THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Towards Prospective Exposure Modeling of Nanoparticles

Applying Particle Flow Analysis and Kinetic Exposure Modeling for the Cases of TiO_2 and Ag Nanoparticles

RICKARD ARVIDSSON

Division of Environmental Systems Analysis, Department of Energy and Environment

CHALMERS UNIVERSITY OF TECHNOLOGY

Gothenburg, Sweden 2010

Towards Prospective Exposure Modeling of Nanoparticles
Applying Particle Flow Analysis and Kinetic Exposure Modeling for the Cases of TiO_2 and Ag Nanoparticles

RICKARD ARVIDSSON

ESA report no 2010:18
ISSN: 1404 8167

Division of Environmental Systems Analysis
Department of Energy and Environment
Chalmers University of Technology
SE-412 96 Gothenburg
Sweden
Telephone + 46 (0)31-772 1000

Cover:
This thesis deals with the exposure of synthetic nanoparticles to aquatic organisms, thus studying the emissions of nanoparticles from society (including applications such as textiles and painted facades) and their fate in water.

Chalmers Reproservice
Gothenburg, Sweden 2010

ABSTRACT

The claims regarding the usefulness of nanoparticles (NPs) in different applications, such as wound dressings, solar cells and soil remediation, has been accompanied by concern that NPs may also pose risks to humans and to the environment. Considering the past century, when many substances later shown to cause unacceptable damage were manufactured in large amounts, there are reasons to thoroughly assess the risks of these NPs. This thesis discusses how the exposure assessment step of a risk assessment of NPs may be conducted, focusing on two research aims.

The first research aim considered is the magnitude of NP emissions from society. In order to address this aim, the methodology of substance flow analysis (SFA) was adapted to the case of NPs, resulting in the particle flow analysis (PFA) methodology. In PFA, particle number is used as flow and stock metric instead of mass, which is used in SFA. Moreover, a prospective approach is applied by developing an explorative scenario of technology diffusion. This method has been applied for titanium dioxide (TiO_2) in sunscreen, paint and self-cleaning cement, and silver (Ag) NPs in wound dressings, textiles and electronics. The second research aim concerns the fate of NPs in the water compartment. It is shown that modeling NP fate using fugacity based on thermodynamic equilibrium, which is normally done when assessing the risks of chemicals (i.e. molecules), is not feasible. Instead, the fate of NPs was modeled using kinetic equations which were borrowed from colloid chemistry. Particle concentration is used as exposure indicator, rather than mass concentration which is normally used in risk assessment of chemicals. This method was applied to the case of TiO_2 NPs.

The results from the PFA case studies indicate that the currently highest use phase emissions of TiO_2 NPs come from the use of sunscreen, and that this will probably be the case in the future as well. However, there is large number of TiO_2 NPs in paint, and in the future maybe also in self-cleaning cement, which are not emitted during their use but continue to the waste handling phase. Their fate during waste handling processes thus remains an interesting topic to investigate. Regarding Ag NPs, it is difficult to tell which application that gives rise to the currently largest emissions, but the results indicate that the emissions from textiles may be highest in the future. The kinetic exposure modeling of TiO_2 NPs identified parameters and mechanisms which affect the concentration of TiO_2 NPs, and the collision efficiency was shown to have the largest effect. Gaps in current knowledge are identifies in all three case studies and recommendations for further studies are given. The methods of PFA and kinetic exposure modeling constitute important steps towards prospective exposure modeling of NPs.

Keywords: Particle flow analysis (PFA), exposure modeling, nanoparticles, environmental risk assessment.

LIST OF PUBLICATIONS

Appended papers

Paper I
Rickard Arvidsson, Sverker Molander and Björn A. Sandén
“Particle Flow Analysis of TiO_2 Nanoparticles”
Submitted to Journal of Industrial Ecology in 2010

Paper II
Rickard Arvidsson, Sverker Molander and Björn A. Sandén
”The Impact of a Silver-Coated Future: Particle Flow Analysis of Silver Nanoparticles”
Submitted to Journal of Industrial Ecology in 2010

Paper III
Rickard Arvidsson, Sverker Molander, Björn A. Sandén and Martin Hassellöv
“Challenges in Exposure Modeling of TiO_2 Nanoparticles in Aquatic Environments”
Accepted for publication in Human and Ecological Risk Assessment in 2010

Other publications

Arvidsson, Rickard; Molander, Sverker; Sandén, Björn A. ”Tracing nanomaterial hotspots in a changing world”. 20th SETAC Europe Annual Meeting, Seville, Spain, 23-27 May 2010.

Arvidsson, Rickard; Molander, Sverker; Sandén, Björn A.; Hassellöv, Martin “Modelling Environmental Fate of TiO_2 Nanoparticles in Water – Implications for Empirical Validation Studies”. 4th International Conference on the Environmental Effects of Nanoparticles and Nanomaterials, Vienna, Austria, 6-9 September 2009.

Arvidsson, Rickard; Molander, Sverker; Sandén, Björn A. ”Fate modeling of titanium dioxide nanoparticles in the water compartment by colloid chemistry”. 1st International Conference on the Environmental Implications and Applications of Nanotechnology, Amherst, USA, 9-11 June 2009.

Arvidsson, Rickard; Molander, Sverker; Sandén, Björn A. ”The fate of titanium dioxide nanoparticles in the water compartment”. SETAC Europe 19th Annual Meeting, Göteborg, Sweden, 31 May-4 June 2009.

Arvidsson, Rickard; Molander, Sverker; Sandén, Björn A. ”Environmental Impact of Titanium Dioxide Nanoparticles – Applying Life Cycle Thinking and Risk Assessment for Swedish Conditions”. 3rd International Conference on the Environmental Effects of Nanoparticles and Nanomaterials, Birmingham University, Birmingham, UK, 15-16 September, 2008.

ACKNOWLEDGEMENTS

There are many who have made this work possible by supporting me in various ways along the way, and I would like to take the opportunity to thank some of them. I would like to thank my supervisor Sverker Molander for his ever positive spirit and his wise guidance regarding environmental risk assessment, toxicology and chemical pollution. I would also like to thank my second supervisor Björn A. Sandén for his critical eye and for sharing his knowledge of technical change and industrial ecology. Their ability to cooperate and complementary areas of expertise have indeed contributed to the contingent merits of this work. Thank you also Anne-Marie Tillman, my examiner, for valuable comments on this thesis and for believing in my abilities to reach this far and beyond.

This work has also benefitted from the interesting discussions I have had with my fellow PhD candidates and other colleagues at our division of Environmental Systems Analysis and my co-author Martin Hassellöv at the chemistry division of the University of Gothenburg. The financial support from the Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (Formas) and from the Swedish Foundation for Strategic Environmental Research (MISTRA) is gratefully acknowledged.

Finally, I would like to thank my parents for supporting my path towards research. Without your help with early ‘research projects’, such as those about the planet Saturn and the Berlin Wall, this research would not have been possible.

TABLE OF CONTENTS

1 INTRODUCTION

1.1 Nano as System Level

The discussion regarding the definition of the word “nano” in the words nanotechnology, nanomaterial (NM) and nanoparticle (NP) is ongoing. Most definitions suggest that a NM is a material with one, two or three dimensions in the size range 1-100 nm, see for instance ISO (2008). This implies that a NP should have a diameter of 1-100 nm. Some authors, however, have argued that from an ecotoxicological point of view, particle sizes up to 500 nm could be of interest (Handy et al. 2008). Regardless of the exact upper limit, this much is clear: Nano can be seen as a system level.[1] Boulding (1954) suggested an approach to a general systems theory: The perspective of the unit of behavior – or the *individual*. In chemistry, individuals are represented by molecules, atoms and ions, and the area is much built up around the molecular system level (about 0.1-1 nm). In cell biology, animal, fungi and plant cells together with various bacteria represent the individuals, and similarly cell biology is largely built around the cellular level (about 1-10 µm). On the nano level, the perhaps most important individuals are NPs. Nano represents the latest level of scientific and societal interest, dwelling somewhere in between the worlds of atoms and cells (Figure 1).[2] This newly appreciated system level brings new promises. Silver (Ag) NPs in wound dressings could be used to battle malicious bacteria in wounds (Silver et al. 2006), iron NPs could be used to remediate contaminated soil (Schmidt 2007) and sintered titanium dioxide (TiO_2) NPs are used as electron mediator in Grätzel cells to convert solar light to electricity (Greijer et al. 2001).

The claims about the usefulness of the nano level are hardly surprising. Already in 1914, surface and colloid chemistry was referred to as “the world of the neglected dimensions”[3] and its usefulness in many applications was highlighted (Ostwald 1914). As described in Paper III, colloid chemistry and nanotechnology refers to approximately the same system level. Apparently, however, it took almost 100 years until the full potential of this dimension or system level was acknowledged, under the new name nano. At the nano level, some mechanisms that are not relevant for molecules become important. These interactions represent what Boulding (1954) denotes the individuals’ *behavior*. In systems studies contexts, the term *mechanisms* is often used, meaning about the same as Boulding’s term behavior. Different agglomeration mechanisms and sedimentation represent two processes which are not relevant for molecules, since molecules generally do not agglomerate and are too small to sediment. New components to be highlighted at the nano level are the natural organic matter and natural NPs, which represents diverse groups of compounds normally found in natural waters (Buffle et al. 1998; Gallego-Urrea et al. 2010). Several of these mechanisms and components give rise to

---

[1] Sometimes it is added to the definition that a NM must have “properties different from those of molecules or bulk materials of the same composition” (Wiesner et al. 2009). But it is unclear how different these properties must be, and which properties that should be considered. For instance, the properties “particle diameter” and “surface area” should always differ between a bulk material and the same material in nanoparticulate form. Thus, this part of the definition is not applied here. Note also that the terms “NP” and “NM” refers to synthetic or manufactured NMs and NPs in this context.

[2] Note, however, that the system levels presented in Figure 1 which are based on size ranges are not self-evident, but should be seen as conceptualizations which have been useful in this context.

[3] ”Die Welt der vernachlässigten Dimensionen“ in the original text.

emergent phenomena, such as for instance the potential change in agglomeration rate caused when natural organic matter bind to the NP surface. Many of these mechanisms have been well known by colloid chemists for a long time, see for instance Elimelech et al. (1995). The NPs can not only interact with each other but also with other objects in their environment at different system levels, for instance molecules, ions, cells and organisms. Another property which makes NPs differ from molecules, and in particular atoms, is that they may be formed or multiply by grinding or weathering, or be destroyed by melting. In addition to nano level mechanisms, the effect of the organism level on the nano level is important. It is at the organism level where the production and use of NPs is decided upon, and original properties of the NPs are given (these may change later due to fate processes in the environment).

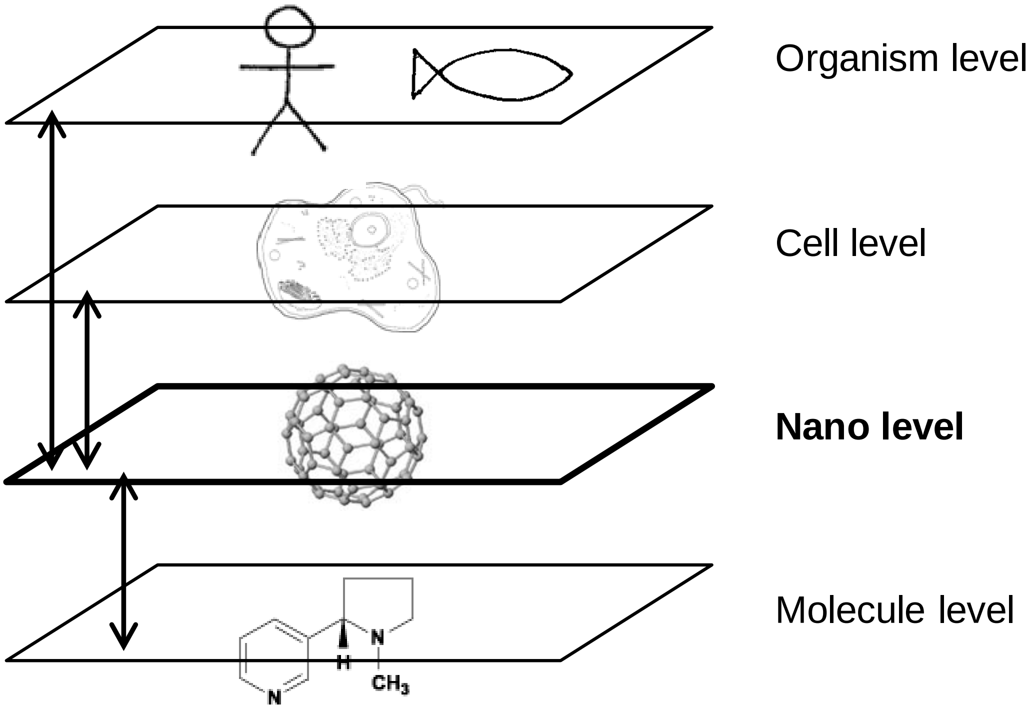

Figure 1. The nano level and its relation to other system levels. Interactions between components can take place within levels and between levels. Note that the system levels outlined here are based on size ranges and are not self-evident, but should be seen as conceptualizations which have been useful in this context.

1.2 Nano Level Hazards

This newly appreciated nano level also brings fear of new risks arising from the material properties at that level (Royal Society and Royal Academy of Engineering 2004; Colvin 2003; Swedish Chemicals Agency 2007; Maynard et al. 2006). Again, this is not surprising, since interactions that could cause harm to organisms exist at all system levels shown in Figure 1. Examples of such interactions between the molecular and organism level is the risk of mercury binding to sulfide groups in enzymes, which can cause extensive nerve damage. Interactions that can cause harm at a cellular level are for instance parasite infections or sickle cell anemia, which causes the afflicted to become excessively tired.

Environmental and health risks related to particles have been addressed for a long time. Particles emitted from combustion engines or wear from asphalt or tires have since long been considered an environmental problem contributing to urban air pollution. The indicators used to assess the impact of airborne particles have been mass concentration of different size classes of particles, such as PM10, PM5 and PM2.5, where PM stands for particulate matter and the figure after tells the upper size limit in µm (Klaine et al. 2008). These categories, although crude and much focused on effects on respiratory systems, reveal the importance of the size of the particles. In addition, the shape of particles has been acknowledged as important, for instance for the case of asbestos (European Environment Agency 2001). The effects of particle characteristics on their ability to cause harm to organisms have thus been acknowledged since long, and risk assessments of their impact on human health have been conducted, see for instance Forsberg et al. (2005). Risks related to particles have, however, caught new attention in the light of the increased production of synthetic or manufactured NPs, and it is the environmental risks related to these novel NPs that are of interest in this thesis.

Andrew Maynard, who is a research fellow of the Woodrow Wilson Institute and an often cited researcher on societal aspects of nanotechnology, sometimes takes the example of the knife and the frying pan in his oral presentations when explaining the novel risks that may emerge at the nano level. A knife and a frying pan can have the same chemical composition, for instance consist of steel. However, despite similar chemistry, the risks related to knives and frying pans are quite different from each other. It is for instance seldom that one gets burn injuries from a knife, and similarly cut wounds from frying pans are rare. So the same chemistry can, even at a macro level, lead to different kinds of risks. The same is true at the nano level: Since NPs are not only characterized by their chemistry, they have other hazardous properties which can give rise to environmental risks. For instance, the high surface area of NPs, which follows from their small size, and the unique surface properties of manufactured NPs have been the major potential hazard often put forward in the literature (Christian et al. 2008; Handy et al. 2008; Nel et al. 2006; Ju-Nam and Lead 2008), and these properties are inherently linked to the nano level. Many authors have highlighted the importance of including NP properties and mechanisms when assessing their risk (Wiesner et al. 2009; Nel et al. 2006; Colvin 2003; Klaine et al. 2008; Handy et al. 2008). Agglomeration and the other mechanisms are inherently different from those of dissolved molecules and thus imply that new methods are required to describe their potentially hazardous properties (Wiesner et al. 2009). Especially emerging technologies, to which many NP applications belong, provides a challenge with regards to estimating production and use since these are affected by technology diffusion (Wiesner et al. 2009). Note, however, that it is not self-evident that all NPs are hazardous. Naturally occurring NPs have been around for ages in soil, oceans, the atmosphere, rivers, glaciers, etc. (Wiesner et al. 2009). Thus, similar to chemicals, of which some are harmless even at very high concentrations whereas some are extremely toxic, the risks of individual NPs must be assessed.

NPs are indeed not the first potentially hazardous substance to be highlighted in the scientific literature. The report *Late lessons from early warnings* describes several cases where scientists issued warnings regarding several chemical compounds and activities (European Environment Agency 2001): The adverse effects of the solvent benzene; lung damage related to asbestos exposure; ecosystem damage due to bioaccumulation of PCB; damage to the ozone layer due to halocarbons; methyl tert-butyl ether as substitute for lead in gasoline; the antifouling agent tributyltin; hormone disrupters; etc. For several of these examples, the adverse environmental effects were due to previously unknown mechanisms, such as the ozone-destroying potential of halocarbons and the bioaccumulation of lipophilic substances such as PCB. However, although the effects were new, warnings of these adverse effects were issued by scientists long before society responded, thus the title *Late lessons from early warnings*. Ulrich Beck writes in his book *Risk Society* that innovation is the main producer of risk in society (Beck 1992), and many of the late lessons above do emanate from innovations, such as new chemical compounds or devices such as the trawl for fishing. It should however be noted that many of the above mentioned compounds have also proven useful for society, which may also be the case for NPs (Schmidt 2007). It has recently been suggested that by assessing the environmental impact of new technologies at an early stage of development, the innovation process can be made reflexive and hazardous side-effects can be avoided (Fogelberg and Sandén 2008). It is in that spirit the risks of NPs are addressed in this work.

1.3 Environmental Risk Assessment

In order to assess the risks connected to NPs, environmental risk assessment (ERA) was applied as the overarching methodology. The framework and procedure of ERA are quite standardized, see for instance Suter et al. (1993), Burgman (2005), van Leeuwen and Vermeire (2007) and US EPA (1998). It is sometimes referred to as *ecological risk assessment* or *risk assessment of chemical*s rather than *environmental risk assessment*. Ecological risk assessment is often more focused on the environment and identifying several potential hazards to a certain organism or population, whereas risk assessment of chemical is more focused on chemical stressors and their effects on several organisms. But these are very closely related and represent, in essence, the same methodology. For instance, if one chemical and one organism are included in a risk assessment study, it is difficult to say which method is being used. Thus no differentiation between them has been made here, and the methodology is referred to by the more general term ERA. Assessing the risk of hazardous substances such as various chemicals has been a major application of ERA (van Leeuwen and Hermens 2004). One important basis for this work is that the method of ERA could be fruitful for assessing the risks of NPs in addition to molecules.

The focus of an ERA is always a *value at stake*, which may be called *endpoint* or *receptor*. The value at stake is threatened by different *stressors*, which could be of various kinds (physical, biological, chemical etc.). In ERA, the stressor is often a toxic chemical. The stressor can reach the endpoint and cause exposure through various *pathways*. One typical exposure pathway of environmental toxins to humans is via food, in which the toxin has been bioaccumulated and biomagnified. The first part of an ERA procedure is often called *problem formulation*. In that stage, *hazard identification* is performed, thus identifying potential hazards such as the use of chemicals known to be toxic. A *conceptual model* is developed, which includes identifying the source of the hazard, the stressor, pathways and receptors or endpoints. The second part of an ERA normally includes conducting an *exposure assessment* and an *effect assessment*, also referred to as *dose-response assessment*. The exposure assessment includes environmental modeling of the *fate* of the stressor or measurements to determine the dose to which the receptor is exposed. That dose or concentration is referred to as the *predicted environmental concentration* (PEC). Often, different *environmental compartments* (water, air, soil and sediment) are considered, and PECs are calculated for each of them. The effect assessment includes using toxicological data to determine the highest dose or concentration at which it is certain that there will be no adverse effects to a certain receptor. This concentration is referred to as the *predicted no effect concentration* (PNEC), and is typically derived from toxicological dose-response curves. Such results are often expressed as the concentration at which half of the organisms died (LC50, where L stands for lethal and C for concentration) or where it was possible to see an effect on half of the organisms (EC50, where E stands for effect). These concentrations must then be divided by a security factor[4] of 10, 100 or even 1000 depending on available data in order to obtain a conservative PNEC. If the toxicological studies have measured a so called no effect concentration or level (NOEC or NOEL), these can be applied directly. However, if the toxicological measurements were not conducted on the exact species that one is interested in, or if there are very few studies that differ considerable in their results, then again security factors may be applied. In the *risk characterization* the PEC and PNEC are compared. If the PEC is higher than the PNEC, i.e. if the ratio PEC/PNEC is higher than one, it indicates risk. If not, there may be no risk. The PEC and PNEC may also be expressed not as single numbers but as ranges or even probability distributions in order to conduct a more detailed risk characterization. PEC is thus *exposure indicator,* and PNEC *effect indicator*, in an ERA. The PEC/PNEC ratio then becomes the *risk indicator*.

1.4 Nano Level Risks in Previous Exposure Assessments

As shown above, the nano level presents some new mechanisms and components that were previously seldom considered in ERAs, and may also require novel risk indicators. It is notable that the early ERAs of NPs and NMs performed, such as Mueller and Nowack (2008) and Boxall et al. (2007), hardly included any of these nano level mechanisms. In Mueller and Nowack (2008) no specific nano level mechanisms are described. Boxall et al. (2007) discusses some of the mechanisms mentioned above, for instance agglomeration, but does not include it formally in the exposure modeling. Boxall et al. (2007) do, however, consider an increased NP inflow due to increased demand in society. In accordance, these models have been deemed to offer “limited guidance” (Wiesner et al. 2009). Later studies, such as those by Gottschalk et al. (2010a; 2010b, 2009), have added some environmental compartments and applied Monte Carlo simulations to account for uncertainties in data, but not included any of the mechanisms specific for the nano level.

In addition, the question of exposure indicator for NPs remains an intriguing one. In environmental and chemical risk assessment, mass concentration has mainly been used as exposure and effect indicator (PEC and PNEC), often in mg/l or similar units (van Leeuwen and Hermens 2004; Suter et al. 1993). A unitless risk ratio of the mass-based PEC and PNEC has been used to estimate the risk. It should be noted that in order to estimate a risk, the exposure and effect should preferably have the same units, or else it will be like comparing apples and pears. Studies by Günter Oberdörster did suggest that the surface area of NPs may be a better effect indicator than mass (Oberdörster et al. 2005). Handy et al. (2008) looked at both toxicological and environmental fate aspects and ended up suggesting particle number as a potential risk indicator. They argued that many important fate mechanisms, such as agglomeration, can only be described mathematically in terms of particle

---

[4] Note that there exist other names for this factor, such as safety factor or uncertainty factor.

number. Particle number is also linked to surface area, since the more particles, the higher surface area. Other authors have also suggested particle number as a possible relevant exposure indicator (Ju-Nam and Lead 2008). As shown in Paper I, the choice between particle number and mass have a huge impact on the results:

“Consider two flows of 1 and 10 kg of TiO_2 NPs respectively, where the second one would normally be described as one order of magnitude larger. However, assume that the first flow consists of 1 nm particles, and the second one of 100 nm particles. Recalculated into particle number, the first flow would be $6 \cdot 10^{22}$ particles and the second one $6 \cdot 10^{16}$ particles, i.e. six orders of magnitude smaller.”

It would be magisterial to claim particle number to be the one and true exposure indicator for NPs. However, particle number as risk indicator for NPs does have certain advantages over mass: (1) it enables the numerical inclusion of fate processes such as agglomeration (Handy et al. 2008), (2) it enables meaningful inclusion of different frameworks for categorization of NPs (see discussion in Paper II) and (3) it may reflect the cumulative toxic effect of NPs (Handy et al. 2008). In addition, it would not be too strong to say that the usefulness of mass concentration as exposure, and effect, indicator for NPs has been seriously questioned (Handy et al. 2008; Oberdörster et al. 2005). Despite this, it is the indicator of choice in previous exposure assessments of NPs (Mueller and Nowack 2008; Boxall et al. 2007; Gottschalk et al. 2010a; Gottschalk et al. 2009, 2010b). There is, in addition, seldom a critical discussion regarding choice of indicator. Similarly, most ecotoxicological studies on NPs have measured their results in terms of mass concentration (Kahru and Dubourguier 2010). Donella Meadows discussed indicators of sustainability in general, and concluded that one common pitfall was to “measure what is measurable, rather than what is important” (Meadows 1998). Considering that mass has previously been used extensively as risk indicator and is easy to measure, it would be tempting to suggest that the extensive use of mass concentration as indicator for NP risk in previous ERAs constitutes an example of this pitfall.

1.5 Methodology and Research Aims

In this thesis, ERA has been applied as overarching methodology, with NPs as stressors rather than molecules, see Figure 2. In addition, since most NPs originate from emerging nanotechnologies, a prospective approach which takes into account technological change was applied, which was suggested by, for instance, Owen and Handy (2007). However, it soon became clear that an ERA of NPs could not be performed without adopting the ERA methodology to be relevant for the case of NPs (Lubick 2008; Wiesner et al. 2009). In addition, the toxicological and ecotoxicological data is scarce, uncertain and points in different directions (Lubick 2008), the fate mechanisms of NPs in the environment, which are discussed above, are only partly understood and quantified (Colvin 2003; Klaine et al. 2008; Handy et al. 2008) and the production and emissions of NPs within the technical system is also very uncertain, which is discussed in Paper III and also noted by other authors (Wiesner et al. 2009). The Woodrow Wilson database list several consumer products presumed to contain NMs (Project on Emerging Nanotechnologies 2009), but it is unclear how much of each that is produced and the NP content of each product.[5] The focus of this work has been put into developing methodology for different parts of the ERA procedure relating to the exposure assessment. Further studies on the effect of NPs on biota have been left to toxicologists. As the famous Taoist philosopher

---

[5] Since the decision of what to include in the database is based on information readily available on the Internet, it is even unclear if the products included actually contain NMs.

Lao Tzu said: “A journey of a thousand miles must begin with a single step.” The following two aims have been addressed.

1. Estimating the emissions of NPs from emerging technologies from the technical to the natural system.

2. Estimating the exposure of NPs from emerging technologies to aquatic organisms given a certain emission scenario.

The first research aim was primarily addressed in Paper I-II, and the second one in Paper III, see Figure 2. In Paper I-II, the methodology of substance flow analysis (SFA), a common method for estimating emissions of chemicals from society (van der Voet 2002), was modified in order to be relevant for NPs. Exposure modeling of chemicals was adapted to the case of NPs in Paper III by applying colloid chemistry, as suggested by Handy et al. (2008). During the work presented here, in particular in the methods developed, there has been an ambition to try to include more mechanisms relevant on the nano level in the exposure models, thus avoiding the trap of routine-like application of the same methods for NPs as for molecules. There has also been an ambition not to be locked-in to mass concentration as exposure indicator, and to take into account that the nano level not only affects organisms at a macro level, but also that the synthetic NPs are affected by the organism level since they are produced in the technical system, and thus technology diffusion affects what exists at the nano level.

The endpoint considered has been aquatic organisms, and thus exposure pathways in aquatic environments have been in focus. In order to verify the developed methodology, TiO_2 and Ag NPs have been used as case studies. These two NPs were selected based on hazard identification: An early risk assessment had shown that TiO_2 NPs constitute a high risk (Mueller and Nowack 2008) and the potential problems of emitting Ag in its nano-form had been highlighted by several studies (Luoma 2008; Wijnhoven et al. 2009; Blaser et al. 2008). In addition, both these NPs are frequently found in consumer products (Project on Emerging Nanotechnologies 2009). Another NP frequently found in consumer products is carbon nanotubes (Project on Emerging Nanotechnologies 2009). Caron nanotubes had also been noted as potentially hazardous due to properties similar to those of asbestos (Poland et al. 2008). However, due to the difficulties of determining the environmental fate of rod-shaped structures, carbon nanotubes were not included. The applications of TiO_2 NPs included were sunscreen, paint and self-cleaning cement and the Ag NP applications included were wound dressings, textiles and electronics. These applications represent an interesting but none-exhaustive selection of products which are frequently mentioned in the literature, see Paper I-II.

Why make the delimitation to exposure of NPs and not include all NMs? Hansen et al. (2007) developed a framework to aid hazard identification of NPs, where NMs are categorized as (1) bulk NMs, (2) surface NMs or (3) NPs. One example of a TiO_2 NM application which does not contain NPs is self-cleaning windows produced by, for instance, Pilkington or Saint Gobain (Sanderson et al. 2003; Parkin and Palgrave 2004). The NM in that application consists of a 15 nm thick film. Such NMs are not included in the exposure modeling conducted here since it has been difficult to identify a stressor. Currently, it is not known if any NMs are emitted from such surfaces. Hence, since it is unclear if there are any stressors related to the first two NM categories in Hansen et al. (2007), i.e. bulk NMs and surface NMs, they have not been included in this work.

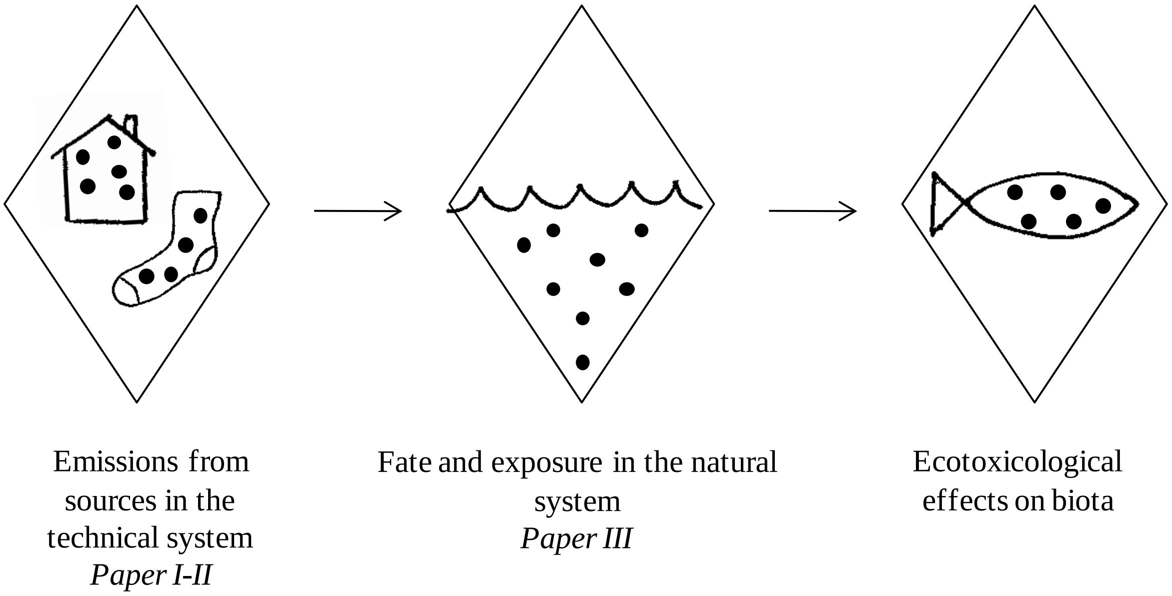

Figure 2. This thesis deals with the two first steps in an ERA of NPs: The emissions from the technical system and the fate mechanisms that lead to exposure to organisms in the natural system.

2 METHODS DEVELOPED

There are essentially two methods that have been developed and applied in Paper I-III. As suggested by the title of this thesis, both these are parts of an exposure model. However, different modeling approaches have been applied for the technical and natural system. Paper I-II deals with the technical system, where flows and stocks of materials and substances are managed by humans. Contrary, Paper III deals with the natural system, in which the fate of NPs is controlled by the forces of nature.

2.1 Particle Flow Analysis

In order to estimate emissions of NPs from the technical system to the environment on a particle number basis the methodology of particle flow analysis (PFA) was developed and applied in Paper I-II. This was done since particle number was suggested to be a more relevant exposure indicator than mass, see the discussion above or in Paper I and III, and Handy et al. (2008). The basis for the method of PFA is SFA, which is a methodology adopted for the study of societal flows and stocks of chemicals (van der Voet 2002). As in standard SFA, the phases of the substance's life cycle are studied to see where emissions to the environment occur. However, instead of using mass as flow and stock metric, particle number was applied. This choice was shown in Paper I-II to have several implications. For instance, a larger mass flow containing large particles may be much smaller than a smaller mass flow containing smaller particles when using particle number as flow and stock metric. In addition, it disrupts one of the basic principles behind SFA, which is the law of mass conservation. A certain amount of mass entering a compartment must leave it or be accumulated, if not converted to energy by nuclear reactions. But for particles, much less dramatic processes than nuclear reactions may erase the equity sign between accumulated particles and the difference between inflow and outflow, for instance processes such as grinding, melting and weathering.

Consider, for instance, an inflow of 100 spherical NPs with a diameter of 100 nm and a density of 1 kg/m^3 to a certain compartment. If these NPs where grinded into 1 nm-sized particles, there would be 1000 000 particles, meaning that 999900 additional NPs emerged. Contrary, consider 1000 000 NPs entering a compartment where these are melted, and reduced to zero or maybe one larger particle (perhaps along with phase transformations). The possibility that such processes may occur is included by using the following equation in Paper I-II:

$$\frac{dN}{dt} = \sum n_{in} - \sum n_{out} + n_s \tag{1}$$

where N is the stock of NPs and n is the flow of NPs. The term n_s, where the index s stands for source, can be both positive and negative and thus accounts for the increase or decrease in particle number due to the processes mentioned above and others. Although no such processes occurred for the studied phases of TiO_2 and Ag NPs in Paper I-II, it is important to include a source factor in the general equation. Besides the inclusion of this factor, changing flow and stock metric to particle number enables a meaningful inclusion of NP typologies, such as the ones by Hansen et al. (2007) and Jiang et al. (2009). See further Paper I-II.

In a standard SFA, much focus lies on finding detailed figures for the current state. But since many nanotechnologies are growing rapidly (Wiesner et al. 2009), these figures will have changed tomorrow. Thus it may be at least equally interesting to consider a future state of the nanotechnologies, which was done in Paper I-II by applying explorative scenarios of technology diffusion. One very basic thought which has guided this work of including technological change in exposure modeling is that the exposure of NPs will increase as the use of the NP applications increase. The growth of technologies follows a well established pattern. The early, formative phase of a technology evolves into a diffusive, growth phase, and later to a mature, saturated phase (Grübler 1996). The examples in the report *Late lessons from early warnings* show that the negative environmental impact for the different cases included, be it DDT, fisheries or halocarbons, first appeared when the substances or activities were used extensively (European Environment Agency 2001). So when evaluating the environmental impact of substances used in emerging technologies, the substance in question may seem misleadingly benign in its early phase. Besides growing, the technologies containing the NP of interest may also become dominant designs, which means that increasing returns will make it difficult to change their performance (Arthur 1996; Utterback 1994). In the light of this knowledge, there are good reasons to not only focus on current exposure of NMs, but also consider the potential exposure levels that may arise due to increased flows and stocks.

Technical change aspects has previously been included in another environmental assessment method: life cycle assessment (Hillman and Sandén 2008; Kushnir and Sandén 2008). In the paper by Hillman and Sandén (2008) different aspects of time and scale on the life cycle environmental performance are discussed, such as changes in electricity sources, transport system fuels and by-product usage. Kushnir and Sandén (2008) showed that the energy use for production of fullerenes and carbon nanotubes will probably become much lower in the future, as the technology develops from lab-based to industrial production. These studies and their results highlight the importance of including technical change in environmental assessments of emerging technologies. The importance of technical change aspects has also been recognized in ERAs of NMs. Boxall et al. (2007) applied different scenarios based on different market penetration of products containing NMs: 10, 50 and 100 percent. The percentage of market penetration was, however, based on current market sizes. Robichaud et al. (2009) assumed that in the future the production of TiO_2 NMs will overtake the production of conventional TiO_2. They also estimated an increase in TiO_2 production based on trend analysis and assumed that the TiO_2 NMs will grow exponentially at the expense of conventional TiO_2.

Börjeson et al. (2006) list some typologies of scenario studies which are helpful when considering the future: predictive, explorative and normative. The future scenarios in Paper I-II are so called *explorative scenarios*, which answer the question *What can happen?* (Börjeson et al. 2006). They are normally used when the knowledge of the development of the system of interest is poor and often take their starting point in the future (Börjeson et al. 2006). Although there exist frameworks to describe the development of emerging technologies, see for instance Bergek et al. (2008), these frameworks are far from being predictive models. The scenarios for market penetration in Boxall et al. (2007) can be regarded as explorative scenarios. However, the scenario in Robichaud et al. (2009) is denoted as a forecast and can thus be regarded as a *predictive scenario* which answers the question *What will happen?*, since the analysis takes the starting point in the present and seems to have quite clear ideas on the mechanisms of the system (Börjeson et al. 2006). Considering the difficulties in estimating the development of an emerging technology, it seems that explorative scenarios are preferred in this case. For instance, nuclear power was once believed to become the world’s major source of electricity, but due to unexpected events such as the Chernobyl accident this scenario did not materialize, at least not within the expected timeframe (Sandén 2004). Such examples illustrate the difficulty of forecasting technological change for technologies in an early phase of development.

In Paper I-II, it is assumed in one scenario that the technologies containing NPs grow until they are limited by per capita demand. It is assumed that the global per capita use of the application containing NPs will be equal to that of today's high income countries, such as Sweden or the US. Further, a population of 10 billion people is assumed, based on a forecast by the United Nations for the years 2050 and beyond (United Nations 2008). One benefit with this method compared to the one in Boxall et al. (2007) is the focus on applications rather than substances, since information regarding which applications, products or technologies that have the potential to cause high emissions of NPs will guide future research and societal interest to that application.

2.2 Kinetic Exposure Modeling

The fate and exposure of potentially toxic chemicals are often modeled by thermodynamic partitioning following the work by Don Mackay and colleagues (Mackay et al. 1996; Mackay et al. 1992). In short, these models can provide information of the partitioning of a certain amount of chemicals emitted to the environment by assuming that thermodynamic equilibrium will be reached. However, for particles this methodology is problematic since colloids, which includes NPs (see Paper III) is never thermodynamically stable (Hunter 1987). This is to say that at thermodynamic equilibrium, there are no particles. However, the world is not at thermodynamic equilibrium, and thus particles may exist. Everyone who has seen, for instance, the Ganges river delta may testify that there is likely a high concentration of particles (mostly natural colloids) in that water, indicating that the agglomeration and sedimentation of particles may sometimes be slow. Particles exist in nature since they are kinetically stabilized by an energy barrier (Elimelech et al. 1995), similar to the activation energy often referred to in chemical kinetics introduced by the Swedish chemist Svante Arrhenius (Atkins and Jones 2002). For instance, at pH values significantly higher or lower than the point of zero charge of TiO_2 NPs the electrostatic energy barrier is large enough to stabilize the particles, making the agglomeration rate very slow (Dunphy Guzman et al. 2006). There is thus a clear scientific basis showing that kinetics may be used for predictions of NP behavior. Although kinetic models hitherto have not been frequently applied in environmental modeling of chemicals, for the case of NPs, where thermodynamic models fail, applying kinetic models provide an interesting path. In some models the existence of particles may be omitted, but modeling of fate and exposure of NPs is obviously not such a case. Hence, the exposure modeling in Paper III was conducted using kinetic equations instead of thermodynamics, in particular the following equation, which was modified from Grant et al. (2001):

$$\frac{dn_j}{dt} = \frac{1}{2}\sum_{i=1}^{i=j-1}\alpha_{i,j-i}K_{i,j-i}n_i n_{j-i} - n_j\sum_{i=1}^{i=\infty}\alpha_{i,j}K_{i,j}n_i - \frac{v_s}{d}j^{\beta}n_j + I_j \qquad (2)$$

where n_j is the particle number concentration of particle j (if j equals three, then particle j consists of three primary particles that have agglomerated), $\alpha_{i,j}$ and $\alpha_{i,j-i}$ are collision efficiencies, $K_{i,j}$ and $K_{i,j-i}$ are rate constants, v_s is the sedimentation rate of primary particles, β describes the increase in sedimentation rate due to increased cluster size (2/3 for spherical particles), d is the depth of the water compartment and I_j is the inflow of particles.[6] Eq. 2 is based on the assumptions that all particles are approximately spherical and that merging of two particles is an irreversible reaction. The first term on the right side of Eq. 2 describes the formation of particle j through agglomeration of particles i and j-i. The second term describes the loss of particle j through agglomeration with other particles i. The third

---

[6] Note that n in Eq. 1 denotes particle flow [particles/year], whereas the n in Eq. 2 denotes particle concentration [particles/m^3]. A slight change of nomenclature is thus needed before mending of these methods.

term accounts for the sedimentation, and the last term for the inflow of particles. A particle number based PEC can be derived from Eq. 2 by solving the differential equation and summing the particle concentrations n_j at a time when the system has reached steady state.

Note that Eq. 2 contains several of the nano level fate mechanisms outlined in the introduction. However, as stated in Paper III, many additional fate mechanisms remain to be included mathematically in this model. The kinetic equations applied in Paper III originate from the early work of Smoluchowski (1917) and Friedlander (1977), which have been well known in colloid chemistry for long. Other important mechanisms for particle kinetics, such as break-up and the formation of fractal agglomerates are also well known, yet difficult to quantify exactly (Elimelech et al. 1995). The modest title “Challenges in Exposure Modeling of Nanoparticles in the Aquatic Environment” was deliberately chosen. Developing a kinetic model to describe particle fate and exposure was proven to be a complex process. As described in Paper III, the lack of formalized equations for many mechanisms constituted a problem for deriving a kinetic exposure model. Thus more effort must be put into the development of such models, where natural scientists and risk analysts try to develop a model which is built on sound knowledge of the behavior of NPs and give relevant information from an environmental point of view. The kinetic model in Paper III should be seen as a contribution to future work in this field.

Recently, modeling exposure using kinetics has been performed for a somewhat different case. The uptake process of environmentally relevant metals, such as heavy metals and radioactive substances, is very much linked to dissolved particulate matter and kinetic models have been applied to describe the uptake of such contaminants via particulate matter in aquatic environments (Barros and Abril 2008; Periáñez 2003). These models share many similarities with the modeling in Paper III. For instance, Barros and Abril (2008) address the difficulty in obtaining reliable rate constant values that apply for a wide range of environments, which is also stressed in Paper III. This provides the perhaps greatest challenge in future exposure modeling of NPs. There is however one significant difference between these models and Paper III. Their primary interest is not to model the particle fate itself, but the fate of contaminants that may attach to the particles. The particulate matter constitutes a box/compartment in these studies, rather than being the stressor of interest, as in Paper III. However, it is clear that the fates of NPs and heavy metals can poorly be described without the inclusion of particles in the fate model. Thus kinetic exposure modeling is considered a valuable tool for such cases.

The two methods described here, kinetic modeling and PFA, are not necessarily separate, but can be linked together as illustrated in Figure 3 in order to perform a full prospective exposure modeling of NPs.

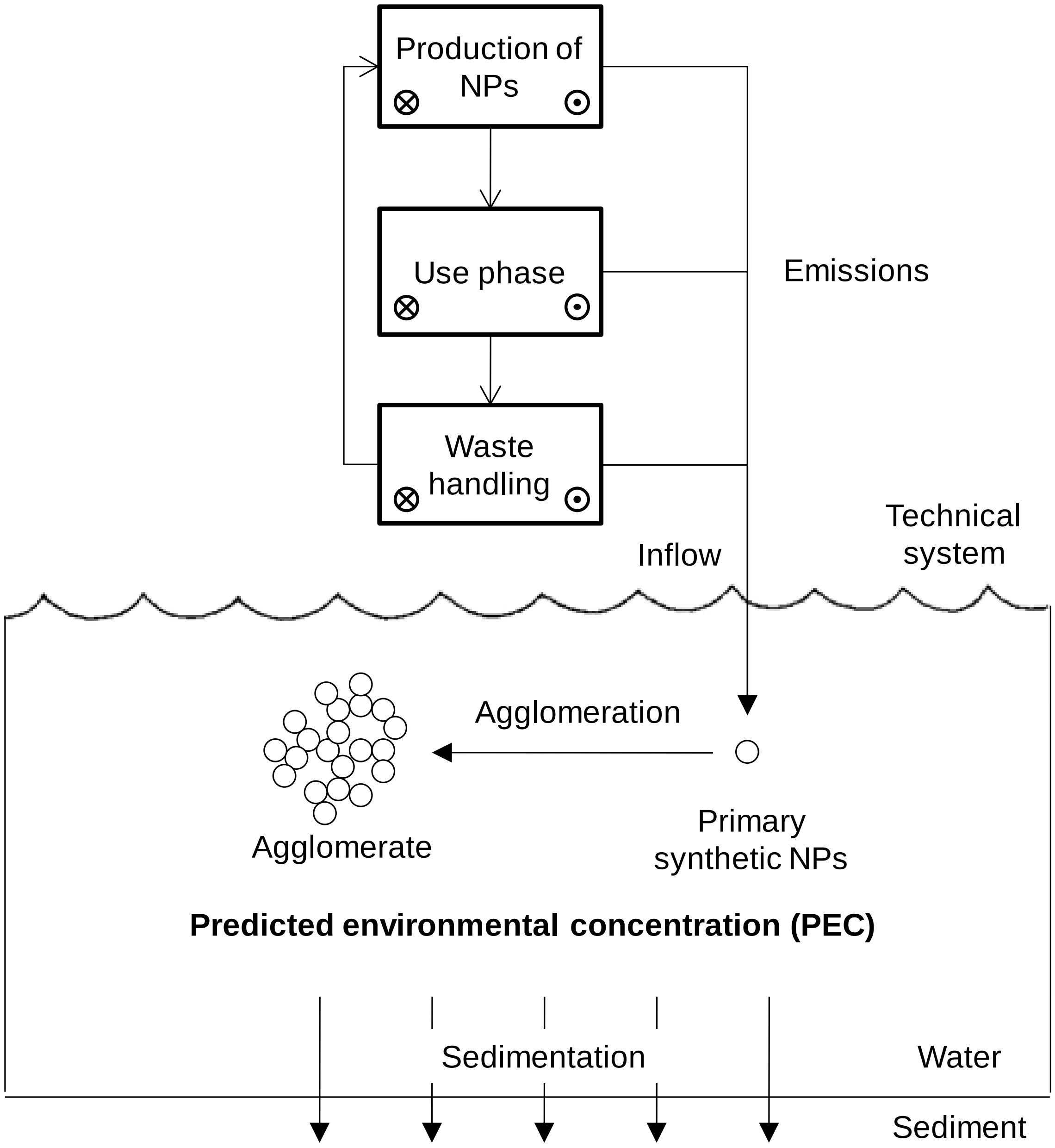

Figure 3. A description of a prospective exposure model of NMs, with a prospective substance flow model linked to a kinetic exposure model. The symbols in the flow chart represent sources and sinks of NPs, see further Paper I-II.

3 RESULTS AND DISCUSSION

Two methods, PFA and kinetic exposure modeling, were developed to answer the two research questions of this thesis. As shown in Paper I-III, the application of these models has led to interesting results. Among other things, it was shown in Paper I that currently, the highest emissions of TiO_2 NPs occur from sunscreen, which will probably be the case in the future as well. Despite estimated large stocks and flows of TiO_2 NPs in paint, and of TiO_2 NPs from self-cleaning cement in the explorative scenario, the estimated use phase emissions from these applications were lower than for sunscreen. For Ag NPs, it is difficult to tell which application that gives rise to the currently highest emissions. However, it is clear from the explorative scenario that textiles have the potential to cause the highest emissions of Ag NPs. See Table 1 for a summary of the estimated emissions in Paper I-II. For the cases of TiO_2 NPs in paint and self-cleaning cement, and for Ag NPs in electronics, it was shown that most NPs probably ended up in the waste handling phase. Regarding the exposure of TiO_2 NPs in water, no full exposure assessment could be performed in Paper III due to lack of data. However, it was shown that some parameters have a major effect on the particle number-based PEC of TiO_2 NPs, whereas some parameters and mechanisms have only a low effect. The collision efficiency and the inflow were the parameters that had the highest effect. The parameters which hardly affected the PEC at all were the shear rate, differential settling and sedimentation. In addition to the numerical results, the case studies performed had methodological implications. Both developed methods, PFA and kinetic exposure modeling, constitute modifications or revisions of methods previously used for assessing the exposure of chemicals, i.e. SFA and thermodynamic exposure modeling, which were modified to address the exposure of NPs and to answer the research aims of this thesis. Thus, the methods developed constitute results as well.

The case studies revealed limitations of both the developed methods described in this thesis, primarily the lack of input data and quantified mechanisms. Parameters that have been difficult to quantify include the collision efficiency (α in Paper III), the shear rate of water (G in Paper III), NP concentrations in various products (x in Paper I-II), emission factors for NPs (k in Paper I-II), lifetimes of different products (τ in Paper I-II), current flows and stocks of products (q_u and Q_u in Paper I) and product surface areas (A_u in Paper I-II). For some of these parameters, ranges of four orders of magnitude were found in the literature. With such uncertainty in input data, modeling becomes difficult. Linked to these parameters are uncertainties in mechanisms, such as the emissions of NPs from surfaces (Paper I-II, linked to the parameter k), the behavior of sintered particles (Paper II), the fate of NPs during waste handling processes such as combustion (Paper I-II), the role of natural organic matter and steric stabilizations of NPs in water (Paper III, linked to the parameter α) and the fractal nature of NP agglomerates (Paper III). In order to refine the results, more research is needed to quantify these mechanisms by measuring experimental parameters and monitoring others, such as flows and stocks of products.

It has been argued that the lack of such specific data and quantified mechanisms makes ERA and other detailed environmental assessment methods inappropriate for the case of emerging technologies (von Gleich et al. 2008). Instead, these authors suggest broader, less detailed, more schematic assessment methods. These methods involve making assessments based on combinations of known, inherent properties of the substance, preliminary life cycle assessments and visionary statements regarding technology development. Although such schematic methods may have their merits, it is seldom that input parameters are completely unknown. For instance, data for the thickness of paint layers was required in Paper I. It was not possible to find an exact value of this parameter, so 0.001 m was assumed. Although this may not be the true value, it is certainly within the correct order of magnitude. Using such reasoning combined with proxy data from the scientific literature, most parameters can be estimated. A few parameters, such as the collision efficiency in Paper III and the Ag NP content in textiles and wound dressings in Paper II, are both unknown and difficult to “guesstimate”. Often, these parameters are measured experimentally and found to vary significantly, sometimes many orders of magnitude. For some cases explorative scenarios and ranges of values can account for some uncertainty in parameter value. The case when mechanisms are not studied well enough to be included in an assessment provides a more difficult challenge. However, if crucial mechanisms are unknown, there is a fundamental lack of knowledge for scientific environmental assessments which cannot be circumvented by applying more schematic methods. Instead, formal environmental assessment methods are recommended, combined with explorative scenarios, ranges of values, and cooperation with experimental scientists and others to obtain data.

Table 1. Estimated emissions of TiO_2 and Ag NPs for a current scenario and an explorative scenario. See further Paper I-II for calculations and assumption connected to the explorative scenario.

Nanoparticle	Application	Use phase emissions [particles/year]	
		Current scenario	Explorative scenario
TiO_2 NPs	Paint	$1.1 \cdot 10^{19}$	$7 \cdot 10^{19}$
	Sunscreen	$2.6 \cdot 10^{25}$	$2 \cdot 10^{26}$
	Self-cleaning cement	Neg.	$3 \cdot 10^{21}$
Ag NPs	Wound dressings	$4.6 \cdot 10^{21}$	$[1 \cdot 10^{21}, 1 \cdot 10^{24}]$
	Textiles	$<8.5 \cdot 10^{23}$	$[6 \cdot 10^{28}, 6 \cdot 10^{32}]$
	Electronics	$<<6.8 \cdot 10^{24}$	$<<9 \cdot 10^{27}$

4 CONCLUSIONS AND RECOMMENDATIONS

Although no full ERA of Ag NPs has been performed here, these results indicate that Ag NPs from textiles may be the NP application which is most urgent to monitor of the ones studied here because of the potentially high emissions. In addition, Ag NPs has been shown to be the perhaps most toxic NP to several organisms with regards to mass-based PNEC (Kahru and Dubourguier 2010). The methods developed have highlighted gaps in current knowledge, and especially the fate of TiO_2 NPs and Ag NPs during the waste handling processes of paint, cement and electronics require more studies. The methods developed here provided interesting insights and knowledge for the cases of TiO_2 and Ag NPs, and can be used on other NPs as well. Interesting study objects include iron NPs for remediation of soil, and cerium oxide NPs in combustion engines.

Obtaining detailed input data and quantification of mechanisms is indeed a multidisciplinary work. It may be guided by risk analysts but require the assistance of chemists and other scientists and perhaps none-scientific organizations. For instance, much of the data on flows and stock of products in Paper I-II are obtained from governmental and industry organizations. Deriving toxicological data to use in an ERA of NPs remains the task of toxicologists. The choice of exposure indicator has been discussed several times in this thesis, and particle number versus mass has been discussed. However, surface area is somewhat of the joker in this deck. Besides the frequently cited study by Günter Oberdörster showing that surface area yielded a clearer dose-response relationship than mass when mice were exposed to TiO_2 NPs (Oberdörster et al. 2005), few toxicological studies have been conducted with surface area as output. Modeling flows and stocks of surface area, and the fate of surface areas in the environment, constitute grand challenges. Case studies using surface area as exposure indicator would highlight these difficulties and perhaps overcome them. A recent review paper summarizes much of the toxicological studies performed on NPs so far (Kahru and Dubourguier 2010), and the data is only provided on a mass basis, and not as particle number or surface area. Obtaining PECs of various units is of little use if the PNECs are only given on mass basis, since the risks of hazardous substances is estimated by comparing exposure and effect. This point at the importance of investigating the relevance of different effect indicators than mass-based.

Note also that the only environmental compartment studied in this thesis is water. Of course, exposure to NPs may also occur in air, soil or sediments. Although there are many experimental studies of NPs in air and soil, few have performed exposure models including nano level mechanisms which aim at estimating a PEC for these compartments. Early work by Elsa Vitorge may prove to be a starting point for exposure modeling of NPs in soil (Vitorge 2009). Particles in air (aerosols and particles from combustions) have been studied intensively by atmospheric and environmental chemists, indicating that there may exist models which can provide starting points for exposure models of NPs in air.

There are, of course, many more NMs than TiO_2 and Ag NPs which could pose environmental risks. For instance, one example of a currently emerging NM is graphene, a one-atom-thick layer of graphite, which is the strongest existing material, has a thermal conductivity twice that of diamond and has among the highest charge mobilities ever measured (Segal 2009; van den Brink 2010). The production of graphene is expected to increase significantly in the coming years (Segal 2009). Unmotivated claims regarding low risks have been made (Segal 2009), but graphene is very stable (Wu et al. 2007) and thus likely to be persistent in the environment. It is also fat soluble, and this together with the polycyclic aromatic hydrocarbon-like structure (Wu et al. 2007) rises question marks regarding its safety, especially if the production will increase as fast as suggested by Segal (2009).

Which indicator(s) that would be appropriate to assess the risks of graphene, and which mechanisms that are of interest, is yet to be investigated. It is by assessing the risks of such novel NMs that I plan to proceed my PhD project.

5 REFERENCES

Arthur, W. B. 1996. Increasing returns and the new world of business. *Harvard Business Review* 74(4).

Atkins, P. and L. Jones. 2002. *Chemical Principles - The Quest for Insight*. New York: W.H. Freeman and Company.

Barros, H. and J. M. Abril. 2008. Kinetic box models for the uptake of radionuclides and heavy metals by suspended particulate matter: equivalence between models and its implications. *Journal of Environmental Radioactivity* 99(1): 146-158.

Beck, U. 1992. *Risk Society. Towards a new modernity*. London: SAGE Publications.

Bergek, A., S. Jacobsson, B. Carlsson, S. Lindmark, and A. Rickne. 2008. Analyzing the functional dynamics of technological innovation systems: A scheme of analysis. *Research Policy* 37(3): 407-429.

Blaser, S. A., M. Scheringer, M. MacLeod, and K. Hungerbühler. 2008. Estimation of cumulative aquatic exposure and risk due to silver: Contribution of nano-functionalized plastics and textiles. *Science of The Total Environment* 390(2-3): 396-409.

Boulding, K. E. 1954. General Systems Theory - The Skeleton on Science. *Management Science* 2(3): 197.

Boxall, A., Q. Chaudhry, C. Sinclair, A. Jones, R. Aitken, B. Jefferson, and C. Watts. 2007. *Current and future predicted environmental exposure to engineered nanoparticles*. York: Central Science Laboratory.

Buffle, J., K. J. Wilkinson, S. Stoll, M. Filella, and J. Zhang. 1998. A Generalized Description of Aquatic Colloidal Interactions: The Three-colloidal Component Approach. *Environmental Science & Technology* 32(19): 2887-2899.

Burgman, M. A. 2005. *Risks and Decicions for Conservation and Environmental Management*. Cambridge: Cambidge University Press.

Börjeson, L., M. Höjer, K.-H. Dreborg, T. Ekvall, and G. Finnveden. 2006. Scenario types and techniques: Towards a user's guide. *Futures* 38(7): 723-739.

Christian, P., F. Von der Kammer, M. Baalousha, and T. Hofmann. 2008. Nanoparticles: structure, properties, preparation and behaviour in environmental media. *Ecotoxicology* 17(5): 326-343.

Colvin, V. L. 2003. The potential environmental impact of engineered nanomaterials. *Nature Biotechnology* 21(10): 1166-1170.

Dunphy Guzman, K. A., M. P. Finnegan, and J. F. Banfield. 2006. Influence of Surface Potential on Aggregation and Transport of Titania Nanoparticles. *Environmental Science & Technology* 40(24): 7688-7693.

Elimelech, M., J. Gregor, X. Jia, and R. I. Williams. 1995. *Particle deposition and aggregation: measurement, modeling, and simulation*. Woburn: Butterworth-Heinemann.

European Environment Agency. 2001. *Late lessons from early warnings: the precautionary principle 1896-2000*. Copenhagen.

Fogelberg, H. and B. A. Sandén. 2008. Understanding reflexive systems of innovation: An analysis of Swedish nanotechnology discourse and organization. *Technology Analysis & Strategic Management* 20(1): 65 - 81.

Forsberg, B., H. C. Hansson, C. Johansson, H. Areskoug, K. Persson, and B. Jarvholm. 2005. Comparative health impact assessment of local and regional particulate air pollutants in Scandinavia. *Ambio* 34(1): 11-19.

Friedlander, S. K. 1977. *Smoke, dust and haze, fundamentals of aerosol behavior*. New York: John Wiley & Sons, Inc.

Gallego-Urrea, J. A., J. Tuoriniemi, T. Pallander, and M. Hassellöv. 2010. Measurements of nanoparticle number concentrations and size distributions in contrasting aquatic environments using nanoparticle tracking analysis. *Environmental Chemistry* 7(1): 67-81.

Gottschalk, F., R. W. Scholz, and B. Nowack. 2010a. Probabilistic material flow modeling for assessing the environmental exposure to compounds: Methodology and an application to engineered nano-TiO2 particles. *Environmental Modelling & Software* 25(3): 320-332.

Gottschalk, F., T. Sonderer, R. W. Scholz, and B. Nowack. 2009. Modeled Environmental Concentrations of Engineered Nanomaterials (TiO2, ZnO, Ag, CNT, Fullerenes) for Different Regions. *Environmental Science & Technology* 43(24): 9216-9222.

Gottschalk, F., T. Sonderer, R. W. Scholz, and B. Nowack. 2010b. Possibilities and Limitations of Modeling Environmental Exposure to Engineered Nanomaterials by Probabilistic Material Flow Analysis. *Environmental Toxicology and Chemistry* 29(5): 1036-1048.

Grant, S. B., J. H. Kim, and C. Poor. 2001. Kinetic Theories for the Coagulation and Sedimentation of Particles. *Journal of Colloid and Interface Science* 238(2): 238-250.

Greijer, H., L. Karlson, S.-E. Lindquist, and H. Anders. 2001. Environmental aspects of electricity generation from a nanocrystalline dye sensitized solar cell system. *Renewable Energy* 23(1): 27-39.

Grübler, A. 1996. Time for a Change: On the Patterns of Diffusion of Innovation. *Daedalus* 125(3): 19-42.

Handy, R., F. von der Kammer, J. Lead, M. Hassellöv, R. Owen, and M. Crane. 2008. The ecotoxicology and chemistry of manufactured nanoparticles. *Ecotoxicology* 17(4): 287-314.

Hansen, S. F., B. H. Larsen, S. I. Olsen, and A. Baun. 2007. Categorization framework to aid hazard identification of nanomaterials. *Nanotoxicology* 1(3): 243 - 250.

Hillman, K. M. and B. A. Sandén. 2008. Time and scale in Life Cycle Assessment: the case of fuel choice in the transport sector. *International Journal of Alternative Propulsion* 2: 1-12.

Hunter, R. J. 1987. *Foundations of Colloid Science*. Oxford: Oxford University Press.

ISO. 2008. *Nanotechnologies — Terminology and definitions for nano-objects — Nanoparticle, nanofibre and nanoplate*. ISO/TS 27687:2008(E).

Jiang, J., G. Oberdörster, and P. Biswas. 2009. Characterization of size, surface charge, and agglomeration state of nanoparticle dispersions for toxicological studies. *J Nanopart Res* 11(1): 77-89.

Ju-Nam, Y. and J. R. Lead. 2008. Manufactured nanoparticles: An overview of their chemistry, interactions and potential environmental implications. *Science of The Total Environment* 400(1-3): 396-414.

Kahru, A. and H. C. Dubourguier. 2010. From ecotoxicology to nanoecotoxicology. *Toxicology* 269(2-3): 105-119.

Klaine, S. J., P. J. J. Alvarez, G. E. Batley, T. F. Fernandes, R. D. Handy, D. Y. Lyon, S. Mahendra, M. J. McLaughlin, and J. R. Lead. 2008. Nanomaterials in the Environment: Behaviour, Fate, Bioavailability, and Effects. *Environmental Toxicology and Chemistry* 27(9): 1825-1851.

Kushnir, D. and B. A. Sandén. 2008. Energy Requirements of Carbon Nanoparticle Production. *Journal of Industrial Ecology* 12: 360-375.

Lubick, N. 2008. Risks of Nanotechnology Remain Uncertain. *Environmental Science & Technology* 42(6): 1821-1824.

Luoma, S. N. 2008. *Silver nanotechnologies and the environment: Old problems or new challanges?* Washington DC: Woodrow Wilson International Center for Scholars, Project on Emerging Nanotechnologies and The PEW Charitable Trusts.

Mackay, D., S. Paterson, and W. Y. Shiu. 1992. Generic models for evaluating the regional fate of chemicals. *Chemosphere* 24(6): 695-717.

Mackay, D., A. Di Guardo, S. Paterson, and C. E. Cowan. 1996. Evaluating the environmental fate of a variety of types of chemicals using the EQC model. *Environ Toxicol Chem* 15(9): 1627-1637.

Maynard, A. D., R. J. Aitken, T. Butz, V. Colvin, K. Donaldson, G. Oberdorster, M. A. Philbert, J. Ryan, A. Seaton, V. Stone, S. S. Tinkle, L. Tran, N. J. Walker, and D. B. Warheit. 2006. Safe handling of nanotechnology. *Nature* 444(7117): 267-269.

Meadows, D. 1998. *Indicators and Information Systems for Sustainable Development - A Report to the Balaton Group*. Hartland Four Corners: The Sustainablility Institute.

Mueller, N. C. and B. Nowack. 2008. Exposure Modeling of Engineered Nanoparticles in the Environment. *Environmental Science & Technology* 42(12): 4447-4453.

Nel, A., T. Xia, L. Madler, and N. Li. 2006. Toxic Potential of Materials at the Nanolevel. *Science* 311(5761): 622-627.

Oberdörster, G., E. Oberdörster, and J. Oberdörster. 2005. Nanotoxicology: An Emerging Discipline Evolving from Studies of Ultrafine Particles. *Environmental Health Perspectives* 113(7): 823-839.

Ostwald, W. 1914. *Die Welt der vernachlässigten Dimensionen. Eine Einführung in die moderne Kolloidchemie mit besonderer Berücksichtigung ihrer Anwendungen*. Dresden: Theodor Steinkopff.

Owen, R. and R. Handy. 2007. Viewpoint: Formulating the Problems for Environmental Risk Assessment of Nanomaterials. *Environmental Science & Technology* 41(16): 5582-5588.

Parkin, I. P. and R. G. Palgrave. 2004. Self-cleaning coatings. *Journal of Matererials Chemistry* 15: 1689-1695.

Periáñez, R. 2003. Kinetic modelling of the dispersion of plutonium in the eastern Irish Sea: two approaches. *Journal of Marine Systems* 38(3-4): 259-275.

Poland, C. A., R. Duffin, I. Kinloch, A. Maynard, W. A. H. Wallace, A. Seaton, V. Stone, S. Brown, W. MacNee, and K. Donaldson. 2008. Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study. *Nat Nano* 3(7): 423-428.

Project on Emerging Nanotechnologies. 2009. http://www.nanotechproject.org/inventories/consumer/analysis_draft/. Woodrow Wilson International Center for Scholars and the Pew Charitable Trusts.

Robichaud, C. O., A. E. Uyar, M. R. Darby, L. G. Zucker, and M. R. Wiesner. 2009. Estimates of Upper Bounds and Trends in Nano-TiO2 Production As a Basis for Exposure Assessment. *Environmental Science & Technology* 43(12): 4227-4233.

Royal Society and Royal Academy of Engineering. 2004. *Nanoscience and nanotechnologies: opportunities and uncertainties*. London.

Sandén, B. A. 2004. Technology path assessment for sustainable technology development. *Innovation: management, policy and practice* 6: 316-330.

Sanderson, K. D., S. Hurst, T. McKittrick, D. Rimmer, and L. Ye. 2003. Photocatalytic Coatings for Self Cleaning Glass. In *Glass Processing Days*. Tampere, Finland.

Schmidt, K. F. 2007. *Green nanotechnilogy: It's Easier Than You Think*. Washington DC: Woodrow Wilson International Center for Scholars, Project on Emerging Nanotechnologies and The PEW Charitable Trusts.

Segal, M. 2009. Selling graphene by the ton. *Nature Nanotechnology* 4(10): 612-614.

Silver, S., L. Phung, and G. Silver. 2006. Silver as biocides in burn and wound dressings and bacterial resistance to silver compounds. *Journal of Industrial Microbiology and Biotechnology* 33(7): 627-634.

Smoluchowski, M. 1917. Versuch einer matematischen Theorie der Koagulationskinetic kolloider Lösungen. *Zeitschrift für Physikalische Chemie* 92: 129-168.

Suter, G. W., L. W. Barnthouse, S. M. Bartell, T. Mill, and S. Patersson. 1993. *Ecological Risk Assessment*. Cambridge: Cambridge University Press.

Swedish Chemicals Agency. 2007. *Nanotechnology – big risks with small particles?* Sundbyberg.

United Nations. 2008. *World Population Proscpects. The 2008 Revision. Executive Summary*. New York.

US EPA. 1998. *Guidelines for Ecological Risk Assessment*.

Utterback, J. M. 1994. *Mastering the dynamics of innovation*. Boston: Harward Business School Press.

van den Brink, J. 2010. GRAPHENE What lies between. *Nature Materials* 9(4): 291-292.

van der Voet, E. 2002. Substance flow analysis methodology. In *A Handbook of Industrial Ecology*, edited by R. U. Ayres and L. W. Ayres. Cheltenham: Edward Elgar.

van Leeuwen, C. J. and J. L. M. Hermens. 2004. *Risk Assessment of Chemicals: An Introduction*. Dordrecht: Kluwer Academic Publishers.

van Leeuwen, C. J. and T. G. Vermeire. 2007. *Risk Assessment of Chemicals*: Springer.

Wiesner, M. R., G. V. Lowry, K. L. Jones, J. M. F. Hochella, R. T. Di Giulio, E. Casman, and E. S. Bernhardt. 2009. Decreasing Uncertainties in Assessing Environmental Exposure, Risk, and Ecological Implications of Nanomaterials. *Environmental Science & Technology* 43(17): 6458-6462.

Wijnhoven, S. W. P., W. J. G. M. Peijnenburg, C. A. Herberts, W. I. Hagens, A. G. Oomen, E. H. W. Heugens, B. Roszek, J. Bisschops, I. Gosens, D. Van De Meent, S. Dekkers, W. H. De Jong, M. van Zijverden, A. J. A. M. Sips, and R. E. Geertsma. 2009. Nano-silver – a review of available data and knowledge gaps in human and environmental risk assessment. *Nanotoxicology* 3(2): 109 - 138.

Vitorge, E. 2009. Mechanisms of transport and retention of silica NPs in saturated porous media - Experimental aspects and modeling. In *International Conference on the Environmental Implications and Applications of Nanotechnology*. Amherst, Massachusetts, USA.

von Gleich, A., M. Steinfeldt, and U. Petschow. 2008. A suggested three-tiered approach to assessing the implications of nanotechnology and influencing its development. *Journal of Cleaner Production* 16(8-9): 899-909.

Wu, J., W. Pisula, and K. Müllen. 2007. Graphenes as Potential Material for Electronics. *Chemical Reviews* 107(3): 718-747.

Particle Flow Analysis of TiO_2 Nanoparticles

RICKARD ARVIDSSON[1*]*, SVERKER MOLANDER*[1] *AND BJÖRN A. SANDÉN*[1]

[1]Chalmers University of Technology, Department of Energy and Environment, Division of Environmental Systems Analysis, Rännvägen 6, 412 96 Gothenburg, Sweden.

[*]Corresponding author phone: +46 (0) 31 772 21 61; e-mail: rickard.arvidsson@chalmers.se.

Summary

Several authors have highlighted the potential risks of nanoparticles (NPs). Still, little is known about the magnitude of emissions of NPs from society. Here, the method of explorative particle flow analysis (PFA), a modification of the more well-known substance flow analysis (SFA), is developed and applied. In explorative PFA, particle number instead of mass is used as flow and stock metric and explorative scenarios are used to account for potential technology diffusion and associated particle flows. The method has been applied to the case of TiO_2 NPs in paint, sunscreen and self-cleaning cement. The results indicate that the current largest emissions of TiO_2 NPs originate from the use of sunscreen. One scenario implies that, in the future, the largest flows and stocks of TiO_2 NPs could be related to self-cleaning cement. Gaps in current knowledge are identified and suggestions for future research are given.

Keywords: Substance flow analysis (SFA), nanomaterials, nanoparticles, titanium dioxide, explorative scenarios, particle flow analysis (PFA).

Introduction

History shows several cases where early calls for precautionary actions regarding emerging technologies have been ignored (European Environment Agency 2001). Several of those examples are related to emissions of human-made substances, such as CFCs, tributyltin, PCBs, DDT and benzene. Recent studies have identified a potential new environmental risk related to man-made substances, which is nanomaterials (NMs) in general and nanoparticles (NPs) in particular (Royal Society and Royal Academy of Engineering 2004; Colvin 2003; Nel et al. 2006; Klaine et al. 2008). NPs may have toxic effects and mechanisms that are not present for ordinary chemical substances (Nel et al. 2006; Oberdörster et al. 2005). There is a fear that NP risks will become yet another unheard call for precaution (Allenby and Rejeski 2009). There are, however, indications that some lessons postulated by the European Environment Agency to some extent have been responded to for the case of NMs and NPs. For instance, critical questions regarding their risk have been asked, cross-disciplinary scientific cooperation are formed and the public has been involved in some cases (Hansen et al. 2008). Still, the research performed on NM and NP risks have not yet led to answers to critical questions such as which NMs that pose harm to the environment and which toxic mechanisms and exposure pathways that are most crucial (Hansen et al. 2008; Lubick 2008).

The environmental risk assessment (ERA) framework and procedure is well-defined and has often been used to assess risks related to chemical substances (Burgman 2005; van Leeuwen and Hermens 2004; US EPA 1998; Suter et al. 1993). In general, the ERA procedure involves identification of stressors (e.g. chemicals) and quantification of exposure in the form of a predicted environmental concentration (PEC) and environmental effects in the form of a predicted no-effect concentration (PNEC). The exposure is estimated through quantification of the stressor's sources, emissions and environmental fate, whereas the effects are extracted from (eco)toxicological studies. The framework of ERA is generally considered applicable for assessing risks related to NP emissions, but authors have stressed the importance of adapting the different parts of the ERA procedure in order to apply for NPs as well as for chemicals (Wiesner et al. 2009; Lubick 2008; Hansen et al. 2007). In Arvidsson et al. (2010), we discuss critical problems of and prospects for improving the exposure assessment step (from emission to PEC) for the case of NPs. It was among other things concluded that the inflow of NPs to the environment, i.e. the emissions from society, were a highly uncertain yet important parameter. The aim of this paper is thus to develop a method to estimate emissions of NPs from society to the environment, i.e. quantify the source of the stressors in the environmental risk assessment framework. This task has previously been undertaken as part of risk or exposure assessments performed by other authors, see for instance Mueller and Nowack (2008), Boxall et al. (2007), Robichaud et al. (2009) and Gottschalk et al. (2010a; 2010b, 2009). In some of these studies, a substance flow analysis (SFA) perspective is applied. SFA has earlier been used to study flows of chemicals related to specific environmental problems (van der Voet 2002). To use SFA to quantify the source in an ERA is in line with Shatkin (2008) and Sweet and Strohm (2006) who proposed the need for integration of life cycle modeling, to which SFA is closely related, and risk analysis. However, we suggest two types of modifications to previous estimations of emissions of NPs from society, and by that a modification of the SFA methodology itself for the cases of NPs and emerging technologies.

The first and perhaps most fundamental modification is to acknowledge the particulate nature of the substance in question by using particle number instead of mass to describe the magnitude of flows and stocks of NPs. In addition, discrimination between different types of NPs is of high importance (Hansen et al. 2007; Jiang et al. 2009) and has thus been applied in this study. This fundamental modification of SFA requires a different denotation, and thus we use the term “particle flow analysis” (PFA) to describe the methodology presented here. The second modification is to, in addition to addressing current emissions, also consider scenarios of technology diffusion. Authors have stressed the importance of assessing risks proactively (Allenby and Rejeski 2009), in particular for the case of NPs (Owen and Handy 2007). Only considering current markets and neglecting technology diffusion could greatly underestimate the potential environmental impact of an emerging technology (Sandén and Karlström 2007; Hillman and Sandén 2008). Explorative aspects are included in Boxall et al. (2007), which include one scenario with a 100 percent market penetration of products containing NPs, and in Robishaud et al. (2009), which assumes that all TiO_2 produced will be in the nano-form in the future. However, the methodology presented here gives information regarding which specific TiO_2 NP applications that may cause large emissions in the future in order to guide scientific and societal attention. Together, these two modifications of SFA lead to the methodology henceforth referred to as “explorative PFA” which is described below and applied for the case of TiO_2 NPs in order to estimate the current emissions and emissions in an explorative scenario in order to determine which applications that need further attention due to its large potential impact. Besides providing some answers regarding current and potential magnitude of emissions, this study highlights important gaps in the current knowledge of TiO_2 NPs.

Method

TiO_2 NPs as Case Study

In this study a selection of TiO_2 NP applications which are frequently mentioned in the literature are applied as case study to illustrate the methodology: Paint (Kaegi et al. 2008), sunscreen (Nohynek et al. 2007) and self-cleaning cement (Cassar et al. 2003). These applications represent different properties possessed by TiO_2 NPs. In paint, the white color of larger TiO_2 NPs and agglomerates is wanted. In sunscreen, the ability of TiO_2 NPs to absorb and block UV light is used. While basically any material could be coated or mixed with TiO_2 NPs to create a photocatalytic surface, cement is a good example of this application with a potential large scale use. Our selection is by no means exhaustive and new commercial applications may emerge in the coming decades. The potential environmental risks of TiO_2 NPs has been highlighted in early risk assessments (Mueller and Nowack 2008), which makes it an interesting case to study.

Particle Flow Analysis

The overarching goal of substance flow models is to estimate the emissions from different parts of a substance's life cycle (van der Voet 2002, see Figure 1). SFA quantifies flows of a certain substance throughout society, from extraction of the substance, via the production and use of products in which it is contained, to the waste handling phase. SFA has successfully been used to quantify diffuse emissions of hazardous substances, such as cadmium, mercury and lead (Månsson et al. 2009). That is similar to the aim of this study. In SFA and other environmental systems studies, the question of magnitude is often of vital importance, and mass is normally used as indicator of magnitude. But mass is a dubious indicator for assessing the magnitude of flows and stocks of NPs when they are linked to exposure and risk. Consider two flows of 1 and 10 kg of TiO_2 NPs respectively, where the second one would normally be described as one order of magnitude larger. However, assume that the first flow consists of particles with a diameter of 1 nm, while the second consists of 100 nm particles. Recalculated into particle number, the first flow would be $6 \cdot 10^{22}$ particles and the second one $6 \cdot 10^{16}$ particles, i.e. six orders of magnitude smaller. Particle number has been suggested as a more relevant exposure and effect indicator than mass for NPs (Handy et al. 2008; Arvidsson et al. 2010; Ju-Nam and Lead 2008). It may reflect the cumulative toxic effect stemming from the size and shape of the NPs and is possible to measure experimentally (Handy et al. 2008). Particle number is thus used as flow and stock metric instead of mass, and this is denoted PFA instead of SFA.

Applying particle number as flow and stock metric has an important implication: The basic principle in SFA is the law of mass conservation, which could be expressed as:

$$\frac{dM}{dt} = \sum m_{in} - \sum m_{out} \tag{1}$$

where m represents mass flows and M represents the mass stock [kg]. However, Eq. 1 does not apply strictly when particle number is applied as flow and stock metric. For particles, there are sources and sinks. Sources exist when NPs are produced intentionally for different purposes, e.g. when larger particles are grinded into smaller particles, or when NPs are formed unintentionally during weathering or combustion. Examples of sinks of particles in society are melting of particles or dissociation into molecules, atoms or ions. These sources and sinks has been represented in the flow model by arrows perpendicular to the others, illustrated by the symbols normally used in electronics to indicate the direction of current in long conductors, see Figure 1. Hence, the equation which describes the particle number flows and stocks of a compartment can be written as:

$$\frac{dN}{dt} = \sum n_{in} - \sum n_{out} + n_s \tag{2}$$

where N represents particle number stock [particles], n particle number flows [particles/yr] and the index s stands for sources. The parameter n_s can be a source or a sink depending on its sign (positive or negative). Due to very limited information about production and waste handling processes, the flows and stocks connected to these processes are not estimated in this case study. Instead, the use phase is focused, and the stock in use, the inflow to use phase and use phase emission (N_u, n_u and n_{eu} in Figure 1) are estimated, where the inflow to use phase is coupled to product consumption. The stock (N_u) and annual use (n_u) of particles are calculated from

$$N_u = Q_u \times c_Q \tag{3}$$

and

$$n_u = q_u \times c_q \tag{4}$$

respectively, where Q_u is the product stock [kg], q_u is the product flow [kg] and c_Q and c_q are the particle number concentrations of TiO_2 NPs in the product stock and product flow [particles/kg]. The particle concentrations (both c_F and c_S) are calculated from

$$c = \frac{6 \times x}{\rho \times \pi \times d^3} \qquad \text{[particles/kg]} \tag{5}$$

where x denotes mass concentration, ρ the particle density [kg/m^3] which isapproxiamtely 4200 kg/m^3 for TiO_2 and d the average primary particle diameter [m]. The average diameter is used as proxy for particle size, since detailed size distributions of TiO_2 NPs are not availible for most products included. Note also that particle number in this case refers to primary particle number.

To calculate emissions a distinction between dissipative and non-dissipative use can be made. Since no sinks or sources are present in the use phase of the TiO_2 NP applications studied here and dissipative use implies that stock changes and waste flows are tiny compared to emissions, Eq. 2 can for the case of dissipative use be reduced to

$$n_{eu} = n_u \tag{6}$$

For none-dissipative use, the emissions depend on an emission factor, the particle concentration in the medium and the surface area from which NPs may be emitted. The equation used here to estimate those emissions is an approximate equation derived to fit the only study that has measured TiO_2 NP emissions from surfaces:

$$n_{eu} = \frac{c_Q}{c_{ref}} \times k \times A_u = \frac{c_Q}{c_{ref}} \times k \times \frac{Q_u}{l \times \rho_Q} \tag{7}$$

where A_u is the use stock effective surface area [m^2], k is an emission factor obtained from Hsu and Chen (2007) [particles/m^2/yr], c_{ref} is the particle concentration in the medium studied in Hsu and Chen (2007) [particles/kg], ρ_S is the product density [kg/m^3] and l is the product depth [m]. As can be seen, the effective surface area, meaning the area from which emissions of NPs may occur, has in lack of better estimations been approximated as the total product volume divided with an average depth, thus assuming a parallelepiped-shaped stock. Eq. 6 is based on equal densities between the reference medium in Hsu and Chen (2007) and the product of interest. Data regarding the product stock Q_u was not available for paint, and thus estimated from

$$Q_u = q_u \times \tau \tag{8}$$

where τ denotes the product lifetime in steady-state. Further, NPs may be of different types and be present in different material types, which affect the magnitude and type of emissions.

Hansen et al. (2007) have suggested a framework for characterizing NPs, which divides NPs into surface bound particles, particles suspended in liquid, particles suspended in solids and airborne particles. For particles suspended in liquid Jiang et al. (2009) have suggested a nomenclature that differentiates between three different configuration states: primary particles, agglomerates and aggregates. Agglomerates, which, for instance, can be formed by TiO_2 NPs in water (Arvidsson et al. 2010), are defined as particles held together by weak van der Waals bonds. Aggregates, on the other hand, are defined as particles held together by stronger covalent bonds, and are sometimes referred to as being “sintered”. The material type and particle configuration state will affect both how many NPs that are emitted, i.e. k in Eq. 4, but also what type of NPs that is emitted which affects the environmental fate and toxicity (Baun et al. 2008; Klaine et al. 2008). In addition, the importance of coatings for particle fate, bioavailability and toxicity has been highlighted in many studies (Christian et al. 2008; Handy et al. 2008; Klaine et al. 2008; Nel et al. 2006) and thus specific attention has been paid to determine whether or not the NPs are coated.

The NP definition of particles 1-500 nm in diameter is chosen since it is the broadest suggested range that has been found in the litterature (Handy et al. 2008), although 1-100 nm is a more frequently used definition (ISO 2008; British Standards Institution 2007; Swedish Chemicals Agency 2007). This implies, for instance, that the TiO_2 in paint counts as NPs due to its average diameter of about 250 nm (IARC 2006). The modeling have been conducted for each product separately.

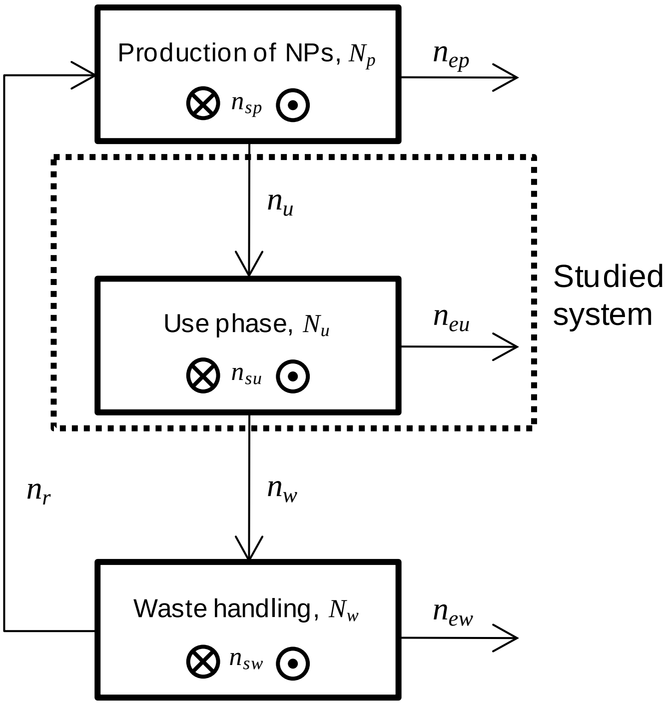

Figure 1. The particle flow model. In the case study, only a part of the system has been described in quantitative terms due to lack of data. *N* stands for particle number stocks, *n* for particle number flows, and the indices *p* stands for production, *u* for use phase, *w* for waste handling, *s* for source, *r* for recycling and *e* for emissions. The potential presence of sinks and sources is illustrated by arrows perpendicular to the others.

Explorative Scenarios

To identify potentially large future sources of TiO_2 NPs a scenario-based method was applied. Note first that the methodology applied here is not a forecast of technology diffusion. The future is to a substantial part unknown, a fact that cannot be circumvented by applying more “advanced” forecasting methods. Instead, explorative scenarios have been applied to generate potential future flows and stocks of TiO_2 NPs, which denotes scenarios which are possible, but no claims regarding their likeliness are made (Börjeson et al. 2006). In the explorative scenario applied here it is assumed that the world average demand per capita for the TiO_2 NP applications included will be equal to the current demand in developed countries such as the U.S. or Sweden. Further, a world population of 10 billion people is assumed, as is forecasted by the United Nations for the year 2050 and beyond (United Nations 2008). Stocks, flows and emissions of this scenario have been given index one, whereas the estimates of current flows, stocks and emissions have been given the index zero. Based on these considerations, the product flow and stock in the explorative scenario can be estimated from

$$q_{u,1} = P \times \frac{q_i}{P_i} \tag{8}$$

$$Q_{u,1} = P \times \frac{Q_i}{P_i} \tag{9}$$

where P stands for population in the scenario (i.e. 10 billion), q_i [kg/year] and Q_i [kg] for the current product flow and stock, respectively, in a developed country and P_i stands for the current population in the same developed country.[1] Thus, q_i/P_i is the current per capita consumption in the developed country in question, and Q_i/P_i is the current per capita stock of the same country.

Model Input Data

Figures on paint flows (q_u) in paint was obtained from the U.S. Geological Survey (2009a), and information of NP size, content and properties (d, x_q and x_Q) are obtained from Tiraks et al. (2003) and different producers' web pages, such as DuPont, Kemira and Tronox. The current stock of paint ($Q_{u,0}$) was estimated by Eq. 8, assuming a lifetime (τ) of 10 years. The emissions of TiO_2 NPs from paint ($n_{eu,0}$) were estimated using Eq. 7, assuming a thickness (l) of 10^{-3} m. The inflow of sunscreen to the use phase ($q_{u,0}$) was obtained from BCC (2008) with the simplifying assumption that all NPs in sunscreen consist of TiO_2 NPs, which may be a reasonable assumption since ZnO as sunscreen ingredient is currently banned in the EU. Information regarding TiO_2 NP properties (d and x_q) in sunscreen was obtained from Nohynek et al. (2007), González et al. (2008) and Serpone et al. (2007). For self-cleaning cement, information of magnitude of inflow to use phase ($q_{u,0}$ and $Q_{u,0}$,) and material characteristics (d, x_Q and x_q) are obtained from Cassar et al. (2003) and from the cement company Cementa (Nilsson 2009).

In order to estimate emission factors (k) from the use phase of paint and self-cleaning cement, average emission factors obtained from Hsu and Chein (2007) were applied. The average

---

[1] The reader may note the similarity between these equations and the well-known IPAT equation, which is described, for instance, in Chertow (2000).

emissions rate for a 10 cm^2 surface coated with 5 weight percent TiO_2 NPs was about 100 particles per minute for a range of materials and conditions, which corresponds roughly to $5 \cdot 10^{10}$ particles$\cdot$year$^{-1}\cdot$m^{-2} (Hsu and Chein 2007). Note that the emission factor (k) derived from Hsu and Chein (2007) has been used rather loosely here: The measurements performed in that study was on TiO_2 NPs sprayed onto a surface, whereas the TiO_2 NPs in paint and self-cleaning cement would rather be categorized as particles suspended in a solid. However, the particles close to the surface of the paint or self-cleaning could be regarded as surface bound, and no specific estimations measurements for the cases of paint or self-cleaning cement have been found.[2] It is also assumed that k is independent of particle size and coatings. Hsu and Chein (2007) studied a spray with 5 weight percent TiO_2 NPs from the company Degussa, Inc., indicating that the particles may be the 21 nm-sized P 25 AEROXIDE® from that company. The reference particle concentration (c_{ref}) can thus be estimated at $3.1 \cdot 10^{17}$ particles/kg.

The future per capita inflow to use phase of paint (q_i/P_i) was estimated as the current per capita inflow to use phase of paint in Sweden (Swedish Paint and Printing Ink Makers Association 2009), and future per capita stock of paint (Q_i/P_i) was estimated by again assuming a lifetime of 10 years. The accuracy of this estimate was checked by comparing it to the per capita façade surface in Sweden in 1984 (Tolstoj et al. 1984), while assuming a paint thickness of 0.001 m. The two estimates were in the same range. Hence, the lifetime of 10 years for paint is considered reasonable. The future per capita inflow to use phase of sunscreen (q_i/P_i) was estimated as the current per capita inflow to use phase of sunscreen in Sweden (Swedish Cosmetic Toiletry and Detergent Association 2009). The U.S. per capita cement inflow to use phase in 2008 (U.S. Geological Survey 2009b) was used to estimate the future per capita inflow to use phase of TiO_2 NPs in cement (q_i/P_i) and the U.S. per capita stock of cement (Kapur et al. 2008) to estimate the future per capita stock of self-cleaning cement (Q_i/P_i). The parameter $n_{eu,1}$ for self-cleaning cement was estimated by assuming a thickness (l) of 1 m. See Table 1 for numerical values of the input data. Note that x_q and x_Q are the same for most products, except for the case of self-cleaning cement, where the cement is mixed with sand and gravel to form concrete, thus changing the concentration of TiO_2 NPs. Similarly, the product stock (Q_u) and the density of the stock (ρ_Q) does not refer to self-

---

[2] Kaegi et al. (2008) did measurements on emissions of TiO_2 NPs painted facades specifically, but did not relate the emitted particles to the amount of paint and can thus not be used in the PFA model presented here.

cleaning cement for that case, but to concrete. This is because it is ultimately the surface area (A_u in Eq. 4) that is of interest for estimating the emissions, and the surface area is in the form of concrete.

Input Parameter	**Paint**	**Sunscreen**	**Self-cleaning cement**
d **[nm]**	250	20	21
x_q **[kg/kg]**	0.1	0.05	0.05
x_Q **[kg/kg]**	0.1	-	0.005
k **[particles/m^2/year]**	$5.0 \cdot 10^{10}$	-	$5.0 \cdot 10^{10}$
l **[m]**	0.001	-	1
q_u **[kton/year]**	29000	72	Neg.
Q_u **[kton]**	550000	Neg.	Neg.
q_i/P_i **[kg/capita/year]**	19	0.07	330
Q_i/P_i **[kg/capita]**	190	Neg.	15000
τ **[years]**	10	Neg.	46
ρ_S **[kg/m^3]**	1500	-	2400

Table 1. Input data to Eq. 3-9. “Neg.” stands for negligible. For references, see Model Input Data.

Output Parameter	**Paint**	**Sunscreen**	**Self-cleaning cement**
$n_{u,0}$ **[particles/year]**	$1.0 \cdot 10^{25}$	$2.6 \cdot 10^{25}$	Neg.
$N_{u,0}$ **[particles]**	$1.0 \cdot 10^{26}$	Neg.	Neg.
$n_{eu,0}$ **[particles/year]**	$1.1 \cdot 10^{19}$	$2.6 \cdot 10^{25}$	Neg.
$n_{u,1}$ **[particles/year]**	$7 \cdot 10^{25}$	$2 \cdot 10^{26}$	$1 \cdot 10^{30}$
$N_{u,1}$ **[particles]**	$7 \cdot 10^{26}$	Neg.	$5 \cdot 10^{31}$
$n_{eu,1}$ **[particles/year]**	$7 \cdot 10^{19}$	$2 \cdot 10^{26}$	$3 \cdot 10^{21}$

Table 2. Current inflow to use phase, use phase stocks and use phase emissions for the TiO_2 NP applications included in this study, along with the same parameters estimated for an explorative scenario. “Neg.” stands for negligible. For references, see Model Input Data.

Results and Discussion

Based on the values in Table 1 inserted into Eq. 3-9 and data found in the litterature, the results in Table 2 have been derived. Note that some of the parameters in Table 2 are derived using very approximate equations and data. The aim of this paper is, however, to develop methodology to estimate emissions of NPs from society, and the figures in Table 2 should thus be seen as indications of magnitude which may help guiding future research. For instance, sunscreen was the application which results in the highest current inflow to use phase of TiO_2 NPs. This is because the NPs in sunscreen are much smaller compared to those in paint. The mass concentration of TiO_2 NPs is about the same in these two products, i.e. about 10-20 percent, and paint is produced in much larger quantities than sunscreen. Compare, for instance, the q_u values in Table 1, which indicate that the mass flow of TiO_2 NPs is much larger for paint. Applying particle number as flow metric thus gives interesting perspectives regarding flow magnitude. Sunscreen dissipates quickly and hence it is the inflow to use phase and not the negligible stock that is of interest from an emission point of view. Regarding self-cleaning cement, only pilot experiments with buildings made from self-cleaning cement exist today (Cassar et al. 2003; Maggos et al. 2008), and thus the current flow and use phase stock of TiO_2 NPs in self-cleaning cement are negligible. However, note that the waste handling was excluded due to lack of data. To our knowledge, very little is known about the behavior of, for instance, TiO_2 NPs during waste handling processes such as combustion, landfill or recycling. It is possible that significant emissions of TiO_2 NPs in paint are emitted during the waste handling phase.

In the explorative scenario, the estimates in Table 2 indicate that the picture outlined above may change significantly. Paint has been produced for many years and is close to its mature stage, and thus the inflow to use phase of TiO_2 NPs in paint will probably increase with less than one order of magnitude. The same appears to be true for sunscreen. Again, the inflow to use phase of TiO_2 NPs in sunscreen is higher than that in paint. Self-cleaning cement, however, is only in the very beginning of its commercialization and may grow significantly in the future. The explorative scenario estimations of flows to use phase in Table 2 show that due to the flow of cement (compare the q_i/P_i value of self-cleaning cement to the others in Table 1) and the small particle size, self-cleaning cement may have the by far largest inflow to use phase and stock of TiO_2 NPs in the future. In fact, the explorative scenario gives a stock of TiO_2 NPs in self-cleaning cement which exceeds the current reserve base of TiO_2 (U.S.

Geological Survey 2009c), which indicate the potential of self-cleaning cement as a major source of TiO_2 NPs even if only a small percentage of the total cement use will contain NPs. Regarding future use phase emissions, sunscreen again has the highest emissions of TiO_2 NPs. The emission factor estimated from data in Hsu and Chein (2007) gives comparatively small emissions for the case of paint and self-cleaning cement. For both paint and self-cleaning cement, this implies that the majority of the TiO_2 NPs are not emitted in the use phase but proceed to the waste handling phase. This in turn strongly highlights the importance of studying the fate of TiO_2 NPs during different waste handling processes.

Applying the categorization frameworks of Hansen et al. (2007) and Jiang et al. (2009) to the TiO_2 NP containing applications included in this study reveals a diversity in particle properties. The stock of TiO_2 NPs in paint consists of particles suspended in liquid, but becomes more like particles suspended in a solid in dried paint. When Kaegi et al. (2008) conducted measurements on TiO_2 NPs emitted from ordinary paint it was concluded that the particles were mostly in the form of agglomerates. Also, most pigments, such as R-706, R-900, R-902+ and R-960 from the leading pigment producer DuPont, have coatings of SiO_2 and Al_2O_3 to increase durability and dispersibility. TiO_2 NPs in sunscreen consist of particles suspended in liquid in the form of agglomerates and is often coated with silicon oils, SiO_2, Al_2O_3 or ZrO_2 to improve their dispersion in the sunscreen and to reduce photosensitivity (Nohynek et al. 2007; Serpone et al. 2007; González et al. 2008). Self-cleaning cement contain TiO_2 NPs that are suspended in a solid. The Degussa P 25 particles used in pilot projects of self-cleaning cement (Cassar et al. 2003) are not coated according to the product information provided by the producer, and no existence of a coating was reported in experimental studies of the P 25 particles (Ohno et al. 2001). This shows that all TiO_2 NPs currently emitted from the use of sunscreen and paint are coated, which has not been included in risk and exposure modeling of NPs (Arvidsson et al. 2010; Mueller and Nowack 2008; Boxall et al. 2007; Robichaud et al. 2009). Thus, considering the different coating, summing up all TiO_2 NP emissions into one figure may not be feasible with regards to fate and toxicity, since the coatings may affect these aspects.

The estimations of stocks, flows and emissions of TiO2 NPs performed in this study may be improved in several ways, especially with regards to experimental data. For instance, the emissions factor for surfaces estimated here draw heavily upon one single reference: Hsu and Chein (2007). Their results need to be confirmed by additional studies, and more similar studies are needed to derive emission factors for the specific products studied in this paper, i.e. paint and self-cleaning cement. This study also indicates that currently, and in particular if self-cleaning cement gains market shares, a significant amount of TiO_2 NPs will end up in the waste handling phase. The fate of particles in the waste handling phase is considered an interesting and important object of future studies. In addition, several parameters used in this study are somewhat uncertain. These include, for instance, particle diameters (d) and estimations of future inflow to use phase and stocks (q_i/P_i and Q_i/P_i). One way to illustrate this uncertainty would be to present ranges of values instead of single figures, or to use more advanced methods such as Monte Carlo simulations, which was applied in Gottschalk et al. (2010a; 2010b, 2009). In general, such methods are considered valuable, but at this stage there is such a fundamental lack of data that the value of applying such methods is in doubt. Consider, for instance, the estimation of TiO_2 NP emissions from surfaces performed in this study (k), which was based on Hsu and Chein (2007). To our knowledge, only one measurement of that parameter had been performed, and on particles sprayed onto a surface rather than paint and self-cleaning cement specifically. Assigning a range or probability distribution to such a parameter is considered impossible and would more reflect the imagination of the author than actual statistical variations of the parameter. Instead, more experimental measurements and closer monitoring is recommended for several of the parameters included, such as emission factors, average particle diameters, and societal flows and stocks of materials such as paint and cement.

Conclusion

In conclusion, this study develops the methodology of explorative PFA and applies it to the case of TiO_2 NPs in paint, sunscreen and self-cleaning cement. This method is a modification of SFA where particle number instead of mass is used as flow and stock metric and explorative scenarios are applied to account for the potential diffusion of technologies. The results indicate that the current largest emissions of TiO_2 NPs originate from the use of sunscreen despite other applications having larger mass flows of TiO_2 NPs. One scenario implies that, in the future, the largest flows and stocks of TiO_2 NPs could be related to self-cleaning concrete. Gaps in current knowledge are identified, and further research is, for instance, needed to develop emission factors of TiO_2 NPs from paint and self-cleaning concrete. In addition, the waste handling processes of paint and cement should be investigated with regards to the fate of TiO_2 NPs. These conclusions underline the importance of an adequate stock and flow metric and considering technical change, which therefore further points to the merits of PFA in combination with explorative scenarios.

Acknowledgements

The financial support from the Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (Formas) and from the Swedish Foundation for Strategic Environmental Research (MISTRA) is gratefully acknowledged.

References

Allenby, B. and D. Rejeski. 2009. The Industrial Ecology of Emerging Technologies: Complexity and the Reconstruction of the World. *Journal of Industrial Ecology* 13: 168-183.

Arvidsson, R., S. Molander, B. A. Sandén, and M. Hassellöv. 2010. Challenges in Exposure Modeling of Nanomaterials in Aquatic Environments. *Human and Ecological Risk Assessment: An International Journal* In press.

Baun, A., N. Hartmann, K. Grieger, and K. Kusk. 2008. Ecotoxicity of engineered nanoparticles to aquatic invertebrates: a brief review and recommendations for future toxicity testing. *Ecotoxicology* 17(5): 387-395.

BCC. 2008. *NANOTECHNOLOGY: A REALISTIC MARKET ASSESSMENT*. BCC Research.

Boxall, A., Q. Chaudhry, C. Sinclair, A. Jones, R. Aitken, B. Jefferson, and C. Watts. 2007. *Current and future predicted environmental exposure to engineered nanoparticles*. York: Central Science Laboratory.

British Standards Institution. 2007. *Terminology for nanomaterials*. London: PAS 136:2007.

Burgman, M. A. 2005. *Risks and Decicions for Conservation and Environmental Management*. Cambridge: Cambidge University Press.

Börjeson, L., M. Höjer, K.-H. Dreborg, T. Ekvall, and G. Finnveden. 2006. Scenario types and techniques: Towards a user's guide. *Futures* 38(7): 723-739.

Cassar, L., C. Pepe, G. Tognon, G. L. Guerrini, and R. Amadelli. 2003. WHITE CEMENT FOR ARCHITECTURAL CONCRETE, POSSESSING PHOTOCATALYTIC PROPRETIES. In *11th Int. Congr. on the Chemistry of Cement*. Durban, South Africa.

Chertow, M. 2000. The IPAT Equation and Its Variants. *Journal of Industrial Ecology* 4(4): 13-29.

Christian, P., F. Von der Kammer, M. Baalousha, and T. Hofmann. 2008. Nanoparticles: structure, properties, preparation and behaviour in environmental media. *Ecotoxicology* 17(5): 326-343.

Colvin, V. L. 2003. The potential environmental impact of engineered nanomaterials. *Nature Biotechnology* 21(10): 1166-1170.

European Environment Agency. 2001. *Late lessons from early warnings: the precautionary principle 1896-2000*. Copenhagen.

González, S., M. Fernández-Lorente, and Y. Gilaberte-Calzada. 2008. The latest on skin photoprotection. *Clinics in Dermatology* 26(6): 614-626.

Gottschalk, F., R. W. Scholz, and B. Nowack. 2010a. Probabilistic material flow modeling for assessing the environmental exposure to compounds: Methodology and an application to engineered nano-TiO2 particles. *Environmental Modelling & Software* 25(3): 320-332.

Gottschalk, F., T. Sonderer, R. W. Scholz, and B. Nowack. 2009. Modeled Environmental Concentrations of Engineered Nanomaterials (TiO2, ZnO, Ag, CNT, Fullerenes) for Different Regions. *Environmental Science & Technology* 43(24): 9216-9222.

Gottschalk, F., T. Sonderer, R. W. Scholz, and B. Nowack. 2010b. Possibilities and Limitations of Modeling Environmental Exposure to Engineered Nanomaterials by Probabilistic Material Flow Analysis. *Environmental Toxicology and Chemistry* 29(5): 1036-1048.

Handy, R., F. von der Kammer, J. Lead, M. Hassellöv, R. Owen, and M. Crane. 2008. The ecotoxicology and chemistry of manufactured nanoparticles. *Ecotoxicology* 17(4): 287-314.

Hansen, S. F., B. H. Larsen, S. I. Olsen, and A. Baun. 2007. Categorization framework to aid hazard identification of nanomaterials. *Nanotoxicology* 1(3): 243 - 250.

Hansen, S. F., A. Maynard, A. Baun, and J. A. Tickner. 2008. Late lessons from early warnings for nanotechnology. *Nature Nanotechnology* 3(8): 444-447.

Hillman, K. M. and B. A. Sandén. 2008. Time and scale in Life Cycle Assessment: the case of fuel choice in the transport sector. *International Journal of Alternative Propulsion* 2: 1-12.

Hsu, L.-Y. and H.-M. Chein. 2007. Evaluation of nanoparticle emission for TiO2 nanopowder coating materials. In *Nanotechnology and Occupational Health*.

IARC. 2006. *Titanium Dioxide (Group 2B).*

ISO. 2008. *Nanotechnologies — Terminology and definitions for nano-objects — Nanoparticle, nanofibre and nanoplate*. ISO/TS 27687:2008(E).

Jiang, J., G. Oberdörster, and P. Biswas. 2009. Characterization of size, surface charge, and agglomeration state of nanoparticle dispersions for toxicological studies. *J Nanopart Res* 11(1): 77-89.

Ju-Nam, Y. and J. R. Lead. 2008. Manufactured nanoparticles: An overview of their chemistry, interactions and potential environmental implications. *Science of The Total Environment* 400(1-3): 396-414.

Kaegi, R., A. Ulrich, B. Sinnet, R. Vonbank, A. Wichser, S. Zuleeg, H. Simmler, S. Brunner, H. Vonmont, M. Burkhardt, and M. Boller. 2008. Synthetic TiO2 nanoparticle emission from exterior facades into the aquatic environment. *Environmental Pollution* 156(2): 233-239.

Kapur, A., G. Keoleian, A. Kendall, and S. E. Kesler. 2008. Dynamic Modeling of In-Use Cement Stocks in the United States. *Journal of Industrial Ecology* 12(4): 539-556.

Klaine, S. J., P. J. J. Alvarez, G. E. Batley, T. F. Fernandes, R. D. Handy, D. Y. Lyon, S. Mahendra, M. J. McLaughlin, and J. R. Lead. 2008. Nanomaterials in the Environment: Behaviour, Fate, Bioavailability, and Effects. *Environmental Toxicology and Chemistry* 27(9): 1825-1851.

Lubick, N. 2008. Risks of Nanotechnology Remain Uncertain. *Environmental Science & Technology* 42(6): 1821-1824.

Maggos, T., A. Plassais, J. Bartzis, C. Vasilakos, N. Moussiopoulos, and L. Bonafous. 2008. Photocatalytic degradation of NOx in a pilot street canyon configuration using TiO2-mortar panels. *Environmental Monitoring and Assessment* 136(1): 35-44.

Mueller, N. C. and B. Nowack. 2008. Exposure Modeling of Engineered Nanoparticles in the Environment. *Environmental Science & Technology* 42(12): 4447-4453.

Månsson, N., B. Bergbäck, D. Hjortenkrans, A. Jamtrot, and L. Sorme. 2009. Utility of Substance Stock and Flow Studies. *Journal of Industrial Ecology* 13(5): 674-686.

Nel, A., T. Xia, L. Madler, and N. Li. 2006. Toxic Potential of Materials at the Nanolevel. *Science* 311(5761): 622-627.

Nilsson, Å. 2009. Personal Communication with Nilsson, Å., Project leader for R&D at Cementa AB. 2009.

Nohynek, G. J., J. Lademann, C. Ribaud, and M. S. Roberts. 2007. Grey Goo on the Skin? Nanotechnology, Cosmetic and Sunscreen Safety. *Critical Reviews in Toxicology* 37(3): 251 - 277.

Oberdörster, G., E. Oberdörster, and J. Oberdörster. 2005. Nanotoxicology: An Emerging Discipline Evolving from Studies of Ultrafine Particles. *Environmental Health Perspectives* 113(7): 823-839.

Ohno, T., K. Sarukawa, K. Tokieda, and M. Matsumura. 2001. Morphology of a TiO2 Photocatalyst (Degussa, P-25) Consisting of Anatase and Rutile Crystalline Phases. *Journal of Catalysis* 203(1): 82-86.

Owen, R. and R. Handy. 2007. Viewpoint: Formulating the Problems for Environmental Risk Assessment of Nanomaterials. *Environmental Science & Technology* 41(16): 5582-5588.

Robichaud, C. O., A. E. Uyar, M. R. Darby, L. G. Zucker, and M. R. Wiesner. 2009. Estimates of Upper Bounds and Trends in Nano-TiO2 Production As a Basis for Exposure Assessment. *Environmental Science & Technology* 43(12): 4227-4233.

Royal Society and Royal Academy of Engineering. 2004. *Nanoscience and nanotechnologies: opportunities and uncertainties*. London.

Sandén, B. A. and M. Karlström. 2007. Positive and negative feedback in consequential life-cycle assessment. *Journal of Cleaner Production* 15(15): 1469-1481.

Serpone, N., D. Dondi, and A. Albini. 2007. Inorganic and organic UV filters: Their role and efficacy in sunscreens and suncare product. *Inorganica Chimica Acta* 360(3): 794-802.

Shatkin, J. A. 2008. Informing Environmental Decision Making by Combining Life Cycle Assessment and Risk Analysis. *Journal of Industrial Ecology* 12(3): 278-281.

Suter, G. W., L. W. Barnthouse, S. M. Bartell, T. Mill, and S. Patersson. 1993. *Ecological Risk Assessment*. Cambridge: Cambridge University Press.

Swedish Chemicals Agency. 2007. *Nanotechnology – big risks with small particles?* Sundbyberg.

Swedish Cosmetic Toiletry and Detergent Association. 2009. http://www.ktf.se/statistik.html. Accessed 10th December 2009.

Swedish Paint and Printing Ink Makers Association. 2009. http://www.sveff.se/STATISTIK.htm. Accessed 13th May 2009.

Sweet, L. and B. Strohm. 2006. Nanotechnology—Life-Cycle Risk Management. *Human and Ecological Risk Assessment: An International Journal* 12(3): 528 - 551.

Tiraks, F., T. Frechen, S. Kirsch, J. Leuninger, M. Melan, A. Pfau, F. Richter, B. Schuler, and C.-L. Zhao. 2003. Formulation effects on the distribution of pigment particles in paints. *Progress in Organic Coatings* 48(140-152).

Tolstoj, N., C. Sjöström, and T. Waller. 1984. *Bostäder och lokaler från energisynpunkt [Eng. Accomodations and locales from an energy aspect]*. Gävle, Sweden: Statens institute för byggnadsforskning [Eng. Swedish institute for construction research].

U.S. Geological Survey. 2009a. *Mineral Commodity Summary - Titanium and Titanium Dioxide*. Reston.

U.S. Geological Survey. 2009b. *Mineral Commodity Summary - Cement*. Reston.

U.S. Geological Survey. 2009c. *Mineral Commodity Summary - Titanium Mineral Concentrates*. Reston.

United Nations. 2008. *World Population Proscpects. The 2008 Revision. Executive Summary*. New York.

US EPA. 1998. *Guidelines for Ecological Risk Assessment*. Washington DC.

van der Voet, E. 2002. Substance flow analysis methodology. In *A Handbook of Industrial Ecology*, edited by R. U. Ayres and L. W. Ayres. Cheltenham UK: Edward Elgar.

van Leeuwen, C. J. and J. L. M. Hermens. 2004. *Risk Assessment of Chemicals: An Introduction*. Dordrecht: Kluwer Academic Publishers.

Wiesner, M. R., G. V. Lowry, K. L. Jones, J. M. F. Hochella, R. T. Di Giulio, E. Casman, and E. S. Bernhardt. 2009. Decreasing Uncertainties in Assessing Environmental Exposure, Risk, and Ecological Implications of Nanomaterials. *Environmental Science & Technology* 43(17): 6458-6462.

The Impact of a Silver-Coated Future: Particle Flow Analysis of Silver Nanoparticles

Rickard Arvidsson[1*], *Sverker Molander*[1] *and Björn A. Sandén*[1]

[1] *Environmental Systems Analysis, Chalmers University of Technology, Rännvägen 6, 412 96 Gothenburg, Sweden.*
[*] *Corresponding author:* rickard.arvidsson@chalmers.se, *+46 (0) 31 772 21 61.*

Summary

Silver has been used for centuries and is well-known for its adverse environmental effects on aquatic organisms. More recently, silver in the form of silver nanoparticles (Ag NPs) have begun to be produced in increasingly larger amounts as coatings, and several authors have highlighted the potential environmental impact of these NPs. In order to contribute to a risk assessment of Ag NPs, the method of particle flow analysis is applied to estimate current emissions from society to the environment. In addition, explorative scenarios are set up to account for potential technology diffusion of the Ag NP applications included. The results are uncertain and need to be refined, but they indicate that all applications included may increase significantly in the future. Ag NPs in textiles and electronic circuitry may increase more than wound dressings due to the limited consumption of that product. Due to the dissipative nature of Ag NPs in textiles, the results indicate that they may cause the highest emissions in the future, thus partly confirming the woes of both scientists and environmental organizations. Gaps in current knowledge have been identified. Especially the fate of Ag NPs during different waste handling processes is outlined as an area which requires more research.

Keywords: Silver, particle flow analysis, explorative scenarios, textiles, wound dressings, electronics, silver ink.

Introduction

The element silver has had a large impact on society for at least a thousand years (Green 1999). For instance, it became one of the main drivers for the colonization of South America and a main aid in forming the Venetian empire. It continues to play an important role in society today due to (1) it's shining appearance which makes it suitable for silverware and jewelry, (2) its superior conductivity which makes it suitable to use in electronic circuitry, (3) its rareness which makes it suitable to use in coins and (4) the sensitivity to light of silver halides which is used in photography (The Silver Institute 1990). There has also been environmental concerns regarding silver since it is one of the most toxic metals to aquatic organisms (Ratte 1999; Eisler 1996; Swedish Environmental Protection Agency 1997) and, hence, it is one of the priority pollutants of the US EPA's Clean Water Act (U.S. Congress 2010). Recently a new application for silver has emerged: the use of silver nanoparticles (Ag NPs). Studies have outlined NPs as a potential environmental risk (Colvin 2003; Klaine et al. 2008; Ju-Nam and Lead 2008; Baun et al. 2008) and Ag NPs in particular (Luoma 2008; Blaser et al. 2008). Nanosilver is today already used in a diverse range of products. According to the Woodrow Wilson Project of Emerging Nanotechnologies, nanosilver is by far the most frequently found NM in consumer products (Project on Emerging Nanotechnologies 2009). It exists as dietary supplements, air purification and antimicrobial dressings (BCC 2008) as well as in tableware, chopsticks, food storage containers, washing machines, refrigerators, computer keyboards, slippers, sportswear, undergarments, socks, hygiene products, beauty soaps, cleansers, cosmetics, disinfection sprays and baby mugs (Luoma 2008), along with computer mice, spatulas, toothpaste, pay phones and handrails (Henig 2007). Besides being used for antimicrobial purposes, Ag NPs are also used in electronic circuitry, since they have the benefits of being easier to apply onto circuitry at low curing temperatures and with a lower resource demand compared to bulk silver, with the drawback of a lower conductivity (Caglar et al. 2008; Kunnari et al. 2009). This application is often called 'nanosilver ink'. Many of these products are currently limited in use, but the few estimates of Ag nanomaterial (NMs) production and consumption show a similar pattern of market growth (Figure 1), implying that a "silver-coated future" (Henig 2007) may be a possible scenario.[1] Especially Ag NPs in wound dressings have gained significant market shares. The global consumption was estimated at $25 million in 2007, possessing four percent of the wound dressings market and growing with a compound annual growth rate of 31 percent since 2003 (BCC 2008). In addition, the use of many of these products, such as toothpaste and cosmetics, is inherently

---

[1] NMs include NPs, but also nanosized surfaces, films, and bulk materials. See further Hansen et al. (2007).

dissipative. The use of antibacterial nanosilver for wound dressings may be motivated considering the efficiency of silver against a wide range of bacteria and since it is not particularly toxic to humans (Brett 2006; Gibbins and Warner 2005), although it is debated whether silver actually improves wound healing (Vermeulen et al. 2009). But the use of nanosilver in consumer products such as socks, refrigerators and computer keyboards in order to kill bacteria or reduce odor has been suggested to be less motivated, especially considering the environmental risks (Henig 2007). The use of these products also threatens the perhaps more motivated use of nanosilver in wound dressings, since there is then a risk to induce silver resistance (Silver et al. 2006). There is currently no regulation for nanosilver and the European legislation REACH does not in general cover NMs and NPs (Hassellöv et al. 2009).

As part of evaluating the risks of Ag NPs, the aim of this study is to estimate emissions of Ag NPs from society to the environment for some product groups. Emissions of Ag NPs has been estimated in previous studies, see Mueller and Nowack (2008), Boxall et al. (2007), Gottschalk et al. (2010a; 2010b, 2009). Silver exposure due to emerging antimicrobial silver applications was studied in Blaser et al. (2008), but that study was not limited to NPs. However, as was pointed out in Arvidsson et al. (2010a), these studies have two major limitations in common. First, mass is used as indicator of magnitude rather than particle number and particle properties are not included. The second limitation is that potential technology diffusion is not accounted for. Boxall et al. (2007) do include market diffusion by assuming a future market share of 100 percent of the included NPs, but focus on Ag NPs as one substance rather than on specific technologies. Thus it gives limited guidance regarding where to focus further societal and scientific attention. In order to address these limitations, this study applies the method of particle flow analysis (PFA) to estimate emissions of Ag NPs (Arvidsson et al. 2010a). In PFA, particle number is used as indicator of magnitude instead of mass, which facilitates the inclusion of specific NP properties in the analysis. In addition, explorative scenarios are used to account for potential technology diffusion. In a way, this scenario accounts for the "silver-coated future", which was the suggestive term introduced by Henig (2007) to denote a world where much Ag NPs and other silver substances would cover larger areas than today. Besides estimating current and future potential emissions of Ag NPs, this methodology highlights gaps in the current knowledge of Ag NPs, which may be addressed by future studies. The none-exhaustive selection of technologies included in this study is wound dressings and textiles containing Ag NPs and nanosilver ink in electronic circuitry. The textile materials included is cotton and polyester, which are common textiles to be coated with Ag NPs (Geranio et al. 2009).

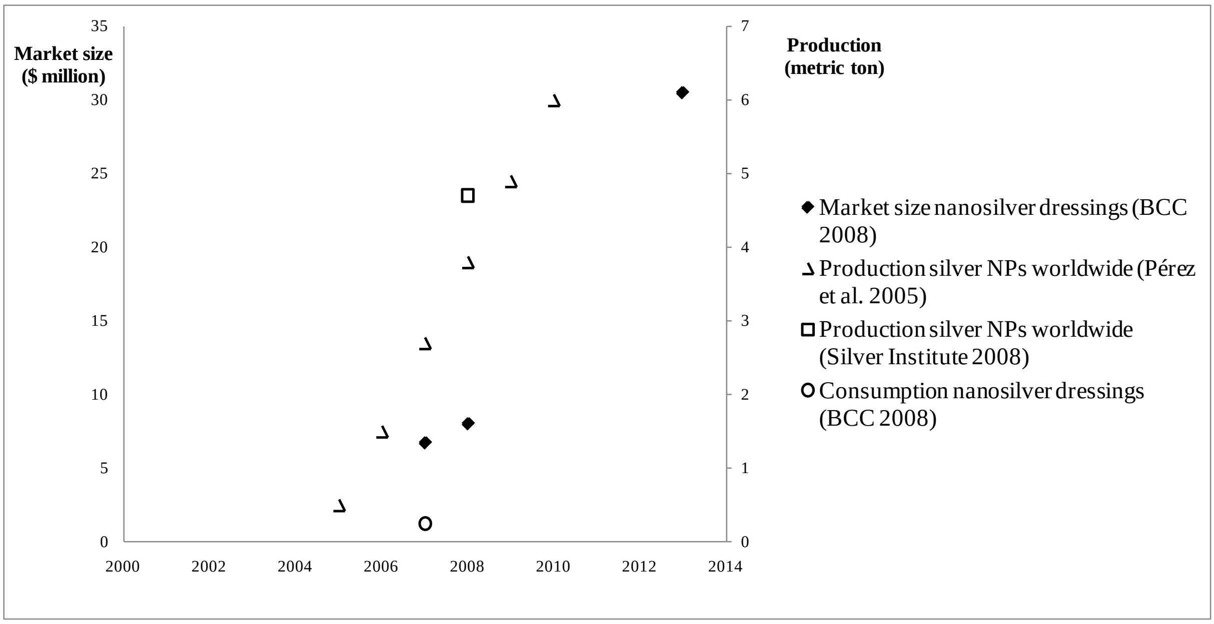

Figure 1. The market size of Ag NPs or Ag NMs according to some estimates (BCC 2008; Pérez et al. 2005; Silver Institute 2008).

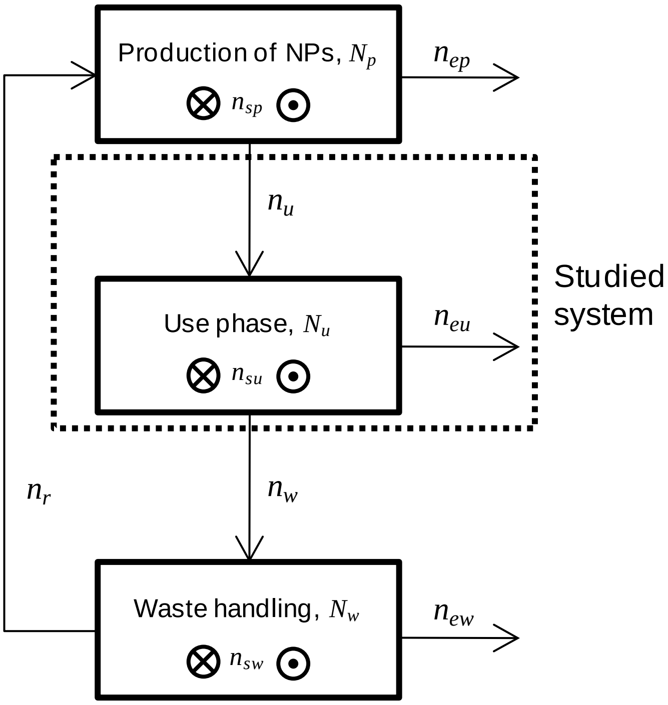

Figure 2. PFA model applied in this study to quantify the flows and stocks of Ag NPs and the emissions of Ag NPs to the environment. *N* stands for particle number stock, *n* for particle number flow, *p* for production, *u* for use phase, *w* for waste handling, *e* for emission, *r* for recycling and *s* for sink or source. Obtained from Arvidsson et al. (2010a).

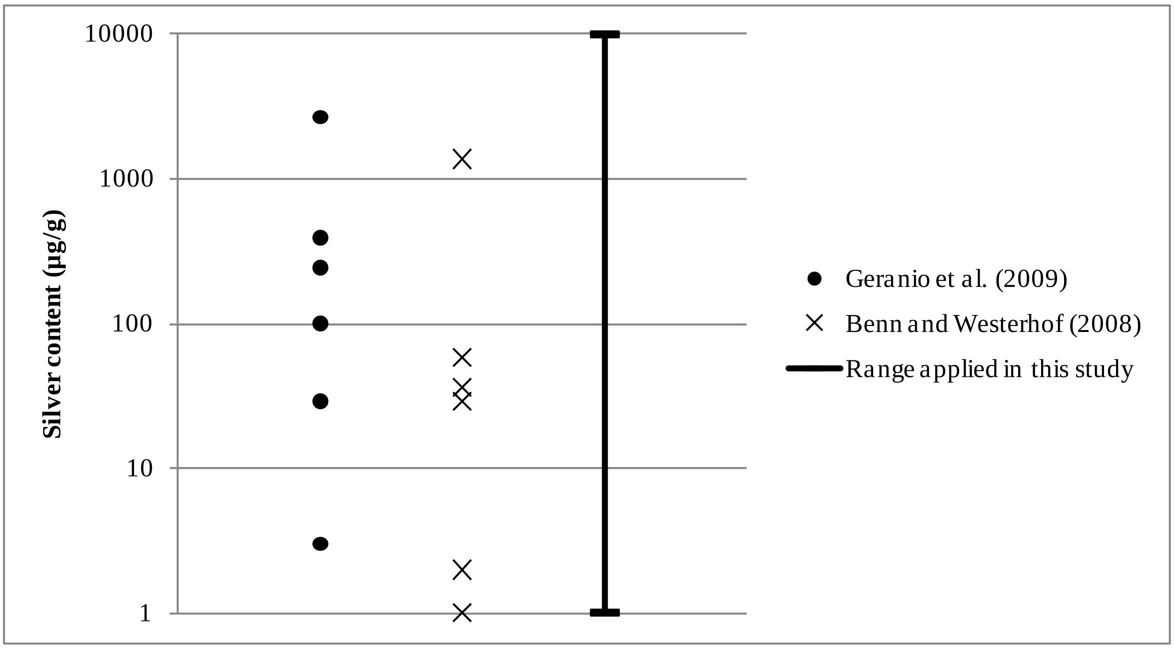

Figure 3. Results from measurements of Ag NP concentrations in antimicrobial textiles in two studies. Also shown is the range applied in this study.

Methods

Particle Flow Analysis

In the method of PFA, particle number is applied as flow and stock metric rather than mass. Mass has previously been used to indicate magnitude of flows and stocks of chemical substances in substance flow analysis (van der Voet 2002) as well as exposure and effect of chemicals in environmental and chemical risk assessments (van Leeuwen and Vermeire 2007; Suter et al. 1993). However, there are strong indications that mass may not be a relevant indicator of magnitude, exposure or toxic effect for the case of NPs (Handy et al. 2008; Ju-Nam and Lead 2008; Arvidsson et al. 2010b; Arvidsson et al. 2010a; Oberdörster et al. 2005). By applying particle number instead of mass as flow and stock metric, relevant particle properties such as size can accounted for. In addition, frameworks describing different types and properties of NPs, for instance those by Hansen et al. (2007) and Jiang et al. (2009), can be utilized in the analysis. The characterization framework for NPs by Hansen et al. (2007) include particles which are surface bound, suspended in liquid, suspended in solids or airborne. The categorization framework of NPs by Jiang et al. (2009) divides particles into primary particles, agglomerates (primary particles held together by weak, van der Waals forces) and aggregates (primary particles held together by strong, covalent bonds). Processes that change particle number, such as melting of particles, dissociation of particles into ions, and grinding which produces more particles, can be included by adding a source (or sink) factor, see Figure 2. Thus, the convenient law of mass conservation on which substance flow analysis is based does not apply. Instead, a similar equation can describe the particle flows and stocks of a compartment, with the source or sink term included:

$$\frac{dN}{dt} = \sum n_{in} - \sum n_{out} + n_S \qquad (1)$$

where N denotes the particle number [particles] stock and n the particle number flow [particles/yr]. Note that the source or sink term (n_S) can be both positive and negative. Due to lack of data, only the NP use phase (same as substance use phase in a substance life cycle) and related flows and stocks has been investigated in this study. The production phase relates to working environment, and NP emissions in that phase may be more dependent on companies' management practices then on NP properties. The waste handling process is not included due to poor knowledge on the fate of Ag NPs during that phase. The parameters estimated in this study are thus the use phase inflow (n_u), the use phase stock (N_u) and the use phase emissions (n_{eu}), see Figure 2. This is done for all three Ag NP applications included. However, data on Ag NP use is often reported on a mass basis. In lack of proper size distributions, the average particle diameter is used as proxy for particle size, and the following equation has been used:

$$n = \frac{6 \times m}{\rho \times \pi \times d^3} \qquad (3)$$

where m is the mass flow, ρ is the density [kg/m^3] which is 10 500 kg/m^3 for silver and d is the average particle diameter [m]. Some applications included are dissipative, meaning that $n_{eu} >> n_w$ and $N_u \approx 0$. For those cases, $n_{eu} \approx n_u$. Typically, dissipative use applies for particles suspended in a liquid or air-born particles, see Hansen et al. (2007). For none-dissipative use of applications consisting of NPs suspended in a solid or on a surface, see Hansen et al. (2007), emissions can for the general case be estimated according to:

$$n_{eu} = A_u \times c_Q \times k \qquad (2)$$

where A_u is the surface area of the product stock [m^2], c_Q is the Ag NP concentration in the product stock, and k is an emission factor. “Product” refers to wound dressing, textile or electronic device in this case. The categorization framework of Hansen et al. (2007) becomes useful here, since depending on whether the product contains NPs suspended in a solid or bound to a surface, the units of c and k will vary. For NPs suspended in a solid, c_Q represents the particle concentration in the solid [particles/m^3] and k has the unit [m/s]. For particles bound to a surface, c_Q is a surface concentration [particles/m^2] and k gets the unit [1/s]. Often, similarly to the case of Ag NP use, concentrations of Ag NPs are given on a mass basis and must be recalculated. By assuming spherical particles, the particle number can then be estimated using:

$$c = \frac{6 \times x}{\rho \times \pi \times d^3} \qquad (3)$$

where x is the mass concentration. No figures on stocks of electronic circuitry have been found, and thus it has been estimated using an approximate equation which assumes that the emissions $n_{eu} << n_u$:

$$N_u = n_u \times \tau \tag{4}$$

where τ is the lifetime of electronic circuitry. The typology of Jiang et al. (2009) will also affect the emission factor (k) since sintered NPs are held together by hard bonds and should have a lower affinity to be emitted, which strengthen the assumption that the emissions are significantly lower than the inflow to use phase for Ag NPs in electronic circuitry.

Explorative Scenario

Modeling technological diffusion is difficult. The formative phase of a technology or product is characterized by various designs, market diversity and high uncertainty (Grübler 1998). There are many examples of forecasts of technology diffusion that have not materialized, such as the forecast that nuclear power would become the dominant source of electricity by the last turn of century (Sandén 2004). To avoid making dubious forecasts, an explorative scenario is applied here in order to assess the potential of the included applications. Explorative scenario denotes a possible scenario which answers the question of what could happen given a certain development (Börjeson et al. 2006). However, no claims are made regarding how likely the scenario is. Examples of this include the emissions scenarios applied by IPCC (Börjeson et al. 2006). The explorative scenario applied here aims at estimating the potential emissions from the included Ag NP applications, and thus involve the following features: (1) The Ag NP application in question will reach 100 percent market share, (2) the per capita inflow to use phase and stock of the applications will be equal to those found in today's high income regions such as the U.S. or Europe, and (3) the world population will increase to 10 billion people, as forecasted by the United Nations for the year 2050 (United Nations 2008). This scenario has been given the index one, whereas the scenario that represents the current situation has been given the index zero. Note that the current situation refers to approximately the year 2008. The use phase inflow and stock of Ag NPs for the explorative scenario has been estimated as:

$$n_{u,1} = P \times \frac{q_i}{P_i} \times c_q \tag{5}$$

$$N_{u,1} = P \times \frac{Q_i}{P_i} \times c_Q \tag{6}$$

where P stands for population in the explorative scenario (i.e. 10 billion), q_i/P_i and Q_i/P_i for the current per capita product flow and stock of product in developed countries respectively, c_q is the concentration of Ag NPs in the product flow.[2] Again, the unites of c_q, c_Q, q_i/P_i and Q_i/P_i will change depending on application. For surface-bound Ag NPs, the product stock is measured in area and for Ag NPs suspended in liquid it is measured in mass. In accordance, A_u in Eq. 2 becomes equal to Q_u for the case of surface-bound particles.

Model Input Data

The current mass based inflow of Ag NPs ($m_{u,0}$) in wound dressings was found in BCC (2008), and information about their particle size (d) in Gibbins (2005). According to interviews with practitioners at Swedish hospitals, both wound dressings that contain silver and those that do not are changed regularly, from several times per day up to one time per week. There is thus no significant stock of wound dressings formed in the use phase. However, some Ag NPs are emitted during the use phase, i.e. when the dressing is taped onto the wound, and some are still in the dressing when it is thrown away. No data on emission factor (k) for Ag NPs in wound dressing has been found, but Gibbins (2005) showed that the release of Ag NPs in SilvaGard is at a rate of about 10 percent of the initial loading in 10 days, given an original concentration of 0.8 µg/cm^2. Since most dressings are changed within 10 days, the release of 10 percent of the particles is considered a worst case and applied in this study, i.e. $n_{eu} \approx 0.1 \times n_u$. Although, the figure 10 percent is probably weight percent, the Ag NPs in wound dressings are quite monodisperse with a size range of only 2-7 nm (Gibbins 2005), making the figure 10 percent fair to use also for particle concentrations. The Ag NP concentration (c_q) on the product SilvaGard can range from 1 to 32 µg/cm^2 (Gibbins 2005), and between 0.84 and 1.34 mg/cm^2 for the product Acticoat (BCC 2008). This variation in mass concentration could be due to the use of smaller particles in SilvaGard, but this has not been possible to confirm. Considering this variations, a range of 1 mg/cm^2 to 1 µg/cm^2 has

---

[2] The reader may note the similarity between these equations and the well-known IPAT equation, which is described, for instance, in Chertow (2000).

been applied for the parameter c_q. The per capita inflow to use phase of wound dressings (q_i/P_i) in the U.S. was calculated from data provided by BCC (2008).

No figures on current inflow to use phase of Ag NPs in textiles ($m_{u,0}$) have been found, but it is stated by the Silver Institute (2008) that the total amount of Ag NPs consumed is 4700 kg, indicating that the figure must be smaller than that. According to the company Uvex, their cloths contain particles <20 nm in size (d), and 10 nm has thus been assumed for Ag NPs in textiles. This is supported by the fact that the smallest size of Ag NPs emitted from textiles measured by Benn and Westerhoff (2008) was 10 nm. Measurements on Ag NP release from textiles indicate that it is reasonable to assume that most particles will be emitted within a few washes (Benn and Westerhoff 2008; Geranio et al. 2009), and thus the use of Ag NPs in textiles is regarded as dissipative. The per capita inflow to use phase of cotton and polyester fiber in the U.S. was obtained from Meyer et al. (2008) and Aizenshtein (2006) respectively and added to obtain Q_i/P_i for textiles. Regarding the Ag NP concentration in textiles (c_q), there is a great variety in the measurements performed.[3] Results from the concentration measurements of the seven products containing Ag NPs included in Benn and Westerhoff (2008) and the six out of nine products containing Ag NPs in Geranio et al. (2009) can be found in Figure 3. To include this uncertainty, a range of 1-10000 µg/g has been applied.

Similar to Ag NPs in textiles, no figures on the current inflow to use phase of Ag NPs in electronic circuitry ($m_{u,0}$) has been found, but it should be smaller than 4700 kg, i.e. the total consumption of Ag NPs estimated by the Silver Institute (2008). The size of the Ag NPs (d) in silver ink is obtained from Caglar et al. (2008). The average content of silver in circuit boards (c_q and c_Q) is obtained from Lanzano et al. (2006). However, experts report that for applications not requiring high current carrying capability, nanosilver ink use 50-75 percent less silver than conventional bulk silver applications (Jablonski 2010). Thus, the silver concentration has been reduced by half for the case of Ag NPs. The European per capita inflow to use phase of electronic circuitry was obtained from Lanzano et al. (2006). A lifetime of 10 years is assumed in order to estimate the stock of Ag NPs in electrical circuits, both current and for the explorative scenario. The figure 10 years has not been possible to confirm with references, but is probably within the right order of magnitude. No information regarding

---

[3] From a technological change point of view this diversity in Ag NP concentration is not surprising: The early phase of the technological life cycle is characterized by varying, competing designs (Grübler 1998). In a similar manner, there was a great diversity in filament material (bamboo, osmium, tantalum and eventually tungsten) in the formative phase of the incandescent light bulb (Smil 2005).

surface areas of electronic circuits (A_u) or emissions of Ag NPs from such areas (k) has been found. The only thing known for sure is that the emissions of Ag NPs from electronic circuits must be lower than the inflow to the use phase, and probably a lot lower since the Ag NPs are sintered.

Input Parameter	Wound dressings	Textiles	Electronic circuitry
d [nm]	10	10	5
m_u [kg/yr]	254	<4700	<4700
x_q	0.001-1 [μg/cm^2]	1-10000 [mg/kg]	1 [mg/kg]
x_Q	-	-	1 [mg/kg]
k [particles/m^2/year]	-	-	N.A.
A_u [m]	-	-	N.A.
q_i/P_i	7 cm^2/capita/year	32 kg/capita/year	12 kg/capita
τ [years]	Neg.	Neg.	10

Table 1. Input data to Eq. 2-6. “Neg.” stands for negligible and “N.A.” for not available. For references, see Model Input Data.

Output Parameter	**Wound dressings**	**Textiles**	**Electronic circuitry**
$n_{u,0}$ **[particles/year]**	$4.6 \cdot 10^{22}$	$<8.5 \cdot 10^{23}$	$<6.8 \cdot 10^{24}$
$N_{u,0}$ **[particles]**	Neg.	Neg.	$<6.8 \cdot 10^{25}$
$n_{eu,0}$ **[particles/year]**	$4.6 \cdot 10^{21}$	$<8.5 \cdot 10^{23}$	$<<6.8 \cdot 10^{24}$
$n_{u,1}$ **[particles/year]**	$[1 \cdot 10^{22}, 1 \cdot 10^{25}]$	$[6 \cdot 10^{28}, 6 \cdot 10^{32}]$	$9 \cdot 10^{27}$
$N_{u,1}$ **[particles]**	Neg.	Neg.	$9 \cdot 10^{28}$
$n_{eu,1}$ **[particles/year]**	$[1 \cdot 10^{21}, 1 \cdot 10^{24}]$	$[6 \cdot 10^{28}, 6 \cdot 10^{32}]$	$<<9 \cdot 10^{27}$

Table 2. Current inflow to use phase, use phase stocks and use phase emissions for the Ag NP applications included in this study, along with the same parameters estimated for an explorative scenario. “Neg.” stands for negligible and “N.A.” for not available. For references, see Model Input Data.

Results and Discussion

According to Table 2, the currently highest inflow to use phase of Ag NPs may occur from their use in electronic circuitry. This result is primarily due to the smaller particle size of the Ag NPs in electronic circuitry compared to those in wound dressings and textiles. However, the figures regarding current inflow to use phase of Ag NPs in textiles and electronic circuitry constitute upper limits rather than exact figures. It is clear that more detailed monitoring of these inflows to use phase rates are needed to accurately assess the emissions of Ag NPs from these applications. Regarding the use phase emissions, the results indicate that the currently largest use phase emissions of Ag NPs originate from textiles. In fact, this pattern remains in the explorative scenario, where the lower boundary of the Ag NP emission from textiles was four orders of magnitude higher than the highest upper boundary of Ag NPs in wound dressings. This is due to the much higher inflow to use phase of textiles compared to wound dressings. It is, of course, much more common to wear cloths than wound dressings, and cloths normally cover a significantly larger part of the body than wound dressings for most people even in the summer time. The results presented in Table 2 thus indicate that the articulated concern regarding Ag NPs in textiles should be taken serious, as suggested by other authors (Henig 2007; Blaser et al. 2008). It is, of course, possible that Ag NPs in textiles remain a niche product only applied in underwear and sports cloths, but the figures in Table 2 show that it has the potential to become a large emitter of nanosilver. It should be noted that the estimations of Ag NP emissions from textiles are very uncertain due to high variation in nanosilver content in experimental studies (Geranio et al. 2009; Benn and Westerhoff 2008). Also, different nanosilver textile designs may emit less nanosilver (Geranio et al. 2009). It is noted in Geranio et al. (2009) that there is a variation in the incorporation of Ag NPs which correlate with the way the silver was attached to the textile and the amount of silver emitted. For instance, when the silver was incorporated into the textile fiber matrix, the emissions were slower compared to when the silver was merely bound to the fiber surface. But since the sample was so small and the correlation not described mathematically, no such considerations have been made in this study. Efforts should be put into revealing that relationship and to further try to establish an average concentration of Ag NPs in textiles. If one of the designs with lower emissions becomes dominant, the emissions may be significantly lower. According to Table 2, Ag NPs in wound dressings will probably never be of major environmental importance due to the limited use of wound dressings. However, as always, effects could arise from locally high emissions.

Note also that an increase in Ag NPs in electronic circuitry would result in a decreased use of bulk silver for that purpose. As stated above, if bulk silver is used instead of nanosilver ink in electronic circuitry, the amount of silver per product may be twice as high or more. This implies that switching to Ag NPs in electronic circuitry may reduce the total use of silver. However, the results in Table 2 also show that even if Ag NPs are used in electronic, the use of Ag NPs may still be as large as that of textiles and larger than that of wound dressings. The emissions of Ag NPs were proven to be a formidable challenge to estimate, since the effective surface area (A_u) may vary depending on the specific application. In addition, the Ag NPs in electronic circuitry are sintered, and to our knowledge no measurements of NP emissions from sintered particles have ever been made. The fact that sintered particles are tightly attached by covalent bonds indicates that emissions may be low, but this needs to be confirmed by experimental studies. The Ag NPs in electronic circuitry may also be encapsulated in other materials.

Apart from the importance of Ag NP emissions from textiles, this study points at the importance of the waste handling phase. According to one study, only 10 percent of the Ag NPs attached to an antibacterial wound dressing are emitted during use (Gibbins 2005). Practitioners at Swedish hospitals report that silver-containing wound dressings are disposed in the everyday garbage, and the nanosilver still attached to the wound dressing is thus likely to end up in an incineration plant. This is probably the fate of most consumer purchased textiles with Ag NPs as well. The fate of Ag NPs during such processes is, to our knowledge, not studied. An incineration plant normally reaches temperatures of above 800ºC, which is much higher than the temperature used for sintering of Ag NPs (Caglar et al. 2008; Kunnari et al. 2009). The Ag NPs may thus undergo a transformation from one configuration state to another according to the typology suggested by Jiang et al. (2009). The fate of Ag NPs from electronic circuitry in the waste handling phase is also unknown, although the waste handling of electronic circuitry has already been acknowledged as a significant environmental problem due to the electronic devises' content of various toxic metals, see for instance Robinson (2009). Ag NPs in electronic circuitry may add to this problem in the future, although at the same time reduce it due to the lower silver content compared to conventional circuitry.

According to Morley and Eatherley (2008), silver is a compound that deserves attention due to potential resource scarcity. The total mining of silver metal in 2009 was approximately 21 000 ton (Brooks 2009), and the known silver reserve base, i.e. silver recoverable from base-metal ores, is estimated at about 570 000 ton in 2009 (Brooks 2009). If the particle number inflow to use phase in the explorative scenario in Table 2 are recalculated into mass flows, they would greatly exceed the current total mining of silver and even the reserve base. Although this shows that the explorative scenario is possible yet unlikely, it also illustrates that the Ag NP applications studied here have the potential to further contribute to the scarcity of silver, in particular when considering the dissipative, i.e. non recyclable, type of use. Finally, the results in Table 2 also show that for the three applications included in this study, significant increases of inflow to use phase and emissions could potentially occur. This highlights the importance of applying explorative scenarios or other methods to account for technology diffusion.

Conclusions

In this paper the methodology of PFA is applied for the case of Ag NPs in wound dressings, textiles and electronic circuits to estimate the emissions of Ag NPs from these applications. Further, explorative scenarios are developed to account for potential technology diffusion. It is assumed in these scenarios that the Ag NP application will reach 100 percent market share and that everybody in a world of 10 billion inhabitants will use as much of the products as today’s Americans or Europeans. The results indicate that current knowledge of Ag NP emissions is very uncertain. However, the results show that textiles may become a large source of Ag NP emissions in the future. Wound dressings will probably remain a smaller source. The future stock of electronic circuits may contain many Ag NPs, but the emissions of these from the use phase are unknown. The waste handling phase was not included in the study, but the estimated low emissions of Ag NPs from wound dressings and the presumed low emissions of Ag NPs from electronic circuits suggest that the fate of Ag NPs in the waste handling phase is an interesting object of study. In addition, effort should be made to derive a factor that describe particulate emissions from electronic circuitry.

Acknowledgements

The financial support from the Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (Formas) and from the Swedish Foundation for Strategic Environmental Research (MISTRA) is gratefully acknowledged.

References

Aizenshtein, E. 2006. World production and consumption of polyester fibres and thread. *Fibre Chemistry* 38(3): 264-271.

Arvidsson, R., S. Molander, and B. A. Sandén. 2010a. Particle Flow Analysis of TiO2 nanoparticles. *Journal of Industrial Ecology* In review.

Arvidsson, R., S. Molander, B. A. Sandén, and M. Hassellöv. 2010b. Challenges in Exposure Modeling of Nanoparticles in Aquatic Environments. *Human and Ecological Risk Assessment: An International Journal* In press.

Baun, A., N. Hartmann, K. Grieger, and K. Kusk. 2008. Ecotoxicity of engineered nanoparticles to aquatic invertebrates: a brief review and recommendations for future toxicity testing. *Ecotoxicology* 17(5): 387-395.

BCC. 2008. *NANOTECHNOLOGY: A REALISTIC MARKET ASSESSMENT*. BCC Research.

Benn, T. M. and P. Westerhoff. 2008. Nanoparticle Silver Released into Water from Commercially Available Sock Fabrics. *Environmental Science & Technology* 42(18): 7025-7026.

Blaser, S. A., M. Scheringer, M. MacLeod, and K. Hungerbühler. 2008. Estimation of cumulative aquatic exposure and risk due to silver: Contribution of nano-functionalized plastics and textiles. *Science of The Total Environment* 390(2-3): 396-409.

Boxall, A., Q. Chaudhry, C. Sinclair, A. Jones, R. Aitken, B. Jefferson, and C. Watts. 2007. *Current and future predicted environmental exposure to engineered nanoparticles*. York: Central Science Laboratory.

Brett, D. W. 2006. A Discussion of Silver as an Antimicrobial Agent: Alleviating the Confusion. *Ostomy Wound Management* 52(1).

Brooks, W. E. 2009. *Mineral Commodity Summary: Silver*. Reston: U.S. Geological Survey.

Börjeson, L., M. Höjer, K.-H. Dreborg, T. Ekvall, and G. Finnveden. 2006. Scenario types and techniques: Towards a user's guide. *Futures* 38(7): 723-739.

Caglar, U., K. Kaija, and P. Mansikkamäki. 2008. Analysis of Mechanical Performense of Silver Inkjet-Printed Structures. In *2nd IEEE International Nanoelectronics Conference (INEC 2008)*. Pudong, Shanghai, China.

Chertow, M. 2000. The IPAT Equation and Its Variants. *Journal of Industrial Ecology* 4(4): 13-29.

Colvin, V. L. 2003. The potential environmental impact of engineered nanomaterials. *Nature Biotechnology* 21(10): 1166-1170.

Eisler, R. 1996. *Silver Hazards to Fish, Wildlife and Invertebrates: A Synoptic Review*. Washington DC: U.S. Department of the Interior.

Geranio, L., M. Heuberger, and B. Nowack. 2009. The Behavior of Silver Nanotextiles during Washing. *Environmental Science & Technology* 43(21): 8113-8118.

Gibbins, B. and L. Warner. 2005. The Role of Antimicrobial Silver Nanotechnology. *Medical Device & Diagnostic Insustry Magazine, August*.

Gibbins, B. L. 2005. *SilvaGard Technology Summary*. AcryMed Inc.

Gottschalk, F., R. W. Scholz, and B. Nowack. 2010a. Probabilistic material flow modeling for assessing the environmental exposure to compounds: Methodology and an application to engineered nano-TiO2 particles. *Environmental Modelling & Software* 25(3): 320-332.

Gottschalk, F., T. Sonderer, R. W. Scholz, and B. Nowack. 2009. Modeled Environmental Concentrations of Engineered Nanomaterials (TiO2, ZnO, Ag, CNT, Fullerenes) for Different Regions. *Environmental Science & Technology* 43(24): 9216-9222.

Gottschalk, F., T. Sonderer, R. W. Scholz, and B. Nowack. 2010b. Possibilities and Limitations of Modeling Environmental Exposure to Engineered Nanomaterials by Probabilistic Material Flow Analysis. *Environmental Toxicology and Chemistry* 29(5): 1036-1048.

Green, T. 1999. *The Millenium in Silver*. London.

Grübler, A. 1998. *Technology and Global Change*. Cambridge, UK: Cambridge University Press.

Handy, R., F. von der Kammer, J. Lead, M. Hassellöv, R. Owen, and M. Crane. 2008. The ecotoxicology and chemistry of manufactured nanoparticles. *Ecotoxicology* 17(4): 287-314.

Hansen, S. F., B. H. Larsen, S. I. Olsen, and A. Baun. 2007. Categorization framework to aid hazard identification of nanomaterials. *Nanotoxicology* 1(3): 243 - 250.

Hassellöv, M., T. Backhaus, and S. Molander. 2009. REACH misses nano! *Sustainability - Journal from the Swedish Research Council Formas* 2.

Henig, R. M. 2007. Our Silver-Coated Future. *OnEarth Magazine*.

Jablonski, G. 2010. Personal Communication with Jablonski, G., PChem Associates, Inc. 2010.

Jiang, J., G. Oberdörster, and P. Biswas. 2009. Characterization of size, surface charge, and agglomeration state of nanoparticle dispersions for toxicological studies. *J Nanopart Res* 11(1): 77-89.

Ju-Nam, Y. and J. R. Lead. 2008. Manufactured nanoparticles: An overview of their chemistry, interactions and potential environmental implications. *Science of The Total Environment* 400(1-3): 396-414.

Klaine, S. J., P. J. J. Alvarez, G. E. Batley, T. F. Fernandes, R. D. Handy, D. Y. Lyon, S. Mahendra, M. J. McLaughlin, and J. R. Lead. 2008. Nanomaterials in the Environment: Behaviour, Fate, Bioavailability, and Effects. *Environmental Toxicology and Chemistry* 27(9): 1825-1851.

Kunnari, E., J. Valkama, M. Keskinen, and P. Mansikkamäki. 2009. Environmental evaluation of new technology: printed electronics case study. *Journal of Cleaner Production* 17(9): 791-799.

Lanzano, T., M. Bertram, M. De Palo, C. Wagner, K. Zyla, and T. E. Graedel. 2006. The contemporary European silver cycle. *Resources, Conservation and Recycling* 46(1): 27-43.

Luoma, S. N. 2008. *Silver nanotechnologies and the environment: Old problems or new challanges?* Washington DC: Woodrow Wilson International Center for Scholars, Project on Emerging Nanotechnologies and The PEW Charitable Trusts.

Meyer, L., S. MacDonald, and J. Kiawu. 2008. *Cotton and Wool Situation and outlook Yearbook*. United States Department of Agriculture.

Morley, N. and D. Eatherley. 2008. *Material Security - Ensuring resource availibility for the UK*. Chester: U.K. Environment Agency and Department for Business Enterprice & Regulatory Reform.

Mueller, N. C. and B. Nowack. 2008. Exposure Modeling of Engineered Nanoparticles in the Environment. *Environmental Science & Technology* 42(12): 4447-4453.

Oberdörster, G., E. Oberdörster, and J. Oberdörster. 2005. Nanotoxicology: An Emerging Discipline Evolving from Studies of Ultrafine Particles. *Environmental Health Perspectives* 113(7): 823-839.

Pérez, J., B. Bax, and C. Escolano. 2005. *Roadmap Report on Nanoparticles*. Barcelona: NanoRoadMap project.

Project on Emerging Nanotechnologies. 2009. http://www.nanotechproject.org/inventories/consumer/analysis_draft/. Woodrow Wilson International Center for Scholars and the Pew Charitable Trusts.

Ratte, H. T. 1999. Bioaccumulation and toxicity of silver compounds: A review. *Environmental Toxicology and Chemistry* 18(1): 89-108.

Robinson, B. H. 2009. E-waste: An assessment of global production and environmental impacts. *Science of The Total Environment* 408(2): 183-191.

Sandén, B. A. 2004. Technology path assessment for sustainable technology development. *Innovation: management, policy and practice* 6: 316-330.

Silver Institute. 2008. The Current State of Nanosilver Markets. *Silver News, Second Quarter*.

Silver, S., L. Phung, and G. Silver. 2006. Silver as biocides in burn and wound dressings and bacterial resistance to silver compounds. *Journal of Industrial Microbiology and Biotechnology* 33(7): 627-634.

Smil, V. 2005. *Creating the twentieth century: Technical innovations of 1867-1914 and their lasting impact*. Cary, NC, USA: Oxford University Press.

Suter, G. W., L. W. Barnthouse, S. M. Bartell, T. Mill, and S. Patersson. 1993. *Ecological Risk Assessment*. Cambridge: Cambridge University Press.

Swedish Environmental Protection Agency. 1997. *Silver - Occurence, distribution and effects of silver in the environment*. Stockholm: Report 4664.

The Silver Institute. 1990. *World Silver Survey 1950-1990*. Washington DC:

U.S. Congress. 2010. *Appendix A in part 423 of the Code of Federal Regulations 40: Protection of Environment*.

United Nations. 2008. *World Population Proscpects. The 2008 Revision. Executive Summary*. New York.

van der Voet, E. 2002. Substance flow analysis methodology. In *A Handbook of Industrial Ecology*, edited by R. U. Ayres and L. W. Ayres. Cheltenham: Edward Elgar.

van Leeuwen, C. J. and T. G. Vermeire. 2007. *Risk Assessment of Chemicals*: Springer.

Vermeulen, H., J. M. van Hattem, M. N. Storm-Versloott, and D. T. Ubbink. 2009. *Topical silver for treating infected wounds (Review)*. The Cochrane Collaboration.

Challenges in Exposure Modeling of Nanoparticles in Aquatic Environments

Rickard Arvidsson,[1] Sverker Molander,[1] Björn A. Sandén,[1] and Martin Hassellöv[2]

[1]Chalmers University of Technology, Department of Energy and Environment, Division of Environmental Systems Analysis, Gothenburg, Sweden; [2]University of Gothenburg, Department of Chemistry, Gothenburg, Sweden

Address correspondence to Rickard Arvidsson, Chalmers University of Technology, Department of Energy and Environment, Division of Environmental Systems Analysis, SE 412 96 Gothenburg, Sweden, E-mail: rickard.arvidsson@chalmers.se, Phone: +46 (0) 31 772 21 61

Running Head: Exposure to Nanoparticles in Aquatic Environments

Received 14 December 2009; revised manuscript accepted 12 April 2010

.

ABSTRACT

Managing the potential environmental risks of nanoparticles requires methods to link nanoparticle properties with macro-scale risks. This study outlines challenges in exposure modeling of nanoparticles in aquatic environments, such as the role of natural organic matter, natural colloids, fractal dimensions of agglomerates, coatings and doping of particles, and uncertainties regarding nanoparticle emissions to aquatic environments. The pros and cons of the exposure indicators mass concentration, particle number concentration, and surface area are discussed. By applying colloid chemistry kinetic equations describing particle agglomeration and sedimentation for the case of titanium dioxide nanoparticles, a limited exposure assessment including some of the factors mentioned is conducted with particle number concentration as the exposure indicator. The results of the modeling indicate that sedimentation, shear flows, and settling are of less importance with regard to particle number based predicted environmental concentrations. The inflow of nanoparticles to the water compartment had a significant impact in the model, and the collision efficiency (which is affected by natural organic matter) was shown to greatly affect model output. Implications for exposure modeling, regulation and science are discussed. A broad spectrum of scientific disciplines must be engaged in the development of exposure models where nano-level properties are linked to macro-scale risk.

Key Words: fate modeling, environmental risk assessment, nanoparticles, titanium dioxide.

INTRODUCTION

In a report from the European Environmental Agency (2001) case studies show several examples of how early calls for precautionary measures regarding emerging technologies have been neglected. There is a possibility that the case of nanoparticles (NPs) will become yet another of these unheard calls (Hansen *et al.* 2008). Many studies outline NPs as a potential environmental risk, and the importance of understanding the fate and exposure routes of NPs has been stressed (Sweet and Strohm 2006; Klaine *et al.* 2008; Colvin 2003; Maynard *et al.* 2006). The lack of knowledge is often highlighted in these studies; production volumes, emissions to the environment, environmental fate and exposure, and toxic effects are stated as highly uncertain. Issues related to fate and exposure modeling of NPs in water are addressed in this study. One main difficulty in exposure modeling of NPs lies in vertical system integration, that is, linking properties on a nano-scale to macroscopic risks. In our terminology, “macro-scale risks” is the outcome in terms of potential effects on defined endpoints, such as specific impacts on human health or environmental endpoints such as fish or crustacean populations. Previous exposure and risk assessments of NPs have not modeled fate processes at the nano level, but at much higher system levels (Mueller and Nowack 2008; Boxall *et al.* 2007; Blaser *et al.* 2008). In those studies NPs are treated as bulk material and material flow analysis is applied, without acknowledging the particulate nature of the material. For instance, fate processes such as agglomeration[1] and sedimentation have not been considered, despite the fact that agglomeration has been pointed out as an important fate mechanism that could affect the exposure and bio-availability of NPs (Velzeboer *et al.* 2008; Klaine *et al.* 2008; Handy *et al.* 2008; Baun *et al.* 2008), and sedimentation was suggested to be an important sink for NPs in Baun *et al.* (2008).

Other important properties that affect NP fate and exposure in the water compartment include the presence of natural organic matter (NOM), the concentration and type of natural colloids (NCs), the fractal dimension of agglomerates and break-up of agglomerates (Christian *et al.* 2008). These properties are nano-level properties that have an impact on particle concentration and size distribution; that is, they are examples of vertical system integration where the nano level affects the macro level. Also, these properties are not covered by the procedures of chemical risk assessment under REACH (Hassellöv *et al.* 2009).

Chemical risk assessment, however, has a long tradition of relating small-scale molecular properties to macro-scale risks. In chemical risk assessment it is normal to calculate a risk quotient (RQ) using the predicted environmental concentration (PEC) of a substance and the predicted no-effect concentration (PNEC) of the same substance (European Chemicals Bureau 2003; van Leeuwen and Hermens 2004). The RQ is calculated according to the formula:

---

[1] Note that sometimes the words “coagulation” or “aggregation” are used instead of “agglomeration” in the colloid chemistry literature. Recently, however, an ISO standard has suggested that “aggregation” should denote when the particles are bound together by tight covalent bonds (sintered) and “agglomeration” should denote when particles are held together by weaker attractive forces such as van der Waals forces (ISO 2008). See also Jiang *et al.* (2009) for a more detailed discussion.

$$RQ = \frac{PEC}{PNEC} \tag{1}$$

A risk quotient greater than 1 indicates risk. The PEC is often estimated using exposure models, where molecular properties such as Henry's law coefficient, the octanol-water partition coefficient and molecular mass, and environmental properties such as water volumes, wind speed, and soil density are inserted into models based on thermodynamically founded natural science theories (van Leeuwen and Hermens 2004; Mackay *et al.* 1996; Mackay *et al.* 1992). Recently, environmental scientists have been encouraged to turn to colloid chemistry to create analogous models of the environmental fate and exposure of NPs (Velzeboer *et al.* 2008; Klaine *et al.* 2008; Handy *et al.* 2008; Christian *et al.* 2008). A reason is that colloids are often defined as particles with a diameter between 1 nm and 1 µm (Elimelech *et al.* 1995; Shaw 1992) while NPs are often defined as particles ranging in diameter from 1 to 100 nm (Royal Society and Royal Academy of Engineering 2004; ISO 2008; Oberdorster *et al.* 2005; Swedish Chemicals Agency 2007). Even with the broad definition of NPs of up to 500 nm suggested by Handy *et al.* (2008), NPs are well within the colloid size range.[2] Therefore it seems reasonable to apply colloidal physical chemistry theories for modeling NP exposure.

This study outlines the possibilities and difficulties in modeling fate and exposure of NPs in water in order to derive a PEC by applying colloid chemistry, using titanium dioxide NPs (TiO_2 NPs) as an example. TiO_2 NPs are among the most frequently used nanomaterials in consumer products according to the Project on Emerging Nanotechnologies (2009), and the risk associated with TiO_2 NPs has been stressed in particular by Mueller and Nowack (2008). Thus TiO_2 NPs provide a relevant case study. The main question investigated in this study is whether a PEC for NPs in water can be derived from colloid chemistry models. Therefore a model is presented, together with some results, which form the starting points for a discussion on the further need for research and development of exposure models for risk assessments of NPs. Also, difficulties in choosing an appropriate exposure indicator for risk assessments of NPs have been discussed (Handy *et al.* 2008). This study thus discusses the pros and cons of three different exposure indicators and the importance of finding indicators relevant to both exposure and effect, that is, of identifying which common unit the PEC and PNEC should have. Suggestions are also given for future studies and possible regulation based on the results from this study.

THE KINETIC MODEL

A kinetic model supporting fate and exposure estimations for NPs can, in principle, be constructed since a colloidal dispersion is never thermodynamically stable, but could be stabilized

---

[2] Note, however, that there exist other definitions of colloids, depending on the scientific field (Gustafsson and Gschwend 1997).

kinetically (Handy *et al.* 2008). The kinetic laws that describe changes in particle concentration in a homogenous fluid have been described by Smoluchowski (1917) and Friedlander (1977), which include both sedimentation and three agglomeration mechanisms: (1) perikinetic agglomeration caused by Brownian motion; (2) orthokinetic agglomeration caused by shear flows; and (3) differential settling caused by sedimentation. A collision efficiency[3] α is included to take into account the electrostatic potential barriers surrounding the NPs due to the electric double layer surrounding particles in a fluid, and it obtains values between 0 and 1, with $\alpha = 1$ meaning that all collisions lead to a merging of the NPs and $\alpha = 0$ meaning that no collisions lead to a merging. A continuous inflow of particles I_j is also added, see Equation 2.

$$\frac{dn_j}{dt} = \frac{1}{2}\sum_{i=1}^{i=j-1} \alpha_{i,j-i} K_{i,j-i} n_i n_{j-i} - n_j \sum_{i=1}^{i=\infty} \alpha_{i,j} K_{i,j} n_i - \frac{v_s}{d} j^{\beta} n_j + I_j \tag{2}$$

Equation 2 is based on the assumptions that all particles are approximately spherical and that merging of two particles is an irreversible reaction. In Equation 2, n_j is the particle number concentration of particle j (if j equals three, then particle j consists of three primary particles that have agglomerated), $\alpha_{i,j}$ and $\alpha_{i,j-i}$ are collision efficiencies, $K_{i,j}$ and $K_{i,j-i}$ are rate constants, v_s is the sedimentation rate of primary particles, β describes the increase in sedimentation rate due to increased cluster size (2/3 for spherical particles), d is the depth of the water compartment and I_j is the inflow of particles. The first term on the right side of Equation 2 describes the formation of particle j through agglomeration of particles i and $j-i$. The second term describes the loss of particle j through agglomeration with other particles i. The third term accounts for the sedimentation, and the last term for the inflow of particles. A particle number based PEC can be derived from Equation 2 by solving the differential equation and summing the particle concentrations n_j at a time when the system has reached steady state. An expression for the agglomeration rate constant, which includes perikinetic agglomeration, orthokinetic agglomeration and differential settling respectively, is shown in Equation 3:

$$K_{i,j} = \frac{2k_B T}{3\mu}\frac{\left(a_i + a_j\right)^2}{a_i a_j} + \frac{4}{3}G\left(a_i + a_j\right)^3 + \left(\frac{2\pi g}{9\mu}\right)\left(\rho_p - \rho_w\right)\left(a_i + a_j\right)^3\left(a_i - a_j\right) \tag{3}$$

where k_B is the Boltzmann constant, T is the temperature, μ is the fluid viscosity, a_i and a_j are the radii of particles i and j respectively, G is the shear rate, g is the gravitational acceleration and ρ_p and ρ_w are the densities of the particles and water, respectively. The sedimentation rate in Equation 2 is calculated according to Grant *et al.* (2001):

---

[3] Note that the collision efficiency is sometimes referred to as the sticking probability or the stickiness coefficient.

$$v_s = \frac{2a^2\left(\rho_p - \rho_w\right)g}{9\mu} \tag{4}$$

where a is the radius of the primary particle. In Equations 2–4 above, most parameters, for example the water viscosity and the gravitational acceleration, are easy to determine. However, some parameters are more difficult to assign a value to and several relevant factors are not included in Equation 2.

In the following, some model parameters and factors are discussed, and then an initial sensitivity assessment illustrating their relative importance is presented. The two most notable parameters that raise difficulties are the collision efficiency and the shear rate. Also, assigning a value to the inflow has been difficult due to lack of information regarding NP production volumes. Equation 2 assumes spherical particles, which is doubtful especially after agglomeration when fractal agglomerates are often formed. The importance of including not only synthetic NPs but also NCs is discussed, and finally the assumption that the agglomerates do not undergo break-up is treated along with the effect of coatings and doping. These parameters and processes are discussed in more depth below. The conceptual model describing the fate of NPs in water that has guided the model construction can be seen in Figure 1.

Collision Efficiency and Natural Organic Matter

Assigning a value to the collision efficiency (α) is not a trivial matter. Approximate equations exist where the collision efficiency depends on pH, point of zero charge, ion valence, concentration, and temperature (Reerink and Overbeek 1954), but they only take into account the electrostatic forces between pure particles in water without NOM and are generally not supported by experimental observations (Wiesner 1992; Ryan and Elimelech 1996). In natural waters the existence of NOM creates a different situation. Several studies have shown that NOM interacts with NPs and it is clear that NOM can affect the collision efficiency of particles significantly, both with regard to electrostatic forces and steric hindrance (Sander *et al.* 2004; Baalousha *et al.* 2008; Buffle *et al.* 1998).

The effect of NOM on the collision efficiency is complex, since it can both enhance and reduce agglomeration. Buffle *et al.* (1998) suggest that agglomeration of natural inorganic colloids is enhanced by rigid biopolymers (*e.g.*, peptidoglycans, hemicelluloses, and microbial cell walls) due to the attachment of particles to the polymers and by bridging flocculation, and decreased by fulvic compounds due to electrostatic and/or steric stabilization. The decreased agglomeration in the presence of fulvic acid was also reported by Domingos *et al.* (2009). Further, the effects of NOM are also interconnected with other parameters such as pH and salt concentration (Sander *et al.* 2004; Baalousha *et al.* 2008; Domingos *et al.* 2009) and the exact composition of the NOM differs between different waters (Buffle *et al.* 1998).

However, the vast majority of natural particles are negatively charged due to NOM coatings (Loder and Liss 1985; Beckett and Le 1990). Loux and Savage (2008) showed that NPs coated with organic matter have a more negative surface charge than uncoated NPs. According to Fang *et al.* (2009), TiO_2 NPs were stabilized by NOM in soil suspensions. In summary, the physiochemistry behind the collision efficiency is not yet fully understood and currently no precise equations exist for calculating the collision efficiency, and this is especially true in the presence of NOM.

Since the interaction between NOM and NPs is not well enough understood, model estimations of the collision efficiency are limited. The collision efficiency must thus be determined experimentally in order to get a reliable value (Wiesner 1992; Ryan and Elimelech 1996), which creates additional problems from an exposure modeling point of view. First, many experimental studies on the effect of NOM on NP fate do not estimate the collision efficiency as output. Instead, other properties such as the size distribution, electrophoretic mobility, mean particle diameter, diffusion coefficient, and zeta potential are the output of many experimental studies (*e.g.*, Baalousha *et al.* (2008), Domingos *et al.* (2009)). Second, several studies do not perform measurements at conditions close to the conditions in relevant environmental compartments, but at pH values or ion concentrations that are very rarely found in nature. For instance, Buffle *et al.* (1998) studied the interaction between hematite NPs and a NOM called polyacrylic acid derivatives, with the collision efficiency as output. The pH in the experiment was 3, which is much lower than normally found in the environment, which is typically from 5 to 8 (Swedish University of Agricultural Sciences 2008). Furthermore, reference to Figure 5 in Buffle *et al.* (1998) shows that the collision efficiency is very sensitive to the concentration of NOM, changing almost four orders of magnitude for a change in NOM concentration from 0.03 to 0.04 mg/l. These values are, however, much lower than the average total organic carbon content in Swedish waters, which is 12 mg/l (Swedish University of Agricultural Sciences 2008).

Assigning a value to the collision efficiency is difficult from a modeling perspective: The complicated dependence of the collision efficiency on NOM and other parameters makes calculation impossible at the present state of knowledge. Furthermore, few empirical studies exist where collision efficiencies have been determined under relevant environmental conditions. Based on current knowledge the only thing that can be said about the numeric value of the collision efficiency in general is that it often varies between 0.001 and 1 (Buffle *et al.* 1998; Chen and Elimelech 2007; Elimelech 1994).

Shear Rates and Differences between Waters

The shear rate *G* in Equation 3 represents laminar flow, which is unusual under natural conditions. Camp and Stein (1943) developed an equation that takes into account theturbulent flow by estimating the mean velocity gradient G_m. Note also that even more refined expressions exist, for example, Peddocchi and Piedra-Cueva (2005). However, a major problem is the large variations in shear rate due to weather conditions and whether the water is running or not. For instance, a still, deep lake should normally have a much lower shear rate than a river. In lakes the shear rate is normally about 0.1-3 s^{-1}, and it is 0.01-10 s^{-1} in oceans (Colomer *et al.* 2005). No shear rates representative for rivers have been found, but they are likely >10 s^{-1}, and thus the shear rate varies at least four orders of magnitude in natural aquatic systems. Hence, although the shear rate in principle can be determined, it is still difficult to assign a general value that is representative for the whole water compartment (contrary to other properties such as water density, which can be assumed to be roughly the same throughout the freshwater compartment).

Fractal Dimension

Synthetic primary NPs can often be regarded as spherical. However, during rapid agglomeration fractal agglomerates are often formed (Meakin 1987). Fractal agglomerates are characterized by their mass fractal dimension d_F, which varies between 1 and 3 for three-dimensional objects (Wiesner 1992). An aggregate so compact that it had no pores would coalesce with a sphere, having a fractal dimension of three. More open aggregates have a fractal dimension closer to 1. The difference in bioavailability and toxicity of primary NPs and particle agglomerates is largely unknown, although it has been suggested that agglomerates are less toxic (Velzeboer *et al.* 2008). However, creation of oxygen radicals has been pointed out as a potential toxicity mechanism for TiO_2 NPs (Hund-Rinke and Simon 2006) and fractal agglomerates may also be able to generate significant amounts of oxygen radicals. The mass fractal dimension is difficult to estimate since it depends on material and fluid properties in a complex way, and must be determined experimentally, similar to the collision efficiency (Elimelech *et al.* 1995). However, Wiesner (1992) showed that neglecting agglomerate porosity could cause an error of less than 10 percent in the collision efficiency, and due to this low impact compared to the range of 0.001-1 as has been reported for the collision efficiency, along with modeling difficulties, the fractal dimension has not been included in the model calculations of this study.

Inflow and Production Volumes

For TiO_2 nanomaterials, approximately 58,800 kg/year enter the Swiss water compartment according to Mueller and Nowack (2008). This figure is based on a company survey stating the amount of several different NPs produced in Switzerland (Schmid and Riediker 2008). Unfortunately such information is not available for most regions. Another source of NP production data in Mueller and Nowack (2008) is a report from the United Nations Environment Program

(UNEP 2007). That report, in turn, states that the data originates from “NanoroadSME, a research project founded by the European Commission, 2006.” However, no information regarding production volumes can be found on the project web page (Project NanoRoadSME 2008), and thus it is unclear where the data originate. A report from the Royal Society and Royal Academy of Engineering (2004) also reports figures for global production of nanomaterials, for instance TiO_2, stating as reference “chemical journals and reviews (2003–2004), and market research BCC (2001).” However, no information on production volumes of specific NPs or nanomaterials can be found in the proceedings of the conference mentioned, that is, BCC (2001). A report from BCC Research gives some information, but it includes no references (BCC 2008). This illustrates the difficulties in finding reliable information about the inflow of NPs to the water compartment, and even if the emissions of NPs to the water compartment could be specified in terms of mass, the input unit in Equation 2 is particle number concentration. If production volumes were well known it would still be a problem that the fate of NPs from the product to the water compartment is not fully understood, such as the fate of NPs in waste incineration plants and in sewage treatment plants. Thus the annual produced mass of a certain NP is not equal to the inflow to the water compartment. The same difficulties described here for TiO_2 NPs apply for other NPs as well.

Natural Colloids

Another important factor with regard to NP fate is the role of NCs that are likely to interact with synthetic NPs (Sweet and Strohm 2006; Klaine *et al.* 2008; Handy *et al.* 2008). Measurements performed by Gallego-Urrea *et al.* (2010) suggest that the amount of natural NPs in water is in the range of 10^{14} particles/m^3, a result that was similar to those found in other studies. Very few particles larger than 500 nm were found. The effect of NCs can be included mathematically into Equation 2 by adding a term describing the heteroagglomeration:

$$\frac{dn_j}{dt} = \frac{1}{2}\sum_{i=1}^{i=j-1}\alpha_{i,j-i}K_{i,j-i}n_i n_{j-i} - n_j\sum_{i=1}^{i=\infty}\alpha_{i,j}K_{i,j}n_i - \frac{v_s}{d}j^{\beta}n_j + I_j - n_j\sum_{i=1}^{i=\infty}\gamma_{i,j}H_{i,j}c_i \qquad (5)$$

where γ is the collision efficiency and H is the rate constant for collisions between NCs and synthetic NPs, and c_i is the concentration of an agglomerate with i primary NCs.

The problem here lies in the diversity of NCs with regard to shape and chemistry. For instance, both organic and inorganic colloids can be found in natural waters. According to measurements performed, the average diameter of these is close to 200 nm for many natural waters, although the size distribution is wide (Gallego-Urrea *et al.* 2010). Besides the diversity of the NCs themselves, they may also be partly or fully covered by NOM, which affects the collision efficiency as described above. To our knowledge, no measurements of the collision efficiency between NPs and NCs have been conducted. Another important question in this context concerns how agglomerates consisting of both natural and synthetic NPs should be classified. Such a heteroagglomerate of a naturally occurring substance and synthetic NPs, outlined as a potential hazard, is indeed difficult to conceptualize from a risk perspective. Are they to be seen as NPs, as NCs, or as something else?

Break-Up and Limiting Size

In Equation 2 the agglomeration is regarded as irreversible in that no agglomerate break-up occurs. Zhang *et al.* (2008) showed that it was very difficult to disaggregate metal oxide NPs below 500 nm, which indicates that break-up may not be of importance, at least not for metal oxide NPs. However, Wiesner (1992) showed that break-up could be of importance and that it is partly controlled by the fractal dimension. Different studies have tried to estimate the maximum size of agglomerates, but these estimations are difficult to confirm experimentally and can be highly system-specific (Elimelech *et al.* 1995). One possibility mentioned by Wiesner (1992) was to model break-up as a reduced agglomeration rate, but to our knowledge no simple expression that can be implemented into Equation 2 exists.

Coatings and Doping

“Coatings” sometimes refers to a layer of NOM surrounding the NPs, as discussed above. More often, however, it refers to a coating that is synthesized along with the particles or right after particle synthesis. Surface properties of particles are important since it is a particle’s surface that can interact with the surroundings, and thus coatings can affect NP fate and effects (Nel *et al.* 2006; Handy *et al.* 2008). For instance, the TiO_2 and zinc oxide NPs in sunscreen are normally coated with silicon oils, SiO_2 or Al_2O_3 in order to improve dispersibility and reduce reactive oxygen species generation in sunscreen (Nohynek *et al.* 2007). The exact extent to which the properties are modified is not known. Whether a TiO_2 NP coated with Al_2O_3 adopts exactly the same properties as an Al_2O_3 NP, or just more Al_2O_3-like properties, is currently unknown. “Doping” refers to the process of purposely introducing impurities into the NPs, which can be done to enhance the UV absorption of TiO_2 NPs (Wakefield *et al.* 2004). The effect of doping on NP behavior is largely unknown.

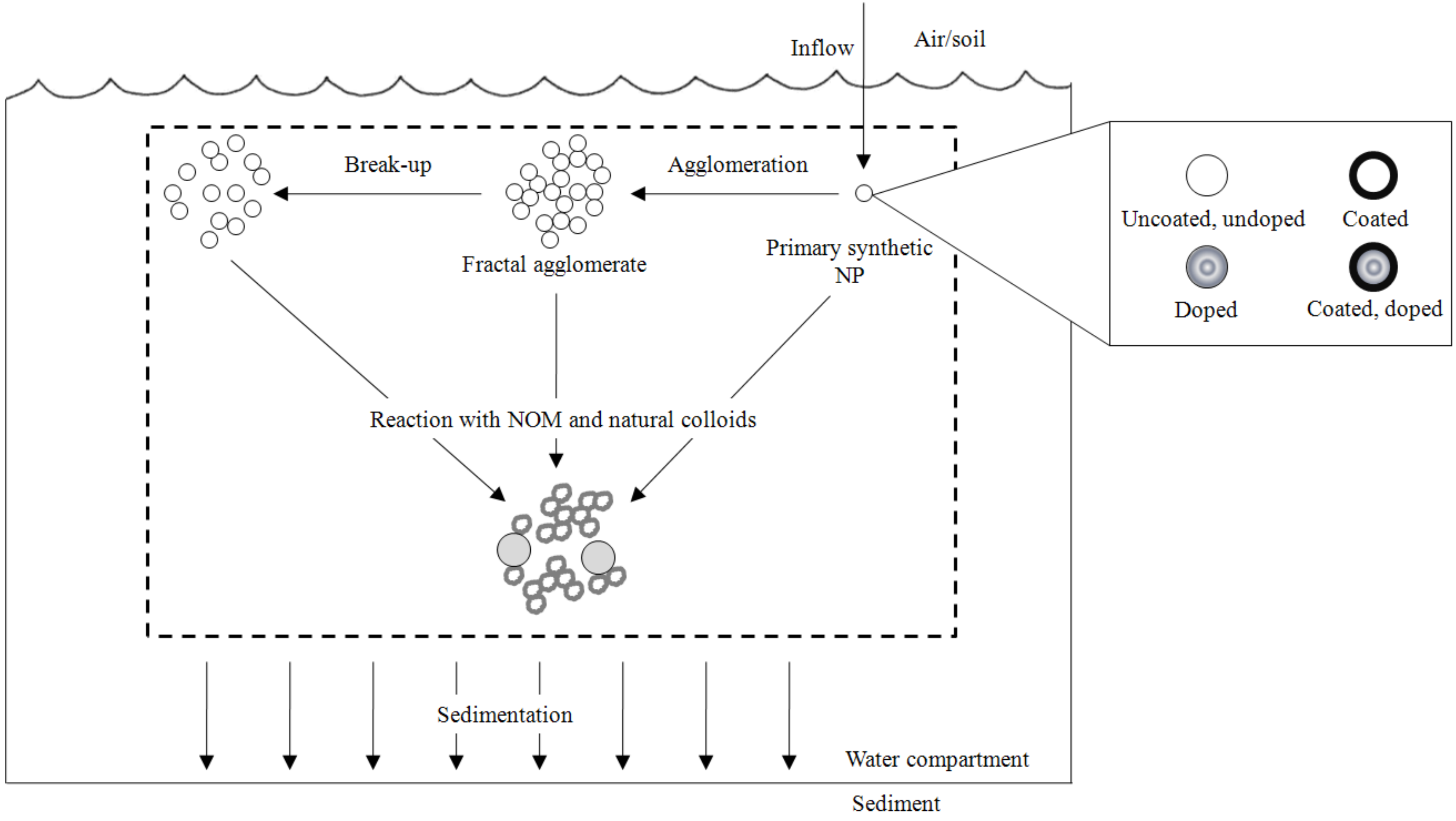

Figure 1. The conceptual model describing NP aquatic fate mechanisms, which have guided the mathematical modeling.

Table 1. A description of the model scenarios tested in this study along with model input and output variables.

Scenario	**Shear rate, G [s^{-1}]**	**Collision efficiency, α**	**Primary particle size, a [nm]**	**Temperature [K]**	**Particle density, ρ_p [kg/m^3]**	**Water density, ρ_p [kg/m^3]**	**Water depth, d [m]**	**Inflow relative to baseline case inflow**	**Output (PEC) relative to baseline case**
Baseline case	0.01	1	21	277	4200	1000	3	1	1
High shear rate	10	1	21	277	4200	1000	3	1	1
High shear rate and larger particles	10	1	500	277	4200	1000	3	1	1
Differential settling excluded and larger particles	0.01	1	500	277	4200	1000	3	1	1
Low collision efficiency	0.01	0.001	21	277	4200	1000	3	1	10
Sedimentation excluded	0.01	1	21	277	4200	1000	3	1	1
High inflow	0.01	1	21	277	4200	1000	3	10	2

MODEL CALCULATIONS

Some limited model calculations were performed for the case of TiO_2 NPs in order to estimate the importance of the collision efficiency (α), shear rate (G), differential settling, sedimentation and inflow rate (I_j), of which all except differential settling and sedimentation have been discussed above. The material TiO_2 NP is chosen as an example since it is one of the major nanomaterials produced today and has been shown to constitute a potential environmental risk (Mueller and Nowack 2008). Break-up, NCs, fractal dimensions, coating and doping were not included in the model due to insurmountable modeling difficulties and lack of data. The model (Equations 2–4) was implemented in MATLAB® along with input values from the literature for the different parameters.

Input Assumptions

A temperature of 277 K was applied, since the temperature at the bottom of lakes is 4°C or 277 K, and it is also a common water temperature during winters in many places in the northern temperate zone. The viscosity of water at 277 K is about 1.5 mPa·s. The NP modeled was selected to be a TiO_2 NP with a primary particle diameter of 21 nm (same diameter as the commercial TiO_2 NP AEROXIDE® P25 from Degussa/Evonik). This is a smaller particle size than the primary particles found in sunscreen and the particles emitted from painted facades, for instance (Nohynek *et al.* 2007; Kaegi *et al.* 2008). The density of water was set to 1000 kg/m^3 and the density of the TiO_2 NPs was set to 4200 kg/m^3. The depth of the water compartment was set to 3 m according to the guidelines of the European Chemicals Bureau (2003). Since no reliable figures for the inflow have been found in the literature, the inflow was set to a random value in Equation 2. This can be done since this study does not seek to determine a PEC, but rather to investigate the feasibility of such models and the importance of some parameters and factors.

Besides the input values listed above, a shear rate of 0.01 s^{-1} and a collision efficiency of 1 have been applied for the baseline case. Regarding shear rate, two additional assumptions were tested: One with the shear rate increased to 10 s^{-1}, and one with the shear rate increased to 10 s^{-1} along with an increased size of the primary particles in the inflow from 21 nm to 500 nm, but with the same number of particles entering the water compartment. The size of 500 nm was chosen since it is the highest suggested upper limit for the definition of NPs known to the authors; see Handy *et al.* (2008). The complete exclusion of the differential settling factor was tested in one case, combined with increasing the primary particle size from 21 nm to 500 nm but with the same number of particles entering the water compartment as for the baseline case, to see the influence on the result. In order to estimate the effect of lower collision efficiency, in one simulation it was decreased to 0.001. One case with the sedimentation term excluded was also tested. Besides the baseline inflow, the impact of a 10-fold increase or decrease in inflow was investigated since existing estimations of annual TiO_2 nanomaterial production vary roughly by a factor of ten or one hundred (Royal Society and Royal Academy of Engineering 2004; Mueller and Nowack 2008). See Table 1 for a summary of the scenarios and assumptions. The results are given as the changes relative to the baseline case.

Model Calculation Results

The low effect of an increased shear rate in the model for the case where a particle size of 21 nm was assumed is not surprising since the orthokinetic agglomeration was shown to be of less importance for small particle sizes (Handy *et al.* 2008). Not even at a primary particle size of 500 nm was the orthokinetic agglomeration significant in the model. The same was true for differential settling as well; not even for 500 nm particles was that effect significant in the model, which was also suggested by Handy *et al.* (2008). The sedimentation term also had a negligible impact on the calculated PEC even for larger 500 nm particles. For all these model parameters, the changes in parameter values or exclusion of factors resulted in a change in PEC at least smaller than 10^{-4} compared to the baseline case. However, significantly lower collision efficiency could increase the PEC by more than a factor of ten according to the model. Also, a 10-fold increase in the model inflow resulted in a twice as high PEC compared to the baseline case, and a 10-fold decrease of the inflow resulted in a reduction of the PEC by a factor of four. It can thus be concluded from the model calculations that for the case of TiO_2 NPs the collision efficiency and the inflow seem to be the most influential parameters of the ones tested. See Table 1 for a summary of the results.

According to Mueller and Nowack (2008) the inflow of TiO_2 NPs to the Swiss water compartment is 58.8 ton/year and the Swiss water compartment is 3.7 km^3. If that inflow is recalculated into primary AEROXIDE® P 25 particles and a total and instant mixing of the water compartment is assumed, the inflow I in Equation 2 is $2.47 \cdot 10^7$ particles$\cdot s^{-1} \cdot m^{-3}$ of P 25. Inserting this value into Equation 2 for our baseline case gives a PEC of approximately $2.5 \cdot 10^{12}$ particles/m^3, which is two orders of magnitude lower than the concentration of NCs reported by Gallego-Urrea *et al.* (2010). However, due to the many uncertainties in the model and especially in inflow data, the authors hesitate to present this figure as a realistic PEC.

EXPOSURE INDICATORS

In the calculation above, particle number based PEC was used as the exposure indicator, leading to the risk quotient indicator. This is because the processes of agglomeration and sedimentation according to Equation 2 are described by the unit particles per volume and also because studies have suggested particle number concentration to be a relevant exposure indicator for NPs (Handy *et al.* 2008). In previous risk assessments, however, mass concentrations have been used for both the exposure and effect assessment (Mueller and Nowack 2008; Boxall *et al.* 2007; Blaser *et* *al.* 2008). This is similar to chemical risk assessment, where mass concentrations are often used in both exposure and effect assessments (van Leeuwen and Hermens 2004). For the case of chemical risk assessment, the choice between mass and molar concentration is not that crucial, since there is an easy way to convert mass to amount of substance using the molar mass. For particles, this is different. For the case of TiO_2, the estimated PEC from Mueller and Nowack (2008) was 16 µg/l, which can correspond to either one particle per liter with a diameter of 200 µm, or 1 million particles per liter with diameters of 2 µm, or 10^{12} particles per liter with diameters of 20 nm and so on.

Toxicological studies have had difficulties confirming the dose-response relationship for mass concentration that applies for many NPs; sometimes dose-response relations are obtained and sometimes not, and in some studies particle and agglomerate size were found to affect the toxicity (Baun *et al.* 2008). Oberdörster *et al.* (2005) found that particle surface area was a better dosimetric exposure indicator than mass, making dose-response curves understandable. Not knowing the proper exposure indicator is a difficulty when performing exposure assessments. The model described in Equations 2-4 can, however, be used to obtain not only particle number concentrations but also mass concentrations, since the amount of particles in each agglomerate (j) is known. Surface area is more complicated to calculate, and is related, for example, to the fractal dimension of the agglomerate.

Mass concentration is a convenient indicator of risk in exposure assessments due to the law of mass conservation and to experimental ease, but problematic for NPs since is cannot discriminate between many small particles and fewer larger particles. Surface area or even bio-active surface area might be more relevant as an exposure indicator, but it would be difficult to make operational since it is difficult to calculate or measure. Changes in surface area along exposure pathways would thus be difficult to monitor. One benefit with particle number concentration, as has been mentioned, is that it is the unit used in agglomeration kinetics equations, although it is also somewhat difficult to monitor along exposure pathways. There is a possibility that an exposure indicator that is suitable from an exposure assessment perspective will prove to be less accurate from an effect assessment perspective, and vice versa. Whether and when mass concentration, particle number concentration, surface area or other indicators of risk are most appropriate is an issue that needs to be addressed by further research.

IMPLICATIONS FOR EXPOSURE MODELING

It is important to notice that an exposure model is not meant to be a perfect representation of reality, but is instead meant to provide a reasonable and conservative estimate of the exposure. An exposure model should include only relevant properties and exclude factors that do not have a large effect on the outcome. Besides the fate processes described above, additional ones of presumed less importance can be added, see for example Elimelech *et al.* (1995). The question posed here thus concerns which of the processes described in this paper and elsewhere are of relevance to the exposure modeling. The calculations above indicate that the orthokinetic agglomeration can be excluded for NPs that enter the aquatic environment. This is convenient considering the variety in shear rate for different waters. Also, differential settling and sedimentation seem to be of less importance. Note, however, that the low impact of the sedimentation is in large part due to the choice of particle number as exposure indicator, and thus the impact of different factors depends partly on the exposure indicator (see discussion above). Changes in collision efficiency related to the amount and type of NOM can increase the PEC of TiO_2 NPs 10-fold according to the model calculations above. Changes in the inflow also had a significant impact, although a 10-fold increase of the inflow only resulted in a doubling of the PEC. The influence of other aspects such as the fractal dimension, the presence of NCs, agglomerate break-up, coatings and doping should be evaluated by models and measurements in order to achieve a reasonably accurate exposure model able to predict environmental concentrations of NPs. The first steps would be to evaluate the importance of break-up, agglomerate fractal dimension and NCs. Here the complexity and diversity of NCs provide perhaps the greatest challenge. In parallel, modeling efforts to estimate current and future inflows (*i.e.*, emissions and leakage from society) are of great importance for an appropriate risk assessment of nanoparticles.

Although the calculations above show that the collision efficiency is an important parameter for exposure modeling, its complex dependence on type and amount of NOM, pH, salt concentration and valence, *etc*. makes it difficult to calculate using existing equations. Thus more accurate equations should be developed. Until then, experimental collision efficiencies relevant for environmental conditions must be derived. However, if the collision efficiency varies greatly within the water compartment, only emissions that are clearly localized, such as peak emissions or point sources, can be modeled with high certainty. For diffuse emissions that are emitted in low amounts to several types of waters, reliable exposure modeling will be more difficult. Unfortunately, many of the known emissions of NPs that have been outlined in the literature are diffuse. Some examples are TiO_2 NPs from ordinary paint (Kaegi *et al.* 2008), TiO_2 and zinc oxide NPs from sunscreen, silver NPs from textiles, iron NPs for soil remediation (O'Brien and Cummins 2008), silica NPs in polishing products and cerium oxide NPs as fuel additives (O'Brien and Cummins 2008). Even if the collision efficiency could be calculated by modeling, the question of exposure indicator is urgent and requires communication between toxicologists, colloid chemists, and risk analysts. It is important to agree on which indicators are relevant for linking exposure and toxic effects. These indicators must also be possible to derive from exposure models. The difficulty in modeling changes in surface area for NPs in the environment in contrast to the presumed merits of surface area as effect indicator (Handy *et al.* 2008) illustrates this great challenge.

Considering the challenges, it is not surprising that previous exposure assessments of NPs have not included specific particulate or colloidal behavior and have used mass concentration as the exposure indicator for a more convenient exposure modeling. However, although excluding the particulate nature of the material makes exposure modeling more feasible, there is no guarantee that the results are relevant and they may offer limited guidance (Wiesner *et al.* 2009). It is thus suggested that scientists working at different system levels relevant for exposure modeling of NPs be given resources to co-operate to develop integrated models where nano-level properties are linked to macro-scale risk.

IMPLICATIONS FOR REGULATION

The problems in exposure modeling of NPs of course lead to regulatory challenges. Several ways to deal with the potential risk of NPs have been suggested. Reinert *et al.* (2006) suggested voluntary information programs similar to the current voluntary program for nanotechnologies established and maintained by the U.S. Environmental Protection Agency. Under this program the producer of nanotechnology can report material characterization, hazard information, use and exposure potential, and risk management practice. However, considering the high uncertainties in exposure modeling of NPs discussed above, it seems unlikely that producers of nanotechnology or NPs could give reliable information about the potential exposure of their products, especially if the products give rise to diffuse emissions. Also, Köhler and Som (2008) showed that innovators of nanotechnology in general did not perceive ecotoxicity of NPs to be a major risk and that they were not sensitive to early scientific warnings regarding risks of nanotechnology. Another option mentioned in Reinert *et al.* (2006) is to create new precautionary regulations, and Köhler and Som (2008) suggested that risk preventive measures should not be postponed until more information about NPs is available. The discussion above about the difficulties in exposure modeling of NPs supports the conclusion that precautionary measures may be the best way to prevent NPs from becoming yet another late lesson.

ACKNOWLEDGEMENTS

The financial support from the Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (Formas) and from the Swedish Foundation for Strategic Environmental Research (MISTRA) is gratefully acknowledged.

REFERENCES

Baalousha M, Manciulea A, Cumberland S, *et al.* 2008. Aggregation and Surface Properties of Iron Oxide Nanoparticles: Influence of pH and Natural Organic Matter. Environ Toxicol Chem 27:1875-82

Baun A, Hartmann N, Grieger K, *et al.* 2008. Ecotoxicity of engineered nanoparticles to aquatic invertebrates: a brief review and recommendations for future toxicity testing. Ecotoxicology 17:387-95

BCC. 2001. In 4th annual BCC conference fine, ultrafine and nanoparticles, October 14-17. Chicago, IL, USA

BCC. 2008. NANOTECHNOLOGY: A Realistic Market Assessment. Report from BCC Research, Wellesley, MA, USA

Beckett R and Le N. 1990. The role of organic matter and ionic composition in determining the surface charge of suspended particles in natural waters. Colloids Surf 44:35-49

Blaser SA, Scheringer M, MacLeod M, *et al.* 2008. Estimation of cumulative aquatic exposure and risk due to silver: Contribution of nano-functionalized plastics and textiles. Sci Total Environ 390:396-409

Boxall A, Chaudhry Q, Sinclair C, *et al.* 2007. Current and Future Predicted Environmental Exposure to Engineered Nanoparticles. Central Science Laboratory, York, UK

Buffle J, Wilkinson KJ, Stoll S, *et al.* 1998. A generalized description of aquatic colloidal interactions: the three-colloidal component approach. Environ Sci Technol 32:2887-99

Camp TR and Stein PC. 1943. Velocity gradients and internal work in fluid motion. J Boston Soc Civ Eng 30:219-38

Chen KL and Elimelech M. 2007. Influence of humic acid on the aggregation kinetics of fullerene (C60) nanoparticles in monovalent and divalent electrolyte solutions. J Colloid Interface Sci 309:126-34

Christian P, Von der Kammer F, Baalousha M, *et al.* 2008. Nanoparticles: structure, properties, preparation and behaviour in environmental media. Ecotoxicology 17:326-43

Colomer J, Peters F, and Marrasé C. 2005. Experimental analysis of coagulation of particles under low-shear flow. Water Res 39:2994-3000

Colvin VL. 2003. The potential environmental impact of engineered nanomaterials. Nat Biotechnol 21:1166-70

Domingos RF, Tufenkji N, and Wilkinson KJ. 2009. Aggregation of titanium dioxide nanoparticles: Role of a fulvic acid. Environ Sci Technol 43:1282-6

Elimelech M. 1994. Particle deposition on ideal collectors from dilute flowing suspensions: Mathematical formulation, numerical solution, and simulations. Sep Technol 4:186-212

Elimelech M, Gregor J, Jia X, *et al.* 1995. Particle Deposition and Aggregation: Measurement, Modeling, and Simulation. Butterworth-Heinemann, Woburn:, MA, USA

European Chemicals Bureau. 2003. Technical Guidance Document on Risk Assessment. Ispra, Italy

European Environmental Agency. 2001. Late lessons from Early Warnings: The Precautionary Principle 1896-2000. Copenhagen, Denmark

Fang J, Shan X-q, Wen B, *et al.* 2009. Stability of titania nanoparticles in soil suspensions and transport in saturated homogeneous soil columns. Environ Pollut 157:1101-9

Friedlander SK. 1977. Smoke, Dust and Haze, Fundamentals of Aerosol Behavior. John Wiley & Sons, Inc. , New York, NY, USA

Gallego-Urrea JA, Tuoriniemi J, Pallander T, *et al.* 2010. Measurements of nanoparticle number concentrations and size distributions in contrasting aquatic environments using nanoparticle tracking analysis. Environ Chem 7:67-81

Grant SB, Kim JH, and Poor C. 2001. Kinetic theories for the coagulation and sedimentation of particles. J Colloid Interface Sci 238:238-50

Gustafsson O and Gschwend PM. 1997. Aquatic colloids: Concepts, definitions, and current challenges. Limnol Oceanogr 42:519-528

Handy R, von der Kammer F, Lead J, *et al.* 2008. The ecotoxicology and chemistry of manufactured nanoparticles. Ecotoxicology 17:287-314

Hansen SF, Maynard A, Baun A, *et al.* 2008. Late lessons from early warnings for nanotechnology. Nat Nanotechnol 3:444-7

Hassellöv M, Backhaus T, and Molander S. 2009. REACH misses nano! Sustainability 2 (Journal from the Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning)

Hund-Rinke K and Simon M. 2006. Ecotoxic effect of photocatalytic active nanoparticles (tio2) on algae and daphnids. Environ Sci Pollut Res 13:225-32

ISO (International Standards Organization). 2008. Nanotechnologies — Terminology and definitions for nano-objects — Nanoparticle, nanofibre and nanoplate. ISO/TS 27687:2008(E), Geneva, Switzerland

Jiang J, Oberdörster G, and Biswas P. 2009. Characterization of size, surface charge, and agglomeration state of nanoparticle dispersions for toxicological studies. J Nanopart Res 11:77-89

Kaegi R, Ulrich A, Sinnet B, *et al.* 2008. Synthetic TiO2 nanoparticle emission from exterior facades into the aquatic environment. Environ Pollut 156:23239

Klaine SJ, Alvarez PJJ, Batley GE, *et al.* 2008. Nanomaterials in the environment: behaviour, fate, bioavailability, and effects. Environ Toxicol Chem 27:1825-51

Köhler AR and Som C. 2008. Environmental and Health Implications of Nanotechnology - Have innovators learned the lessons from past experiences? Hum Ecol Risk Assess 14:512-31

Loder TC and Liss PS. 1985. Control by organic coatings of the surface charge of estuarine suspended particles. Limnol Oceanogr 30:418-21

Loux N and Savage N. 2008. An assessment of the fate of metal oxide nanomaterials in porous media. Water, Air, Soil Pollut 194:227-41

Mackay D, Paterson S, and Shiu WY. 1992. Generic models for evaluating the regional fate of chemicals. Chemosphere 24:695-717

Mackay D, Di Guardo A, Paterson S, *et al.* 1996. Evaluating the environmental fate of a variety of types of chemicals using the EQC model. Environ Toxicol Chem 15:1627-37

Maynard AD, Aitken RJ, Butz T, *et al.* 2006. Safe handling of nanotechnology. Nature 444:267-9

Meakin P. 1987. Fractal aggregates. Adv Colloid Interface Sci 28:249-331

Mueller NC and Nowack B. 2008. Exposure modeling of engineered nanoparticles in the environment. Environ Sci Technol 42:4447-53

Nel A, Xia T, Madler L, *et al.* 2006. Toxic potential of materials at the nanolevel. Science 311:622-7

Nohynek GJ, Lademann J, Ribaud C, *et al.* 2007. Grey goo on the skin? Nanotechnology, cosmetic and sunscreen safety. Crit Rev Toxicol 37:251 -77

O'Brien N and Cummins E. 2008. Recent developments in nanotechnology and risk assessment strategies for addressing public and environmental health concerns. Hum Ecol Risk Assess 14:568 -92

Oberdorster G, Oberdorster E, and Oberdorster J. 2005. Nanotoxicology: An emerging discipline evolving from studies of ultrafine particles. Environ Health Perspect 113:823-39

Pedocchi F and Piedra-Cueva I. 2005. Camp and Stein's velocity gradient formalization. J Environ Eng 131:1369-76

Project NanoRoadSME. 2008. Available at: http://www.nanoroad.net/

Project on Emerging Nanotechnologies. 2009. Wilson International Center for Scholars and the Pew Charitable Trusts. Available at: http://www.nanotechproject.org/inventories/consumer/analysis_draft/.Woodrow

Reerink H and Overbeek J. 1954. The rate of coagulation as a measure of stability of silver iodide sols. Discuss Faraday Soc 18:74-84

Reinert K, Andrews L, and Keenan R. 2006. Nanotechnology nexus - intersection of research, science, technology, and regulation. Hum Ecol Risk Assess 12:811-8

Royal Society and Royal Academy of Engineering. 2004. Nanoscience and Nanotechnologies: Opportunities and Uncertainties. London,United Kingdom

Ryan JN and Elimelech M. 1996. Colloid mobilization and transport in groundwater. Colloids Surf, A 107:1-56

Sander S, Mosley LM, and Hunter KA. 2004. Investigation of interparticle forces in natural waters: effects of adsorbed humic acids on iron oxide and alumina surface properties. Environ Sci Technol 38:4791-6

Schmid K and Riediker M. 2008. Use of nanoparticles in swiss industry: A targeted survey. Environ Sci Technol 42:2253-60

Shaw DJ. 1992. Introduction to Colloid and Surface Chemistry. Elsevier Science Ltd, Oxford. UK

Smoluchowski M. 1917. Versuch einer matematischen Theorie der Koagulationskinetic kolloider Lösungen. Z Phys Chem 92:129-68

Swedish Chemicals Agency. 2007. Nanotechnology – Big Risks with Small Particles*?* Sundbyberg, Sweden

Swedish University of Agricultural Sciences. 2008. Available at: www.slu.se

Sweet L and Strohm B. 2006. Nanotechnology—life-cycle risk management. Hum Ecol Risk Assess 12:528 -51

UNEP (United Nations Environment Programme). 2007. Geo Year Book - An Overview of Our Changing Environment. Nairobi, Kenya

Wakefield G, Lipscomb S, Holland E, *et al.* 2004. The effects of manganese doping on UVA absorption and free radical generation of micronised titanium dioxide and its consequences for the photostability of UVA absorbing organic sunscreen components. Photochem Photobiol Sci 3:648-52

van Leeuwen CJ and Hermens JLM. 2004. Risk Assessment of Chemicals: An Introduction. Kluwer Academic Publishers, Dordrecht, The Netherlands

Velzeboer I, Hendriks AJ, Ragas AMJ*, et al.* 2008. Aquatic ecotoxicity tests of some nanomaterials. Environ Toxicol Chem 27:1942-7

Wiesner MR. 1992. Kinetics of aggregate formation in rapid mix. Water Res 26:379-87

Wiesner MR, Lowry GV, Jones KL*, et al.* 2009. Decreasing uncertainties in assessing environmental exposure, risk, and ecological implications of nanomaterials. Environ Sci Technol 43:6458-62

Zhang Y, Chen Y, Westerhoff P*, et al.* 2008. Stability of commercial metal oxide nanoparticles in water. Water Res 42:2204-12