulated natural sunlight and water chemistry, where the authors



found that depending on solution pH, ionic strength, and NOM concentration, variable amounts of aggregation and settling of TiO<sub>2</sub> MNMs were observed<sup>178</sup>. In a continuation of these two studies, Foltete et al. exposed *V. gaba* plantlets to the altered TiO<sub>2</sub> MNMs where the particles were found to be internalized in the root tissue, yet no toxic biological effects were observed<sup>179</sup>. The authors suggest that this is in contrast to other plant studies involving bare nano-TiO<sub>2</sub>, where adverse genotoxic effects were demonstrated upon particle uptake<sup>180</sup>. Thus, it was concluded that particle behavior is dictated by surface modifications. Aging commercial sunscreens to access transformations over their life cycle, Botta et. al found that a significant fraction of TiO<sub>2</sub> MNM residues were released from four commercially available sunscreens tested. The creams were submitted to artificial aging simulating drastic environmental conditions (UV/visible irradiation, water and stirring)<sup>37</sup> which resulted in agglomeration and sedimentation of the MNMs. With the use of FFF-ICP-MS, Nischwitz et al. developed a method to extract and size the composition of primary particles in a selection of sunscreen formulations<sup>181</sup>, though no prior aging of the sunscreens took place.

ZnO particles will experience the same light and aqueous environment as TiO<sub>2</sub> particles, but transformation products will be significantly different<sup>182</sup>. Photo transformations possible include transformation on the skin and involve consideration of how the coating of the material reacts when exposed to UV which can be different for different formulations of sunscreens/cosmetics. Exposure to water will induce dissolution of ZnO particles if/when the surface coating is desorbed<sup>168</sup>, and in certain water systems, such as pool water, oxidants present may increase the rate of coating degradation. After ion formation, Zn carbonate may precipitate, especially in fresh and sea waters<sup>169</sup>.

Both TiO<sub>2</sub> and ZnO MNMs may also be altered via soaps and/or detergents during shampooing the hair/body or laundering of clothing. Addition of surfactants may result in a more stable MNM suspension as a whole by creating micelles. However, since shampoo is always used with water (where dissolution may be a prominent factor in the case of ZnO), the resulting transformation(s) may not be easily determined. Phosphate containing detergents (where sold) may form Zn phosphates. EDTA, a chelating agent, is known to dissolve and subsequently stabilize metals in solution. Notably, some of these transformations may happen in tandem (e.g. UV plus oxidation in pool water) while others have sequential transformation steps (e.g. ZnO dissolution in water then re-precipitation as zinc carbonate or zinc phosphate). In swimming pool water, protective coatings may be stripped from TiO<sub>2</sub> particles<sup>167</sup>, and in some cases even result in dissolved species in the water<sup>170</sup>.

Ag MNM are used in cosmetics such as creams and lotions, in addition to soaps and toothpastes. Traditionally, conventional forms of Ag (e.g. silver salts, etc.) have been shown to be a safe and stable preservative. Previously the Ag active ingredient was physically separated from cosmetic components either through precipitation or micellation, which compromised its antimicrobial effectiveness. The use of Ag MNM could alleviate this problem by forming stable suspensions and preventing both primary contamination of the products during formulation, production or manufacturing and secondary microbial contamination when consumers open and close cosmetics containers. To date, Ag MNMs are generally considered safe since the first results show that they are not able to penetrate healthy human skin<sup>183</sup>. However, when the barrier function of the skin is disrupted, either through irritations such as rashes/allergies or cuts/abrasions on the surface, MNMs could penetrate the skin surface. In these cases, low cytotoxicity is still expected because the proportion of Ag MNM penetrating the skin barrier is still likely to be low. As was the case with ZnO particles, when Ag MNM is exposed to UV light through wearing the product, surface transformations of the particle capping agent can be expected. These transformations will vary depending on the specific capping agent in question. Furthermore, when the product is exposed to water, dissolution of Ag MNM to Ag<sup>+</sup> will occur, especially when the capping agent has been compromised.

## 2.4. Paints and Coatings

Many commercial paints used for both indoor and outdoor application contain substances which protect against microbial, physical, and/or chemical deterioration. Addition of MNM to coatings can upgrade many properties of the coating and produce multipurpose coatings with little cost difference<sup>184</sup>. Touted advantages include better surface appearance, good chemical resistance, decreased permeability, optical clarity, increased thermal stability, easy to clean surface, anti-reflective properties, and more. Modern formulations may implement MNMs to



accomplish preservation and anti-fouling through the use of nano-Ag, nano-Cu, nano-ZnO, nano-TiO<sub>2</sub> and nano-SiO<sub>2</sub><sup>185</sup>. Photoactive MNMs, such as ZnO and TiO<sub>2</sub>, are used because they adsorb UV-light and generate reactive oxygen species, which negatively impact bacterial growth, again with the intention of keeping the paints and coatings clean. However, in addition to working as an anti-microbial agent, this process may either initiate or accelerate the degradation of the paint matrix itself.

**Table 4:** Possible transformations of Ag, TiO<sub>2</sub> and ZnO MNM in paints and coatings. Specific studies cited when possible.

Transformation Process	MNM Affected	Life cycle activity	Change to Particle	Possible Implications	Representative Example(s)
Dissolution	Ag	Contact with rain water	Ion formation	Leaching to soil, increased toxicity	Outdoor ambient weather produced strong Ag runoff <sup>33</sup>
	Ag Zeolite	Contact with rain water	Ion formation	Leaching to soil, increased toxicity	N/A
	ZnO	Contact with rain water	Ion formation	Leaching to soil, increased toxicity	Dissolution of NM in paint matrix, especially true with acid rain <sup>33</sup>
UV Irradiation	Ag	Surface finishing	Dissolution	Leaching to soil, increased toxicity	N/A
	ZnO	Surface finishing	Surface reactivity	Change in transformations	N/A
	TiO <sub>2</sub>	Surface finishing	Surface Transformations	Only surface functionality effected	N/A
	CNT	Surface finishing	Surface Transformations	Only surface functionality effected	N/A
Oxidation	Ag	Exposure to air	<ul style="list-style-type: none"> <li>•Oxidation by gaseous oxidants such as NOx or ozone</li> <li>• Surface changes due to cleaning</li> </ul>	<ul style="list-style-type: none"> <li>• Surface less stable/degrade coating(s)</li> <li>• Increased dissolution if cleaned with aqueous solution</li> </ul>	N/A
Release	all	Weathering	Release in matrix-bound form	NM less reactive	NM released in matrix <sup>33, 34, 186</sup>
	all	Renovation, Disposal	Release in matrix-bound form into air	Transfer to soils via atmosphere	NM released in matrix <sup>33, 186</sup>

Physical transformation of MNMs embedded in paints and coatings can begin before they are even subjected to environmental weathering. Direct or indirect MNM exposure may occur in both the production and application of nano-paint formulations, in addition to subsequent finishing and renovation. Dust particles will inevitably be generated during sanding and other finishing or renovation processes<sup>187, 188</sup>. While there is only inconclusive evidence that there is a change in the number concentration of different size fractions of dust after sanding nano-enhanced surfaces compared to sanding conventional paints, it was evident that any released MNM during sanding did not occur as individual particles<sup>103, 189</sup>. Rather, Koponen et al. suggested that emitted particles agglomerate and or attach onto coarser particles generated by the sanding machine and so generally the sanding dust particles consisted of product fragments with embedded or attached MNMs<sup>103</sup>.

Many paints and coatings will experience outdoor weathering conditions, such as UV irradiation, rain, and pollution, which can both chemically and physically change the MNMs. TiO<sub>2</sub> has a capability to absorb UV radiation and this property can extend excellent weatherproofing properties to paints, which may prolong the life of



products, though more detailed study is needed to understand under which conditions this is possible<sup>190</sup>. While initial UV illumination and ROS generation appears to positively influence paint qualities, during the weathering of paint containing these pigments, the oxidation which occurs at the surface layer of the material eventually erodes the particle coating leaving an exposed particle surface<sup>191, 192</sup>. This may give rise to either “chalking” of the paint surface or release of MNM (agglomerates) as the paint ages. In just one example, Kaegi et al (2008) found that TiO<sub>2</sub> particles were detected in aged paint runoff, and 85-90% of the total Ti was in the 20-300 nm size range<sup>33, 34</sup>. Electron microscopy revealed that the released particles occurred either as agglomerates or as individual particles, but of specific importance was that they were still embedded in the organic binder. The same authors found a similar result when investigating Ag MNMs in aged paint, though in this case some evidence was provided from EDX analysis to suggest the formation/release of Ag<sub>2</sub>S (but not AgCl). Depending on the nature of the TiO<sub>2</sub> MNMs (synthesis process, annealing), the “TiO<sub>2</sub> MNM film” can show super hydrophilic properties<sup>135</sup> that are susceptible to increase the surface degradation rate. TiO<sub>2</sub> reacts with NO to form NO<sub>2</sub> and oxidizes organic molecules to form CO<sub>2</sub> but its photo-activity readily decreases when it is coated<sup>154</sup>. These studies suggest that the behavior of actually used MNMs in their respective matrix is much more complex than the study of pure MNMs in water<sup>193</sup>.

Conversely, the incorporation of ZnO MNMs significantly reduces the extent of photo degradation of the host matrix due to its superior UV light screening effects, which increase the durability of paints and as the particles dissolve there is no issue with chalking or MNM release.<sup>194, 195</sup> Thus, unlike TiO<sub>2</sub> particles which degrade, the ZnO MNMs will dissolve. This would be especially evident in areas suffering from acid rain, which with a pH ranging from 5 – 6, has the capability to totally leach the Zn from the paint matrix over time.

Interest is growing in the use of nano-Ag in paints because of its biocidal properties. Ag is not always added as particles or salts, but also as silver zeolite (paints containing on average just 2.5% silver)<sup>196</sup>. However, regardless of the form it is in, because Ag dissolves readily it will likely wash out of the paint into rain water, and thus release Ag<sup>+</sup> directly to the environment. In one example, paints containing nano Ag that were exposed to ambient outdoor weather for one year showed strong leaching of MNMs (mostly < 15 nm, attached to the organic binders of the paint) during initial runoff events<sup>197</sup>. The released particles showed the possible presence of Ag<sub>2</sub>S formed with trace amounts of sulfur species present in the atmosphere and/or Ag<sub>2</sub>O.

Considering that paints have a longer lifespan than other applications (10 – 20 years), other hypothetical considerations can be made concerning the release and degradation rate of MNM from the paint matrix. In city situations, effects of NO<sub>x</sub> from car exhausts and the effects of ozone may both oxidize the surface of the particles over time. Additionally, the influence of seasons with hot/cold cycles can degrade the paint matrix allowing increased release of NM into the environment. However, this would not necessarily change the type of transformations incurred by the MNM.

Innumerable coatings exist which all aim to improve the characteristics of the base material. MNM coatings being developed range from fabric coating for water and stain resistance<sup>198</sup>, to antimicrobial coatings for infection prevention<sup>199</sup>, to product preservation, to conductive coatings for solar cells, to scratch resistant coatings in the field of optics, to anti-fouling coatings for marine applications<sup>198, 200</sup>. The products generally focus around the medical field<sup>201</sup> and include coatings on medical instruments<sup>202</sup> and surfaces<sup>201</sup>, in catheters<sup>203, 204</sup> and in wound dressings<sup>205, 206</sup>. Exposure to oxidants in cleaning agents, likely will dissolve the particles. Depending on oxidant strength/exposure time, this may just oxidize the particle surface or capping agent of the particle. More degradation (oxidation, transformation, etc.) may occur after multiple exposures to oxidants, i.e. multiple cleaning events. This subsequent use would change the transformation behavior but there has been little study on how these dilute multiple exposures to oxidants (such as with cleaning) effect MNM persistence in coatings.

## 2.5. Plastics and Polymers

While the MNMs used in commercial plastics and polymers may be transformed during the use of these materials, the major transformations will likely be during the disposal of the materials (Table 5). Ag MNMs, ZnO, TiO<sub>2</sub>, and CNT are all currently being implemented in a variety of products on the market today. The purpose of implementing MNM into these materials ranges from antibacterial properties to increased strength.



**Table 5:** Possible transformations of Ag, TiO<sub>2</sub> and ZnO MNM in plastics and polymers. Specific studies cited when possible.

Transformation Process	MNM Affected	Life cycle activity	Change to Particle	Possible Implications	Representative Example(s)
UV	All	Outdoor weathering	Oxidation of surface	Destroys polymer binder	Coating particles inhibits binder destruction <sup>207</sup>
Incineration	CNT	Waste incineration	Destruction	Removes CNTs from further environmental consideration	N/A
	MNM coating	Waste incineration	Removal of organic coating	Destroy coating	N/A
	Ag	Waste incineration	Oxidation	Oxidize particle	N/A
Dissolution	All	Acid washing incineration ash	Dissolution	Dissolved species (Ag, Zn) and bare particles (TiO <sub>2</sub> )	N/A
Structural Transformation	TiO <sub>2</sub>	Waste Incineration	<ul style="list-style-type: none"> <li>• Change in crystal structure</li> <li>• Calcination</li> </ul>	<ul style="list-style-type: none"> <li>• Rutile less photo-reactive than anatase but rutile is more stable</li> <li>• Change in reactivity or effectiveness</li> </ul>	Calcination and change in particle crystal structure
Aggregation	TiO <sub>2</sub>	Waste incineration	Aggregation	Decreased thermal stability of composites	Aggregation of particles <sup>208</sup>

Many MNM-enhanced (composites) plastics and polymers are intended for outdoor use and thus will be exposed to UV rays. Destructive oxidation of the polymer matrix may be reduced through surface treatments of the imbedded particles. For TiO<sub>2</sub> MNM composites, part of the process leading to the polymer breakdown is induced by the photoactivity of TiO<sub>2</sub> MNMs via localized sites on the particle surface. Coating the particles would occupy these “defect sites” and inhibit the reduction of TiO<sub>2</sub> by UV light and, consequently, prevent some destruction of the polymer binder<sup>207</sup>. Exposure of nano-doped polymers to UV light was studied by Nguyen et al.<sup>209</sup> Amine-cured epoxies doped with either SiO<sub>2</sub>NP or MWCNT exposed to realistic environmental conditions (50°C, 75% RH) showed variable mass losses created by photo-oxidative chain scission. The same behavior was observed with other polymer composites (see Najafi et. al, for instance<sup>210</sup>). In such configurations, aging proceeds via oxidation on the surface layers of the composite material, which eventually erodes. Continuing on the work of Nguyen et al., Gorham and colleagues observed macroscopic changes to the polymer matrix through degradation, such as increased roughness and the appearance of cracks<sup>211</sup>. MNMs tended to gather at the surface and thus release of the embedded particles was made possible, provided that extra mechanical energy was applied and/or there was poor dispersion of the particles in the matrix<sup>212</sup>.

Plastics may be acid washed during recycling, where an acid wash is used as a preparation/cleaning step to remove dirt or debris from the surface. Here, TiO<sub>2</sub> and ZnO will behave as described above, with TiO<sub>2</sub> being resistant to change and ZnO entirely dissolving. Other MNMs incorporated into the packaging, such as Ag MNM into food packaging, would also likely be dissolved during this cleaning process. At the end of their life cycle, plastics will generally be disposed of in solid waste, either as raw products transported directly to a landfill or as incineration byproducts. Here, landfills are considered a final sink for the MNMs and, if incinerated, residual material is either found in the bottom ash or the filter ash, where either process would burn away any organic coatings the particles processed initially, as discussed previously.

If CNTs are embedded in a polymer and the polymer degrades, then the coating/functionality on the CNT surface would also likely degrade. Essentially no outright transformation of CNTs would be observed. However, transformation may include breaking, such as when CNTs are released from polymers. General transformations of CNTs include shortening of tubes, oxidation of whole tubes, and surface oxidation of the tubes (either the coating or the surface of the tubes themselves). Natural water and/or sunlight (photo-oxidation) can affect the colloidal stability of CNT.



## 2.6. Consumer Electronics, Semiconductors and Magnets

A large number of MNMs are encountered in this domain of application. ZnO, ZnS, Ag, Al oxides, TiO<sub>2</sub>, Ag, SiO<sub>2</sub>, Co, CdS and CdSe quantum dots, CNTs: virtually all MNMs are possible candidates for nanostructures to improve materials in this sector. For the review here, we consider the transformations of TiO<sub>2</sub> and Ag (Table 6), as these were the two most prominent MNM categories found in Figure 2.

**Table 6:** Possible transformations of MNMs in consumer electronics, semiconductors and magnets. No studies could be cited here.

Transformation Process	MNM Affected	Life cycle activity	Change to Particle	Possible Implications	Representative Example(s)
Acid Wash	Ag	Treatment of e-waste	Dissolution	Ion formation	N/A
	TiO <sub>2</sub>	Treatment of e-waste	Surface Transformations	Dissolve surface coating, bare particles behave differently	N/A
Incineration	CNT	Waste incineration	Destruction	Decreased risk from CNT	N/A
	MNM coating	All	Removal of organic coating	Change in stability	N/A

Considering TiO<sub>2</sub> MNMs, if products are treated as e-waste after disposal then the products will be acid washed, and metals fractionated and collected. This would only affect the surface or capping agent of the TiO<sub>2</sub> particles, as acid washes are unlikely to dissolve the entire particle. If, however, consumer electronics are not specially recycled and are disposed of into a standard landfill, we could consider this a final sink as discussed earlier.

Ag MNMs possess a strong surface plasmon-polariton resonance that make them an interesting candidate for nanophotonics applications. However, this property was found to be altered after tarnishing of the surface during aging in ambient air of nano-Ag arrays, observed as a decrease and red shift of the resonance peak<sup>213</sup>. The authors attribute this to the chemisorption of sulfur (via H<sub>2</sub>S present in the air) and the conversion of Ag to Ag<sub>2</sub>S on the nano-array surface. It is noteworthy that this reaction proceeds at a greater rate than at bulk Ag surfaces (a few nm/day) but preserves the spherical shape of the particles. There are not many possibilities for Ag to be released during the use of consumer electronics, but as with the TiO<sub>2</sub> particles discussed above, it is possible during recycling. Both the acid and heating steps could dissolve the particles.

## 2.7. MNM in the Food Sector (Additives and Supplements)

Numerous nanostructures are used in the food and drug industry today, many of which are naturally occurring, i.e. traditional food nanotechnology that has been used to improve the textural and nutritional properties of food for many years<sup>214</sup>. Examples of these include proteins, lipids, and nanostructured emulsions. On the other hand, MNMs are being developed that have the potential to improve foods: making them tastier, healthier, more nutritious, longer lasting, safer and even more vibrant (visually appealing) with nano-dyes and colorants. MNMs in the food industry can be divided into two groups: organic engineered MNMs and inorganic, surface-functionalized materials, the latter of which is focused on in this review. 57.3% of the food and beverage products currently on the market contain colloids of zinc, TiO<sub>2</sub>, or other inorganic substances and a sizeable portion of products also contain nanosilver, with nanosilver coating being used in kitchen ware<sup>215</sup>.

Nanotechnology applications in the food sector are relatively recent, but the main developments thus far have been aimed at altering the texture of food components, encapsulating food components or additives, developing





new tastes and sensations, controlling the release of flavors, and/or increasing the bioavailability of nutrients<sup>216</sup>. Ag MNM incorporation into food products has been increasing, either implemented as an additive or as a nutraceutical (health supplement). Two recent patents integrate Ag MNM into products to inhibit bacterial and fungal growth<sup>217</sup>. The first claims to improve the quality of freeze-dried food using ozone, ultra violet light, and a nanosilver coating to sterilize the product and control microbial growth<sup>217</sup>. The second product uses Ag as an antibacterial additive during the production of wheat flour<sup>216</sup>. Taken as a supplement, aqueous dispersions of nanosilver are available from a number of commercial sources.

Food grade TiO<sub>2</sub> is available by the tonne for use in the food and beverage markets and it represents the bulk of commercially used whiteners in these industries. However, few studies are available that report the content of TiO<sub>2</sub> in commercial products<sup>39, 218</sup>, and they do not necessarily discriminate to studying materials only in the nano-range. Weir et al. found that only a small percentage of the products with the highest overall Ti concentrations would pass through a 0.45 micron filter, but attributed this to incomplete degradation of the food product due to their sample preparation methods<sup>39</sup>. The authors suggest additional research be conducted simulating stomach digestion fluids to better understand the ultimate size fractions of Ti in digested food.

Ingestion of MNM-enhanced food or drink is the main pathway for both human exposure and MNM transformation (Table 7). A healthy digestive system only allows absorption of nutrients from the gut after digestion of foods. As nano-sized particles are likely to have a greater ability to cross the gut wall than larger sized particles and therefore increased internal exposure of some substances may result because of their enhanced absorption and bioavailability. The potential effects of MNMs, and their transformations, as they move through the gastrointestinal (GI) track have not been definitively documented for a wide range of test subjects, let alone humans. One must consider the transformations inside the stomach and gut, where it is very acidic and a multitude of enzymes are present. Subsequently, once the material moves to the intestine, there is a drastic change in environment: both changing the pH and becoming anaerobic. The behavior, interaction and fate of MNM in the GI tract makes it unlikely that NMs will remain as free particles given the chemical environment. Transformations in the gut may include agglomeration, adsorption or binding with other food components, reaction with acid and digestive enzymes etc. A more complete discussion of possible MNM translocation within the gut and potential health effects can be found in a review by Chaudhry et al.<sup>216</sup>. These knowledge gaps make it difficult to speculate regarding the precise changes an MNM may experience after consumption. Ultimately, nanomaterials (or MNM transformation by-products) from foods will be discharged as feces/urine and enter wastewater treatment plants.

**Table 7:** Possible transformation reactions of MNM in food. Specific studies cited when possible.

Transformation Process	MNM Affected	Life cycle activity	Change to Particle	Possible Implications	Representative Example(s)
Dissolution	Ag, ZnO	GI tract after ingestion	Interaction with enzymes in acidic environment	Unknown	N/A
Phase transformation	Ag	GI tract after ingestion	Sulfidation, AgCl complexes formed	Unknown	<ul style="list-style-type: none"> <li>• Formation of Ag/Cl/S complexes from Ag MNM and AgNO<sub>3</sub><sup>219</sup></li> <li>• Production of AgCl from Ag MNM<sup>220</sup></li> </ul>
Degradation	MNM coating	GI tract after ingestion	Degradation of coating	Unknown	N/A
Physical Transformation	Ag	Oral ingestion	Agglomeration, complexation with Cl, S	Liver damage (rats)	<ul style="list-style-type: none"> <li>• Oxidative and inflammatory effects to rats from orally fed Ag MNMs, 81 days<sup>221</sup></li> <li>• Review of oral toxicity to Ag MNM, ions and colloids<sup>222</sup></li> </ul>
	All MNM	Ingestion and movement through the body	Agglomeration, aggregation adsorption or binding with other	Unknown	<ul style="list-style-type: none"> <li>• Aggregation of smaller Ag NP more larger particles in stomach acid<sup>223</sup></li> <li>• Review of physical</li> </ul>





food components

transformation and  
translocation in cells<sup>216</sup>

Initial experiments determining alterations in physical state of Ag MNMs exposed to synthetic human stomach fluid have shown that the particles change in zeta potential, aggregation and morphology in addition to the production of silver chloride which appeared physically associated with particle agglomerates<sup>224</sup>. A second study exposing Ag MNMs and AgNO<sub>3</sub> to saliva, gastric and intestinal digestion also found silver chloride associated with Ag NP clusters and noted importantly that intestinal digestion of AgNO<sub>3</sub> in the presence of proteins resulted in particle formation, comprised of silver, sulphur and chlorine<sup>219</sup>. Short 30 minute exposures of a variety of Ag MNMs to synthetic stomach fluid suggested that smaller particles (<10 nm) aggregated more readily than larger particles (75 nm) and there was a suggestion that particle surface coating could vary transformations<sup>223</sup>. More complex dietary exposure tests have been performed where the authors found liver damage to rats orally fed Ag MNMs for 81 days, demonstrating possible oxidative and inflammatory effects of Ag MNMs<sup>221</sup>. A broader review on the oral toxicity of Ag ions, Ag MNMs and colloidal silver has also recently been published<sup>222</sup>. Some additional experiments which may prove useful to determine exposure would be the PBET test (physiologically based extraction test) which could be useful to determine how much of the metal can be solubilized when ingested and investigation into how MNMs with strong antimicrobial activity (e.g. Ag MNM) would affect the natural microflora of the gut.

## 2.8. Food Containers and Packaging

The incorporation of MNMs in food packaging materials may have several advantages compared to traditional materials ranging from extension of food life to improved food safety to alerting consumers of food contamination or spoiling. Incorporation of MNMs may add various functionalities to the matrix, such as antimicrobial activity or acting as a barrier against movement of gasses, volatile components (such as flavors) or moisture, depending on the MNM composition. MNMs can also be beneficial to the polymer itself, such as increasing polymer mechanical strength, addition of reinforcing compounds (fillers), decreasing package weight and eco-friendly biodegradable qualities. A few comprehensive discussions of the use of MNMs, nanocomposites and carbon nanotubes in food packaging can be found in a number of recent reviews,<sup>214, 216, 217, 225-228</sup> including details about creating food packaging (nanocomposite structures, formations, distributions within the matrix), intelligent design (self-heating/cooling packages, nanosensors, biosensors) and more. Compared to inert substances, functionalized MNMs may be more likely to react with food components or be bound to the food and hence be inadvertently consumed. However, while nanoclays, nanosilica, and cellulose are frequently incorporated into food packaging, in terms of the MNMs reviewed for this lifecycle oriented review, there are fewer products being developed.

**Table 8:** Possible transformations of MNMs in food packaging. Specific studies cited when possible.

Transformation Process	MNM Affected	Life cycle activity	Change to Particle	Possible Implications	Representative Example(s)
Dissolution	Ag	Storing food	Ion formation	Release of Ag ions from impregnated containers leached onto food for consumption	Leaching Ag <sup>+</sup> from containers in food simulants <sup>229</sup>
UV Irradiation	TiO <sub>2</sub>	Storing food	Surface transformations	Unknown	N/A
Release of MNM from material	All	Storing food	Unbound from manufactured matrix	Release of MNM from impregnated containers leached onto food for consumption	<ul style="list-style-type: none"> <li>Some MNM release but consumer health risks minimal<sup>230</sup></li> <li>Longevity of release dependent on many</li> </ul>

Some food storage products featuring nanosilver for their antimicrobial properties are available commercially, including some storage containers, plastic bags, and baby milk bottles in addition to kitchenware, tableware and refrigerators that have active coatings<sup>216</sup>. However, the growth potential for products using Ag MNMs in food packaging has been stunted because the US Food and Drug Administration (FDA) has approved its use in <5% of applications for use in food contact surfaces<sup>231</sup>. Additionally, Ag in nanoparticulate form has to be registered in the United States by the Environmental Protection Agency and the use of Ag NMs in plastic food containers is not currently authorized in the European Union<sup>232, 233</sup>. The European Food Safety Authority has listed Ag zeolites in a provisional list of additives, as long as the current migration limit of 0.05 mg Ag (in ionic form generally, but for NMs this would be both nano and ionic forms) kg<sup>-1</sup> food is observed. Since nano-sized silver (and limited nano-silver zeolite) particles for food packaging and storage are not yet a wide-spread viable option, the incorporation of micro and macro-sized silver zeolites have been alternatively investigated<sup>234</sup>. This approach has proven useful as larger sized Ag particles also function as an anti-bacterial agent through the release of Ag<sup>+</sup> and are used in other products such as plastics, stainless steel and fabrics<sup>196, 235, 236</sup>. Therefore, the food industry may soon follow suit. While nominally the silver-zeolite particles are outside the nanoscale, their release of Ag<sup>+</sup> contributes to a similar bactericidal mode of action as MNMs, and thus these transformation processes may still be relevant.

While not representing a large market share of their material categories, it is worth mentioning that other MNMs are used in food containers. Nano-ZnO and TiO<sub>2</sub> have also demonstrated antimicrobial properties. Compared to nanoAg, these compounds may provide a more affordable and safe food packaging solution. A nano Plastic Wrap from SongSing Nano Technology Co. Ltd contains a nano-ZnO based light catalyst, which the company claims can be sterilized with indoor lighting. TiO<sub>2</sub> MNMs have shown promising results for incorporation into food packaging<sup>228</sup>, but since the antibacterial properties are derived from TiO<sub>2</sub> photocatalysis<sup>237</sup>, these products are only active in the presence of UV light.

Inorganic MNM can be easily incorporated into polymers and Ag MNMs can be engineered for controlled release allowing the antimicrobial agents to remain potent for a long period of time. Several factors influence the longevity of Ag MNM or ionic release from polymers including the degree of polymer crystallinity, filler type (i.e. silver particles, zeolites, etc.), hydrophobicity of the matrix and particle size<sup>228</sup>. Hypothetically, when Ag MNM enhanced food containers and packaging are recycled or disposed of, Ag<sup>+</sup> ions may leach from the product either during acid washing (pre-recycling step) or when in contact with water (disposed in landfill).

As is the case with many plastic additives, Ag MNM are not covalently bound to the plastic matrix and are intended to be released during use. The main consumer concern around nano-enhanced food storage is the migration onto/into the food or drink for consumption. If this were to happen, the NMs would experience a similar fate moving through the GI tract as the MNMs used as food additives detailed above. Migration of Ag MNMs from plastic bags into food simulants was studied by Huang et al., where they found a maximal migration rate of 8 ng Ag cm<sup>-2</sup> after 10 days at 25°C in 4% acetic acid<sup>238</sup>. Ag-impregnated plastic food containers were shown to release a maximum Ag concentration of 0.9 mg/L in 5% acetic acid after 7 days<sup>239</sup>. However, in both these studies, the Ag form was not determined. Research presented by Goetz et al. differentiated between ionic and particulate Ag release from plastic food containers using different food simulants<sup>229</sup>. Most of the Ag release was in ionic form, but approximately 12% was found to be Ag MNMs. The authors determined the released Ag exposure potential to be low in relation to general background silver exposure, especially since multiple testing cycles of the plastic showed decreased release rates of Ag. Therefore, consumer health risks from Ag MNMs leaching into food from Ag-doped food containers seems unlikely.

## 2.9. Air Filters



Nanocatalysts can play a crucial role in air filtration applications related to odor removal and chemical remediation. Indoor air quality can be a serious health problem, especially in highly dense cities where vehicle exhaust and new construction materials can lead to lengthy exposure to volatile organic compounds (VOCs) and oxides of nitrogen and sulfur ( $\text{NO}_x$  and  $\text{SO}_2$ ). Conventionally, air purifiers are used to sorb VOCs to filters (e.g. granular activated carbon) but this only transfers contaminants from a gaseous to solid phase, requiring further disposal, instead of eliminating the VOCs directly. To combat this issue, a photocatalytic process using thin film nano- $\text{TiO}_2$  as an advanced oxidation process has emerged as a promising alternative to degrade VOCs directly<sup>240-242</sup> (Table 9). In general,  $\text{TiO}_2$  is immobilized on beads, hollow tubes, woven fabric, or silica gel using various deposition methods such as dip coating and sol-gel formation<sup>243</sup>. The photocatalytic oxidation of VOCs by nano- $\text{TiO}_2$  can be further enhanced by coupling the technology with activated carbon (AC) or CNTs<sup>244</sup>. These electro-spun nanofibers of CNT- $\text{TiO}_2$  photocatalysts could be produced into mats that can be directly placed into current high-efficiency particulate air (HEPA) glass-fiber filter systems<sup>245</sup>, which could potentially extend the life of the filters, prevent secondary re-aerosolization of organic contaminants or biological organisms during maintenance and facilitate regeneration of the filters with UV illumination thereby decreasing the need for frequent replacement<sup>246</sup>. It is not only traditional air filtration systems, such as HEPA filters, where such approaches can be implemented, but MNM can also be incorporated into everyday items to increase their functionality. Thus, nanophotocatalysts can be used in curtains, blinds, or glass where naturally available UV sources are used to activate and purify air, as well as to destroy pathogenic microorganisms<sup>247-249</sup>.

A number of studies indicate that nano- $\text{TiO}_2$  exhibits cytotoxicity in different cell cultures because it catalyzes the formation of superoxide,  $\text{H}_2\text{O}_2$ , and hydroxyl radicals. However, the  $\text{TiO}_2$  embedded in air filters are unlikely to leach into an environmental setting. Rather,  $\text{TiO}_2$  MNMs incorporated into the filter matrix will be disposed of as e-waste (in Switzerland) while in many other countries, this and similar products may end up in landfills. Landfills are very complex systems, but when they are built to the newest standards they can be considered final sinks for the purposes of this review, and so no further transformation of either nano- $\text{TiO}_2$  or CNTs needs to be considered for this scenario.

**Table 9:** Possible transformations of MNMs in air filters and fuels. No studies can be cited at this time.

Transformation Process	MNM Affected	Life cycle activity	Change to Particle	Possible Implications	Representative Example(s)
UV Irradiation	All	Air filtration	Surface Transformations	Oxidation of capping agent or direct oxidation of surface	N/A
Incineration	$\text{TiO}_2$	After disposal	Surface Transformations	Organic particle coating/functionality burned but core intact	N/A
	CNT	After disposal	Combustion	Dependent on CNT structure and incineration temperature. No trace of MNM	N/A
	CNT	Product use	Incomplete Combustion	Dependent on CNT structure and incineration temperature. Preservation of CNT or change in surface properties	N/A
Combustion	CeO	Use of fuel	Surface Transformations	Coating completely oxidized. Particle may stay intact but change from $\text{Ce}^{+3}$ to $\text{Ce}^{+4}$ .	Hypothetical Only

Conversely, if disposal of the filters ends in incineration, only surface transformations would occur on the  $\text{TiO}_2$  particles and the core would stay intact, to be either accumulated in the bottom ash or fly ash. Some CNTs may be burned and some may not, depending on the CNT structure and temperature of incineration. In some incinerators, there may be cooler pockets inside where all CNTs may not combust and thus also be deposited in the ash from the incinerator. The non-combusted tubes may have been transformed through oxidation of the surface or



physical breakage of the tubes themselves. At this time, only mathematical modeling is available to determine the flows of MNM during waste handling and so specific transformations are not confirmed experimentally<sup>250</sup>.

## 2.10. Fuels, the energy sector and catalysts

CeO<sub>2</sub> MNMs are used as a diesel additive directly into fuel to catalytically promote soot oxidation and degradation. While it is not one of the four main material types covered by this review, it is included here because it involves the most rapid release and alteration process among the other transformation processes covered in this review. The fuel is exposed to high temperatures during use and any coatings on the MNM would be completely oxidized prior to release into the environment. The particle itself may stay intact, but the Ce<sup>3+</sup> on the surface could be changed to Ce<sup>4+</sup>, though no data currently exists on this possible reduction during or after the combustion process<sup>4</sup>. Sintering of the particles could be an important transformation, but for natural conditions this is not a relevant transformation because even in fuels, the particles would likely be too disperse and too dilute for this to be a major transformation pathway. Because most of the CeO<sub>2</sub> MNMs are likely to be captured by diesel filters or the catalytic converter<sup>251</sup>, its pathway to the landfill and/or to recycling is considered to be very important<sup>252</sup>. However, little is known about how materials flow through recycling plants for any MNMs and so determining how CeO<sub>2</sub> will make it back into the environment via this route remains to be investigated. Little is known on the fate and reactivity of nano CeO<sub>2</sub> once released into the atmosphere. CeO<sub>2</sub> MNMs can form secondary organic aerosols by adsorption of organic molecules onto their surface<sup>253</sup>. Because of its ability to adsorb oxygen at its surface defects (oxygen vacancies), CeO<sub>2</sub> MNMs were shown to efficiently reduce H<sub>2</sub>O<sub>2</sub>, a common constituent in the atmosphere<sup>254</sup> and to decarboxylate and polymerize small organic molecules<sup>255</sup>, thus altering a number of other atmospheric species.

Soot oxidation can also be promoted via catalytic converters. The thermal and chemical aging processes of the catalysts (Pt/Al<sub>2</sub>O<sub>3</sub>, Pd/Al<sub>2</sub>O<sub>3</sub>, etc.) are well documented. Physical modifications of the catalysts induced by thermal aging (at 700°C) only (i.e. no other treatments) include decreased surface area and increased heterogeneity of the spatial distribution of Pt or Pd within the alloy<sup>256, 257</sup>.

Carbon NMs, like CNTs, fullerene or soot, are the result of the incomplete combustion of hydrocarbons. Their fate and transformation in the environment are still in debate. CNTs have been found to display adsorption properties towards O<sub>2</sub><sup>258</sup> and N<sub>2</sub><sup>259</sup> but these highly crystalline structures seem to be quite stable towards oxidation by O<sub>2</sub> or O<sub>3</sub><sup>154</sup>. Soot, meanwhile, is an amorphous entity that is readily coated by organic molecules. A secondary organic aerosol is then formed via nucleation on the soot seeds with modification of their physico-chemical properties (absorption coefficient, hygroscopic growth factor).

The catalytic properties of MNMs are also utilized in both fuel cells and solar energy applications. The catalysts usually consist of nano-composites derived from mixtures of precursor MNMs with a defined stoichiometry. They are subjected to high temperatures and/or high irradiance during use and the major concern in terms of aging is the alteration/reduction of the performances of these assemblies. It was found, for instance, that Au NPs deposited on Indium Tin Oxide electrodes<sup>260</sup> and Pt-Cu alloy NPs electrocatalyst precursors<sup>261</sup> decreases their electrocatalytic activities, even at ambient temperature. In the case of solar energy thermal absorbers made of MWCNT/NiO composites, 200 h aging at 250°C, simulating a 25 year aging under normal use conditions, which induced a slight decrease in reflectance, correlated with decreases of C/Ni and of particle size<sup>262</sup>. As these are essentially closed systems that will go through a controlled disposal process (i.e. e-waste processing or disposal centers), there is little opportunity for MNMs to leach into the environment.

## 2.11. Remediation

Fe(0) MNMs have found interesting applications in contaminated groundwater and soil remediation. The fate of these MNMs is particularly interesting to study, as they will undergo aging processes under real environmental conditions. Oxidation will generally be the first transformation: once released into the atmosphere, Fe(0) will form Fe oxides and/or hydroxides. The question remains as to how reactive the MNMs will be and what parameters



may influence the rate of oxidation. Through passivation of pristine Fe(0) particles with a controlled air flow, the formation of a shell composed of iron oxides (magnetite, maghemite) and thickness-controlled to 5 nm, resulted in stable chemical patterns under atmospheric conditions<sup>263</sup>. Namely, the Fe(0) core seems to be protected from further oxidation by the oxidized shell, compared with pristine Fe(0) MNMs for which passivation seems to proceed throughout the whole material. Parameters such as the shape and size of the synthesized MNMs play a role in determining the thickness and evolution of this passivated protective shell upon aging<sup>264</sup>.

### 3. Conclusions

#### 3.1. Implication for Future Risk Assessment Protocols

Nanostructured materials have come into play in the consumer market after a relatively short development period. MNMs have been studied extensively for their desirable characteristics in relation to the development of products with distinct performance advantages but decidedly less is known about how the materials will transform under biological and environmental stresses. This situation is further complicated because materials that are chemically similar could be implemented into a variety of different products, each having a different life cycle. Depending on product specific transformations, different toxicological profiles and environmental fates could be possible for the same particle under different use conditions. Undertaking exposure and hazard assessment procedures is common practice in industry<sup>265</sup>. However, concerning MNMs, most products are assessed for toxicity and potential environmental harm on a cradle-to-gate basis, rather than on a cradle-to-grave basis. This leaves the onus for safe disposal on the consumer, public waste facilities, and regulatory bodies<sup>10</sup>.

First results indicate that much of the MNMs released from products are present in a matrix-bound form or as agglomerates, with lesser fractions of single, dispersed particles. This physical alteration could be beneficial for environmental health, as smaller sized agglomerates appear to be less toxic, have decreased reactivity compared to free NMs, and settle in sediments thereby slowing the movement of particles through the environment<sup>52</sup>. When released, MNMs that are still embedded in the nano-product will have environmental behavior closely linked with the properties of the matrix. However, this is product specific and will be highly dependent on the manufactured, tunable interactions between the particle surface coating and the matrix. With more research and development in this area, this interaction may be optimized over time, either to purposefully leach particles or retain them in the matrix. Surface coatings of the particles can play an important role in the stability of particles in both the short and long term. Alternatively some MNMs, such as Ag and ZnO, will dissolve in many environments and release ions. Agglomeration of particles, such as when used in sprays and sunscreens, will effect the particles fate in the longer term because once the particles become agglomerated there is little evidence they would revert to their initial primary particle suspension<sup>36, 178</sup>. The story of NOM and agglomeration is complex, however, and some studies indicate that depending on the NOM concentration (e.g. when NOM concentration is representative of environmental conditions), disagglomeration processes can play important roles and that kinetics (time) effects are important for the NM/NOM interactions<sup>266, 267</sup>. Finally, various temporal scales for assessment of fate & behaviour would be appropriate depending on the product and/or the environment that the particles are released in.

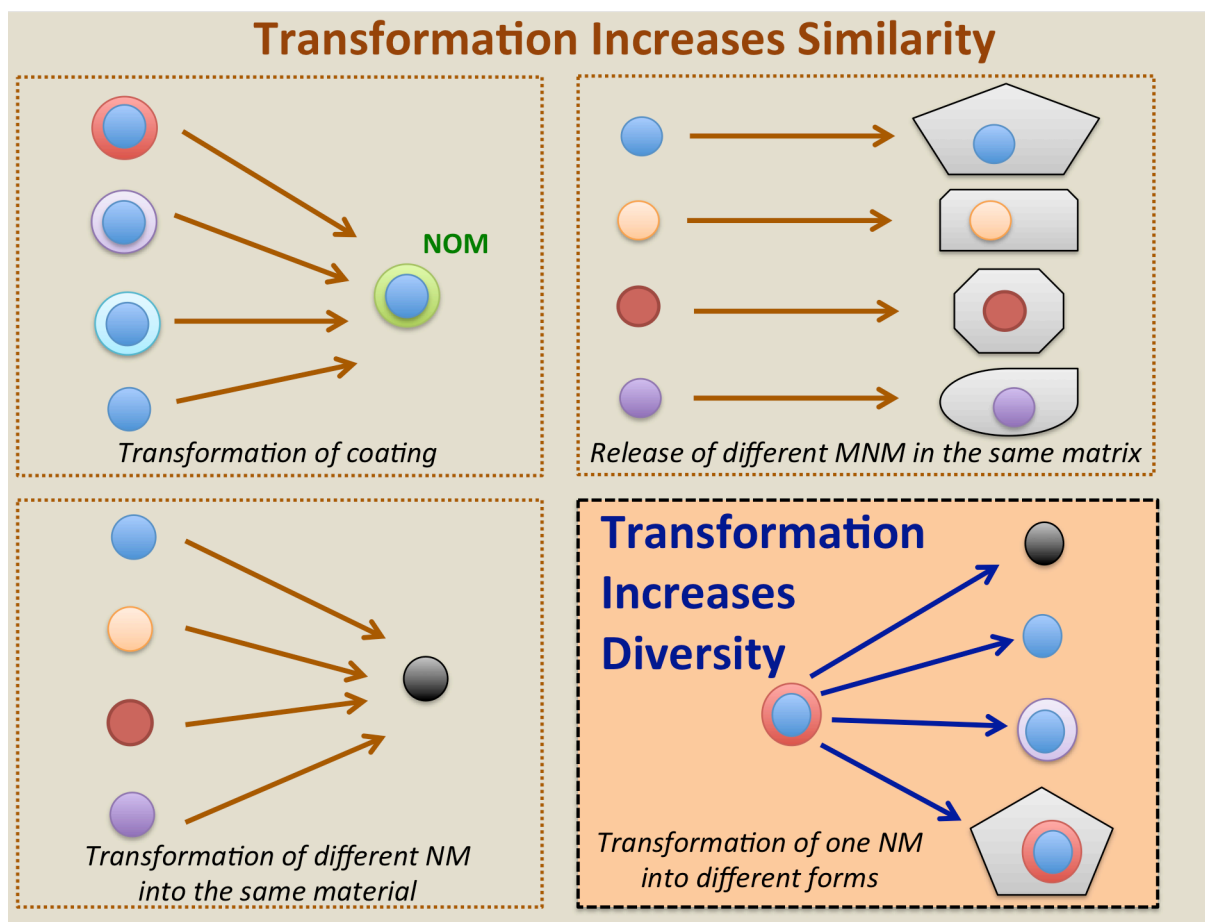
Regardless, it is clear that the released fraction of MNMs from nano-products no longer contains the primary particles uniformly dispersed in the matrix, but rather, a variety of different fragments, agglomerates, and transformed products that have significantly different physical and chemical properties than the original, as manufactured, MNMs. The implementation of additional real-world studies is called for to produce realistic information on the fate of MNMs after product release for environmental, toxicological, and modeling efforts. The true challenge lies in determining if the alteration of commercial MNMs/nano-products will release particles that have high(er) reactivity, or rather, if weathering will lead to various kinds of passivation (compared to the pristine or as-manufactured MNMs) through surface morphology, adsorption, surface redox evolution, or other mechanisms. This may necessitate guidance regarding which material testing protocols should be employed for different MNM that differ to a certain degree. While the results of some environmental and toxicological studies may seem ominous, the results should be kept in perspective. In many studies particles have been poorly characterized or not characterized at all making the relationship between cause and effects difficult to parse out. As risk assessment begins to adopt the incorporation of product modified MNM in EHS studies, and not just the



pristine material, scientists and the public will begin to have a more holistic picture of the true health and environmental impacts the growing field of nanotechnology may pose.

### 3.2. Moving toward building a useable database

Life cycle thinking in the context of nanotechnology is currently in its infancy. Potential advantages and improvements using MNMs are promoted constantly with less systematic understanding of what properties of MNMs in products could be harmful or produce unintended side-effects. Specifically, better understanding how the particles could transform through the life cycle to produce “unexpected” health and environmental consequences is important. The key here is to make information useful in a wider context, standardizing experimental results and determining which metric(s) are crucial for characterizing and predicting MNM transformations during release and exposure throughout the product life cycle. From the above discussion, it will be of interest to determine if the released and subsequently transformed MNMs result in a more similar or more diverse set of MNMs (Figure 6). Though extensive data are not available in this area, some scenarios may be: 1) environmental constituents, such as DOC, binding to particle surface effectively making MNMs more similar, 2) chemical reactions on the particle surface making different MNMs more similar (e.g. conversion of different Ag MNM in WWTP to  $\text{Ag}_2\text{S}$ ), 3) particles released but bound in the matrix (e.g. released  $\text{TiO}_2$  and Ag MNM from paints) may be more similar than the initial particles, at least in the short term, or 4) different transformation reactions acting on one MNM-type that result in different transformation products.



**Figure 6:** Transformation reactions can make different MNM more similar (coating of various forms with NOM; transformation into same phase, e.g. of Ag-forms into  $\text{Ag}_2\text{S}$ ; release of different MNM inside the same matrix) which may determine whether their fate and exposure scenarios would be simplified. Conversely, transformations may increase MNM diversity, where different transformations result in various forms of one MNM-type.





The prioritization which transformations are most important depends on the question that needs to be answered. These will be different if the prioritization is based on:

- One selected NMN (e.g. “what is the most important transformation for nano-Ag”),
- One product type (e.g. “what is the most important transformation for sunscreen particles”),
- Environmental fate and effects (e.g. “what is the most important transformation reaction affecting the environmental behavior of a specific MNM”),
- Total mass flows of all MNMs (e.g. “what is the most important transformation over all MNMs?”).

For different stress situations (mechanical, thermal, chemical) important processes should be identified for either product groups (i.e. textiles, polymers, etc.) and/or MNM groups (i.e. chemical makeup) and standardized release risk assessment protocols implemented for defined conditions. As a start, existing standardized procedures for other purposes could be modified to approximate the risk of MNMs from similar conditions, such as using ISO color fastness test adjusted to study MNM release from textiles. Finally, reporting the results of experiments should be standardized to include a key set of metrics upon which to more easily compare one study to the next. Important MNM characteristics, including size, concentration, and capping agent should be reported in addition to key environmental/test conditions such as full water chemistry characterization. Within NanoMILE, the ISA Tab Nano format is being adopted for all data capture and reporting, as this seems to be the emerging consensus format. This will provide detailed information regarding the investigation, study, assay and material.

### 3.3. Gaps in Knowledge

Unlike dissolved metals or organic chemicals, where a mass per volume metric had been sufficient under most circumstances to approximate risk, no single metric is available (or has proven useful) to characterize exposure and risk assessment for MNMs, due to their enormous variability and diversity. Particle characteristics that are most important to exposure (and risk) still need to be identified. Particle numbers (and if it changes over time), size (distribution), total metal and particle concentration, the speciation of the various components, surface area, surface functionality/coating, being coated or complexed to natural particles/microbes/biofilms, stability (change in size e.g. dissolution or agglomeration) and impurities in the MNM matrix that could be released may all potentially be important. Small changes in these factors can affect the propensity for MNMs to be released and their behavior and fate following release.

A significant gap appears to be identifying each stage of the MNM life cycle and thus potential exposure hot-spots, which may include (but are not limited to): occupational exposure during full-scale and down-stream uses, consumer exposure during product use, and environmental release during product recycling or after disposal. Industry surveys<sup>106</sup> were generally more detailed than academic reports/publications in terms of research and development activities but lacked detailed descriptions of the precise MNM under study, precautions taken to prevent environmental release, or the use patterns of the MNM in question.

In terms of predicting MNM fate, at this stage simple correlations between transformations and physical-chemical properties of pristine MNMs are still difficult because of the myriad of particle types, capping agents, and complexity of the systems being studied. Often, a change in one parameter will significantly change the extent of transformation, and determining how multiple factors may co-vary is exceedingly difficult. While some studies give suggestions as to the persistence of MNMs under relevant environmental conditions, fewer delve into the topic of biopersistence and toxicity of matrix bound particles. Since this is a likely release scenario, these aged products needs to be investigated. Generally, environmental exposures are likely to be at low concentrations over long time scales, allowing for slow or multiple transformations of the MNMs. A number of analytical techniques will likely have to be used in conjunction with extrapolating calculations to understand the multitude of MNM interactions with exposure media.

### 3.4. Next steps in NanoMILE





The information derived from this review will be used in task 3.2 to identify the transformation processes that will be studied for the particle types that are being provided under WP2. The selection of MNM for aging studies will then be made in MS5 "Selection of MNMs for ageing studies with reference to needs of WPs 5-8". The type of transformation reactions and MNMs that are going to be chosen will be built on the life-cycle approach presented in this report but also on the identification of product use/life cycle stage/particle combinations that have not been studied or only to a limited extend in order not to duplicate research.



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