DYNAMIC PROBABILISTIC MODELLING OF ENVIRONMENTAL EMISSIONS AND CONCENTRATIONS OF ENGINEERED NANOMATERIALS

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TIANYIN SUN

Master of Science in Sustainable Resource Management (TU München)
born 6 January 1982
citizen of China

accepted on the recommendation of
Prof. Dr. Konrad Hungerbühler, examiner
Prof. Dr. Bernd Nowack, co-examiner
Prof. Dr. Stefanie Hellweg, co-examiner

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ABSTRACT

A prosperous development in a wide and increasing field of applications for engineered nanomaterials (ENM) has been predicted and already observed. A relevant quantity of ENM ending up in the environment is inevitable. To evaluate the potential risks of ENM for the environment, a primary step is to have knowledge of the quantity of the environmental release and concentrations. On the effect side, a considerable number of researches have been conducted and critically reviewed. In contrast, on the side of environmental exposure, quantitative knowledge and appropriate methods for detecting, characterising and quantifying ENM in complex natural media are still largely missing. Currently, to perform a proactive environmental risk assessment of ENM, the only way to obtain information on existing levels of ENM in the environment is to model predicted environmental concentrations (PEC). To derive these, we particularly need information on the flows of ENM to the environment. Material flow modelling, which predicts and quantifies flows and stocks of materials or substances in a well-defined system, is an established method of deriving flows of materials to the environment.

To date, only a few modelling studies have presented quantitative estimations of the environmental concentrations of ENM. Many studies only targeted one or two ENM and were considering just a few applications. Studies using material flow modelling covering the complete spectrum of applications were also published. Some of these studies applied a probabilistic approach to addressing the uncertainty associated with data and the inherent variability introduced by the model. However, these studies were based on the limited information available a few years ago on the behaviour of ENM in technical and natural systems. Moreover, these studies used static models that cannot reflect the rapid development of nanotechnology and are not able to represent the dynamics of the development of ENM applications, disposal and transport to the environment.

The main goal of this thesis is to develop a dynamic probabilistic mass-flow model and apply it to estimate realistic environmental emissions and concentrations of ENM. The emission and concentration information can then serve as either the input data for environmental fate modelling or can be used for environmental risk assessment where both exposure and ecotoxicological data are quantitatively linked.

For this purpose, comprehensive knowledge is needed on the production of ENM and the behavior of ENM in technical and natural systems. A collection of the latest available information was made to parameterize the static model with a more comprehensive description of the whole system. This extended probabilistic material flow analysis model (P-MFA) was applied to estimate the environmental flows and concentrations of five ENM (nano-TiO₂, nano-ZnO, nano-Ag, CNT and fullerenes) for the European Union and Switzerland. The resulting estimated concentrations of nano-TiO₂, nano-ZnO and nano-Ag in sewage effluent, surface water, sediments and sludge treated soils were compared with that of their conventional materials. The comparison results showed that, in most cases, the environmental concentrations of corresponding conventional materials are between one and
seven orders of magnitude higher than those for ENM. The data collection and the description of the technical and environmental systems can serve a primary step to model other ENM and other regions so far not covered.

One further application of this extended P-MFA was to model the mass-flows and concentrations of gold nanoparticles (GNP) from medical applications for the UK and the US. GNP based medical applications are rising, and an increasing amount of GNP can eventually end up in the environment. To model GNP flows, it was necessary to estimate the prospective maximal consumption of GNP from medical applications. By combining the estimated prospective consumption of GNP, the technical and environmental parameters and the extended P-MFA, the mass-flows and environmental concentrations of GNP were modelled. The PEC were then compared to the probabilistic species sensitivity distribution (pSSD) to see whether environmental risks exist. The results showed that based on the GNP amounts originating from prospective medical applications, no environmental risk is expected.

Another application of the extended P-MFA was the modelling of five ENM in South Australia (SA). Soils and sediments are considered sinks for ENM, and thus a better understanding of the spatial and temporal variability of concentrations in these compartments is needed. In this part of the thesis, we used South Australia as a case study for a region with significant biosolids and treated wastewater application on soils. The extended P-MFA was built to include a temporal modelling of ENM production and biosolids handling and transfer onto soils. The results thus not only incorporate the uncertainty on ENM flows but also the spatial and temporal variability of ENM concentrations between 2005 and 2012. The ENM concentrations in different waste amended soils were found to vary by more than two orders of magnitude due to different biosolids and wastewater application rates. The results from this modelling highlight that regional and site-specific conditions need to be considered when assessing the environmental risks of nanomaterials.

In the last part of this thesis, a dynamic probabilistic material flow model (DP-MFA) was developed to predict former, current and future flows of four ENM (nano-TiO₂, nano-ZnO, nano-Ag and CNT) to the environment. Another aim of the DP-MFA is to quantify their amounts in stocks with accumulation such as the in-use stock, soils and sediments. The accumulated ENM masses in sinks and the average concentrations in technical compartments quantified in this part of the thesis provide necessary data for risk assessors and scientists in need of quantitative knowledge on the presence of ENM in various compartments. The flows to the environment provided here will constitute the most up-to-date input masses for environmental fate models that are using process-based descriptions of the fate and behavior of ENM in natural system but rely on accurate mass input parameters.

This thesis represents an important contribution to the improved understanding of ENM emissions and concentrations in technical and natural systems. It provided new knowledge for both new regions and new materials not covered by previous studies. The newly developed DP-MFA provides a new method for estimating more reliable environmental emissions and concentrations of these materials.
ZUSAMMENFASSUNG


Zu diesem Zweck wird ein umfassendes Wissen über die neusten Daten zur ENM Produktion und zum Verhalten von ENM in technischen und natürlichen Systemen benötigt. Es wurden zunächst die
neuesten verfügbaren Informationen zusammengetragen, um das Gesamtsystem in ein vollständiges
statisches Modell abzubilden. Dieses erweiterte probabilistische statische Modell (P-MFA) wurde
verwendet, um die Umweltflüsse und Konzentrationen von fünf ENM (Nano-TiO$_2$, Nano-ZnO, Nano-
Ag, CNT und Fullerene) für die Europäische Union und die Schweiz zu bestimmen. Die resultierenden
geschätzten Konzentrationen von Nano-TiO$_2$, Nano-ZnO, und Nano-Ag in Kläranlagen-Abfluss,
Oberflächenwasser, Sediment und klärschlammgedüngten Böden wurden mit denen des jeweiligen
konventionellen Materials verglichen. Die Ergebnisse dieses Vergleiches zeigten, dass in den meisten
Fällen die Konzentration des konventionellen Pendants der ENM um 1 bis 7 Größenordnungen
größer war, als die des ENM.

Die sorgfältig zusammengetragenen Parameterdaten zusammen mit dem erweiterten statischen
probabilistischen Modell und seiner Beschreibung der technischen und der Umweltsysteme dienen als
erster Schritt zur Modellierung anderer Regionen, die bisher noch nicht Gegenstand von
Modellierungsstudien waren. Eine andere Anwendung dieses erweiterten P-MFA war die
Modellierung der Massenflüsse und Konzentrationen von Gold Nanopartikeln (GNP) aus
medizinischen Anwendungen in Grossbritannien und den USA. Die Verwendung von GNP in
medizinischen Anwendungen steigt und diese wachsende Menge an GNP endet potentiell in der
Umwelt. Als Basis für die Modellierung war es dazu nötig, den zukünftigen maximalen Verbrauch an
GNP in medizinischen Anwendungen abzuschätzen. So konnten durch die Verknüpfung des
geschätzten zukünftigen Verbrauchs, der technischen und der Umweltparameter mit Hilfe des
erweiterten P-MFA die Massenflüsse und die Umweltkonzentrationen von GNP modelliert werden.
Die prognostizierten Umweltkonzentrationen (PEC) wurden dann den entsprechenden
probabilistischen Spezies-Sensitivitätsverteilungen gegenüber gestellt, um etwaige Umweltrisiken
ezurückzuführen. Die Ergebnisse zeigen, dass für GNP aus medizinischen Anwendungen keine
Umweltrisiken absehbar sind.

In einem weiteren Fall wurde das erweiterte P-MFA zur Untersuchung von fünf ENM für die Region
South Australia (SA) verwendet. Wir verwendeten South Australia in diesem Teil der Arbeit als
Fallstudie für eine Region mit erheblicher Klärschlammübertaugung und der Ausbringung von gereinigten
Abwässern auf Böden. Böden und Sedimente sind Senken von ENM, weshalb ein besseres
Verständnis der räumlichen und zeitlichen Varianz der Umweltkonzentrationen nötig ist. Das
erweiterte P-MFA wurde dazu angepasst, um eine Zeit-abhängige Modellierung der ENM Produktion
und der Behandlung von Böden mit Klärschlammbildung zu ermöglichen. Die Ergebnisse berücksichtigen damit
nicht nur die ENM Flüsse unter Unsicherheit, sondern auch zeitliche und räumliche Variabilität der
ENM Konzentrationen in den Jahren 2005 bis 2012. Auf Grund der unterschiedlichen Raten mit denen
das Wasser bzw. der Klärschlammbildung ausgetragen wurde, variieren die resultierenden ENM-
Konzentrationen in unterschiedlichen behandelten Böden um mehr als zwei Größenordnungen. Diese
Ergebnisse zeigen auf, dass bei der Beurteilung von Umweltrisiken durch Nanomaterialien regionale
und standortspezifische Begebenheiten berücksichtigt werden müssen.

PUBLICATIONS

The Introduction (chapter 1) and Conclusions and Outlook (Chapter 6) contain content from the following publication:


The main part of this thesis (chapter 2 to 5) consists of the following publications:


Furthermore, the Appendix contains the following publication:

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<th>Description</th>
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<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
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<tr>
<td>CNT</td>
<td>Carbon nanotubes</td>
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<tr>
<td>CWM</td>
<td>Community wastewater management systems</td>
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<tr>
<td>DP-MFA</td>
<td>Dynamic probabilistic materials flow analysis model</td>
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<tr>
<td>DoB</td>
<td>Degree of belief</td>
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<td>EC50</td>
<td>Median effect concentration</td>
</tr>
<tr>
<td>ECB</td>
<td>European chemicals bureau</td>
</tr>
<tr>
<td>EFM</td>
<td>Environmental fate model</td>
</tr>
<tr>
<td>ENM</td>
<td>Engineered nanomaterial(s)</td>
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<tr>
<td>ERAM</td>
<td>Environmental risk assessment and management</td>
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<tr>
<td>GNP</td>
<td>Gold nanoparticle(s)</td>
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<tr>
<td>HONEC</td>
<td>Highest observed no-effect concentration</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively Coupled Plasma Mass Spectrometry</td>
</tr>
<tr>
<td>LC50</td>
<td>Median lethal effect concentration</td>
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<tr>
<td>MC</td>
<td>Monte Carlo</td>
</tr>
<tr>
<td>MCMC</td>
<td>Markov Chain Monte Carlo</td>
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<tr>
<td>MEC</td>
<td>Measured environmental concentration(s)</td>
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<tr>
<td>MFA</td>
<td>Material flow analysis</td>
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<tr>
<td>NOEC</td>
<td>No observed effect level or concentration</td>
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<tr>
<td>PEC</td>
<td>Predicted environmental concentration(s)</td>
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<td>PMC</td>
<td>Production, manufacture and consumption process</td>
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<td>P-MFA</td>
<td>Probabilistic materials flow analysis model</td>
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<td>PNEC</td>
<td>Predicted no effect concentration(s)</td>
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<td>pSSD</td>
<td>Probabilistic species sensitivity distribution</td>
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<tr>
<td>STM</td>
<td>Scanning Tunnelling Microscope</td>
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<td>STP</td>
<td>Sewage Treatment Plant</td>
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<tr>
<td>TC</td>
<td>Transfer Coefficient</td>
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<td>WIP</td>
<td>Waste Incineration Plant</td>
</tr>
<tr>
<td>WW</td>
<td>Waste water</td>
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<td>Wastewater treatment plant(s)</td>
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1 INTRODUCTION

1.1 Brief history of nanotechnology

Nanoscience, nanotechnology and nanoparticles have now become common words not only in research publications but also in daily life. One valid question quite often asked is “when was nanotechnology invented?” There is probably no simple answer to this question because nanotechnologies are an evolution of other materials engineering disciplines, such as thin film technology or physics. The term is indeed an “umbrella term” that covers disciplines that have very old historic roots. Tools are now available to study ancient artifacts and discover that they contained nanomaterials in several cases (The Guardian, 2012).

Despite the increased excitement surrounding the nanoscale, nanomaterials have been around for millions of years. Mother Nature is the penultimate nanomanufacturer. However, the concept of nanotechnology and its birth as a research subject started only a few decades ago. Generally, nanotechnology can be understood as a technology, which allows in a controlled way not only to create materials at the nanoscale but also to operate them, i.e. to influence them or use them according to their intended purpose (Tolochko, 2009).

The first reference of purposely created and applied technological processes and means that can be understood as nanotechnology is usually assigned to a well-known lecture of Mr. R. Feynman, a Professor at the Californian Institute of Technology. He delivered a speech in 1959 at a session of the American Physical Society, saying “The principles of physics, as far as I see, do not speak against the possibility of maneuvering things atom by atom” (Feynman, 1960).

The word “nanotechnology” was introduced into the scientific world by N. Taniguchi at an international conference on industrial production in Tokyo in 1974 in order to describe the super-thin processing of materials with nanometer accuracy and the creation of nano-sized mechanisms (Taniguchi, 1974).

The development of nanotechnology has been greatly driven by the invention of two analytic tools that have revolutionized the imaging (and manipulation) of surfaces at the nanoscale. These are the Scanning Tunneling Microscope (STM) and the Atomic Force Microscope (AFM). The STM and the AFM are capable of imaging surfaces with atomic resolution. These tools have practically opened the doors of the nano-world to scientists. This led to some historical events in terms of the recent development of nanoscience and nanotechnologies: the discovery of the Buckyballs by Robert Curl, Harold Kroto and Richard Smalley (Kroto et al., 1985); the implementation of the IBM logo spelled by individual atoms by Don Eigler at IBM Almaden (Eigler and Schweizer, 1990); the discovery of Carbon Nanotubes by Sumio Iijima at NEC, Japan (Iijima, 1991) and the discovery of Graphene by Andre Geim and Konstantin Novoselov (Novoselov et al., 2004).
1.2 Definition of Engineered nanomaterials (ENM)

Generally, nanomaterials can be understood as materials that are characterized by having at least in one of the three spatial dimensions a size between 1 and 100 nm, concerning both the material as a whole and its structural elements (Tolochko, 2009). On 18 October 2011 the European Commission (EC) published the following recommendation on the definition of a nanomaterial (European Commission., 2011). According to this recommendation a "Nanomaterial" means: “A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm. In specific cases and where warranted by concerns for the environment, health, safety or competitiveness the number size distribution threshold of 50 % may be replaced by a threshold between 1 and 50 %.” “Engineered or manufactured nanomaterials” refers to the materials that are intentionally produced and designed with very specific properties related to shape, size, surface properties and chemistry and meanwhile fulfill the general definition of “nanomaterials” by the EC.

1.3 ENM today

As the results of their small size, ENM exhibit special properties compared to their bulk counterparts. While some of these properties are purely an effect of the increased surface-to-mass ratio of the ENM (e.g. higher reactivity or faster dissolution), they can also have unique properties which are the results of quantum effects due to their small size (Roduner, 2006). The unique properties of ENM make them highly interesting for a wide range of industrial and consumer applications, and their production and use has increased in recent years. The 2000s can be seen as the beginning of the wide application of nanotechnology in commercial products. Examples include nano titanium dioxide (nano-TiO$_2$) and nano zinc oxide (nano-ZnO) in sunscreen, cosmetics and some food products; nano silver (nano-Ag) in food packaging, clothing, disinfectants and household appliances; carbon nanotubes (CNT) for polymer composites; and cerium oxide (nano-CeO$_2$) as a fuel catalyst (American Elements., 2015). Other more sophisticated applications are for example novel devices based on nano-opto-electronic materials, molecular devices and quantum structures that create new directions for miniaturization; the development of nanosensors for biomonitoring, environmental control, and process control; the application for diagnostic tools and advanced therapy; the development of smart textiles with built-in sensors and functional ENM for both military as well as for public use; enhancing efficiencies of green energy technologies, like solar cells, hydrogen cells (Murty et al., 2013).

The development of the production of nanomaterials has been dramatic since its emergence. In the past 20 years, the demand for nanomaterials has exploded from almost complete non-existence to an estimated $5.5 billion in 2016 (Freedonia, 2012). Moreover, the consulting firm McKinsey predicts the market of products incorporating nanotechnology to be $150-500 billion annually by 2025 (Manyika et al., 2013). The recent growth in nanotechnology has been driven by a combination of
increased market penetration of existing materials and ongoing development of new materials and applications (American Elements., 2015). Along with an increased demand has come a large increase in the number of nano-products available to consumers. According to an inventory by The Project on Emerging Nanotechnology, there are now 1600+ consumer products being sold in the US that contain nanomaterials (The Project on Emerging Nanotechnologies., 2015). It is noteworthy that this number only counts the nano-products registered by this inventory, the actual number of nano-products on the market may be much larger.

Significant opportunities for market expansion exist for the applications of ENM. However, a potential limiting factor in the development will be the growing public and regulatory concern about the environmental impact and toxicity of ENM. Increased regulatory scrutiny may slow the adoption of nanomaterials in consumer-oriented products (American Elements, 2015).

1.4 Quantification of ENM for environmental risk assessment

New properties always represent a potential for new risk. The expected increase in the manufacturing and use of ENM in commercial products is likely to cause exposure of the natural environment to these materials. The release of ENM into the environment may occur during the production of the ENM, the manufacturing of ENM-containing products, and the use and reuse phases of these products. Risks from ENM emissions may emerge if both exposure (due to ENM presence in the environment) and hazards (in the form of toxic effects) are observed (Alvarez et al., 2009; Aschberger et al., 2011). Thus, research into the environmental concentrations and on the toxicity of ENM provides the basis for assessing the potential risks these compounds pose to the environment. Knowledge on the hazard side is increasing almost exponentially, caused by a massive interest of the scientific community and increased funding. A large number of reviews focusing on environmental behavior and ecotoxicity are available (Baun et al., 2008; Handy et al., 2012; Handy et al., 2008a; Handy et al., 2008b; Kahr and Dubourguier, 2010; Klaine et al., 2008; Klaine et al., 2012; Peralta-Videa et al., 2011). These reviews integrate the available knowledge and estimate the behavior and effects of nanoparticles based on the information currently available.

In contrast, for the exposure and concentration assessment part, we are still facing a lack of quantitative knowledge and appropriate methods for detecting, characterizing and quantifying ENM in complex natural media (Hassellöv and Kaegi, 2009; Mitrano et al., 2012a; von der Kammer et al., 2012). However, some analytical evidence on ENM release into the environment has been published. The first case reported that nano-TiO₂ is emitted from paints on building facades into an urban runoff (Kaegi et al., 2008). Later the same evidence was shown for Ag released from paints containing nano-Ag (Kaegi et al., 2010). ENM release was also observed during washing of textiles (Benn et al., 2010; Benn and Westerhoff, 2008; Farkas et al., 2011; Geranio et al., 2009; Kulthorn et al., 2010; Lorenz et al., 2012; Windler et al., 2012) and from different abrasion processes of surface coatings (Guiot et al., 2009; Hsu and Chein, 2007; Vorbau et al., 2009). Based on the evidence that ENM are released to the
environment, several authors have made first modeling attempts to predict the environmental concentration of ENM or combine analytical techniques to get first quantitative information on their occurrence in technical and natural systems (Gottschalk et al., 2009a; Mueller and Nowack, 2008a; Sun et al., 2014).

In the following chapters, the quantification of ENM in the environment both with analytical and modelling approaches is presented.

### 1.4.1 Quantification of ENM with analytic approaches

The analytical studies were characterized according to the analytical techniques the experiment applied, the spatial resolution of the focused study area, the ENMs targeted and the size distribution of the ENMs. The techniques that have been employed by these studies for experimental analysis are filtration, microscopic examination, spectroscopic analysis and chromatography. Although it would be nice to group the studies according to their common features, a thematically structured text classifying all the studies might be impossible, because the each study involves more than one aspect with which we are trying to synthetize them. Therefore, instead of text, we summaries the studies into a table, see Table 1-1.

| Park et al. (2008) | assessed nano-CeO$_2$ air contamination using archived PM10 filter data from city center monitoring sites in London and Newcastle. Background CeO$_2$ concentrations were evaluated before nanoparticulate CeO$_2$ was used as fuel additive. The concentrations after the introduction of this diesel additive in the PM10 samples were derived after acid extraction of the filtered PM based on an ICP-AES (inductively coupled plasma atomic emission spectroscopy) method. The nanosized fraction of CeO$_2$ was estimated by taking the difference between samples taken prior and after use of nanosized CeO$_2$ as diesel additive. The results are therefore not nano-specific at all but may still serve as starting point to evaluate the possible contribution of nano-CeO$_2$ in soils. |
| Kiser et al. (2009a) | quantified Ti (< 700 nm) at wastewater treatment facilities in Arizona, Colorado, California, Maryland, Iowa, and New York (USA). The collected solid phases were transformed into ionic forms through acid digestion (HNO$_3$/H$_2$SO$_4$ digestion method). Those digested samples were then analyzed by ICP-OES (inductively coupled plasma optical emission spectroscopy). A scanning electron microscopy/electron dispersive X-ray microanalysis (SEM/EDX) was performed for visualizing and characterizing the Ti in solids. Concentrations in effluents and settled solids from these wastewater treatment sites were obtained. The results are not nano-specific as all Ti smaller than 700 nm was quantified but can serve to define the upper limit on possible nano-TiO$_2$ concentrations. |
| Farré and colleagues (2010) | developed a method for analyzing fullerenes in natural samples. After the ultrasonic extraction of ENM adsorbed on suspended solids in wastewater, these authors coupled liquid chromatography to a hybrid triple quadrupole linear ion trap mass spectrometry to perform the trace quantification of fullerenes in wastewater effluents in Catalonia (Spain). This work is the first to
quantitatively present trace concentrations of an ENM in the environment; however, the method is not able to distinguish between natural and engineered fullerenes.

Neal et al. (2011) analyzed Ti concentrations in river water in Mid Wales and northwest England. Their filtration was performed using 0.45 μm cellulose nitrate filters. Special efforts were made to minimize sampling artifacts by filtering several times aliquots of water and by frequently changing the filters. Concentrations were provided for river water that drains from natural, industrial and agricultural land types. The measured values include the nano-TiO$_2$ fraction but also larger colloids and are therefore also providing an upper limit for nano-TiO$_2$ concentrations.

Johnson et al. (2011d) measured Ti in wastewater after filtration of the samples through a 0.45 μm cellulose nitrate membrane. The sludge samples were filtered through 0.2 μm filters. Concentrations were obtained for WWTP effluent and sludge from an activated sludge plant in the UK serving about 200’000 people. Again, the measured values also include larger colloids and provide therefore also an upper limit for nano-TiO$_2$ concentrations.

Another monitoring study (Johnson et al., 2011b) aimed to measure particulate/colloidal silver (including the nanosized material) in the influents and effluents of English WWTP. For removing the large particulate fraction, 0.45 μm cellulose nitrate filter membranes were used. The filtrates were passed over a 1kDa ≈ 0.02 μm cross flow ultrafiltration membrane retaining the colloidal fraction from 0.02 to 0.45 μm size. The truly dissolved fraction <0.02 μm was stored for future analysis waiting for adequate methods. The colloidal sample was digested with dilute HNO$_3$, the Ag content was then measured by IC-PMS. Concentrations from WWTP across northern, central and southern England were presented. The measured values are therefore again not specific for nano-Ag but may be used to define an upper limit for nano-Ag concentrations.

Westerhoff et al. (2011a) studied the presence and morphology of nano-TiO$_x$ in WWTP effluents. First, the authors isolated the colloidal material using rota-evaporation, dialysis and lyophilization. High-resolution transmission electron microscopy and energy dispersive X-ray analysis were then used to verify the presence of TiO$_2$ particles between 4 and 30 nm in size in these effluents. Since this material is almost insoluble, it occurs only in the solid phase. After acid digestion (HNO$_3$/H$_2$SO$_4$) the total Ti concentration was quantified using ICP-OES with a detection limit of 0.5 μg Ti /l. Concentration of (TiO$_x$) for wastewater effluents could be obtained from selected municipal facilities in southern and central Arizona (USA). Whereas with the electron microscopy analysis it was possible to specifically detect nanoparticulate TiO$_2$, the total Ti analysis targeted all Ti in the 0.9 μm filtered sample, therefore including a large fraction of particles in the non-nano range.

Sanchis et al. (2011) presented the first atmospheric measurements for fullerenes. These authors used filters (<0.7 μm) to collect aerosol-bound fullerenes. Mediterranean Sea samples were taken in the Spring of 2010 and 2012 (Berrojalbiz et al., 2011; Castro-Jimenez et al., 2010). Those samples were analyzed by means of a method coupling liquid chromatography to mass spectrometry (LCMS).
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Isotope dilution using labeled C\textsubscript{60} as internal surrogate standard was conducted for the quantification purposes.

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

Khosravi et al. (2012) also presented measured (ICP-MS) data on Ti in wastewaters and sewage sludge, therefore providing further estimates on nano-TiO\textsubscript{2} in these matrices. The water samples were filtered with 0.22 μm, a much lower pore size than in many other studies using filtration to remove larger particles.

Majedi et al. (2012) optimized cloud point extraction to separate the nanoparticulate fraction from water samples and applied the method to waste water effluents. The subsequent nanoparticle identification was done by combining transmission electron microscopy with energy dispersive X-ray and UV-visible spectroscopy. A 0.05 μg/l detection limit was achieved for ZnO nanoparticles and recoveries of spiked nano-ZnO in the range from 80 to 110%.

Gondikas et al. (2014) identified titanium dioxide nanoparticles stemming from sunscreens in the suspended matter in the Old Danube Lake (Vienna, Austria) using electron microscopy. However, the techniques are not able to distinguish sunscreen nanoparticles from natural Ti-bearing nanoparticles. They further applied ICPMS and ICPOES, in combination with single particle ICPMS analysis to establish local background values of Ti.

Lee et al. (2014) described a method to estimate the size detection limit using spICP-MS and then apply it to nanoparticles composed of 40 different elements. They found the detectable sizes vary substantially among the 40 elements: from ≤10 nm to greater than 200 nm. This work identifies the elements and nanoparticles to which current spICP-MS approaches can be applied, in order to enable quantification of very small nanoparticles at low concentrations in aqueous media.

Cornelis et al. (2014) developed a signal deconvolution method for spICP-MS analysis using gold (Au) NPs of nominally 10, 15 or 30 nm diameter. The signal distributions of dissolved Au standards were parameterized as a function of concentration using a mixed Polyagaussian probability mass function. The applicability domain of this method lies with relatively small NPs and/or when a relatively high concentration of dissolved ions of the element of interest is present, where overlapping between dissolved and particulate signals occurs.

Peters et al. (2014) used three principally different methods - electron microscopy, asymmetric flow field-flow fractionation combined with inductively coupled mass spectrometry, and single-particle inductively coupled mass spectrometry - to determine the number-based size distribution of TiO\textsubscript{2}
particles. These TiO$_2$ particles are either food grade or used in personal care products. Although the applied methods are considered state of the art, they showed practical size limits for TiO$_2$ particles in the range of 20–50 nm, which may introduce a significant bias in the size distribution because particles <20 nm are excluded.

Montano et al. (2014) improved the spICP-MS technique by employing 100 microsecond dwell times. The short dwell time provides detection of two elements in the same nanoparticle, opening the door for possible environmental applications with the prospect of obtaining particle-by-particle elemental compositions. These improvements help further establish spICP-MS as a leading analytical technique for the detection and characterization of metal-containing ENMs, and introduces new possibilities for differentiating engineered nanomaterials from their naturally occurring analogues.

Baalousha et al. (2014) present a validated quantitative sampling technique for atomic force microscopy (AFM) that allows full recovery and representativeness of the NPs under consideration by forcing the NPs into the substrate via ultracentrifugation and strongly attaches the NPs to the substrate by surface functionalization of the substrate or by adding cations to the NP suspension. This method enables the use of the full capabilities of microscopy tools to quantitatively and accurately determine the number size distribution and number concentration of NPs at environmentally relevant low concentrations (i.e. 0.34-100 ppb).

Overall, the analytical detection possibilities of ENM in the environment have been rapidly expanding in recent years. The improvement of traditional techniques to work with nano-sized particles and the invention of new techniques specifically aimed at quantifying and characterizing ENM in environmental and biological samples have been under intense development. While detection of nanomaterials in “real” environmental samples (i.e. samples taken directly from streams, rivers, WWTP, etc.) has not been fruitful, this may be as much due to the fact that the concentration of ENM in these systems is still too low in addition to the analytical techniques not being robust enough. A specific challenge remains in distinguishing the engineered nanomaterials from the naturally occurring nanomaterials, specifically with particles such as TiO$_2$, ZnO, or Ce which already are abundant in the environment in natural form. However, even here, techniques are being devised which investigate the (deviation) of the measured sample from naturally occurring isotopic ratios to present hints if particles may be of engineered origin.
# Table 1-1: Summary of analytical studies of measurement and detection of ENM in environmental samples

<table>
<thead>
<tr>
<th>Analytical Studies</th>
<th>Analytical techniques used</th>
<th>Spatial resolution</th>
<th>Compartments mass-flows or concentration are given</th>
<th>ENM targeted</th>
<th>Size distributions (nm)</th>
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1.4.2 Modelling ENM concentrations

In order to perform a proactive environmental risk analysis, modelling of predicted environmental concentrations (PEC) currently constitutes a necessary and valuable substitute for measurement studies in the current situation with limited trace measurements of ENM (Gottschalk et al., 2009a). Dependent on the focal points, models aiming at providing information on environmental exposure of ENM can be classified into two groups: material flow models (MFA) with a life cycle concept and the environmental fate models (EFM) with the detailed mechanistic description of processes. The following sections list and describe these two types of models in details.

1.4.2.1 Material flow analysis models

The material flow analysis models for ENM in our definition are models that track the mass flows of ENM (in specific cases this can also be the particle number) over the life stages of products containing ENM. These models can be top-down models, which start with the production of a certain mass of an ENM, distribute the mass to different product categories, and then identify the releases to the environment during production, use and disposal, and finally quantify the mass flows to technical and environmental compartments (Gottschalk et al., 2009a; Sun et al., 2014). Or they can be bottom-up models, which start with product usage and market penetration of nano-products and then track mass flows of ENM from use to technical and environments (Boxall et al., 2007a; Tiede et al., 2011). In MFA behaviour of ENM during technical processes, e.g. in wastewater treatment plants or during waste incineration, are described using transfer factors.

Uncertainty within the models originates from the limited coverage of realistic environmental fate processes, e.g. dissolution, agglomeration and sedimentation in various compartments. Current MFA models do not distinguish between single ENM, aggregated particles and ENM attached to larger particles (including microbes) but rather track the total mass of a specific ENM through the system.

The MFA modelling began with Boxall et al. (2007a) who presented the first quantitative scenarios at all of ENM release and concentrations for environmental media. Several equations were developed for calculating PEC for a series of ENM (see Table 1-2) in water, biosolids and soils. However, because the modeling was based on pure hypothetical and high release scenarios (10%, 50% and 100% market penetration of ENM-containing products), this study does not provide realistic PEC values but aims at defining the upper possible concentration range. The results were therefore not further used in our evaluation.

Mueller and Nowack (2008b) went one step further and used for the first time a comprehensive material flow analysis (MFA) to replace hypothetical calculations with two more concrete scenarios: a realistic one to reflect the best available knowledge and a comprehensive spectrum of ENM release into natural compartments; and a worst-case one for a conservative estimation of parameters. Using a life-cycle perspective, this MFA combined assumptions and first initial empirical information on ENM.
production quantities, release rates and behavior in technical compartments. The environmental concentrations were calculated according to the European technical guidance assuming well-mixed and homogeneous compartments (ECB, 2003). Sedimentation and degradation processes in the aquatic environment were excluded due to a total lack of data. PEC were computed for nanosized Ag, TiO$_2$ and CNTs for Switzerland. The results provided in this work constitute the first realistic assessment of ENM concentrations in the environment, although environmental fate processes were covered only to a limited extent. However, they provided a starting point with which all future modeling studies can be compared.

Park et al. (2008) applied emission and atmospheric dispersion models for their work on CeO$_2$ emissions from its use as a diesel additive. Calculations for different emission scenarios for vehicles were performed by varying the traffic intensities, geographic locations and distances from the ENM sources (e.g. from the edge of the highway). PEC were calculated for different areas of street canyons. Terrestrial PEC were modeled for soils near highways considering the ENM accumulated during a 40-year period. This work is restricted to a single application (CeO$_2$ use in fuels) and only considers one possible transfer of CeO$_2$ into soils, e.g. neglecting transfer via wastewater and sludge application. However, it can provide a worst-case evaluation of a use with significant potential for environmental release and assuming some worst-case events, e.g. all diesel cars use CeO$_2$ and the particle filter does not trap the particles in the exhaust. Ulrich and Wichser (2003) have shown that diesel particulate filters have a removal efficiency of 99.9% for Ce and thus in reality little Ce will escape into the environment.

Blaser et al. (2008a) presented modeled concentrations of Ag originating from the use of biocidal Ag-applications including nano-Ag. However, the nano-Ag only served as a source for dissolved Ag and no nano-Ag concentrations were modeled. The PEC values provided in this work were therefore not further used in our evaluation.

Koelmans et al. (2009a) made the first steps in environmental fate modeling for carbon-based nanomaterials in sediments. These authors combined the output of Mueller and Nowack’s release model (2008b) with mass balance calculations involving aggregation, sedimentation, and ENM burial in deeper layers of the sediment. Three main assumptions were made within the fate model: due to bioturbation the biologically relevant sediment thickness on the top was assumed to be homogeneously mixed; the CNTs entered this top layer due to constant annual sedimentation; due to degradation/aggregation the examined carbon material could be removed from such a layer following a first-order elimination rate constant. This work was the first to include a mechanistic description of the behavior of particles, thus going beyond the mass-transfer approach used in the preceding approaches.

Gottschalk and co-workers (2009b; 2010b) used a probabilistic material flow analysis (P-MFA) approach (Gottschalk et al., 2010a) that builds on Monte Carlo (MC) computer simulations for
predicting PEC of five ENM (TiO$_2$, ZnO, Ag, CNT, fullerenes) in water, sediments, biosolids, soils and air. This stochastic model thrives on the full use of probability distributions for all parameters at any stage of the MFA. Insight into the likelihood of each single material transfer event can be obtained by applying probability distributions. The material transfers include ENM emission from ENM production and incorporation into products, abrasion during washing/consumption/use (of textiles, cosmetics, plastics, coatings, etc.), wastewater treatment, waste incineration plants and other disposal procedures, ENM import, export, recycling and feedback loops into consumption processes and others. PEC have been presented for different metallic and carbon materials (see Table 1-2) using the mode and 15–85% quantiles of the modeled probability distributions. Compared to the previous life-cycle based MFA for Switzerland (Mueller and Nowack, 2008b) updated ENM production information and all the main environmental compartments (ENM in sediments and groundwater were modeled for the first time) as well as more geographical regions (Europe and US) were considered. The PEC provided by this model were, therefore, the most comprehensive and realistic values that were made available.

Tiede et al. (2010) used the equations of the first environmental concentration assessment (Boxall et al., 2007a) for their aquatic exposure modeling. Such exposure estimations were based on adapted algorithms usually used for assessing exposure to medicinal products in surface water environments (CHMP, 2006). The calculations required data on the ENM content in products (aquarium treatment, car polish wax, textiles, coatings, cosmetics, food, fuel additive, paints, hair loss, toothpaste, washing machine) and the amount of products daily used per capita as well as market penetration information. ENM were assumed to be mainly released via WWTP and then diluted in surface water (raw drinking water) before entering into the process of drinking water treatment plants. The model output was mostly determined by the removal efficiency of WWTP. For a conservative case and in cases where no information was available 0% removal was considered, 97% removal efficiency was assumed for a more realistic scenario based on data from others (Omelia, 1980). A 'worst case' was also modeled that ignored ENM dissolution and aggregation in the environment. PEC were provided for WWTP effluents and biosolids at regional resolution (UK) including comprehensive application scenarios “all products” (C60, nano-Ag, nano-TiO$_2$) and “sunscreen” ENM (nano-TiO$_2$) applications. In this modeling only some product categories were included, and thus the results can only provide a lower estimate of the concentration range.

O’Brien and Cummins (2010a) included calculations for pharmaceutical and metal removal efficiencies in WWTP in their aquatic exposure assessment in addition to calculations for pathogen removal during drinking water treatment. The latter estimates were based on available information for known representative contaminants commonly found in Irish water supplies. Average ENM removal efficiencies of 59.8% and 70.2% were assumed for WWTP and a removal rate between 0% and 96.95% seen for Irish drinking water facilities. The ENM contents and release amounts from relevant products and processes used (such as market penetration of nanomaterial containing products) were computed by probability distributions, as described in detail elsewhere (O’Brien and Cummins,
A few further release scenarios were considered, e.g. emissions from paints and coatings directly into surface water or via runoff as a result of material abrasion/degradation, release from plastics and packaging due to water contact/abrasion or direct emissions of fuel additives to WWTPs, such as during maintenance of filters. The market penetration for Ireland (5% of the products in a product group contain ENM) and release coefficients for ENM products were modeled with a standard deviation of 20% to account for uncertainty and variation. Surface water PEC were presented for nano-sized TiO$_2$, Ag and CeO$_2$. Similar to other modeling studies, these authors also used a combination of a contemporary assessment parameters (e.g. on removal) and scenario building (e.g. when assuming a certain market penetration for nano-products). However, only some product categories were considered and no comprehensive assessment was targeted.

Another study (Musee, 2010) used a simplistic deterministic MFA to calculate ENM emissions from cosmetic products into the water and terrestrial environments by focusing geographically on Johannesburg Metropolitan City (South Africa). The MFA included material transmission via untreated and treated streams from WWTP, deposition of biosolids on soils, landfilling of biosolids and landfill leachate. Low and high WWTP removal efficiencies were combined with three different ENM release assumptions (minimum, probable, and maximum) computed based on ENM production taken from others (Mueller and Nowack, 2008b) and adapted based on GDP information and wastewater generation per capita for JHB City. PEC (nano-Ag, nano-TiO$_2$) originating from cosmetic products was estimated for surface water, biosolids and soils treated with such biosolids. This study, therefore, investigated only a very small group of products and can thus provide only a lower estimate of the targeted ENM.

Gottschalk et al. (2011b) combined P-MFA (Gottschalk et al., 2010a) and graph theory (Ort et al., 2009) to model first aquatic PEC for ENM at higher spatial and temporal resolutions (nanosized TiO$_2$, Ag, ZnO). Values for the Swiss stream network were modeled by spreading the total ENM release computed at the regional level (Gottschalk et al., 2009b) over a network based on the distribution of the relevant population. The spatial dependent variation was achieved by linking diffusive ENM discharge with local dilution (stream flow data). The temporal variation was considered by integrating into the modeling flow measurement data collected during a 20-year period. Two scenarios accounted for the wholly possible spectrum of variability and uncertainty of ENM fate in the river water: a conservative one assuming no ENM degradation/deposition, and an optimistic scenario considering rapid and complete ENM removal.

Johnson et al. (2011d) estimated sunscreen TiO$_2$-PEC for soils by basing their PEC modeling on own measured concentrations in biosolids (see corresponding part in the section analytic studies). Those measured values were related to the proportion of Ti present as nano-TiO$_2$ (derived from market information) and data of recommended sludge applications to soils. Surface water PEC were then modeled based on commercial information on the consumption of Ti products by the relevant population and data on dilution in the Thames and Anglian rivers in Southern England. For this
purpose, a GIS-based water-quality model (Williams et al., 2009) was employed. However, the PEC provided in this work can only serve as an indicative lower estimate of total nano-TiO$_2$ in the environment, because only a single use (TiO$_2$ in sunscreen) was considered.

Johnson et al. (2011b) used their own effluent monitoring results for their silver ENM modeling (see again corresponding part in the section analytic studies). The results were converted into a typical per capita effluent load, to model river concentrations on the basis of different dilution conditions (mean and 90% quantiles). A GIS model (Williams et al., 2009) was applied for computing PEC in English and Welsh rivers based on mean per capita loads derived from normally distributed load quantities. Similar to Gottschalk et al. (2011b), this model, therefore, provided local estimates of nano-Ag concentrations, and thus included additional complexity compared to the regional modeling performed in all previous studies.

Arvidsson et al. (2012) proposed a particle flow analysis approach (PFA), to assess anthropogenic ENM release into the environment. In this modeling study, particle numbers instead of mass were calculated. ENM inflow to the use phase, stocks in use and release from the use phase to the environment were considered. Release scenarios were produced based e.g. on predictions for the technology diffusion, per capita consumption of nano products, their lifetime and ENM concentrations. Case studies were conducted for nano-TiO$_2$ in sunscreen, self-cleaning cement and paints (Arvidsson et al., 2012) and for nano-Ag in textiles, wound dressings and electronics (Arvidsson et al., 2011). Unfortunately, PEC were not presented. This work does not aim to present environmental concentrations but limits itself to discussing general aspects of the feasibility of such modeling and the sensitivity of the model output on the mentioned main input parameters.

The modeling studies presented so far revealed that significant amounts of ENM enter the waste stream and therefore waste incineration plants and landfills. Mueller et al. (2013a) aimed to model the flows of ENM during waste incineration and landfilling in greater depth by including a more detailed description of the different processes and considering ENM-specific transformation reactions. Four substances were modeled: nano-TiO$_2$, nano-ZnO, nano-Ag and carbon nanotube (CNT). The modeling showed that the major ENM flows go from the waste incineration plant to the landfill as bottom ash. on some ENM (e.g. combustion of CNT, dissolution of ZnO in acid washing) but that the majority of the ENM-mass is still expected to end up in landfills.

Keller et al. (2013a) combined ENM market information and MFA and produced the first global assessment of the likely ENM emissions to the environment and landfills. They studied the ten most produced ENM by mass covering major applications of these materials. There are considerable uncertainties in the estimates because the only data source they used is a market report with no access to how the company collected the information. A follow-up study by the same group scaled the global emissions to regional and local level by using scaling factor combining economic and population indicators Keller et al. (2013b).
Markus et al. (2013) went through a bottom-up approach and combined the indicative figures on the content of nanomaterials in various products and the usage profiles to estimate the potential releases of nano-forms of zinc, titanium and silver into the environment in the Netherlands. The estimated release flows of ENM sourced from products containing ENM were compared to the total loads, based on measurements of the total concentration.

1.4.2.2 Environmental fate models

Environmental fate models are models that include a mechanistic handling of agglomeration, hetero-agglomeration, sedimentation and other processes of ENM and allow a more process-based description (Liu and Cohen, 2014; Meesters et al., 2014; Praetorius et al., 2012). These models can be coupled to MFA models and may potentially enable a more accurate description of the actual form of the ENM. However, they are strongly dependent on the input size distribution of the ENM, which is currently not available.

Praetorius et al. (2012) developed a new concept for environmental fate modeling of ENM with process descriptions based on the specific properties of ENM. These authors used nano-TiO$_2$ as a case study, and investigated the fate and transport of ENM in the Rhine River. A fundamental process, the heteroaggregation between nano-TiO$_2$ and suspended particulate matter (SPM) was analyzed in detail.

Arvidsson et al. (2011) apply the “particle flow analysis” method to estimate nano-Ag emission from society to the environment. They set up explorative scenarios to account for potential technology diffusion of selected nano-Ag applications. Processes that change particle numbers, such as agglomeration, melting of particles, dissociation of particles into ions, and grinding (which produces more particles), were included by the model.

Hendren et al. (2013) developed a mass-balanced representation of ENM behavior based on a minimal number of input variables to describe release quantities to the environment. In their study the WWTP is modelled as a completely mixed reactor where heteroaggregation, biouptake, etc. result in a distribution between “free” nanomaterials and those associated with other particulate species (such as bacteria).

Praetorius et al. (2014) presented a method for determining $\alpha_{\text{hetero}}$ values by using a combination of laser diffraction measurements and aggregation modelling based on the Smoluchowski equation. Nano-TiO$_2$ (15 nm) were used to demonstrate this new approach together with larger silicon dioxide particles (SiO$_2$, 0.5 μm) representing natural colloids. The heteroaggregation experiments were performed at different environmentally relevant solution conditions.

Liu et al. (2014) developed a multimedia environmental distribution model for ENM considering the environment as a collection of compartments, linked via fundamental environmental intermedia transport processes. ENM attachment to suspended solids in water, atmospheric dry and wet
depositions, and ENM dissolution were taken into account to assess the multimedia mass distribution of ENM and associated potential exposure concentrations.

Meesters et al. (2014) presented the SimpleBox4Nano (SB4N) model which is a screening level model for environmental assessment of ENM. They assessed its validity and evaluated it by comparisons with a known material flow model. SB4N expresses ENM transport and concentrations in and across air, rain, surface waters, soil, and sediment, accounting for nano-specific processes such as aggregation, attachment, and dissolution. The model solves simultaneous mass balance equations (MBE) using simple matrix algebra. The MBEs link all concentrations and transfer processes using first-order rate constants for all processes known to be relevant for ENM. The output of SB4N are mass concentrations of ENM as free dispersive species, heteroaggregates with natural colloids, and larger natural particles in each compartment in time and at steady state. The author then applied the ENM release results from MFA for Switzerland (Gottschalk et al., 2009a) to demonstrate the impact of the transport processes included in SB4N on the prediction of environmental concentrations.

Liu et al. (2015) went further on the basis of their multimedia compartmental model. They developed an integrated simulation tool for assessing the potential release and environmental distribution of nanomaterials (RedNano) coupling the MFA and mechanistic intermedia transport processes. The model allows the investigation of the impact of geographical and meteorological parameters on ENM distribution in the environment, comparison of the impact of ENM production and potential releases on different regions, and estimation of source release rates based on monitored ENM concentrations.

Praetorius et al. (2015) presented a combined mass-flow and environmental fate modelling approach for predicting the concentration of nano-TiO$_2$, nano-ZnO, and nano-Ag in a network of all Swiss rivers and streams connected to a sewage treatment plant. The fate model for ENMs used here includes nano-specific process descriptions such as heteroaggregation with suspended particulate matter (SPM) and deposition to the sediment. The physical and chemical properties of all river sections (width, discharge, temperature, pH, water chemistry, SPM concentration) are parameterized to enable location-specific fate process calculations. Through this modelling approach, the authors obtained the concentration of free and SPM-bound ENMs in the water and sediment compartments of the entire Swiss river network.

Figure 1-1 categorizes the different modeling approaches discussed in this section according to the complexity of the model and the year published. The complexity increases from studies targeting only single uses of a selected ENM over scenario-based models to comprehensive approaches that aim to model all relevant flows of a specific ENM. The highest level of complexity is found in those comprehensive models that provide concentration estimates at a local level rather than just providing regional estimates based on well-mixed compartments. Figure 1-1 also shows the relationships between the models, as some of them use results from another study as input parameters or use the same methodology, and the results are therefore not completely independent from each other. This
applies especially to all those models that are descendants from the Mueller and Nowack (2008b) study. This work has influenced several subsequent models from the same research group (Gottschalk et al., 2009, 2010b, 2011; Mueller et al., 2013) or groups from other institutions (Koelmans et al., 2009; Musee, 2010).

A summary of the MFA and EFM modelling studies including their methodologies, environmental compartments and materials used is given in Table 1-2. The spatial resolution tells the level of the representative of the modelled results. The types of models and spectrum of applications the study covers are indicated. The types of model are classified according to the ways of handling parameters in terms of uncertainty and variability and the temporal spectrums the studies represent. A detailed description of the classification of the models is given in the following section.
Table 1-2: Overview and characterization of modelling methodologies used to assess concentrations of engineered nanomaterials (ENM) in the environment. The studies listed in the blue block are studies of material flow analysis modelling studies; the studies listed in the light blue block are environmental fate modelling studies. Studies in bold are the contribution of this dissertation and are included in the main chapters of this thesis.

<table>
<thead>
<tr>
<th>Modelling Studies</th>
<th>Spatial resolution</th>
<th>Compartments targeted</th>
<th>Targeting ENM</th>
<th>Spectrum of applications</th>
<th>Size distributions (nm)</th>
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<tr>
<td>Material Flow Analysis models</td>
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<td>Environmental Fate Models</td>
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1.4.3 Classification of MFA models for ENM

MFA, which predicts and quantifies flows and stocks of materials or substances in a well-defined system, is an established method of deriving flows of materials to the environment (Baccini and Brunner, 2012). It is used at different spatial and temporal scales accounting for material flows within and between anthropogenic and connected ecosystems.

MFA models for ENM can be classified into categories according to their features such as deterministic models or probabilistic models and static models or dynamic models. Whether a model is deterministic or probabilistic depends on how the data for model’s input parameters are treated and used. If the data for parameterizing the model are treated in a stochastic manner and used as probabilistic distribution then this model is probabilistic. Similarly, if the data are used as deterministic values then the model is a deterministic model. MFA models for ENM also differentiate themselves being as static and dynamic. Generally, static models only study “one-year’ event” of the MFA systems. In the context of MFA for ENM, static models only consider one-year’s ENM input into a defined economic entity. And it only investigates the mass distribution of ENM to technical and environmental compartments taking place in one year. A general definition of dynamic MFA is that it aims for a long-term quantification of material flows and uses historic development patterns of physical stocks and flows to create robust scenarios for the years and decades to come (Müller, 2006). For the case of MFA for ENM we classify a model as dynamic once a long-term or a periodic production volume as input into the MFA systems is taken into account (if only this aspect is considered we call it a partial dynamic model) and the time dependent ENM release from products over their life-time is included. If in a MFA model both the periodic input and the release kinetic are taken into account, then it is considered as a fully dynamic model. If none of them is included in a model, then this model is a static model.

Clearly, probabilistic models are more advantageous compared to deterministic models by being able to address the uncertainty and variability associated with the raw data for input parameters. This is truly important under the current circumstances where only little and often conflicting data is available. Compared to static models, dynamic models have a more realistic representation of the real system. However, most of the MFA models for ENM before this dissertation are not probabilistic, and almost none of these are really dynamic models. This provides research space and the starting point for this dissertation.

A classification of the MFA models for ENM according to their deterministic-probabilistic and static-dynamic features is shown in Table 1-3.
Table 1-3: Classification of MFA studies for ENM according to their features into static-dynamic and deterministic-probabilistic. Studies in bold are the contribution of this dissertation and are included in the main chapters of this thesis.

<table>
<thead>
<tr>
<th>Modelling Studies (MFA)</th>
<th>Classification</th>
<th>Static</th>
<th>Dynamic</th>
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<td></td>
<td>Deterministic</td>
<td>Probabilistic</td>
<td>Deterministic</td>
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<td>ENM Production development</td>
<td>ENM release kinetics</td>
<td>ENM production development</td>
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Figure 1-1: Categorization of modeling approaches used to assess environmental exposure to engineered nanomaterials (ENM). Blue boxes represent the exposure models that only accounting mass-flows. Orange boxes indicate models that incorporate a mechanistic description of ENM behavior, e.g. agglomeration or sedimentation. For references see footnotes on next page.
Footnotes to Figure 1-1: 1. Algorithms for single hypothetical ENM applications and release estimations (e.g. cosmetics) (Boxall et al., 2007); 2. Diesel fuel ENM application and release scenario study (Park et al., 2008); 3. Modeling the contribution of nano-functionalized plastics and textiles on the total Rhine river (silver) exposure (Blaser et al., 2008); 4. First life cycle based ENM flow model covering comprehensive ENM applications based on a current and a high release scenario for different environmental compartments (Mueller and Nowack, 2008); 5. First mechanistic modeling (for manufactured carbon-based nanomaterials) of sedimentation fluxes including agglomeration and burial in deeper sediment layers (Koelmans et al., 2009); 6. First stochastic/probabilistic life cycle based ENM flow model for a complete inventory of ENM applications and all important environmental compartments (Gottschalk et al., 2009; Gottschalk et al., 2010a; Gottschalk et al., 2010b); 7. Simple predictive algorithms on release of ENM to raw and treated drinking water (Tiede et al., 2010); 8. ENM study on removal rates for sewage treatment and ENM use in sunscreens (Johnson et al., 2011b); 9. Study on ENM release (via sewage treatment) to surface water from a few nano-applications (O’Brien and Cummins, 2010a); 10. Study of colloid chemistry kinetics for describing nanoparticle agglomeration and sedimentation (Arvidsson et al., 2011a; Arvidsson et al., 2011b); 11. ENM release (into waters and soils) scenarios from the use of ENM in cosmetics (Musee, 2010); 12. Combined measurement and modeling exercise on release of ENM from sewage treatment (Johnson et al., 2011b); 13. Stochastic/probabilistic modeling of local ENM concentrations in Swiss rivers by varying ENM release and natural dilution for different geographical and hydrological conditions (Gottschalk et al., 2011); 14. Particle number instead of mass is discussed for material flow modeling (Arvidsson et al., 2012); 15. Modeling and analysis of heteroagglomeration between ENM and suspended particulate matter in river water (Praetorius et al., 2012); 16. Predictive simulation of ENM flows during waste incineration and landfilling based on available knowledge (Mueller et al., 2013); 17. Modeling of nano-Ag flows during wastewater treatment (Hendren et al., 2013a); 18. A deterministic and static life cycle mass-flow modelling for 10 ENM in a global perspective (Keller et al., 2013); 19. A update from their last study, which based on economic and populations scaling factor, scaled the global mass-flows of 10 ENM into national and regional level (Keller and Lazareva, 2013); 20. Modelling ENM discard to regional rivers in Netherland on the basis of consumptions of ENM containing products such cosmetics and the ENM removal efficient in sewage treatment plant (Markus et al., 2013); 21. A full life cycle probabilistic mass-flow modelling of ENM with comprehensive description of technical processes (Sun et al., 2014); 22. Modeling and analysis of heteroaggregation of nano-TiO$_2$ with model natural colloids under environmentally relevant conditions (Praetorius et al., 2014); 23. A multimedia model to evaluate dynamic environmental multimedia mass distribution and concentrations of ENM (Liu and Cohen, 2014); 24. SimpleBox4nano, a multimedia model express ENM transport and concentrations in and across environmental compartment accounting nanospecific processes such as aggregation, attachment, and dissolution (Meesters et al., 2014); 25. A life cycle probabilistic mass-flow modelling accounting complete ENM applications for South Australia with a spatial and temporal approach (Sun et al., 2015b); 26. Prospective probabilistic mass-flow modelling for GNP applied in medical sector (Mahapatra et al., 2015); 27. Fully dynamic and probabilistic mass-flow modeling accounting complete ENM applications, ENM production development and ENM release kinetics (Sun et al., 2015a). 28. An integrated simulation tool for assessing the potential release and environmental distribution of nanomaterials based on a life cycle assessment approach and multimedia compartmental modeling coupled with mechanistic intermediate transport processes (Liu et al., 2015). 29. A combined mass-flow and environmental fate modelling approach for predicting the concentration of ENM in a network of all Swiss rivers and streams connected to a sewage treatment plant (STP). The fate model for ENMs used here includes nano-specific process descriptions such as heteroaggregation with suspended particulate matter (SPM) and deposition to the sediment. The physical and chemical properties of all river sections (width, discharge, temperature, pH, water chemistry, SPM concentration) are parameterized to enable location-specific fate process calculations. Dashed red arrows indicate the inheritance relationship of the modelling work by the group of Empa and the other institute influenced by the work of Müller and Bernd 2008.
1.5 Motivations of the thesis

1.5.1 Latest knowledge on ENM uses, release and behaviour

The basis for material flow modeling is the knowledge about the total use of a certain ENM in a defined region, the distribution of the mass to different product categories and the transfer of the mass along the entire life-cycle of the products into technical and environmental compartments. Data on environmental concentrations using material flow models for ENM were published in 2008 (Mueller and Nowack, 2008a) and 2009 (Gottschalk et al., 2009a). These were necessarily based on the limited information available at that time on the behavior of ENM in technical and natural systems. Modelled results may rapidly change due to the fast development of ENM production and applications. Moreover, the availability and quality of published information on fate and behavior of ENM have increased enormously in the last few years and thus we now have a much better understanding of the behavior of ENM in the technical systems. These two factors call for a more comprehensive and up-to-date prediction of ENM flows to the environment (surface water, soil, sediment, air) and therefore for an update of the previous models published by the ERAM group at Empa.

1.5.2 Necessity to take the conventional counterparts of ENM into account

ENM constitute only a portion of the nanomaterials existing on earth and conventional materials produced in high volumes (such as TiO$_2$ pigment) may contain a nano-sized fraction (Weir et al., 2012). Also, several studies (Akaighe et al., 2011; Glover et al., 2011) have reported that metallic silver nanoparticles can be generated under environmental conditions from sources such as silver wire or jewellery. Therefore, it is necessary to compare the environmental concentrations of ENM with that of their corresponding conventional materials in order to have a holistic understanding of the environmental exposure to nanomaterials.

1.5.3 Extended applications of the P-MFA

1.5.3.1 Extension to other material

There is a growing interest in the environmental fate of gold nanoparticles (GNP) due to its increased use in medical applications. This interest relates both to its potential ecotoxicological impacts and the financial benefits associated with its recovery post-use for recycling. Probabilistic material flow analysis provides a useful tool to address both of these considerations. The exchange of expertise on material flow modelling and the knowledge on GNP application in the medical sector form the ground for a collaboration between Prof. Jamie Lead’s group at the University of Birmingham and Empa.

1.5.3.2 Extension to other regions

Almost all the previous studies of MFA for ENM are only able to provide regional average concentrations of ENM. This is largely due to the lack of sufficient data for site-specific distributions
of ENM. The group of Prof. Enzo Lombi at the University of South Australia possesses the expertise in soil science and a high abundance of good quality of input data for South Australia. The detailed information on biosolids applied for soil amendment and sewage effluent used for grassland irrigation offer the opportunity to calculate the South Australian specific ENM distributions onto regional biosolids-treated soils and STP effluent-treated soils within a better spatio-temporal resolution.

1.5.4 Development and application of the DP-MFA

All the models published so far are static and do not consider time-dependent processes with respect to the use and release of ENM. The current models consider only the input into the system that occurs in one year and subsequently distribute the mass over the entire system in the same year. The models also assume that all ENM produced and applied to products are released to waste streams and environmental compartments in the same year when they enter the system. So in this way ENM accumulation in in-use stocks is not considered. With these two oversimplifications of the true situation, the static models do not represent the actual ENM flows to environmental compartments under conditions where a rapid increase in production of ENM is taking place and when they are entering in-use stocks. Moreover, the static models cannot predict concentrations in environmental sinks, such as soils or sediments, because these compartments accumulate inputs over many years. First attempts in considering accumulation in environmental sinks have been made by Gottschalk et al. (2009a) who used a simplistic model to scale the input for previous years to calculate final concentrations in soils and sediments. However, it considered only one aspect of the dynamic nature of the system - a periodic production input into the system, but another aspect - the residence time of ENM remaining in in-use stock - is completely missing.

A more realistic prediction of ENM flows to the environment therefore requires a complete dynamic material flow analysis model. Unlike the static models, a dynamic MFA is able to track the flows over many years and it also no longer uses the simplified assumption of immediate ENM release.
1.6 Objective of the thesis

The overall objective of this thesis is to provide a better understanding of environmental exposure to ENM, which is a fundamental basis for the environmental risk assessment of ENM. To derive this, the sub-objectives are:

- to extend the existing probabilistic MFA model with more extensive descriptions of processes within technical systems such as STP and WIP, and based on that predict the environmental mass flows and concentrations of nano-TiO$_2$, nano-ZnO, nano-Ag, CNT and fullerenes incorporating the latest data on production, use and behaviors of ENM;
- to collect information about environmental concentrations of the corresponding conventional materials of ENM (pigment TiO$_2$, metal Ag and Zn), and to identify the significance of ENM compared to their conventional counterpart;
- to predict the mass flows and environmental concentrations (PEC) of gold nanoparticles from selected medical applications that are currently on the market or have the potential to be introduced in the near future by applying P-MFA modelling, and to evaluate the environmental risks of gold nanoparticles by combining the PEC with the obtained hazard data;
- to develop a P-MFA model for South Australian with a detailed description of the spatial and temporal biosolids and sewage efﬂuent distributions onto crop soils and grassland and to predict the local PEC of ENM;
- to build a dynamic probabilistic material flow model (DP-MFA) accounting both the development of the ENM production volumes and their release kinetics, and to predict the former, current and future mass flows of nano-TiO$_2$, nano-ZnO, nano-Ag, and CNT to technical and environmental compartments and the resulting concentrations in these compartments.
1.7 Structure of the thesis

The structure of the thesis is illustrated in Figure 1-2. The thesis consists of six chapters.

Chapter 1 (Introduction)

Chapter 2 (Improvement of the static model)
A comprehensive P-MFA modelling for nano-TiO$_2$, nano-ZnO, nano-Ag, CNT and fullerenes in the EU and CH using newest input data; and comparison between the PEC of ENM and the environmental concentrations of their conventional counterparts.

Chapter 3 (Application of the improved static model to a new material)
Application of P-MFA for the prospective GNP consumption in the medical sector and environmental risk assessment of GNP based on PEC and hazard data.

Chapter 4 (Development and application of a partially dynamic model)
Developing a P-MFA model for the South Australian situation; predicting local PEC of ENM incorporating spatial and temporal distributions of biosolids and sewage effluent.

Chapter 5 (Development and application of a fully dynamic model)
Development and application of a DP-MFA model for nano-TiO$_2$, nano-ZnO, nano-Ag, CNT to derive the to-date most reliable mass-flows and PEC in the EU.

Chapter 6 (Conclusions & Outlook)

Figure 1-2: Structure of the thesis. EU= European Union, CH= Switzerland, P-MFA=probabilistic material flow analysis (model), CNT=Carbon nanotubes, GNP= gold nanoparticles, PEC=predicted environmental concentrations, DP-MFA=dynamic probabilistic material flow analysis (model) Arrows indicate the heritage and development from the comprehensive P-MFA to the full DP-MFA.
Chapter 1, the introduction, provides background information on engineered nanomaterials (ENM) as emerging contaminants and highlights the need to quantify their environmental exposure. This chapter reviews all the analytical and modelling studies for quantifying the environmental exposure of ENM available to date. It points out that specific trace analytical methods for ENM detection and quantification are not available and currently modelling predicted environmental concentrations (PEC) constitutes the only way to obtain information on existing levels of ENM in the environment. It discusses the feasibility of material flow modeling (MFA) to estimate the PEC of ENM and the limitations of the previous MFA studies for ENM. It also demonstrates the necessity of extending the application of MFA to other materials and regions. This chapter provides the motivation and the theoretical basis for the further development and application of the MFA tools to predict the mass flows and PEC for ENM as presented in the following chapters.

Chapter 2 presents an updated and more extensive probabilistic material flow model to calculate the concentrations of five ENM (nano-TiO$_2$, nano-ZnO, nano-Ag, CNT and fullerenes) in environmental and technical compartments in the EU and Switzerland. The model applies the newest data on ENM production volumes, their allocation to and subsequent release from different product categories, and their flows into and within those compartments. This improved static model enables comprehensive modelling prediction for other ENM and in other regions. It also provides a fundamental basis for later development of a dynamic model. In this study, the newly predicted ENM concentrations are compared to estimates from 2009 and corresponding measured concentrations of the conventional materials of ENM, e.g. pigment TiO$_2$, metal Zn and Ag. The new ENM production estimates are higher than those a few years ago. In most cases, the environmental concentrations of the corresponding conventional materials are between one and seven orders of magnitude higher than those for ENM. The incorporation of the latest data of the production and use of ENM, and the more comprehensive description of technical processes in sewage treatment plants (STP) and waste incineration plants (WIP) made the model a good basis to be extended for applications to other regions and materials.

Chapter 3 presents an application of improved probabilistic material flow modelling for gold nanoparticles (GNP) in the UK and the US. In this study, the prospective maximal consumptions of GNP from medical applications in the UK and US are estimated. On this basis, the GNP flows post-use, and the resulting environmental concentrations are predicted. Furthermore, the environmental risks of GNP are assessed by comparing the predicted environmental concentrations (PEC) with ecological threshold (PNEC) values. The conclusion of this chapter is that no environmental risk from GNP in surface waters and agricultural soils amended with biosolids is currently expected.

Chapter 4 presents the development and application of a partially dynamic probabilistic material flow model for the case of South Australia, where significant amount of biosolids and treated
wastewater are applied on soils. The probabilistic material flow modelling approach was extended to include a temporal modelling of the ENM production and the biosolids handling and transfer onto soils. This part of the thesis focuses on nano-TiO₂, nano-ZnO, nano-Ag, carbon nanotubes (CNT) and fullerenes. The inclusion of a temporal aspect in this study, the production development modelling, provides a first step for further development of a full dynamic probabilistic material flow model.

**Chapter 5** presents the new concept of a fully dynamic probabilistic material flow model for ENM, which is urgently needed for a realistic prediction of mass-flows and PEC of ENM. It describes the two major components for a dynamic model for the case of ENM, the production development of ENM in a given period and the time dependent ENM release kinetics from products. These aspects are necessary to address the rapid development of ENM production volume and includes the fact that a lot of ENM are entering an in-use stock before they are released from a particular product (i.e. have a lag phase). Given the rapid increase in production, this approach is necessary in order to capture the dynamic nature of ENM flows. The predicted accumulated masses in sinks and the average concentrations in technical compartments quantified in this work provide necessary data for risk assessors and scientists in need of quantitative knowledge on the presence of ENM in various compartments. The flows to the environment that this study provides constitute the most accurate and reliable input of masses for environmental fate models. The latter use process-based descriptions of the fate and behavior of ENM in natural system but rely on accurate mass input parameters.

**Chapter 6** closes the thesis with more general thoughts on possible strategies to handle the challenges emerging from the significant complexities in the context of ENM exposure and risk assessment. Emphasize is placed on the importance of considering a better spatial resolution of the modelled mass flows and PEC of ENM and the technical changes over time i.e. the evolution of ENM applications. The inclusion of these two aspects can largely improve the level of accuracy of the derived results and enable a proactive and well-founded ENM risk assessment.
1.8 References


Dynamic Probabilistic Modelling of Environmental Emissions and Concentrations of Engineered Nanomaterials


Dynamic Probabilistic Modelling of Environmental Emissions and Concentrations of Engineered Nanomaterials


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2 COMPREHENSIVE PROBABILISTIC MODELLING OF ENVIRONMENTAL EMISSIONS OF ENGINEERED NANOMATERIALS

Tian Yin Sun\textsuperscript{ab}, Fadri Gottschalk\textsuperscript{ac}, Konrad Hungerbühler\textsuperscript{b} and Bernd Nowack\textsuperscript{a}

\textsuperscript{a} Empa – Swiss Federal Laboratories for Materials Science and Technology, Technology and Society Laboratory, CH-9014 St. Gallen, Switzerland
\textsuperscript{b} Institute for Chemical and Bioengineering, ETH Zürich, CH-8093 Zürich, Switzerland
\textsuperscript{c} ETSS, CH-7558 Strada, Switzerland

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Abstract

Concerns about the environmental risks of engineered nanomaterials (ENM) are growing, however, currently very little is known about their concentrations in the environment. Here, we calculate the concentrations of five ENM (nano-TiO$_2$, nano-ZnO, nano-Ag, CNT and fullerenes) in environmental and technical compartments using probabilistic material flow modelling. We apply the newest data on ENM production volumes, their allocation to and subsequent release from different product categories, and their flows into and within those compartments. Further, we compare newly predicted ENM concentrations to estimates from 2009 and corresponding measured concentrations of their conventional materials, e.g. TiO$_2$, Zn and Ag. We show that the production volume and the compounds’ inertness are crucial factors determining final concentrations. ENM production estimates are generally higher than a few years ago. In most cases, the environmental concentrations of corresponding conventional materials are between one and seven orders of magnitude higher than those for ENM.
2.1 Introduction

The rapid increase in the production and use of ENM makes it likely that increasing environmental exposure to them will occur (Gottschalk and Nowack, 2011). Release of ENM into the environment may occur throughout their entire lifecycle: from their production to the fabrication of ENM-containing products, to the use and end of life phase of those products. Risks from ENM emissions may emerge if both exposure (due to the presence of ENM in the environment) and hazard (in the form of toxic effects) are observed (Aschberger et al., 2011). Therefore, understanding environmental exposure and the toxicity of ENM provides the basis for assessing the environmental risks posed by these compounds. Knowledge on the hazard side is increasing exponentially (Klaine et al., 2008; Scown et al., 2010); however, there are currently almost no specific trace analytical methods available to quantify ENM in environmental samples, e.g. water, wastewater or biosolids (von der Kammer et al., 2012; WWI, 2013). Currently, to perform a proactive environmental risk analysis, the only way to obtain information on existing levels of ENM in the environment is to model predicted environmental concentrations (PEC). To derive these, we particularly need information on the flows of ENM into the environment. Material-flow modeling, which predicts and quantifies flows and stocks of materials or substances in a well-defined system, is an established method of deriving flows of materials to the environment (Baccini and Brunner, 2012). It is used at different spatial and temporal scales accounting for material flows within and between anthropogenic and connected ecosystems.

To date, only a few modeling studies have presented quantitative estimations of the environmental concentrations of ENM (Blaser et al., 2008; Boxall et al., 2007; Gottschalk, 2013; Gottschalk et al., 2009a; Johnson et al., 2011a; Keller et al., 2013; Mueller and Nowack, 2008; Sun et al., 2014c). Furthermore, most of these studies only targeted one or two ENM and focused on scenarios considering just a few applications, e.g. nano-TiO2 use in sunscreens (Arvidsson et al., 2011; Musee, 2011). These scenario-based models, therefore, cannot be representative of the total real levels of ENM currently in the environment. Data on environmental concentrations using a material flow model of ENM were published in 2008 (Mueller and Nowack, 2008) and 2009 (Gottschalk et al., 2009a), but these were necessarily based on the limited information available at that time on the behavior of ENM in technical and natural systems. The recently published study by Keller et al. (2013) provided the first global assessment of the likely ENM emissions to the environment for ten most produced ENM applications by combining ENM market information and material flow modeling. However, the production and use input data of the whole study relied solely on one single market report, and it is thus not transparent as to how the information was compiled. Because of this it is difficult to access the amount of uncertainty in the dataset itself, which therefore leads to unknown uncertainty of all their results. Mechanistic models specifically considering agglomeration and sedimentation reactions of ENM have also been developed in (Arvidsson et al., 2011; Praetorius et al., 2012). Modelled results may rapidly change due to the fast development of ENM production and
applications; what is more, the availability and quality of published information on fate and behavior have increased enormously in the last few years and thus we have a much better understanding of the behavior of ENM in the environment. These two factors call for a more comprehensive and up-to-date prediction of ENM flows to the environment (surface water, soil, sediment, air), which is the main aim of this study. The new modeling effort is necessary to identify possible trends in production and concentrations and with the current knowledge a much more robust and comprehensive understanding of the flows is possible.

We must also remember that ENM constitute only a portion of the nanomaterials existing on earth and conventional materials produced in high volumes (such as TiO$_2$ pigment) may contain a nano-sized fraction (Weir et al., 2012). Also, several studies (Akaighe et al., 2011; Glover et al., 2011) have reported that metallic silver nanoparticles can be generated under environmental conditions from sources such as silver wire or jewellery. Therefore, an additional aim of this work was to compare the environmental concentrations of ENM with that of their corresponding conventional materials.

We modelled for nano-TiO$_2$, nano-ZnO, nano-Ag, CNT and fullerenes. These materials were selected because either they are used in large amounts (nano-TiO$_2$, nano-ZnO), are contained in many products (nano-Ag), or because a relatively large amount of information is available about their properties (CNTs and fullerenes). The material flows of TiO$_2$ pigment were modelled as the conventional counterpart to nano-TiO$_2$. The modelled concentrations of nano-Ag and nano-ZnO were compared to the measured concentrations of total Ag and Zn metal in the different environmental compartments.

2.2 Methods

2.2.1 Model structure, system boundary and assumptions

Figure 2-1 presents the general material flow model. The basis for the modeling is knowledge about the total use of certain ENM in a defined region (in our present model, the EU and Switzerland) and the distributions of their mass to different product categories. Product life-cycles then determine any possible releases of ENM into the environment. Apart from releases during their production and incorporation into products, the majority of the releases of ENM into the environment take place during the use and disposal phases. The model grew from the approach developed by Gottschalk et al. (2010b), but with a more comprehensive description of the processes in technical systems, for example, sewage treatment plants (STP) and waste incineration plants (WIP). The model applies a stochastic approach to computing probability distributions of mass flows and PEC, by means of Monte Carlo simulations and Markov Chain Monte Carlo (MCMC) (Martin, 2011) modeling. This allows the model to cope with the uncertainties and inherent variability of its parameters (ENM production volumes, transfer coefficients etc.).
The material flows of ENM can be used to predict averaged concentrations of ENM in technical and environmental systems. This was achieved by calculating the total input flows into compartments using the material flow calculation and then dividing the amounts remaining in each compartment by the volumes of the respective compartments. For air and surface water, a retention time of 10 (Anastasio and Martin, 2001) and 40 (ECB, 2003a) days were used, therefore 10/365 and 40/365 of the total input flows into these compartments were considered as the fraction of ENM remaining in the two compartments. Different compartmental volumes were calculated based upon ECHA’s technical guidance (ECHA, 2012b), as explained in detail in Gottschalk et al. (2009a), with environmental concentrations assuming well-mixed, homogeneous compartments. A summary of the calculated compartment volumes is shown in Table A2-6. The concentrations calculated are therefore average values. For surface water the concentrations correspond to a no-sedimentation scenario which means no fate of ENM in water was considered, representing the initial concentration after mixing of surface water and wastewater effluents. Sediment concentrations on the other hand reflect the full-sedimentation scenario, representative of the sediment concentrations over the long-term with complete sedimentation (Gottschalk et al., 2011a). The method used to estimate the masses of solid waste, bottom ash and fly ash in WIP can also be found in Appendix 2.

The modeling for the EU considers average data for the European Union, for example the household waste water connection rate to wastewater treatment plants, the percentage of waste going to landfill or incineration. It thus represents an “averaged EU”. The numbers are based on the standard risk assessment of chemicals as performed according to REACH (2007), so these parameters are generally accepted to represent an averaged region in material flow and environmental fate modelling. Transfer factors from one compartment to another were estimated, incorporating the current knowledge on fate and behavior in these compartments. Details about the mathematical model, the system equations, the modelling of distributions and the Monte Carlo simulations are given in Gottschalk et al (2010b).
2.2.2 Input data preparation

All the model input parameters were treated as probability distributions; the methodologies for these probability distributions were chosen by analyzing the raw data. Raw data – obtained from published papers and reports, but also from experts – were classified according to a degree of belief (DoB) scale (80% for high and 20% for low DoB are used, respectively). The DoB of the data were judged according to their reliability: e.g. for ENM production volumes, a high DoB was assigned to data from peer reviewed papers explicitly investigating this topic, with detailed, clear descriptions of how data were obtained. First hand commercial market information via personal communication also scored a high DoB. Surveys of companies also received a high DoB. Data from reports or presentations where
only numbers were available, without further reference or explicit explanations as to their sources scored a lower DoB. For transfer coefficients, like STP removal efficiency, the highest DoB was assigned to experimental results from full-scale STP, a medium DoB was given to data from pilot STP, and the lowest DoB was assigned to results from laboratory scale or batch reactor experiments. Complete data on ENM production volumes and STP removal efficiency, together with their DoB, are summarized in Appendix 2 Table A2-1 and Table A2-3. DoB was reflected in the Monte Carlo modeling by assigning more or fewer samples (proportional to their DoB) to the corresponding input data. For example, if in total there are three data sources for one parameter are available and they are assigned DoBs of 20%, 30% and 50%. If the total simulation for this parameter is 100,000 times, we will assign 20,000, 30,000 and 50,000 samples respectively for these data sources to express their likelihood and differentiate their reliability. MCMC, as a combination of Bayes inference and Monte Carlo method, is considered to include data with different DoB from different sources and to produce a normal distribution (Gottschalk et al., 2010b) e.g. for nanomaterial production and use (see section on Characterization of production volume of ENM).

In many cases we have only a single data point for a certain parameter; in such cases this single value is deviated ±50% and a triangular distribution is obtained. This approach was applied for the major part of the parameters in our modelling, e.g. ENM release rate from product to disposal or environment (see Appendix 2 Table A2-2), connection rate of wastewater to STP, or STP sludge disposal. For all the parameters where minimal, mode (mean) and maximal values were available, such as for the allocation of ENM to product categories, triangular distributions were also applied. Many data were available in the form of a range or pair of values. For these data a general uniform distribution was used to produce the input distributions. Examples are the filter removal efficiency of WIP, or TC from soil to surface water. For parameters exhibiting uncertainty and variability, and where there were many different data sources – such as STP’s ENM removal efficiency (Appendix 2 Table A2-3) – a simple random Monte Carlo sampling of empirical raw data, combined with a uniform distribution (ranging from 0 and 1 by the inherence of these parameters), was used to produce probability distributions for these parameters. The distribution generated includes all the information contained in these data and at the same time is able to represent the inherent variability of these Transfer Coefficients (TC) (the inhomogeneity of the same type of ENM can lead to a variety of TC for the same process). Our modeling also used a standard normal distribution for overflow rates, for example, for which both mean value and standard deviation were known (Stauf, 2012).

2.2.3 Characterization of ENM production volumes

Production volume is an important input parameter for any material flow model. We therefore screened all the available publications and studies published after 2008 reporting information on ENM production or use (data sources and raw data are summarized in Appendix 2 Table A2-1). Global and
regional (e.g. U.S.A.) production or use data were extrapolated to Europe and Switzerland in proportion to Gross Domestic Product; detailed principles are given in Appendix 2 “Production volume of ENM”. The production/use probability distributions were obtained by feeding these data into simple MCMC algorithms (Martin, 2011) that produce for each ENM studied a sample from the posterior distribution of a normal likelihood with known variance and a normal prior (see Figure 2-2). Prior mean and variance values (derived from the 20% weighting factor data, see Appendix 2 Table A2-1)

![Figure 2-2: Yearly ENM production distribution and mode values in the EU (t) in 2012. Raw data of ENM production or use (see Appendix 2 Table A2-1) were classified into groups according to their degree of belief (DoB), which, according to Huber (2009) formally represent the strength with which we believe in the truth of various propositions, e.g. data from peer-reviewed studies received a higher DoB than values extracted from reports without information on the methods used to obtain them. DoB was reflected in the modelling by assigning more or less samples (in proportion to their DoB) to the corresponding input data. These data were treated with MCMC (Martin, 2011) to obtain annual probability distributions of the production/use amounts in the EU for the five ENM investigated.](image)

were combined with newer evidence on central tendency and spread (derived from the 80% weighting factor data), so as to benefit from Bayes inference and compute the joint posterior distributions. In the EU, the most produced/used ENM of the five studied is nano-TiO₂, with an annual production of about 10’000 tonnes (t); followed by nano-ZnO with a production of around 1’600 t; then CNT,
around 400 t; nano-Ag, around 30 t; and finally fullerenes, with about 20 t per year. The full probability curves were used as input into the material flow modeling described below.

### 2.2.4 Characterization of model parameters

Our model tracks ENM release throughout the entire life cycle of the products containing them, therefore knowing how much ENM is incorporated into which products is essential. Information from various sources was combined to allocate ENM to different products. A company survey by Piccinno et al. (2012) provided direct distribution data for various ENM. These data were complemented using publicly available nano-product inventories that were analysed and summarized so as to make them ready for modeling purposes: the inventory of the Woodrow Wilson Centre for Scholars’ Project on Emerging Nanotechnologies (WWI, 2012); the ANEC/BEUC Inventory (ANEC/BEUC, 2010); the BUND inventory (BUND, 2011); a summary of recent nanotechnology patents, (Lem et al., 2012) and a comprehensive nano market report (Future Markets, 2011). We also conducted an internet search using Google, Yahoo and EC21 for counting the numbers of products for wide variety of applications available on the market. The information obtained from these sources was either the share of ENM in certain applications (which can be used directly) or product numbers that were used to obtain product shares as described by Gottschalk et al. (2009a). Each product category was assigned relative shares according to different sources. Minimal, maximal and average values were calculated from these assigned shares for each product category and form the basis for building triangular distributions, see Appendix 2 Table A2-7. Appendix 2 Table A2-2 shows the mean percentages of ENM allocated to different product categories, calculated from the sources mentioned above, which were used as modes for generating triangular distributions.

The next important modeling step was to define during which life cycle stages ENM release occurs and how much is released into which technical or environmental compartments. Appendix 2 Table A2-2 shows the transfer factors for ENM released from products into these compartments. These transfer factors were estimated based on published release studies, for example for textiles (Geranio et al., 2009; Lorenz et al., 2012) and paints (Kaegi et al., 2008; Kaegi et al., 2010); fate studies in STP (Kaegi et al., 2011; Lombi et al., 2012) and WIP (Walser et al., 2012). Release can occur onto technical compartments, e.g. wastewater treatment plants or directly into the environment, e.g. from bathing in natural waters after application of sunscreen.

Our modeling is based on transfer factors that summarize the overall transport behavior from one compartment to another. For sedimentation from air for example we base the transfer factor on the known life-time of ultrafine particles because no data about ENM in the atmosphere are available (Anastasio and Martin, 2001). However, we don’t use one single value for these transfer coefficients but produce probability distributions that consider variability between different studies and uncertainty based on the available knowledge. As stated above, our primary source of data are studies
that are able to deliver an overall transfer factor. Top soils are treated as final sinks and thus no fate processes are modelled. Also the sedimentation in natural waters was not modelled in this work because empirical data describing the important heteroagglomeration process are not yet available (Praetorius et al., 2012). The flow from surface water into sediments was therefore predicted based on two extreme scenarios: no sedimentation and complete sedimentation. Dissolution, phase transformation, degradation, incineration and other removal processes were modelled as flows going into an “elimination” compartment. CNT and fullerenes, for example, can be burned in WIP (Mueller et al., 2013); the majority (85%-100%) (Kaegi et al., 2011) of nano-Ag is transformed into silver sulphide in STP; and nano-ZnO can be completely transformed into other non-nano forms during the anaerobic digestion process in STP (Lombi et al., 2012). The fate and behaviour of the ENM relevant for transfer between the compartments is described in detail in Appendix 2. All transfer factor are given in the Appendix 2 Table A2-2.

2.3 Results

2.3.1 ENM flows

Flows of the five ENM, from production and use through release into all the compartments, were modelled by combining the modelled production volumes, product distributions and transfer factors between all the compartments. The material-flows calculated for nano-TiO₂, nano-ZnO, nano-Ag, CNT and fullerenes in the EU are shown in Figure 2-3. The corresponding material flows for Switzerland can be found in Appendix 2 Figure A2-3: Modelled results (mode values) of material flows for nano-TiO₂, nano-Ag, pigment-TiO₂, nano-ZnO, CNT and fullerene in Switzerland (CH) in t for the year 2012. The thickness of the arrows indicates the proportion of flow quantity. Dotted arrows between surface water and sediments/export indicate two different scenarios with either complete ENM sedimentation or 100 % of ENM remain in surface water with 0 % sedimentation. Flows leaving the system describe ENM flows out of the system boundary considered, e.g. export or river flow into the sea. ENM might be transformed or degraded before they end up in environment. Nano-Ag and nano-ZnO can be transformed into other forms in the anaerobic phase in a STP or be dissolved in the acid washing process in a WIP. Carbon-based ENM can be completely destroyed through the combustion processes in WIP (Mueller et al., 2013). All these processes are regarded as ENM elimination and the corresponding flows lead to a virtual elimination compartment representing the loss of these materials. ENM can also accumulate in landfills, soils and sediments, as indicated by the black squares in Figure 2-3, with a yearly increment.
PMC: Production, Manufacture and Consumption; N&U soil: natural and urban soil; ST soil: sludge treated soil

Figure 2-3: Modelled results (mode values) of material flows for nano-TiO$_2$, TiO$_2$ pigment, nano-ZnO, nano-Ag, CNT and fullerenes in the EU in t for 2012. In the model, technical compartments (e.g. PMC, STP, WIP, landfill, recycling and elimination) and environmental
compartments (air, soil, water and sediments) are expressed as boxes; flows between these processes and compartments are expressed as arrows, the thickness of these arrows indicates the magnitude of the flows. The flows are determined by transfer coefficients (TC) that describe the exchange of ENM between and within these boxes. The mathematical structure of the material flow model describes the processes by rates of changes of stocks and flows by TC; the model is a stationary input-output system consisting of set n linear equations containing n unknowns. Matrix algebra is embedded in Monte Carlo algorithms for material flows and solutions are found by computing inverse matrices. For details refer to Gottschalk et al. (2010, 2010b) All the ENM mass-flows are computed regardless of their agglomerated and aggregated form, therefore tracking the mass of the primary particles. Degradation (e.g. combustion of CNT and fullerenes in WIP) and transformation (e.g. nano-Ag transformation in STP and nano-ZnO transformation in the STP anaerobic digestion process) are treated as disappearance entering into an “elimination” box. All the values are rounded to three significant numbers; therefore the balance between input and put flows from one compartment might not be 100% closed.

The most prominent flows for nano-TiO$_2$ and nano-ZnO were from production, manufacturing, and consumption (PMC) to waste water (and further to STP), for both the EU and Switzerland. This is due to the fact that the major applications for these two ENM are in cosmetics (Appendix 2 Figure A2-2 shows shares for all ENM applications). In the case of TiO$_2$ pigment, the dominant flows were from PMC to landfills. For nano-Ag, the major flows were from PMC to recycling and to waste water. The most prominent flows for carbon-based ENM (CNT and fullerenes) were from PMC to recycling and to WIP, and from there to further elimination. Initially ENM flows going through STP would mainly be captured and settled in STP sludge, and further transported to WIP and landfill (in Switzerland), and some of ENM end up in soil from the part of STP sludge that is used as fertilizer (in the EU, but not in Switzerland). In our modeling we track the mass of the primary particles. Agglomeration plays a role in transferring particles from one compartment to another (e.g. from water to sediment), but does not affect the total mass of the primary particles.

### 2.3.2 ENM concentrations in technical and environmental systems

Table 2-1 shows the predicted ENM concentrations in STP effluent, surface water, STP sludge, air, solid waste, WIP bottom ash and WIP fly ash, as well as yearly incremental concentration increases in sediments, soils, and STP sludge treated soils (only for the EU). The values presented are the most probable values (mode values) and their 15th and 85th percentiles ($Q_{0.15}$ and $Q_{0.85}$) from each distribution. No concentrations in sludge-treated soil were calculated for Switzerland since sewage sludge is not applied to soils; instead it goes to waste incineration plants or is used as solid fuel in cement plants. In general, all the ENM showed their highest concentrations in STP sludge, followed by concentrations in solid waste, WIP bottom ash and WIP fly ash. Among the environmental compartments (soil, surface water, air and sediments), sediments had the most considerable concentrations, followed by STP-sludge treated soil (in the case of EU), then untreated soil and surface water, followed by air, with the lowest concentration of ENM overall. This appears quite
reasonable due to the low release of ENM into the air and their short persistence time there. For soils and sediments, the simulations provided the annual amount of ENM deposited in these compartments in recent years.

In all the considered compartments, nano-TiO$_2$ had far higher concentrations than the other four ENM modelled; it was followed by nano-ZnO. This reflects on the one side the correlation between the total input production volume and the consequent concentration in different compartments but also the allocation to product groups with similar release pathways to the environment (for both groups cosmetics are major uses). Significant flows of nano-TiO$_2$ and nano-ZnO were found going into wastewater and then from STP to landfill, WIP and soil (only for EU). For nano-Ag, the major part coming from PMC went to recycling, which is believed to be due to its use in various consumer products with antibacterial effects; a quite considerable amount also went to wastewater and this part is assumed to originate from nano-Ag applied to textiles and released during washing. For CNT and fullerenes, the flows from PMC to WIP, landfill and recycling were of similar magnitude.
Table 2-1: Predicted ENM concentrations in different technical and environmental compartments shown as mode (most frequent value) and as a range of lower and upper percentiles (Q_{0.15} and Q_{0.85}). Black values designate concentrations; grey values designate yearly increases in concentrations. ENM concentrations in surface water and sediments represent no and complete sedimentation, respectively.

<table>
<thead>
<tr>
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<th>Switzerland</th>
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<tbody>
<tr>
<td></td>
<td>Mode</td>
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<td></td>
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<td>0.000</td>
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<td>110</td>
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<tr>
<td><strong>Nano-ZnO</strong></td>
<td></td>
<td></td>
</tr>
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<td>1.3</td>
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<td>Surface water</td>
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<td>STP sludge</td>
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<td>Natural and urban soil</td>
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<tr>
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Sediments, where most ENM entering surface water end up, showed concentration increases ranging from 0.4 µg/kg·per year (fullerenes) to nearly 2'000 µg/kg·per year (nano-TiO₂). In most cases the concentrations in WIP materials (solid waste, WIP bottom ash and WIP fly ash) were at the “mg/kg” level, exceeding concentrations in sediments.

Although in reality there may well be ENM in landfill leachates, our model did not take into account this possibility due to the insufficient existing quantitative information on this process. Furthermore, we did not track the fate of ENM during and after recycling, again due to the limited understanding of the behaviour of ENM associated with different products during recycling.

Compared to the results of Gottschalk et al. (2009a), the newly predicted concentrations of ENM were in general 1 to 70 times higher, mainly due to the larger production in our new evaluation, well matching the rapid development of nanotechnology. For nano-TiO₂, newly predicted concentrations were 1 (in STP sludge) to 5 (in STP effluent) times higher. This equated to an increase from 140 mg/kg to a newly predicted concentration of 170 mg/kg in STP sludge, and from 3.5 µg/l in 2009 to a predicted concentration of 16 µg/l in STP effluent. For CNT the new values were 2 (in STP sludge) to 3 times higher (in soil).

However, nano-ZnO and nano-Ag were exceptions by showing lower concentrations in some compartments in the new modeling: lower predicted concentrations of nano-Ag in wastewater resulted from lower production estimates based on more reliable data than was previously available. The comprehensive consideration of transformation reactions (e.g. of nano-Ag and nano-ZnO in STP) resulted in much lower estimated releases into natural waters and into STP sludge, and thus much lower environmental concentration estimates than in 2009, despite higher production of nano-ZnO. The newly predicted increment in nano-ZnO concentration in sludge-treated soil was 0.01 µg/kg·per year, versus 3 µg/kg·per year in 2009. For nano-Ag, the newly predicted incremental increase in concentrations in soil and sludge-treated soil were 1.2 ng/kg and 110 ng/kg·per year respectively; the corresponding increments for 2009 were 23 ng/kg and 1’580 ng/kg·per year – very much higher. This comparison shows that the knowledge gained in the last years on behaviour of ENM in technical systems such as wastewater treatment plants that was not available in 2009, especially about the transformation reactions of ENM that lead to their destruction, can have a very strong influence on the mass flows and the concentrations in the environmental compartments.

The ranges presented in Table 2-1 include both the uncertainty in some of the parameters as well as the variability that is caused by our approach, which considers all different forms of an ENM (e.g. coatings, functionalization) and thus provides information for a generic ENM, e.g. “nano-TiO₂”. The concentrations in the technical compartment, e.g. wastewater, sludge or bottom ashes, may be used as input values to more sophisticated environmental fate models incorporating a mechanistic description of fate processes, e.g. agglomeration and sedimentation. Praetorius et al. for example used the mass
flow to natural waters from Gottschalk et al. (2009a) as input to their mechanistic river fate modeling of nano-TiO$_2$ (Praetorius et al., 2012), also Gottschalk et al. (2011a), used the release from wastewater as input for a local modeling study with high spatial resolution of ENM within the Swiss river network. In a next step the new material flow model will be coupled with the mechanistic environmental fate model provide realistic concentrations in natural waters and sediments.

We also have to consider that our modeling did not take into account accidental releases but only the standard handling and use of ENM and ENM-containing products. During major accidents locally elevated concentrations may be present, however, such events are normally not considered during risk assessment of chemicals but are part of process risk analysis and covered by accident regulations (Krug, 2013).

No current analytical methods are able to distinguish and quantify ENM in environmental samples containing naturally occurring nanoscale materials (von der Kammer et al., 2012), thus a direct validation of our modelled results is impossible. However, there are some data available that might be used to provide an initial comparison. The concentration of Ti smaller than 700 nm was, for example, found to be 5-15 µg/l in STP effluents in the USA (Kiser et al., 2009), therefore close to our predicted value. Using single-particle ICP-MS, a concentration of nano-Ag of 100 ng/l was found in one STP (Mitrano et al., 2012), including however, all forms of Ag, e.g. nano-Ag$_2$S which was considered a transformed nano-Ag in our modeling. This compares well to the upper range of 16 ng/l for engineered nano-Ag in our model. As soon as more analytical data become available, better validations will be able to be performed. However, our modelled data provides analytical chemists with an indication of the expected concentrations that their methods will need to be able to detect in a certain compartment.

2.3.3 Comparison with conventional materials

We made the same material flow calculations for TiO$_2$ pigment as for nano-TiO$_2$ (material flows of TiO$_2$ pigment, see Figure 2-3) and we also searched for measured concentrations of TiO$_2$ for comparison and validation. For the measured environmental concentrations of total metals (silver and zinc), relevant publications and studies were screened and the results were summarised in Appendix 2 Table A2-5: Summary of measured total conventional materials’ (titanium dioxide, silver and zinc) concentrations in different compartments. Numbers in superscripts after each value are the numbers of references. Despite the 150 times higher production of pigment-TiO$_2$, the environmental concentrations are only about 1 order of magnitude higher, reflecting the prime importance of product allocation and release over the whole life cycle in determining the final concentrations.
Figure 2-4: Box and Whisker plots for comparison between logarithmical concentrations of ENM predictions and their corresponding conventional materials in sewage effluent, surface water, soil and sediments in the EU; green bars indicate modelled concentrations of ENM, yellow bars indicate modelled concentrations of TiO$_2$ pigment and orange bars indicate measured concentrations of their conventional materials. The diagrams were generated based on the modelled concentration values of ENM and TiO$_2$ pigment and measured concentrations (see Appendix 2 Table A2-5) of TiO$_2$ and total silver and zinc.

Figure 2-4 shows the comparison between the modelled concentrations of ENM (green bar) and their conventional materials (orange bar) in sewage effluent, surface water, soil and sediments. In all compartments the modelled concentrations of TiO$_2$ pigment (yellow bar) are about one order of magnitude higher than those of nano-TiO$_2$; the concentration of TiO$_2$ measured in sewage effluent is 1 and 2 orders of magnitude lower than that of modelled nano-TiO$_2$ and TiO$_2$ pigment, respectively. The concentrations of TiO$_2$ measured in sewage effluent were obtained by filtration at 700 nm (Kiser et al., 2009), 220 nm (Khosravi, 2012) or 100 nm (Westerhoff et al., 2011), and thus capture only a small fraction of the total modelled TiO$_2$ in that effluent. We also need to consider that a fraction of the pigment-TiO$_2$ has particles sizes below 100 nm (Weir et al., 2012) and thus not all TiO$_2$ particles below 100 nm are thus actually “engineered NM” but some may be unintentional by-products from pigment manufacturing. Weir et al. (2012) measured 36% of the particle number of a food-grade
pigment sample to be below 100 nm. The measured concentration of TiO$_2$ in surface water was around the same levels as those modelled for TiO2 pigment, which validates our modelled results well. Due to high background concentrations in sediments and soil, measured TiO$_2$ concentrations in these two compartments were 3 to 4 orders of magnitude higher than those for modelled nano-TiO$_2$ and TiO$_2$ pigment.

Total metal concentration levels for Ag and Zn were 1 to 3 orders of magnitude higher than for their corresponding ENM in sewage effluent, surface water and sediments. In soil, the total metal level concentrations were up to 7 orders of magnitude higher (e.g. for Zn) due to high natural background concentrations. Any assessment of ENM risks, e.g. nano-Ag in water or nano-ZnO in soils, therefore needs to consider these much higher total metal concentrations, which are of course also toxic at higher concentrations. Figure 2-4 also highlights the “needle-in-a-haystack” problem: any analytical method needs to be able to be specific for very low concentrations of ENM in the presence of high background total metal concentrations, many of which are present in colloidal or particulate form (Hochella and Madden, 2005; Theng and Yuan, 2008), further complicating the analysis of ENM.

2.4 Acknowledgements

This work was funded by the Swiss National Science Foundation within the National Research Programme "Opportunities and Risks of Nanomaterials" (NRP 64).

2.5 Supporting Information Available

Detailed information about production of ENM, allocation (share) of ENM applied to product categories, transfer coefficients for the model, calculation of the volumes of technical and environmental compartments, as well as the materials charts of ENM for Switzerland are provided in Appendix 2.
2.6 References


(3) ANEC/BEUC, 2010. ANEC/BEUC inventory of products claiming to contain nanoparticles available on the EU market.


Dynamic Probabilistic Modelling of Environmental Emissions and Concentrations of Engineered Nanomaterials


(51) WWI, 2012. The Project on Emerging Nanotechnology Inventory.
3 PROBABILISTIC MODELLING OF PROSPECTIVE ENVIRONMENTAL CONCENTRATIONS OF GOLD NANOPARTICLES FROM MEDICAL APPLICATIONS AS A BASIS FOR RISK ASSESSMENT

Indrani Mahapatra,1 Tianyin Sun,2,3 Julian Clark,1 Peter J. Dobson,4 Konrad Hungerbuehler,3 Richard Owen,5 Bernd Nowack2 and Jamie Lead1,6

1 School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, Birmingham, B15 2TT, U.K.
2 Empa – Swiss Federal Laboratories for Materials Science and Technology, Technology and Society Laboratory, Lerchenfeldstrasse 5, CH-9014 St. Gallen, Switzerland
3 Institute for Chemical and Bioengineering, ETH Zürich, CH-8093 Zürich, Switzerland
4 Warwick Manufacturing Group, University of Warwick, Coventry, CV4 7AL, U.K.
5 Business School, University of Exeter, Exeter, EX4 4PU, U.K.
6 Center for Environmental Nanoscience and Risk, Department of Environmental Health Sciences, Arnold School of Public Health, University of South Carolina, Columbia, South Carolina 29208

1 Joint first authors
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1 As a joint first author, I. Mahapatra was responsible for practically collecting the data of GNP consumptions, waste water treatment, waste incineration and the data for environmental compartments and ecotoxicity of GNP. She also jointly wrote the text of this part. T.Y. Sun was responsible in guiding the collection of data, reviewing the data, building the model and producing the results tables and figures. He also co-wrote the text of this part.
Abstract

The use of gold nanoparticles (GNP) based medical applications is rising due to their unique physical and chemical properties. Currently, no information on GNP consumption, material flows to and concentrations in the environment are available. We estimated prospective maximal consumption of GNP from medical applications in the UK and US. We then modelled the GNP flows post-use and predicted their environmental concentrations. Furthermore, we assessed the environment risks of GNP by comparing the predicted environmental concentrations (PEC) with ecological threshold (PNEC) values. The mean annual estimated consumption of GNP from medical applications is 540 kg for the UK and 2’700 kg for the US. Among the modelled concentrations of GNP in environmental compartments, the mean annual PEC of GNP in sludge for both the UK and US was estimated at 124 μg/kg and 145 μg/kg, respectively. The mean PEC in surface water was estimated at 468 pg/l and 4.74 pg/l, respectively for the UK and US. No environmental risk from GNP in surface waters and from agricultural soils amended with biosolids is currently expected.
3.1 Introduction

There has been an increased focus on developing gold nanoparticle (GNP) based applications in fields ranging from electronics to medicine. Between 2000 and 2013, gold nanotechnology related patents increased exponentially, with about 1’600 patents published in 2013 (World Gold Council). The number of publications related to GNP in the health sector in Thomson Reuters’ Web of Science database also show an exponential increase from 54 to 9’083 publications between 2004 to 2014, of which 2’150 articles were published in 2014 alone (search conducted on 28 Dec 2014) (Thomson Reuters’ Web of Science). The unique chemical and physical properties of GNP (Eustis and El-Sayed, 2006; Masitas and Zamborini, 2012; Trudel, 2011) make them excellent candidates for exploitation in the medical field to help in disease diagnosis and treatment. Furthermore, their ease of synthesis in a variety of sizes and shapes and their amenability towards surface functionalization creates the possibility for multi-functionality including imaging and targeted drug delivery (Arnaiz et al., 2012; Kircher et al., 2012; Lukianova-Hleb et al., 2014; Setua et al., 2014; Shilo et al., 2014).

Drug delivery applications based on GNP are forecast to have a 21% share of the USD 136 billion total market of nano-drug delivery applications by 2021 (Cientifica Ltd., 2012). The enormous range of potential applications of GNP and their increased future use could result in greater risk of environmental release and exposure at low concentrations, as is the case with many pharmaceutical products (Jobling and Owen, 2013; Miller et al., 2015; Ramirez et al., 2009; Roberts and Thomas, 2006). Proliferation and increased application of single use and disposable cheap medical diagnostic devices (Keel, 2013) could add to this environmental burden.

Uptake, biodistribution, accumulation and biomagnification of GNP by environmental organisms have been studied by many investigators (Ferry et al., 2009; Judy et al., 2011; Sabo-Attwood et al., 2012) and it has also been shown that GNP can be toxic to animals and plants (Geffroy et al., 2012; Kim et al., 2013; Perreault et al., 2012; Tsyusko et al., 2012) thus indicating that these supposedly biocompatible materials could present a significant hazard to plants and wildlife. GNP have been shown to have different modes of action for creating toxic effects dependent on their properties and the organism studied (Coradeghini et al., 2013; Cui et al., 2012) and show promise as an antibacterial agent.

In terms of environmental risks, studies on potential flows and concentrations of GNP in anthropogenic and ecological systems are non-existent. Overall there is limited environmental hazard data and no exposure data, making risk assessment highly problematic. Since there is potential for an exponential increase in use of GNP, it is timely to model their environmental flows and concentrations to help frame the risk analysis (Owen and Handy, 2007; Pastoor et al., 2014), as has been done also for other nanomaterials (Gottschalk et al., 2009b; Keller et al., 2013; Keller and Lazareva, 2014; Sun et al., 2014a).
In this study we have estimated the environmental concentrations of GNP from selected medical applications that are currently on the market or have potential to be introduced in the near future by developing a conceptual environmental exposure model and by combining this with the hazard data. We have used a probabilistic material flow analysis (Gottschalk et al., 2010a) (PMFA) to track the flow and fate of GNP during use and disposal. This approach attempts to address the large uncertainty and variability in the data by creating probability distributions for all input data (Gottschalk et al., 2010a; Gottschalk et al., 2010c). Where there is limited toxicity data and where experimental procedures and methodologies have large variability, use of probabilistic/stochastic methods to establish and quantify environmental risks can help to increase the robustness of the risk quotients. Thus, probabilistic species sensitivity distribution (pSSD) for quantifying ecotoxicological risks, by comparing the modeled PEC to the predicted no effect concentration (PNEC) based on toxicity data for the corresponding environmental compartment, forms the basis of our approach to derive risk levels for the ecosystem (Gottschalk and Nowack, 2013).

3.2 Methodology

3.2.1 General model layout

We have used the geographical regions of the UK and US (excluding dependent areas) as the units of analysis for our study. Similar to the approach proposed by the Guidelines for environmental risk assessment (ERA) of human pharmaceuticals (EMA, 2006; US FDA, 1998), (hereinafter referred to as ‘Guidelines’) where the consumption data of a drug per year is the key input factor, the model input in this study is based on population based estimates of use and consumption of the selected medical applications in a given year and disregards the manufacturing and processing facilities as a potential source. The model is a step-wise process where the selected application’s post usage life cycle has been mapped through the technical compartments of sewage treatment plants (STP), waste incineration plants (WIPs), landfills and the environmental compartments of soil, water and sediments. In addition to GNP based therapeutic agents which are in early stages of clinical trials, we have estimated GNP concentrations in medical devices approved by regulatory agencies or in late stages of product development. A deviation from the Guidelines is the use of excretion rates from pre-clinical studies as opposed to assuming 100% excretion. We have considered possible variable retention of GNP in sewage treatment plants (STP). PEC in various compartments and risk assessment results considering 100% excretion are provided in Appendix 3 as Alternate Scenarios. The data and values used to arrive at gold amounts per use are based on broad estimates derived from the available literature and the patient population and hence the study is a bottom up, high release scenario study. We have assumed GNP to be spherical in shape and have used mass concentrations to estimate consumption amounts.
Transfer coefficients (TC) have been used to model the behavior of GNP in various environmental and technical compartments included within the model (see Figure 3-1 for details). The data used in the model have high uncertainty, compounded by large variability and hence we built probability distributions for the majority of input data. Estimated consumption values of products which have the same life-cycle pathway have been summed by adding their individual probability distributions. Table A3-1 in the Appendix 3 illustrates the probability distributions for all data used in the study.

To estimate the volumes of the environmental compartments, we have used ECHA’s guidance on environmental exposure estimation for chemicals for a regional scale model (ECHA, 2012a). The mass and volumes along with the assumptions of the transition and final environmental compartments are detailed in Table A3-3. Seawater is not included in our model. The assumptions of a well-mixed, homogenous and stationery system have been applied in this study. The model tracks the GNP mass and not the total gold mass. Loss of the nano-property (e.g. by vaporization) therefore constitutes an elimination flow.

3.2.2 Methodological approach for input data

An extensive literature search was carried out to identify relevant peer reviewed scientific publications of GNP or gold colloids in the medical field, administration doses, distribution, excretion, environmental fate and behavior and environmental toxicity. Our aim was to identify GNP enabled medical applications which are approved, in clinical trials or show promise of translation from preclinical models. Reports published by UK and US Government Department and Agencies have been relied upon for estimating population, environment and technical compartment data. The transfer coefficients have been estimated by reviewing literature and/or soliciting expert viewpoints. Triangulations between various publications were performed and the approach of the best available data was adopted to arrive at the estimates used in this study. Details regarding consumption data and assumptions and references therein are included in ‘Estimation of GNP amount’ in the Appendix 3 and Table A3-2.

3.2.2.1 Transfer factors

Therapeutics based on GNP, after use, will end up either in solid waste, when the containers with the remnants of the therapeutic and associated procedural implements are disposed of as part of hazardous medical/clinical/infectious waste (HMCIW) and/or in the sewerage system when it is excreted from the body in urine or faeces. In vitro diagnostic devices used in hospitals and other healthcare settings will likely be part of HMCIW. Over-the-counter (OTC) single use medical devices are likely to end up in household waste. Therefore, wastewater (WW)/sewerage, HMCIW and household waste are defined as the key potential sources of entry of GNP from medical products to the environment.

**GNP flow into sewage treatment plants and surface water**
Not all houses are served by a centralised STP. The connection rates to STP are 96% (DEFRA, 2012) and 74% (USEPA, 2008) for the UK and the US respectively. Untreated sewer overflows, misconnections whereby grey water from households is connected to the storm water drainage systems, and exfiltration from sewerage pipes can result in untreated WW reaching surface waters, groundwater and subsurface soil directly. GNP from WW can also enter the environment due to failure of decentralized STP. Since the connection rate to STP for the UK is 96%, we have neglected the contribution of individual septic tanks, cess pools, etc. to the pollution load. However, for the US, nearly 25% of the total population is served by decentralised systems and the US EPA suggests a failure rate of 6% annually of these systems. (US EPA, 2004) Therefore, for the US we have considered failures of decentralised systems as a source of GNP reaching the environment. Additionally, discharge of untreated WW due to the dilapidated state of sewerage infrastructure (ASCE, 2013) and polluted outfalls from combined sewers during rains (USEPA, 2008) can add to the pollution load of surface waters.

**Behaviour of GNP in surface water**

Data was non-existent with regard to GNP fate in surface waters and we have therefore assumed that GNP entering the surface freshwater compartment were either 100% deposited to the sediment to derive sediment concentrations, or remained 100% in the water phase to derive freshwater concentrations, representing worst case conditions for both compartments.

**Behaviour of GNP in Sewage Treatment Plant**

Only one published study is available where an estimate of the removal efficiency of GNP in STP has been provided (Kaegi et al., 2013). This study found 99% removal rate of polymer coated GNP of sizes 10 nm and 100 nm in activated sludge batch experiments irrespective of coating, sizes and treatment. We have therefore used a removal efficiency of 99% for wastewater treatment. However, we acknowledge that removal efficiencies will differ based on the WW treatment systems used (Jarvie et al., 2009; Johnson et al., 2014).

**GNP flow into waste compartment**

Household waste is non-hazardous in nature and hence in addition to incineration, discarding to landfill is another preferred mode of treatment. OTC disposable *in vitro* diagnostic devices containing GNP will be part of the household and similar waste category as defined in the European Union Waste catalogue (Eurostat, 2010). In the UK, the proportion of landfilled and incinerated waste for the category of household and similar waste is 85% and 15% respectively for the year 2008 (EC, 2013b). For the US, the proportion of household waste sent to landfill and incinerated is 82% and 18% respectively of the total waste discarded after the recovered fraction (USEPA, 2013).

Wastes from healthcare settings are both hazardous and non-hazardous in type. Hazardous waste from healthcare facilities are generally sent for high temperature treatments like incineration and pyrolysis,
or alternatively non-burn low temperature treatments or chemical treatments to disinfect the infectious waste (Tudor et al., 2009). These alternative treatment technologies use wet or dry steam at temperatures lower than 200°C and use chemical disinfection methods. We have assumed that GNP will not be transformed/destroyed when waste is treated via non-burn alternative treatment technologies and will eventually end up in landfill.

**Behaviour of GNP during Waste Incineration**

No information is available about the fate of GNP in incinerators. Depending on the type of waste, type of incinerator and operating temperatures, configuration of the air pollution control devices (APCDs), and the particle size, it is likely that GNP will partition into bottom ash, APCD residues and stack emissions from APCDs.

Emissions from incinerators are under strict regulatory control; therefore it has been assumed that all municipal waste incinerators (MWI) and HMCIW incinerators (HMCIWI) will have associated APCDs. Both the UK and US use dry or semi–dry scrubbing systems with fabric filters or electrostatic precipitators (ESPs) as the main types of APCDs in the MWIs (DEFRA, 2013b; USEPA, 2010).

The temperatures in HMCIWI having secondary chambers can reach as high as 1’100°C, which is higher than the melting temperature of bulk gold. Melting temperature depression related to particle size, both for free GNP and substrate supported GNP, has been proven by many investigators (Buffat and Borel, 1976; Dick et al., 2002; Lee et al., 2009; Luo et al., 2012; Nanda et al., 2007). Furthermore, the presence of chlorine generated from Polyvinyl chloride in the incinerator can increase metal volatility and release into gas phase (Kakumazaki et al., 2014). The vapour pressure of gold at 1095°C is about 1 x 10⁻⁵ torr (1.33*10⁻³ Pa) (Honig and Kramer, 1969) and that means typically around one monolayer of gold will be vaporized in 0.1 seconds. Hence, GNP entering the HMCIW incinerators will either melt or vaporize. In both cases the nano-property of the gold is lost and the GNP is no longer distinguishable from the other gold forms. We have used both the case of 0% and 100% elimination of the gold mass. In the case of 0% elimination, we assume GNP to be distributed 81% in the bottom ash and 19% in the fly ash using the values found by Walser et al. (2012) for removal of Ceria nanoparticles in MWI. Of the 19% of GNP in the fly ash, we assume 50% of the GNP pass through the wet scrubbers and the remaining 50% through the fabric filter for both the UK and US. This assumption was extrapolated from the type of APCD installed in the HMCIW incinerators in the US (RTI International, 2012) since no data was available with regard to APCDs for HMCIW incinerators in the UK.

The operating temperatures in MWIs are around 850°C, so we assume that 81% of GNP mass will be removed in the bottom ash and 19% in the fly ash of which 99.99% will be removed by the ESP and fabric filter as APCD residue (Booker et al., 2014). These residues are treated as hazardous waste and
are finally disposed to secured landfills or abandoned underground mines (Amutha Rani et al., 2008). Bottom ash from municipal waste combustors can be used in the construction sector (Ørnebjerg et al., 2006). However, due to non-uniformity in available data for the selected regions and to simplify the model, we have neglected bottom ash recycling rate and have presumed that 100% of the bottom ash from both types of incinerators will be landfilled.

We have not included the leachate from landfill and subsequent contamination of the ground water compartment. The technical compartment of cremation has been considered in the model boundary with the assumption that some percentage of GNP might remain in the human body post treatment when GNP has been administered as a last line treatment. The temperature in crematoria is not high enough to vaporize or melt GNP (Mari and Domingo, 2010) and hence we assume that untransformed GNP will form part of the ash.

Therefore, human body, landfills, sediments, subsurface soils and burial grounds have been considered as the final sink of the product life cycle post usage.

3.2.3 Ecological risk assessment

To derive species sensitivity distributions for environmental effects of GNP, an extensive search of the ecotoxicological literature was conducted. Fourteen relevant studies were found published between 2008 and Feb 2014. Twenty six data points across five taxonomically different environmental organisms - bacteria, fish, algae, crustacean and ciliates - were included in the assessment. The endpoints selected were mortality and malformations, growth inhibition and reproductive performance. If in a study only one concentration has been tested on an organism and it had shown no effect for the selected toxicity endpoint, we have used that concentration as no-observed-effect concentration (NOEC), acknowledging that this could in reality be higher. When a range of concentrations were tested (Asharani et al., 2011; Bar-Ilan et al., 2009), the highest concentration at which no statistically significant adverse effect was observed was used as the highest-observed-no-effect-concentration (HONEC). The raw data were converted to species sensitive values below which long-term negative impacts on the species were considered to be excluded using two assessment factors (AF) based on the REACH guidelines (ECHA, 2008). The first AF was used to convert acute toxicity to chronic toxicity (AF time = 1, in the case of chronic and long-term test; AF time = 10, in the case of acute and short-term test). All but two data points represented acute or short-term exposures. The second AF was used to convert the various endpoints to NOEC values (AF no effect = 1 for NOEC, AF no-effect = 2, if $L(E)C_{10} \leq L(E)Cx < L(E)C_{50}$ and AF =10, if $L(E)_{50} \leq L(E)Cx \leq L(E)C_{100}$). In studies where effect concentrations were reported in terms of molar concentrations, we have converted the values to mass concentration (μg/l), because regulatory limits are expressed as such. The studies selected and the associated end points arranged species wise are
detailed in Appendix 3 Table A3-6 and Table A3-7. Probabilistic species sensitivity distributions were constructed for soil and freshwater as explained in reference (Gottschalk and Nowack, 2013).
3.3 Results and Discussion

3.3.1 Estimation of nano gold consumption from prospective medical applications

Table 3-1 details the estimated quantity of GNP from nano-enabled medical applications. As the table depicts, very small amounts – in the range of milligram to less than a few kilograms – are estimated to originate from in vitro medical devices or devices used for detection of specific disease biomarkers. Larger quantities of GNP are estimated to be released from applications used for treating or managing a particular disease, for example, for the treatment of gum infections, cancer and diabetes. The amount of GNP per patient was estimated to range from 0.05 mg to 5’000 mg for the whole treatment cycle, the higher values corresponding to the treatment modality of photothermal ablation of cancer using gold nanoshells. A study (Booker et al., 2014) conducted in Northwest England estimated the consumption of anticancer drugs from hospital records and showed total consumption of all the identified anticancer drugs to be around 350 kg. Thus, the annual GNP consumption amount in the range <1 kg to 250 kg for the UK for treatment of breast, lung, pancreatic and bowel cancer, which have high incidence rates, could be reached in the near future even though we have used the high release scenario of 100% patient access and treatment by the same GNP based therapeutic.

The GNP consumption data could be estimated due to the strict regulatory governance framework associated with approval of pharmaceutical products for human use and also because of the availability of disease incidence and prevalence data for widespread diseases such as cancer, diabetes. In contrast, estimating GNP quantities from in vitro diagnostic devices was challenging due to the dependence on the patenting literature, wherein specific details are obscured and also because of the less stringent regulatory pathway for in vitro medical devices. Hence, the estimated data relied on vast number of assumptions and data was extrapolated from various literature sources.
Table 3-1: Prospective amount (per annum) of Gold particles in selected medical applications (high release scenario); data rounded off to 2 significant digits for values below 1 or to the nearest integer or ten. Unit: gram. Refer to Appendix 3 for details related to assumptions and references.

<table>
<thead>
<tr>
<th>Application</th>
<th>Consumption</th>
<th>Waste compartment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab based lateral flow assay to detect the presence of Methicillin Resistant and Methicillin Sensitive Staphylococcus aureus in blood</td>
<td>0.34</td>
<td>6</td>
</tr>
<tr>
<td>In vitro lab based diagnostic test kit for detection and genotyping warfarin metabolism</td>
<td>0.36</td>
<td>3</td>
</tr>
<tr>
<td>In vitro lab based diagnostic test kit for detection of single nucleotide polymorphism to detect risk from venous thrombosis</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>OTC pregnancy and ovulation test kits to detect hormones in urine</td>
<td>3 to 100</td>
<td>20 to 460</td>
</tr>
<tr>
<td>Lab based in vitro rapid test kits for qualitative detection of antibodies to HIV-1 and HIV-2 in human serum, plasma and blood</td>
<td>2 to 80</td>
<td>20 to 830</td>
</tr>
<tr>
<td>Home based in vitro HIV test kits</td>
<td>20</td>
<td>90</td>
</tr>
<tr>
<td>Lab based in vitro tests for detection of CD4 cells and viral loads for HIV patients</td>
<td>60</td>
<td>540</td>
</tr>
<tr>
<td>Lab based diagnostic test kits for infectious diseases</td>
<td>70</td>
<td>350</td>
</tr>
<tr>
<td>Removal of Staphylococcus aureus from the nasal passage of patients to reduce risks of nosocomial infections</td>
<td>30 to 53300</td>
<td>110 to 164640</td>
</tr>
<tr>
<td>Treatment of periodontitis</td>
<td>270 to 106560</td>
<td>940 to 365160</td>
</tr>
<tr>
<td>Sensors for diagnosing diseases from breath samples</td>
<td>0.01 to 1590</td>
<td>0.03 to 4620</td>
</tr>
<tr>
<td>Treatment for solid tumors (colorectal, pancreas, breast)</td>
<td>70 - (480) -1100</td>
<td>310- (2020) – 4600</td>
</tr>
<tr>
<td>Last line treatment for patients with colorectal, pancreatic and breast cancer</td>
<td>420</td>
<td>1500</td>
</tr>
<tr>
<td>Treatment for patients diagnosed with head &amp; neck and lung cancer</td>
<td>140290 to 233820</td>
<td>744750 to 1241260</td>
</tr>
<tr>
<td>Last line treatment for patients with head &amp; neck and lung cancer</td>
<td>104710 to 174520</td>
<td>468250 to 780410</td>
</tr>
<tr>
<td>Transbuccal insulin delivery platforms</td>
<td>128250</td>
<td>841620</td>
</tr>
</tbody>
</table>

3.3.2 Mass flows of GNP

The annual mean prospective GNP use estimates for the UK and US are 540 kg and 2’700 kg respectively. The yearly disease incidence rates of HIV AIDS and cancer were found to be relatively stable over the last few years (Cancer Reasearch UK; CDC, 2011; Prejean et al., 2011; Siegel et al., 2014; Yin Z et al., 2014), so the data estimated in this study (which uses incidence and prevalence data compiled in the recent national disease registries and are for the years between 2007-2014) can be assumed to remain constant for the next 5 years. By combining the estimated maximal possible consumption of GNP with the technical and environmental transfer coefficients, we were able to obtain GNP flows from the end user to technical compartments and then further to receiving
environmental compartments. Currently this represents an unrealistically high use of GNP and therefore our PEC values also represent highest possible concentrations. If GNP-based applications for the healthcare sector are realised over the coming years, it may result in very high market penetration. For example, seven in vitro diagnostics, based on GNP for determining pregnancy and ovulation, were approved by the USFDA between 2009 and 2012.

Figure 3-1 shows that the most prominent GNP flows arise from consumption, leading to accumulation in the human body for both the UK and US. Based on pre-clinical data, we assumed 35% (Goel et al., 2009) and 85% (Gad et al., 2012) accumulation of GNP in the body for the two cancer therapeutics used as model input data. For other GNP based applications we assumed 100% excretion (Longmire et al., 2008; Zhang et al., 2012). Of the total yearly consumption of GNP, around 160 kg and 850 kg of GNP respectively for the UK and the US would remain in the body of treated patients.
Dynamic Probabilistic Modelling of Environmental Emissions and Concentrations of Engineered Nanomaterials

Figure 3-1: Modelled annual prospective mass flows of GNP in the UK and US in kg. Technical and environmental compartments are expressed as boxes and flows are expressed as arrows. The flow volumes used are mean values from the probability distribution of each flow. Each box (compartment) is given a code. Mean values, mode, quantile 15 (Q$_{15}$) and Quantile 85(Q$_{85}$) values are also given. These are indicated with compartment codes on the right side of the flowchart. The flow volumes are visualised by the thickness of the arrows. The compartments which we assumed to be the final sink are indicated by a black square box (body of living patients, crematorium, burial, landfill, soil, sediments and subsurface soils). Complete GNP suspension in surface water and complete GNP sedimentation from surface water to sediment are assumed in the calculation of mass flow (indicated by dashed arrow) and concentrations.

The second largest flow of GNP for both the UK and US is via sewage to STP. About 230 kg and 1’300 kg of GNP from the total consumption for the UK and US, respectively, end up in sewage. In the UK, small amounts of GNP are directly transported to surface water due to misconnections and overflows. No data about misconnection for the US could be found, hence we have not modelled this value, but it is a potentially important source of uncertainty. In addition to misconnections, leakages from sewer pipes result in GNP mass transfer to subsurface soils. GNP reaching the STP might additionally not flow into the STP processes due to overflow discharges during rainy seasons. Compared to the US, overflows for the UK are more significant; direct discharge to surface waters accounts for nearly one fifth of the total GNP initially reaching STP; whereas for the US only 0.04% of the total GNP by-passes the STP and reaches the surface waters.

Significant removal of GNP into the sludge, for both regions, results in significant quantities of GNP entering STP, ending up in biosolids, which is partially further distributed onto agricultural soils as a
fertilizer. Total GNP inputs in soil were modeled to be around 150 kg/y and 730 kg/y for the UK and US respectively. For the UK, around 32 kg of GNP present in the sludge reach the MWI and a negligible quantity pass to the landfill i.e. the majority is applied as sludge to land. For the US, of the 990 kg of GNP present in sludge from centralized treatment works, around 280 kg and 150 kg were estimated to reach the landfill and MWI compartments respectively. GNP from decentralized systems such as septic tanks, cesspools, etc. can be released to land and/or surface water, or underground water, based on the implementation status of relevant regulations. We assumed all GNP passing through the decentralized systems end up in sludge treated soils.

The third major flow of GNP is to the hazardous waste compartment for both regions. For the UK, 60% of the 27 kg of hazardous waste was estimated to reach landfill, with the remainder in HMCWIWI, whereas for the US, 90% of the 84 kg of GNP in the hazardous waste end up in landfills. These values indicate that clinical waste treatment via incineration is not a prevalent practice for both regions, and hence there is a possibility of GNP becoming accumulated in landfills in the future. However, these values need to be treated with caution because of the scarcity of national scale data with regard to waste management from healthcare facilities. Comprehensive and updated reports for medical waste for the US were not available and we depended on extrapolations from data reported in non-peer reviewed literature sources (details in Appendix 3). For the UK, only one peer reviewed paper (Tudor et al., 2009) containing data for the year 2007 was available. Furthermore, the difference in the healthcare and biological waste (H&B) generation data in the EU Stat database, updated on Dec 6, 2013 (EC, 2013b) and DEFRA (2013a) report for the years 2004, 2006, 2008 indicate the need for coherent definitions and reporting. H&B generation data in the EU Stat database for the year 2010 was approximately 3 times more than the waste generated in 2008. Since there was no publication from DEFRA for the year 2010, the data reported in the EU stat database could not be verified/triangulated and the reason for the increase was undecipherable. This indicates the poor state of environmental reporting, monitoring and updating between national scale and regional scale databases and between organizations in the EU.

### 3.3.3 GNP concentrations in technical and environmental compartments

Table 3-2 shows the predicted GNP concentrations in STP effluent, surface water, STP sludge, and yearly concentration in sediments and biosolid-treated soils for the UK and US. The values presented are mean values, mode values (the most probable values) and their 15th and 85th percentiles ($Q_{15}$ and $Q_{85}$) from each distribution. When comparing the two regions, predicted GNP concentrations were higher in the UK in nearly all the compartments when compared to those in the US, except for STP sludge which shows similar mean concentrations. The PEC in surface water in the US is the lowest among all the modeled technical and environmental compartments for UK and US.
Table 3-2: Predicted GNP concentrations in technical and environmental compartments; mean, mode (most probable values), quantile 15 (Q_{15}) and quantile 85 (Q_{85}) are given. Black values designate concentrations; grey values designate yearly increases in concentrations. GNP concentrations in surface water and sediments represent no and complete sedimentation respectively. The results are expressed up to three significant digits.

<table>
<thead>
<tr>
<th></th>
<th>UK</th>
<th></th>
<th></th>
<th>US</th>
<th></th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Mode</td>
<td>Q_{15}</td>
<td>Q_{85}</td>
<td>Mean</td>
<td>Mode</td>
</tr>
<tr>
<td>STP Effluent</td>
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<td>359</td>
<td>217</td>
<td>665</td>
<td>135</td>
<td>128</td>
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<tr>
<td>Surface water</td>
<td>468</td>
<td>268</td>
<td>214</td>
<td>725</td>
<td>4.74</td>
<td>4.02</td>
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<tr>
<td>STP sludge</td>
<td>124</td>
<td>126</td>
<td>94.3</td>
<td>154</td>
<td>145</td>
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<tr>
<td>Sludge treated soil</td>
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<td>301</td>
<td>227</td>
<td>368</td>
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<td>Sediments</td>
<td>289</td>
<td>165</td>
<td>132</td>
<td>447</td>
<td>5.27</td>
<td>4.47</td>
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<td>Hazardous waste</td>
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<td>78.2</td>
<td>23.4</td>
<td>130</td>
<td>65.0</td>
<td>68.8</td>
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<td></td>
<td></td>
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<tr>
<td>Fly ash</td>
<td>266</td>
<td>30.0</td>
<td>36.4</td>
<td>534</td>
<td>263</td>
<td>32.2</td>
</tr>
<tr>
<td>Bottom ash</td>
<td>203</td>
<td>24.5</td>
<td>27.4</td>
<td>407</td>
<td>201</td>
<td>25.8</td>
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<tr>
<td>Municipal WIP</td>
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</tr>
<tr>
<td>Fly ash</td>
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<td>69.7</td>
<td>52.8</td>
<td>91.6</td>
<td>38.9</td>
<td>38.0</td>
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<tr>
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<td>51.7</td>
<td>38.8</td>
<td>71.5</td>
<td>29.7</td>
<td>27.5</td>
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</tbody>
</table>

In the UK, the predicted GNP concentration in surface water is higher than in sewage effluent. This is due to the fact that a significant amount of GNP is estimated to be released directly to surface waters via overflows. In contrast, the lower GNP concentration in STP effluent and the lower PEC in surface water for the US can be explained by the much larger STP effluent volume produced per capita. According to USEPA, 625 liters of STP effluent is produced per capita per day (USEPA, 2000) whereas for the UK, it is 150-180 liters per capita per day (British Water, 2009, 2013) (see Appendix 3 Table A3-3). The mean modeled GNP concentration in surface waters for both regions is in the range of 5 to 470 pg/l which is similar to the background gold concentration reported in freshwaters (reviewed in (McHugh, 1988)). PEC in surface water of Germany for iron oxide nanoparticles (IONP) based MRI contrast agents were estimated to be 400 and 3’140 pg/l for the year 2015 for two different scenarios used by author (Filser et al., 2013). Measured environmental concentrations in surface waters of various anticancer drugs in use are in the range 500 to 41’000 pg/l (Booker et al., 2014), indicating that the results of our model are at a similar level.

Predicted mean concentrations of GNP in STP sludge are 124 μg/kg and 145 μg/kg for the UK and US, respectively. The PEC in sludge is considerably less than the measured total gold concentration of 790 μg/kg reported in a Swedish study (Eriksson, 2001). The second highest concentration of GNP is in biosolid - treated soils, although yearly concentrations are only in ng/kg levels. However, continuous application of biosolids on agricultural land might lead to GNP accumulation in soil over years. The lower predicted concentration of GNP in US agricultural soils is because of the larger area of the country and hence larger mass of biosolid treated agricultural soils in comparison to the UK.
3.3.4 Risk assessment with probabilistic species sensitivity distribution (pSSD)

Aquatic species show a wide range of responses to GNP, with no observed effect concentrations (NOECs) ranging from 0.12 μg/l up to 26'800 μg/l; a spread of five orders of magnitude, although most values are in the 1’000 μg/l range. The most sensitive species was the single cell green algae, *Chlamydomonas reinhardtii*, (an acute toxicity study done using 2 nm GNP capped with D-manno-pyranoside terminated PAMAM (polyamidoamine) G0 generation dendrimer) (Perreault et al., 2012). PAMAM dendrimers of different cores and generations (G2 to G6) have been shown to exert toxic effects in fish, freshwater crustaceans and algae with L(E)C₅₀ values in the range 0.13 to 194 μM (reviewed in Suarez et al (2011)). Figure 3-2 shows the cumulative probabilistic species sensitivity distribution (pSSD) for GNP in water. The results lacked sufficient resolution to decipher which taxa are most affected, though it seems fish (*Danio rerio*) were the least sensitive species when exposed to GNP in an aquatic environment, and what particle properties are related to toxicity. Publications with properly designed experiments (ICMM, 2007; Wheeler et al., 2002) or environmentally relevant exposure concentrations for studying toxic effects of GNP on environmental organisms are sparse. Barring a few, the studies selected do not report the L(E)Cₓ (lethal / toxic effect shown by x% of the organisms at a particular concentration) values, or the statistical method used to arrive at the reported data, do not mention acceptable control performance, and lack characterization of the NPs throughout the exposure duration. These results indicate the high variability of input model data, reflecting the varied toxic potential of GNP of different sizes and coating to different species. Overall there are inadequate data with regard to environmental toxic effects of GNP researched for biomedical application. Therefore, reliable toxicity studies with specific GNP used for medical applications are needed for improved environmental risk assessment to influence policy makers for aiding regulatory decision making and responsible innovation (Stilgoe et al., 2013).
Figure 3-2: Probabilistic species sensitivity distribution (pSSD) for GNMs in fresh water and soils (red lines) compared with the raw sensitivity data used (blue diamond). The red diamonds are the geometric means of the raw sensitivity data if there are more than one data available. The number of blue diamonds for each species corresponds to the number of raw sensitivity data available and used. The raw sensitivity data indicate the no observed effect concentrations (NOEC).

Figure 3-3 shows the probability distributions of the PEC and the pSSD for GNP in the aquatic and terrestrial environment for both the UK and US. The PEC and pSSD for surface water and soils are compared and risks may arise where the PEC and pSSD overlap. It is clear that there is no overlap between the PEC and pSSD in both environmental compartments considered for the UK and US. The narrowness of the PEC probability density curves is due to the fact that few of the GNP application categories dominate the total consumption resulting in a narrow distribution of the total input into the system.
Probabilistic Modelling of Prospective Environmental Concentrations of Gold Nanoparticles

Figure 3: Probabilistic species sensitivity distribution (pSSD) reflecting the no observed effect concentration data compared to the probability distributions of predicted environmental concentrations (PEC) of GNP in surface water and sludge treated soils in the UK and the US. Environmental risk is observed where the PEC overlaps the pSSD.

Many human pharmaceuticals occur in the aquatic environment in ng/l concentrations (Ashton et al., 2004; Roberts and Thomas, 2006; Thomas and Hilton, 2004) and studies have shown accumulation of these chemicals in aquatic organisms (Liu et al., 2015a; Liu et al., 2015b; Miller et al., 2015) and their adverse effects (Jobling and Owen, 2013; Sanchez et al., 2011). The very defining property of nanoparticles – size and surface area – coupled with their ability to interact at subcellular levels to generate subtle biochemical changes (Shvedova et al., 2010), their novel properties and gaps in knowledge regarding relationship between chronic and acute toxicity, calls for the inclusion of sub-lethal toxicity endpoints for regulatory decision making. In this study, we included selected sub-lethal endpoints in the pSSD, which suggest that there may be no risk to the organisms in the aquatic
environment. The results are provided in the SI as Alternate Scenarios. Moreover, transformation and fate of nanoparticles (Lowry et al., 2012) in the environment calls for the need for long term or chronic toxicity data.

Both exposure and hazard data are limited and uncertain and the model attempts to deal with this uncertainty. However, ideally, ecosystem risk assessment should be based on robust characterization of the toxicant and its transformation products in the environment; in the case of nanomaterials such exhaustive risk assessments are not available and might be logistically impossible or at least extremely challenging (Owen and Handy, 2007). The complex challenge can be addressed in a number of ways. For instances, expert judgment and multi-criteria decision analysis (Linkov et al., 2007; Owen et al., 2009), species sensitivity distributions (Garner et al., 2015) probabilistic species sensitivity distributions with available hazard data (Gottschalk and Nowack, 2013) and probabilistic mass flow models (Gottschalk et al., 2010a). This study uses the stochastic mass balance partitioning approach to predict concentrations in the environment to arrive at a crude estimate of risk characterisation. The results from the model can be used to provide a baseline for realistic and environmentally relevant exposure/toxicology studies and can help in iterative problem formulation and solution, as more concrete data becomes available. The modelling performed here suggest that freshwater (and hence sediments) and biosolids treated soils would likely receive highest loads of GNP for the UK. No risk from GNP to aquatic organisms and soil organisms is expected in the near future at a regional scale, although variations will exist temporally and spatially. However, hazard assessment data for soil organisms is severely limited and so uncertainty is particularly high. Empirical fate and transformation data of GNP for incinerators as well as freshwater systems is non-existent and research is needed for GNP transformation in STP with different treatment processes using GNP with surface coatings used in medical applications.

3.4 Acknowledgement

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3.5 Supporting information (Appendix 3)

Details regarding estimation of annual gold nanoparticles consumption (Table A3-2) from selected medical applications, the probability distribution functions of the input parameters used to create the
probabilistic mass flow model (Table A3-1), the data used to develop the pSSD (Table A3-6 and Table A3-7) summary of volumes or mass of environment and technical compartment (Table A3-3) and PEC in various compartments and risk assessment results considering 100% excretion and using lethal and sublethal endpoints are provided as Alternate Scenarios (Figure A3-1, Figure A3-2, Figure A3-3 and Figure A3-4) in the supporting information.
3.6 References


(2) Thomson Reuters’ Web of Science Title search = (health* or medic* or therap* or dis eas* or cancer* or HIV or AID*) AND title search = (nano* or ultra small) AND (gold or Au) - Time period: 2004-2014 Search conducted on 28 December 2014


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4 PROBABILISTIC MODELLING OF ENGINEERED NANOMATERIAL EMISSIONS TO THE ENVIRONMENT: A SPATIO-TEMPORAL APPROACH

Tian Yin Sun,‡ab Gulliver Conroy, ‡cd Erica Donner,⁵ Konrad Hungerbühler,⁶ Enzo Lombi⁵ and Bernd Nowack⁶

‡Empa – Swiss Federal Laboratories for Materials Science and Technology, Technology and Society Laboratory, Lerchenfeldstrasse 5, CH-9014 St. Gallen, Switzerland.
⁵Institute for Chemical and Bioengineering, ETH Zürich, CH-8093 Zürich, Switzerland
⁶CERAR, University of South Australia, Building X, University Boulevard, Mawson Lakes, South Australia 5095, Australia
⁷CRC CARE, PO Box 486, Salisbury, South Australia 5106, Australia
DOI: 10.1039/c5en00004a
‡2 Joint first authorship.

‡ T.Y. Sun guided the collection of data and reviewed and compiled the data, built the model and produced all results. He also wrote the text. G. Conroy collected all the input data for modelling, and involved in writing the text.
Abstract

For the environmental risk assessment of engineered nanomaterials (ENM) knowledge about environmental concentrations is crucial. Soils and sediments are considered sinks for ENM and thus a better understanding of the spatial and temporal variability of concentrations is needed. In this work we use South Australia as a case study for a region with significant biosolids and treated wastewater application on soils, representing a system with almost “closed loops”. The probabilistic material flow modelling approach was extended to include a temporal modelling of ENM production and biosolids handling and transfer onto soils, focusing on nano-TiO₂, nano-ZnO, nano-Ag, Carbon Nanotubes (CNT) and fullerenes. The results thus not only incorporate the uncertainty on ENM flows but also the spatial and temporal variability of ENM concentrations between 2005 and 2012. The ENM concentrations in different waste amended soils vary by more than 2 orders of magnitude due to different biosolids and wastewater application rates. Because of the almost complete transformation of nano-ZnO and nano-Ag during wastewater treatment, we also modelled the total flows of Zn and Ag derived from the nanoparticles and compared their modelled concentrations to measured total Ag and Zn concentration in biosolids and soils in South Australia. The modelled Ag concentration derived from nano-Ag is 50-times smaller than measured Ag in soils and 10-times in biosolids. For Zn the respective values are 250 and 7. If in the future the accumulation continues with the same rate as in 2012 it would take about 170 years until a regulatory threshold value of 500 ug Ag per kg of soil would be reached. For Zn, it will take 930 years. The results from this modelling highlight that regional and site-specific conditions need to be considered when assessing the environmental risks of nanomaterials.
4.1 Introduction

To date, quantification of engineered nanomaterials (ENM) at the trace concentrations relevant in environmental samples is, in most cases, not feasible (Kim et al., 2012; von der Kammer et al., 2012). A modelling approach is thus required in order to fill the existing data gaps and gain information about current environmental emissions and concentrations of ENM, and subsequent environmental exposures (Gottschalk et al., 2013c). Müller and Nowack (Mueller and Nowack, 2008) used a material flow model and took all known commercial products containing ENM into account to predict their environmental release. In their study, uncertainty and variability of data were addressed by including a realistic emissions scenario, as well as a worst case (i.e. high emissions) scenario. Gottschalk et al. went further and developed a stochastic material flow model by applying a Monte Carlo approach (Gottschalk et al., 2010b; Gottschalk et al., 2009a). This stochastic method enabled a full range of possible values to be inserted as model parameters and generated results in the form of probability distributions (Gottschalk et al., 2009a). Both studies were necessarily based on the limited information available at that time about the behavior of ENM in technical and natural systems. Taking advantage of the considerably greater amount of published information now available on production, fate and behavior of ENM, Sun et al. recently carried out a comprehensive and up-to-date prediction of ENM flows to the environment by extending the stochastic method (Sun et al., 2014c). At almost the same time, Keller et al. (2013) for the first time revealed a mass-flow analysis of different ENM at a global level.

All of the studies mentioned above were limited in their assessment of ENM accumulation in environmental compartments, e.g. sediments and soils, because they were restricted to an incremental yearly input of ENM into the system. Only Gottschalk et al. (2009a) made a simple projection of the increasing concentrations of ENM in sediments and biosolids-treated soils, forecasting the period from 2001 to 2012 for the USA, based on some ENM market projections. These projections indicated that a range of responses are to be expected for different ENM with different sources and properties. The possible accumulation of ENM in soils and sediments is now recognized as a very important issue, as the development and application of nanotechnology has grown exponentially in recent years (LUX RESEARCH INC, 2004; Roco, 2011) and previous modelling studies have indicated that these compartments can act as ENM sinks.

Aside from the limited temporal aspects, these studies (Gottschalk et al., 2009a; Keller et al., 2013; Keller and Lazareva, 2013; Markus et al., 2013; Mueller and Nowack, 2008; Sun et al., 2014c) also generally assumed well-mixed and homogenous environmental compartments for a given country or region (e.g. the European Union). Some local information was reported by Gottschalk et al. (2011b) who modelled spatially resolved ENM concentrations in 543 river sections at base flow, and in 21 locations based on 20-year flow data. The ENM input was allocated to the river sections by population-adjusted inflows from wastewater treatment plants (WWTP). Markus et al. (2013) combined the potential release of nano-forms of zinc (Zn), titanium (Ti), and silver (Ag) from nano-
enhanced products per person and then predicted, by using this bottom-up approach, the contribution of these nanoparticles to the annual load in the Dutch reaches of the Rhine and Meuse rivers. A very similar principle was used by Dumont et al. (2015). By combining the information of household connectivity to sewerage, sewage treatment efficiency, the spatial distribution of sewage treatment plants, and their associated populations they calculated the monthly nano-Ag and nano-ZnO load from households to individual river sections. They used these loadings to model temporally varying nanoparticle concentrations in rivers, lakes and wetlands by considering dilution, downstream transport, water evaporation, water abstraction, and nano-particle sedimentation. Keller et al. (2013) provided a global assessment of ENM emissions to the environment for ten ENM by combining ENM market information and material flow modelling. In a follow-up study, Keller et al. (2013) down-scaled the global values to the regional and local level according to the population in each region and their developmental status based on the United Nations inequality-adjusted human development index (IHDI) for the major countries in each region. However, the production and use input data of the whole study relied solely on one single market report, and it is thus not transparent as to how the information was compiled. As a result, it is difficult to access the amount of uncertainty in the dataset itself, which therefore leads to an unknown uncertainty in all the results. An accurate prediction of localized environmental concentrations, especially ENM concentrations in soils, has therefore not yet been achieved.

As noted above, it is clear that, in addition to landfills as technical compartments, soils and sediments are the main sinks for ENM following the use and release of products containing them. For soils, the main transfer occurs due to the application of biosolids onto certain agricultural soils and, in this situation, time-resolved modelling is the key to an accurate prediction of current concentrations. As only a small fraction of soils receive biosolids, and often in varying amounts, the inclusion of spatial aspects is also required to support the realistic prediction of soil concentrations. Recently Yang et al. (2014) showed the presence of nano-TiO$_2$ particles in biosolids-treated soils, thereby adding experimental evidence to the predicted transfer and accumulation of ENM in soils.

The goal of this study was to develop a mass flow model combining spatial and temporal aspects. The model is able to calculate the ENM emissions and concentrations for five materials (nano-TiO$_2$, nano-ZnO, nano-Ag, CNT, and fullerenes) in a highly regionalized context, and is able to account for the accumulation of ENM in environmental compartments that represents sinks, e.g. soils and sediments. South Australia has been selected as a suitable case study for the elaboration of this model as it is a region where treated waste products such as biosolids and wastewater are very actively recycled, and for which detailed spatial and temporal data documenting the application of biosolids and treated wastewater to regional farms, gardens and pastures is available.
4.2 Methods

4.2.1 General system boundary

The mass-flow modelling approach used in this study follows the life-cycle principle. Initially, it tracks ENM distribution from their production to allocation in consumer products, and from the ‘use’ phase of products containing ENM to their ‘end of life’ disposal/recycling stage. Then, the ENM distribution within and between disposal processes (technical compartments) and from disposal to the environment is considered. In this study, nano-TiO₂, nano-ZnO, nano-Ag, CNT and fullerenes were modelled. These ENM were selected on the basis of their significant production and application quantities, or due to the relatively abundant information available with respect to their production, applications and environmental fate and behaviour.

The geographical focus of this study was the state of South Australia (SA). The life-cycle tracking of ENM in SA started from the point of consumption (i.e. use phase), rather than production. This is a reasonable starting point for SA based on the assumption that in a small region (in terms of population size) like SA, there is minimal ENM production and manufacturing of ENM enabled products. During and after the use phase of ENM enabled products, ENM will however be released into technical and environmental compartments, and these transfers and subsequent accumulations were the focus of the model. The technical compartments included in this study were landfill, wastewater treatment plants (WWTP), community wastewater management systems (CWMS, which handle the primary treated effluent derived from septic tanks), recycling, and export (i.e. outside of SA). The environmental compartments considered were the atmosphere, the two ocean gulfs within South Australia (St. Vincent and Spencer gulfs), and the biosolids and sewage effluent treated soils in the region. ENM flows to air and atmospheric deposition were calculated but a comprehensive calculation of ENM concentration in air was excluded from this modelling study. A preliminary calculation of ENM concentration in air suggested very low values, which are negligible to the purpose of this study (Sun et al., 2014c). ENM concentrations in ocean water were not calculated because complete sedimentation was assumed; only ENM flows (emissions) to ocean were calculated. The soil compartment in this study is a combination of biosolids treated soils (well-defined regional agricultural soils in this context), sewage effluent treated soils, and other soils (i.e. soils not receiving biosolids or sewage effluent and receiving ENM only from atmospheric deposition and direct release during the use of products containing ENM). Inland surface water was excluded from our study because unlike in Europe or the U.S.A, treated wastewater in SA is either recycled for soil irrigation or discharged into the ocean, as over 90% of the population live in coastal urban centres (Australian Bureau of Statistics). Although ENM leaching from landfill, soils and resuspension from sediments is possible, in our study due to inadequately available knowledge they are assumed as final sinks, no output flows are modelled from these compartments.
Chemical transformations of nano-ZnO and nano-Ag during the wastewater treatment processes were also taken into account (Kaegi et al., 2011; Lombi et al., 2012). Unlike treating all the transformed nano-ZnO and nano-Ag as eliminated as done in our previous study (Sun et al., 2014c), here we also tracked the flows of nano-ZnO and nano-Ag that are transformed into non-nano forms. We call them “nano-ZnO derived Zn” and “nano-Ag derived Ag” respectively for the transformed forms of nano-ZnO and nano-Ag. It is noteworthy to point out that the “nano-Ag derived Ag” includes both the transformed forms of nano-Ag and the remaining nano-Ag.

### 4.2.2 Probabilistic material flow modelling

The model consists of three modules: module 1. anthroposphere; module 2. ENM transfer to soils; and module 3. ENM transfer to oceans. Module 1 calculates the yearly ENM flows in treated wastewater and to biosolids for the period considered (2005-2012). This module was based on the previous mass flow models (Gottschalk et al., 2010b; Gottschalk et al., 2009a; Mueller and Nowack, 2008; Sun et al., 2014c) but with adaptions to SA conditions. The first part of module 2 calculates the annual distribution and the accumulated load of ENM transferred with biosolids into different government-defined regional areas (see Appendix 4) where soils were amended with biosolids between 2005 and 2012. The second part of module 2 calculates the annual distribution of ENM and accumulated ENM load in soils irrigated with treated sewage effluent over this period. Module 3 calculates the annual and accumulated ENM load into ocean gulf waters and ocean sediments.

Only a portion of the biosolids produced in SA was transported to soils for application in the year produced; the rest was stockpiled and gradually transported and applied onto soils over the following years, together with some proportion of biosolids produced in previous years. The annual mass of ENM flowing into the soil in each regional area is thus the sum of each year’s ENM input from biosolids that are sourced from different production years. One aim of this study was to calculate the total accumulated ENM load into the regional soils over the period from 2005 to 2012. This was done by summing up the yearly ENM loads from 2005 to 2012, as Figure 4-1 shows. The ENM concentrations in these regional soils were then calculated by dividing the accumulated ENM load by the corresponding receiving soil volume. This approach is well defined by REACH (2007), but also adapted according to the Australian guidelines by using a different soil depth proposed (SA EPA, 2009). 0.10 m (CSIRO, 2007) and 0.03 m (ECB, 2003a) of depth for agricultural soils and sediments are used respectively for the calculation of compartment volumes.

The approach used to calculate ENM loads to soils treated by sewage effluent differs from that used for biosolids treated soils. Unlike the temporal variation in biosolids application onto soils, all the treated wastewater (sewage effluent) produced in one year is used in the same year. Hence, in this case, the ENM load to soils is directly related to the ENM concentration of that year’s sewage effluent. As no data was available to define the area (therefore the volume) of these soils treated by sewage
effluent, and only application rates of recycled water onto these soils were available (Laurenson et al., 2010; South Australian Wine Industry Incorporated, 2013), we calculated the ENM load to one unit area of these soils by combining the ENM concentration in treated wastewater given by module 1 and the wastewater application rates to these soils. The accumulated ENM loads carried by recycled water in these soils are then the sum of all the considered years’ loads.

Module 3 calculates the ENM load to the two ocean gulfs and their sediments. These values are actually provided directly by the output of module 1. The portion of the treated wastewater that is not used for irrigation is discharged into the two ocean gulfs. For nano-TiO$_2$ and nano-ZnO there is also a direct release of these ENM into the ocean due to the on-beach use of sunscreen, in which nano-TiO$_2$ and nano-ZnO are important active ingredients. As shown in Figure 4-1, this presents an additional flow to the ocean besides the wastewater discharge. Each gulf has three major WWTP effluent discharge points, so in order to obtain more accurate estimates of ENM concentrations in sediments, the spatial distribution of these different discharge points is taken into account and the accumulated ENM loads are divided by the mass volume of the defined area that is affected by each discharge point (see Appendix 4). The accumulated ENM loads to individual discharge points are the sum of the products of the annual WWTP effluent discharge and the corresponding ENM concentrations in that effluent. The yearly discharge of WWTP effluent at each discharge point is given in the summary of Table A4-3 (Appendix 4); and the definition of discharge point areas is documented in the “Gulf Sedimentation Area Estimates & WWTP Discharges for 2005 – 2012” section of the Appendix 4. It is important to note that strong agglomeration and sedimentation is expected to occur in seawater (Keller et al., 2010). Therefore the calculation of concentrations in sediments is based on the assumption of complete sedimentation from seawater.

The definition of the areas of the biosolids treated soils in the seven regions is according to the areas of crop land in these regions. This information is given in the local government report (PIRSA, 2013a). A summary of all compartment volumes used in the model is given in Table A4-1 (Appendix 4), with detailed information on the parameters and data used for the calculations.
4.2.3 ENM parameters, system parameters and assumptions

Given that no specific data for ENM use in South Australia is available, we estimated these values by downscaling the modelled European Union (EU) ENM use to that of SA according to the proportional difference in their Gross Domestic Product (GDP) (Sun et al., 2014c). This is based on the assumption that regional GDP is proportional to purchase power (Keller and Lazareva, 2013). It is an imperfect scaling factor but is stated to be more reasonable than using other factors such as population which...
disregards the difference in purchasing power of people living in countries with different development status (Keller and Lazareva, 2013). The base year data used was 2012. The extrapolation of annual ENM consumption between 2005 and 2011 was made by scaling the 2012 base year data according to the estimated development of world ENM production. The estimation was modelled on the basis of several market and patent studies (European Commission, 2006; LUX RESEARCH INC, 2004; Piccinno et al., 2012). Each market and patent study provides a projection of how the technology or market can develop over time; this supports the use of quantitative ratios between the base year 2012 and other years over the period from 2005 to 2012. Projections of this ratio for the same year based on different studies were used as raw input data for probability modelling. The results can be found in Figure A4-1 (Appendix 4).

The evolution of all ENM flows over time in Module 1 is based on the total ENM consumption in SA. It assumes all the transfer parameters in Module 1 remain unchanged compared to 2012 and the ENM flows are proportional to the initial yearly total consumption. Our assumption is that the allocation of ENM to different consumer products and applications is region-independent, therefore the data used for Europe by Sun et al. (2014c) can also be applied in the case of SA. ENM releases to the environment and waste streams are generally dependent on the product-type, irrespective of where they are used; however, when it comes to the end of life treatment of products different regional regulations may apply. In SA, 10% of plastics are recycled and 6% exported; 30% of consumer electronics are recycled and 19% exported; 66% of glass is recycled and 3% is exported (Brulliard et al., 2012); 23% of metals are recycled and 67% are exported (Colby et al., 2012). Centralized wastewater treatment plants serve 92% of the population in SA, and the 8% of people living in rural areas dispose of their wastewater via septic tanks (Local Government Association of South Australia, 2013). No SA specific WWTP removal efficiencies are available for the five studied ENM, therefore these data were drawn mostly from the summary by Sun et al. (2014c) and updated by adding newly available WWTP removal studies (Hedberg et al., 2014; Li et al., 2013; Ma et al., 2013). There is only one waste incineration plant in SA, and that is used to burn the small volume of medical, quarantine and pharmaceutical waste produced (SA EPA, 2013). Farmers in SA have used biosolids since the late 1960s and the use of biosolids is regulated by the SA Environmental Protection Authority (SA EPA, 2009; UN-HABIATAT, 2008). The biosolids applied to SA soil between 2005 and 2012 also include some stockpiled biosolids produced prior to this period, but due to their very low ENM concentrations compared to the biosolids produced in the last few years, we excluded this portion of ENM from our calculation. According to a relevant report (Darvodelsky, 2012), 100% of biosolids are applied in agriculture in SA (92% directly used for agriculture, 8% composted and then applied in soils). The official data for stockpiled and transported biosolids produced between 2005 and 2012 is given in Table A4-2 (Appendix 4). About 30% of treated wastewater produced in SA is reused for irrigation, while the vast majority of the remaining 70% is discharged into the two ocean gulfs (SA Water, 2013). On the basis of the available information for treated wastewater application rates in different soil
types, we were able to calculate the ENM load per unit area of soil. For the category of grass, gardens and pastures 4.48 million litres (ML) of treated wastewater per hectare (ML/ha·yr) are applied on average each year. The value for viticulture is 2.10 ML/ha·yr and for horticulture it is between 3 and 5 ML/ha·yr (Laurenson et al., 2010). A summary of these data is made in Table A4-4 in Appendix 4.

Like most of the populated regions in Australia, SA is a state with a long coastline. A considerable amount of sunscreen application takes place near the beach, where ENM contained in sunscreen are released directly into ocean water instead of going through wastewater treatment plants. About 13% of the total sunscreen used in SA is estimated to be used during beach visits (Conroy et al., 2014).

A summary of the transfer coefficients (TC) of ENM from production to technical and environmental compartments can be found in Table A4-8 (Appendix 4).

4.3 Results

4.3.1 ENM mass flows in South Australia

The flows of the five ENM were modelled using the volumes of ENM used in SA, ENM allocation to products, and SA-specific ENM transfer factors from products to technical and environmental compartments. Figure 4-2 shows the mass flow for nano-TiO$_2$ in 2012. Mass-flow charts for nano-ZnO, nano-Ag, CNT and fullerenes can be found in Figure A4-4 (Appendix 4). The technical compartments (e.g. PMC, WWTP, WIP, landfill, recycling) and environmental compartments (air, soil, water and sediments) are expressed as boxes; flows between these processes and compartments are expressed as arrows, and the thickness of the arrows indicates the magnitude of the flows. The flows are determined by transfer coefficients (TC) that describe the exchange of ENM between and within these boxes. Flows leaving the system describe ENM flows out of the considered system boundary, e.g. export. ENM can also accumulate in landfills, soils and sediments, as indicated by the black squares in Figure 4-2 with the accompanying yearly rate. In Figure 4-2 the soil box is a combination of all regional soils receiving biosolids and/or treated wastewater, as well as the soils not receiving ENM via biosolids and sewage effluent but via ENM deposition from air and direct release during the use of ENM enabled products. The ocean and sediment compartment values shown in Figure 4-2 represent the sum for the two gulfs and gulf sediments. The mass flow values shown on the flowchart are the mean values from the probability distributions, and mode values (values having the highest probability) and the quantile 15 and 85 are also presented in the Figures.

The total nano-TiO$_2$ consumption in SA in 2012 was estimated to be 54 tonnes, and this value was used as the total input into our modelling system. The most prominent flow for nano-TiO$_2$ in SA was from production, manufacturing, and consumption (PMC) to waste water (and further to WWTP). This is due to the fact that, like anywhere else, the major use of nano-TiO$_2$ in SA is in cosmetics (Sun et al., 2014c). During wastewater treatment more than 90% of nano-TiO$_2$ is captured in biosolids. All of the nano-TiO$_2$ contained in biosolids ends up in soils, either directly or in the form of compost. The nano-
TiO_2_ flow from PMC to landfill constitutes another significant flow, which is a result of dumping all municipal solid wastes in landfills. In total about 5% of nano-TiO_2_ may be directly released into the ocean due to sunscreen use on beaches.

In our modelling we track the mass of the primary particles. Agglomeration plays a role in transferring particles from one compartment to another (e.g. from water to sediment), but does not affect the total mass of the primary particles. It should be noted, however, that ENM can be transformed or degraded before they reach environmental compartments. Nano-Ag and nano-ZnO can be transformed into other forms during product use and especially in wastewater transfer and in the anaerobic phase in WWTP (Kaegi et al., 2011; Lombi et al., 2013; Lombi et al., 2012; Ma et al., 2013). According to Lombi et al. (2012) and Ma et al. (2013) all nano-ZnO is transformed to other Zn compounds during WWTP processes, which means that all of the Zn contained in WWTP biosolids and effluent is no longer nano-ZnO. These transformed flows are called “nano-ZnO derived Zn”. For nano-Ag, the above mentioned authors indicated in their studies that a small fraction can survive the WWTP processes. So the Ag flows from WWTP and CWMSs are mainly transformed species of Ag together with a very small fraction of original nano-Ag. In the mass flow charts these forms are presented together (see Figure A4-4, Appendix 4), but separate mass flow charts differentiating the nano and transformed flows of Ag are given in Figure A4-5 (Appendix 4).

The modelled total consumptions of nano-ZnO, nano-Ag, CNT and fullerenes in SA are 10 tonnes, 0.18 tonnes, 2.1 tonnes and 0.12 tonnes respectively. Very similar to the findings for nano-TiO_2_ the prominent flows of nano-ZnO are from consumption to waste water due to a considerable fraction of nano-ZnO being used in personal care products. After WWTP processes, nano-ZnO is transformed into different chemical forms such as ZnS, Zn-ferrihydrite and Zn_3(PO_4)_2 (Lombi et al., 2012; Ma et al., 2013) and then transported to soils. For nano-Ag the most prominent flow is to landfill; this is because one of its major applications is in plastics and electrical appliances. This is followed by lesser flows to waste water and downstream compartments. As mentioned above, after passing through wastewater transfer and treatment, most of the nano-Ag is transformed to Ag sulfides. Most of the CNT and fullerenes end up either in landfill or recycling, and this can be explained by the fact that most of these materials are applied in polymer composites.
Figure 4-2: Modelled mass flows (in tonnes/year) of nano-TiO₂ in SA in 2012. Technical compartments (e.g. PMC, WWTP, WIP, landfill, recycling and export) and environmental compartments (air, soil, water and sediments) are expressed as boxes; flows between these processes and compartments are expressed as arrows, sinks are expressed as black squares, and the thickness of these arrows indicates the magnitude of the flows. The values shown are mean values from each probability distribution; while mode values and quantile 15(Qₐₓₜ₁) and quantile 85(Qₐₓₜ₈) values are also given in the right text field. A compartment code is used to identify each compartment and these are shown at the corner of each compartment box. Arrows between any two compartment codes in the right text field indicate flows from one such compartment to another. The volumes of flows are determined by transfer coefficients (TC) that describe the exchange of ENM between and within these boxes. All the values are rounded to three significant digits; therefore the balance between input and output flows from one compartment might not be exactly 100%.

4.3.2 Environmental concentrations of ENM

In Figure 4-3 the development of the accumulated nano-TiO₂ concentrations between 2005 and 2012 is shown for biosolids treated soils, effluent treated soils and the gulf sediments. The nano-TiO₂ concentrations increased over time due to the yearly input into these compartments that function as nano-TiO₂ sinks. The yearly input by biosolids varied, resulting in a non-linear increase. The accumulation curves for nano-TiO₂ in soils and sediments provide references for the other four ENM, which follow similar trends. A summary table of accumulated concentrations of all five ENM in 2012 is given in Table A4-9 (Appendix 4).
Comparing the concentrations in the different compartments, nano-TiO$_2$ concentrations in soils amended with biosolids cover the broadest range, varying from 0.05 µg/kg for farms on Eyre and Western in 2005 to 450 µg/kg for farms in the Greater Adelaide area in 2012 (i.e. 4 orders of magnitude difference). These concentrations can effectively be divided into two clusters: the concentration for Greater Adelaide and the concentrations for the other six regions. The concentrations of nano-TiO$_2$ in WWTP effluent treated soils and gulf sediments are in a very similar range as the concentrations in biosolids treated soils of the six regions except Greater Adelaide, which vary from 0.05 to 17 µg/kg. In summary, the model indicates that the concentrations of nano-TiO$_2$ in biosolids and WWTP effluent treated soils and in ocean sediments have increased 30-40 times over the 7 year period. The nano-TiO$_2$ concentrations in the soils of the Greater Adelaide region are projected to be the highest among all environmental compartments considered within the model boundaries. This is due to the fact that, compared with the other regions, in the Greater Adelaide region a similar or even larger yearly biosolids load is applied to a much smaller area (i.e. smaller receiving soil volume). The soil volumes in some other regions are 1 to 2 orders of magnitude higher than that of the Greater Adelaide region. In contrast to Greater Adelaide, soils of Kangaroo Island receive the lowest loads and have the lowest concentrations due to the relatively low biosolids production and use in this area.

Concentrations in WWTP effluent treated soils including horticulture; viticulture; and grassland, gardens, and pastures are less variable than concentrations in biosolids treated soils and in gulf sediments. Among the three land-use categories irrigated with WWTP effluents, nano-TiO$_2$ concentrations are almost the same, increasing from less than 1 µg/kg in 2005 to more than 10 µg/kg in
2012. Concentrations in viticultural soils are only half that of the other two land-uses due to the lower application rate of sewage effluent in viticulture.

With respect to the concentrations in sediments, overall the predicted concentrations increase 30-fold over the seven years between 2005 and 2012. The lowest concentration predicted by the model is for the sediment at Whyalla. This is estimated to increase from 0.09 µg/kg in 2005 to 2.5 µg/kg in 2012. The highest concentration is linked to the sediment affected by Bolivar (the largest WWTP in SA), with the concentration in the affected area predicted to be more than 10 times higher than the concentration in the least affected sediment.

A direct comparison between the accumulations of the five ENM has been made for the Greater Adelaide soils, the region where the highest ENM concentrations were found. We can see from Figure 4-4 that the order of ENM concentrations is well correlated with the order of the total input volumes of the ENM. Nano-TiO$_2$ is predicted to be present in the highest concentrations, accumulating from about 9.5 µg/kg in 2005 to 450 µg/kg in 2012, followed by nano-ZnO (in this case the “nano-ZnO derived Zn”), with the “nano-ZnO derived Zn” concentrations predicted to be 5 times lower than those for nano-TiO$_2$. As mentioned in the previous section, after wastewater treatment processes, all nano-ZnO is expected to be transformed into other chemical forms; therefore none of the original nano-ZnO released from products is predicted to be transported onto soils with biosolids. The majority of the nano-Ag in biosolids is also known to be transformed into non-nano forms e.g. Ag$_2$S (Kaegi et al., 2011). We therefore calculated the concentrations of the “nano-Ag derived Ag” (here both the transformed forms of nano-Ag and the remaining nano-Ag) ending up in soil as well as the concentration of only remaining nano-Ag. The concentration of “nano-Ag derived Ag” is about 2 orders of magnitude lower than that of “nano-ZnO derived Zn”. The concentration of CNT and fullerenes are a further order of magnitude lower. Nano-Ag has the lowest concentration in soil, ranging from 0.0002 µg/kg in 2005 to 0.02 µg/kg in 2012.
4.4 Discussion

Compared to previous ENM mass flow studies (Gottschalk et al., 2009a; Mueller and Nowack, 2008; Sun et al., 2014c), the present study increased the temporal and spatial resolution of the predicted environmental concentrations of ENM. It includes temporal aspects by considering the accumulation of ENM in environmental sinks over a seven-year period instead of only one single year’s input and accumulation of ENM in soils, therefore provides actual concentrations instead of only the predicted yearly increase in concentration. The increase of ENM concentrations in biosolids amended soils is caused by a combination of increasing production of ENM – and therefore increasing concentrations in biosolids – and the yearly addition of biosolids to the soils. We have used the conservative assumption that soils are the final sink for the ENM transported along this pathway. Leaching and runoff are minimal in SA as due to the small amount of precipitation the large majority of the watercourses are dry for the majority of the year and potential evapotranspiration exceeds water supply, although it should be noted that wind erosion may occur. The model was also conservative in that it did not consider the possible transformations of ENM in soil/sediments. These compartments were considered in our model as final sinks, although of course dissolution/phase transformation or leaching or sediment transport may affect the concentrations. However, to include these reactions in the model a coupling with process-based environmental fate models would be needed (Praetorius et al., 2013).

When compared to the studies by Sun et al. (2014c) and Gottschalk et al. (2009a), the results for biosolids treated soils in the EU are 3-4 times higher than the ENM concentrations predicted for soils
in the Greater Adelaide area. We note that the nano-ZnO concentrations cannot be directly compared because results in Sun et al. (2014c) indicate the concentration of untransformed nano-ZnO reaching the soils while the results presented here only report the concentrations of total “nano-ZnO derived Zn” because no nano-ZnO survives in biosolids, the only source modelled in our study. The differences between the results for the EU and for this study are caused by the smaller biosolids production and relatively larger volumes of soils in Greater Adelaide. The soils of Greater Adelaide with the highest ENM load received accumulatively 292 tons/km² of biosolids between 2005 and 2012; in contrast, European soils received 2'000 tons/km² in a single year in 2012. Even within SA the accumulated concentrations of ENM in biosolids treated soils vary by two orders of magnitude, ranging from 1.9 μg/kg of nano-TiO₂ in Eyre and Western soils to 450 μg/kg of nano-TiO₂ in Greater Adelaide soils. These results indicate that ENM soil concentrations will be very strongly influenced by local practices. For SA, one important practice is the transportation of biosolids produced in metropolitan Adelaide (SA state capital) to different regions across the state for use in soil amendment by farmers. This practice helps explain the soil concentrations for the two groups of regions in Figure 4-3a. Greater Adelaide is likely to receive most transported biosolids per unit area because it is the closest to metropolitan Adelaide. Since farmers pay the cost of transportation, the cluster of regions beyond Greater Adelaide (Murray-Mallee, Limestone Coast, Yorke and Mid North, Eyre and Western, Kangaroo Island) are likely to receive less transported biosolids per unit area because transport is relatively expensive.

SA is also special in that a significant part of the treated wastewater is used for irrigation of some crops and trees. These results in an almost closed loop for ENM as on the one hand the ENM captured by the WWTP (this is the major part of the ENM released to wastewater) are transferred to some soils whereas the ENM not captured are transferred directly other soils. In such a situation an almost complete transfer of all ENM to soils can be expected which is completely different to a region that does not allow biosolids transfer onto soils (instead landfilling or incineration may be used). In such a region landfills and sediments will be final sinks for ENM whereas in SA these final sinks are mainly soils.

The availability of extensive data detailing the annual distribution of biosolids to individual regional farms enabled a more precise positioning on target soils receiving biosolids and therefore a higher resolution of the predicted environmental concentrations of ENM. In order to visualize the importance of spatial and temporal variability, in Figure 4-5 the probability distributions of nano-TiO₂ concentrations from different stages of the modelling are plotted. The black curve shows the uncertainty of the model output from production/use/fate in technosphere and represents the average nano-TiO₂ concentration in biosolids treated soils in SA. This curve was calculated by dividing the total annual flow of nano-TiO₂ onto soils in 2012 by the total volume of these soils. Here only the uncertainty of nano-TiO₂ production and transfer along its life cycle before ending up in soils is reflected. The blue curve represents the additional spatial variability and is the probability density
distribution of the 2012 incremental nano-TiO$_2$ concentrations comprising all regional soils of SA. It involves the uncertainty of the model output from production, use and fate in technosphere as well as the regional variability of nano-TiO$_2$ concentrations. Compared to the average curve, both higher and lower concentrations are observed. The red curve is the probability density distribution of the accumulated nano-TiO$_2$ concentrations over the period between 2005 and 2012 comprising the seven regional soils. Compared to the blue curve apart from uncertainty in production, use, fate in technosphere and local variability it also takes the temporal variability of biosolids application onto soils into account. We can clearly see that the concentration variability derived from spatial and temporal biosolids application practice is much larger than the uncertainty caused by production data and transfer parameters.

As this study provides accumulated concentrations in soils, it can be directly used for environmental risk assessment. This is particularly relevant as metal concentrations in soil are already used as a critical indicator for assessing risk in soils. In this study we not only modelled nano-Ag and nano-ZnO flows and concentrations but also the total “nano-Ag derived Ag” and the total “nano-ZnO derived Zn”. This was done by applying the transformation rate suggested by studies about the fate of metal
nanomaterials during the wastewater processes (Kaegi et al., 2011; Lombi et al., 2013; Lombi et al., 2012; Ma et al., 2013). The inclusion of total “nano-ZnO derived Zn” and “nano-Ag derived Ag” modelling helps to see how much contribution nanomaterials make to the total metal concentrations in soils. We therefore compared modelled and measured concentrations of Ag and Zn in both biosolids and soils in SA (total measured concentrations of Ag and Zn are summarised in Table A4-10 of the Appendix 4). Figure 4-6 shows these comparisons with boxplots. Here the modelled concentrations of biosolids treated soils in Greater Adelaide were taken to represent the highest soil metal concentration induced by biosolids. Modelled nano-Ag concentrations and the concentration of nano-Ag derived Ag are separated by almost 2 orders of magnitude. The modelled concentration of nano-Ag derived Ag in biosolids is about 1'000 µg/kg, the measured concentration of total Ag in biosolids is about 10'000 µg/kg. About 10% of the total Ag contained in biosolids could be contributed by and derived from nano-Ag. The concentration of measured background Ag in soil is around 50 µg/kg, which is between the modelled Ag concentrations in soils and the Ag concentrations in biosolids. Zinc is quite similar to Ag, but with all the corresponding concentrations increased by about 2 orders of magnitude. There is no modelled nano-Zn concentration in soils but only “nano-ZnO derived Zn”, because no nano-Zn survives the WWTP processes. The red line in the figure represents for the upper limits of maximally permitted Zn concentrations in soils in South Australia, which is 195 mg/kg for soils with a moderate pH as given by the SA biosolids guideline for the safe handling and reuse of biosolids (SA EPA, 2009). No corresponding value is available for Ag in Australia, so the upper limit for Ag in Figure 4-6 is based on existing regulations in other countries, here the lowest value of 500 µg/kg was shown (ESdat, 2000; L.S. Sonon and J. Gaskin, 2009; Ministry of the Environment., 2011).

The modelled Ag and Zn concentrations are 50 and 250 times respectively smaller compared to the measured background soil concentrations of Ag and Zn. The difference between the current background soil concentration of Ag and the lowest upper limit concentration is 450 µg/kg, as it is shown in Figure 4-6. If assuming the current load of Ag onto soil remains constant - the biosolids induced Ag yearly increase in soil concentration is 2.6 µg/kg·y it will take 170 years to reach the lowest threshold in SA. The difference between the currently measured Zn background concentration in soils and the upper limit in SA is about 170 mg/kg. The current yearly increase in concentrations of Zn in soils in Greater Adelaide is 182 µg/kg·y According to this rate, it will take 930 years to reach the limit.

Two issues in relation to soil concentrations need to be highlighted: we assumed soils to be final sinks for ENM, so no downward leaching or surface erosion was considered, also further dissolution/degradation reactions were not included. The modelled soil concentrations therefore represent maximal values and more process-based models will be needed to quantify the importance of these processes for the long-term fate of ENM in soils.
Notes: mod. = modelled; meas. = measured;

Figure 4-6: Comparison of modelled and measured concentrations of Ag and Zn in biosolids and biosolids treated soils of South Australia. The modelled concentrations in soils are for Greater Adelaide which represents the case of the highest concentrations among the regions studied. The modelled concentrations in biosolids represent the general concentrations across SA. The concentrations are given as boxplots (mean, 25% and 75% quantiles, interquartile range=Q₃−Q₁). The red line represents the upper limits of threshold concentration of Zn and Ag for soils in Australia.

Our work also provides the first concentration prediction for marine sediments in two different ocean gulfs. The concentrations are in the µg/kg range for nano-TiO₂ and are thus much lower than predicted for river sediments (Sun et al., 2014c). These concentrations can serve as baseline concentrations for marine ecotoxicologists when studying sediment-dwelling organisms. These concentrations were obtained by assuming complete sedimentation in the area affected by ENM, an assumption that it is reasonable given the fast sedimentation of ENM in seawater (Garner and Keller, 2014). However, we have to consider that highest sedimentation will occur close to the discharge point and thus a gradient in sedimentation with increasing distance from the coast is expected.
4.5 Acknowledgments
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4.6 Supporting information (Appendix 4)
More details about the geographical information of South Australia, the distribution and applications of biosolids and treated effluent to regional soils and the discharge of effluent to ocean are given in the Appendix 4.
4.7 References

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5 DYNAMIC PROBABILISTIC MODELLING OF ENVIRONMENTAL EMISSIONS OF ENGINEERED NANOMATERIALS

Tian Yin Sun, Nikolaus A. Bornhöft, Konrad Hungerbühler and Bernd Nowack

1) Empa – Swiss Federal Laboratories for Materials Science and Technology
   Technology and Society Laboratory, Lerchenfeldstrasse 5, CH-9014 St. Gallen, Switzerland
2) Institute for Chemical and Bioengineering, ETH Zürich, CH-8093 Zürich, Switzerland
3) Department of Informatics, University of Zurich, Binzmühlestrasse 14, 8050 Zurich, Switzerland

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Abstract

The need for an environmental risk assessment for engineered nanomaterials (ENM) necessitates the knowledge about their environmental concentrations. Despite significant advances in analytical methods, it is still not possible to measure the concentrations of ENM currently in natural systems. Material flow and environmental fate models have been used to fill this gap and to provide predicted environmental concentrations. However, all current models are static and consider neither the rapid development of ENM production nor inclusion of the fact that a lot of ENM are entering an in-use stock and are released from products (i.e. have a lag phase). Here we use a dynamic probabilistic material flow modelling to predict former, current and future flows of four ENM (nano-TiO₂, nano-ZnO, nano-Ag and CNT) to the environment and to quantify their amounts in (temporary) sinks such as the in-use stock and (“final”) environmental sinks such as soils and sediments. Given the rapid increase in production, this approach is necessary in order to capture the dynamic nature of ENM flows. The accumulated masses in sinks and the average concentrations in technical compartments quantified in our study provide necessary data for risk assessors and scientists in need of quantitative knowledge on the presence of ENM in various compartments. The flows to the environment that we provide will constitute the most accurate and reliable input of masses for environmental fate models which are using process-based descriptions of the fate and behavior of ENM in natural system but rely on accurate mass input parameters.
5.1 Introduction

Previous modelling efforts have attempted to show the concentration of ENM in environmental and technical compartments (Blaser et al., 2008; Boxall et al., 2007; Gottschalk et al., 2009a; Gottschalk et al., 2013b; Johnson et al., 2011a; Keller et al., 2013; Keller and Lazareva, 2013; Mueller and Nowack, 2008; Sun et al., 2014c). However, all the models published so far are static and do not consider time-dependent processes with respect to the use and release of ENM. The current models consider only the input by production, manufacturing and consumption (PMC) into the system that occurs in one year and subsequently distributes the mass over the entire system in the same year. The models also assume that all ENM produced are released to waste streams and environmental compartments in the same year that they enter the system and so in this way no in-use stocks are considered. With these two oversimplifications of the true situation, the static models do not represent the actual ENM flows to environmental compartments under conditions where a rapid increase in production of ENM is taking place and when they are entering in-use stocks. Moreover, the static models cannot predict concentrations in environmental sinks, such as soils or sediments, because these compartments accumulate inputs over many years. First attempts in considering accumulation in environmental sinks have been made by Gottschalk et al. (2009a) who used a very simplistic model to scale the input in previous years to calculate final concentrations in soils and sediments. Sun et al. made a spatio-temporal prediction of mass-flows and concentrations for five ENM in biosolids amended soils in South Australia over a period between 2005 and 2012 (Sun et al., 2015). However, both of them only considered one aspect of the dynamic nature of the system a periodic production inputs into the system, but another aspect the delayed ENM release from in-use stock is completely missing.

A realistic prediction of ENM flows to the environment therefore requires a complete dynamic material flow analysis model (MFA). Unlike the static models, a dynamic MFA is able to track the flows over many years and it also no longer uses the simplified assumption of immediate ENM release. Dynamic MFA is a well-established modelling technique. Mueller et al. (2014) performed a review on dynamic MFA methods with respect to uncertainty treatment. More than half of the methods covered did not consider uncertainty at all; 37% used sensitivity analysis, Gaussian error propagation (6%) or parameter ranges (5%), but none supported a full probabilistic uncertainty representation. The dynamic probabilistic MFA (DP-MFA) method recently developed by Bornhöft et al. (2015) is able to fill this gap. This method represents all system dimensions under uncertainty as probability distributions in the respective model parameters and propagates these values to the dependent model variables using Monte-Carlo simulation. The aim of this work was to build a customised DP-MFA model based on this new method for four ENM - nano-TiO$_2$, nano-ZnO, nano-Ag, and CNT - and predict their former, current and future mass-flows to technical and environmental compartments and the resulting concentrations in these compartments.
5.2 Methods

5.2.1 General principle

The general principle of the DP-MFA model for the four ENM can be summarized by the following three features: 1) dynamic considerations, 2) the use of a life-cycle concept and 3) a probabilistic approach. The dynamic feature distinguishes the current model from all previous static models by a more realistic representation of the true system dynamics as developed by Bornhöft et al. (2015). The dynamic considerations in this study are comprised of two aspects: the input dynamics and the release dynamics. The input dynamics describe the annual production of ENM as inflows into the system within a given period. The release dynamics describe the time-dependent ENM release kinetics from a specific product category over the entire life-cycle.

Following a life-cycle concept, the model tracks the ENM mass-flows from ENM production to incorporation into the commercial product and finally from the products to technical and environmental compartments during/after their use and disposal (Mitrano et al., 2015). Probabilistic methods are employed for all the parameters used in the modelling processes to address the inherent uncertainty in the raw data used (Gottschalk et al., 2010b). This means data from varied sources, with inherently different reliability, are combined into an appropriate probability density distribution. The input data for the model are the annual production amounts of ENM in the EU, the estimated shares of ENM applied onto product categories, the process-based transfer coefficients within and among the technical systems and the transfer coefficients between environmental compartments. All these parameters are treated as appropriate probability distributions depending on the data available. For each of the parameters, 100’000 random iterations are made to represent the comprehensive picture of the probability density distribution as described in the previous study (Gottschalk et al., 2010b).

The scheme of the DP-MFA is shown in Figure 5-1. It consists of two modules: the Release Module and the Distribution Module. The Release Module addresses the input and release dynamics. It describes the annual ENM production/consumption entering the system, the estimated share onto product categories, the flows from product categories by immediate release or into in-use stocks and finally the release from in-use stocks. The total annual release of ENM is then transferred to the compartments of the Distribution Module. The Distribution Module is built upon the previous static model (Sun et al., 2014c), which describes the ENM transfers within and between technical and environmental compartments.

5.2.2 System boundary

The geographical focus of this study is the European Union (EU) due to the abundant information available. But modelling for other regions can be easily expanded once data needed are provided. The technical compartments included in this study are landfills, sewage treatment plants (STP), waste incineration plant (WIP), recycling and export. The environmental compartments considered are
atmosphere, natural and urban soils, sewage sludge treated soils, surface waters and sediments. Among these compartments, landfills, soils and sediments are defined as sink compartments. From sink compartments no downstream flows are modelled. A study by Caballero et al (2015) was included providing an explicit description of ENM fate during and after recycling processes.

**System boundary**

**Release Module**

- **Use/stock**
  - PC1: Input/year
  - PC1: Release/year

- **Annual release**
  - PC1: Input/year
  - PC1: Release/year

**Distribution Module**

- **Technical systems: landfills, sewage treatment plants, waste incineration, recycling, export**
- **Environment**
  - Sinks
  - Sinks

**Figure 5-1: Schematic of the probabilistic dynamic material flow model for ENM. It consists of two modules, the Release Module and the Distribution Module. The Release Module focuses on dynamic system behaviour, describing both the input dynamics and the release dynamics. The Distribution Module describes ENM distributions within and between technical and environmental systems after they are released out of the use phase.**

In this study we track the mass of the initial ENM. Transformed ENM (in our definition which lose their nano features i.e. gasification, dissolution, chemical reactions) will be viewed as loss of the ENM and flow to a virtual compartment called “Elimination”.

### 5.2.3 Input dynamics

We considered a time frame from 1990 to 2020. Explanations of the definition of the time frame are given in the Appendix 5. The estimation of production of ENM over time is made by multiplying the base year production (2012) with retrospective and prospective scaling factors. The production of the four ENM in 2012 is based on the probability distributions provided by Sun et al. (2014c) updated with newly available data. Table A5-1 shows the raw data used for building the probability distribution of the ENM production in 2012. The scaling factors for each individual year are based on ENM market projections, nanotechnology patent analysis, and direct information on ENM production (Piccinno et al., 2012) when available. We use the assumption that the development of ENM
production is proportional to nanotechnology development with respects to e.g. patents registrations, funding etc. A summary of all the data used for estimating probability distributions of the scaling factors are summarized in Table A5-2. The probability distribution of ENM production in 2012 and the distribution of scaling factors are multiplied to obtain the probability distribution of ENM production for the period from 1990 to 2020.

For nano-Ag, an additional estimation of the production development for a period from 1900 to 2020 has been made. This longer time period is founded in the historic applications of “silver colloids” that are in fact nano-Ag (Nowack et al., 2011). Detailed information on how this is done can be found in the Appendix 5.

5.2.4 Release dynamics

“Release” in our definition refers to ENM that leave the production, manufacturing, and consumption phase and are transferred to technical or environmental compartments. The total ENM production is assigned to different nano-enabled product categories in shares based on the information provided by a previous study (Sun et al., 2014c). This allocation of ENM to product categories is assumed to remain constant over the time considered in this study. Figure 5-2 shows the scheme of how time dependent ENM release from products is expressed in the model. It proceeds in three steps: separation of ENM allocated to one product category into the Use release and End of Life (EoL) release ❶, scheduling of Use and EoL release ❷, distribution of ENM to technical and/or environmental compartment after Use release and EoL release ❸.
Figure 5-2: Schematic visualization of the time dependent ENM release dynamics. For ENM contained in a product category, the first step is the division of the total ENM-content between the Use release and EoL release. The ENM contained in a product category allocated to use release is the fraction supposed to be released during its use phase; the part allocated to EoL release is the fraction supposed to be remaining in the product and be released once the products come to their end of life. The second step is the definition of the duration of the Use release and the EoL release as well as the release schedule; in other words in how many years the release events take place for one product category and how much of the fraction is released each year. The EoL release depends on the life-time distributions of each product category; here normal distributions are assumed. The third step is the distribution of the released ENM from the scheduled Use release and EoL release to technical and environmental compartments.

5.3 Results and discussion

5.3.1 ENM production over time

Figure 5-3a shows the modelled production development of nano-TiO$_2$ in the EU between 1990 and 2020. The corresponding diagrams for nano-ZnO, CNT and nano-Ag are given in Figure A5-2. The full probability spectrum of the production development is used as main input for the dynamic flow modelling. The grey lines represent single model runs with single values randomly selected out of the underlying probability distributions. The denser the grey lines appear, the more likely the modelled
value is true. The mean values are shown by the red line. The uncertainty can be quantified by the width of the gap between the 15% and 85% quantiles (dashed blue lines).

### 5.3.2 Release dynamics

Table 5-1 depicts the dynamic release parameters for nano-Ag as an example. Data for nano-Ag was shown here as an example because relatively more extensive information is available. The respective data for the other ENM are given in the Appendix 5. This table demonstrates the division of the release between Use release and EoL release, the release schedule over time and the allocation to different compartments after release. As Table 5-1 shows, important products categories such as Electronics and appliances, Medtech and Paints have the major part of nano-Ag remaining in the product and it is released when it reaches the end of life. In contrast, product categories like Textiles, Cosmetics, Foods, Cleaning agents and Plastics have their nano-Ag component released mainly during the use phase.

Product life times are often independent of the ENM application, therefore they are either well known or can be easily estimated. The release kinetics of ENM is specific to which ENM is applied to and how the material is bound to a product. This information is based preferably on experimental data when it is available or estimated on the basis of expert judgement. The use of realistic data compared to worst-case assumptions (Boxall et al., 2007; Gottschalk et al., 2009a; Johnson et al., 2011a; Keller et al., 2013; Keller and Lazareva, 2013; Mueller and Nowack, 2008; Sun et al., 2014c) ensures a realistic modelling effort.

Product categories of Electronics and Electricals, Plastics, Paints, Metals and Filters have life-times normally longer than 5 years. With 20 years of use release, Metals is the product category with the longest use release. Electronics and appliances, the most important product category for nano-Ag, has an average life-time of 8 years (SENS SWICO SLRS., 2014). Fast release is found in non-durable product categories for instance Cosmetics, Foods, Cleaning agents and Medtech. For these, we have estimated general use release duration of 1 to 2 years. Experimental studies indicated that the majority of nano-Ag release takes place in the early stage of their life-time (Kaegi et al., 2010; Limpiteeprakan, 2014). Therefore, in the use release schedule release is mostly allocated to the first year. Most nano-Ag released during use release end up in waste water, which was evaluated on the basis of a previous study (Sun et al., 2014c).

In our approach, the EoL release schedule of ENM for a product category is represented by its life-time distribution, i.e. the time it takes until it is discarded. The longest EoL release is estimated for Paints. Although, Paints have an average use release duration of 8 years, the EoL release duration is in average 80 years, governed by the life-time of the buildings they are applied to (ATD Home inspection, 2014; Hischier et al., 2015). Complete use release in the first year is assumed for product categories with fast use release, such as Foods, Cleaning agents and Medtech. Distribution of nano-Ag
to landfill, WIP, recycling and export after EoL releases are made according to solids waste management statistics in the EU for general solid waste (Bakas et al., 2011) and specific waste (EEA, 2012; EEA Website, 2013; ERPC, 2011; Friend of the Earth Europe, 2013; Glass International, 2014; Kiddee et al., 2013).
Table 5-1: Summary of parameters for the release dynamics used in the model for nano-Ag; the respective information for nano-TiO₂, nano-ZnO and CNT is provided in Table A5-3. The column Priority is based on the share of nano-Ag applied in the different product categories. Columns 1, 2 and 3 correspond to the three allocation steps shown in Figure 5-2. Values of X in the column Use release in step 1 indicate the fraction of nano-Ag contained in a product released during the use phase; values of 1-X in the column EoL release indicate the fraction of nano-Ag released at the product’s end of life (EoL). Use release duration in step 2 means the estimated number of years during which release takes place; Use release schedule in step 3 describes during the use phase how much nano-Ag is released from a product each year; Distribution after use release and Distribution after EoL release in step 3 contains information about the transfer coefficients defining the nano-Ag allocation to different compartments after release; the life-times of the products categories are assumed to be normally distributed. Average life-time and standard deviations are either based on literature if available or estimated based on expert judgement; 3σ is used to show the whole span of the life-time.

<table>
<thead>
<tr>
<th>Priority (share of the total nano-Ag application)</th>
<th>nano-Ag (product categories)</th>
<th>Use release (m)</th>
<th>Use release duration (years)</th>
<th>Use release schedule</th>
<th>Distribution after use release(h)</th>
<th>EoL release</th>
<th>Lifetime distribution (normal) Note: α is the standard deviation</th>
<th>Distribution after EoL release</th>
</tr>
</thead>
<tbody>
<tr>
<td>38.1%</td>
<td>Electronics &amp; Appliances</td>
<td>0.30(m)</td>
<td>8(i)</td>
<td>1/8(i)</td>
<td>1.00</td>
<td>0.70(k)</td>
<td>mean=8; 3σ=8(i); Y1=1.0(k)</td>
<td>Landfill</td>
</tr>
<tr>
<td>25.1%</td>
<td>Textiles</td>
<td>0.60(m)</td>
<td>3(ii)</td>
<td>0.2(ii)</td>
<td>0.80</td>
<td>0.40(l)</td>
<td>mean=3; 3σ=2(ii)</td>
<td>Soil</td>
</tr>
<tr>
<td>10.2%</td>
<td>Cosmetics</td>
<td>0.95(m)</td>
<td>2(ii)</td>
<td>0.1(ii)</td>
<td>0.90</td>
<td>0.05(b)</td>
<td>Y1=0.90; Y2=0.10(b)</td>
<td>Air</td>
</tr>
<tr>
<td>6.6%</td>
<td>Foods</td>
<td>0.90(m)</td>
<td>1(ii)</td>
<td>1.0(ii)</td>
<td>1.00</td>
<td>0.10(c)</td>
<td>Y1=1.0(c)</td>
<td>Surface water</td>
</tr>
<tr>
<td>6.0%</td>
<td>Cleaning agents</td>
<td>0.95(m)</td>
<td>1(ii)</td>
<td>1.0(ii)</td>
<td>1.00</td>
<td>0.05(k)</td>
<td>Y1=1.0(k)</td>
<td>Waste water</td>
</tr>
<tr>
<td>3.6%</td>
<td>Medtech</td>
<td>0.05(m)</td>
<td>1(ii)</td>
<td>1.0(ii)</td>
<td>1.00</td>
<td>0.95(l)</td>
<td>Y1=1.0(l)</td>
<td>Recycling</td>
</tr>
<tr>
<td>3.3%</td>
<td>Plastics</td>
<td>0.80(m)</td>
<td>8(iii)</td>
<td>1/6(iii)</td>
<td>1.00</td>
<td>0.20(l)</td>
<td>mean=8; 3σ=5(iii)</td>
<td>Recyling</td>
</tr>
<tr>
<td>3.0%</td>
<td>Paints</td>
<td>0.35(m)</td>
<td>7(iii)</td>
<td>0.9(iii)</td>
<td>0.50</td>
<td>0.65(k)</td>
<td>mean=80; 3σ=20(iii)</td>
<td>0.10(m)</td>
</tr>
<tr>
<td>2.4%</td>
<td>Metals</td>
<td>0.05(m)</td>
<td>20(iii)</td>
<td>1/20(iii)</td>
<td>1.00</td>
<td>0.5(i)</td>
<td>mean=20; 3σ=5(iii)</td>
<td>0.10(m)</td>
</tr>
<tr>
<td>0.6%</td>
<td>Glass &amp; Ceramics</td>
<td>0.35(m)</td>
<td>10(iii)</td>
<td>0.9(iii)</td>
<td>0.25</td>
<td>0.65(n)</td>
<td>mean=10; 3σ=5(iii)</td>
<td>0.10(m)</td>
</tr>
<tr>
<td>0.6%</td>
<td>Soil remediation</td>
<td>0.98(m)</td>
<td>1(ii)</td>
<td>1.0(ii)</td>
<td>1.00</td>
<td>0.02(h)</td>
<td>Y1=1.0(h)</td>
<td>Soil</td>
</tr>
<tr>
<td>0.3%</td>
<td>Filter</td>
<td>0.30(iii)</td>
<td>8(iii)</td>
<td>1/8(iii)</td>
<td>0.80</td>
<td>0.70(m)</td>
<td>mean=8; 3σ=8(iii)</td>
<td>WIP</td>
</tr>
<tr>
<td>0.2%</td>
<td>Diapers</td>
<td>0.05(m)</td>
<td>1(ii)</td>
<td>1.0(ii)</td>
<td>1.00</td>
<td>0.95(j)</td>
<td>Y1=1.0(j)</td>
<td>Export</td>
</tr>
<tr>
<td>0.1%</td>
<td>Paper</td>
<td>0.0(iii)</td>
<td>1(ii)</td>
<td>1.0(ii)</td>
<td>1.00</td>
<td>1.00(i)</td>
<td>mean=5; 3σ=4(ii)</td>
<td>0.07(i)</td>
</tr>
</tbody>
</table>

(a) (Sun et al., 2014c) (b) Revised from (Sun et al., 2014c) (c) SENS SWICO SLRS. , 2014 (d) (Expert Judgement, 2014) (e) (Bakas et al., 2011) (f) Kiddee et al., 2013 (g) VEA, 2012 (h) Limpiteeprakan, 2014 (i) Eastonstewartsvilledrycleaner36, 2014 (j) (Friend of the Earth Europe, 2013) (k) (EEA Website, 2013) (l) Kaegi et al., 2010 (m)(ATD Home inspection, 2014) (n) (Hischier et al., 2015) (o) (EEA, 2009) (p) (Glass international, 2014) (q) (ERPC, 2011)

Note: Yn = year n, e.g. Y1 = year 1
5.3.3 Evolution of ENM in stocks and sinks

One of the reasons to conduct a dynamic modelling endeavour is to calculate the accumulated ENM loads in compartments that accumulate ENM. Figure 5-3b shows a full picture of the distribution of the nano-TiO$_2$ amount development in in-use stocks of product in the EU from 1990 to 2020. This is visualized by single simulation (grey lines) out of 100'000 runs with mean value (red line) and 15\% and 85\% quantiles (dashed blue lines). Figure 5-3c highlights the mean values for the accumulated production and the amount accumulated in the use stock, landfills, sludge treated soils and sediments. All the stocks exhibit an exponential-like increase over time. This is caused by both the accumulation in the compartment and the yearly increasing input into these stocks. Results for nano-TiO$_2$ were demonstrated here as an example because it is the most interesting ENM in terms of production size among the four ENM.
**LF=Landfill, WIP=waste incineration plant.**

Figure 5-3: **a.** Modelled production development of nano-TiO$_2$ in the EU from 1990 to 2020. Short grey lines indicate the single modelled values. The red curve is the average trend of all simulated values. Dashed blue lines indicate the 15% and 85% quantile range of the probability density distribution of the production. **b.** The evolution of nano-TiO$_2$ amount in the in-use stock. The grey lines are development trend of a single iteration out of 100’000 simulation runs; here only 2’000 are shown. The mean (red trace) and 15% and 85% quantile are shown (blue traces). The whole cluster area consisting of grey curves builds up the range of the probability distribution of the overall trend. The vertical width of the grey area indicates the degree of uncertainty. **c.** Mean values of the evolution of nano-TiO$_2$ in the in-use stock and in landfills, sludge treated soils and sediments as well as the total accumulative production in the EU from 1990 to 2020. **d.** The evolution of the concentrations in selected technical and environmental compartments in logarithmic scale. “Soils” here indicate the STP sludge treated soils.
5.3.4 Mass-flows of ENM

Flows of the four ENM, from production and use through to release into all compartments, were modelled by combining the modelled production volumes, shares of ENM applied in products and transfer factors between all the compartments for the year 2014, incorporating the dynamics of the system from 1990 to 2014, as shown in Figure 5-4. The mean total productions of nano-TiO$_2$, nano-ZnO, CNT and nano-Ag estimated for EU in 2014 were 38’000, 6’800, 730 and 50 tonnes respectively. Depending on the products applying these materials, different shares of amounts currently produced are entering into in-use stock or are released into technical and environmental compartments. For nano-TiO$_2$, nano-ZnO and nano-Ag, about half of the year’s total input into the system enters the in-use stock and the rest is directly released during the same year. With respect to CNTs, less than 1% (0.4 out of 730 tons) is directly released and nearly 100% is allocated to the stock phase. The amount in the in-use stock up to 2014 for nano-TiO$_2$, nano-ZnO and nano-Ag is in general around two times of their input in 2014; for CNT it is four times because the majority is stocked. Releases from in-use stock together with the immediate release from 2014’s input constitute the total release in 2014. Compared to the immediate release, the release from stocks (previous year’s input into the system) is in most cases much smaller, being about 15-25% of the total annual release. The one exception are CNTs, for which more than 99% of the annual release in 2014 is coming from in-use stock, again showing their particular applications in polymer nano-composites which corresponds with little immediate release. This importance of releases from in-use stocks justifies the need for a dynamic modelling of ENM. Because flows into a certain product category are split into stocked and released amounts, it is not possible to compare the new results to those of static models such as from Sun (2014b) or Keller (2014). In these models the production in one year was completely distributed to the environment, an assumption that our dynamic modelling has clearly shown to be not representative for the ENM investigated.

The most prominent flows for nano-TiO$_2$ and nano-ZnO after release were from production, manufacturing, and consumption (PMC) to wastewater (and further to STP). This is due to the fact that the major applications for these two ENM are in cosmetics (the priority columns in Table 5-1 and Table A5-3 shows the shares for all ENM applications). For nano-Ag, the major flows are from PMC to landfill and to waste water. The most prominent flows for CNT were from PMC to landfill, followed by the flow to WIP, and from there to elimination. This can be explained by the fact that most of these materials are applied in polymer composites. ENM flows through the STP are mainly captured in STP sludge, and further transported to WIP and landfill, and some ENM end up in soil from sludge application. After wastewater treatment processes, nano-ZnO is transformed into different chemical forms such as ZnS, Zn sorbed to iron oxides and Zn$_3$(PO$_4$)$_2$ (Lombi et al., 2012; Ma et al., 2013) and thus allocated to the virtual elimination compartment. As mentioned above, after passing through wastewater transfer and treatment, most of the metallic nano-Ag is transformed to Ag
sulphides and is therefore also ending up in the elimination compartment (and therefore left the system because the metallic nano-Ag property was lost.
PCNE: “Product Categories Not Evaluated” by Caballero-Guzman (2015), based on which the recycling process are modelled; NU Soil: natural and urban soil. ST Soil: Sludge treated soil, for values of ENM annual inflows and accumulations to/in ST soil, only the amount carried by sludge is accounted here.
Figure 5-4: Mass-flow of dynamic modelling of nano-TiO$_2$, nano-ZnO, nano-Ag and CNT in the EU for the year 2014 in ton/year. The nano-Ag flow chart displays the 1990-2020 scenario. The values for flow quantities are mean values from the respective probability distributions. The thickness of the arrows reflects the quantities of flows; the blue/black squares in some compartments represent stocks in these compartments, e.g. in-use stock, landfill, soils, and sediments. Values in these stocks are given to represent the current status of ENM accumulation in 2014. Colours of flow arrows are only for differentiating flows. The dynamic component, the Release Module, is highlighted with the red dashed line. The dashed lines from Surface water to Sediments or Export indicate worst case scenarios: either the ENM are completely transferred to sediments or are fully stable in water and are carried by water out of the system boundary (exported).

5.3.5 Concentrations

The compartments for which concentrations of ENM are calculated are assumed to be well-mixed and homogenous, although natural and urban soils and sewage sludge treated soils are differentiated. These concentrations are therefore representative for an average hypothetical region as defined in the REACH guidance (ECHA, 2012b). All details about the parameters used are given in the Table A5-4. Table 5-2 shows the predicted ENM concentrations in STP effluent, surface water, STP sludge, air, solid waste entering landfill, solid waste entering WIP, WIP bottom ash and WIP fly ash, as well as accumulated concentrations in sediments, soils, and STP sludge treated soils for the EU in 2014. The values presented are the mean values, mode values, median values and the 15% and 85% quantiles ($Q_{0.15}$ and $Q_{0.85}$) from each distribution. This feature of our results is unique compared to other deterministic models because it allows assessing the range and the likelihood of expected concentrations. In general, for all ENM, the highest concentration is found in STP sludge, followed by solid waste, WIP bottom ash and WIP fly ash. Among the environmental compartments (soil, surface water, air and sediments), sediments had the most considerable concentrations, followed by STP-sludge treated soil, then untreated soil and surface water, followed by air, with the lowest concentration of ENM overall. For soils and sediments, the simulations provided the accumulative amount of ENM deposited in these compartments in since 1990.

In all the compartments considered, nano-TiO$_2$ had far higher concentrations than the other three ENM. This reflects the correlation between the total input production volume and the consequent concentration in different compartments. Sediments, where most ENM entering surface water end up in our worst-case scenario, showed accumulated concentration ranging from 6.7 µg/kg (CNT) to nearly 40'000 µg/kg (nano-TiO$_2$). In most cases the concentrations in WIP materials (solid waste to WIP, WIP bottom ash and WIP fly ash) are at the “mg/kg” level.

Comparing the results for the concentrations of nano-Ag based on the two scenarios with different time scope, the results of the scenario with the time frame “1900-2020” are only slightly higher than the results of the scenario “1990-2020”. For most compartments the difference is less than a factor of two. Larger differences are found in the accumulated amounts in sludge treated soils and sediments.
There, the results from the scenario “1900-2020” are a factor of five larger than that of the scenario of depicting “1990–2020”. Here, certainly the longer accumulation effect plays a role, although historic nano-Ag uses were modelled to be much lower than current ones.

With respect to recycling, unlike previous static modelling studies, we were able to include the fate of ENM during recycling based a recent modelling study of ENM flows during recycling (Caballero-Guzman et al., 2015). Although in reality there may well be ENM in landfill leachates, our model did not take this account due to the insufficient quantitative information that exists on this process. It also needs to be noted that the concentrations in surface water and sediments reflect worst-case scenarios for both compartments. No fate modelling was performed and the water concentrations assume no sedimentation or other losses while the sediment concentrations reflect complete sedimentation from water. However, our flow results can be used as input data for dedicated mechanistic fate models that all rely on accurate predictions of the input flows.

Due to the different dynamic and static modelling concepts applied, it is not really possible to draw a direct comparison between the newly predicted concentrations results with all previous studies (Gottschalk et al., 2009a; Keller et al., 2013; Keller and Lazareva, 2013; Mueller and Nowack, 2008; Sun et al., 2015; Sun et al., 2014c). As stated in the mass flow section above, the previous models distributed the produced mass in one year to the whole system in that year while our dynamic modelling clearly revealed that in-use stocks and delayed releases are highly important and essentially define the system behavior. However, this does not necessarily lead to lower predicted concentrations because releases from previous years are also considered and in some cases may dominate the flows. Similar concentrations in 2014 predicted by static and dynamic models may therefore by chance have the same magnitude. Extending the simulation time will reveal larger and larger differences between the two approaches due to additional releases from stocks.

The values presented in Table 5-2 include both the uncertainty in some of the parameters as well as the variability that is caused by the representation of a range of different forms of an ENM (e.g. coatings, functionalization), which are subsumed under the label of a generic ENM, e.g. nano-TiO$_2$. In our approach, single numbers are treated with a deviation factor of two and with triangular distributions. Data for which a range is given are treated with uniform distributions. Normal and other distributions are used alone or combined in accordance to available data. This treatment of the available data allows us to consider for each parameter the knowledge that is available by including always the specific uncertainty associated with each parameter.

The major purpose of the dynamic modelling is to track the historical concentrations and project the future concentrations of ENM in accumulative compartments. Therefore, besides the ENM concentrations predicted for the year 2014, we also provide the concentrations in 2020 in Table A5-5. Additionally, predicted evolutions of ENM concentrations in major compartments are provided in
Figure 5-3d and Figure A5-2d. These predictions are based on the combined estimates of different market research companies and are grounded in the increase in the market in the last years and are probably valid if the technology continues to develop as it does today.
Table 5-2: Predicted (Accumulated) concentrations of nano-TiO₂, nano-ZnO, nano-Ag and CNT in waste streams and environmental compartments in the EU in 2014. Mean, mode, median and 15% and 85% quantiles are presented for both the time intervals of the 1900-2020 and 1990-2020 scenarios.

<table>
<thead>
<tr>
<th>Material</th>
<th>EU (2014)</th>
<th>Mean</th>
<th>Mode</th>
<th>Median</th>
<th>Q₀.₁₅</th>
<th>Q₀.₈₅</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nano-TiO₂</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STP Effluent</td>
<td>44.4</td>
<td>13.7</td>
<td>16.3</td>
<td>2.77</td>
<td>76.1</td>
<td>µg/L</td>
</tr>
<tr>
<td>STP sludge</td>
<td>1.60</td>
<td>0.471</td>
<td>0.841</td>
<td>0.155</td>
<td>3.42</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Solid waste to Landfill</td>
<td>12.9</td>
<td>7.67</td>
<td>10.3</td>
<td>5.37</td>
<td>21.3</td>
<td>mg/kg</td>
</tr>
<tr>
<td>Solid waste to WIP</td>
<td>10.3</td>
<td>6.19</td>
<td>7.93</td>
<td>4.24</td>
<td>16.9</td>
<td>mg/kg</td>
</tr>
<tr>
<td>WIP bottom ash</td>
<td>395</td>
<td>161</td>
<td>237</td>
<td>93.6</td>
<td>729</td>
<td>mg/kg</td>
</tr>
<tr>
<td>WIP fly ash</td>
<td>543</td>
<td>238</td>
<td>327</td>
<td>129</td>
<td>979</td>
<td>mg/kg</td>
</tr>
<tr>
<td>Surface water</td>
<td>2.17</td>
<td>0.607</td>
<td>1.10</td>
<td>0.191</td>
<td>4.40</td>
<td>µg/L</td>
</tr>
<tr>
<td>Sediment</td>
<td>43.1</td>
<td>30.0</td>
<td>38.7</td>
<td>21.3</td>
<td>65.0</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Natural and urban soil</td>
<td>2.94</td>
<td>1.86</td>
<td>2.57</td>
<td>1.44</td>
<td>4.53</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Sludge treated soil</td>
<td>61.1</td>
<td>40.8</td>
<td>54.6</td>
<td>30.9</td>
<td>93.3</td>
<td>mg/kg</td>
</tr>
<tr>
<td>Air</td>
<td>2.05</td>
<td>0.858</td>
<td>1.235</td>
<td>0.429</td>
<td>3.98</td>
<td>ng/m³</td>
</tr>
<tr>
<td><strong>Nano-ZnO</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STP Effluent</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>µg/L</td>
</tr>
<tr>
<td>STP sludge</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Solid waste to Landfill</td>
<td>1.69</td>
<td>0.959</td>
<td>1.21</td>
<td>0.520</td>
<td>2.64</td>
<td>mg/kg</td>
</tr>
<tr>
<td>Solid waste to WIP</td>
<td>1.27</td>
<td>0.641</td>
<td>0.86</td>
<td>0.342</td>
<td>2.04</td>
<td>mg/kg</td>
</tr>
<tr>
<td>WIP bottom ash</td>
<td>6.43</td>
<td>3.13</td>
<td>4.10</td>
<td>1.49</td>
<td>10.2</td>
<td>mg/kg</td>
</tr>
<tr>
<td>WIP fly ash</td>
<td>12.2</td>
<td>4.85</td>
<td>7.32</td>
<td>2.16</td>
<td>20.8</td>
<td>mg/kg</td>
</tr>
<tr>
<td>Surface water</td>
<td>0.376</td>
<td>0.161</td>
<td>0.227</td>
<td>0.046</td>
<td>0.641</td>
<td>µg/L</td>
</tr>
<tr>
<td>Sediment</td>
<td>6.97</td>
<td>4.95</td>
<td>6.26</td>
<td>3.64</td>
<td>10.5</td>
<td>mg/kg</td>
</tr>
<tr>
<td>Natural and urban soil</td>
<td>1.82</td>
<td>1.01</td>
<td>1.52</td>
<td>0.738</td>
<td>2.96</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Sludge treated soil</td>
<td>1.82</td>
<td>1.01</td>
<td>1.52</td>
<td>0.738</td>
<td>2.96</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Air</td>
<td>0.940</td>
<td>0.388</td>
<td>0.475</td>
<td>0.081</td>
<td>1.67</td>
<td>ng/m³</td>
</tr>
<tr>
<td><strong>Nano-Ag (1990-2020)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STP Effluent</td>
<td>2.53</td>
<td>0.946</td>
<td>1.22</td>
<td>0.293</td>
<td>4.60</td>
<td>ng/L</td>
</tr>
<tr>
<td>STP sludge</td>
<td>64.2</td>
<td>18.3</td>
<td>35.4</td>
<td>6.73</td>
<td>128</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Solid waste to Landfill</td>
<td>84.0</td>
<td>39.0</td>
<td>55.0</td>
<td>20.5</td>
<td>152</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Solid waste to WIP</td>
<td>20.7</td>
<td>11.0</td>
<td>15.1</td>
<td>7.42</td>
<td>35.3</td>
<td>µg/kg</td>
</tr>
<tr>
<td>WIP bottom ash</td>
<td>173</td>
<td>113</td>
<td>146</td>
<td>79</td>
<td>209</td>
<td>µg/kg</td>
</tr>
<tr>
<td>WIP fly ash</td>
<td>349</td>
<td>190</td>
<td>268</td>
<td>116</td>
<td>578</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Surface water</td>
<td>1.60</td>
<td>0.673</td>
<td>1.06</td>
<td>0.446</td>
<td>2.94</td>
<td>µg/L</td>
</tr>
<tr>
<td>Sediment</td>
<td>30.6</td>
<td>26.5</td>
<td>28.6</td>
<td>18.1</td>
<td>43.8</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Natural and urban soil</td>
<td>0.020</td>
<td>0.014</td>
<td>0.018</td>
<td>0.011</td>
<td>0.029</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Sludge treated soil</td>
<td>2.36</td>
<td>0.680</td>
<td>1.89</td>
<td>0.451</td>
<td>4.31</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Air</td>
<td>0.011</td>
<td>0.004</td>
<td>0.007</td>
<td>0.003</td>
<td>0.020</td>
<td>ng/m³</td>
</tr>
<tr>
<td><strong>Nano-Ag (1900-2020)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STP Effluent</td>
<td>4.74</td>
<td>1.80</td>
<td>2.56</td>
<td>0.664</td>
<td>8.12</td>
<td>ng/L</td>
</tr>
<tr>
<td>STP sludge</td>
<td>59.4</td>
<td>21.0</td>
<td>33.7</td>
<td>8.03</td>
<td>109</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Solid waste to Landfill</td>
<td>82.2</td>
<td>37.6</td>
<td>54.6</td>
<td>25.0</td>
<td>145</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Solid waste to WIP</td>
<td>25.0</td>
<td>15.2</td>
<td>20.1</td>
<td>11.5</td>
<td>40.1</td>
<td>µg/kg</td>
</tr>
<tr>
<td>WIP bottom ash</td>
<td>286</td>
<td>255</td>
<td>266</td>
<td>146</td>
<td>416</td>
<td>µg/kg</td>
</tr>
<tr>
<td>WIP fly ash</td>
<td>572</td>
<td>380</td>
<td>481</td>
<td>201</td>
<td>923</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Surface water</td>
<td>1.52</td>
<td>0.778</td>
<td>1.07</td>
<td>0.481</td>
<td>2.71</td>
<td>µg/L</td>
</tr>
<tr>
<td>Sediment</td>
<td>167</td>
<td>165</td>
<td>164</td>
<td>126</td>
<td>203</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Natural and urban soil</td>
<td>0.067</td>
<td>0.059</td>
<td>0.064</td>
<td>0.045</td>
<td>0.088</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Sludge treated soil</td>
<td>13.1</td>
<td>4.23</td>
<td>10.7</td>
<td>2.84</td>
<td>24.2</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Air</td>
<td>0.010</td>
<td>0.004</td>
<td>0.006</td>
<td>0.002</td>
<td>0.018</td>
<td>ng/m³</td>
</tr>
<tr>
<td><strong>CNT</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STP Effluent</td>
<td>8.58</td>
<td>6.50</td>
<td>7.00</td>
<td>0.925</td>
<td>15.6</td>
<td>ng/L</td>
</tr>
<tr>
<td>STP sludge</td>
<td>326</td>
<td>273</td>
<td>277</td>
<td>33.9</td>
<td>593</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Solid waste to Landfill</td>
<td>1.26</td>
<td>0.716</td>
<td>1.08</td>
<td>0.541</td>
<td>1.99</td>
<td>mg/kg</td>
</tr>
<tr>
<td>Solid waste to WIP</td>
<td>0.98</td>
<td>0.603</td>
<td>0.832</td>
<td>0.419</td>
<td>1.60</td>
<td>mg/kg</td>
</tr>
<tr>
<td>WIP bottom ash</td>
<td>0.433</td>
<td>0.170</td>
<td>0.295</td>
<td>0.089</td>
<td>0.787</td>
<td>mg/kg</td>
</tr>
<tr>
<td>WIP fly ash</td>
<td>0.915</td>
<td>0.304</td>
<td>0.543</td>
<td>0.145</td>
<td>1.74</td>
<td>mg/kg</td>
</tr>
<tr>
<td>Surface water</td>
<td>0.359</td>
<td>0.284</td>
<td>0.298</td>
<td>0.043</td>
<td>0.646</td>
<td>ng/L</td>
</tr>
<tr>
<td>Sediment</td>
<td>6.74</td>
<td>6.34</td>
<td>6.46</td>
<td>4.32</td>
<td>9.24</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Natural and urban soil</td>
<td>35.0</td>
<td>33.8</td>
<td>33.9</td>
<td>23.6</td>
<td>46.2</td>
<td>ng/kg</td>
</tr>
<tr>
<td>Sludge treated soil</td>
<td>11.7</td>
<td>10.2</td>
<td>11.1</td>
<td>7.42</td>
<td>15.8</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Air</td>
<td>0.018</td>
<td>0.014</td>
<td>0.015</td>
<td>0.005</td>
<td>0.030</td>
<td>ng/m³</td>
</tr>
</tbody>
</table>
5.3.1 Considerations for the applicability of model results

The concentrations that we provide for the technical compartment, e.g. wastewater, sludge or bottom ashes, can be used as input values for more sophisticated environmental fate models that incorporate a mechanistic description of fate processes, e.g. agglomeration and sedimentation. Praetorius et al. for example used the ENM mass flow to natural waters from Gottschalk et al. (2009a) as input to their mechanistic river fate modelling of nano-TiO$_2$ (Praetorius et al., 2012). Also, Gottschalk et al. (2011b) used the release from wastewater as input for a local modelling study with high spatial resolution of ENM within the Swiss river network. In another example using the same dataset, Dumont et al. (2015) used for their spatial modelling on ENM in European watersheds. Meesters et al. (2014) took the emissions data to air, water and soils from the Mueller and Nowack (2008) mass-flow model as their SimpleBox4Nano model input. Liu et al. (2014) used the ENM emission results from Gottschalk et al. (2009a) and Keller et al. (2013) as input data for their MendNano fate model. This list exemplifies that the data provided by mass flow models are absolutely crucial for the fate models to come up with correct environmental concentrations as they all rely on mass inputs into one or several environmental compartments. Clearly the to date most reliable and accurate results modelled here by incorporating the true situations of ENM accumulation and release constitute the fundamental input information for realistic concentrations results by environmental fate models.

The concentrations in natural compartments, although based on worst-case assumptions such as no/complete sedimentation or no further dissipation from soils and sediments, provide ecotoxicologists and risk assessors with crucial exposure data needed for first ecological risk assessments. As long as analytical chemists are not able to quantify ENM at the natural concentrations and distinguish them from the natural background particles, the modelled concentrations constitute the only source of environmental exposure information that we have available. The modelled concentrations have previously been used to compare the exposure levels used in toxicological studies (Holden et al., 2014) or to perform a full environmental risk assessment based on the comparison of PEC values with NOEC values (no observed effect concentrations) extracted from the ecotoxicological literature (Gottschalk et al., 2013a). These assessments rely on the provision of accurate environmental exposure data and our dynamic modelling is able to provide the most realistic and accurate numbers on flows and accumulated amounts in sinks.
5.4 Acknowledgements

The authors would like to thank Prof. Dr. Martin Scheringer for valuable discussions on the manuscript. The authors would also like to thank Dr. Denise Mitrano for reviewing the manuscript and improving the English. Tian Yin Sun was supported by project 406440_131241 of the Swiss National Science Foundation within the National Research Program 64. Nikolaus A. Bornhöft was supported by the European Commission within the Seventh Framework Programme (FP7; MARINA project - Grant Agreement n° 263215).

5.5 Supporting information (Appendix 5)

More detailed information about the estimation of ENM production development, ENM release dynamics from product is provided in the Appendix 5.
5.6 References


(26) Friend of the Earth Europe. Less is More, resource efficiency through waste collection, recycling and reuse of aluminium, cotton and lithium in Europe; 2013.


(32) EEA. EU as a Recycling Society Present recycling levels of Municipal Waste and Construction & Demolition Waste in the EU Copenhagen: European Topic Centre on Sustainable Consumption and Production; 2009.


6 CONCLUSIONS & OUTLOOK

6.1 Analytical approach vs modelling approach: does a validation make sense?

A validation of a model by analytical data is often and generally called for to check whether the model is accurately capturing the main aspects of the system or if significant deficiencies in the model exist (Nowack et al., 2015). Unlike for many other modelling works, it is not readily to compare the results generated by the MFA modeling for ENM with the results from analytical studies. As stated in a previous comparative review of modelled and measured values by Gottschalk et al. (2013b), modelled and measured concentrations are hardly comparable due to the different underlying assumptions in the models or the different measurement techniques. These assumptions eventually determine what exactly the modelling or analytical approaches are targeting.

![Figure 6-1: Spectrum of modelled and measured environmental concentrations of nanomaterials. In addition to engineered nanomaterials (ENM) measurements refer also to bulk derived NM (nanosized-fraction of pigments), combustion-generated NM and natural NM. The ENM-fraction consists of agglomerates in the nano-range (that are measured by the analytical methods) and larger agglomerates (that are not detected). Source: (Gottschalk et al., 2013b)](image_url)

Another study discussing the mutual validation of modelling and analytical studies by Nowack et al (2015), emphasized again that when attempting to validate modelling results, there is a need to
consider the presence of large concentrations of natural NMs in samples and methodological shortcomings in the current analytical methods to quantify all ENM forms, especially those bound to larger particles. The issues are explained with the help of Figure 6-1. The modeling predictions of ENM have in most cases targeted the primary particles and did not distinguish between single and agglomerated particles even if the agglomerates were much larger than 100 nm. This could potentially be an important omission or over simplification. We would therefore expect that modeled concentrations of ENM are higher than measured ENM concentrations, especially if the analytical procedure involved a size fractionation step. On the other hand, modelled concentration could possibly overestimate the environmental concentrations of nanomaterials remaining in their initial form. A critical review (Isaacson et al., 2009) of the quantitative analysis of ENM showed that under natural conditions only a small part of ENM can persist in the environment, transformation reactions rapidly change the initial form of the ENM. ENM only constitute a portion of the nanomaterials existing on earth. Conventional materials produced in high production volumes such as pigment TiO$_2$ may contain a nano-sized fraction. The measured results from environmental samples often indicate often not only the ENM but also naturally occurring nanomaterials (NMs), unintentionally produced NMs by human actions as well as the bulk derived NM which has been found for instance in pigment-TiO$_2$ (Weir et al. (2012)). All these factors make the concentrations results approached by analytical and modelling methods hardly comparable.

Although using modeling and analytical measurements to validate the other is not always possible, both modelling and analytics provide an orthogonal view on nanomaterials. Modelling can provide estimates of the presence of ENM and analytics can provide estimates of the total NM concentration and their characterization. In the current state of the science, the results from the models and the available analytical data both provide the necessary information to obtain an up-to-date view on exposure of NMs and ENM in the environment (Nowack et al., 2015).

6.2 MFA as tools to tackle the problem: strength and limitations

6.2.1 The ability of addressing uncertainty, variability and the inherent flexibility of the MFA models

From the first life-cycle concept based MFA with deterministic scenarios (Mueller and Nowack, 2008) to the P-MFA (Gottschalk et al., 2009) and to today’s DP-MFA, the development of MFA for ENM’s environmental exposure assessment has been rigorous. As shown in this thesis, MFA together with EFM constitutes an indispensable part of the overall toolset to assess environmental risks of nanomaterials. The stochastic property of the general P-MFA models coupling uncertainty analysis, Monte Carlo simulation, Bayesian and Markov Chain modelling that has been used and further developed at Empa, adequately handles the problem of the distinct lack of model input data today. The inclusion of the latest information on ENM production, behaviors in technical and environmental
compartments, and the more comprehensive description of the ENM distribution during technical processes such as in STP and WIP enabled a “complete” presentation of the whole transfer routine of ENM post release from products. The further application of P-MFA to GNP used for future medical purpose proves that P-MFA can be easily adapted to other ENM and regions, and can even be applied in a prospective way once requested data are in hand. The extended P-MFA model developed for and applied in South Australia includes a temporal modelling of ENM production and biosolids handling and transfer onto soils. The model is thus not only able to incorporate the uncertainty in ENM flows but also the spatial and temporal variability of ENM concentrations in a given time range.

6.2.2 The fully dynamic features of DP-MFA

Being the major objective of this thesis, a full dynamic probabilistic materials flow model was developed. The dynamic nature of the DP-MFA model encompasses the inclusion of not only the periodic production input (input dynamics) into the systems studied but also the concept of time dependent ENM release kinetic (release dynamics) from products (in-use stocks). The importance of releases from in-use stocks justifies the need for a dynamic modelling of ENM, because flows into a certain product category are split into stocked and released amounts. Conceptually, the new dynamic model is different from previous static models in which production in one year was completely distributed to the environment, an assumption that the dynamic modelling has clearly shown to be not representative for the ENM investigated. This makes the dynamic model much more sophisticated and of higher accuracy. Therefore, the applicability of the modelled results for EFM is highly raised in this new approach. In general, it can be summarized that the developed DP-MFA possess an adequate capability to cope with uncertainty and variability associated with model parameters in the case of distinct lack of information; it is also fully flexible and robust to include other aspects (e.g. spatial resolution, temporal changes of waste handling regulations or technical changes) needing to be addressed and can be easily adapted and extended to other materials and regions that undergo different processes and routines.

6.2.3 Limitations of the current model

When comparing the DP-MFA to the previous generations of static MFAs and to other de-terministic MFAs, it is obvious that it is a very advanced tool to model environmental emissions of ENM. However, the discussion of its limitations is essential to ensure a good scientific use of the simulation outputs and to discuss the requirements for improvements to provide more accurate results in the future. There are a few main limitations within the presented DP-MFA approach.

First of all, the general MFA approach including DP-MFA considers all different forms of an ENM (e.g. coatings, functionalization) together and thus provides information for a generic ENM, e.g.
“nano-TiO$_2$”. Differentiation of ENM into categories according to different properties e.g. size, coatings, or morphology is missing in the current approach.

Secondly, although the dynamic feature takes into account the annual ENM production development, the technology changes over time are not considered. Currently it is assumed that the shares and applications of ENM in different products remain the same as they were in 2012.

Moreover, very often in the current modeling, a certain region, e.g. the EU, is treated as being homogeneous with respect to production, use and waste handling and no local specific technological and regulatory information is taken into account which is particularly important in the waste stream sector.

Furthermore, although some experimental data of kinetics of ENM release from products are available, which constitute one of the two most important pieces of information for dynamic modelling, the available information is limited to a few ENM such as nano-TiO$_2$ and nano-Ag. Even for those two ENM, the availability of data is solely restricted to the applications of paints and textiles.

Last but not least, although in reality there may well be ENM in landfill leachates, our model did not take into account this possibility due to the insufficient existing quantitative information on this process.

### 6.3 Environmental implications of the modelled output

With respects to the environmental implications of the modelled PEC of the ENM studied, based on the comparison between PEC and the measured background concentrations of the conventional materials as well as the comparisons between PEC and species sensitivity distributions, we conclude that:

- Measured background concentrations of conventional materials of ENM are often several orders of magnitude higher than that of ENM (Sun et al., 2015; Sun et al., 2014b).
- Based on the current knowledge of ecotoxicity of ENM, no environmental risk is expected (Coll et al., 2015; Mahapatra et al., 2015).
- The concentrations that we provide for technical compartments, e.g. wastewater, sludge or bottom ashes, can be used as input values for more sophisticated environmental fate models that incorporate a mechanistic description of fate processes (Dumont et al., 2015; Gottschalk et al., 2011; Liu and Cohen, 2014; Meesters et al., 2014; Praetorius et al., 2012). Our to-date most reliable and accurate results modelled here by incorporating the dynamics of ENM accumulation and release constitute the fundamental input information for environmental fate models.
- The concentrations in natural compartments, although based on worst-case assumptions such as no/complete sedimentation or no further dissipation from soils and sediments, provide ecotoxicologists and risk assessors with crucial exposure data needed for first ecological risk assessments. As long as analytical chemists are not able to quantify ENM at the natural
concentrations and distinguish them from the natural background particles, the modelled concentrations constitute the only source of environmental exposure information that we have available.
6.4 Outlook

As discussed above, although the DP-MFA up to today is already a very capable and comprehensive tool to address the issues of estimation of emissions and environmental concentrations of ENM in a more realistic manner, there are still a few of open points that can be addressed for a better prediction of flows and concentrations.

The conclusions regarding the future work are the following:

- To obtain comprehensive data for model parameterization is an arduous process. Insufficient data is not just a challenge of today, but it is also foreseen that even in the future a distinct lack of data will remain. Using probability distributions to represent limited available and often conflicting data has been proven to be a very effective approach to tackle this challenge as shown in the series of studies using P-MFA (Gottschalk et al., 2013a; Gottschalk and Nowack, 2013a; Gottschalk et al., 2009; Sun et al., 2015b; Sun et al., 2014). However, the determination of specific probability distributions for each parameter is laborious. The determination has to consider both the inherent properties of the parameters and to evaluate the available data. The properties of the parameters define their value and their variability. In terms of the parameters value, these can be either absolute values or fractional values (0 to 1). Likewise, the variability of the parameters can be expressed with only a single (true) value or with variant true values. Currently treating the available data set case by case is not done according to a systematic principle nor is it ensured that always a consistent handling for the same kind of data is made. Therefore, a generic guidance is required to facilitate a systematic decision on determining probability distribution when facing an available data set for a parameter. Single or combined approaches of data fusion (Castanedo, 2013; Destercke et al., 2009; Smets, 2007), assignment of degree of belief or belief function (Smets, 2005) or Bayesian updating (Gelman et al., 2013) can be used for formulating a specific probability distribution. A well explained and organized document would help not only the reader to understand the method part better, but would also help the modeller selecting a distribution in a consistent and systematic way.

- In general, the PEC predicted by DP-MFA are for well-mixed and homogenous regions; these concentrations are representative for an average hypothetical large region as defined in the REACH guidance. But in fact PEC can vary a lot between specific regions; sometimes the magnitude of this difference can even be larger than the uncertainty associated with the parameters data. This has been shown in chapter 4 of this thesis to be the case for South Australia. An effective risk assessment requires not only a generic big picture such as the average PECs representing the general level of ENM in a given region, but also site-specific information. A better spatial resolution of PECs requires a better understanding of the local
practices with regards to ENM production and use and the technical and regulatory handling of waste streams. For instance, nano-ZnO is prohibited in some European countries in cosmetics and thus the significant release from that product category will not exist in these regions. The treatment of solid waste in the EU varies a lot between nations (EEA, 2013) and consumer behavior and habits in Mediterranean countries such as Greece, Spain and Italy are certainly different to those in inland countries such as Germany, Poland, or Austria. A generic handling of the EU as a whole, disregarding the diversity in terms of country specific policies, life styles, and technological development, will affect the final ENM distributions. Furthermore, the ENM relevant policies together with the waste handling policies change over time in a dynamic process rather than being constant, as shown in Figure 6-2 for the changes in the waste handling system over time. A more accurate dynamic modelling also need to take this aspect into account in order to represent the reality, because the output flows from these different waste treatment processes lead to totally different emissions, for instance to air.

Figure 6-2: Municipal waste treatment by type of treatment, EU-27, (kg per capita), 1995 - 2013. (Eurostat, 2015)

Currently in the DP-MFA approach the share of ENM applied to different product categories over time is kept constant as it was in 2012 (Sun et al., 2014) for both retrospective and prospective modelling. The life cycles of products are critical factors determining the release scenarios of ENM and therefore the share of ENM allocated to a product category determines to a large extent the final ENM emission to a particular environmental compartment. For instance, ENM applied in cosmetics mainly flow to wastewater and are then mostly captured
in STP and eventually end up in biosolids (to soils or WIP) and STP effluent (to surface water), while the ENM applied on metal as coating will finally come to an end in recycling. Nanotechnology has been one of the most innovative and rapidly developing fields in the past decades. This can be seen from the increasing and diversifying list of products registered in inventories (WWI, 2013) and also from the development of nanotechnology related patents (Chen et al., 2013; Chen et al., 2008; Dang et al., 2010). Simply assuming a constant technology status over time will substantially dismiss a crucial factor that will have a large influence on determining the ENM flows from consumption to technical and environment compartments. This is particularly relevant in a dynamic modelling approach in which the temporal flows to and/or accumulated in compartments are subject not only to the current immediate ENM release but also to the ENM accumulated in the in-use stock from previous years. This is already shown in chapter 5 of the DP-MFA study. Therefore, more investigations about technological changes with regards to ENM applications need to be included in modelling for a true representation of the dynamic system.

Another current simplified assumption made in the DP-MFA model is that aggregation and agglomeration of ENM during release to the environment are not taken into account, although chemical transformations of ENM (in this regard ENM lose their initial nano property and chemical composition e.g. CNT changed to CO$_2$ due to combustion or nano-Ag changed to Ag$_2$S because of sulfidation) are considered (Sun et al., 2015a). Additionally, the DP-MFA model considers all different forms of an ENM (e.g. coatings, functionalization) together, variants for the same ENM with different characteristics are neglected. Ecotoxicity studies show that the size, coating, and morphology of an ENM all play a strong role in determining its toxic effects (Johnston et al., 2010). We have to raise the question about the need to model explicitly all different ENM species compared to just modelling an average ENM, so the justification for scientific models with a rigorous description of all processes compared to simpler models relevant for risk assessment. The explicit description of all ENM species would also facilitate the coupling of MFA and EFM. Eventually the models used for risk assessment should contain a level of detail needed in the risk assessment process and have to be compatible to the hazard data generated in ecotoxicological studies. Similarly, the detailed reporting of the properties of the ENM while conducting ecotoxicological experiments should be also requested or encouraged. In this way, the PECs and hazard data can find a valid comparison focusing on the same target in order to enable a meaningful environmental risk assessment of ENM.
6.5 References


Appendix 1: A Dynamic Probabilistic Material Flow Modelling Method

Nikolaus A. Bornhöft\textsuperscript{a,b}, Tian Yin Sun\textsuperscript{a}, Lorenz M. Hilty\textsuperscript{a,b,*}, Bernd Nowack\textsuperscript{a}

\textsuperscript{a} Empa, Swiss Federal Laboratories for Materials Science and Technology, Lerchenfeldstrasse 5, CH-9014 St. Gallen

\textsuperscript{b} University of Zurich, Department of Informatics, Binzmühlestrasse 14, CH-8050 Zurich
Abstract

Material flow modeling constitutes an important approach to predicting and understanding the flows of materials through the anthroposphere into the environment. The new “Dynamic Probabilistic Material Flow Analysis (DP-MFA)” method, combining dynamic material flow modeling with probabilistic modeling, is presented in this paper. Material transfers that lead to particular environmental stocks are represented as systems of mass-balanced flows. The time-dynamic behavior of the system is calculated by adding up the flows over several consecutive periods, considering changes in the inflow to the system and intermediate delays in local stocks. Incomplete parameter knowledge is represented and propagated using Bayesian modeling. The method is implemented as a simulation framework in Python to support experts from different domains in the development of their application models. After introduction of the method and its implementation, a case study is presented in which the framework is applied to predict the environmental concentrations of carbon nanotubes in Switzerland.

Software Availability

The simulation framework has been made available as software package via PyPI - the Python Package Index: https://pypi.python.org/pypi/dpmfa-simulator
Appendix 1: A Dynamic Probabilistic Material Flow Modelling Method

A 1.1 Introduction

The quantification of the environmental concentration of an anthropogenic pollutant is a crucial step toward the determination of risks for humans and ecosystems emerging from the application of new materials. While direct, quantitative measurements are often not feasible, the representation of material flows that lead to those concentrations provides means for an indirect assessment. The knowledge about these flows is the starting point for multimedia environmental fate models, which regard systems as sets of clearly separated, distinguishable compartments and allow the investigation of material transfers between them (MacLeod et al., 2010). "Multimedia" in this context refers to the fact that multiple environmental media (air, surface water, groundwater, soil) are considered parts of the system under study.

The production of a material, its application and use in different products, and subsequent waste handling are the most important flow processes for assessing the material releases to the environment. However, depending on the particular material and the scope of the study, further aspects such as geographic distribution are taken into account. The material flows along these pathways allow an assessment of the changes in environmental releases and stocks. Adding up these changes over time permits the determination of absolute values for the materials in stock.

Existing mass flow modeling approaches such as material flow analysis (MFA) (Baccini et al. 1991) regard systems of stocks and flows using mass equations to derive dependent system dimensions. They are supported by the software tool Stan (TU Vienna 2012) for general flow modeling purposes and the Umberto software (ifu Hamburg GmbH 2014) for material flows in the area of corporate environmental informatics. These programs (STAN and Umberto) also support uncertainty representation and propagation, but are restricted to a set of given distribution functions. They also support the representation of a system over time. However, the update of the system state is determined by an explicit definition of the flow model for every period and not based on an underlying set of rules (e.g., for the residence times in stocks).

Substantial uncertainties often exist about the volume of a flow, the rates with which the total amount divides into partial flows, and the particular pathways they take. Available data sources may be based on imprecise, incomplete or even contradictory assumptions. The explicit representation of these uncertainties and their propagation through the model can lead to more meaningful simulation results, thus allowing more reliable predictions of the resulting environmental concentrations. Bayesian modeling provides a technique for representing and propagating incomplete system knowledge and translates uncertainty about the true value of a system variable to the model as a probability distribution for the model parameter in question. It represents the modelers’ assumptions about the true value, which can vary both concerning the type and the parameters of the probability distribution. Based on the given distributions, the distributions of the dependent values are then inferred using
Monte-Carlo (MC) simulation. Money et al. (2012) propose a Bayesian network of several stages for forecasting environmental concentrations of nano-particles.

A predecessor of the approach presented in this article, the probabilistic material flow analysis (PMFA) approach, was developed by Gottschalk and colleagues (Gottschalk et al. 2010). They built a flow model that includes a complete assessment of uncertainties in all model parameters. It applies Bayesian modeling to propagate incomplete knowledge about the absolute inflow to the system and the internal dependencies between the downstream flows. Over a large sample size, steady states of flows are calculated, each based on a sampled set of random values. From that the resulting absolute material flows are determined. PMFA has mainly been applied for assessing environmental flows of nanomaterials (Gottschalk et al. 2009, Gottschalk et al. 2010, Gottschalk et al. 2011, Sun et al. 2014).

In order to predict absolute pollutant accumulations in a particular area over time, changes in the inflows to the system (e.g. a varying production volume), local stocks, and temporal delays need to be considered. The simulation method has to investigate the changes in the model dynamically over a longer time span. Müller et al. (2014) performed a survey on dynamic material flow modeling methods in which the uncertainty handling of these methods is investigated as well. While a large share of the methods do not consider uncertainty at all (>50%), there are some that use sensitivity analysis (37 %), Gaussian error propagation (6%) or parameter ranges (5%), but none supports full Bayesian uncertainty representation and propagation.

Dynamic Bayesian networks that are mainly used to learn and reproduce time-dependent system behavior (Daly et al. 2011) process uncertain knowledge in a time-dynamic model. However, this approach focuses on variances in state transitions and does not include flow-specific behavior.

A method for investigating the development of environmental stocks of a pollutant has to:

- represent a system of mass balanced dependent flows,
- consider changing material releases and intermediate delays in local stocks over a significant time horizon, and
- provide means to represent and process incomplete parameter knowledge.

In (Bornhöft et al. 2013) we investigated several existing methods regarding their capabilities for meeting these requirements in more detail and revealed that no existing method fulfills these requirements.

In the present article, we present a modeling approach that merges the advantages of the existing techniques of probabilistic material flow modeling with the existing approaches to dynamic material flow modeling. The combined method forms the basis for a software framework that supports the development, implementation, and simulation of dynamic probabilistic material flow models. We will describe how we implemented this framework as a software package using the Python language.
Appendix 1: A Dynamic Probabilistic Material Flow Modelling Method

(Python Software Foundation 2014) to support experts in building specific models in their field of application.

Finally, we will demonstrate the application of the framework using a realistic case study. This case includes the implementation of a model to investigate the system of flows of engineered Carbon Nanotubes (CNT) in Switzerland. Due to their toxic properties to humans and ecosystems, CNTs pose potential risks (Savolainen et al. 2010). Sun et al. (2014) presented a steady-state model to assess the inflows to different environmental compartments based on data for the year 2012. However, CNTs are very stable and accumulate in the environment over time. Moreover, they are usually applied in products with long life-times, which leads to significant material amounts bound in use-stocks. A dynamic model is therefore needed to provide a more detailed and adequate system representation. Based on this example application, the new approach is discussed in more detail regarding general functionality and its opportunities and limitations.

A 1.2 Description of the method

We propose a new method that combines the advantages of the existing approaches to probabilistic and dynamic material flow modeling: dynamic probabilistic material flow analysis (DP-MFA). It aims to close the gap in existing techniques for exposure assessment by providing a method that models and simulates systems of complex, dependent material flows, considers the dynamic behavior of the system over time, and explicitly represents and propagates incomplete parameter knowledge.

In a first step, the main idea of the approach is outlined, describing the basic structure of the models and the simulation processes and how the elements of the previously introduced modeling methods are combined. The implementation of the framework as a software package in Python is described on that basis in a second step.

Each DP-MFA model is an abstraction and idealization of an original system of flows in the technosphere and the ecosphere. The model is reduced to the parts and aspects that determine the behavior investigated. In accordance with the scope of the simulation study the system is first subdivided into a set of compartments. They constitute the static model structure and structure the system into spatially or logically separated units (e.g., as in Figure A1-1). The actual breakdown depends on the objective and the scope of the study. All material inflows, transfers, accumulations, and releases refer to these compartments.
Simulation experiments need to be performed with the model to assess material stocks and flows over time. Based on the results of these experiments, conclusions about the processes of the original system are drawn. The general simulation mechanism for investigating the flows between the compartments is structured as a 3-layer process (see Figure A1-2). On the first – the Bayesian – layer, parameter uncertainty about the flow dependencies between the system compartments and the absolute annual inflow is represented by Bayesian probability distributions. These uncertainties are then propagated through the model for the entire simulation time using Monte-Carlo techniques.

The second layer refers to the time-dynamic model behavior. Time is represented as a sequence of successive periods (usually years). For each period within the time horizon of the simulation, the external inflows to the model, the material accumulation in stocks, and their local material releases are determined and added up.

To enable this, the third layer provides a mechanism that calculates the absolute material flows for a period based on absolute material releases and the flow matrix, taking all transfer dependencies into account.

**Figure A1-1: Pathways of material flows of anthropogenic pollutants from the technosphere via different product categories, waste incineration and sewage treatment plants to the ecosphere.** Specific system compartments and flow dependencies need to be implemented for each particular material and scope.
A 1.2.1 Static structure

The static structure of the model consists of a set of persistent entities. They represent the local behavior of the compartments and are assembled to derive the aggregated system behavior. The basic model components are stock, flow and sink compartments and external inflows.

- A stock compartment is a component with a temporary total or partial material accumulation and later re-release of the material.
- A flow compartment is a component where a flow is split up into several partial flows without a delay of the material transfer.
- A sink compartment is a component with permanent material accumulations.
- An external inflow is a source that implies a time dependent exogenous input to a stock or flow compartment (e.g., through production or import).

The dynamic model behavior emerges from the interplay of these static components over time.

A 1.2.1.1 Material flows

The calculation of absolute values for the material transfers is derived from existing material flow analysis approaches. It represents the material flows of one period as immediate and simultaneous. While exogenous inflows to the system are defined as absolute material inflow values to a compartment, endogenous flows from a compartment are defined as transfer coefficients (TC). The transfer coefficient $T_{Cjs}$ defines the relative mass flow $m$ from compartment $j$ to $s$ as proportion of the sum of all inflows to compartment $j$ (Equation 1).
To determine the absolute flows of the model, all transfer coefficients are aggregated to the flow matrix $A$ (Figure A1-3). The flow rates from one compartment to another are read diagonally from top to left. The compartments $C_1$ to $C_m$ represent immediate flow dependencies, $C_{m+1}$ to $C_n$ sinks. The absolute material inflows to the system are expressed as an input vector $I$ (Figure A1-4). It comprises the sum of the external inflows and the releases from the model stocks for all compartments 1 to n. Solving the System $AX = I$ for an unknown column vector $X$ leads to a steady state of flows. The column vector $X$ determines the inflows to the compartments with which the stocks are incremented. If the sum of each column of a flow compartment in the coefficient matrix is zero and the entire inflow is allocated to the sink columns as a non-zero value, the system is mass-balanced. All material inflows are distributed to the sinks based on the relative local flow dependencies.

$$TC_{js} = \frac{m_{js}}{\sum_r m_{rj}} \quad \text{Eq. [1]}$$

**Figure A1-3:** Flow dependencies between the model compartments $C_1$ to $C_n$ (read as flow from top to left) as flow matrix $A$.

$$I = \begin{pmatrix} g_1 \\ g_2 \\ g_3 \\ \vdots \\ g_n \end{pmatrix}$$

**Figure A1-4:** Input vector $I$; the elements $g_1$ to $g_n$ represent inflows to the compartments $C_1$ to $C_n$. 
A 1.2.1.2 Flow Compartments

In the model, the relative transfer dependencies are bound to flow compartments, which represent points in the system where material flows are gathered and split up. Several transfers can be bound to one flow compartment. Each transfer includes a target compartment and a transfer coefficient.

To ensure the equilibrium of the flows of the system, the local in- and outflows of a compartment need to be balanced – which implies that the transfer coefficients of the outflows from each compartment have to sum up to 1. This constraint allows deriving some of the dependent transfer coefficients under large uncertainties from TCs about which more reliable information is available.

A 1.2.2 Time-dynamic behaviour

Time advancement is represented in the model as a series of subsequent periods of equal length. At the end of each of these periods, the model state is updated with the flows of the respective period as follows:

- First, the external inflows and the material releases from stocks are determined.
- Based on this input the flow matrix is solved.
- Then the stocks and sinks are incremented with their particular inflows.

Once the model is simulated over the required time interval, the total material in a sink at the end of this interval can be predicted.

A 1.2.2.1 External inflows

Exogenous material inflows to the system are defined as absolute material inputs for a particular system compartment and period. A time dynamic development of these inflows is either represented by a list defining an input volume for each period or as a function of time over all periods.

A 1.2.2.2 Stock compartments

Stock compartments represent system areas through which the material flows are non-immediate. They act as sinks in one period and later release the material again, either in one period, or distributed over several future periods. The distribution among the other model compartments is defined in the same way as in flow compartments – as a set of transfers. However, including both immediate and delayed material transfers from the same compartment, a stock can partly act as a flow compartment for the material share immediately released and as a source to the flow system for the material releases in subsequent periods. As for transfers from flow compartments, the sum of the relative outflows from stocks has to be one in total to ensure the mass balance.

The internal structure of a stock includes several elements:
• an inventory that keeps track of the stocked amount,
• a release list with the times and amounts of material releases,
• a release strategy consisting of rules for the residence times of newly stocked material and the proportions of future releases at various points in time,
• a set of transfer objects defining target compartments and rates from the total release,
• and an internal flow compartment for the share that is released immediately.

At the beginning of each period, the material releases from the stocks are determined from the internal release list. The inventory of the stock is reduced by that value. Based on the rates defined in the transfer objects, the release is distributed to the particular target compartments and added to the respective positions of the model input vector.

During the calculation of the immediate flows of a period, the stock acts as a flow compartment for the share that is transferred without delay. Its transfer coefficients for the proportion of the immediate material release are included in the flow matrix of the model and taken into account in the calculation of the absolute material flows.

After the determination of the absolute flows of a period, the material amount in the stock is incremented by its particular inflow. Based on the point in time of the material input and the relative resident times and release proportions, absolute points in time and amounts are calculated and scheduled by adding them to respective target period of the release list.

A 1.2.2.3 Uncertainty representation and processing

Incomplete knowledge about the system primarily concerns the point in time, the location and the extent of a flow. Our method considers epistemic uncertainty about the absolute inflows to the system and the relative allocation of subsequent flows is represented as the marginal distribution for the model parameter and propagated using Monte-Carlo simulation. With that, simulation results for dependent model variables such as the material amount in a stock during a certain period are derived as a sample of values, which are further statistically evaluated.

The marginal distributions are either regarded as parametric distribution functions or as non-parametric distributions. Depending on the origin of the available data, there may by samples from direct observations, results of previous simulation steps, or probability distribution functions representing the assumed characteristics of the distribution. Since it is possible to sample random values from either variant for the Monte-Carlo simulation, both are suitable for representing uncertain knowledge about absolute inflows and transfer coefficients in the model.

The representation of uncertainty in transfer coefficients and external inflows has some important characteristics. For modeling TCs the mass balance of the system needs to be preserved. While in a
deterministic mass balanced flow model the sum of the outgoing TCs from one flow compartment or stock have to sum up to 1, in the probabilistic case the marginal distributions for the model parameters have to be chosen in such a way that their expected values sum up to 1.

Moreover, in the simulation process, dependent random values are adjusted after sampling to avoid combinations violating mass balance constraints. The modeler can choose to do so either by a normalization factor over all involved TCs or – in the case of transfer coefficients from underlying information of strongly differing reliability – by defining an order of priority to first adjust the parameter values based on the least reliable data.

The external inflow to a particular compartment over time can be represented either as a list of single probability distributions for each period, or by one marginal distribution representing an uncertain base value and a deterministic growth function. The two variants imply different underlying assumptions. The use of a common base value for all periods emphasizes the inter-periodic dependencies while the absolute value is not exactly known. Expressed as a list of single inflows, the random samples for the periods are assumed to be independent. They implicitly show variant behavior and increasing degrees of freedom of the model with the number of simulated periods and thus a growth of the complexity of model behavior for longer time spans.

A 1.3 Implementation of the method

Based on the DP-MFA Method a software framework was developed to support the design and use (i.e., the simulation) of Dynamic Probabilistic Material Flow Models. It is designed as a Python (2014) package and utilizes the SciPy library (Jones et al. 2001) for statistical computation and in particular the NumPy package (van der Walt et al. 2011) for matrix representation and calculation.

The program package implements the principle of separation of model and experiment (Page et al. 2005). At its core, it provides the infrastructure to perform simulation experiments using the Simulator class. This class is provided as a black-box component and is used unchanged by a modeler working with the package. The modeler implements the system-specific logic by assembling predefined components. These are provided as white-box components that the modeler has to adapt to fit the particular behavior of the system under study.

A 1.3.1 Simulator

The Simulator performs experiments to generate and evaluate the Model behavior. As part of the simulation process – as described by our overall simulation algorithm above (Fig. 2) – the model parameters specified under uncertainty are assigned random values from the underlying Bayesian probability distributions. Statistical evaluations of the observations over sufficiently large sample
sizes approximate the distribution of the variables under the assumptions of the marginal distributions. For each of these parameter sets, the model is simulated over the total investigated time span.

In an iteration over all periods, the Simulator determines the external inflows to the system and the local inflows from the stocks. These flows are then distributed to the different model compartments by solving the flow matrix of the model – which is aggregated from the internal flow dependencies – with the current inflow vector. Based on the inflows, the model stocks and sinks are updated. During the experiment, the Simulator keeps track of the values of model variables (e.g., the amount of material in a stock).

All of these values are logged in form of a matrix over all samples and periodic values for later statistical evaluation. To facilitate an aggregated evaluation, categories can be assigned to the model compartments. After a simulation experiment is executed, the Simulator provides several functions for a category-based evaluation, e.g., to provide total material inflow or outflow or the total material stocked.

A 1.3.2 Model

The model builder implements a specific simulation model by customizing and combining basic model components:

- **Model Compartments** representing system entities, which all material flows, accumulations, and releases are related to,
- **Transfers** defining the internal, relative flow dependencies,
- **LocalReleases** defining the residence times of materials from Stocks and the release rates, and
- **ExternalInflows** representing exogenous inputs to the system.

An overview of the model structure is shown in Figure A1-5. The Compartments are specified by subclasses. FlowCompartments are branches of a flow within one period; Sinks mark the material accumulation at an endpoint of a flow process, and Stocks represent material flows that are delayed for a particular period of time and later transferred further. Different Transfer types are used to model flow dependencies as relative transfer coefficients to particular subsequent target Compartments. ConstTransfers define deterministic values as transfer coefficients. StochasticTransfer, RandomChoiceTransfer, and AggregatedTransfer use probability distributions to represent incomplete knowledge about the true values of transfer coefficients. Random values are sampled for those Transfers during the simulation process. StochasticTransfers are parameterized with probability distribution functions and respective parameter lists. RandomChoiceTransfers hold lists of values to
randomly draw from. AggregatedTransfers allow weighted combinations of the previously stated Transfers.

All transfers are bound to sources, which can either be FlowCompartments or Stocks. To ensure the mass balance of the system, the local transfer coefficients for the relative outflows from such a source have to sum up to 1. This adjustment step is performed after the random values are sampled from the underlying probability distributions. The modeler can either choose to apply a normalization of the corresponding transfers or to define a prioritization to adjust the random numbers from the least credible underlying data. Combinations of both approaches are feasible as well.

Stocks represent delayed flow processes. The model builder defines their particular release times and rates as LocalRelease strategies. The target compartments and the relative transfer coefficients are defined as Transfer objects the same way as for FlowCompartments. To implement LocalReleases, their subclasses need to be implemented. FixedRateRelease defines constant rates for all following periods, ListRelease an explicit list of all future release rates, and FunctionRelease gives a mathematical function for the particular rates and periods.

ExternalInflows are implemented as ExternalListInflow to define explicit inflow amounts for each period or as ExternalFunctionInflow with a (growth) function on a base value. To define the base value or the individual values for the list, the model builder has to define SinglePeriodInflows. These can be either deterministic FixedValueInflows or a probability distribution function, namely StochasticInflow or RandomChoiceInflow from a given sample.

![UML diagram; composition of the DP-MFA model structure](image_url)

**Figure A1-5: UML diagram; composition of the DP-MFA model structure**

**A 1.4 Application of the method**

The capabilities of the DP-MFA method and the corresponding Python package are illustrated by applying them in an exemplary case study of practical relevance. Here, we modeled the flows of carbon nanotubes (CNT) in Switzerland to predict current and future material stocks in the
technosphere and the environment. This system was previously modeled using MFA (Mueller et al. 2008) and PMFA (Gottschalk et al. 2009, Sun et al. 2014). The investigated flows include the production of the CNTs, their application in different product categories, their release during the life cycles of the products to technical and environmental system compartments, and the subsequent environmental fate, namely their final accumulation as a pollutant.

The model was simulated on a standard laptop\(^3\) with an Intel i5-4200U CPU @1.6 GHz processor and 8 Gb memory.

### A 1.4.1 Static model structure

The basic structure of the model is derived from a steady-state model which we developed to predict CNT flows in Switzerland (Sun et al. 2014). This model includes 31 model compartments and sinks and 80 transfer coefficients. It was originally implemented in the R programming language. From that work we adopted the subdivision of the system into particular compartments and the probability distribution functions which define the transfer coefficients of the flow dependencies between the compartments.

![Inflow to sediment compartment](image)

**Figure A1-6: CNT inflow to sediment compartment in the static model: Density function, mode and mean value of the sample.**

We first re-implemented this static model using our new approach to cross-check the consistency between the two approaches for the static case. To facilitate the cross-check, we created a deterministic version of the model by replacing the parameter distributions with their expectation

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\(^3\) HP EliteBook 840 G1
values and then implemented the deterministic version both in R (as the original model of Sun et al. 2014) and in Python using the new package. With that, it was possible to compare the functionality of the flow calculations of the two implementations.

Then we re-implemented the stochastic version of the original model of Sun et al. (2014) using the new Python package as well to see the influence of the randomness of the underlying probability distributions on the simulation results. For the stochastic version, we used the same probability distributions as Sun et al. (2014) did. We simulated 50'000 runs to reach a sufficient sample size.

Table A1-1 shows the material inflows to the model sinks as simulation results; in columns 1 and 2 for the deterministic versions of the model in R and using the new Python package, respectively, and in column 3 for the probabilistic version.

The agreement between the simulation results was high. Small discrepancies between the two deterministic implementations can be explained by small numerical errors caused by differences in the underlying algorithms, i.e., for solving the flow matrix, or in number representation. But all in all, the two implementations can be seen as almost equivalent. Differences between the deterministic and the probabilistic model can be explained by the stochastic error, introduced by the randomness of the probabilistic model, which is small due to the large sample size.

Table A1-1: Simulation results – model sinks in tons of CNT/year: Comparison of the mean values of the inflows to the model sinks for 2012. The left column shows the results of the deterministic model in R, using the expectation values of the parameter distributions from Sun et al 2014. The middle column shows the results of the same deterministic model implemented using the new simulation package. The right column shows the simulation outcome of the probabilistic version of the model implemented with the new package (mean values).

<table>
<thead>
<tr>
<th></th>
<th>Deterministic model based on (Sun et al., 2014d), implemented in R</th>
<th>Deterministic model, implemented using the new simulation package</th>
<th>Probabilistic model, implemented using the new simulation package (mean values)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elimination</td>
<td>7.83</td>
<td>7.82</td>
<td>7.82</td>
</tr>
<tr>
<td>Landfill</td>
<td>0.96</td>
<td>0.96</td>
<td>0.97</td>
</tr>
<tr>
<td>Soil</td>
<td>0.14</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Sediment</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Cement Plant</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Recycling</td>
<td>3.10</td>
<td>3.10</td>
<td>3.08</td>
</tr>
<tr>
<td>Export</td>
<td>0.87</td>
<td>0.86</td>
<td>0.87</td>
</tr>
<tr>
<td>Sum</td>
<td>12.94</td>
<td>12.94</td>
<td>12.93</td>
</tr>
</tbody>
</table>

In previous works by Gottschalk et al. (2009, 2010, 2011) and Sun et al. (2014), we focused on the mode value to represent a sample by its most probable single value. Here we mainly use the mean value of the sample. This has some advantages because the mean values show a system of balanced
flows. Also, mean values are more robust, especially on small and scattered samples. The computation of a “real” mode value can be performed only for a discrete set of different values. For continuous variables, the maximum of a density function of the sample, such as the Gaussian kernel-density estimator (Scott 1992), are often used instead. Depending on the used estimator and its parameters, different maximum values are chosen. However, both the mean value and the mode value represent only a single aspect of a probability sample (Figure A1-6). For more comprehensive insights, the sample itself or at least several dimensions of it have to be considered.

**A 1.4.2 Dynamic modeling**

We extended the static model to a dynamic one by applying historical production volumes as model inflows for previous periods and projections for future periods. This extension demonstrates the advantage of the DP-MFA package. It enables the assessment of the absolute material amount in a stock from the sum of the preceding material flows.

The modeled time span begins in 2003 to cover the significant time period in which CNT have been applied on industrial scale. The annual production volumes are derived from Sun et al. (2014) and Piccinno et al. (2012). Missing values for past and future periods are estimated using a quadratic regression function (Figure A1-7). To represent uncertainty about the true production volumes, a standard deviation (SD) is assumed that complies with the relative SD in the sample of the system input from the Sun data. This is implemented as ExternalListInflow of single StochasticInflows using normal distributions with a respective parameterization.

CNTs applied in some products have a considerable residence time. This constitutes material stocks with releases after a delay period. Polymer composites, consumer electronics, and automotive have been identified as product categories forming significant intermediate stocks of CNTs (Sun et al. 2014). The delay period of consumer electronics is approximated by a list of relative circulation times of computer notebooks (Stiftung Entsorgung Schweiz et al. 2014) as ListRelease. The mean circulation time in the automotive industry is modeled as a normal distribution with a mean of 11.9 years (Kraftfahrt-Bundesamt 2013) and a standard deviation of 5 years. For polymer composites, a mean delay of 7 years is assumed and approximated by a normal distribution with a mean of 7 and an SD of 3 years. The material releases from both stocks are modeled using a FunctionRelease.
A 1.4.3 Simulation Results

The dynamic model was investigated for the period from 2003 to 2025 to predict its material stocks and flows over time. The environmental concentrations of CNTs in soil were determined for the years 2014 and 2025 as examples. Afterwards, a second scenario was simulated to investigate the assumption of an immediate production stop of CNTs from 2015 on. Both scenarios were run over a sample size of 50’000 simulation runs. The computation of each took approximately 8:30 minutes. In the first scenario, growing production volumes (Figure A1-7) were assumed.

The change in the amount of CNTs in the soil compartment over time is shown in Figure A1-8. Each individual curve represents the progress of the material amount in the compartment for one random set of parameter values from the underlying probability distributions, so areas of a high density of curves indicate values with a high likelihood. In the diagram, the number of curves was limited to 500 to increase the clarity of the representation. However, the mean values and quantiles stated still refer to the full sample. For the years 2014 and 2025, each of the samples of CNTs accumulated in the soil compartment were projected to a density distribution, from which mean and mode values as well as quantiles were derived (Figure A1-8). Based on the mean values and the significant mass of natural and urban soil of 6.25E+12 kg in Switzerland (Sun et al. 2014), the predicted environmental concentration in soil is 74 ng/kg for 2014 and 486 ng/kg for 2025.
Figure A1-8: Amount of CNT in soil over time; each grey curve represents a random set of parameter values. For the years 2014 and 2025 the sample is projected to a density function.

Besides the growth of the amount of material stocked (and with it the environmental concentration), the uncertainty about the true values increases over time as well. While for 2014 the range between the 15% and the 85% quantile is approximately 0.16 tons, for 2025 it is 1.02 tons. The distribution of the CNTs among the different stocks for the years 2012 and 2014 is presented as mean values of the respective samples in Table A1-2 and Table A1-3 (columns 1 and 2).

Table A1-2 shows the in-use stocks of CNTs for the years 2012 and 2014 and for both scenarios in 2025. Table A1-3 shows the aggregated amounts for the model sinks of the technosphere and environmental media. Currently, a large part of the material is still bound in products (in-use stock) – 36.47t (2012), 55.50t (2014) – while only 18.91t (2012) and 33.51t (2014) have been further transferred. This means that in 2012 a share of 65.85% (62.35% in 2014) of the mass that entered the system has not yet been released to the environment. The material that is released from the product categories leaves the system to a large extent via export (3.86t) and recycling (15.57t). Waste incineration and sewage treatment eliminate 10.74t, and subsequently, 2.59t are bound in landfills. The release to the environment has resulted in an amount of 0.46t in soils and 0.22t in sediments (2014) so far. The progress of the stocked material in “polymer composites” as a compartment of the technosphere and in “landfill” as a model sink are pictured in Figure A1-9 and Figure A1-10, respectively.

The second scenario investigates the system under the assumption of an immediate production stop from the year 2015 on. This leads to a peak of CNTs bound in the technosphere and a subsequent steady release (Figure A1-9 and Figure A1-10).
Appendix 1: A Dynamic Probabilistic Material Flow Modelling Method

Table A1-2: Mean values (in tons) of the samples of CNTs bound in the technosphere in different product categories, predicted values for 2012 and 2014, and prognoses for 2025 using the assumption of growing production volumes or of an immediate production stop in 2015.

<table>
<thead>
<tr>
<th></th>
<th>2012</th>
<th>2014</th>
<th>2025</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Growing Prod.</td>
<td>Stopped Prod.</td>
<td></td>
</tr>
<tr>
<td>Polymer Composites</td>
<td>30.60</td>
<td>46.47</td>
<td>172.72</td>
</tr>
<tr>
<td>Consumer Electronics</td>
<td>4.00</td>
<td>6.08</td>
<td>22.86</td>
</tr>
<tr>
<td>Automotive</td>
<td>1.87</td>
<td>2.95</td>
<td>12.84</td>
</tr>
<tr>
<td>Sum</td>
<td>36.47</td>
<td>55.50</td>
<td>208.42</td>
</tr>
</tbody>
</table>

Table A1-3: Mean material amounts in sinks in tons, predicted values for 2012 and 2014 and prognoses for 2025 using the assumption of growing production volumes or of an immediate production stop in 2015.

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<th>2025</th>
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<td>Sum</td>
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The simulation results of the projected “growth”-scenario show a strong increase of both the amount of CNTs bound in polymer composites products and in landfill over time. The development of the material amounts in landfill is delayed relative to the material stock in polymer composites and shows a significant increase in the years from 2020 on. In the “production stop” scenario, the amount of CNTs bound in polymer composites slowly runs out, leaving only 5.09 t in 2025. The total amount in landfill stabilizes at an amount of 7.63 t at the end of the time considered, and the predicted soil concentration is 192 ng/kg. Both scenarios show relatively little uncertainty about the product stocks. In contrast, the spread between the 15% and 85% quantiles of the landfill stock is approximately the same as the mean value. Outliers even reach roughly three times the mean amount.
Figure A1-9: Growth Scenario – CNTs bound in products containing polymer composites as stock of the technosphere and in the landfills over time.

Figure A1-10: Production stop in 2015 scenario – CNTs bound in products containing polymer composites as stock of the technosphere and in the landfills over time.
A 1.5 Discussion and Outlook

Dynamic probabilistic material flow modeling (DP-MFA) as a new approach to material flow modeling provides a method for indirectly assessing material accumulations in stocks – both in the environment and in the technosphere – considering a variety of dependent partial flows and epistemic uncertainties. The suitability of the method and that of the Python package supporting it for modeling and simulating these systems were shown through their application to predicting stocks of engineered CNTs in the environment. This is an exemplary case and the new method is applicable virtually to all MFA and dynamic MFA modeling cases, e.g., the ones reviewed by Müller et al. (2014), if and when the modelers want to consider the uncertainties for all relevant model parameters.

The DP-MFA method enables the assessment of environmental concentrations, exposure to humans and ecosystems, and emerging risks. Moreover, the implementation of the example model showed that in the case of CNTs, delayed material transfers and the existence of intermediate stocks in the technosphere have a large impact on estimated current and future environmental concentrations. Whereas it was possible before to perform such simulations with traditional dynamic material flow models, it was so far not possible to fully include the uncertainties of the model parameters. Considering the intermediate stocks enables a closer investigation of the actual material amounts released to the environment and the prospective future releases. Within the scope of exposure assessment modeling the new DP-MFA method represents a significant step forward compared to established MFA methods because it allows consideration of a large range of different types of uncertainty for all relevant model parameters. The modeler can choose freely whether to use distributions, functions, or discrete data to describe the uncertainty of all parameters, thus making full use of the available data while representing the varying quantities and qualities of uncertainty as adequate as possible.

The time representation as a series of subsequent periods of equal length is an abstraction from the continuous nature of the flows in the real system. There are two good reasons for this abstraction. First, it enables efficient computation. Second, it corresponds to the way most data is available – as time series, namely as periodic (e.g., annual) values. Given that a continuous model would introduce assumptions (by implicit interpolation) that are often not warranted by data, this would induce a potential discretization error that would be rather inherent to the data than explicitly introduced during the modeling process.

The implementation of our approach as a Python package leads to several advantages. It allows the modeler to use the package within a larger project and to utilize the full functionality provided by Python and further associated libraries, e.g., for the preparation and management of large amounts of data such as pandas (McKinney 2014) and the plotting and evaluation of simulation output as in matplotlib (Hunter et al. 2007). Moreover, it provides for large flexibility in representing specific
system characteristics, e.g., by implementing particular distribution functions for specific behaviors. As a tradeoff, the model needs to be implemented at the code level, which requires programming skills and knowledge of the language Python.

To ensure the computability also of larger models, the method accepts some limitations. The package does not support the representation of uncertainty about the time of a particular release from stock. However, material amounts in environmental stocks depend primarily on the total inflow to the system and the proportion transferred to the compartment. Especially for longer observation periods, the exact duration of a delay process has comparatively little impact on the total amount stored. Accordingly, uncertainty about these processes has only little influence and is therefore considered less relevant. Moreover, the transfer coefficients describing the relations between flows are considered stable over the investigated time (simulation length). Under this assumption, the model complexity mainly depends on the number of included model compartments and flow dependencies.

In general, the required computational effort to simulate a DP-MFA model can be a limiting factor regarding model complexity, simulation length, time granularity, and desired precision of the simulation outcome. For the case-study investigated herein, however, the computation of the model did not pose particular difficulties.

For the given scope of the method – the assessment of environmental stocks and flows under substantial uncertainties – the simulation package was shown to be suitable. Considering a much higher degree of detail either of the system representation or the time resolution, might be desirable in some cases. However, a particular degree of detail of the model only makes sense if it is not considerably exceeded by existing uncertainties about the system.

As probabilistic – Bayesian – prediction model, incomplete knowledge about the true value of a model parameter is represented as probability distribution. To ensure to comprise the true parameter value also wrong, but plausible values are included. Instead of a validation the model in terms of confirming or rejecting it, it can be improved by proving or rejecting some of the assumptions made and thus reduce the incorporated uncertainty.

Future work could provide additional components that are adapted to particular application domains. Moreover, the modeling process could be enhanced by higher-level modeling constructs, in particular for hierarchical modeling and graphic model representation. Also, while the actual processing of uncertain knowledge about material flows is clear, support for the modeler in the formulation of a probability distribution based on heterogeneous, diverse, and incomplete knowledge about a system variable could be improved.
A 1.6 Acknowledgement

Nikolaus A. Bornhöft was supported by the European Commission within the Seventh Framework Programme (FP7; MARINA project - Grant Agreement n° 263215). Tian Yin Sun was supported by project 406440_131241 of the Swiss National Science Foundation within the National Research Program 64.
A 1.7 References


Appendix 2: Comprehensive Probabilistic Modelling of Environmental Emissions of Engineered Nanomaterials
A 2.1 Production volume of ENM

The US EPA (2010) suggested a global production for nano-TiO$_2$ of 12’500 tons; while a study by Nightingale et al. (2008) reported for this with a volume of 5’000 tons. Another study by Piccinno et al. (2012) that based on industry survey gave a range of 55-3’000 tons for nano-TiO$_2$ produced in Europe. Studies by Hendren et al. (2011) and Robichaud et al. (2009) that explicitly investigated production of ENM suggested the nano-TiO$_2$ production in the U.S. with a range of 7’800-44’400 tons. Schmid et al. (2008) gave a production of nano-TiO$_2$ for Switzerland with 436 tons through a targeted survey. For global nano-ZnO production, Nightingale et al. (2008) reported 18 ton; Zhang and Saebfar reported 528 tons; and Aschberger et al. (2011) reported 10’000 tons. Schmid et al. (2008) reported 70 ton for the nano-ZnO production in Switzerland; Piccinno et al. (2012) suggested a range of 5.5-28’000 tons for nano-ZnO production in Europe. For nano-Ag, global productions were reported ranging from 5.5 to 500 tons (Aschberger et al., 2011; Piccinno et al., 2012; Sahasrabudhe, 2010; Scheringer et al., 2010; Windler et al., 2013); for CNT, global production were reported ranging from 55 to 3’300 tons (Aschberger et al., 2011; Future Markets, 2011; Healy et al., 2008; Piccinno et al., 2012); and for Fullerene, global production were reported ranging from 0.6 to 1620 (Aschberger et al., 2011; Future Markets, 2011; Piccinno et al., 2012; Ray et al., 2009a).

These global and regional production or use data were extrapolated to Europe and Switzerland in proportion to Gross Domestic Product. The reason we used regional/national GDP instead of population (which was used as scaling factor for our previous studies (Gottschalk et al., 2009a; Mueller, 2007) ) as our scaling factor is based on the consideration that the consumption capability of people in poor and richer countries vary a lot (in this context, US and Swiss data cannot be simply scaled up to EU’s data according to population, because the average individual consumption capability in eastern Europe is not comparable to those living in US and in Switzerland), and GDP as an economic indicator is very much correlated to a nation’s consumption (Anghelache, 2011). In this regard, actually we improved our scaling method for production compared to our previous study by applying GDP rather than population. The summary of the raw data used for producing the probability distribution is given in Table A2-1.
A 2.2 Fate parameters

The dissolution of nano-ZnO and nano-Ag in product use phase was modeled as elimination for different products upon contact with water. Table A2-2 shows all the middle values of the nano-ZnO and nano-Ag eliminations which are used for triangular distribution. A complete dissolution of nano-ZnO contained in food is assumed due to the existence of gastric acid in stomach. Nano-ZnO incorporated in other product like cosmetics, paints, textiles and filters that can easily be in contact with water, is assumed to dissolve ranging from 5% to 10%. This also applies to nano-Ag containing product that can very possibly in touch with water. Dissolution of nano-Ag was quantified based on information given by Blaser et al. (2008) for the release of Ag from biocidal plastics. No complete dissolution of Ag was considered for natural waters, although a continuous dissolution is in principle possible, the particle form can persist long enough to open new pathways for silver partitioning and transport (Liu and Hurt, 2010). For nano-TiO$_2$, CNTs and Fullerenes, no dissolution or elimination during PMC was considered.

Wastewater from household containing ENM is discharged either into Sewage Treatment Plant (STP) or directly into environment when STP is not connected. The connection rate of waste water to STP in EU was summarized from European Commission’s Technical Guidance Document on Risk Assessment (ECB, 2003a) with a mean value of 0.80; for that of Switzerland, a range between 0.967 and 0.98 was taken from the Swiss yearbook of wastewater (SVGW, 2012) to model a uniform distribution. However, not all the wastewater entering STP is treated, due to heavy rain and flood, overflows escaping STP treatment processes occur at STP and flow into environment. A normal distribution for Swiss STP overflows was modelled with the median value of 0.032 and standard deviation of 0.040 obtained via personal communication with Philipp Staufer (2012) and the same data is used for EU because there is no such EU data found.
Regarding STP removal efficiency, Kiser et al. (2009) reported results of their experiments from full scale wastewater treatment plant that the average overall removal of Ti was $82 \pm 21\%$, and for the filterable Ti (Titanium) ($< 0.7 \mu m$ in size) the value was $42 \pm 22\%$. Another real plant study by Westerhoff et al. (2011) reported a much higher overall removal efficiency of Ti, ranging from 96.1% to 99.4% with an average of 98.3%. Gomez-Rivera et al. (2012) investigated a laboratory-scale activated sludge system to simulate the removal of CeO$_2$, which probably can also represent the removal of TiO$_2$, and they concluded an overall total CeO$_2$ removal of 96.6% and a removal of 98.5% for the CeO$_2$ smaller than 200 nm. Another CeO$_2$ removal study by Limbach et al. (2008) who used a model wastewater treatment plant and concluded a efficiency between 95% and 98%. Other STP removal studies (Hwang et al., 2011; Johnson et al., 2011b; Kiser et al., 2010; Kiser et al., 2009; Wang et al., 2012; Zhang et al., 2008) for nano-TiO$_2$ studies (Hou et al., 2012; Kaegi et al., 2011; Kiser et al., 2010; Tiede et al., 2010; Wang et al., 2012) for nano-Ag, and studies (Kiser et al., 2012; Kiser et al., 2010; Wang et al., 2012) for Fullerene are summarized in Table A2-3. There is no specific nano-ZnO and CNT removal study available, considering the similarity of chemical property, nano-TiO$_2$ and Fullerene data were also used for nano-ZnO and CNT respectively. In modeling of STP removal the results from these studies were treated differently. The highest weighting factor was given to the result from these full scale STP investigations, lower weighting factor was given to the removal concluded from pilot STP experiments, and the lowest weighting factor was assigned to the results of the batch laboratory experiments. Exact assignment of weighting factors is depending on the number of the removal values obtained for different ENM. Table A2-3 also shows comprehensively how these data were weighted with DoB. And these data are then modeled as a uniform distribution taking their DoB into account. Figure A2-1 shows the modeled probability distribution of ENM removal in STP. In STP, ENM may be transformed into other compounds and no longer nano form. Kaegi et al. (2011) reported 85%-100% of the metallic nano-Ag is transformed into Ag$_2$S, which means only less than 15% of initial nano-Ag entering into STP with wastewater can survive STP process. Lombi et al. (2012) studied the fate of zinc oxide nanoparticles during anaerobic digestion of wastewater and post-treatment processing of sewage sludge and they conclude that after anaerobic digestion zinc oxide nanoparticles completely disappear and is transformed into other non-nano forms. All these factors were also included into our modeling.

For the use of STP sludge in Switzerland, 22% of the sludge from wastewater treatment is used in cement production (Huegi et al., 2008), the remaining 78% is burnt in Waste Incineration Plant (WIP) or separately in sludge incineration plants. While in EU, according to EEA (2001) and Blaser et al. (2008) about 55% of the STP sludge is applied as fertilizer in soil, and about 20% of them is. The remaining 25% is incinerated for which no differentiation between WIP and cement plant incineration is clarified, therefore, we can imagine that most of the incinerated sludge goes into WIP, thus, in the case of absent clear information we assumed all 25% of the sludge is incinerated in WIP in EU for our modeling.
The burnable Municipal Solid Waste (MSW) in Switzerland is around 2.59 million tons (Hanser et al., 2005; Huegi et al., 2008) of which 100% is assumed to be incinerated and that of EU according to EUROSTAT (2012) the latest available information in 2008 was around 190 million tons, out of which between 20% (Koehler et al., 2011) and 30% (Salzmann, 2008) were incinerated. After burning, these wastes become bottom ash or slag and fly ash with very much reduced volume. Salzmann (2008) stated after burning, 1 tonne of MSW produce 221 kg of bottom ash and 33 kg of fly ash; the study by Chang et al. (2006) gave similar results with 110-150 kg for bottom ash and 20-30 kg for fly ash. With the above information given, the amount of MSW incinerated and the amount of correspondingly produced bottom ash and fly ash were modeled and calculated.

For waste incineration plant (WIP), according to the study by Müller et al. (2013) there are mainly three processes of WIP in Switzerland: burning, filtration, and acid washing (wet-flue gas cleaning facility). In EU only around half amount of the household waste are incinerated by wet-flue-gas cleaning facility equipped WIP, the remaining half is incinerated by the WIP without this process (Koehler et al., 2011). According to Walser et al. (2012) the partition of ENM between bottom ash and fly ash is supposed to be constantly at 81% to bottom ash and 19% to fly ash, refer to Table A2-4. In Switzerland, the bottom ash is supposed to be wholly landfilled; and 39% of the fly ash goes through the acid washing process, 39% is used in cement consolidation and 22% is exported. In EU, bottom ash is recycled and used as e.g. construction materials or landfilled if limit values of leachability exceed the criteria for recycling (Chang and Wey, 2006; Mueller et al., 2013; Reijnders, 2005; Van Gerven et al., 2005). In Germany, 50% of the ash produced from incinerated waste is used for the manufacture of sound insulation in walls along highways, as well as for sublayers of city roads. In the Netherlands, 60% of the bottom ash is used for the construction of asphalt and for a sublayer of roads. The aim is to reuse 80% of the bottom ash. In Denmark, over 72% of the ash is reused for the construction of parking lots, cycling tracks and other roads (Reijnders, 2005). With the information given by the European waste incineration report (EC, 2006) (page11), we calculated approximate bottom ash recycling rate result of 42% in EU. For fly ash, because these was no quantitative information found on diversified cases in different countries and due to the fact that fly ash is regarded as hazardous that has to be landfilled or used for filling up old coalmines; we assumed all of it will end up in landfill. Depending on ENM types, there is substance-specific elimination/destruction of ENM during burning and acid washing processes, these parameters were summarized on Müller et al. (2013). The efficiency of filter in WIP is particle-size dependent rather than substance-specific. According to Walser et al. (2012) the removal efficiency of filter is between 99.6% and 99.9% which corresponds quite well to the result of Burtscher et al. (2002) of which the efficiency is > 99.5%. For the removal efficiency of wet scrubber (acid washing), the both studies also agreed on >99.9%.

For landfills, we assume that there is no leaching out of them. The ENM suspending in air can persist only a short time and eventually will settle down on earth surface, here we assumed ten days of persistence time for the modeling (Anastasio and Martin, 2001). Under some circumstances, ENM in
soil can be transferred to surface waters during storm events, a modelled transfer coefficient with mean of 0.549% was given by O’Brien and Cummins (2011) who adapted the data from diffuse transfer of linear alkylbenzene sulphonate (LAS) from soils to surface water reported by Kannan et al. (2007)
Table A2-2: Transfer coefficients (TCs) from product categories to environmental and technical compartments in the EU and Switzerland (CH).

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<td>CH</td>
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<tr>
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<td>Production</td>
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<td>0.75</td>
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<tr>
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<tr>
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<td>CH</td>
<td>EU</td>
<td>CH</td>
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<td>CH</td>
<td>EU</td>
<td>CH</td>
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<td>Production</td>
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</tbody>
</table>

*For Nano-Ag contained in textiles the release to waste water during washing and rinsing there are minimal; mean and maximal values concluded from empirical data in literature.

This is shown in a way of min-mean-max. And the "Rest" indicate the rest fraction of nano-Ag remaining in textiles after release to waste water, air and after elimination or transformation.
Table A2-3: Sewage Treatment Plant (STP) removal efficiency with categorization of Degree of Belief (DoB). Numbers in superscripts after each value are the numbers of references.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Sewage treatment plant (STP) removal efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Real STP study (50% DoB)</td>
</tr>
</tbody>
</table>
| TiO₂ Pigment | 61-100%\textsuperscript{22}  
96.1-99.4% (mean: 98.3%)\textsuperscript{23} | 80-98%\textsuperscript{27} | 96.6%\textsuperscript{34} |
| Nano TiO₂ | 20-64%\textsuperscript{22}  
89.5%\textsuperscript{26} | 95-98%\textsuperscript{25}  
80-98%\textsuperscript{27} | 23%\textsuperscript{28}  
95%\textsuperscript{29}  
98.5%\textsuperscript{24}  
91.3%\textsuperscript{30} |
| Nano ZnO | Use the information of nano-TiO₂ |
| Nano Ag | 97%\textsuperscript{31} | 39-97%\textsuperscript{28}  
88%\textsuperscript{29}  
90%\textsuperscript{36}  
40-62%\textsuperscript{34}  
99-100%\textsuperscript{33} |
| Fullerene | 88%\textsuperscript{28}  
95%\textsuperscript{29}  
93%\textsuperscript{34} |
| CNT | Use the information of Fullerene |
Figure A2-1: Modelled probability distribution of STP removal efficiency of ENM

Table A2-4: Removal efficiency of ENM (including TiO$_2$ pigment) in Waste Incineration Plant (WIP) (refer to paper Mueller et al. (2013))

<table>
<thead>
<tr>
<th></th>
<th>TiO$_2$ (nano &amp; pigment)</th>
<th>ZnO</th>
<th>Ag</th>
<th>CNT</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td>mode</td>
<td>max</td>
<td>min</td>
</tr>
<tr>
<td>Destruction by burning/melting</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Destruction by acid washing</td>
<td>0</td>
<td>100%</td>
<td>0</td>
<td>2.5%</td>
</tr>
<tr>
<td>Fly ash</td>
<td>19%</td>
<td>19%</td>
<td>19%</td>
<td>19%</td>
</tr>
<tr>
<td>Bottom ash</td>
<td>81%</td>
<td>81%</td>
<td>81%</td>
<td>81%</td>
</tr>
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</table>
### Table A2-5: Summary of measured total conventional materials’ (titanium dioxide, silver and zinc) concentrations in different compartments.

Numbers in superscripts after each value are the numbers of references.

<table>
<thead>
<tr>
<th>Materials</th>
<th>TiO₂</th>
<th>Ag</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surface water</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Summary⁵⁷</td>
<td>(0.012, 0.3, 70)⁹⁸</td>
<td>(0.09-40)⁹⁰, (0.09-510)⁹⁷, (2-2000)⁹³</td>
<td>1-12⁳⁵, 0.09-40⁹⁰, (0.09-310)⁹⁷, (2-2000)⁹³, (0.3-0.6, 250’000)⁹⁴, 1.2⁶⁴, (10-430)⁹³, (87-570)⁹⁴, (40-2970)⁹⁵, (5-10)⁹⁰, 18.7⁳⁵, (12.2-20)⁹³, Summary⁷³</td>
</tr>
<tr>
<td><strong>STP Effluent</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Summary²¹, Summary²⁴, 1.6⁴⁶</td>
<td>0.56⁶⁶, 7.1⁷⁵, (0.069-2.25) (0.712)⁹⁵, (0.028-0.139)⁹⁴, (0.042-0.053)⁹⁵, 0.055⁹⁵</td>
<td>(2,36,120,16)³⁵, (10,100,3,133,300)⁷⁵, 1.437⁷⁰, 4’900⁷⁰, 180⁷⁰, 60⁷⁰, (5-5’500)⁹⁵, (680-60’840)⁹³, (64-77)⁹³</td>
<td></td>
</tr>
<tr>
<td><strong>STP Sludge</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>317’000⁹⁰</td>
<td>7’000-39’000 (24’000)²¹, Summary¹⁷, (7’400, 1’100, 2’000, 3’100, 5’400, 9’900, 16’000, 33’000)⁸³</td>
<td>(275’300-361’500)⁹⁵, 250’000⁹⁵, ([55/23/32/40/50/62/70/230]×10⁴)³⁵, 864’400⁹⁵</td>
<td></td>
</tr>
<tr>
<td><strong>Sediment</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Summary⁵⁷, Summary⁷⁷, 70⁸⁷, 1’100⁸⁸, 2’000-16’000 (6’000)⁹⁵, (50-1’100)⁹⁵</td>
<td>(82’000-3’700’000)⁹⁵, (70’000-175’000)⁹⁵, (4’000-13’900’000)⁹⁵, 65’000⁹⁵, Summary²⁷, 830⁹⁷, 510⁹⁸</td>
<td>μg/kg</td>
<td></td>
</tr>
<tr>
<td><strong>Soil</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Summary²⁷, 3’340⁹⁰</td>
<td>(20, 10, 25, 27, 289, 304, 500, 509, 2’070, 3’150)⁹⁷, 2’600⁹⁴</td>
<td>(10’000-300’000)⁹⁸, (3’000-3’060’000)⁹⁷, (5’000-2’900’000)⁹⁸, 48’00⁴⁸, 49⁴⁸, (48’000-180’000)⁹⁴, 29’20⁹⁸, (50’000-100’000)⁹⁸, 40’000⁹⁴, 50’00⁹⁴, 90’00⁹⁴, 126’00⁹⁴, 906’00⁹⁴, 830⁹⁴, 100’00⁹⁴, (117’000-1286’000)⁹⁸, (114-173)³⁵, Summary⁶⁴, (477, 30, 60, 50, 36)³⁵, (74.2’10⁴, (74.2’10⁴), (174’10⁴), (250-2’500)³⁵, 419’00³⁵, (1’800-4’990)³⁵, (68’000-290’000)³⁵</td>
<td></td>
</tr>
<tr>
<td><strong>Air</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.00003⁹⁸</td>
<td>(0.1-1.7)³⁵, (0.01, 0.02, 0.05, 0.16)⁹⁸, 0.003⁹⁸</td>
<td></td>
</tr>
<tr>
<td><strong>Note:</strong> Summary: a set of data are summarised from the corresponding literatures or reports, not directly shown here studies reporting the concentration of the studied materials either provide a single value, or a range expressed here as (min-max), or a range with mean expressed here as (min- max)(mean); or a few of values expressed as (value1, value2, value3.).</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table A2-6: Summary of volumes of different technical and environmental compartments. Numbers in superscripts after each value are the numbers of references.

<table>
<thead>
<tr>
<th>Compartments</th>
<th>Formula</th>
<th>Volumes</th>
<th>Unit</th>
<th>Comments</th>
</tr>
</thead>
</table>
| **Air**                       | EU $4326337*1*10^4$            | $4.33E+15$| m$^3$  | $4326337$ km$^2$ is the area of EU27$^{105}$  
10 days was used for the residence time in air for ultrafine particles$^{10}$  
1 km was taken for the depth of air will be affected by ENM$^{15}$  
$10^9$ is the transformation from km$^3$ to m$^3$ |
| CH $41285*1*10^4$            |                                | $4.13E+13$| m$^3$  | $41285$ km$^2$ is the area of Switzerland$^{106}$                                                                                     |
| **Natural and urban soil**    | EU $4326337*0.97*10^6*[C.2*0.47+0.05*0.53]*1500$ | $7.59E+14$| kg     | $0.97$ is the proportion of terrestrial land in EU$^{105}$  
$10^6$ is the transformation factor from km$^3$ to m$^3$  
$0.2$ is the depth considered for agricultural soil suggested$^{10}$  
$0.47$ is the share of agricultural land area in EU$^{102}$  
$0.05$ m depth of natural and urban soil$^{10}$  
$0.53$ is the share of natural and urban land in EU$^{107}$  
$1500$ kg/m$^3$ is the density of dry soil$^{19}$ |
| CH $41285*0.958*10^6*[0.2*0.369+0.05*0.631]*1500$ |                                | $6.25E+12$| kg     | $0.558$ is the proportion of terrestrial land in Switzerland$^{108}$  
$0.631$ share of urban and natural soil in Switzerland$^{108}$  
$0.369$ share of agricultural soil in Switzerland$^{108}$ |
| **Biosolid treated soil**     | EU $(9000000*0.55/20)*10^4*0.2*1500$ | $7.43E+11$| kg     | $9000000$ tons is the volume of sewage sludge EU yearly produced$^{109}$  
$0.55$ is the share of sewage sludge going to agricultural soil$^{17}$  
$20$ tons/ha is the average sludge application rate in EU$^{110}$  
$10^4$ is the transformation factor from ha$^3$ to ton$^3$ |
| **Surface water**             | EU $4326337*0.03*10^6*3*1000$  | $3.89E+14$| litre  | $0.03$ is the share of water area in EU$^{105}$  
$3$ m is the depth of water compartment considered$^{19}$  
$1000$ is the transformation factor from m$^3$ to litre |
| CH $41285*0.042*10^6*3*0.000$ |                                | $2.02E+10$| litre  | $0.042$ is the share of water area in Switzerland$^{106}$                                                                 |
| **Sediments**                 | EU $4326337*0.03*10^6*0.03*260$ | $1.01E+12$| kg     | $0.03$ m is the depth of sediments considered to be affect by ENM$^{13}$  
Another $0.03$ is the share of water area in EU$^{105}$  
$260$ kg/m$^3$ is the density of sediments soil$^{15}$ |
| CH $41285*0.042*10^6*0.03*260$ |                                | $1.35E+10$| kg     | $0.042$ is the share of water area in Switzerland$^{106}$                                                                 |
| **STP effluent**              | EU $0.8*200*365*509000000$     | $2.97E+13$| litre  | $0.8$ is the average proportion of EU families connected to central sewage facility$^{25}$  
$200$ l/head is the average daily water consumption of EU citizens$^{35}$  
$509000000$ is the number of EU population$^{106}$ |
| CH $200*365*7997000$          |                                | $5.83E+12$| litre  | $7997000$ is the number of population in Switzerland$^{106}$                                                                       |
| **STP sludge**                | EU $9.00E+09$                  | $9.00E+09$| kg     | $9'000'000'000$ kg is the volume of sewage sludge EU yearly produced$^{109}$ |
| CH $2.03E+08$                 |                                | $2.03E+08$| kg     | $203'000'000$ kg is the volume of sewage sludge Switzerland yearly produced$^{111}$                                              |
Table A2-7: Lower, upper boundary and mean percentage of ENM (including TiO$_2$ pigment) allocation to different product applications calculated from varied sources that mentioned in “Characterization of model parameters” in paper main text. These percentages values were used for modelling triangular (and uniform) distributions.

<table>
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<th>Product categories</th>
<th>Lower Boundary</th>
<th>Mean</th>
<th>Upper Boundary</th>
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</tr>
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<tr>
<td>Waste water treatment</td>
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</tr>
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</tr>
<tr>
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</tr>
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<td>0.0001</td>
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<td>0.0100</td>
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<td>0.1500</td>
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<td>0.1500</td>
</tr>
<tr>
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<td>0.6000</td>
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<td>0.1000</td>
<td>0.3100</td>
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<td>0.0400</td>
<td>0.1500</td>
</tr>
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<td>Plastics</td>
<td>0.0000</td>
<td>0.0300</td>
<td>0.0700</td>
</tr>
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<td>Food</td>
<td>0.0000</td>
<td>0.0700</td>
<td>0.2400</td>
</tr>
<tr>
<td>Glass &amp; ceramics</td>
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<td>0.0100</td>
<td>0.0400</td>
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<tr>
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<td>0.1200</td>
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<td>0.0100</td>
<td>0.0400</td>
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<td>0.0010</td>
<td>0.0100</td>
</tr>
<tr>
<td><strong>Carbon nanotubes (CNTs)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>0.8400</td>
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<td>0.0100</td>
<td>0.1000</td>
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<tr>
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<td>0.0002</td>
<td>0.0007</td>
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<tr>
<td>Automobile</td>
<td>0.0000</td>
<td>0.0100</td>
<td>0.1000</td>
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<tr>
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<td>0.0300</td>
<td>0.2400</td>
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<tr>
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<td>0.0900</td>
<td>0.5000</td>
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<td>Sensor</td>
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<td>0.0040</td>
<td>0.0300</td>
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<td>0.0053</td>
<td>0.0500</td>
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<td><strong>Fullerenes</strong></td>
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<td>Polymer composites</td>
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<td>Cosmetics</td>
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<td>0.1700</td>
<td>1.0000</td>
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<tr>
<td>Consumer electronics</td>
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<td>0.0300</td>
<td>0.2000</td>
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<td>0.0200</td>
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</tr>
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<td>Aerospace</td>
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<td>0.0030</td>
<td>0.0200</td>
</tr>
<tr>
<td>Energy/environment</td>
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<td>0.0030</td>
<td>0.0200</td>
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<td><strong>Pigment-TiO$_2$</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paints</td>
<td>0.5700</td>
<td>0.5800</td>
<td>0.5900</td>
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<td>0.0900</td>
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<td>Textiles</td>
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<tr>
<td>Foods</td>
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<td>0.0050</td>
<td>0.0090</td>
</tr>
<tr>
<td>Others</td>
<td>0.0200</td>
<td>0.0300</td>
<td>0.0400</td>
</tr>
</tbody>
</table>
Figure A2-2: Mean percentage of ENM (including TiO$_2$ pigment) allocation to different product applications calculated from varied sources that mentioned in “Characterization of model parameters” in paper main text. These percentage values were used as middle values for modelling triangular distributions, which are also the most probable values on the distribution curves.
Figure A2-3: Modelled results (mode values) of material flows for nano-TiO2, nano-Ag, pigment-TiO2, nano-ZnO, CNT and fullerene in Switzerland (CH) in t for the year 2012. The thickness of the arrows indicates the proportion of flow quantity. Dotted arrows between surface water and sediments/export indicate two different scenarios with either complete ENM sedimentation or 100 % of ENM remain in surface water with 0 % sedimentation.
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A 2.3 References


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(29) Europa, 2013. The common agricultural policy (CAP) and agriculture in Europe – Frequently asked questions.


(31) FOREGS, 2005. Forum of European Geological Surveys FOREGS project


Dynamic Probabilistic Modelling of Environmental Emissions and Concentrations of Engineered Nanomaterials

(66) Migros, 2012. Personal communication with Migros.
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(86) Scheringer, M., MacLeod, M., Behra, R., Sigg, L., Hungerbuhler, H., 2010a. Environmental risks associated with nanoparticulate silver used as biocide. Household and Personal Care TODAY 1, 34-37.

(87) Scheringer, M., MacLeod, M., Behra, T., Sigg, L., Hungerbühler, K., 2010b. Environmental risks associated with nanoparticulate silver used as biocide. Household & Personal Care Today 1, 34-37.


Appendix 3: Supporting Information for Chapter 3: Probabilistic modelling of prospective environmental concentrations of gold nanoparticles from medical applications as a basis for risk assessment
## A 3.1 Estimation of the prospective annual GNP consumption from medical applications

### Table A3-1: The probabilistic distribution functions of the input parameters used to create the probability mass flow model.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Probabilistic Distribution Functions(PDFs)</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UK</td>
<td>US</td>
</tr>
<tr>
<td></td>
<td>UK</td>
<td>US</td>
</tr>
<tr>
<td>Lateral Flow Immunoassay to detect the presence of Methicillin Resistant</td>
<td>Triangular</td>
<td>0.34</td>
</tr>
<tr>
<td>and Methicillin Sensitive Staphylococcus aureus in blood</td>
<td>Triangular</td>
<td>0.36</td>
</tr>
<tr>
<td>Test kit for detection and genotyping Warfarin metabolism</td>
<td>Triangular</td>
<td>1</td>
</tr>
<tr>
<td>Test kit for detection of single nucleotide polymorphism to detect risk</td>
<td>Triangular</td>
<td>3 to 100</td>
</tr>
<tr>
<td>from venous thrombosis</td>
<td>Triangular</td>
<td>2 to 80</td>
</tr>
<tr>
<td>OTC test kits to detect pregnancy and ovulation</td>
<td>Uniform</td>
<td>0.34</td>
</tr>
<tr>
<td>Test kits for qualitative detection of antibodies to HIV-1 and HIV-2</td>
<td>Uniform</td>
<td>20 to 460</td>
</tr>
<tr>
<td>in human serum, plasma and blood</td>
<td>Uniform</td>
<td>3 to 100</td>
</tr>
<tr>
<td>Home based in vitro HIV test kits</td>
<td>Triangular</td>
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</tr>
<tr>
<td>Test kits to establish viral load In HIV patients</td>
<td>Triangular</td>
<td>60</td>
</tr>
<tr>
<td>Test kits to diagnose infectious diseases</td>
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<td>70</td>
</tr>
<tr>
<td>Nasal decolonization of Staphylococcus aureus</td>
<td>Uniform</td>
<td>30 to 53'300</td>
</tr>
<tr>
<td>Periodontal disease treatment</td>
<td>Uniform</td>
<td>270 to 106'560</td>
</tr>
<tr>
<td>Sensors for diagnosing diseases from breath samples</td>
<td>Uniform</td>
<td>0.01 to 1’590</td>
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<td>Treatment modality for Cancer : TNF delivery (Can_T1)</td>
<td>Triangular</td>
<td>70 - (480) - 1’100</td>
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<tr>
<td>Treatment modality for Cancer : TNF delivery (last line) Can_T1_LS</td>
<td>Triangular</td>
<td>420</td>
</tr>
<tr>
<td>Treatment modality for Cancer: Thermal ablation (Can_T2)</td>
<td>Uniform</td>
<td>140’290 to 233’820</td>
</tr>
<tr>
<td>Treatment modality for Cancer: Thermal ablation (last line) Can_T2_L2</td>
<td>Uniform</td>
<td>104’710 to 174’520</td>
</tr>
<tr>
<td>Transbucical insulin delivery platforms (Dia_T)</td>
<td>Triangular</td>
<td>128’250</td>
</tr>
<tr>
<td>Can_T1 to wastewater</td>
<td>Fixed data</td>
<td>0.65</td>
</tr>
<tr>
<td>Can_T1 remains in body</td>
<td>Fixed data</td>
<td>0.35</td>
</tr>
<tr>
<td>Can_T2 to wastewater</td>
<td>Fixed data</td>
<td>0.15</td>
</tr>
<tr>
<td>Can_T2 remains in body</td>
<td>Fixed data</td>
<td>0.85</td>
</tr>
<tr>
<td>From STP</td>
<td>From Waste Incinerator Plant</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>-----------------------------</td>
<td></td>
</tr>
<tr>
<td>Dia_T to wastewater</td>
<td>Fixed data</td>
<td>fixed data</td>
</tr>
<tr>
<td>Can_T1_LS to body</td>
<td>Fixed data</td>
<td>fixed data</td>
</tr>
<tr>
<td>Can_T2_LS body</td>
<td>Fixed data</td>
<td>fixed data</td>
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<td>Body to crematorium</td>
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<tr>
<td>Body to burial</td>
<td>Triangular</td>
<td>Triangular</td>
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<td>Percentage of population not connected to Sewage Treatment Plant</td>
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<td>Triangular</td>
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<td>Overflows from STP</td>
<td>Log normal</td>
<td>Uniform</td>
</tr>
<tr>
<td>Leakage from sewerage networks</td>
<td>Uniform</td>
<td>Uniform</td>
</tr>
<tr>
<td>STP misconnection</td>
<td>Uniform</td>
<td>--</td>
</tr>
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<td>STP removal efficiency</td>
<td>Triangular</td>
<td>Triangular</td>
</tr>
<tr>
<td>Sludge to Incinerators (WIP)</td>
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<td>Uniform</td>
</tr>
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<td>Sludge to Landfill</td>
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<td>Sludge to soil</td>
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<td>Dependent</td>
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<td>Hazardous waste to landfill</td>
<td>Triangular</td>
<td>Triangular</td>
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<td>Non-hazardous waste to MWI</td>
<td>Triangular</td>
<td>Triangular</td>
</tr>
<tr>
<td>Non-hazardous waste to landfill</td>
<td>Triangular</td>
<td>Triangular</td>
</tr>
<tr>
<td>Stack emissions from MWI</td>
<td>Triangular</td>
<td>Triangular</td>
</tr>
<tr>
<td>Bottom-ash from MWI</td>
<td>Triangular</td>
<td>Triangular</td>
</tr>
<tr>
<td>MWI bottom-ash to landfill</td>
<td>fixed data</td>
<td>fixed data</td>
</tr>
<tr>
<td>MWI Fly-ash to air</td>
<td>Triangular</td>
<td>Triangular</td>
</tr>
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<td>MWI Fly-ash to landfill</td>
<td>Triangular</td>
<td>Triangular</td>
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<td>GNP in HMCIWI</td>
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<td>Uniform</td>
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<td>Gold eliminated from HMCIWI</td>
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<td>Uniform</td>
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<tr>
<td>GNP from HMCIWI to stack emissions</td>
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<td>Uniform</td>
</tr>
<tr>
<td>GNP from HMCIWI to bottom-ash</td>
<td>Triangular</td>
<td>Triangular</td>
</tr>
<tr>
<td>Bottom ash from HMCIWI to landfill</td>
<td>fixed data</td>
<td>fixed data</td>
</tr>
<tr>
<td>Stack emissions from HMCIWI to wet scrubber</td>
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<table>
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<tr>
<th>TCs between Eco systems</th>
<th>Stack emission from HMCIWI to Dry scrubber and Fabric Filter (APCD)</th>
<th>APCD to landfill</th>
<th>APCD to air</th>
<th>HMCIWI wet scrubber to waste water</th>
<th>HMCIWI wet scrubber to air</th>
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<td></td>
<td>Triangular Triangular 0.5 Triangular 0.5</td>
<td>Triangular Triangular 0.9999 0.9999</td>
<td>Triangular Triangular 0.0001 0.0001</td>
<td>Uniform Uniform 0 to 1 0 to 1</td>
<td>Uniform Uniform 1 to 0 1 to 0</td>
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<td>Air to soil</td>
<td>Triangular Triangular 0.9866 0.9324</td>
<td>Triangular Triangular 0.0134 0.0676</td>
<td>Uniform Uniform 0 to 1 0 to 1</td>
<td>Uniform Uniform 1 to 0 1 to 0</td>
<td>Uniform Uniform 0 to 1 0 to 1</td>
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<td>Air to surface water</td>
<td>Worst-case scenario 0 or 1 Worst-case scenario 0 or 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface water to sediments(S2S)</td>
<td>Worst-case scenario 0 or 1 Worst-case scenario 0 or 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Our aim was to identify GNP enabled medical applications which are approved, in clinical trials or show promise of translation from pre-clinical models. We have crosschecked our selection of applications used in this study by using corporate websites, company annual reports, press releases, and clinical trials.gov database including US FDA and EMA websites. The subscription database of ‘Citeline’\(^d\) and ‘Adis R&D Insight’ \(^e\) was used between the period of 17-21 December 2012, 18-19 January and 26-27 April 2013. Information obtained from personal communication has also been included to arrive at some generic estimates since the empirical data base is insufficient. United States Patent and Trademark Office’s website and ‘Patent Buddy’ websites were relied upon for finding out related patents to arrive at an estimate of the amount of gold (Au) per test/per patient.

For arriving at population estimates, sources of information include data from the World Health Organization (WHO), www.cancerresearchuk.org, and U.S. federal agencies such as National Institutes of Health (NIH), National Cancer Institute’s SEER data base, and the Centers of Disease Control and Prevention (CDC), to name a few has been used. For the UK, data was extracted from the website of the ONS (Office of the National Statistics) and reports from NICE (National Institute of Clinical Excellence) and the NHS (the National Health Services). Where possible and practicable, the most recent data available have been used. Broad assumptions have been used with the intent to come up with best plausible estimates. Attempts have been made to reduce risks due to double counting (Exception: There is double counting of two applications selected for testing of \textit{Staphylococcus aureus}. However, the inclusion of this data does not impact the share of these applications significantly in the total consumption amount. The assumptions are:

- It has been assumed that each product by a company for a particular application serves 100\% of the market of the US and UK (i.e. no competition) and all patients, irrespective of socio-economic status etc., have access to these products. For example, when a therapy is in clinical trials for head and neck cancer, we have used the latest publicly available data for number of people diagnosed with head and neck cancer in a particular year and used this data as a prospective population for treatment. Innovative medicines might create excitement with regard to possibility of increasing the life expectancy of a patient; hence we have assumed that all deaths could be prevented if this medicine is used as a last line treatment under the auspices of “expanded access or compassionate use”\(^f\). Therefore, mortality figures of people suffering from a particular type of cancer were used. We are aware that not all people will have access to these ‘trial’ drugs and devices, however, our objective is to model high emission worst case scenario and hence we have included these numbers. Various different

\(^d\) http://www.citeline.com/
\(^e\) http://www.springer.com/gp/adis/products-services/adisinsight-databases/r-d-insight
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disease types and stages of cancer have not been taken into consideration. It is assumed that all patients get treated in the same year, since the model (in the current state of development) doesn’t allow for time-based-releases.

- Attempts have been made to reduce risks due to double counting (Exception: There is double counting of two applications selected for testing of *Staphylococcus aureus*). However, the inclusion of this data does not impact significantly the share of these applications in the total consumption amount.

- Estimates of health and health care related statistics are based on the most recent data available in the public domain, except for incidences of Venous Thromboembolism for the UK.

- In most cases, dose of the therapeutic agent is used to arrive at estimates and the gold amounts that would be present in drug delivery equipments, containers containing the drug, etc. have not been included in our estimates.

- Census data of the US (2010) and UK (2011) have been used to arrive at the prospective population.

The details of the data and assumptions used to calculate annual consumption of GNP from medical applications selected for the study is presented below. The two step approach:

1. Estimate the range of nano gold amount per application
2. Estimate the prospective affected population/total number of tests
Table A3-2: Prospective amount of Gold nanomaterials in select medical applications (high emission scenario)

<table>
<thead>
<tr>
<th>Application</th>
<th>Description</th>
<th>Amount per test / intake (unit)</th>
<th>Number of Applications per patient</th>
<th>Possible Population (UK and USA)</th>
<th>Prospective consumption amount(^a)</th>
<th>Refer to pages 10 to 20 for specific assumptions to estimate Au amount</th>
<th>End of Life</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diagnostic devices for Pregnancy and Ovulation detection</td>
<td>Lateral flow assay kits to detect the presence of select biomarkers in urine</td>
<td>(2.5 to 8.52)(\times)(10^{-7}) g</td>
<td>1/year</td>
<td>12'770'000</td>
<td>3.19 to 10.85</td>
<td>Refer to Bullet A.</td>
<td>Household waste</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2.5 to 8.52)(\times)(10^{-7}) g</td>
<td>1/year</td>
<td>61'601'000</td>
<td>15.40 to 52.36</td>
<td>Refer to Bullet A.</td>
<td>Medical waste</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2.5 to 8.52)(\times)(10^{-7}) g</td>
<td>6/year</td>
<td>19'557'000</td>
<td>29.34 to 136.10</td>
<td>Refer to Bullet A.</td>
<td>Medical waste</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2.5 to 8.52)(\times)(10^{-7}) g</td>
<td>6/year</td>
<td>90'732'000</td>
<td>99.74 to 462.73</td>
<td>Refer to Bullet A.</td>
<td>Medical waste</td>
</tr>
<tr>
<td>Diagnostic devices for HIV tests</td>
<td>Rapid Lab based test kits for HIV AIDS</td>
<td>8.52(\times)(10^{-7}) to 3.75(\times)(10^{-7}) g</td>
<td>Once/year</td>
<td>2'073'700</td>
<td>1.77 to 77.76</td>
<td>Refer to Bullets B.1. and B.2.</td>
<td>Medical waste</td>
</tr>
<tr>
<td>HIV Oral test kits</td>
<td></td>
<td>8.52(\times)(10^{-7}) to 3.75(\times)(10^{-7}) g</td>
<td>Once/year</td>
<td>22'000'000</td>
<td>18.74 to 825</td>
<td>Refer to Bullet B.3.</td>
<td>Household waste</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.52(\times)(10^{-7}) g</td>
<td>Once/year</td>
<td>20'853'000</td>
<td>17.77</td>
<td>Refer to Bullet B.3.</td>
<td>Medical waste</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.52(\times)(10^{-7}) g</td>
<td>Once/year</td>
<td>101'777'000</td>
<td>86.71</td>
<td>Refer to Bullet B.3.</td>
<td>Medical waste</td>
</tr>
<tr>
<td></td>
<td>Lab based test kits for HIV AIDS</td>
<td>0.000517 g</td>
<td>2 times/year</td>
<td>11600(^b)</td>
<td>59.97</td>
<td>Refer to Bullet G.</td>
<td>Medical waste</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.000517 g</td>
<td>2 times/year</td>
<td>105000(^b)</td>
<td>542.85</td>
<td>Refer to Bullet G.</td>
<td>Medical waste</td>
</tr>
<tr>
<td>Diagnostic device for MRSA/MSSA test</td>
<td>Test is conducted on a positive blood culture report to detect the presence of Methicillin Resistant and Methicillin Sensitive Staphylococcus aureus in blood</td>
<td>1.7(\times)(10^{-5}) g</td>
<td>Once</td>
<td>20000</td>
<td>0.34</td>
<td>Refer to Bullet C.</td>
<td>Medical waste</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.7(\times)(10^{-5}) g</td>
<td>Once</td>
<td>325000</td>
<td>5.25</td>
<td>Refer to Bullet C.</td>
<td>Medical waste</td>
</tr>
<tr>
<td>Modality for Removal of</td>
<td>(1.36 to 5.12)(\times)(10^{-2}) g</td>
<td>2</td>
<td>439014</td>
<td>11'976.29 to 44'911.1</td>
<td>Refer to Bullet D.</td>
<td>Medical waste</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Unless mentioned, reported unit is gram

\(^b\) Total no. of tests per year

\(^1\) Total no. of tests per year
<table>
<thead>
<tr>
<th>Application</th>
<th>Description</th>
<th>Amount per test / intake (unit)</th>
<th>Number of Applications per patient</th>
<th>Possible Population (UK and USA)</th>
<th>Prospective consumption amount</th>
<th>Refer pages 10 to 20 for specific assumptions to estimate Au amount</th>
<th>End of Life</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Infection Prevention</strong></td>
<td><em>Staphylococcus aureus</em> in the nasal passages to prevent nosocomial infection</td>
<td>(1.36 to 5.12) * 10^{-2} g</td>
<td>2</td>
<td>1'600'000</td>
<td>43'648 to 163'680</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.52 * 10^{-3} to 1.32 * 10^{-4} g</td>
<td>2</td>
<td>439'014</td>
<td>30.90 to 115.899</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.52 * 10^{-4} to 1.32 * 10^{-5} g</td>
<td>2</td>
<td>1'600'000</td>
<td>112.64 to 422.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Treatment of dental diseases</strong></td>
<td>Treatment of chronic periodontitis, endodontitis, peri-implant diseases</td>
<td>5.28 * 10^{-6} g</td>
<td>1</td>
<td>5'208'200</td>
<td>274.99</td>
<td>Refer to Bullet E.</td>
<td>Waste water</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.28 * 10^{-7} g</td>
<td>1</td>
<td>17'847'400</td>
<td>942.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.05 * 10^{-7} g</td>
<td>1</td>
<td>5'208'200</td>
<td>106'559.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.05 * 10^{-8} g</td>
<td>1</td>
<td>17'847'400</td>
<td>365'151.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Diagnostic test kits for detecting infectious diseases</strong></td>
<td>Gram positive blood culture tests (Septicaemia)</td>
<td>5.66 * 10^{-6} g</td>
<td>1</td>
<td>200'000</td>
<td>0.11</td>
<td>Refer Bullet G.1.1.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.66 * 10^{-7} g</td>
<td>1</td>
<td>325'000</td>
<td>1.84</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gram negative blood culture tests</td>
<td>5.66 * 10^{-6} g</td>
<td>1</td>
<td>75'000</td>
<td>0.42</td>
<td>Refer Bullet G.1.2.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.66 * 10^{-7} g</td>
<td>1</td>
<td>280'000</td>
<td>1.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>C. difficile</em> test (gram positive bacteria)</td>
<td>5.66 * 10^{-6} g</td>
<td>1</td>
<td>20'851</td>
<td>0.12</td>
<td>Refer Bullet G.1.3.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.66 * 10^{-7} g</td>
<td>1</td>
<td>370'260</td>
<td>2.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Respiratory Virus test</td>
<td>5.66 * 10^{-6} g</td>
<td>1</td>
<td>12'636'400</td>
<td>71.52</td>
<td>Refer Bullet G1.4.</td>
<td>Medical waste</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.66 * 10^{-7} g</td>
<td>1</td>
<td>60'856'000</td>
<td>344.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Diagnostic test kit to evaluate hypercoaguable state</strong></td>
<td>Detection of single nucleotide polymorphism (F2/F5) to establish risk from venous thrombosis (VTE)</td>
<td>5.66 * 10^{-6} g</td>
<td>1</td>
<td>225'000</td>
<td>1.27</td>
<td>Refer Bullet G.2.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.66 * 10^{-7} g</td>
<td>1</td>
<td>550'000</td>
<td>3.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Diagnostic test kit for genotyping drug metabolism</strong></td>
<td>Genotyping Warfarin metabolism</td>
<td>5.66 * 10^{-6} g</td>
<td>1</td>
<td>64'000</td>
<td>0.36</td>
<td>Refer Bullet G.3.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.66 * 10^{-7} g</td>
<td>1</td>
<td>550'000</td>
<td>3.11</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

188
<table>
<thead>
<tr>
<th>Application</th>
<th>Description</th>
<th>Amount per test / intake (unit)</th>
<th>Number of Applications per patient</th>
<th>Possible Population (UK and USA)</th>
<th>Prospective consumption amount</th>
<th>Refer pages 10 to 20 for specific assumptions to estimate Au amount</th>
<th>End of Life</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensors for diagnosing diseases from breath samples</td>
<td>Diagnosing of lung, prostate, head and neck cancer, breast, colorectal cancer and Chronic Kidney disease</td>
<td>$2.21 \times 10^6$, $2.21 \times 10^6$, $1.43 \times 10^5$ g</td>
<td>$1$</td>
<td>718'401</td>
<td>0.01 to 1'588.71</td>
<td>Refer Bullet F.</td>
<td>Medical waste</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2.21 \times 10^{5}$, $2.21 \times 10^{6}$, $1.43 \times 10^{5}$ g</td>
<td>$1$</td>
<td>2'087'211</td>
<td>0.02 to 4'615.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Treatment for solid tumors (colorectal, pancreas, breast, ocular)</td>
<td>Treatment of cancer by delivery of hrTNF (tumor necrosis factor) bound to gold nanoparticles</td>
<td>95.39% of (95 to 1432 μg)</td>
<td>8 doses for full treatment cycle</td>
<td>100'639</td>
<td>0.07-(0.48)-1.10 kg</td>
<td>Refer Bullet I.</td>
<td>Waste water</td>
</tr>
<tr>
<td></td>
<td></td>
<td>95.39% of (95 to 1432 μg)</td>
<td></td>
<td>421'610</td>
<td>0.3-(2.024)-4.61 kg</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Last line treatment</td>
<td>95.39% of 1432 μg</td>
<td></td>
<td>36'565</td>
<td>0.42 kg</td>
<td></td>
<td>Waste water + burial cremation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>95.39% of 1432 μg</td>
<td></td>
<td>130'640</td>
<td>1.50 kg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Treatment for patients diagnosed with head &amp; neck and lung cancer</td>
<td>Photothermal ablation of head and neck cancer and Lung tumor</td>
<td>2'793 to 4'655 mg$^1$</td>
<td>2 doses per treatment cycle</td>
<td>50'230</td>
<td>140 to 234 kg</td>
<td>Refer Bullet J.</td>
<td>Waste water</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>266'650</td>
<td>744.75 to 1'241.25 kg</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Last line treatment</td>
<td></td>
<td></td>
<td>37'490</td>
<td>104.7 to 174.52 kg</td>
<td></td>
<td>Waste water + Burial/cremation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>167'650</td>
<td>468.246 to 780.41 kg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diabetes Management</td>
<td>Transbuccal Insulin delivery Platform</td>
<td>0.366 mg</td>
<td>One dose every day*365 days</td>
<td>960'000</td>
<td>128.35 kg</td>
<td>Refer Bullet K.</td>
<td>Waste water</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6'300'000</td>
<td>841.62 kg</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^1$Includes two doses recommended per treatment cycle
### Appendix 3: Supporting Information for Chapter 3

<table>
<thead>
<tr>
<th>Application</th>
<th>Description</th>
<th>Amount per test / intake (unit)</th>
<th>Number of Applications per patient</th>
<th>Possible Population (UK and USA)</th>
<th>Prospective consumption amount(^a)</th>
<th>Refer pages 10 to 20 for specific assumptions to estimate Au amount</th>
<th>End of Life</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>UK (total)</td>
<td></td>
<td></td>
<td>540 kg</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>US (total)</td>
<td></td>
<td></td>
<td>2700 kg</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
A. **Test kits to detect pregnancy and ovulation**

Seven Pregnancy and ovulation test kits containing colloidal Gold approved by USFDA:

- Atlas Medical
- IND Diagnostics
- Polymed therapeutics
- NewScen Coast Bio-Pharmaceutical
- Tianjin New Bay Bioresearch Co., Ltd.
- Nantong EGENS Biotechnology Co., Ltd.
- Church and Dwight

Assumptions to estimate amount of Au per application:

- GNP size = 60-80 nm size (Nazareth et al., 2012)
- Conjugate release pad’s width is 15 mm (Wong and Tse, 2009)
- 1µl/mm of conjugate (gold + anti hCG) is used (Zhou et al., 2004)
- Mass of 60 nm GNP/ml = 5.68*10^{-5} g/ml (BBI Solutions)
- Range: 5-15 µl of conjugate per test device (BioAssay Works LLC). Therefore, use 15 µl of conjugate solution per test device: mass of Au = 8.52*10^{-7} g per test device
- Amount of gold antibody conjugate = 0.03 to 0.25 µg /test device, i.e., 3*10^{-8} g per test device and 2.5*10^{-7} g per test device (Wong and Tse, 2009)

Therefore, we use two estimates of Au per test device for high emission worst case scenario:

- 2.5*10^{-7} g/test device
- 8.52*10^{-7} g/test device

Assumptions for annual total number of tests:

- All women in the child bearing (15-44 yrs) age group conduct one pregnancy test per year. The age range of child bearing age has been taken from the reported age range of 15-44 yrs in Table 13 of the report Health, United States, 2011 (National Centre for Health Statistics, 2012)
- 50% women of child bearing age group from (30-44 yrs) conduct 6 ovulation tests per year
- 20 million pregnancy and ovulation tests in the US per year (BIO-AMD, 2014)
- Total female population, aged 15 to 44 yrs, for the US = 61’606’000 (U.S. Census Bureau, 2011)
- Total female population, aged 30-44 yrs, for the US = 30’244’000 (U.S. Census Bureau, 2011)
- Total female population, aged 15 to 44 yrs, for the U.K. = 12’777’000 (ONS, 2012)
- Total female population, aged 30-44 yrs, for the U.K. = 6’519’000 (ONS, 2012)

B. **Test kits to diagnose HIV**

B.1. **Four Rapid HIV tests approved by USFDA based on colloidal gold**

- Clearview® COMPLETE HIV ½ (Alere)
- Clearview® HIV 1/2 STAT-PAK (Alere)
- Uni-Gold Recombigen (TRINITY BIOTECH)
- OraQuick® ADVANCE Rapid HIV-1/2 (Orasure technologies)
- CE marked (European Union)
- Genie™ Fast HIV ½ (Bio-Rad)

Assumptions to estimate amount of Au per application:

- Particle size: 5-50 nm (Krutzik)
- Mass of GNP/ml = 5.68*10^{-5} g/ml (BBI Solutions)
Appendix 3: Supporting Information for Chapter 3

- Gold conjugate solution = 10 µl/test strip (Rohrman et al., 2012)
- Gold conjugate solution = 15 µl/test strip (BioAssay Works LLC)
- We use 15 µl/test strip = 8.52*10^{-7} g Au/test strip


Assumptions to estimate amount of Au per application
- GNP size = 80 nm (Nazareth et al., 2012)
- 10 ml vial (MedMira Laboratories Inc, 2003)
- Per vial caters to 15 tests (MedMira Laboratories Inc, 2003). So, amount of gold solution per test is 0.66 ml
- Mass of Au/ml = 5.68*10^{-5} g/ml (BBI Solutions)
- Mass concentration of Au (80 nm) per 0.66 ml or per test device = 3.75*10^{-5} g

Assumptions for annual total number of tests

Number of HIV tests conducted per year in the US = 16-22 millions (Centers for Disease Control and Prevention)

To estimate for high emission scenario, we use the higher value = 22 million tests for the US

For the UK
- All people who attended Sexual Health Clinics are tested for HIV AIDS in 2013 = 1373700 (Yin Z et al., 2014)
- Total no. of women tested under antenatal screening program in 2013 = 700000 (Yin Z et al., 2014)

Therefore, total number of HIV tests for the UK in 2013 = 2073700

B.3. Colloidal Gold based HIV home based test kits

Approved by US FDA on 3 July 2012 (OraSure Technologies Inc., 2015)

Assumptions to estimate amount of Au per application
1. 15 µl/test device = 8.52*10^{-7} g/test strip (BioAssay Works LLC)
2. 15 µl of gold conjugate solution per strip (BioAssay Works LLC)

Assumptions for annual total number of tests

Since this is a home based test based on oral fluids, we assume 50% of people from age 15 to 64 years conduct one home based HIV test per year, though legally the self-testing kit is to be sold to population aged 17 years or more, we have used 15-64 yrs because of the class intervals provided in the population tables.

- Population in the age group of 15 to 64 yrs for the US (Year 2010) = 203 554 000 (U.S. Census Bureau, 2011)
- Population in the age group of 15 to 64 yrs for the UK (Year 2011) = 41 706 000 (ONS, 2012)

C. Lateral flow Immunoassay test for detection of Methicillin Resistant and Methicillin Sensitive Staphylococcus aureus in blood

Assumptions to estimate amount of Au per application
- GNP size = 80 nm (20-80 nm for Lateral Flow Devices and Conjugates)
- Mass gold /ml = 5.69*10^{-5} g/ml (BBI Solutions)
- 15 µl of gold conjugate solution per strip (BioAssay Works LLC)
- Two test kits per test (Microphage Inc., 2013). Therefore, 30 µl of gold conjugate per test, i.e., 0.03 ml = 1.7*10^{-5} g of Au per test device

Assumptions for annual total number of tests

US:
No. of discharges with septicaemia = 1665400. Around 15% (approx 250000) of the above discharges were diagnosed to be due to gram positive bacteria (Elixhauser et al., 2011). 50% of patients suffering from septicaemia, the bacteria is unspecified. And, 15% have bacteria present in blood, but without the response. Keeping these factors into consideration, assume 30% more tests to be done. (Elixhauser et al., 2011)
Therefore, total no. of tests = 25’000 + 30% of 250’000. Ca.325’000

UK:
No. of MSSA and MRSA reports in England (above 2 years of age) year 2013 = ca. 10’000 (PHE, 2014)
Population for England above 4 years is ca. 50 million (ONS, 2012).
Total population over 4 yrs for UK = ca. 60 million (ONS, 2012)
So, for the UK = estimated number of MRSA and MSSA cases is 12000 (above 4 years of age) approx. = assume 15’000 for all age groups.
Therefore, total no. of tests = 15’000 + 30% more tests = 15’000 + 4’500 = ca. 20’000

D. Nasal decolonization of Staphylococcus aureus

Assumptions to estimate amount of Au per application
- GNP size = 2 and 15 nm (Wilson et al., 2008)
- One vial = 1.5 ml, 54 vials in a pack (MRSAid)
- Two treatments per patient (MRSAid)
- 2nm GNP has ca. 270 atoms (M_Au = 53000 Da)(Gibson et al., 2007)
- Mass of one GNP of 2 nm = 53000 dalton = 8.8*10^{-20} g(Gibson et al., 2007)
- Particle mass of 15 nm GNP= 3.41*10^{-17} g(BBI Solutions)
- Total particles in 1 ml = (1*10^{13} to 1 * 10^{15}) (Wilson et al., 2008). Use: 1 * 10^{15} particles /ml. Therefore, no. of particles in 1.5 ml =1.5*10^{15}
- 1 drop = approx. 0.05 ml
- 8 drops per patient= 0.4 ml per patient. Therefore, no. of particles in 0.4 ml = 0.4*10^{15}. Therefor, we use two estimates of Au per treatment for high emission scenario based on assumed particle size of 2 nm and 15 nm and volume of 0.4 ml and 1.5 ml:
- Amount per treatment (2 nm size)= 3.52*10^{-5} g (0.4 ml) to 1.32*10^{-4} g (1.5 ml)
- Amount per treatment (15 nm size) = 1.36*10^{-2} g (0.4 ml) to 5.12 *10^{-2} g (1.5 ml)

Assumptions for annual total number of tests
- 10-40% of population as outpatients or upon admission have nasal colonisation of S. aureus (von Eiff et al., 2001)
- ca. 2% - 5% is the rate of Surgical Site Infections (Deverick J. Anderson et al., 2008)
- We assume screening/treatment of 10% of the all surgical procedures (inpatients), because people with surgical procedures are at risk of contracting MRSA
- Therefore, 10% of 16 million gives are the prospective number of patients treated = 1600000 for the US
- UK – Sum of Scotland, England, Wales and Northern Ireland =10% of (0.25 million + 3749225+0.25 million +0.18 million) = 439014 patients treated

Scotland: Total main procedures/operations and inpatients stay greater than zero days for year 2011-2012 is 242’518 = ca. 0.25 million (NHS Scotland, 2012)
England: Total main procedures (minus drug therapy and diagnostic) = 8520965 (2011-2012). Inpatients = ca. 44% of 8520965 = 3749225 (HSCIC, 2012)

Wales: Total inpatients for the year 2011 = 226911 = ca. 0.25 million (NHS Wales)

Northern Ireland: Total main procedures for the year 2011-12 = 350651 (DHSSPS, 2012), 48.9% (Myers et al., 2012) were inpatients = 48.9% *350651 = 171483 = ca. 0.18 million

E. Periodontal disease treatment

Assumptions to estimate amount of Au per application

- GNP size = 2nm and 15 nm (Wilson et al., 2008)
- Mass of 2 nm GNP = 8.8*10^-20 g (BBI Solutions)
- Mass of 15 nm GNP = 3.41*10^-17 g (BBI Solutions)
- Application dose = 0.2 ml of solution per pocket (Ondine Biomedical Inc.)
- Total dose: 0.6 ml per patient (3 teeth treated per patient)
- No. of GNP/ml = (1*10^15) (Wilson et al., 2008)

Therefore, we use two estimates of amount of Au per patient based on particle size of 2nm and 15 nm:

- 2 nm GNP size = 5.28*10^-5 g
- 15 nm GNP size = 2.05*10^-2 g

Assumptions for annual total number of tests

Background data to arrive the assumption for total number of tests

US:

Definitions (Eke et al., 2012)

i. Severe periodontitis: Two or more interproximal (IP) sites in different teeth having >= 6 mm Attachment loss AND 1 or more IP site >= 5 mm pocket depth

ii. Moderate periodontitis: Two or more I.P. sites >= 4 mm attachment loss OR two or more I.P. sites >= 5 mm pocket depth

- 47.2% of adults over 30 yrs of age in the United States have some form of periodontal disease (Eke et al., 2012)
- 8.5% of the adult population (30 years or more) in the U.S suffer from severe periodontitis

30% of the adult U.S. Population suffer from moderate periodontitis

UK:

- 45% of all dentate (at least 1 teeth) adults, age 16 yrs or more, have pocketing depth of 4 mm or more (HSCIC, 2011)
- 8% of all dentate adults, greater than 16 yrs of age, pocket depth >6 mm (HSCIC, 2011)
- 8% of all dentate adults, greater than 16 yrs of age, loss of attachment > 5.5 mm and 5% of all dentate adults aged 16 yrs or more = Pocketing depths > 5.5 mm (Morris et al., 2001)
- Percentage of total finished admission episodes dealing with periodontitis and gingivitis = 9% (NHS England, 2014)

10-15% of world adult population (greater than 15 yrs of age) -severe periodontitis, i.e. Community Periodontal Index = 4, Pocket depth of >= 6 mm (Petersen and Ogawa, 2005)

Assumptions for annual total number of tests

- 10% of the population of the U.S. above 30 yrs of age will seek treatment for periodontitis
- 10% of the population of the U.K. above 15 yrs of age will seek per seek periodontitis treatment
• Total population of the US above 30 years = 178’474’000 (U.S. Census Bureau, 2011)
• Total Population of the UK above 15 years of age = 52’082’000 (ONS, 2012)

F. Sensors for diagnosing diseases from breath samples

Assumptions to estimate amount of Au per application

• GNP Size = 5nm; an array of monolayer capped spherical AuNPs.
• Mass of 5 nm GNP = 1.26*10^{-18} g (BBI Solutions)
• One drop as 180 pl (Raguse et al., 2007)
• Or, 1 drop as 0.05µl (Steinecker et al., 2011)
• Or, 1 drop as 0.05 ml
• 9 sensors with 9 different surface cappings (Haick et al., 2011)
• The sensor consists of 10 pairs of circular interdigitated (IDE) gold electrodes of 3 mm diameter and 20 µm electrode width and 20 µm electrode gap (Peng et al, 2009).
• 10 drops per circular IDE (Chow et al., 2009; Chow et al., 2010; Cooper et al., 2010; Raguse et al., 2009)
• Disposal of sensors array every 10 tests\(^{11}\).

Therefore,

• 9 sensors*0.05 ml per drop *10 drops = 4.5 ml/per sensor array
• 9 sensors*0.05µl per drop *10 drops= 4.5 µl/ = 0.0045ml
• 9 sensors*180 pl*10 drops =9*1.8*10^{-6}*10=0.00162 ml/sensor

- 25 ml of 31.5 mM HAuCl\(_4\) solution = 0.0315 moles/litre of HAuCl\(_4\) solution (Haick et al., 2011)
- Moles of HAuCl\(_4\) solution in 25 ml = 7.875*10^{-4} moles/l (Lewis et al., 2006)
- No. of atoms in a 5 nm particle = (Radius of GNP divided by radius of one atom of Gold NP) = (5/0.137)\(^3\) = 48612 atoms of Au per NP.
- No of nanoparticles formed = 4.74*10^20 atoms of Au divided by No. of atoms of Au per NP
  = 48612 = 9.75*10^{15} AuNPs
- Therefore 25 ml of 31.5 mM of HAuCl\(_4\) forms = 9.75*10^{15} GNP
- Number and Mass of GNP in different volumes:
  - Volume 4.5 ml = 1.76*10^{15} GNP; Mass of Au = 1.76*10^{15} * 1.26*10^{-18} = 2.21*10^{-13} g
  - Volume 0.0045ml = 1.75*10^{12} GNP; Mass of Au =1.75*10^{12} AuNPs * 1.26*10^{-18} g
  =2.21*10^{-6} g
  - Volume 0.000162 ml = 1.26*10^{8} GNP; Mass of Au = 1.26*10^{8} AuNPs * 1.26*10^{-18} g
  =1.59*10^{-10} g

Assumptions for annual total number of tests

<table>
<thead>
<tr>
<th>Type of cancer</th>
<th>US (estimated cases in 2014)(Howlader N et al., 2014)</th>
<th>UK (cases for 2011) <a href="http://www.cancerresearchuk.org/">http://www.cancerresearchuk.org/</a></th>
</tr>
</thead>
<tbody>
<tr>
<td>Lung</td>
<td>224’210</td>
<td>43’463</td>
</tr>
<tr>
<td>Colorectal</td>
<td>136’830</td>
<td>41’581</td>
</tr>
<tr>
<td>Head and neck cancer</td>
<td>42’440</td>
<td>6’767</td>
</tr>
<tr>
<td>Prostate</td>
<td>233’000</td>
<td>41’736</td>
</tr>
<tr>
<td>Breast</td>
<td>235’630</td>
<td>50’285</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>872’110</strong></td>
<td><strong>183’832</strong></td>
</tr>
</tbody>
</table>

Chronic Kidney disease (CKD):

\(^{11}\) Disposal of sensor after every 100 tests for asthma diagnosis http://www.niox.com/en/ordering/)
Appendix 3: Supporting Information for Chapter 3

US = 20 million (Centers for Disease Control and Prevention)
UK = Range of CKD 44’607 to 7’291’480 = ca 7 million (Roderick et al., 2011).

G. Tests To Diagnose Disease Conditions

G.1. Infectious Disease

Assumptions to estimate amount of Au per application
- GNP size = 13-20 nm (Nanosphere Inc.); assume GNP size = 20 nm
- Volume per test cartridge: 0.1 ml, i.e., ca. 2 drops
- Mass of gold per ml = 5.66*10^-5 g (BBI Solutions); mass of gold in 0.1 ml or mass of Au per application = 5.66*10^-6 g

Assumptions for annual total number of tests

G.1.1 Septicaemia (Gram positive blood culture test)
Refer to details in Page 12 for assumptions for annual number of tests.
US = 325’000
UK = 20’000

G.1.2 Gram Negative Blood culture test
US = No. of discharges with septicemia = 1’665’400 (Elixhauser et al., 2011)
No. of discharges with gram negative bacterial incidences = 215’000 (Elixhauser et al., 2011)
Assume, 30% more tests are done. Total no. of tests = 215’000 + 30% of 215’000 = 280’000
Total no. of E-coli infections in England = 33’366 for year 2013 (PHE, 2014)
Assume 50’000 for the UK for all gram negative infections
Assume, 30% more tests are done. Therefore, total no. of tests for the UK = 30% of 50’000 + 50’000 = 75’000.

G.1.3. C. difficile infections (CDI)
- 336, 600 hospitalizations that involved CDI in 2009 (Locado et al., 2012)
- Assume 10% more diagnostic tests have been performed
- So, no. of tests/year for the US = 10% of 336’600 + 336’600 = 370’260
- For England, reported cases is 13756 for the year 2013 (PHE, 2014)
- To estimate reported cases for CD infections for the UK, using the rate of 30 per 100’000 of population = 18’955 (PHE, 2014)
- Assume 10% more tests conducted
- No. of tests done per year for the UK = 20’851

G.1.4 Respiratory Virus
- USA = 5 to 20% of the population every year (Centers for Disease Control and Prevention)
- Assume, all people having flu like symptoms are tested for respiratory virus.
- Incidences of flu = 20% of total population of the US = 60’856’000
- UK = Same assumption as that for the US, i.e. 20% of population
- Flu season = October to May (Centers for Disease Control and Prevention)

G.2. Test kit for detection of single nucleotide polymorphism (F2/F5) to establish risk from venous thrombosis (VTE)

Assumptions to estimate amount of Au per application
- GNP size = 13-20 nm (Nanosphere Inc.); assume GNP size = 20 nm
- Volume per test cartridge: 0.1 ml, i.e., ca. 2 drops
• Mass of gold per ml = $5.66 \times 10^{-5}$ g (BBI Solutions); mass of gold in 0.1 ml or mass of Au per application = $5.66 \times 10^{-6}$ g

Assumptions for annual total number of tests
• Prevalence of Factor V Leiden in European Whites = 3-15% (Kujovich, 2011)
• Prevalence of Factor V Leiden in UK = 8.8% (Kujovich, 2011)
• Prevalence of Factor V Leiden in United States, white population = 5.2% (Kujovich, 2011)

Assume, 8% of the white population will carry Factor V gene mutation

US white population = $223'553'265^{12} = 8\%$ of $223'553'265 = 17'884'261$

White population for England and Wales = $54'809'000$(ONS, 2011b) = 8% of $54809000 = 4'384'720 = \text{approx. 4'400'000}$

Estimated annual average of hospitalizations with VTE ($\geq 18$ years in the United States) = 547596 among those aged $\geq 18$ years in the United States (Centers for Disease Control and Prevention, 2012)

547596 hospitalisations shows 3% of the white population of the US who might carry one of the risk factors for VTE are hospitalised in a given year.

Therefore, we assume 5% of the white population of the US and UK gets the genetic test done.

5% of 4’400’000 for the UK = approx. 225’000

G.3. Test kit for detection and genotyping Warfarin metabolism

Assumptions to estimate amount of Au per application
• GNP size = 13-20 nm (Nanosphere Inc.); assume GNP size = 20 nm
• Volume per test cartridge: 0.1 ml, i.e., ca. 2 drops
• Mass of gold per ml = $5.66 \times 10^{-5}$ g (BBI Solutions); mass of gold in 0.1 ml or mass of Au per application = $5.66 \times 10^{-6}$ g

Assumptions for annual total number of tests
To establish Warfarin dosages in patients diagnosed with VTE, we assume all hospitalisations/diagnosis with VTE are advised the genetic test for Warfarin metabolism to establish sensitivity to Warfarin and rate of metabolism.

UK, 64000 Finished Consultant Episodes of VTE for the year 2004-05 (NICE, 2009)

For the US, VTE diagnosis = 547'596 = approx. 550'000 (Centers for Disease Control and Prevention, 2012)

H. Test To Establish Viral Load In HIV Patients

Assumptions to estimate amount of Au per application
• GNP size = 80 nm (Hansen and Krauledat, 2004)
• One polypropylene vial for 20 tests (Hansen et al., 2012)
• Assume each vial is 2.5 ml. Therefore, 0.125 ml per test.
• No. of particles per ml = $8 \times 10^{11}$ (Hansen and Krauledat, 2004)
• Mass of one gold NP of 80 nm size = $5.17 \times 10^{-15}$ g (BBI Solutions)
• Amount of Au in 0.125 ml = 0.000517 g. Therefore, amount of Au per test device = 0.000517 g

The test is to manage disease progression (start ARV therapy or change drugs when the disease becomes drug resistant).

Population assumptions for annual total consumption
US:

Appendix 3: Supporting Information for Chapter 3

- HIV prevalence (year end 2010) = 872’990 (CDC, 2013)
- HIV incidence (new diagnosis) is = ca. 50’000 every year (CDC, 2013)
- Stage 3 HIV prevalence = ca. 500’000 (end of 2010) (CDC, 2013)
- 500’000/872’990 = ca. 60% of people are in Stage 3 of total people living with HIV/AIDS
- Assume people with Stage 3 HIV infection and are on regular Anti-retroviral therapy
- Assume device is used once every 6 months to check their CD4 count. Therefore, Total tests done for patients living with Stage 3 HIV per year =500’000 * 2 = 1 million (AVERT)
- Total tests per year = Newly diagnosed + test for HIV stage 3 = 1 million + 50’000 = 1’050’000

UK:
- Newly diagnosed = 6’000 (Yin Z et al., 2014)
- 107’800 people are living with known HIV infection. Assume 50% of the people living with known HIV infection are late stage = 53’900 = approx. 55’000 (Yin Z et al., 2014)
- Total tests done for patients living with Stage 3 HIV per year = 55’000*2 = 0.11 million =116’000
- Total tests = Newly diagnosed + test for HIV stage 3 = 0.11 million + 50’000

I. Treatment modality for Cancer : TNF delivery

Assumptions to estimate amount of Au per application
- GNP size = 30-34 nm (Paciotti et al., 2004)
- Total dose range of CYT-6091 = 90 ± 5 to 1208 ± 214 µg; therefore, use dose = 95µg to 1’432 µg (Libutti et al., 2010)
- SH- PEG = 20 kDa (Paciotti and Tamarkin)
- TNF monomer = 17 kDa. Assume = 20 kDa (Paciotti et al., 2004)
- One GNP has 400 TNF molecules bound to it (Paciotti et al., 2004)
- Since the available literature doesn’t inform of the number of PEG on one GNP (Tsai et al., 2012). Assume, both SH-PEG and rhTNF are bound to the GNP and they do not cross-link with each other.
- Mass of 1 GNP of size 30 nm = 2.73*10^-16 g (BBI Solutions)
- Mass of 400 TNFs = 400* 20 kDa = 400* 3.32*10^-20 g = 1.32*10^-17 g (Conversion from Da to grams)
- Ratio=GNP: TNF = (2.73*10^-16 /1.32*10^-17) = 20.76: 1. Thus, percentage weight of gold is (20.76/21.76)*100 = 95.39%
- No. of doses per treatment cycle (high dose) = 8 ; 4 courses where 1 course = 2 doses) (Libutti et al., 2010)

Amount of Au per patient:
- Estimates of range of Au per patient: 95.39% of (95*8) µg to 95.39% of (1’432*8) µg
- Estimate of average amount of Au per patient = 95.39% of (4801 µg)

Population assumptions for annual total consumption
Type of enrolled patients in clinical trial phase I (Libutti et al., 2010):
- Ocular melanoma
- Adenocarcinoma of the colon and pancreas
- Ductal carcinoma of breast
- Carcinoma of rectum

Combine adenocarcinoma of the colon and carcinoma of rectum as colorectal cancer or bowel cancer.
Dynamic Probabilistic Modelling of Environmental Emissions and Concentrations of Engineered Nanomaterials

<table>
<thead>
<tr>
<th>Type of cancer</th>
<th>US</th>
<th>UK</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Estimated cases in 2014</strong> <em>(Howlader N et al., 2014)</em></td>
<td><strong>Estimated deaths for 2014</strong> <em>(Howlader N et al., 2014)</em></td>
<td><strong>Diagnosed Cases for 2011</strong></td>
</tr>
<tr>
<td>Colorectal</td>
<td>136'830</td>
<td>50'310</td>
</tr>
<tr>
<td>Pancreatic</td>
<td>46'420</td>
<td>39'590</td>
</tr>
<tr>
<td>Breast</td>
<td>235'630</td>
<td>40'430</td>
</tr>
<tr>
<td>Ocular</td>
<td>2'730</td>
<td>310</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>421'610</td>
<td>100'639</td>
</tr>
</tbody>
</table>

J. Treatment modality for Cancer: Thermal ablation

Assumptions to estimate amount of Au per application

- Dosage = 21 to 35 mg/kg body *(Gad et al., 2012)*
- Two infusions is the expected clinical dose *(Gad et al., 2012)*
- Average body weight = 70 kg
- 95% of the weight of Auroshells is gold weight *(Gad et al., 2012)*

Auroshells: 155 nm in diameter *(120 nm diameter is the silica core)* with a coating of polyethylene glycol 5000.

Estimates of Amount of Au per patient
- 95% of (21*70*2) = 2'793mg
- 95% of (35*70*2) = 4'655mg

Population assumptions for annual total consumption

<table>
<thead>
<tr>
<th>Type of cancer</th>
<th>US</th>
<th>UK</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Estimated cases in 2014</strong> <em>(Howlader N et al., 2014)</em></td>
<td><strong>Estimated deaths for 2014</strong> <em>(Howlader N et al., 2014)</em></td>
<td><strong>Diagnosed Cases for 2011</strong></td>
</tr>
<tr>
<td>Lung cancer 13</td>
<td>224'210</td>
<td>159'260</td>
</tr>
<tr>
<td>Head and Neck Cancer</td>
<td>42'440</td>
<td>8'390</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>266'650</td>
<td>167'650</td>
</tr>
</tbody>
</table>

K. Transbuccal Insulin Delivery Platforms

Assumptions to estimate amount of Au per application

- GNP size = 3.5 nm = 102 atoms of Au *(Williams et al.)*
- Mass of 3.5 nm GNP = 102 atoms *196.96 g/mol = 3.33*10^-20 g
- 1 IU of insulin = 0.0385 mg *(Joshi et al., 2007)*
- Average body weight = 70 kg
- Total daily insulin intake dose = 0.55 IU/kg of body weight 14 (without giving consideration to insulin resistance, other oral medications, etc.) = 0.55*70 = 38.5
- Molecular weight of insulin monomer = 5808 Da *(Joshi et al., 2007)* = ca 5808 g/mol
- No. of Insulin monomer required per day = 38.5 * 0.0385 mg *(Mass of Insulin) = 1.48mg of Insulin/day = 2.5*10^-7 moles of Insulin = 1.5*10^17 molecules of Insulin
- Binding of Insulin to NP is in the ratio of 14:1 *(14 insulin monomer)* *(Williams et al.)*

13 [http://www.nanospectra.com/clinicians/trialinfo.html]: The clinical trials include metastatic lung cancer and refractory head and neck cancer
Appendix 3: Supporting Information for Chapter 3

- No. of GNP required for binding $1.5 \times 10^{17}$ molecules of Insulin = $1.07 \times 10^{16}$
- Gold concentration = 4.037 mg of Au/ml = $1.21 \times 10^{17}$ GNP/ml (Williams et al.)
- Mass of $1.07 \times 10^{16}$ GNP = 0.366 mg of Au.

Therefore, Amount of Au per day per patient = 0.366 mg

Population assumptions for annual total consumption

- Total diagnosed diabetic population in the US of all age groups (all ages, 2012) = 21 million (Centers for Disease Control and Prevention, 2014)
- Total diagnosed adults (greater than 18 years) take insulin = 6 million, i.e. 28% of the diagnosed adult population (Centers for Disease Control and Prevention, 2014)
- People with diagnosed diabetes (20 years and less) = 215,000 (Centers for Disease Control and Prevention, 2014)

Therefore, assume 30% of the diagnosed population of all age groups take insulin = 6.3 million

UK = 3.2 million people have been diagnosed with diabetes (2013) (Diabetes UK, 2014)
Also, assume 30% of UK’s diabetic patients will take insulin (as derived from the American numbers) = 30% of 3.2 million = 960,000
### A 3.2 Summary of volumes of technical and environmental compartments

Table A3-3: Summary of volume or mass of environment compartment – air, water, sediment and soil – as input parameters for the probabilistic mass flow model. The Comments column provides the values used to calculate the mass/volume. The mass of soil and sediment compartment has been arrived at by multiplying the area, the mixing depth and the density. The area of natural and urban soils has been calculated by subtracting the area occupied by agricultural soils and other soils. Littoral sediments (beaches and intertidal mud flats and salt marshes) have been included for the UK as it represents a key ecosystem of the UK.

<table>
<thead>
<tr>
<th>Compartments</th>
<th>Countries</th>
<th>Formula/ Calculation</th>
<th>Mass/Volume</th>
<th>Unit</th>
<th>Comments</th>
</tr>
</thead>
</table>
| Sludge treated soils | UK | $1.65 \times 10^9 \times 0.2 \times 1.5 \times 10^3$ | 4.95E+11 | kg | • 1.65\times 10^9 \text{ m}^2: total sludge treated agricultural land area in the UK (Water UK, 2010)  
• 0.2 m: the depth of agricultural soil (ECB, 2003b)  
• 408,139,000 acres is the total cropland/arable land in the US\(^{16}\) = ca. 1.65\times 10^9 \text{ m}^2 (Trading Economics; USDA, 2011)  
• 1.5\times 10^3 \text{ kg/m}^3: the density of dry soil (ECHA, 2012a; OECD, 2013) |
| | US | $1.65 \times 10^{10} \times 0.2 \times 1.5 \times 10^3$ | 4.95E+12 | kg | • Total area of sludge treated soil the US; 1% (UN-HABITAT, 2008) of arable land= 1.65\times 10^{10} \text{ m}^2 |
| Surface water | UK | $3.25 \times 10^9 \times 1\,000 \times (365/40)$ | 8.90E+13 | litre | • 3.25\times 10^9 \text{ m}^2: the total freshwater area in the UK (Morton et al., 2011)  
• 3 m: the mixing depth of surface water  
• 1000: the conversion from \text{ m}^3 to litre  
• 86,409 sq. Miles: the area of Inland water (U.S. Census Bureau, 2013)  
• 59,959 sq. Miles: the area of Great Lakes (U.S. Census Bureau, 2013)  
• 2.59\times 10^4: the conversion factor from \text{ sq. mile to m}^2  
• 40:ENM residence time in the system (Gottschalk et al., 2009b)  
• 365 days: 1 year |
| | US | $(86,409+59,959) \times 2.59 \times 10^9 \times 3 \times 1000 \times (365/40)$ | 1.04E+16 | litre | • 3.25\times 10^9 \text{ m}^2: the total freshwater area (Morton et al., 2011)  
• 2.59\times 10^4: the conversion factor from \text{ sq. mile to m}^2  
• 365 days: 1 year |
| Surface water Sediments | UK | $(3.25+2.59) \times 10^9 \times 0.03 \times 0.82 \times 10^3$ | 1.44E+11 | kg | • 3.25\times 10^9 \text{ m}^2: the total freshwater area (Morton et al., 2011)  
• 0.82\times 10^3 \text{ kg/m}^3: the bulk density of dry sediments (ECHA, 2012a),(Dedeh et al.)  
• 86,409+59,959 sq. Miles: the surface water area in the US (U.S. Census Bureau, 2013)  
• 2.59\times 10^4: the conversion factor from \text{ sq. mile to m}^2 |
| | US | $(86,409+59,959) \times 2.59 \times 10^9 \times 0.03 \times 0.82 \times 10^3$ | 9.33E+12 | kg | • 3.25\times 10^9 \text{ m}^2: the total littoral sediment area(Morton et al., 2011)  
• 0.82\times 10^3 \text{ kg/m}^3: the bulk density of dry sediments (ECHA, 2012a),(Dedeh et al.)  
• 86,409+59,959 sq. Miles: the surface water area in the US (U.S. Census Bureau, 2013)  
• 2.59\times 10^4: the conversion factor from \text{ sq. mile to m}^2 |
| STP Effluent | UK | $11 \times 10^9 \times 365$ | 4.02E+12 | litre | • 11 billion L: the amount of wastewater collected/day in the UK (DEFRA, 2012)  
• 365 days: 1 year |
| | US | $3.09 \times 10^8 \times 165 \times 3.785 \times 365$ | 7.04E+13 | litre | • 3.09\times 10^8: US population (2010) (U.S. Census Bureau, 2011)  
• 165 US gallons wastewater is assumed per capita per day (USEPA, 2000)  
• 3.785: gallons to litres |
| STP sludge | UK | $1.41 \times 10^9$ | 1.41E+09 | kg | • 1.41\times 10^9 \text{ kg : STP sludge (dry weight) generated in the UK (DEFRA, 2012)} |
| | US | $6.5 \times 10^9$ | 6.5E+09 | kg | • 7.18\times 10^9\text{ tons: Biosolids generated in the U.S. (NEBRA, 2007, UN-HABITAT, 2008)}  
• 0.9072: Short Ton to metric Ton |

\(^{15}\) 1 acre = 0.004046 km\(^2\)  
\(^{16}\) In the US, treated sewage sludge is termed as biosolids.
Table A3-4: Summary of non-hazardous household and hazardous healthcare and biological waste

<table>
<thead>
<tr>
<th>Compartments</th>
<th>Countries</th>
<th>Formula/ Calculation</th>
<th>Mass/Volume</th>
<th>Unit</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hazardous healthcare and biological (H&amp;B) waste</td>
<td>UK</td>
<td></td>
<td>1.4*10^8</td>
<td>kg</td>
<td>• 144’000 tonnes of H&amp;B waste incinerated in year 2008, i.e., 40% of hazardous H&amp;B waste generated (DEFRA, 2013a)</td>
</tr>
<tr>
<td>treated by incineration</td>
<td>US</td>
<td>146'502*0.9072</td>
<td>1.1*10^8</td>
<td>kg</td>
<td>• 146'502 tons: Estimated throughput of 54 medical waste incinerators in year 2011 (RTI International, 2012)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hazardous H&amp;B waste sent to landfill</td>
<td>UK</td>
<td>Total hazardous H&amp;B waste generated – waste incinerated</td>
<td>2.1*10^8</td>
<td>kg</td>
<td>• 350’000 tonnes: Total hazardous H&amp;B generated in the year 2008 (DEFRA, 2013a)</td>
</tr>
<tr>
<td></td>
<td>US</td>
<td>Total hazardous H&amp;B waste generated – waste incinerated</td>
<td>1.2*10^9</td>
<td>kg</td>
<td>• 5.9 million tons: Total H&amp;B waste generated per year (Practice Greenhealth)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• 24% (Kwakye et al., 2011) of 5.9 million tons: Total hazardous waste generated per year</td>
</tr>
<tr>
<td>Non hazardous household waste treated by</td>
<td>UK</td>
<td>15%*19 million tonnes</td>
<td>2.8*10^9</td>
<td>kg</td>
<td>• 19'354'616 tonnes of household and similar waste generated in the year 2010 (EC, 2013a)</td>
</tr>
<tr>
<td>incineration</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• 15% of waste treated (2008) (EC, 2013b)</td>
</tr>
<tr>
<td></td>
<td>US</td>
<td></td>
<td>2.6*10^{10}</td>
<td>kg</td>
<td>• Assume waste generated = waste treated</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• 29 million tons: Incineration with energy recovery (USEPA, 2013)</td>
</tr>
<tr>
<td>Non hazardous household waste sent to landfill</td>
<td>UK</td>
<td>85%*19 million tonnes</td>
<td>1.6*10^{10}</td>
<td>kg</td>
<td>• 85% of waste treated is landfilled (2008)</td>
</tr>
<tr>
<td></td>
<td>US</td>
<td></td>
<td>1.2*10^{11}</td>
<td>kg</td>
<td>• 134 million tons: Municipal waste Landfilled in Year 2011 (USEPA, 2013)</td>
</tr>
</tbody>
</table>
### A 3.3 Information for Transfer Coefficients

#### Table A3-5: Summary of parameters related to waste water

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Countries</th>
<th>Values</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Connection rate to STP</td>
<td>UK</td>
<td>0.96</td>
<td>• 96%: Percentage of population connected to STP (DEFRA, 2012)</td>
</tr>
<tr>
<td></td>
<td>US</td>
<td>0.74</td>
<td>• 74%: Percentage of population connected to centralised STP (USEPA, 2008)</td>
</tr>
<tr>
<td>Misconnection of STP pipes</td>
<td>UK</td>
<td>0.0026 to 0.018</td>
<td>• Range estimated from (Personal communication with Bryan Ellis, 2014; Ellis, 2013; ONS, 2011a). Please see explanation in Notes</td>
</tr>
<tr>
<td></td>
<td>US</td>
<td>No data available</td>
<td>• None</td>
</tr>
<tr>
<td>Leakage of STP pipes</td>
<td>UK</td>
<td>0.03 to 0.05 of effluent collected</td>
<td>• Range estimated from (DEFRA, 2012; Ellis et al., 2004; Ellis et al., 2008; Rutsch et al., 2008). Please see explanation in Notes</td>
</tr>
<tr>
<td></td>
<td>US</td>
<td>0.05 to 0.06 of effluent collected</td>
<td>• Range estimated from (Ellis et al., 2004; Jr. Sharp, 2010)</td>
</tr>
<tr>
<td>Overflows</td>
<td>UK</td>
<td>Mean= 0.161, Sd=0.079</td>
<td>• 16.1% of dry weather flow (std dev =7.9% with lognormal distribution)(Constantino Carlos, 2014)</td>
</tr>
<tr>
<td></td>
<td>US</td>
<td>0.01 to 0.07</td>
<td>• Range estimated from (ASCE, 2013; USEPA, 2008). Please see explanation in Notes</td>
</tr>
</tbody>
</table>
NOTES

Dry weather flow

- Dry weather flow = Population served * per capita water output + Infiltration + trade effluent
- Total Population (2010) census = 63,182,000
- Population served by WWTP = 96%
- Population served = 96% * 6318'200 = 60654720
- Per capita waste water output = 0.15 m$^3$/day (British Water, 2013)
- Total population output = 60'654'720*0.15 m$^3$ * 365 days = 3.32 billion m$^3$
- Per capita industrial output = 0.028 m$^3$/day (Scott Wilson, 2010)
- Infiltration = 25% of population WW load = 25% * 3.32E+09 = 8.30E+08 m$^3$ = 830 million m$^3$ (Ellis, 2001; Scott Wilson, 2010)
- Trade flow per year = 0.028 m$^3$/day * 60'654'720 * 365 = 6.20E+08 m$^3$ = 620 million m$^3$
- Total days in a year = 365
- DWF/year = 4.77E+09 m$^3$ = 4.77 billion m$^3$ (nearly same as waste water collected - 4.02 billion m$^3$)
- Storm tank discharges = 16.1% of dry weather flow (Constantino Carlos, 2014)

Misconnections Volume (UK)

- Total no. of unshared dwellings in 2011 (whole house or bungalow) (ONS, 2011a) = 20’514’994
- Misconnection rate = 1 to 7% and national average = 3% (Bryan Ellis, 2014; Ellis, 2013)
- 1% to 7% of 20’514’994 = 205’150 to 1’436’050
- 138 litres WW per day per household discharged due to misconnections (Ellis, 2013)
- Misconnection volume = 0.138*365*205’150 to 0.138*365*1’436’050 = 10’333’402 to 72’333’817 m$^3$
- Volume percentage of WW discharged due to misconnections = 10’333’402/4.02E+09 * 72’333’817/4.02E+09 = 0.26% to 1.8%

Exfiltration/leakage for the UK

- Exfiltration rate: 0.0014 l/s/km or 2.8% of DWF for the city of Dresden (cited in Rutsch et al., 2008)
- Exfiltration = 3% of total average annual flow for Thames region (Ellis et al., 2004)
- 5-20% leakage rate for gravity sewers above water table. 5% is the lower value used in various studies (mentioned in Ellis et al., 2004); Other studies give very high exfiltration rate (see Ellis et al., 2008; Rueedi et al., 2009) (see ref. 27 summary and ref. 35 for recent study for Doncaster, UK)
- Range used for our study = 3 to 5% of effluent volume
- Sewer length in the UK = 347,000 km (DEFRA, 2012)
- Effluent volume (2011) = 4.05 billion m$^3$ (DEFRA, 2012)

Overflows/intermittent discharges for the US

- Discharges from decentralized water treatment systems due to failures: 66 to 144 billion Gallons (USEPA, 2008)
- Discharges from sanitary sewerage = 900 billion gallons (ASCE, 2013)
- Total overflows = 144+900 = 1’044 billion gallons

17 Comments for the team: Ellis’s paper gives the range of 15-50%. Have used the data by Scott Wilson which is a recent publication. However, 25% still seems to be too high to me.
Dynamic Probabilistic Modelling of Environmental Emissions and Concentrations of Engineered Nanomaterials

- Total centralized + decentralized effluent = $5.21 \times 10^9 + 5.96 \times 10^9 = 5.81 \times 10^9$ m$^3$
- Percentage $= \frac{3.95 \times 10^9}{5.80 \times 10^{10}} = 6.8\% = \text{ca. } 7\%$ (higher estimate because the infrastructure report card rates the waste water treatment infrastructure status of US to be 'D', i.e., poor and at risk (ASCE, 2013))
- Conservative estimate from USEPA’s Report to Congress (2008): 10 billion gallons from Sewer overflows and 160 billion gallons from Combined Sewer Overflows = 1.1% or ca. 1% of total effluent volume
- Range = 1 to 7%

Sludge distribution
UK – (DEFRA, 2012)

<table>
<thead>
<tr>
<th>Total sludge generated/annum</th>
<th>(tonnes dry weight)</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Land application</td>
<td>0.791</td>
<td>79.10%</td>
</tr>
<tr>
<td>Incineration</td>
<td>0.184</td>
<td>18.40%</td>
</tr>
<tr>
<td>Landfill</td>
<td>0.006</td>
<td>0.60%</td>
</tr>
<tr>
<td>Other disposal</td>
<td>0.019</td>
<td>1.90%</td>
</tr>
</tbody>
</table>


| Total biosolids from Treatment works treating domestic sewage | 7'180'000 dry tons | S |
| Conversion to metric tonnes | 6'513'586.43 | 6.5 to 9.1 million tonnes |
| Agriculture /farmlands | 2'651'029.68 | 41% | 41% to 45% |
| Incineration | 967'267.59 | 15% | 15% to 17% |
| Landfill+Monofill | 1'963'846.31 | 30% | 29% to 30% |
| Class A exceptional quality as biosolids or heat dried pellet fertilizer/Compost - silviculture, horticulture, gardens, etc. | 788'143.96 | 12% | 9% to 14% |
| Forest land and reclamation, other beneficial uses | 143'298.90 | 2% |

Cremation of bodies:
UK: Cremation – 74% for year 2012 (Cremation Society of Great Britain)
US: Cremation - 38% for year 2012 (National Funeral Directors Association)

Hospital waste estimates from various sources for the US:
- More than 4 billion pounds of waste disposed in 2007 (Kagoma et al., 2012) 1 pound = 0.45 kg
- Year 2007 = $4 \times 0.45 \times 10^9 = 1.8 \text{ million metric tonnes}$
- 2 million tons/year (Brennan, 2009) = $2 \times 0.9072 = 1.8 \text{ million tonnes}$ (if 7000 tons of waste per day = 2.32 million tonnes of waste per year)
- 1 ton = 0.9072 tonnes
  1 year = 365 days
  Hospital waste generation range = $1.8 \text{ to } 2.32 \text{ million tonnes}$
- 13-15 pounds of waste/patient/day = 5.85 to 6 kg/patient/day (Rutala and Mayhall, 1992)
Use = 6 kg/patient/day
Total waste = waste/patient/day * total no. of discharges in a year * average length of stay in a hospital
Total no. of discharges (in non-federal, short stay hospital) in 2008-2009 = 35908000 (Table 104)(National Centre for Health Statistics, 2012)
Average length of stay (both federal and non-federal hospitals) = 6.2 days (Table 108)(National Centre for Health Statistics, 2012)
Total waste generated in year 2008 to 2009 = 1.34 million tonnes

- World Health Organisation (WHO, 1999)
  Medical waste generation = 1.1 to 12.0 kg/capita
  Population of USA in 2010 = 30428000
  Hospital waste generation range = 0.3 million tonnes to 3.6 million tonnes

- Hospital waste = 5.9 million tons = 5.35 million tonnes (Practice Greenhealth)
- In 1994, USA generated around 3.361 million tons of medical waste = 3.05 million tonnes (USEPA, 2010)

The higher estimate of 5.35 million tonnes has been used in the study:
  - Due the futuristic perspective of nanomedicine waste
  - Increasing stringency in regulations concerning hospital waste
A 3.4 Information of ecological toxicity of GNP

Table A3-6: Data for aquatic toxicity extracted from 12 related scientific papers. Ecological effects selected to create probabilistic species distribution were mortality and malformation, growth inhibition, reproductive impairment and acute immobilisation. Twenty three toxicity endpoints spread across four different taxonomic groups – fish, algae, crustacean and bacteria – were used to construct the Species Sensitivity Distribution for the aquatic compartment. The term Highest Observed No Effect Concentration (HONEC) was used when a range of concentrations were tested and the effects reported at the highest concentration tested was not statistically different from the control for the selected endpoint. The term No Observed Effect Concentration (NOEC) was used when two or less than two concentrations were tested and the reported concentration was not statistically significantly different from the control treatment. The concentration which caused an adverse effect in 10% of the test organisms was termed as Lowest Observed Effect Concentration (LOEC). The lowest concentration which caused an adverse effect in x% of the test organisms has been termed as ECx or if x% of the test organisms died, it has been represented as LCx. We used Assessment Factors (AF) to account for chronic toxicity (AF time) and to extrapolate to no observed effect values (AF-no effect) for deriving the species sensitivity values. For short time or acute exposure studies, the factor used for AF time was 10. AF no-effect factor used was 1 for the concentration which showed no difference in comparison to the control treatment, AF no-effect factor used was 2, if L(E)C 10· L(E)Cx < L(E)C 50 and a factor of 10 was used to derive NOEC if L(E) 50· L(E)Cx·L(E)C 100. Various units of exposure concentrations reported in the studies were standardised to microgram/litre.

<table>
<thead>
<tr>
<th>Gold nanomaterial tested (particle size in nm and coating)</th>
<th>Test organism</th>
<th>Exposure concentrations</th>
<th>Toxic endpoint</th>
<th>Effect concentration (μg/l)</th>
<th>Type of toxicity test</th>
<th>AF time</th>
<th>AF no-effect</th>
<th>Species sensitivity values (μg/l)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>15-35 nm Capping: Poly vinyl alcohol</td>
<td>Danio rerio</td>
<td>10, 25, 50, 75, 100 μg/ml</td>
<td>Mortality</td>
<td>HONEC=100000</td>
<td>Acute toxicity test</td>
<td>10</td>
<td>1</td>
<td>10000</td>
<td>(Asharani et al., 2011)</td>
</tr>
<tr>
<td>0.8 nm Capping - TMAT (N,N,N-trimethylammonium ethane thiol)</td>
<td>Danio rerio</td>
<td>(16, 80, 400 ppb), (2,10,50, 250) ppm</td>
<td>Mortality and malformation</td>
<td>ECx=2000 (p&lt;0.01)</td>
<td>Acute toxicity test (120 hpf)</td>
<td>10</td>
<td>10</td>
<td>20</td>
<td>(Harper et al., 2011)</td>
</tr>
<tr>
<td>1.5 nm Capping - TMAT (N,N,N-trimethyl ammonium ethane thiol)</td>
<td>Danio rerio</td>
<td>(16, 80, 400 ppb), (2,10,50, 250) ppm</td>
<td>Mortality and malformation</td>
<td>ECx=80 (p&lt;0.05)</td>
<td>Acute toxicity test (120 hpf)</td>
<td>10</td>
<td>2</td>
<td>4</td>
<td>(Harper et al., 2011)</td>
</tr>
<tr>
<td>15 nm Capping - TMAT (N,N,N-trimethyl ammonium ethane thiol)</td>
<td>Danio rerio</td>
<td>(16, 80, 400 ppb), (2,10,50, 250) ppm</td>
<td>Mortality and malformation</td>
<td>ECx=50,000 (p&lt;0.01)</td>
<td>Acute toxicity test (120 hpf)</td>
<td>10</td>
<td>2</td>
<td>2500</td>
<td>(Harper et al., 2011)</td>
</tr>
<tr>
<td>0.8 nm Capping: 2-mercapto ethane sulfonic acid (MES)</td>
<td>Danio rerio</td>
<td>(16, 80, 400 ppb), (2,10,50, 250) ppm</td>
<td>Mortality and malformation</td>
<td>LOEC=50000 (p&lt;0.01)</td>
<td>Acute toxicity test (120 hpf)</td>
<td>10</td>
<td>2</td>
<td>2500</td>
<td>(Harper et al., 2011)</td>
</tr>
<tr>
<td>1.5 nm Capping: 2-mercapto ethane sulfonic acid (MES)</td>
<td>Danio rerio</td>
<td>(16, 80, 400 ppb), (2,10,50, 250) ppm</td>
<td>Mortality and malformation</td>
<td>LOEC=2000 (p&lt;0.01)</td>
<td>Acute toxicity test (120 hpf)</td>
<td>10</td>
<td>2</td>
<td>100</td>
<td>(Harper et al., 2011)</td>
</tr>
<tr>
<td>Gold nanomaterial tested (particle size in nm and coating)</td>
<td>Test organism</td>
<td>Exposure concentrations</td>
<td>Toxic endpoint</td>
<td>Effect concentration (μg/l)</td>
<td>Type of toxicity test</td>
<td>AF time</td>
<td>AF no-effect</td>
<td>Species sensitivity values (μg/l)</td>
<td>Source</td>
</tr>
<tr>
<td>----------------------------------------------------------</td>
<td>--------------</td>
<td>------------------------</td>
<td>----------------</td>
<td>----------------------------</td>
<td>----------------------</td>
<td>---------</td>
<td>--------------</td>
<td>---------------------------------</td>
<td>--------</td>
</tr>
<tr>
<td>0.8 nm, 1.5nm, 15 nm capped with MEE (2,2 mercapto ethoxy ethanol) and MEEE (2-(2-(2-mercaptopethoxyethoxy)ethanol)</td>
<td><em>Danio rerio</em></td>
<td>(16, 80, 400 ppb), (2,10,50, 250) ppm</td>
<td>Mortality and malformation</td>
<td>HONEC=250000</td>
<td>Acute toxicity test(120 hpf)</td>
<td>10</td>
<td>1</td>
<td>25000</td>
<td>(Harper et al., 2011)</td>
</tr>
<tr>
<td>1.2 nm (3-mercaptopropionic acid-functionalized)</td>
<td><em>Danio rerio</em></td>
<td>0.08 to 50 μg/ml</td>
<td>Mortality and malformation</td>
<td>HONE=50,000</td>
<td>Acute toxicity test(120 hpf)</td>
<td>10</td>
<td>1</td>
<td>5000</td>
<td>(Truong et al., 2012)</td>
</tr>
<tr>
<td>3 nm (4-9 nm) Triphenylphosphine monosulfonate (TPPMS)-functionalised</td>
<td><em>Danio rerio</em></td>
<td>0.25,2.5,25,250 μM</td>
<td>Mortality, embryonic malformations</td>
<td>HONEC=49000</td>
<td>Acute toxicity test(120 hpf)</td>
<td>10</td>
<td>1</td>
<td>4900</td>
<td>(Bar-Ilan et al., 2009)</td>
</tr>
<tr>
<td>10 nm (14-21nm) TPPMS functionalised</td>
<td><em>Danio rerio</em></td>
<td>0.25,2.5,25,250 μM</td>
<td>Mortality, embryonic malformations</td>
<td>HONEC=49000</td>
<td>Acute toxicity test(120 hpf)</td>
<td>10</td>
<td>1</td>
<td>4900</td>
<td>(Bar-Ilan et al., 2009)</td>
</tr>
<tr>
<td>50 nm (31-60nm) TPPMS functionalised</td>
<td><em>Danio rerio</em></td>
<td>0.25,2.5,25,250 μM</td>
<td>Mortality, embryonic malformations</td>
<td>HONEC=49000</td>
<td>Acute toxicity test(120 hpf)</td>
<td>10</td>
<td>1</td>
<td>4900</td>
<td>(Bar-Ilan et al., 2009)</td>
</tr>
<tr>
<td>100 nm (75-115nm) TPPMS functionalised</td>
<td><em>Danio rerio</em></td>
<td>0.25,2.5,25,250 μM</td>
<td>Mortality, embryonic malformations</td>
<td>HONEC=49000</td>
<td>Acute toxicity test(120 hpf)</td>
<td>10</td>
<td>1</td>
<td>4900</td>
<td>(Bar-Ilan et al., 2009)</td>
</tr>
<tr>
<td>1.3 nm TMAT (N,N,N-trimethylammoniummethanethiol) functionalised</td>
<td><em>Danio rerio</em></td>
<td>0.08, 0.4, 2, 10, 20, 30, 40, and 50 mg/l</td>
<td>Mortality</td>
<td>LC50=30000</td>
<td>Acute toxicity test(120 hpf)</td>
<td>10</td>
<td>10</td>
<td>300</td>
<td>(Kim et al., 2013)</td>
</tr>
<tr>
<td>2 nm (alkane thiol-ethylene glycol and then functionalised A1- Hydrophilic positive charge)</td>
<td><em>Oryzias latipes</em> (adult)</td>
<td>20 nM of AuNPs(800-1000ppb of Au)</td>
<td>Mortality</td>
<td>NOEC = 973</td>
<td>Acute toxicity test (120 hrs)</td>
<td>10</td>
<td>1</td>
<td>97</td>
<td>(Zhu et al., 2010)</td>
</tr>
<tr>
<td>2 nm (alkane thiol-ethylene glycol and then functionalised A2- Hydrophilic negative charge)</td>
<td><em>Oryzias latipes</em> (adult)</td>
<td>20 nM of AuNPs(800-1000ppb of Au)</td>
<td>Mortality</td>
<td>NOEC = 973</td>
<td>Acute toxicity test (120 hrs)</td>
<td>10</td>
<td>1</td>
<td>97</td>
<td>(Zhu et al., 2010)</td>
</tr>
<tr>
<td>2 nm (alkane thiol-ethylene glycol and then functionalised ; A3- Hydrophilic neutral)</td>
<td><em>Oryzias latipes</em> (adult)</td>
<td>20 nM of AuNPs(800-1000ppb of Au)</td>
<td>Mortality</td>
<td>NOEC = 973</td>
<td>Acute toxicity test (120 hrs)</td>
<td>10</td>
<td>1</td>
<td>97</td>
<td>(Zhu et al., 2010)</td>
</tr>
<tr>
<td>2 nm (alkane thiol-ethylene glycol and then functionalised; A4- Hydrophobic positive charge)</td>
<td><em>Oryzias latipes</em> (adult)</td>
<td>20 nM of AuNPs(800-1000ppb of Au)</td>
<td>Mortality</td>
<td>LC50 = 973</td>
<td>Acute toxicity test (24 hrs)</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>(Zhu et al., 2010)</td>
</tr>
<tr>
<td>20 nm (15-21 nm) Capping: citrate</td>
<td><em>Daphnia magna</em></td>
<td>Not clear from the study</td>
<td>Acute immobilisation and reproductive test</td>
<td>LC50=70000</td>
<td>Acute toxicity test</td>
<td>10</td>
<td>10</td>
<td>700</td>
<td>(Li et al., 2010)</td>
</tr>
</tbody>
</table>
### Table A3-7: Data for terrestrial toxicity extracted from one paper. Ecotoxicity endpoint data transformed to species sensitivity values as explained in Table A3-6.

<table>
<thead>
<tr>
<th>Gold nanomaterial tested (particle size in nm and coating)</th>
<th>Test organism</th>
<th>Exposure concentrations</th>
<th>Toxic endpoint</th>
<th>Effect concentration (μg/l)</th>
<th>Type of toxicity test</th>
<th>AF time</th>
<th>AF no-effect</th>
<th>Species sensitivity value (μg/kg)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.6 nm Capping: Dodecanethiol coated with Amphiphilic Polymer (hydrophobic part -dodecylamine and a hydrophilic part, poly-sobutylene-alt-maleic anhydride)</td>
<td><em>Pseudokirchneriella subcapitata</em></td>
<td>0.0012 to 0.12 μM (0.46 to 46 mg/l)</td>
<td>Growth inhibition test</td>
<td>EC₅₀ =7500</td>
<td>Acute toxicity test (24 and 48 hrs)</td>
<td>10</td>
<td>10</td>
<td>75</td>
<td>(Van Hoecke et al., 2013)</td>
</tr>
<tr>
<td>4.6 nm (4 to 5.5 nm) Capping: 10 kD PEG coating on the amphipilic coating</td>
<td><em>Pseudokirchneriella subcapitata</em></td>
<td>0.0012 to 0.12 μM (0.46 to 46 mg/l)</td>
<td>Growth inhibition test</td>
<td>EC₃₀ =39000</td>
<td>Acute toxicity test (24 and 48 hrs)</td>
<td>10</td>
<td>10</td>
<td>390</td>
<td>(Van Hoecke et al., 2013)</td>
</tr>
<tr>
<td>2 nm Capping: α-D-mannopyranoside terminated PAMAM (polyamidoamine) dendrimer) G-0 generation</td>
<td><em>Chlamydomonas reinhardtii</em></td>
<td>6 and 12 ng/ml</td>
<td>Growth inhibition test</td>
<td></td>
<td>Acute toxicity test (24 and 48 hrs)</td>
<td>10</td>
<td>10</td>
<td>0.12</td>
<td>(Perreault et al., 2012)</td>
</tr>
<tr>
<td>4 nm (5-9 nm) Capping: Citrate</td>
<td><em>Caenorhabditis elegans</em></td>
<td>0, 2.5, 5.5, 7, 15, and 30 mg/l</td>
<td>LC 10</td>
<td>LC₅₀ = 5900</td>
<td>Acute toxicity test (24 hrs)</td>
<td>10</td>
<td>2</td>
<td>295</td>
<td>(Tsusko et al., 2012)</td>
</tr>
<tr>
<td>10 nm Capping: Citrate</td>
<td><em>Photobacterium phosphoreum</em></td>
<td>28 μg/ml</td>
<td>Decrease in bioluminescence</td>
<td>NOEC = 2800</td>
<td>Microtox test</td>
<td>10</td>
<td>1</td>
<td>2800</td>
<td>(Barrena et al., 2009)</td>
</tr>
<tr>
<td>5.1 nm Capping: Bovine Serum Albumin</td>
<td><em>Bacteria</em></td>
<td>Not clear from the study</td>
<td>Toxicity test</td>
<td>EC₅₀ = 2.68*10^6ug/l</td>
<td>Microtox test</td>
<td>10</td>
<td>10</td>
<td>26800</td>
<td>(Zheng et al., 2010)</td>
</tr>
</tbody>
</table>

---

209
A 3.5 Results of alternate scenarios

This document details the scenario and possibilities:

1. Where modelled PEC of GNP is arrived at by considering 100% excretion of the therapeutic in waste water and is named as Scenario 2 (worst case).
2. Where the environment risk is estimated by comparing this worst case PEC with lethal endpoints and sub-lethal endpoints for the aquatic compartment.
3. Where the environment risk is estimated by comparing the realistic scenario 1 (with accumulation of therapeutics in the body) and pSSD with sublethal endpoint.

Predicted GNP concentration in technical and environmental compartments of Scenario 2 (worst case)

Table A3-8: PEC of GNP without accumulation of GNP (from drugs) in body, i.e., 100% excretion. Black values designate concentrations; grey values designate yearly increases in concentrations. GNP concentrations in surface water and sediments represent no and complete sedimentation respectively. The results are expressed up to three significant digits.

<table>
<thead>
<tr>
<th></th>
<th>UK</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th>Units</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Mode</td>
<td>Q15</td>
<td>Q85</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STP Effluent</td>
<td>979</td>
<td>930</td>
<td>498</td>
<td>1,460</td>
<td></td>
<td></td>
<td></td>
<td>pg/L</td>
</tr>
<tr>
<td>Surface water</td>
<td>1,040</td>
<td>594</td>
<td>492</td>
<td>1,600</td>
<td></td>
<td></td>
<td></td>
<td>pg/L</td>
</tr>
<tr>
<td>STP sludge</td>
<td>276</td>
<td>288</td>
<td>230</td>
<td>324</td>
<td></td>
<td></td>
<td></td>
<td>µg/kg</td>
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<tr>
<td>Sludge treated soil</td>
<td>648</td>
<td>673</td>
<td>541</td>
<td>760</td>
<td></td>
<td></td>
<td></td>
<td>ng/kg/y</td>
</tr>
<tr>
<td>Sediments</td>
<td>644</td>
<td>367</td>
<td>304</td>
<td>987</td>
<td></td>
<td></td>
<td></td>
<td>ng/kg/y</td>
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<tr>
<td>Hazardous waste</td>
<td>76.7</td>
<td>26.5</td>
<td>23.5</td>
<td>130</td>
<td></td>
<td></td>
<td></td>
<td>µg/kg</td>
</tr>
<tr>
<td>Medical WIP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fly ash</td>
<td>258</td>
<td>29.6</td>
<td>35.8</td>
<td>517</td>
<td></td>
<td></td>
<td></td>
<td>µg/kg</td>
</tr>
<tr>
<td>Bottom ash</td>
<td>197</td>
<td>24.1</td>
<td>27.0</td>
<td>393</td>
<td></td>
<td></td>
<td></td>
<td>µg/kg</td>
</tr>
<tr>
<td>Municipal WIP</td>
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<td></td>
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<td></td>
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<tr>
<td>Fly ash</td>
<td>30.1</td>
<td>29.0</td>
<td>23.8</td>
<td>36.7</td>
<td></td>
<td></td>
<td></td>
<td>µg/kg</td>
</tr>
<tr>
<td>Bottom ash</td>
<td>22.9</td>
<td>21.9</td>
<td>17.2</td>
<td>28.8</td>
<td></td>
<td></td>
<td></td>
<td>µg/kg</td>
</tr>
</tbody>
</table>
Environmental risk assessment of alternate scenarios

Scenario 1: PEC vs pSSD (with the PEC considering accumulation of GNP in body)

Figure A3-1: PEC vs pSSD in water with sublethal end points. PEC vs pSSD for water with sublethal end points: The graphs don’t overlap and hence indicates no risk.

Scenario 2: PEC without accumulation of GNP in body and pSSD with lethal and sublethal endpoints

Figure A3-2: PEC vs pSSD for water and using lethal endpoints. PEC vs pSSD for water and using lethal endpoints: The graphs don’t overlap and hence indicates no risk.
Appendix 3: Supporting Information for Chapter 3

Figure A3-3: PEC vs pSSD in soil with lethal endpoints. The graphs don’t overlap and hence indicates no risk.

Figure A3-4: PEC vs pSSD in water with sublethal end points. The graphs don’t overlap and hence indicates no risk.
A 3.6 References

(8) U.S. Census Bureau Age and Sex Composition: 2010 (2010 Census Briefs); C2010BR-03; U.S. Census Bureau: 2011; p 15.
(20) MRSaid Nasal Decolonization of MRSA. http://www.mrsaid.com/for-clinicians/how-can-i-get-mrsaid/ (21 May 2014)
Appendix 3: Supporting Information for Chapter 3


(25) CDC CDC/NCHS NATIONAL HOSPITAL DISCHARGE SURVEY; Centers for Disease Control and Prevention: Maryland, 12 May 2014, 2012.

(26) NHS Scotland Table 2: Number of Procedures performed in acute hospitals (All Admission Types) Information Services Division, NHS National Services Scotland: Edinburgh, September 2012, 2012.


(28) NHS Wales Principal Procedure Summary: PEDW Statistics - 2011/12; NHS Wales Informatics Service.


(31) Ondine Biomedical Inc. User Manual: Photodisinfection System; UG1000 Rev B.


Howlader N; Noone AM; Krapcho M; Garshell J; Miller D; Altekruse SF; Kosary CL; Yu M; Ruhl J; Tatalovich Z; Mariotto A; Lewis DR; Chen HS; Feuer EJ; KA, C., SEER Cancer Statistics Review, 1975-2011. National Cancer Institute: Bethesda, MD, 2014; Vol. based on November 2013 SEER data submission, posted to the SEER web site, April 2014.

Centers for Disease Control and Prevention, Chronic Kidney Disease.


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Appendix 3: Supporting Information for Chapter 3


(73) ECB Technical Guidance Document on Risk Assessment: Part II; EUR 20418 EN/2; European Chemicals Bureau: Luxembourg, 2003; p 328.


(82) Dedeh, A.; Ciutat, A.; Treguer-Delapierre, M.; Bourdineaud, J. P., Impact of gold nanoparticles on zebrafish exposed to a spiked sediment. Nanotoxicology 2014, 0, (0), 1-10.


(84) USEPA Progress in Water Quality: An Evaluation of the National Investment in Municipal Wastewater Treatment; EPA-832-R-00-008; United States Environmental Protection Agency: Washington DC, 2000.


(87) RTI International Memorandum: Inventory of Hospital/Medical/Infectious Waste Incinerators Potentially Covered by the Proposed Section 111(d)/129 Federal Plan; EPA Contract No. EP-D-07-019; 2012.


(96) Bryan Ellis, Middlesex University, UK. Personal Communication 2014


(102) ASCE 2013 Report Card for America's Infrastructure; American Society of Civil Engineers: 2013; p 74.


(113) WHO Safe management of wastes from healthcare activities; World Health Organisation: Geneva, 1999; p 230.


(122) Perreault, F.; Bogdan, N.; Morin, M.; Claverie, J.; Popovic, R., Interaction of gold nanoglycodendrimers with algal cells (Chlamydomonas reinhardtii) and their effect on physiological processes. Nanotoxicology 2012, 6, (2), 109-120.


Appendix 4: Probabilistic modelling of engineered nanomaterial emissions to the environment: A spatio-temporal approach
A 4.1 System parameters

A brief introduction of SA

South Australia is a state located in southern central Australia with a land area of 975,612 km² (South Australian Government, 2011-12) and is divided into 12 distinctive government identified regions, encompassing 4 metropolitan, 3 greater metropolitan and 5 country regions (SA Government Regions). Each region comprises a set of local councils and is spatially zoned to assist in planning and management according to a range of demographic, economic and geographic features. Approximately three quarters of the population live in metropolitan and greater Adelaide, the state capital. Metropolitan Adelaide is home to a number of important manufacturing industries such as defense and provides the gateway to a number of regional tourist attractions and economies. Greater Adelaide extends from McLaren Vale and the Fleurieu Peninsula in the south around the Adelaide Hills to the Barossa in the north, providing world renowned vineyards. The Murray-Mallee and Limestone Coast regions of the south and south-east provide temperate geographies amenable to agriculture and orchards, whereas the temperate and semi-arid landscape of the Yorke and Mid-North produces cereals and wool. In contrast to crop-centred economies, the Far North and Eyre and Western regions are characterised by a greater dependence on mining and aquaculture, respectively (SA Government Regions). Figure A4-1 shows the administrative geographical regions and the locations of the regions studied.
Figure A4-1: The administrative geographical regions and the locations of the regions studied in South Australia. Map was taken from website of South Australian Government (2011-12).
Definition of the seven regions:
The 12 South Australian government regions provided the basis by which to define the flow and fate of engineered nanomaterials throughout the state. This approach was significant because it enabled the use of existing demographic and geographic data when defining each region. Metropolitan and greater Adelaide regions were coalesced into a single region with the exception of Kangaroo Island. Kangaroo Island was defined as a separate region in recognition of differences in the use and recycling of biosolids and treated wastewater on the island in contrast to the mainland. The 5 remaining regions corresponded to the country South Australian government regions resulting in a total of 7 regions (see Figure A4-1), each with a distinctive population (Australian Bureau of Statistics, 2013) and size (South Australian Government, 2011-12). The flow and fate of engineered nanomaterials for South Australia were then characterized by studying (i) the flow of materials out of the state for recycling, (ii) the fate of materials such as wastewater and biosolids within regions, and (iii) the flow and fate of biosolids between regions.

The areas of the agricultural soils receiving biosolids covered by each region were defined by the areas of soil in each region aiming for crop farming. This is given in PIRSA report (PIRSA, 2013b).
Table A4-1: Summary of volumes of different technical and environmental compartments used for South Australia. Numbers in superscripts in the comments after each sentence are numbers of references.

<table>
<thead>
<tr>
<th>Compartments</th>
<th>Formula</th>
<th>Mass/Volumes</th>
<th>Unit</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Agricultural soil</strong></td>
<td>Far North</td>
<td>4278<em>10^6</em>0.10*1333</td>
<td>5.70E+11</td>
<td>kg 10^9 is the conversion factor from km^2 to m^2</td>
</tr>
<tr>
<td></td>
<td>Yorke &amp; Mid North</td>
<td>10781<em>10^6</em>0.10*1333</td>
<td>1.44E+12</td>
<td>kg 0.10 m is the depth of agricultural soil considered to be affected by pollutant. ^5</td>
</tr>
<tr>
<td></td>
<td>Eyre &amp; Western</td>
<td>14087<em>10^6</em>0.10*1333</td>
<td>1.88E+12</td>
<td>kg 1333 kg/m^3 is the density of agricultural soil (same as above) ^5</td>
</tr>
<tr>
<td></td>
<td>Greater Adelaide</td>
<td>214<em>10^6</em>0.10*1333</td>
<td>2.85E+10</td>
<td>kg 4278 km^2, 10781 km^2, 14087 km^2, 214 km^2, 182 km^2, 7101 km^2, 3214 km^2 are the area of agricultural soil in region of Far North, Yorke &amp; Mid North, Eyre &amp; Western, Greater Adelaide, Kangaroo Island, Murray-Mallee and Limestone Coast ^5</td>
</tr>
<tr>
<td></td>
<td>Kangaroo Island</td>
<td>182<em>10^6</em>0.10*1333</td>
<td>2.43E+10</td>
<td>kg</td>
</tr>
<tr>
<td></td>
<td>Murray-Mallee</td>
<td>7101<em>10^6</em>0.10*1333</td>
<td>3.47E+11</td>
<td>kg</td>
</tr>
<tr>
<td></td>
<td>Limestone Coast</td>
<td>3214<em>10^6</em>0.10*1333</td>
<td>4.28E+11</td>
<td>kg</td>
</tr>
<tr>
<td><strong>Ocean gulfs</strong></td>
<td>St. Vincent</td>
<td>75000<em>50000</em>30*1000</td>
<td>1.13E+14</td>
<td>litre 75000 m is the length of the gulf; 1000 is conversion factor from m^3 to litres</td>
</tr>
<tr>
<td></td>
<td>Spencer</td>
<td>200000<em>40000</em>21*1000</td>
<td>1.68E+14</td>
<td>litre 200000 m is the length of the gulf; 30 m is the depth of the gulf suggested ^8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>30 m is the width of the gulf ^8</td>
</tr>
<tr>
<td><strong>Ocean sediments</strong></td>
<td>St. Vincent</td>
<td>Bolivar</td>
<td>1761.3<em>10^6</em>0.03*260</td>
<td>1.37E+10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Glenelg</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Christies</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Spencer</td>
<td>Whyalla</td>
<td>628.3<em>10^6</em>0.03*260</td>
<td>4.90E09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pirie</td>
<td>628.3<em>10^6</em>0.03*260</td>
<td>4.90E09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Augusta</td>
<td>104.7<em>10^6</em>0.03*260</td>
<td>3.17E08</td>
</tr>
</tbody>
</table>

^5 Data from EUROSIONS (2018), http://www.euroions.org/technologies/urban-subsurface-water/.

^8 Source: South Australian Government (2019).

^9 Economic Commission for Europe (2020).
WWTP biosolids stockpiles and transfer

Regional biosolids production was determined on a per capita basis using SA Water figures for the average total biosolids produced in metropolitan Adelaide over the study period using SA Water Activity Reports for 2005–2012 (Australian Bureau of Statistics, 2013; SA Water, 2005-12). It was assumed that the per person rate of biosolids production would be stable between metropolitan and regional WWTP (Daminato, 2013). Due to the complexity of the system we also assumed that regionally produced biosolids would be applied to soils in the year of production, but we acknowledge that this may not be the case. Quantities transported between regions were determined by identifying and charting post-2005 biosolids movements as part of the SA Water Biosolids Re-use Scheme (SA Water, 2005-12). This approach provided the rationale for calculating the total quantities of biosolids applied to agricultural soils for soil amendment within each region.

Table A4-2: Temporal production and distribution of WWTP biosolids between 2005 and 2012 from SA water (unit: tons)

<table>
<thead>
<tr>
<th>Year</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
<th>2012</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Far North and Kangaroo Island biosolids produced and applied</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Far North</td>
<td>633</td>
<td>688</td>
<td>697</td>
<td>706</td>
<td>712</td>
<td>717</td>
<td>721</td>
<td>723</td>
<td>5′597</td>
</tr>
<tr>
<td>Kangaroo Island</td>
<td>116</td>
<td>116</td>
<td>117</td>
<td>118</td>
<td>118</td>
<td>119</td>
<td>120</td>
<td>120</td>
<td>944</td>
</tr>
</tbody>
</table>

Eyre & Western

<table>
<thead>
<tr>
<th>Biosolids Produced</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
<th>2012</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>2005</td>
<td>1′534</td>
<td>55</td>
<td>592</td>
<td>563</td>
<td>26</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2′770</td>
</tr>
<tr>
<td>2006</td>
<td>0</td>
<td>1′606</td>
<td>0</td>
<td>0</td>
<td>14</td>
<td>14</td>
<td>0</td>
<td>0</td>
<td>1′634</td>
</tr>
<tr>
<td>2007</td>
<td>0</td>
<td>0</td>
<td>1′615</td>
<td>0</td>
<td>158</td>
<td>297</td>
<td>139</td>
<td>0</td>
<td>2′209</td>
</tr>
<tr>
<td>2008</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1′581</td>
<td>25</td>
<td>0</td>
<td>77</td>
<td>77</td>
<td>1′760</td>
</tr>
<tr>
<td>2009</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1′590</td>
<td>27</td>
<td>55</td>
<td>55</td>
<td>1′727</td>
</tr>
<tr>
<td>2010</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1′572</td>
<td>30</td>
<td>30</td>
<td>1′632</td>
</tr>
<tr>
<td>2011</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1′869</td>
<td>293</td>
<td>2′162</td>
</tr>
<tr>
<td>2012</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1′587</td>
<td>1′587</td>
</tr>
<tr>
<td>Total</td>
<td>1′534</td>
<td>1′661</td>
<td>2′207</td>
<td>2′144</td>
<td>1′813</td>
<td>1′910</td>
<td>2′170</td>
<td>2′042</td>
<td>1′,481</td>
</tr>
</tbody>
</table>
Table A4-2 continues:

<table>
<thead>
<tr>
<th>Biosolids Produced</th>
<th>Yorke &amp; Mid North</th>
<th></th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2005</td>
<td>2006</td>
<td>2007</td>
</tr>
<tr>
<td>2005</td>
<td>3'783</td>
<td>2'375</td>
<td>5'401</td>
</tr>
<tr>
<td>2006</td>
<td>0</td>
<td>2'165</td>
<td>0</td>
</tr>
<tr>
<td>2007</td>
<td>0</td>
<td>0</td>
<td>2'716</td>
</tr>
<tr>
<td>2008</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2009</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2010</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2011</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2012</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>3'783</td>
<td>4'540</td>
<td>8'117</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Biosolids Produced</th>
<th>Greater Adelaide</th>
<th></th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2005</td>
<td>2006</td>
<td>2007</td>
</tr>
<tr>
<td>2005</td>
<td>4'396</td>
<td>237</td>
<td>577</td>
</tr>
<tr>
<td>2006</td>
<td>0</td>
<td>4'397</td>
<td>0</td>
</tr>
<tr>
<td>2007</td>
<td>0</td>
<td>0</td>
<td>4'805</td>
</tr>
<tr>
<td>2008</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2009</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2010</td>
<td>0</td>
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</tr>
<tr>
<td>2011</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2012</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>4'396</td>
<td>4'634</td>
<td>5'382</td>
</tr>
</tbody>
</table>
Table A4-2 shows the temporal year of production and distribution of biosolids into seven defined regional farms between 2005 and 2012. Due to the mechanism of biosolids stockpile and biosolids transport between regions, biosolids produced in one region were not applied in the same regional farms in which they were produced; similarly biosolids were not applied in their totality to the soils in the same year when they were produced. The matrix of table S2 shows in rows how much of each year biosolid is distributed over time; in column it shows one year’s application of biosolid into soils consisted of different years product input. In the farms of Far North and Kangaroo Island there were no stockpiled biosolids applied; only “fresh” biobolids, which means biosolids were applied in the same year of production. Determination and differentiation of the biosolids produced and applied in different years is important; because ENM concentrations in biosolids produced in different year vary considerably. This is crucial for the calculation of annual as well as total ENM load into a regional farm.
Distribution of treated waste water

Regional ocean wastewater discharge figures for South Australia were determined on a per capita basis using wastewater produced in metropolitan Adelaide. The average rate of wastewater produced in metropolitan Adelaide was calculated by integrating population and wastewater production figures (Australian Bureau of Statistics; SA Water, 2013). Regional wastewater production was correlated to metropolitan wastewater production on the basis of population. This approach provided the rationale for calculating regional discharge by multiplying the population serviced by WWTP in respective regions by the quantity of wastewater not recycled (Engineers Australia, 2010; SA Water, 2009-10). In Table A4-3 the summary of wastewater production and distribution in SA over the period 2005-2012 is given.

**Table A4-3: Summary of wastewater production and distribution in SA over the period 2005-2012.**

<table>
<thead>
<tr>
<th>Year/units/sources</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
<th>2012</th>
<th>Units</th>
<th>References/Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Produced WWTP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gt. Adelaide</td>
<td>104,916</td>
<td>103,475</td>
<td>95,549</td>
<td>91,266</td>
<td>91,520</td>
<td>92,706</td>
<td>98,676</td>
<td>96,801</td>
<td>10^4 m^3</td>
<td>SA Water report (2013)</td>
</tr>
<tr>
<td>Regions</td>
<td>10,890</td>
<td>11,002</td>
<td>11,090</td>
<td>11,080</td>
<td>11,237</td>
<td>11,312</td>
<td>11,342</td>
<td>11,412</td>
<td>10^4 m^3</td>
<td>Extrapolation based on SA Water information (2013)</td>
</tr>
<tr>
<td>Sum</td>
<td>115,806</td>
<td>114,477</td>
<td>106,639</td>
<td>102,346</td>
<td>102,757</td>
<td>104,018</td>
<td>110,018</td>
<td>108,213</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CWMS</td>
<td>16,712</td>
<td>16,973</td>
<td>17,141</td>
<td>17,359</td>
<td>17,486</td>
<td>17,640</td>
<td>17,721</td>
<td>17,858</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>132,518</td>
<td>131,450</td>
<td>123,780</td>
<td>119,705</td>
<td>120,243</td>
<td>121,658</td>
<td>127,739</td>
<td>126,071</td>
<td>10^4 m^3</td>
<td></td>
</tr>
<tr>
<td>Recycled</td>
<td>27,084</td>
<td>29,934</td>
<td>34,061</td>
<td>35,769</td>
<td>37,131</td>
<td>35,368</td>
<td>28,392</td>
<td>24,041</td>
<td>10^4 m^3</td>
<td>SA Water (2013)</td>
</tr>
<tr>
<td>Discharge to Ocean</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>St.Vincent</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bolivar</td>
<td>49,100</td>
<td>49,978</td>
<td>40,704</td>
<td>37,948</td>
<td>37,450</td>
<td>39,215</td>
<td>45,884</td>
<td>42,816</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glenelg</td>
<td>19,476</td>
<td>19,825</td>
<td>16,146</td>
<td>15,053</td>
<td>14,855</td>
<td>15,555</td>
<td>18,201</td>
<td>16,984</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Christie</td>
<td>13,257</td>
<td>13,494</td>
<td>10,990</td>
<td>10,246</td>
<td>10,112</td>
<td>10,588</td>
<td>12,389</td>
<td>11,560</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spencer</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Whyalla</td>
<td>976</td>
<td>980</td>
<td>976</td>
<td>990</td>
<td>994</td>
<td>1,000</td>
<td>1,003</td>
<td>1,010</td>
<td>10^4 m^3</td>
<td>(Engineers Australia, 2010; SA Water, 2009-10)</td>
</tr>
<tr>
<td>Pirie</td>
<td>1,114</td>
<td>1,118</td>
<td>1,125</td>
<td>1,129</td>
<td>1,135</td>
<td>1,138</td>
<td>1,139</td>
<td>1,145</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Augusta</td>
<td>583</td>
<td>634</td>
<td>641</td>
<td>649</td>
<td>655</td>
<td>660</td>
<td>661</td>
<td>666</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sum of discharge</td>
<td>84,506</td>
<td>84,506</td>
<td>84,506</td>
<td>84,506</td>
<td>84,506</td>
<td>84,506</td>
<td>84,506</td>
<td>84,506</td>
<td>10^4 m^3</td>
<td></td>
</tr>
</tbody>
</table>

**Table A4-4: Summary of the application rate of treated waste water in grass, gardens and pastures (GGP), viticulture (VC), horticulture (HC) from 2005 to 2012**

<table>
<thead>
<tr>
<th>Soil types</th>
<th>Application rate</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grass, gardens and pastures (GGP)</td>
<td>4.48 million litres per hectare per year</td>
<td>Laurenson, S., et al. 2010 (Laurenson et al., 2010)</td>
</tr>
<tr>
<td>Viticulture (VC)</td>
<td>2.10 million litres per hectare per year</td>
<td></td>
</tr>
<tr>
<td>Horticulture (HC)</td>
<td>3-5 million litres per hectare per year</td>
<td></td>
</tr>
</tbody>
</table>
Appendix 4: Supporting Information for Chapter 4


Two separate approaches were taken to calculating the likely ENM exposure areas in the Spencer Gulf and the Gulf of St Vincent due to differences in the availability of suitable data.

Spencer Gulf

The strategy used for WWTP in the Upper Spencer Gulf were based on Kämpf et al’s (2009) observation that slow flushing times in this region indicated that the accumulation of materials at 0.3% concentration in the far field would reach 20 km. As such, it was reasoned an area of sediment exposed to ENM from discharge could be estimated based on a 20 km radius around each of the three WWTP discharging into the Upper Spencer Gulf. Figure A4-2.a shows how the geography of the region influenced the calculation of sediment areas. Since the coast surrounding both Whyalla and Port Pirie WWTP is relatively open (ie. 180⁰), it was assumed that half the area of a circle with a radius of 20 km would produce a fair estimate. In contrast, the coast adjacent to Port Augusta provides a relatively narrow body of water in which wastewaters are discharged. It was assumed that this would equate to approximately 30⁰.

Figure A4-2: a. Upper Spencer Gulf; b. Gulf of St Vincent

Whyalla

It was assumed that approximately half of a hypothetical circle of 20km radius would cover ocean sediment.
The area of sediment affected by discharge from Whyalla WWTP was calculated as:

\[ \text{Area} = \frac{1}{2} \pi r^2 = 0.5\pi \times (20)^2 = 628.3 \text{ km}^2 \]

**Port Pirie**

It was assumed that approximately half of a hypothetical circle of 20km radius would cover ocean sediment.

The area of sediment affected by discharge from Port Pirie WWTP was calculated as:

\[ \text{Area} = \frac{1}{2} \pi r^2 = 0.5\pi \times (20)^2 = 628.3 \text{ km}^2 \]

**Port Augusta**

It was assumed that approximately one eighth of a hypothetical circle of 20 km radius would cover ocean sediment.

The area of sediment affected by discharge from Port Augusta WWTP was calculated as:

\[ \text{Area} = \frac{1}{12} \pi r^2 = 0.083\pi \times (20)^2 = 104.7 \text{ km}^2 \]

**Discharge**

Table A4-3 provides a summary of the volumes of wastewater discharge by each of the WWTP into the receiving environment.

<table>
<thead>
<tr>
<th>Year</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
<th>2012</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Whyalla</strong> 628.3 km$^2$</td>
<td>976</td>
<td>980</td>
<td>976</td>
<td>990</td>
<td>994</td>
<td>1,000</td>
<td>1,003</td>
<td>1,010</td>
</tr>
<tr>
<td><strong>Port Pirie</strong> 628.3 km$^2$</td>
<td>1,114</td>
<td>1,118</td>
<td>1,125</td>
<td>1,129</td>
<td>1,135</td>
<td>1,138</td>
<td>1,139</td>
<td>1,145</td>
</tr>
<tr>
<td><strong>Port Augusta</strong> 104.7 km$^2$</td>
<td>583</td>
<td>634</td>
<td>641</td>
<td>649</td>
<td>655</td>
<td>660</td>
<td>661</td>
<td>666</td>
</tr>
</tbody>
</table>

**Gulf of St. Vincent Strategy**

This was estimated using data contained in a South Australian EPA report which detailed the state of the marine/coastal zone environment of the Gulf of St Vincent according to the concept of a bioregion. A bioregion is a part of the environment identified by conservation ecologists for its distinctive and unique properties with respect to flora and fauna etc. The EPA report listed a range of activities that threatened each of the bioregions of the Gulf of St Vincent which listed the Clinton (2.491.4 km$^2$) and Yankalilla (515.6 km$^2$) (Figure A4-2b) bioregions as those under significant threat from WWTP and Community Wastewater Management Systems (CWMS, formerly called Septic Tank Effluent Drainage Scheme or STED; [http://www.lga.sa.gov.au/page.aspx?id=253](http://www.lga.sa.gov.au/page.aspx?id=253)) contamination (SA EPA, 2011). Since the constituents of wastewater are widely acknowledged as a direct threat to the health of Gulf St Vincent seagrass (Bryars and Neverauskas, 2004; Edyvane, 1999), it was reasoned that the relationship between seagrass die back and wastewater could provide the basis for estimating sediment
areas from bioregion data. Given that the prevailing currents of the Gulf of St Vincent move in a clockwise direction and die back of seagrass north of Bolivar had not extended more than 6 km between 1949 and 1993 (Edyvane, 1999; Kinhill, 1995), it was assumed that WWTP/CWMS threats further north in the Clinton bioregion could be attributed to CWMS alone. Accordingly, it was assumed that approximately 50% of the Clinton bioregion area was likely to be affected by WWTP wastewater. Therefore, in combination, the total area of sediment in the Gulf of St Vincent that is likely to be exposed to ENM from discharged wastewaters is 1’761.3 km². In addition, Wear and Tanner (2007) describe distance gradients from the point source for pH and dissolved nutrients. While they do not characterise the gradient, this information could be used to consider an ENM gradient. These authors state: “From the present study, it appears that water quality improves out to a distance of 2 km after which it stabilizes. However, the spatial resolution of the data is insufficient to determine if there is a gradual change or abrupt transition” and then go on to say “Lara et al (1985) demonstrated that water quality rapidly declined within 900 m of a sewage outfall, reaching normal values at approximately 1’700 m”.

**Metropolitan WWTP**

Bolivar is the largest of the three metropolitan Adelaide WWTP, serving 60% of the population (Water Services Association of Australia, 2013), which equated to 705,016 people in 2012. Christies Beach treats 45 ML/day (water-technology.net, 2013) and using the per person rate of treatment (0.08631 ML/year) calculated by dividing the metropolitan total wastewater produced (SA Water, 2013) by the average metropolitan population (Australian Bureau of Statistics, 2013) over the study. It was inferred that this equated to a population of 190’433. In the absence of specific data for Glenelg, population and wastewater figures were estimated by subtracting Bolivar and Christies Beach WWTP populations from the Adelaide total population of 1’175’026 for 2012. Based on the information and specific wastewater recycling knowledge of the treated wastewater recycling rates for metropolitan Adelaide over the study period, the volumes of wastewater discharged was calculated, as shown in Table A4-6.
Table A4-6: Upper Spencer gulf wastewater discharge (ML) for 2005–2012

<table>
<thead>
<tr>
<th>Year</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
<th>2012</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bolivar 1’761.3km²</td>
<td>45’331</td>
<td>43’768</td>
<td>42’210</td>
<td>43’833</td>
<td>44’427</td>
<td>43’557</td>
<td>43’563</td>
<td>43’850</td>
</tr>
<tr>
<td>Glenelg 1’761.3km²</td>
<td>22’432</td>
<td>22647</td>
<td>22’924</td>
<td>23’213</td>
<td>21’551</td>
<td>21’188</td>
<td>20’798</td>
<td>20’540</td>
</tr>
<tr>
<td>Christies Beach 1’761.3km²</td>
<td>11’980</td>
<td>11’654</td>
<td>11’483</td>
<td>11’262</td>
<td>11’075</td>
<td>10’863</td>
<td>10’593</td>
<td>10’773</td>
</tr>
</tbody>
</table>

A 4.2 ENM parameters

Production volume:
Global and regional production and consumption data of ENM have been reported by quite a few studies (Hendren et al., 2011; Keller et al., 2013; Keller and Lazareva, 2013; Piccinno et al., 2012; Sun et al., 2014c). However, to the best knowledge of the authors of this study, no specific report of ENM consumption especially for South Australia (SA) is available. Keller et al. (Keller and Lazareva, 2013) is the only study that reported ENM emission in Australia. Yet they did not report any explicit figures of how much ENM is consumed in Australia, but only ENM emissions to technical and environmental compartments. By summing up the total emission amount, we were able to estimate an approximate consumption volume for four ENM that is of interest to this study suggested by them. We followed a top-down approach to estimate the ENM consumption in SA on the basis of the known EU ENM production. This was done by scaling the known ENM consumption data in European Union(EU) (Sun et al., 2014c) down to the number of SA in proportional to the ratio of their Gross Domestic Product(GDP), which is an index that we think is very correlated to its power of purchase and consumption of products. According to World Bank statistics in 2012 (The World Bank, 2012), EU has a GDP of 16.67 trillion the U.S. dollar, the number for Australia is 1.532 trillion (The World Bank, 2012), and for SA is 86 billion (Australian Bureau of Statistics, 2010). Sun et al.(Sun et al., 2014c) reported the EU nano-TiO₂, nano-ZnO, nano-Ag, CNT and fullerenes production (also taken as consumption) for 10’200 tons, 1’580 tons, 32 tons, 380 tons and 22 tons respectively. These values are the most probable values from the probability distribution. Combining the information of GDP in the EU, Australia and South Australia and the predicted ENM consumption data in EU, we calculated the ENM consumption of Australia and SA. Table A4-7 shows the results of a comparison between our estimation and the estimation of Keller et al. in tons.
Table A4-7: The comparison of ENM consumption estimation in Australia and SA between Keller et al. 2013 and this study, unit: ton.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>nano-TiO₂</td>
<td>867</td>
<td>961</td>
<td>54</td>
</tr>
<tr>
<td>nano-ZnO</td>
<td>334</td>
<td>178</td>
<td>10</td>
</tr>
<tr>
<td>nano-Ag</td>
<td>4</td>
<td>3.2</td>
<td>0.18</td>
</tr>
<tr>
<td>CNT</td>
<td>31</td>
<td>37</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Because there is no data of fullerenes from Keller’s study, we just compared the estimation of nano-TiO₂, nano-ZnO, nano-Ag and CNT. From table S6 we can see out of the four ENM compared, except nano-Zn, the estimated consumption from the two studies for all the other three ENM matches very well. For the case of nano-ZnO, Keller et al. has a higher estimation of 334 tons which is around twice of the estimation of this study. While this discrepancy between the two figures is just relatively bigger than the others, they still fall within the same range. The estimation of Australian data was not necessary for our modelling, but together with the comparison it was intended for cross validation. The result implies estimations of both methods are in very good agreement; this increases the reliability of the approach we used.

The extrapolation of the ENM consumption for the years before 2012 were made by proportionating the value of 2012 to other years according to ENM development trend analysis (Piccinno et al., 2012) and nanotechnology market projections (European Commission, 2006; LUX RESEARCH INC, 2004) together with a direct production trend estimation for the case of CNT by Piccinno et al. (2012) The final development tendency estimation of ENM between 2005 and 2012 is an information combination of all these studies. Modelled estimations of the five ENM consumption developments between 2005 and 2012 are shown in Figure A4-3.
Figure A4-3: Estimation of five ENM production/consumption developments in South Australia between 2005 and 2012. Curves of mode values (most probable values) and ranges between quantile 15 and quantile 85 are shown.
A 4.3 Transfer coefficients of ENM from production to technical and environmental compartments

ENM release from products to wastewater, to air, and direct to soil, is normally dependent only on the way they are attached to products and the scenarios of how these products are used. In this case, release is assumed independent of where they are consumed but only dependent on the product categories. Therefore, it is reasonable to assume that the ENM release from products to these compartments in South Australia is the same as it is in Europe (Sun et al., 2014c), which was summarized from literature reviews or if not on expert judgement. There is no incineration plant in South Australia; therefore all the solid wastes if not recycled or exported go to landfill.

The distribution of ENM contained in cosmetics especially those in sunscreen to wastewater and to ocean water is very much dependent on where the applications of these products take place. An unpublished study by Conroy et al. (2014) suggested a ratio of 6.78:1 for sunscreen applications inland (ending up in wastewater) and on beach. According to a local government report (Brulliard et al., 2012), around 10% of plastic products are recycled, 6% is exported out of South Australia; for glass 66% is recycled and 3% is exported; for household electronics 30% is recycled, 19% is exported; for textile 18% is exported; 60% of cement is recycled and reused; for paper 1% is recycled. Metal in South Australia according to a report prepared for government of South Australia (Colby et al., 2012), in average 23% is recycled and 67% is exported. Table S8 below shows the ENM release transfer into technical and environmental compartments. In probabilistic modelling, to cover the unknown uncertainty of these data, minus and plus 50% of these single numbers are deviated to get a range for a transfer coefficient, together with their original values they were used to build a triangular distribution for each ENM transfer coefficient.
Table A4-8: Transfer coefficients of ENM from production to technical and environmental compartments on the basis of Sun et al. (2014c).

<table>
<thead>
<tr>
<th></th>
<th>Wastewater</th>
<th>Landfill</th>
<th>Air</th>
<th>Soil</th>
<th>Ocean water</th>
<th>Recycling</th>
<th>Export</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>nano-TiO₂</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Production</td>
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<td>0.30</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manufacture</td>
<td>0.45</td>
<td>0.30</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plastics</td>
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<td>0.79</td>
<td></td>
<td></td>
<td>0.10</td>
<td>0.06</td>
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<tr>
<td>Cosmetics</td>
<td>0.83</td>
<td>0.05</td>
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<td></td>
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<td></td>
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</tr>
<tr>
<td>Coating</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Batteries &amp; Capacitors</td>
<td>0.51</td>
<td></td>
<td></td>
<td></td>
<td>0.30</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>Metals</td>
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<td>0.05</td>
<td></td>
<td></td>
<td>0.23</td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td>Paints</td>
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<td>0.35</td>
<td>0.01</td>
<td>0.01</td>
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<td></td>
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</tr>
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<td>Textiles</td>
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<td>0.01</td>
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<td>Dietary Supplyment</td>
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<td>0.50</td>
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<td><strong>CNT</strong></td>
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</tr>
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<td>0.30</td>
<td>0.25</td>
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<tr>
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<td>0.30</td>
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<td>0.95</td>
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<td>Motor oil (Lubricant)</td>
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<td></td>
<td>0.30</td>
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<tr>
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<td>0.01</td>
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<td>0.60</td>
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A 4.4 Results

Mass flowchart of nano-ZnO, nano-Ag, CNT and fullerenes:
Dynamic Probabilistic Modelling of Environmental Emissions and Concentrations of Engineered Nanomaterials

Figure A4-4: Annual mass flow of nano-ZnO, nano-Ag, CNT and fullerenes in South Australia in 2012, unit: ton. The values taken are MEAN values from each probability distribution; meanwhile mode values and quantile 15(Q15) and quantile 85(Q85) are also given in the right text field. A compartment code is given to each compartment in the corner of each compartment box. Arrows between two compartment codes in the right text field indicate flows from one compartment to the other. The volumes of flows are determined by transfer coefficients (TC) that describe the exchange of ENM between and within these boxes. All the ENM mass-flows are computed regardless of their agglomerated and aggregated form; the balance between input and put flows from one compartment might not be 100% closed due to rounding. Blue arrows indicate all the nano flows which is in contrast to red arrows indicating ENM flows transformed into other chemical variants; yellow arrows is the mixture of nano flows and transformed flows, in other words the mixture of blue and red flows. In this concrete case, red flows means the transformed nano-ZnO flows after waste water treatment processes; yellow flows are the flows comprising both transformed nano-Ag after waste water treatment and the survived nano-ZnO flows from waste water treatment. Black squares indicate the ENM sinks such as landfills, soils and sediments.
In Figure A4-4 the Ag flow after waste water treatment is shown as a mixture of flows of nano-Ag and transformed nano Ag. The differentiation of them is not given. Therefore, a more explicit description of the nano-Ag flows, transformation and distributions from waste water treatment plant (WWTP) to ocean water, soils, stockpile and landfill is demonstrated by Figure S5 below.

Over the processes of WWTP, majority of ENM including nano-Ag end up in biosolids, there are many studies in this context. (Brar et al., 2010; Gómez-Rivera et al., 2012; Hou et al., 2012; Kaegi et al., 2011; Kim et al., 2010) In sewage effluent between 86% and 100% of nano-Ag is transformed to Ag$_2$S and in biosolids only 1% to 2% of nano-Ag can survive and remains its original nano form, the rest is transformed into Ag$_2$S too due to the presence of abundant sulphate primarily from urine. (Kaegi et al., 2011) In South Australia around 70% of the sewage effluent is discharged into ocean, the remaining 30% is recycled for irrigation of grassland, garden, viticulture and horticulture etc. So the flows of surviving nano-Ag and transformed nano-Ag are proportional to the distribution of sewage effluent to soils and ocean. All of biosolids is used in soils, either directly applied in agricultural soils or first composed or stockpiled for later soil use. Again these values are also valid for the distribution of nano-Ag and transformed nano-Ag contained in biosolids to soils, stockpile and landfill.

![Figure A4-5: Mass flow, transformation and distributions of nano-Ag from Waste Water Treatment Plant (WWTP) to ocean gulf, soils and stockpile in South Australia in 2012, unit: tons. Mass balance due to individual rounding might not be 100% closed.](image-url)
Table A4-9: Summary of accumulated concentration of five ENM in 2012. Values are mode values (most probable values) taken from the probability distributions.

<table>
<thead>
<tr>
<th>Compartments</th>
<th>nano-TiO$_2$</th>
<th>Zn from nano-ZnO</th>
<th>Ag from nano-Ag</th>
<th>nano-Ag</th>
<th>CNT</th>
<th>fullerenes</th>
<th>Units</th>
</tr>
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<tr>
<td>Greater Adelaide</td>
<td>4.5E+02</td>
<td>9.2E+01</td>
<td>9.8E-01</td>
<td>2.3E-02</td>
<td>2.1E-01</td>
<td>1.5E-01</td>
<td></td>
</tr>
<tr>
<td>Yorke &amp; Mid North</td>
<td>1.7E+01</td>
<td>3.7E+00</td>
<td>3.8E-02</td>
<td>9.0E-04</td>
<td>8.1E-03</td>
<td>6.0E-03</td>
<td></td>
</tr>
<tr>
<td>Limestone Coast</td>
<td>1.0E+01</td>
<td>2.2E+00</td>
<td>2.3E-02</td>
<td>4.7E-04</td>
<td>4.7E-03</td>
<td>3.7E-03</td>
<td></td>
</tr>
<tr>
<td>Murray-Mallee</td>
<td>6.9E+00</td>
<td>1.5E+00</td>
<td>1.5E-02</td>
<td>3.2E-04</td>
<td>3.1E-03</td>
<td>2.4E-03</td>
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</tr>
<tr>
<td>Kangaroo Island</td>
<td>9.5E+00</td>
<td>1.7E+00</td>
<td>2.0E-02</td>
<td>1.1E-04</td>
<td>3.9E-03</td>
<td>2.5E-03</td>
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<tr>
<td>Far North</td>
<td>2.3E+00</td>
<td>4.4E-01</td>
<td>5.0E-03</td>
<td>2.8E-05</td>
<td>1.0E-03</td>
<td>6.4E-04</td>
<td></td>
</tr>
<tr>
<td>Eyre &amp; Western</td>
<td>1.9E+00</td>
<td>4.0E-01</td>
<td>5.0E-03</td>
<td>9.8E-05</td>
<td>8.4E-04</td>
<td>6.1E-04</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Grass/gardens/pastures</td>
<td>1.8E+01</td>
<td>4.1E+00</td>
<td>3.5E-02</td>
<td>1.2E-03</td>
<td>2.3E-02</td>
<td>1.4E-02</td>
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</tr>
<tr>
<td>Horticulture</td>
<td>1.6E+01</td>
<td>4.1E+00</td>
<td>3.1E-02</td>
<td>1.0E-03</td>
<td>2.1E-02</td>
<td>1.4E-02</td>
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<tr>
<td>Viticulture</td>
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<td>4.5E-04</td>
<td>1.1E-02</td>
<td>7.0E-03</td>
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<td></td>
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<tr>
<td>Bolivar</td>
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<td>9.0E+00</td>
<td>7.4E-02</td>
<td>2.5E-03</td>
<td>4.8E-02</td>
<td>3.1E-02</td>
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<tr>
<td>Glenelg</td>
<td>1.5E+01</td>
<td>3.6E+00</td>
<td>2.9E-02</td>
<td>9.7E-04</td>
<td>1.9E-02</td>
<td>1.2E-02</td>
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</tr>
<tr>
<td>Christies Beach</td>
<td>1.0E+01</td>
<td>2.4E+00</td>
<td>2.0E-02</td>
<td>6.6E-04</td>
<td>1.3E-02</td>
<td>8.4E-03</td>
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</tr>
<tr>
<td>Whyalla</td>
<td>2.5E+00</td>
<td>5.9E-01</td>
<td>4.9E-03</td>
<td>1.6E-04</td>
<td>3.2E-03</td>
<td>2.1E-03</td>
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<tr>
<td>Pirie</td>
<td>2.8E+00</td>
<td>6.8E-01</td>
<td>5.6E-03</td>
<td>1.8E-04</td>
<td>3.6E-03</td>
<td>2.4E-03</td>
<td></td>
</tr>
<tr>
<td>Augusta</td>
<td>9.8E+00</td>
<td>2.3E+00</td>
<td>2.0E-02</td>
<td>6.3E-04</td>
<td>1.3E-02</td>
<td>8.1E-03</td>
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Table A4-10: Summary of the measured Zinc and Silver concentrations in SA biosolids and soils. Numbers in superscript after each value are numbers of references.

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<tr>
<th>Metals</th>
<th>Compartments</th>
<th>Values or Range</th>
<th>References</th>
</tr>
</thead>
</table>
| Zn     | Biosolids    | 1. 300-1,300 mg/kg  
2. 503-688 mg/kg | 1. Personal communications with SA Water\(^{43}\)  
2. Unpublished data from University of South Australia\(^{54}\) |
|        | Soils        | 1. 12-69 mg/kg  
2. 11-18 mg/kg  
3. 50 mg/kg  
4. 7-58 mg/kg  
5. 10-43 mg/kg  
6. 4-110 mg/kg  
7. 4-61 mg/kg  
8. 11-86 mg/kg | 1. Unpublished data from University of South Australia\(^{44}\)  
2. Betrand et al.\(^{45}\)  
3. Donner et al.\(^{46}\)  
4. Broos et al.\(^{47}\)  
5. Donner et al.\(^{48}\)  
6. Blackburn et al.\(^{49}\)  
7. Tiller et al.\(^{50}\)  
8. McKenzie et al.\(^{51}\) |
| Ag     | Biosolids    | 1. 6-10 mg/kg | 1. Unpublished data from University of South Australia\(^{44}\) |
|        | Soils        | 1. 0-0.1 mg/kg  
2. 0-0.1 mg/kg  
3. 0-0.04 mg/kg  
4. 0.01-1.01 mg/kg | 1. Cornelis et al.\(^{52}\)  
2. Cornelis et al.\(^{53}\)  
3. Settimio et al.\(^{54}\)  
4. Unpublished work\(^{45}\) |
A 4.5 References

(5) Blackburn, G., Giles, J.B., 1963. Trace element concentrations in certain soils of the lower south east of South Australia. CSIRO.
(14) CSIRO. 2007. The Adelaide Coastal Waters Study, final report. CSIRO.


(28) Kämpf, J., Brokensha, C., Bolton, T., 2009. Hindcasts of the fate of desalination brine in large inverse estuaries:

(29) Spencer Gulf and Gulf St. Vincent, South Australia. Desalination and Water Treatment 2, 325-333.


(36) Lombi, E., 2009. Unpublished data about Zn and Ag concentration in biosolids and soils of South Australia.


(43) SA Government Regions.

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(53) University of South Australia, 2013. Unpublished work about Ag soil concentration in South Australia

(54) water-technology.net, 2013. Christies Beach Wastewater Treatment Plant Upgrade, Adelaide, Australia.


Appendix 5: Supporting Information for Chapter 5: Dynamic Probabilistic Modelling of Environmental Emissions of Engineered Nanomaterials
**A 5.1 Input dynamics**

The estimation of the development of ENM production over time is made by multiplying the base year’s (2012) production with the scaling factors of the other years. The production distribution of five ENM in 2012 is given in Sun et al. (2014c). This forms the basis of the updated production distribution of nano-TiO$_2$, nano-ZnO, nano-Ag and CNT in 2012 used in this study. Table A5-1 shows the raw data of ENM production volume reported which are used for building the probability distribution. The figures in black are taken from the study by Sun et al. 2014, and the figures in red are new data found after that study. These figures are subjectively assigned a degree of belief (DoB) based on the reliability and degree of depth the cited source acquired the figures which hinges on how precisely the author collected information to arrive at the given figures. To cover the unknown uncertainty of these data, a single number is deviated by 50% and factor 2 to have a triangular distribution; for data in a range, a uniform distribution is built. Finally these individual distributions based on the data from different sources are combined to represent the compiled knowledge of all information. The scaling factors for each individual years are based on ENM market projections, nanotechnology patent analysis, and the direct ENM production projection (Piccinno et al., 2012) when available. Data for general nanotechnology are used for all the four ENM studied; there are also data especially for CNT. A second reference year is made in 2005 for the data that do not reach to 2012, so that all the data can be compared to the year 2012. A summary of all the data used for estimating the scaling factors is given in Table A5-2. These variable scaling factors for each individual year are used for building a normal distribution. Once both the updated ENM production distribution of 2012 and the distribution of scaling factors are given, they are multiplied to get the production distribution of the years retrospective and prospective.
Table A5-1: Raw data of production volume of nano-TiO2, nano-ZnO, nano-Ag and CNT in 2012 in Europe with Degree of Belief (DoB) for modelling the base year 2012’s production distribution. Numbers in black are those from study Sun et al. (2014); numbers in red are newly available data after that study. DoB are made based on expert judgement. Unit is tons.

<table>
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<th>ENM</th>
<th>80% (DoB)</th>
<th>20% (DoB)</th>
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<tr>
<td></td>
<td>246(^{(a)})</td>
<td>4'037(^{(b)})</td>
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<tr>
<td>Nano-TiO(_2)</td>
<td>13'398(^{(a)})</td>
<td>49'373(^{(a)})</td>
</tr>
<tr>
<td></td>
<td>55-3’000(^{(b)})</td>
<td>1285(^{(c)})</td>
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<tr>
<td></td>
<td>13’360-14’080(^{(d)})</td>
<td>2570(^{(f)})</td>
</tr>
<tr>
<td>Nano-ZnO</td>
<td>2’151(^{(f)})</td>
<td>6(^{(h)})</td>
</tr>
<tr>
<td></td>
<td>5’040-5’440(^{(g)})</td>
<td>136(^{(j)})</td>
</tr>
<tr>
<td></td>
<td>1’815(^{(i)})</td>
<td></td>
</tr>
<tr>
<td>Nano-Ag</td>
<td>6.6-55(^{(n)})</td>
<td>129(^{(n)})</td>
</tr>
<tr>
<td></td>
<td>3.1-22(^{(o)})</td>
<td></td>
</tr>
<tr>
<td>CNT</td>
<td>848(^{(p)})</td>
<td>11-23(^{(q)})</td>
</tr>
<tr>
<td></td>
<td>31-1224(^{(r)})</td>
<td>13-26(^{(r)})</td>
</tr>
</tbody>
</table>

Sources:
(a) (Migros, 2012), (b) (Piccinno et al.), (c) (Keller and Lazareva), (d) (Schmid and Riediker), (e) (Hendren et al.), (f) (RAPPORT d’étude), (g) (EPA), (h) (Nightingale et al.), (i) (Robichaud et al.), (j) (Aschberger et al.), (k) (Zhang and Saebfar), (l) (Future Markets), (m) (Windler et al.), (n) (PC), (o) (Blaser et al.), (p) (Sahasrabudhe), (q) (Ray et al., 2009b), (r) (Healy et al.)
Table A5-2: Summary of the scaling factors for extrapolation of ENM production development. Data are based on projection of nanotechnology market development, nanotechnology patents registration development, and direct historical ENM production and future projection data. These information are transformed into the proportion to the reference year in 2005 (numbers marked in green) and 2012 (numbers marked in orange). Data having only one reference year of 2005 are again extrapolated to reference year 2012 according their proportion year 2012 (numbers in column 2005 that are not 1).

<table>
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<td>Scheu et al. (2006)</td>
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<td>Dorey (DORSEY, 2005)</td>
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<td>Parrish 2010 (Parrish, 2010)</td>
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General nanotechnology

| Patents analysis | Nanowerk 2011 (Patel, 2011) | 0.120 | 0.235 | 0.375 | 0.619 | 1 | 1.716 |
| | Dorsey CNT (DORSEY, 2005) | 0.070 | 0.141 | 0.235 | 0.722 | 0.767 | 1 | 1.689 |
| Market projection | BCC Research (bcc Research, 2012a) | 0.020 | 0.032 | 0.048 | 0.072 | 0.104 | 0.148 | 0.204 |
| | Piccinno et al. 2012 (Piccinno et al., 2012) | 0.003 | 0.050 | 0.083 | 0.228 |
| | Future Markets (Future Markets, 2012) | 0.120 | 0.235 | 0.375 | 0.619 | 1 | 1.716 |
| | Nanowerk 2011 (Patel, 2011) | 0.070 | 0.141 | 0.235 | 0.722 | 0.767 | 1 | 1.689 |
## Appendix 5: Supporting Information for Chapter 5

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Colloidal silver has been used for medical applications since 120 years (Nowack et al., 2011). This means nano silver has been long used before the term “nano-Ag” was invented. To take all the man-made nano-Ag actually applied in history into account, besides the time from 1990 to 2020, for nano-Ag we also modelled another period from 1900 to 2020, which represents a more realistic history of nano-Ag application. In this case, the production distribution of nano-Ag in 2012 is still used as the base. The scaling factor for each individual year is made under the assumption that there is a linear increase of the nano-Ag share compared to total Ag produced worldwide from 1900 to 2020 (U.S. Geological Survey, 2014). By combining this information with the data of the development of total Ag production the scaling factor for each individual year is obtained.

**Figure A5-1:** Estimated scaling factor for production development of nano-Ag from 1900 to 2020. The year 2012 is taken as a reference year. The curve is obtained based on the information of development of total Ag production and the assumed linear increase of the share of nano-Ag compared to total Ag from 1900 to 2020. The use of nano-Ag from 1900 to 1970 is assumed to be only for medical applications; from 1970 to 2020 applications of nano-Ag is assumed to be the same as in the year 2012.
Dynamic Probabilistic Modelling of Environmental Emissions and Concentrations of Engineered Nanomaterials

a. Productions

b. In-use stock

c. Accumulations

d. Concentrations
**LF** = Landfill, **WIP** = waste incineration plant

Figure A5-2: a. Modelled production development of nano-ZnO, nano-Ag (from 1900 to 2020 and from 1990 to 2020), CNT in the EU from 1990 to 2020. Short grey lines indicate the single modelled values. The red curve is the average trend out of the whole simulated values. Dashed blue lines indicate the quantile 15% and 85% range, showing the range of the probability density distribution of the production. b. The evolution of nano-TiO$_2$ amount in the in-use stock. The grey lines are the development trend of single simulations out of 100’000 simulations; here only 2000 of them are shown. The average and quantile 15% and 85% are also shown. The whole cluster area consisting of grey curves builds up the range of the probability distribution of the overall trend. The vertical width of the grey area indicates the degree of uncertainty. c. The evolution of nano-TiO$_2$ in the in-use stock and in landfills, sludge treated soils and sediments as well as the total accumulative production in the EU from 1990 to 2020. Average values are taken here. d. The concentrations evolution in the important technical and environmental compartments in logarithmic scale. “Soils” here indicate the STP sludge treated soils.
A 5.2 Release parameters

The release schedules were determined based on empirical data if relevant experimental data were available, or on the basis of expert opinions, if no relevant data were available. To quantify and schedule the time-dependent release during use, we searched for all the available studies regarding ENM release over time. A handful of studies for some important nanomaterials and applications are available that make a detailed modelling possible. Among the four ENM studied, most studies are available for nano-TiO₂. These studies are mainly about release from textile and paints. Kaegi et al. (2010) conducted a one-year long experiment on a model facades to investigate the release of nano-Ag (to certain extent also TiO₂). The cumulative TiO₂ release was about 1 %. A clear decrease over the first half year was observed and for the rest almost no further release was observed. Al-Kattan et al. 2013 (2013) studied the release of nano-TiO₂ from paints by weathering. Their results show that after 120 cycles of weathering less than 1 % of nano-TiO₂ was released to waster. A study conducted by Windler and colleagues investigated the nano-TiO₂ release from textiles during washing (Windler et al., 2012). After ten cycles of washing experiment, functional textiles released some TiO₂ particles, normally less than 1% of the initial content. In another study by Olabarrieta et al. (2012), TiO₂ nanoparticles release from glasses under water flow was observed over a four-week experiment duration. No information of percentage of nano-TiO₂ loss and the distribution of TiO₂ release over time was given.

Several studies about nano-Ag release from product such as textiles are available. Goetz et al. (2013) and Lorenz et al. (2012) investigated the nano-Ag migration into artificial sweat under physical stress and nano-Ag release from commercially available functional textiles respectively. They showed that up to 20% of nano-Ag can be released from textiles, but no information about the temporal development is available. So the results cannot be used for the purpose of time dependent ENM release modelling. Another unpublished work by Limpiteprakan et al. (2014) looked at release of Ag from three commercial textiles, one cotton based, one PET based and one TC based. After ten washes, 51%, 65% and 48% of nano-Ag was released into washing solution (lab water without detergent). After 20 times wash, the numbers were 55%, 72%, and 48%, respectively. This indicates that the release distribution over time follows a dramatically declining trend. The major release occurred during the first washing cycles.
Table A5-2: Summary of use phase and EoL release for ENM (nano-TiO$_2$, nano-ZnO and CNT). Column Priority is based on the share of ENM applied in products categories. Values of X in column Use release indicate the fraction of ENM contained in a product released during the use phase; values of 1-X in column EoL release indicate the fraction of ENM released during the product’s end of life (EoL). Use release duration means the estimated number of years in which release takes place; Use release schedule is the schedule that each year after a product enters the system how much ENM is released; Distribution after use release is the allocation factor to different environmental compartments after ENM is released during use; Life time of products categories are assumed as being normally distributed. Average life time and deviations are either based on literature if available or estimated based on expert judgement. Similar to Distribution after EoL release, Distribution after EoL release describes the allocations of ENM flows when they come to the end of their life.

<table>
<thead>
<tr>
<th>Priority (share of the total nano-TiO$_2$ application)</th>
<th>nano-TiO$_2$ (product categories)</th>
<th>Use release</th>
<th>Use release schedule</th>
<th>Distribution after use release</th>
<th>EoL release</th>
<th>Lifetime distribution (normal)</th>
<th>Distribution after EoL release</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>X</td>
<td>Y1</td>
<td>Y2</td>
<td>Y3</td>
<td>Y4</td>
<td>...</td>
</tr>
<tr>
<td>59.4%</td>
<td>Cosmetics</td>
<td>0.95$^{(b)}$</td>
<td>2$^{(a)}$</td>
<td>0.6$^{(a)}$</td>
<td>0.1$^{(a)}$</td>
<td>0.9</td>
<td>0.1</td>
</tr>
<tr>
<td>8.9%</td>
<td>Paints</td>
<td>0.01$^{(a)}$</td>
<td>7$^{(a)}$</td>
<td>0.9$^{(a)}$</td>
<td>0.1*(1/6)$^{(a)}$</td>
<td>0.5</td>
<td>0.25</td>
</tr>
<tr>
<td>6.5%</td>
<td>Electronics &amp; A</td>
<td>0.30$^{(a)}$</td>
<td>8$^{(a)}$</td>
<td>0.1*(1/8)$^{(a)}$</td>
<td>1</td>
<td>0.7$^{(a)}$</td>
<td>mean=8; 3o=8$^{(a)}$</td>
</tr>
<tr>
<td>6.2%</td>
<td>Cleaning agent</td>
<td>0.95$^{(b)}$</td>
<td>1$^{(a)}$</td>
<td>1$^{(a)}$</td>
<td>1</td>
<td>0.05$^{(a)}$</td>
<td>Y1=1.0$^{(a)}$</td>
</tr>
<tr>
<td>5.8%</td>
<td>Filter</td>
<td>0.30$^{(a)}$</td>
<td>8$^{(a)}$</td>
<td>1/8$^{(a)}$</td>
<td>0.8</td>
<td>0.2</td>
<td>0.70$^{(a)}$</td>
</tr>
<tr>
<td>3.6%</td>
<td>Plastics</td>
<td>0.03$^{(a)}$</td>
<td>8$^{(a)}$</td>
<td>1/8$^{(a)}$</td>
<td>1</td>
<td>0.97$^{(a)}$</td>
<td>mean=8; 3o=5$^{(a)}$</td>
</tr>
<tr>
<td>3.7%</td>
<td>Coating</td>
<td>0.35$^{(b)}$</td>
<td>10$^{(a)}$</td>
<td>0.9$^{(a)}$</td>
<td>0.1*(1/9)$^{(a)}$</td>
<td>0.8</td>
<td>0.1</td>
</tr>
<tr>
<td>1.7%</td>
<td>Glass &amp; Ceramics</td>
<td>0.35$^{(b)}$</td>
<td>10$^{(a)}$</td>
<td>0.9$^{(a)}$</td>
<td>0.1*(1/9)$^{(a)}$</td>
<td>1</td>
<td>0.65$^{(a)}$</td>
</tr>
<tr>
<td>1.5%</td>
<td>Sport goods</td>
<td>0.04$^{(a)}$</td>
<td>7$^{(a)}$</td>
<td>1/7$^{(a)}$</td>
<td>0.7</td>
<td>0.3</td>
<td>0.96$^{(a)}$</td>
</tr>
<tr>
<td>0.7%</td>
<td>WWTP</td>
<td>0.98$^{(b)}$</td>
<td>1$^{(a)}$</td>
<td>1$^{(a)}$</td>
<td>1</td>
<td>0.02$^{(a)}$</td>
<td>Y1=1.0$^{(a)}$</td>
</tr>
<tr>
<td>0.4%</td>
<td>Batteries</td>
<td>0$^{(a)}$</td>
<td>1$^{(a)}$</td>
<td>1.0$^{(a)}$</td>
<td>1</td>
<td>1.0$^{(a)}$</td>
<td>mean=4; 3o=2</td>
</tr>
<tr>
<td>0.4%</td>
<td>Food</td>
<td>0.90$^{(a)}$</td>
<td>1$^{(a)}$</td>
<td>1.0$^{(a)}$</td>
<td>1</td>
<td>0.10$^{(a)}$</td>
<td>Y1=1.0$^{(a)}$</td>
</tr>
<tr>
<td>0.3%</td>
<td>Textiles</td>
<td>0.03$^{(a)}$</td>
<td>3$^{(a)}$</td>
<td>0.5$^{(a)}$</td>
<td>0.3$^{(a)}$</td>
<td>0.2$^{(a)}$</td>
<td>0.8</td>
</tr>
<tr>
<td>0.2%</td>
<td>Light Bulbs</td>
<td>0$^{(a)}$</td>
<td>1$^{(a)}$</td>
<td>1.0$^{(a)}$</td>
<td>0.9</td>
<td>0.1</td>
<td>0.05$^{(a)}$</td>
</tr>
<tr>
<td>0.2%</td>
<td>Spray</td>
<td>0.95$^{(b)}$</td>
<td>1$^{(a)}$</td>
<td>1.0$^{(a)}$</td>
<td>0.9</td>
<td>0.1</td>
<td>0.05$^{(a)}$</td>
</tr>
<tr>
<td>0.1%</td>
<td>Metals</td>
<td>0.05$^{(a)}$</td>
<td>20$^{(a)}$</td>
<td>1/20$^{(a)}$</td>
<td>1</td>
<td>0.95$^{(a)}$</td>
<td>mean=20; 3o=5$^{(a)}$</td>
</tr>
<tr>
<td>0.1%</td>
<td>Cement</td>
<td>0.01$^{(a)}$</td>
<td>80$^{(a)}$</td>
<td>0.9$^{(a)}$</td>
<td>1/79$^{(a)}$</td>
<td>1</td>
<td>0.95$^{(a)}$</td>
</tr>
<tr>
<td>&lt;0.1%</td>
<td>Ink</td>
<td>0$^{(a)}$</td>
<td>1$^{(a)}$</td>
<td>1.0$^{(a)}$</td>
<td>1</td>
<td>1.0</td>
<td>mean=5; 3o=4$^{(a)}$</td>
</tr>
<tr>
<td>&lt;0.1%</td>
<td>Paper</td>
<td>0$^{(a)}$</td>
<td>1$^{(a)}$</td>
<td>1.0$^{(a)}$</td>
<td>1</td>
<td>1.0</td>
<td>mean=5; 3o=4$^{(a)}$</td>
</tr>
</tbody>
</table>
Appendix 5: Supporting Information for Chapter 5

<table>
<thead>
<tr>
<th>Priority (share of the total nano-ZnO application)</th>
<th>nano-ZnO (product categories)</th>
<th>Use release</th>
<th>Use release duration (years)</th>
<th>Use release schedule</th>
<th>Distribution after use release (^{(a)})</th>
<th>EoL release</th>
<th>Lifetime distribution (normal) Note: (\alpha) is the standard deviation</th>
<th>Distribution after EoL release</th>
</tr>
</thead>
<tbody>
<tr>
<td>82.6%</td>
<td>Cosmetics</td>
<td>0.95 (^{(h)})</td>
<td>(X)</td>
<td>2 (^{(h)})</td>
<td>0.9 (^{(h)})</td>
<td>0.1 (^{(h)})</td>
<td>0.9 (^{(h)})</td>
<td>0.1 (^{(h)})</td>
</tr>
<tr>
<td>14.3%</td>
<td>Paints</td>
<td>0.35 (^{(h)})</td>
<td>(X)</td>
<td>7 (^{(h)})</td>
<td>0.9 (^{(h)})</td>
<td>0.1 (^{(h)})</td>
<td>10 (^{(h)})</td>
<td>1 (^{(h)})</td>
</tr>
<tr>
<td>2.0%</td>
<td>Plastics</td>
<td>0.80 (^{(h)})</td>
<td>(X)</td>
<td>8 (^{(h)})</td>
<td>0.9 (^{(h)})</td>
<td>0.1 (^{(h)})</td>
<td>1 (^{(h)})</td>
<td>0.20 (^{(h)})</td>
</tr>
<tr>
<td>0.7%</td>
<td>Glass</td>
<td>0.35 (^{(h)})</td>
<td>(X)</td>
<td>10 (^{(h)})</td>
<td>0.9 (^{(h)})</td>
<td>0.1 (^{(h)})</td>
<td>1 (^{(h)})</td>
<td>0.65 (^{(h)})</td>
</tr>
<tr>
<td>0.2%</td>
<td>Electronics &amp; A &amp; 0.30 (^{(h)})</td>
<td>(X)</td>
<td>8 (^{(h)})</td>
<td>0.9 (^{(h)})</td>
<td>0.1 (^{(h)})</td>
<td>1 (^{(h)})</td>
<td>0.70 (^{(h)})</td>
<td>mean=8; 3=8 (^{(h)})</td>
</tr>
<tr>
<td>0.1%</td>
<td>Filter</td>
<td>0.30 (^{(h)})</td>
<td>(X)</td>
<td>8 (^{(h)})</td>
<td>0.9 (^{(h)})</td>
<td>0.1 (^{(h)})</td>
<td>1 (^{(h)})</td>
<td>0.70 (^{(h)})</td>
</tr>
<tr>
<td>0.1%</td>
<td>Cleaning agent</td>
<td>0.95 (^{(h)})</td>
<td>(X)</td>
<td>1 (^{(h)})</td>
<td>1 (^{(h)})</td>
<td>0.20 (^{(h)})</td>
<td>0.1 (^{(h)})</td>
<td>0.05 (^{(h)})</td>
</tr>
<tr>
<td>&lt; 0.1%</td>
<td>Foods</td>
<td>0.90 (^{(h)})</td>
<td>(X)</td>
<td>1 (^{(h)})</td>
<td>1 (^{(h)})</td>
<td>0.20 (^{(h)})</td>
<td>0.1 (^{(h)})</td>
<td>0.10 (^{(h)})</td>
</tr>
<tr>
<td>&lt; 0.1%</td>
<td>Textiles</td>
<td>0.60 (^{(h)})</td>
<td>(X)</td>
<td>3 (^{(h)})</td>
<td>0.9 (^{(h)})</td>
<td>0.2 (^{(h)})</td>
<td>0.2 (^{(h)})</td>
<td>0.80 (^{(h)})</td>
</tr>
<tr>
<td>&lt; 0.1%</td>
<td>Metals</td>
<td>0.05 (^{(h)})</td>
<td>(X)</td>
<td>20 (^{(h)})</td>
<td>0.9 (^{(h)})</td>
<td>0.1 (^{(h)})</td>
<td>1 (^{(h)})</td>
<td>0.95 (^{(h)})</td>
</tr>
<tr>
<td>&lt; 0.1%</td>
<td>Woods</td>
<td>0.30 (^{(h)})</td>
<td>(X)</td>
<td>20 (^{(h)})</td>
<td>0.9 (^{(h)})</td>
<td>0.1 (^{(h)})</td>
<td>1 (^{(h)})</td>
<td>0.70 (^{(h)})</td>
</tr>
<tr>
<td>&lt; 0.1%</td>
<td>Paper</td>
<td>0 (^{(h)})</td>
<td>(X)</td>
<td>0 (^{(h)})</td>
<td>0 (^{(h)})</td>
<td>0 (^{(h)})</td>
<td>0 (^{(h)})</td>
<td>1.00 (^{(h)})</td>
</tr>
</tbody>
</table>

Note: Yn = year n, e.g. Y1 = year 1; Electronics & A = "Electronics and Appliances

(a) (Sun et al., 2014c)
(b) Revised based on (Sun et al., 2014c)
(c) (Expert judgement, 2014)
(d) (Bakas et al., 2011)
(e) (EEA Website, 2013)
(f) (Al-Kattan A, 2013)
(g) (ATD Home inspection, 2014)
(h) (Hischier et al., 2015)
(i) (EEA, 2009)
(j) (SENS SWICO SLRS., 2014)
(k) (Kiddie et al., 2013)
(l) (EEA, 2012)
(m) (Windler et al., 2012)
(n) (Olabarrieta et al., 2012)
(o) (Eastonstewardsvilledrycleaners36, 2014)
(p) (Friend of the Earth Europe, 2013)
(q) (The Telegraph, 2009)
(r) (Kaegi et al., 2010)
(s) (Glass International, 2014)
(t) (Limpiteeprakan, 2014)

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### A 5.3 Estimation of volumes of technical and environmental compartments

**Table A5-3: Summary of volumes of different technical and environmental compartments used for the EU**

<table>
<thead>
<tr>
<th>Compartments</th>
<th>Formula</th>
<th>Volumes</th>
<th>Unit</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Air</strong></td>
<td>4'326'337<em>1</em>10^9</td>
<td>4.33E+15</td>
<td>m³</td>
<td>4'326'337 km² is the area of EU27 (Wikipedia, 2012) 10 days was used for the residence time in air for ultrafine particles (Anastasio and Martin, 2001) 1 km was taken for the depth of air will be affected by ENM (ECB, 2003a) 10^9 is the transformation from km³ to m³</td>
</tr>
<tr>
<td><strong>Natural and urban soil</strong></td>
<td>4'326'337<em>0.97</em>10^6*(0.2<em>0.47+0.05</em>0.53)*1'500</td>
<td>7.59E+13</td>
<td>kg</td>
<td>0.97 is the proportion of terrestrial land in EU (Wikipedia, 2012) 10^6 is the transformation factor from km² to m² 0.2 is the depth considered for agricultural soil suggested (ECB, 2003a) 0.47 is the share of agricultural land area in EU (Europa, 2013) 0.05 m depth of natural and urban soil (ECB, 2003a) 0.53 is the share of natural and urban land in EU (Europa, 2013) 1'500 kg/m³ is the density of dry soil (ECB, 2003a)</td>
</tr>
<tr>
<td><strong>Biosolid treated soil</strong></td>
<td>(9'000'000<em>0.55/20)<em>10^4</em>0.2</em>1'500</td>
<td>7.43E+11</td>
<td>kg</td>
<td>9'000'000 tons is the volume of sewage sludge EU yearly produced (EC, 2009) 0.55 is the share of sewage sludge going to agricultural soil (Blaser et al., 2008) 20 tons/ha is the average sludge application rate in EU (Eamens, 2006) 10^4 is the transformation factor from ha to m²</td>
</tr>
<tr>
<td><strong>Surface water</strong></td>
<td>4'326'337<em>0.03</em>10^6<em>3</em>1'000</td>
<td>3.89E+14</td>
<td>litre</td>
<td>0.03 is the share of water area in EU (Wikipedia, 2012) 3 m is the depth of water compartment considered (ECB, 2003a) 1'000 is the transformation factor from m³ to litre</td>
</tr>
<tr>
<td><strong>Sediments</strong></td>
<td>4'326'337<em>0.03</em>10^6<em>0.03</em>260</td>
<td>1.01E+12</td>
<td>kg</td>
<td>0.03 m is the depth of sediments considered to be affect by ENM (ECB, 2003a) The another 0.03 is the share of water area in EU (Wikipedia, 2012) 260 kg/m³ is the density of sediments soil (Gottschalk et al., 2009a)</td>
</tr>
<tr>
<td><strong>STP effluent</strong></td>
<td>0.8<em>200</em>365*509'000'000</td>
<td>2.97E+13</td>
<td>litre</td>
<td>0.8 is the average proportion of EU families connected to central sewage facility (ECB, 2003a) 200 l/head is the average daily water consumption of EU citizens (ECB, 2003a) 509'000'000 is the number of EU population (Wikipedia, 2012)</td>
</tr>
<tr>
<td><strong>STP sludge</strong></td>
<td>9.00E+09</td>
<td>9'000'000'000 kg is the volume of sewage sludge EU yearly produced (EC, 2009)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Solid waste landfilled</strong></td>
<td>7.31E+10</td>
<td>73.1 kg</td>
<td></td>
<td>73.1 million tonnes of municipal waste is landfilled in the EU in 2013 (Eurostat, 2015)</td>
</tr>
<tr>
<td><strong>Solid waste incinerated</strong></td>
<td>6.16E+10</td>
<td>61.6 kg</td>
<td></td>
<td>61.6 million tonnes of municipal waste is incinerated in the EU in 2013 (Eurostat, 2015)</td>
</tr>
</tbody>
</table>
A 5.4 Predicted concentration results of EU in 2020

Table A5-4: Predicted (Accumulated) concentrations of nano-TiO2, nano-ZnO, nano-Ag and CNT in waste streams and environmental compartments in the EU in 2020. Mean, mode, median, quantile 0.15 and quantile 0.85 are shown. Values are rounded off to three significant digits. Results for nano-Ag are presented for both the time scopes of the 1900-2020 and 1990-2020 scenarios.

<table>
<thead>
<tr>
<th>Compartment</th>
<th>EU (2020)</th>
<th>Mean</th>
<th>Mode</th>
<th>Median</th>
<th>Q0.15</th>
<th>Q0.85</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nano-TiO2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STP Effluent</td>
<td>106</td>
<td>20.1</td>
<td>33.9</td>
<td>4.80</td>
<td>176</td>
<td>µg/L</td>
</tr>
<tr>
<td>STP sludge</td>
<td>4.37</td>
<td>1.09</td>
<td>1.856</td>
<td>0.318</td>
<td>8.23</td>
<td>g/kg</td>
</tr>
<tr>
<td>Solid waste to Landfill</td>
<td>37.4</td>
<td>23.6</td>
<td>31.3</td>
<td>16.2</td>
<td>56.5</td>
<td>mg/kg</td>
</tr>
<tr>
<td>Solid waste to WIP</td>
<td>29.5</td>
<td>18.4</td>
<td>24.2</td>
<td>11.9</td>
<td>45</td>
<td>mg/kg</td>
</tr>
<tr>
<td>WIP bottom ash</td>
<td>1.12</td>
<td>0.493</td>
<td>0.617</td>
<td>0.245</td>
<td>1.82</td>
<td>g/kg</td>
</tr>
<tr>
<td>WIP fly ash</td>
<td>1.53</td>
<td>0.557</td>
<td>0.829</td>
<td>0.314</td>
<td>2.54</td>
<td>g/kg</td>
</tr>
<tr>
<td>Surface water</td>
<td>5.76</td>
<td>1.26</td>
<td>2.41</td>
<td>0.376</td>
<td>11.5</td>
<td>µg/L</td>
</tr>
<tr>
<td>Sediment</td>
<td>123</td>
<td>85.6</td>
<td>11.1</td>
<td>62.9</td>
<td>186</td>
<td>mg/kg</td>
</tr>
<tr>
<td>Natural and urban soil</td>
<td>8.57</td>
<td>6.11</td>
<td>7.75</td>
<td>4.36</td>
<td>13.1</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Sludge treated soil</td>
<td>0.177</td>
<td>0.129</td>
<td>0.158</td>
<td>0.092</td>
<td>0.265</td>
<td>g/kg</td>
</tr>
<tr>
<td>Air</td>
<td>5.48</td>
<td>1.87</td>
<td>3.14</td>
<td>0.909</td>
<td>9.45</td>
<td>ng/m³</td>
</tr>
<tr>
<td><strong>Nano-ZnO</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STP Effluent</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>µg/L</td>
</tr>
<tr>
<td>STP sludge</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Solid waste to Landfill</td>
<td>4.58</td>
<td>2.38</td>
<td>3.00</td>
<td>1.30</td>
<td>6.94</td>
<td>mg/kg</td>
</tr>
<tr>
<td>Solid waste to WIP</td>
<td>3.43</td>
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<td>0.839</td>
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<td>WIP bottom ash</td>
<td>17.5</td>
<td>6.19</td>
<td>9.64</td>
<td>3.62</td>
<td>28.2</td>
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<td>WIP fly ash</td>
<td>32.2</td>
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<td>16.8</td>
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<td>Surface water</td>
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<td>0.354</td>
<td>0.496</td>
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<td>Sediment</td>
<td>20.2</td>
<td>14.6</td>
<td>18.1</td>
<td>10.9</td>
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<tr>
<td>Natural and urban soil</td>
<td>5.28</td>
<td>3.24</td>
<td>4.47</td>
<td>2.11</td>
<td>8.20</td>
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<td>Sludge treated soil</td>
<td>0.056</td>
<td>0.043</td>
<td>0.052</td>
<td>0.033</td>
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<td>Air</td>
<td>2.33</td>
<td>0.593</td>
<td>0.947</td>
<td>0.162</td>
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<td>STP Effluent</td>
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<td>1.42</td>
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<td>53.1</td>
<td>129</td>
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<td>0.043</td>
<td>0.052</td>
<td>0.033</td>
<td>0.081</td>
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<td>6.77</td>
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<td>5.47</td>
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<td>285</td>
<td>332</td>
<td>193</td>
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<td>0.011</td>
<td>0.087</td>
<td>ng/m³</td>
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A 5.5 References


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Curriculum Vitae

Tianyin Sun

Personal Information

Date of birth: 06.01.1982
Nationality: Chinese
Email: sty1882@hotmail.com
Languages: Chinese (native), English (fluent), German (fluent)

Education

2011 – 2015: Doctoral Studies in Environmental Science
ETH Zurich (Switzerland)

TU München (Germany)

2001 – 2005: Bachelor of Engineering in Software Engineering
South China University of Technology (China)

Professional Occupations

04/2010 – 05/2011: LCA Consultant at PE INTERNATIONAL
Stuttgart, Germany

Essen, Germany

06/2009 – 09/2009: Intern at the UNEP/Wuppertal Institute CSCP Centre
Wuppertal, Germany

New York, United States