Henning Wigger

Environmental Release of and Exposure to Iron Oxide and Silver Nanoparticles

Prospective Estimations Based on Product Application Scenarios



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Henning Wigger Department of Technological Design and Development, Faculty of Production Engineering, University of Bremen Germany

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Supervisors

Prof. Dr. Arnim von Gleich

Department of Technological Design and Development Faculty of Production Engineering University of Bremen, Germany

Prof. Dr. Klaus Kümmerer

Chair for Sustainable Chemistry and Material Resource Director of the Institute of Sustainable and Environmental Chemistry Leuphana University of Lüneburg, Germany

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German abstract (deutsche Zusammenfassung)

Nanotechnologien und Nanomaterialien wird ein signifikantes Marktpotenzial zugesprochen, und sie zählen zu einer der viel versprechendsten Technologien dieses Jahrhunderts. Diese Erwartungen basieren auf den neuen oder verstärkten Materialeigenschaften, die insbesondere Metalle und Metalloxide im nanoskaligen Größenbereich aufweisen. So wird beispielsweise das normalerweise magnetische Eisenoxid erst im Nanometerbereich superparamagnetisch — ein Zustand in welchem das Material selbst nicht magnetisiert wird. Diese Eigenschaft ermöglicht es das Material durch das Anlegen eines elektromagnetischen Feldes kurzfristig zu magnetisieren. Viele dieser unterschiedlichen Eigenschaften von Nanomaterialien können durch das vergrößerte Oberflächen-Volumen-Verhältnis erklärt werden, wobei bei gleichbleibendem Volumen und annehmender Partikelgröße sich die spezifische Oberfläche und somit das Verhältnis zum Volumen erhöht. Neben den vielen Einsatzmöglichkeiten, welche Nanomaterialien bieten, lassen die andersartigen Eigenschaften aber auch Besorgnis für potenzielle Risiken aufkommen. Insbesondere greifen die Nanotechnologien in niedrige Hierarchieebenen ein, d.h. auf der Ebene von Atomen, Molekülen oder Genen. Dies hat das Potenzial von irreversiblen sowie entgrenzenden negativen Wirkungsketten in Raum und Zeit. Daher verbietet sich die oft angewendete "Versuch und Irrtum Strategie", um Wissenslücken zu überbrücken, sondern es muss nach dem Vorsorgeprinzip gehandelt werden.

Der Umfang des Nichtwissens und das Noch-Nichtwissens über mögliche negative Folgen ist in einer frühen Innovationsphase der Nanotechnologien besonders groß. Daher wurde in den letzten Jahren verstärkt Risikoforschung betrieben, die zum größten Teil ökotoxikologische Studien und weniger Umweltexpositionsstudien abdeckte. Zwar konnten schon erste Effekte und Wirkungsmechanismen identifiziert werden, diese reichen jedoch nicht für eine letztliche Risikoeinstufung aus. Wenn im Sinne des Vorsorgeprinzips gehandelt werden soll, sind Studien zu Expositionen und potenziellen Umweltkonzentrationen besonders relevant, da Ansätze zur Expositionsminderung wichtige Elemente einer Vorsorgestrategie sind. Daher werden Methoden dringend benötigt, die vor einer Freisetzung von Nanomaterialien ansetzen, um dem Vorsorgeprinzip zu folgen und Wissenslücken überbrücken.

Vor diesem Hintergrund fokussiert diese Arbeit auf eine prospektive Abschätzung der potenziell freigesetzten Nanomaterialien aus Produkten in die Umwelt. Dabei konnte gezeigt werden, dass trotz erheblicher Wissenslücken in frühen Innovationsphasen begründete Aussagen über potenzielle Umweltkonzentrationen gemacht werden können.

Die entwickelte Methodik wurde an zwei Fallbeispielen für Silber- und Eisenoxidnanopartikeln (AgNP und IONP) demonstriert.

Basierend auf einer Technologiecharakterisierung wurden Materialeigenschaften von AgNP und IONP bestimmt. Anschließend wurden gegenwärtige und zukünftige Anwendungen ermittelt. Ersteres basierte auf der Analyse von Produktdatenbanken, letzteres nutzte die ermittelten Materialeigenschaften in einer bibliometrischen Analyse von wissenschaftlichen Publikationen und in einer Patentdatenbankanalyse, um auch zukünftige relevante Anwendungen zu identifizieren.

die vergleichsweise großen Des Weiteren wurden Unsicherheiten durch Produktanwendungsszenarien überbrückt, worin relevante Freisetzungseigenschaften der ausgewählten Produkte enthalten sind. Diese Szenarien umfassten ein dreistufiges Verfahren zur Ermittlung von begründeten Freisetzungsfaktoren innerhalb des Produktlebenszyklus von Textilien (AgNP Fallstudie) und von Kontrastmitteln für die Magnetresonanztomographie (IONP Fallstudie). Sofern keine experimentellen Daten vorhanden waren, wurden begründete Analogieschlüsse oder worst-case Annahmen verwendet. Durch die zusätzliche Berücksichtigung von minimalen und maximalen Freisetzungsfaktoren wurden dann, im Rahmen einer Materialflussanalyse, potenzielle Umweltkonzentrationen für die primären Umweltkompartimente ermittelt.

Dennoch besitzt diese Methodik einige Limitationen. Die in den Fallstudien angenommenen Freisetzungsfaktoren bilden die Unsicherheiten nur in einem groben Bereich ab und vernachlässigen dabei die wechselseitigen Einflüsse von Produktmatrixmaterial und Nanomaterial. Hier sollten in zukünftigen Studien bereits bekannte Methoden aus der Ökobilanzierung (z.B. Pedigree Approach) verwendet werden, um die hier entwickelte Methodik um diesen Aspekt zu ergänzen. Des Weiteren werden die Transfers in und zwischen den Kompartimenten sowie letztendliche Transformationen, welche die Nanoobjekte in Umweltmedien erfahren können, aufgrund des prospektiven Charakters nicht berücksichtigt. Dies sollte ebenfalls in zukünftigen Studien aufgegriffen werden, um einen weiteren Beitrag zur prospektiven Risikoabschätzung zu leisten.

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List of abbreviations

AgNP	Silver nanoparticle	LED	Light emitting diode
ANEC	European Association for the Co-ordination of Consumer Representation in Standardisation		Monte Carlo simulation
BUND	Friends of the Earth	MRI	Magnetic resonance imaging
СТА	Center for Technology Assessment	NOAA	Nanomaterials, nanoobjects, -agglomerates, and -aggregates
DNA	Deoxyribonucleic acid	NOEL	No-observed effect level
DNEL	Derived no-effect level	OECD	The Organisation for Economic Co-operation and Development
DPTA	Diethylene triamine pentaacetic acid	РВТ	Very persistent, bioaccumulative, and toxic
EC ₅₀	Effective concentration that can be observed at 50% of the population/organisms	PEC	Predicted environmental concentration
ECHA	European Chemicals Agency	PNEC	Predicted no-effect concentration
EEA	Environmental exposure assessment	PNEL	Predicted no-effect level
EHS	Environmental, health, and safety aspects	PVP	Polyvinylpyrrolidon
EMF	Electro-magnetic field	REACH	Registration, Evaluation, Authorization, and Restriction of Chemicals
EOL	End-of-life	SERS	Surface enhanced raman spectroscopy
EPO	European Patent Office	spERC	Specific environmental release category
ERC	Environmental release category	SPION	Superparamagnetic iron oxide nanoparticle
EWG	Environmental Watch Group	sw	Surface water
Gd	Gadolinium	TA	Technology assessment
GMR	Giant magnetoresistance	uv	ultraviolett
HEA	Human exposure assessment	vPvB	very persistent and very bioaccumulative
ICT	Information and communication technology	WIP	Waste incineration plant
IPCS	International Programme on Chemical Safety	WMS	Waste management system
IONP	Iron oxide nanoparticle	WoS	Web of Science
ISO	International Organization for Standardization	wwi	Woodrow Wilson Institute
LCA	Life cycle assessment	WWTP	Wastewater treatment plant
LCD	Liquid crystal display	ww	Wastewater

1 Background and motivation

Nanotechnologies are promising for various product applications that are accompanied with a significant market potential (Roco 2011). Innovations based on nanomaterials address global challenges like energy, health care, clean water, and climate change (Palmberg et al. 2009) promising to satisfy the economical, social and environmental needs of the society. Consequently, nanotechnologies are often declared as the key technology of the 21st century combining several research disciplines including physics, chemistry, biology and biochemistry.

Interestingly, nanomaterials, nano-objects, -agglomerates, and -aggregates (NOAAs) show different or enhanced material properties in the nanometer range compared to their bulk counterparts. For instance, iron oxide nanoparticles (IONP) have superparamagnetic properties and are only magnetic in presence of an electromagnetic field. Moreover, titanium dioxide appears transparent at submicron scales as for example in thin-film coatings. Many of these effects can be explained by the higher surface-to-volume ratio. Due to the smaller particle size more atoms and electrons are (closer) placed at the particle surface compared to surfaces of bulk materials, which influence material characteristics such as reactivity or optical properties. Hence, many biological and physical processes are dependent on the size of the surface area. Furthermore, it is expected that NOAAs can also contribute to a higher resource efficiency by reducing the required material and energy inputs in applications (NNI 2015; Wigger et al. 2015b).

Accordingly, companies increasingly use NOAAs in products in order to deploy such advantages and bring innovations to market. Entrepreneurs are challenged by an intensified global competition, accelerating innovation cycles, and a shortened time-to-market (Spur 2006). Thus, innovations are viewed as key requirements for companies and society to sustain in this context. Hence, a shift towards shorter development times and product life cycles is noticeable (Cucculelli and Ermini 2012; Gmelin and Seuring 2014).

Generally, innovations are often associated with potential (environmental) risks, which are constituted by potential adverse effects (i.e., hazards) and exposure likelihood. In the case of NOAAs concerns are raised due to the new or enhanced properties, which may be the cause of unprecedented risks. This situation is typical for technologies in early innovation stages with prevailing ignorance and uncertainties regarding potential environmental health and safety (EHS) risks. On the other hand, there are still possibilities for creating more benign by design alternatives, which will vanish in later innovation stages due to decisions made previously (Gleich et al. 2008). Consequently, it would be ideally preferable to make use of both the advantages of NOAAs and minimizing potential risks in an early innovation stage. However, even though an ideal arrangement of both objectives seems to be mutually

exclusive, the technology and risk assessment have to face several challenges in order to handle and allow a sustainable development.

1.1 Problem description

In the light of the accelerating innovation cycles and the need to innovate, technology assessment (TA) and risk assessment are confronted with very complex and uncertain issues, because one cannot reliably predict the future and foresee every possible risk. Nevertheless, the urgent need to act before a technology is fully developed, is illustrated by the "Collingridge Dilemma" in the context of innovation processes. Collingridge (1980) described this dilemma as follows: In early innovation stages a high uncertainty and ignorance exist about potential risks of a technology, which is referred to as the information problem. Additionally, in this stage many opportunities are available to realize intended functionalities and to avoid or minimize potential detrimental impacts. This is because no far-reaching decisions that would lead to path dependencies have been made so far. Path dependence is a concept generally describing the "lock-in" situation, in which a change towards another (more promising) path is aggravated (cf. Beyer 2005). On the other hand, in later innovation stages the knowledge gaps on potential EHS impacts can be stepwise filled, but path changes would be difficult and expensive, because relevant decisions and investments were already made. Wrong decisions now can only be revised, if at all, with respective monetary efforts (i.e., sunk costs that are later added to the market price). This mutual dependency is illustrated in Figure 1. Additionally, this figure shows some of the available methods that can be applied for TA in the corresponding innovation stage in a prospective manner.

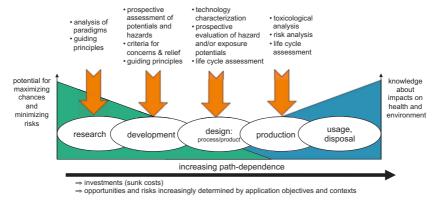


Figure 1. Challenges in early innovation stages and some available methodologies for technology assessment. (Gleich 2013)

Besides, technologies and related innovations differ in several aspects not only regarding chances but also regarding risks. These characteristics can be investigated by the technology characterization and by prospective risk assessment approaches. Following Gleich (1999), technologies especially differ in their "power" or "capability", which in certain cases are based on their "depth of intervention" into physical, chemical or biological structures. The criterion "depth of intervention" concerns the approach on how a technology creates the desired effect or function, which can be technologically exploited. Technologies with a very high depth of intervention do not apply on the highest hierarchical level of immediate phenomena (like stones or trees), but exploit elementary mechanisms at low hierarchical levels (e.g., atoms, molecules, or genes) to create or influence the desired phenomenon. Such technologies are nuclear power, genetic engineering as well as synthetic biology, for instance.

To illustrate two different kinds of depth of intervention, the following example is provided (Gleich 1999): A technology with low depths of intervention is the mechanical splitting of stones. In contrast, a high depth of intervention is the splitting of the atom. Both approaches differ in their strategy on how to construct the technical phenomenon and also in the existing knowledge gaps regarding potential consequences. This lack of knowledge on potential consequences is described by the second criterion capability. Gleich (1999) postulated the increase of knowledge gaps together with higher depth of interventions. Additionally, potential severe consequences of such interventions are often uncontrollable and irreversible especially almost unlimited in space and time (Gleich 1999; Giese and Gleich 2015). To continue the example of splitting stones and atoms: While splitting of stones is more or less easy to analyze regarding its consequences, the splitting of the atom has more severe and far reaching effects in space and time (e.g., the half-life of plutonium is approx. 240,000 years). Therefore, a precautionary approach should be applied for technological developments based on a high depth of invention, since the wide spread and conventional trial-and-error approach is not justifiable due to the severity and irreversibility of the expectable consequences (Gleich 1999; Giese and Gleich 2015). The question if nanotechnologies belong to the category "high depth of intervention" is not yet completely answered. However, nanotechnologies use effects or functionalities, which are created by intervening at the lowest hierarchical level potentially leading to unprecedented long-term consequences. Therefore, precautionary approaches should be applied and are needed to perform prospective assessments.

Besides, (environmental) risk assessments are used to investigate potential adverse effects and exposure likelihoods, which both are constituents of risks. Currently, there is the common sense that these assessments should be completely and quantitatively conducted in order to identify potential risks based on "evidence" (Gleich et al. 2008). On the one hand,

it would be necessary to follow a case-by-case analysis as it was recommended by Aitken et al. (2011) to understand certain observed effects. On the other hand, however, such complete assessments are not possible due to time and financial limitations in particular with view on the shortened innovation cycles. This concern is increased, because pristine NOAAs (i.e., the originally synthesized particles) can be environmentally transformed during their life cycle (Mitrano et al. 2015). Hence, the number of potential NOAAs species would additionally increase, which have to be investigated in risk assessments (Harper et al. 2015). Potential strategies to reduce the required time for experimental testing and to improve testing strategies are still in development such as high throughput screening (i.e., large quantity of miniaturized samples for accelerated testing) (see e.g., Watson et al. 2014) or the grouping of NOAAs to implement intelligent toxicological testing strategies (e.g., Delmaar et al. 2015; Godwin et al. 2015). The high number of NOAA species that have to be analyzed, complicates the derivation of potential adverse effects of NOAAs. Hence, major challenges for determining potential hazards still remain. Additionally, the diversity in NOAA characterization protocols applied in experiments and the lack of reference materials complicate predictive hazard estimations (Schafer et al. 2013; Powers et al. 2014). These challenges still hinder the determination of specific physico-chemical properties responsible for the mode of action as well as related risks. Thus, researchers mostly focus on uncovering potential hazards arising from NOAAs, which has been a long time the traditional approach for risk assessment despite that exposure assessment is as important as hazard assessment (Hansen et al. 2007).

On the other hand, exposure assessments also rely on retrospectively gained data. In principle two main approaches exist: experimental measurements and model based simulations. First, retrospective exposure assessments comprise the measurement and analysis of concentrations of a substance in the respective environmental compartment after the release (Lioy 2010), which is the starting point of exposures. Furthermore, the retrospective exposure assessment can be conducted in a biomonitoring perspective. This is usually applied in human toxicology in order to determine past exposures via the analysis of organs, breaths, urine, or feces (Paustenbach 2000; Lioy 2010). These methodologies are well developed for already known substances (Paustenbach 2000). However, in the case of new substances such approaches are not adequate to analyze and to evaluate the expected exposure to a new agent.

Moreover, environmental models were developed for predicting environmental concentrations of chemicals that mainly rely on already known data on environmental fate and behavior or substance-related properties (see fugacity approach in e.g. Mackay et al. (2001)). In contrast, unlike chemicals, NOAAs are mainly present in a solid particulate form and thus show a different environmental behavior. Therefore, currently existing fate and behavior models, which are widely used for organic chemicals, need to be adapted

(Westerhoff and Nowack 2013). Such a modified approach using partition coefficients (e.g., octanol-water coefficient) can identify the distribution of NOAAs in environmental compartments and their major exposure pathways in risk assessment (Westerhoff and Nowack 2013). Consequently, several studies focus on the applicability of partition coefficients for NOAAs to predict their environmental behavior. However, recent findings have highlighted that partition coefficients seem not applicable for NOAAs and thus alternative methods are required. This is mainly because the transport and behavior of NOAAs in environmental compartments represents a major determinant of exposure (Praetorius et al. 2012; Praetorius et al. 2014; Meesters et al. 2014; Cornelis 2015; Dale et al. 2015b).

In this way, the crucial information for exposure (and also hazard) assessment is the finally transformed NOAA species, its mobility and quantity present in the environmental compartment causing exposures, which is still needed for risk assessments. Consequently as previously implied, several knowledge gaps exist for the corresponding NOAA species (Painter et al. 2014). Irrespectively of the kind of finally transformed NOAA, which may be the origin of adverse effects, the strength of the emission source defines the exposure and thus determines the potentially necessary precautionary measures (IPCS 2004; Kümmerer 2010). Besides environmental emissions caused by industrial processes, products can be regarded as the main output source (Held 1991) and are thus related to their environmental release and exposure. Up to now, NOAA release studies for products are rare. However, they are urgently needed to determine reliable predicted environmental concentrations (PEC) in a complete life cycle perspective (Som et al. 2010a; Markus et al. 2013). Thus far, only some knowledge on potential releases (i.e., the source of exposure) and related risks has been gained in a retrospective view, primarily due to the early stage of research and development of nanotechnologies.

1.2 Research objectives and methodologies

The previous subsections emphasized the urgent necessity of a prospective approach for assessing innovations in an early technological development stage. Additionally, existing knowledge gaps particularly prevail in environmental exposure assessments. Thus, the prospective approach should additionally analyze the source of exposure, which is determined by releases from products. This approach would in turn serve also the precautionary principle by operating before any environmental releases have occurred, which was one major demand due to the technology character (see previous subsection). However, a prospective approach has also to deal with corresponding uncertainties due to the limited data availability. Furthermore, it still should be able to give recommendations for decision-makers. In this thesis a prospective approach will be developed for estimating environmental NOAAs releases of products in early innovation stages. Subsequently, the

prospective approach will be applied to the selected case studies addressing the following objectives:

Objective 0.1

Identification of current and future product application with embedded NOAAs

The basis for the prospective approach is the identification of innovations and products, which contain NOAAs. Hence, three subgoals have to be defined for fulfilling this main objective. At first, the subgoal O.1.1 will consider the characterization of the technology with regard to the material properties, which are used in potential product applications. The identified material properties will be used in subgoal O.1.3 for identifying upcoming products. Particularly, in early stages of innovations there is little knowledge about possible aims and application contexts, which to an important extend influence positive or negative effects (Gleich et al. 2008). Nevertheless, there are explicitly formulated hopes or intentions combined with potentials (i.e., functionalities and properties) based on the new technology (Liebert and Schmidt 2010). Consequently, quite a lot of knowledge about the technology is available in an early innovation stage that can be investigated to derive potential chances as well as risks (Liebert and Schmidt 2010; Gleich 2013). The research focus changes from potential consequences to the characteristics of the technology, which may be the source of effects.

Second, the subgoal O.1.2 will determine current product applications on the market, whereas subgoal O.1.3 will consider upcoming future product applications. Thereby, both current and future product applications will cover different innovation cycles (i.e., market entry vs. developmental stage, respectively) and will be checked against each other. Accordingly, different methodologies have to be applied for each subgoal.

In subgoal O.1.2 different existing *product databases* will be analyzed to outline the current situation of commercially available NOAA-enhanced products. For subgoal O.1.3 other data sources have to be considered for enabling the prospective assessment. First, technological trends have to be analyzed for identifying relevant product applications. Several methods are at hand for analyzing technological trends, which originate from the field of technology forecasting and road mapping that are applicable in different innovation stages. Watts and Porter (1997) and Martino (2003) provided an overview on the potential information sources related to the respective innovation stage as illustrated in Table 1. Generally, it is assumed that each invention or progress is published in corresponding media. Consequently, the science citation index is a common representative for the stage of basic research. This index focuses on selected journals and related publications on basic research issues (Kostoff et al. 2001). The Compendex (formerly known as Engineering index) is related to the applied research stage also comprising different selected journals and conference papers with special focus on the application of researches in different contexts (Järvenpää et al. 2011).

Additionally, patenting trends can be investigated via patent database analysis, which is assigned to the developmental stage (Daim et al. 2006), but it has to be noted that not always strict differentiations are possible between applied research and developmental stage. Moreover, following Watts and Porter (1997), indicators for the application stage and the social impact represent newspapers, print medias, or respectively the business and popular print medias.

Table 1. Potential sources of information in different research and development stages.

Research and development stage	Potential sources of information
Basic research	Science citation index
Applied research	Engineering index (until 1969) / Compendex (from 1970)
Development	Patents
Application	Newspaper, print media, product databases
Social impact	Business and popular print media

Reference: adapted from Watts and Porter (1997); Martino (2003)

Since NOAAs are supposed to be in an early innovation stage, the analysis of technological trends and potential products should be in the research focus.

Therefore, in O.1.3 a *bibliometric analysis* of scientific publications will be used together with the identified material properties in O.1.1 covering the early basic and applied research stage. Additionally, a *patent database analysis* will be conducted to identify potential applications of NOAAs in the development stage. Finally, two case studies will be chosen as examples for the development of the prospective approach to estimate environmental releases of NOAAs.

Objective 0.2

Characterization of the key parameters of environmental releases from NOAA-products Subsequently, in objective O.2 the identified case studies will be analyzed with regard to the key parameters that are relevant for potential environmental releases. In order to analyze these characteristic a technology characterization will be conducted focusing on potential influencing factors of environmental releases. Objective O.2 will identify these factors.

Objective 0.3

Creating an approach for regarding related uncertainties of objective O.2

The early innovation stage of NOAAs is characterized by a high degree of uncertainty and ignorance regarding potential chances and risks. The specified set of criteria in objective O.2 covering key parameters of potential environmental releases has to include respective methods to deal with uncertainty. Objective O.3 will work out an adequate approach to handle these uncertainties for the estimation of environmental releases and concentrations of NOAAs. This approach will use the *scenario methodology* to create corresponding *prospective product application scenarios* for considering uncertainty aspects.

Objective 0.4

Modeling of NOAA material flows throughout the life cycle and prospective estimation of environmental releases and concentrations

The fourth objective O.4 regards the modeling of material flows throughout the life cycle of the selected case studies. The focal points are the environmental release quantities for specific environmental compartments, which are calculated by considering the list of criteria of objective O.3. Finally, releases from product applications into environmental compartments will be calculated. Thereby, the *material flow analysis* is applied that also considers the complete life cycle (production, use, and end-of-life (EOL) of the product application) of the chosen case studies. Finally and based on the modeling results, preliminary environmental concentrations will be determined that will allow drawing conclusions for decision-making.

1.3 Structure of the dissertation

The thesis is structured in eight chapters as it is illustrated in Figure 2. Chapter 1 describes the background and motivation for this thesis and defines the research objectives as well as the applied methods. Chapter 2 lays the theoretical foundation by describing relevant terms and the state-of-the-art for a common understanding. Chapter 3 introduces the applied approach for release and material flow modeling in more detail, whereas chapter 4 develops the methodology of product application scenarios to regard existing uncertainties. Subsequently, chapter 5 deals with the identification of current and potential future product applications. The product applications of AgNPs in textiles and IONPs in magnetic resonance imaging (MRI) are selected as two representative case studies. Chapter 6 and 7 employ the material flow modeling together with the product application scenarios in order to determine potential release points and quantities throughout the life cycle. Finally, chapter 8 summarizes the thesis and gives an outlook for future research needs.

Chapter I
MOTIVATION AND STRUCTUR

Chapter II

RISK ASSESSMENT OF TECHNOLOGICAL INNOVATIONS

Chapter III

APPROACHES FOR RELEASE ESTIMATION AND PRODUCT LIFE CYCLE MODELING

Chapter IV

PRODUCT APPLICATION SCENARIOS FOR PROSPECTIVE ASSESSMENTS

Chapter V

CURRENT AND FUTURE PRODUCT APPLICATIONS

Chapter VI
SILVER NANOPARTICLES IR

Chapter VII
IRON OXIDE NANOPARTICLES

DEVELOPMENT AND MODELING OF PRODUCT LIFE CYCLE SCENARIOS

Chapter VIII
CONCLUSION AND OUTLOOK

Figure 2. Structure of the dissertation

2 Risk assessment of technological innovations

This chapter will introduce relevant terms laying the foundation for the subsequent chapters of this thesis. At first, technological innovation will be defined and described and the relation to the precautionary principle and TA will be shown. Second, technology characterization is shown in the context of TA to systematically analyze technologies in early innovation stages. Third, the components of risk will be introduced together with the risk governance framework. Fourth, the subsequent sections will focus on exposure assessment and its significance in the European chemicals regulation framework. Fifth, the selected materials AgNP and IONP will be characterized with respect to their bulk and nano-specific material properties, which will be used for the bibliometric analysis in chapter 5. Finally, the state-of-the-art and the existing challenges for prospective release and exposure assessment of NOAAs will be summarized.

2.1 Technological innovations

Innovations constitute a key requirement for companies and society to sustain in turbulent contexts. These contexts are characterized by several factors as for example global competition, the need of shorter product life cycles, and the related demand to develop and to innovate (Spur 2006). Innovations promise to ensure the competitiveness and growth of companies and national economies (Hahn 2013). The term "innovation" has several differentiations that were discussed since the 1960s. Even though, this thesis cannot focus on all aspects of the historical scientific discussion, it is important to differentiate between invention and innovation. While the term invention considers new or improved artifacts, innovation also implies its successful introduction to the market that is demanded by society. Thus, not every invention is an innovation as emphasized by Schumpeter (Hahn 2013). The artifacts of innovations comprise products, processes, and services that are related to technical, economical, or societal changes and improvements (Hacklin et al. 2004). Innovations are also differentiated by the degree of improvement and novelty by having an incremental or disruptive character, respectively, which is still controversially discussed (Yu and Hang 2010; Hahn 2013). Disruptive innovations are revolutionary and lead to significant changes, whereas incremental innovations have an evolutionary character with small and continuous improvements (Yu and Hang 2010). However, Hacklin et al. (2004) pointed out that incremental innovations can have a delayed disruptive character. Particularly for converging technologies, incremental innovations can be revealed as disruptive in a cumulatively long-term perspective. Accordingly, criticisms on the rather vague definitions of disruptive and incremental innovations are formulated due to their unclear differentiation.

¹ It has to be noted that since the early 1970th (Club of Rome) the economical concept of growth and its limitations are in critical discussion (cf. Meadows et al. 1972; Meadows et al. 2004).

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