

THE FINNISH ENVIRONMENT 26 | 2010

Environmental aspects related to nanomaterials

A literature survey

**Meri Tuominen
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Helsinki 2010

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Lauout: Ritva Koskinen

ISBN 978-952-11-3813-3 (PDF)

ISSN 1796-1637 (online)

PREFACE

The use of nanomaterials (NM) and nanotechnologies (NT) has been said to revolutionize many industries. The potential benefits of NMs are enormous, and positive impacts are expected from green energy, medicine and diagnostics, optics, electronics, water treatment systems, more durable but lighter material, for example. The increase in applications and utilization of engineered nanomaterials will inevitably lead to the release of these materials into the environment. Therefore, it is essential to understand the fate and possible effects of the NMs on the environment.

Materials in the nanoscale can have different chemical, physical, electrical, and biological characteristics. NMs are not a homogenous group of materials but encompass a large number of various types and forms of materials. Nanotechnology is a relatively new field of science and suffers from gaps in knowledge, definition problems and general lack of data regarding many issues related to environmental safety and life cycle assessment (LCA). All the data gaps lead to difficulties and uncertainties when environmental risk assessment and LCA are being made.

The Life Cycle Assessment Framework and Tools for Finnish Companies –project (FINLCA) started in 2009. The project identifies problems and obstacles in the use of life cycle methods, especially from a corporate perspective, and develops knowledge and know-how on LCA and related methods. A network of research institutes and companies was established to create a national roadmap on how life cycle methods can be promoted in Finnish industries. The project aims at developing life cycle approaches and a framework to help companies determine which are the most feasible methods and best practices. The aim is also to improve the environmental competitiveness of Finnish companies. The research project consists of a theoretical part and several case studies. The theoretical part focuses on recent developments in life cycle methods. Case studies and information from companies is used to support the theoretical findings. FINLCA Work package 2 “Development of methodologies” consists of six sub-items, and this report is the outcome of the sub-item entitled “Environmental effects of nanomaterials”.

The aim of this literature survey was to introduce readers to environmental issues that are important in connection with LCA and the use of engineered nanomaterials.

The Finnish Environment Institute (SYKE) acts as the coordinator of the FINLCA –project, other partners being VTT, Åbo Akademi, The University of Oulu, and The School of Science and Technology, Aalto University. The project has been financed by Tekes, and Finnish Forest Industries, Finnish Plastics Recycling Ltd, Scandinavian Development Association, Outotec Oyj, Metals Industry, Neste Oil Oyj, the Federation of Finnish Technology Industries and Tikkurila Oyj.

The authors gratefully acknowledge the financiers of the project, the two anonymous reviewers of the text, and all the persons who gave useful comments during the work. Special thanks are given to Dr. Markus Sillanpää for his interest and valuable comments.

CONTENTS

Preface	3
Abbreviations	6
Executive summary	7
Yhteenveto	8
1 Introduction	9
2 General properties of nanomaterials	11
2.1 Definitions.....	11
2.2 Classifications of nanomaterials	12
2.2.1 Carbon-based nanomaterials	13
2.2.2 Metal-based nanomaterials	14
2.2.3 Dendrimers	16
2.2.4 Composites.....	16
2.3 Physical characterization	16
2.4 Chemical properties	17
2.5 Manufacturing of nanomaterials	17
2.6 Characterization techniques.....	18
2.7 Potential risks and benefits of nanotechnology	20
3 Environmental fate of nanomaterials	23
3.1 Characteristics affecting behaviour of nanomaterials.....	23
3.2 Emission of nanomaterials	24
3.3 Environmental fate and transport of nanomaterials.....	25
3.4 Monitoring of nanomaterials in the environment.....	29
4 Environmental exposure assessment	30
5 Environmental effects assessment	34
5.1 Environmental effects.....	34
5.2 Health effects	37
6 Risk analysis and oversights	39
6.1 Legislation and recommendations	39
6.2 Risk analysis and classification methods	41
6.3 Risk perception and risk management	42
7 Nanotechnology and nanomaterials in life cycle assessment	44
References	49
Documentation page	54
Kuvailulehti	55
Presentationsblad	56

Abbreviations

ANEC	European consumer voice standardize
BEUC	European Consumers' organization
BSI	British Standards Organization
CNF	Carbon nanofibre
CNT	Carbon nanotube
EC	European Commission
EIO-LCA	Economic Input – Output Life Cycle Assessment
ENM	Engineered Nanomaterial
ISO	International Organization for Standardization
LCA	Life Cycle Assessment
MCDA	Multi- criteria decision analysis
MWCNT	Multi-walled carbon nanotube
NM	Nanomaterial
NNI	National Nanotechnology Initiative
NOM	Natural organic matter
NP	Nanoparticle
OECD	Organization for Economic Co-operation and Development
PEC	Predicted environmental concentration
PNEC	Predicted no effects concentration
QD	Quantum dot
RA	Risk assessment
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
ROS	Reactive oxygen species
RQ	Risk quotient
SCENIHR	Scientific Committee on Emerging and Newly Identified Health Risks
SWCNT	Single-walled carbon nanotube
TOC	Total organic carbon
US EPA	United States environmental protection agency
WFD	Water framework directive
WPMN	Working Party on Manufactured Nanomaterials

Executive summary

Nanotechnology employs the use of materials which have at least one dimension in the nanoscale i.e. between approximately 1-100nm. Materials at that size range exhibit novel chemical and physical properties that are not seen in the larger size scale. Nanotechnology is a relatively new field of science and suffers from gaps in knowledge, definition problems and general lack of data regarding many issues related to its risk and life cycle assessment.

Nanotechnology is an increasing sector in technology, and it has great expectations for the future. It has the potential to revolutionize many industries. Special emphasis has been placed on energy and environmental and medical sectors. The increase in applications and utilization is bound to end up with the release of these materials into the environment and lead to human exposure at some level.

The current legislation controlling chemicals within the European Union is REACH (1907/2006). A problem with this legislation and nanomaterials as a whole relates to the classification of nanomaterials. In the case of carbon nanotubes in particular, small modifications in the size and manufacturing process can result in thousands of variants with diverse features. To tackle this problem several organisations (e.g. OECD; ISO; EC) are working with the issue of finding characterization methods for the use of nanomaterials. Additionally, definitions are varied and a uniform nomenclature is lacking.

Under REACH regulations, nanomaterials have so far been treated as materials in bulk form. Manufacturers have had no legal requirements to disclose the use of nanomaterials in their products. Therefore, information regarding the use of nanomaterials is based on voluntary information, which leads to a situation where consumers and regulatory bodies may not have enough information about the use of nanomaterials and nanotechnology. As a result, information regarding exposure and possible exposure routes is scarce. Studies have shown that nanomaterials are released into the environment as a product of their utilization but what happens to them in the environment is still largely unknown. There are some toxicity and ecotoxicity data concerning nanomaterials but the problem is that they are very inconsistent and fragmentary. There is also debate over what characteristics should be looked for in the evaluation of these toxicity studies. What is common to most studies is that the nanomaterials do cause some kind of biological alterations and responses.

Another problem relating to the environmental impacts of nanomaterials is the methods of the analytical detection of the nanomaterials. There are potentially several characteristics needed for the evaluation of nanomaterials, but no real official guidelines. Sampling and isolation techniques for environmental samples need to be developed so that nanomaterials are conserved until analysis. All the gaps in the data lead to a very difficult scenario when risk assessment and life cycle assessments are being made. The European Commission's Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) recently maintained that risk assessment should be conducted on a case by case basis. The same can be said for life cycle analysis.

The general public knows relatively little about nanotechnology and nanomaterials. The attitudes towards this new technology are being formed at present. The potential of this new technology is enormous but there should be critical evaluation of the potential benefits and hazards related to this field. As a new technology that will allegedly revolutionize the world, facts should be established amidst the hype. It is critical to establish some general guidelines relating to how these new materials should be characterized and find some consensus so that the real impacts of these materials could be evaluated.

Yhteenveto

Nanoteknologia hyödyntää materiaaleja, joilla on vähintään yksi ulottuvuus nanoskaalassa eli alueella 1-100nm. Tämän kokoluokan aineiden kemialliset ja fysikaaliset ominaisuudet poikkeavat oleellisesti niin sanottujen tavanomaisten materiaalien ominaisuuksista. Nanoteknologia on verrattain uutta, nopeasti kehittyvää, ja siihen on asetettu suuria tulevaisuuden toiveita monella teollisuuden ja tieteen alalla. Erityisesti odotetaan ratkaisuja energian tuottamisessa ja talteenotossa, ja vähemmän energiaa kuluttavien tuotteiden valmistamisessa sekä lääketieteen sovelluksissa. Koska nanomateriaaleja käytetään entistä enemmän, on väistämätöntä, että niitä jossain vaiheessa joutuu myös ympäristöön. Teknologian nopeasti kehittyessä on materiaalien ja tuotteiden turvallisuuden arviointi kuitenkin jäänyt vähemmälle huomiolle. Niinpä turvallisuuden arviointiin samoin kuin elinkaarianalyysien tekemiseen tarvittavasta perustiedosta on suuri puute.

Euroopan unionissa kemikaalien turvallisuudesta säädetään REACH-asetuksella (1907/2006). Nanomateriaaleja koskeva ohjeistus on kuitenkin vasta kehitteillä, samoin luokittelua koskevat periaatteet. Esimerkiksi hiilinanoputket ovat kemialliselta koostumukseltaan samaa ainetta, mutta muuntelemalla kokoa tai valmistusmenetelmää voidaan valmistaa tuhansia erilaisia materiaaleja, joilla on keskenään erilaisia ominaisuuksia. Monet kansainväliset organisaatiot, kuten OECD, ISO, ja EC, ovat laatimassa ohjeita nanomateriaalien määrittelyä ja karakterisointimenetelmistä.

Erityisesti nanomateriaalien turvallisuutta koskevaa sääntelyä ei ole vielä, vaikka tuotteita on ollut markkinoilla jo useita vuosia. Koska pakotteita ei ole ollut, on sekä kuluttajien että viranomaisten tiedonsaanti teollisuuden vapaaehtoisen tiedottamisen varassa. Osittain tästäkin johtuen ei ole mahdollista tehdä luotettavia arvioita ihmisten tai ympäristön altistumisesta nanomateriaaleille. Tutkimuksissa on kyetty osoittamaan, että kuluttajatuotteiden käytön aikana vapautuu nanomateriaaleja. Varsin hankalaa on tutkia nanomateriaalien käyttäytymistä ja muuntumista ympäristössä, mistä johtuen näitä ilmiöitä ei juuri tunneta. Joitakin selviä haittavaikutuksia on havaittu testauksissa, mutta yhtenäisten menetelmien puuttuessa, tieto on hajanaista ja vertailujen tekeminen on mahdotonta.

Ympäristöriskien arvioinnin kannalta olisi tärkeätä saada luotettavaa tietoa pitoisuuksista, joille eliöt altistuvat elinympäristössään. Tätä tietoa ei ole vielä riittävästi. Vain joistakin harvoista aineista on tehty arvioita mahdollisista ympäristöpitoisuuksista, mutta tulosten yleistämiseen suhtaudutaan varoen. Euroopan komission tieteellinen komitea (SCENIHR) on todennut viime kannanotossaan vuonna 2009, että ympäristöriskien arviointi on tehtävä kunkin aineen kohdalla erikseen. Elinkaariarvioiden suhteen tilanne on samanlainen, eikä ole mahdollista yleistää jotakin tiettyä nanomateriaalia koskevaa tulosta toisiin materiaaleihin.

Kuluttajien tiedot nanoteknologiasta ja -materiaaleista ovat toistaiseksi melko vähäiset. Nanoteknologian käytön lisääntyessä myös tiedontarve kasvaa. Mielenkiintoisten muodostamiseksi ihmiset tarvitsevat luotettavaa tietoa sekä hyödyistä että mahdollisista haitoista. On tärkeätä löytää yhteiset menettelytavat nanomateriaalien ominaisuuksien ilmaisemiseksi ja tuotteiden koko elinkaaren aikaisten ympäristövaikutusten arvioimiseksi.

1 Introduction

Nanomaterials (NM) are being used in an ever-increasing number of products and applications. Nanotechnology is rapidly developing, which leads to the need for safety assessment with regard to both human health and environmental impacts. Nanoscale materials can behave differently from larger materials, even if the basic material is the same. Materials in the nanoscale can have different chemical, physical, electrical and biological characteristics. For example, nanosized aluminium can be used as material for bombs as it is highly explosive. The nanotechnology industry is experiencing challenges in both environmental effects assessment and therefore risk assessment. There are multiple characteristics that influence the toxicity. These novel materials can also be designed to change their characteristics under specified circumstances. These changes can be either temporal or irreversible. The overwhelming number of characteristics and possible interactions generates a general lack of risk assessment methods. The number of nanomaterials is great and increasing.

Nanotechnology is the study and control of material which has one or more dimensions in the nanoscale i.e. in the size range between approximately 1-100nm. Nanotechnology is a very multifaceted technology ranging from the extensions of conventional physics to the new approaches and the developing of new materials and devices that have at least one dimension in the nanoscale. Nanotechnology also deals with the investigation of whether material in the nanoscale can be directly controlled.

Materials in the nanoscale have quantum size effects which lead to new physical properties. These novel properties are at the heart of nanotechnology. The nanoscale of 1-100nm is what is called the quantum realm, where quantum mechanics become important. Quantum mechanics is a set of scientific principles that predominate and describe the behaviour of matter at the atomic levels. Classical mechanics cannot describe the working of an atom for example. Within the nanoscale materials can have molecular organizations and properties different from the same chemical substance in a larger size. These properties have led to an accelerated growth in the production of manufactured nanomaterials and in the applications in which they can be used.

The global market for nanotechnology is increasing rapidly. According to the results of Nanotechnology in The Finnish Industry 2008 Survey (Kajander and Koponen, 2008) the Finnish nanotechnology sector size in 2008 was 317 million euros, employing approximately 2900 professionals. In revenues this sector has increased 25% from 2006. By 2013 the sector is estimated to reach 1.3 billion euro and will employ 11 000 – 12 000 professionals. On a global scale, Lux Research (2008) predicts that by 2015 nano will be incorporated in \$3.1 trillion of manufactured goods and will account for 11 percent of manufacturing jobs worldwide (Lux Research, 2006.)

Nanotechnology is said to be the next scientific revolution. The potential benefits are enormous and the industry holds great expectations. Positive impacts are expected from green energy, treatment and remediation of pollutants and more durable and yet lighter materials. Applications lie in biomedicine, optics, electronics, catalysts and in material science. The rapid increase of the industry has raised questions regarding the

health and safety of the industry. Discharges of nanomaterials occur, and nanomaterials appearing in consumer products are a cause of debate. Consumer organizations have expressed their concern about consumer safety regarding products containing nanomaterials. For example, consumer organisations such as BEUC and ANEC have stated that previous assessments on a material cannot reflect the safety of the same substance in nanosize (BEUC and ANEC, 2009).

Nanomaterials are not a homogenous group of materials but encompass a magnitude of various types and forms of materials. One of several problems regarding nanomaterials is the difficulties of classifying them and their various forms. Another issue with the environmental assessment of the NMs is the general lack of information regarding them and the analytical difficulties in trying to characterize them. The outcome is that information regarding exposure and potential routes and exposures is scarce. Many NMs have been shown to cause biological alterations and responses in laboratory conditions. Lack of exposure data causes difficulties for the risk assessment and life cycle assessment of nanomaterials. Some LCA methods have been applied for nanomaterials but information for a good full LCA is not currently available.

For the future of nanotechnology M.C. Roco, the driving force behind the U.S National Nanotechnology Initiative (NNI), has developed a typology that identifies four generations of nanotechnologies: passive nanostructures, active nanostructures, systems of nanostructures and molecular nanostructures. Passive nanotechnology most often encompasses the adding of nanomaterials to another material to increase functionality or value. Second generation nanotechnology, active nanostructures, typically involves nanometer-scale structures that change their behaviour in response to changes in the environment. Examples include new transistors and other electrical components, and targeted drugs. The third and fourth generation nanotechnologies are a bit more abstract. There are difficulties distinguishing between the last few generations, even amongst experts. The third generation nanotechnologies encompasses systems of nanosystems, and self-assembly and artificial tissues. The fourth generation technologies will bring heterogenous molecular nanosystems, designed macromolecules, and the interface between human and machines at the tissue and nervous system level (Roco, 2004 and 2007). Currently we are between the second generation and the third.

The idea of generations in nanotechnologies has been considered by others as well. The general features of these generations are that the first stage is the use of passive nanotechnology. This stage will be followed by technology that is responsive to a change in its environment. Following generations will include the miniaturizing of current technologies and the last stage will include the combination of nanotechnology with biotic tissues at some level (Davies, 2009).

It is obvious that the environmental safety of nanomaterials needs the expert co-operation of different sectors of society: natural science (physicists, chemists, material scientist, biologists, and toxicologist) as well as risk assessors and regulators and policy makers (Handy *et al.*, 2008a). This report will focus on the nanomaterials which are manufactured thus excluding the naturally occurring background nanomaterials and those unintentionally produced like particles in exhaust gas from vehicles. This report is a literature survey on the current knowledge of environmental effects assessment of nanomaterials, and will focus on the following topics: possible exposure scenarios and routes of nanomaterials, the known adverse effects of nanomaterials on various organisms, and risk assessment. Life cycle assessment for nanotechnology and nanomaterials will be (briefly) discussed in the last section.

2 General properties of nanomaterials

The first scientific paper which contained the word “nanotechnology” was from the title from a 1974 paper published by Norio Taniguchi from the University of Tokyo (Taniguchi, 1974). Nevertheless, the word did not become popular until the late 1980s (Nanotechnology facts and figures, 2010). The field of nanotechnology was born with the manufacturing of the first carbon-based nanomaterial C_{60} . The discovery of the fullerenes resulted in the awarding of the Nobel Prize for Chemistry to Curl, Kroto and Smalley in 1996. However, on a conceptual level the first ideas were laid out already in 1959. Physicist Richard Feynman gave a lecture by the title “There’s Plenty of Room at the Bottom” where he considered and explored the possibility of the manipulation of individual atoms and molecules (The Royal Society and The Royal Academy of Engineering, 2004).

As a relatively new and dynamic industry the development of definitions and concepts by different institutions and organizations has led to inconsistencies and confusions with the terms. There is no clear consensus about the definitions and classification systems relating to nanomaterials. Generally materials can be divided into how many dimensions they have in the nanoscale. Nanomaterials have one dimension less than 100nm, and nanoparticles have three dimensions less than 100nm. (SCENIHR, 2007). The following section will go through a few chosen definitions relating to this field.

2.1

Definitions

Nanotechnology

Nano- is the S.I prefix for 10^{-9} which written in full is 0,000 000 001. A spherical nanoparticle called a fullerene, consisting of 60 carbon atoms has a diameter of 1nm (nanometer). When thinking about scaling, a fullerene is to a soccer ball what the soccer ball is to the planet Earth. The Finnish Tekes programme FinNano refers to nanotechnology as

Nanotechnology refers to science and technology operating at the level of atoms and molecules, i.e., in the nano size class, as well as scientific phenomena and new characteristics which one can learn to understand when operating at this level. These characteristics can then be observed and utilised in the micro- and macro size class.¹

¹ Tekes, FinNano, nanotechnology – name and definition: [<http://akseli.tekes.fi/opencms/opencms/OhjelmaPortaali/ohjelmat/NANO/en/nanodefinition.html>]

The scientific aspect can be excluded from the definition as does The Royal Society and The Royal Academy of Engineering (2004) report.

Nanotechnologies are the design, characterisation, production and application of structures, devices and systems by controlling shape and size at nanometrescale.²

A definition can also include both the size and the properties such as in the U.S National Nanotechnology Initiative (NNI) definition for nanotechnology:

Nanotechnology is the understanding and control of matter at dimensions between approximately 1 and 100 nanometers, where unique phenomena enable novel applications. Encompassing nanoscale science, engineering, and technology, nanotechnology involves imaging, measuring, modelling, and manipulating matter at this length scale.³

The International Organization for standardization has produced the following terminology and definitions for nano-objects (ISO/TS 27687: 2008):

Nanoscale	Size range from approximately 1nm-100nm
nano-object	material with one, two or three external dimension in the nanoscale
nanoparticle	nano-object with all three external dimensions in the nanoscale
nanoplate	nano-object with one external dimension in the nanoscale and two significantly larger
nanofibre	nano-object with two similar external dimensions in the nanoscale and the third dimension significantly larger
nanotube	hollow nanofibre
nanorod	solid nanowire
nanowire	electrically conducting or semi-conducting nanofibre
quantum dot	crystalline nanoparticle that exhibits size-dependant properties due to quantum confinement effects on the electronic states

The definitions above vary and encompass different aspects of nanomaterials. However, it is generally agreed that the nanoscale is between approximately 1-100nm, and materials can be classified according to how many dimensions they have in that size range. Several institutions include the novel properties and the utilization of these properties into their nanotechnology definition. For this report the term nanomaterials (NM) will be used to encompass all various kinds of materials and objects that have at least one dimension within the nanoscale. Nanoparticles (NP) include those NMs, which have all three dimensions within the nanoscale.

2.2

Classifications of nanomaterials

The classification of nanomaterials is not a straightforward issue and, as in the case of the definitions for nanotechnology, a clear consensus is missing. NMs can be classified according to their chemical and physical qualities. However, different structural types with various sizes produced in several manufacturing processes, combined with different surface coatings, can complicate the classification. In the case of single-walled carbon nanotubes, the outcome can be up to 50 000 variants of essentially of the same carbon nanotube. These variants are not expected to behave similarly (Schmidt, 2007).

² The Royal Society and the Royal Academy of Engineering, (2004).

³ National Nanotechnology Initiative: What is nanotechnology [http://www.nano.gov/html/facts/whatIsNano.html]

For (eco)toxicological purposes nanomaterials could be classified on the basis of the mechanism of toxicity. However, making such classification when there is lack of data is not worthwhile. NMs can also be classified depending on whether they are natural or engineered or even according to their point of origin (Nowack and Bucheli, 2007); they can even be classified for a specific purpose such as risk-based classification (Tervonen *et al.*, 2009).

In this report the following classification of nanomaterials is employed. NMs can be produced either via natural or anthropogenic processes. NMs produced naturally can be divided according to the method of formation into biogenic, geogenic, atmospheric and pyrogenic (Nowack and Bucheli, 2007). Anthropogenic NMs can be divided into intentionally engineered NMs and NMs produced unintentionally (Figure 1). Unintentional NMs are produced for example as a by-product from combustion processes (Nowack and Bucheli, 2007). This report will only look at the intentionally produced engineered nanomaterials. They are further classified in a similar way to what, for example, the US EPA uses. The intentionally produced nanomaterials can be divided into five categories: carbon-based materials, metal-based materials, dendrimers, polymeric particles and composites.

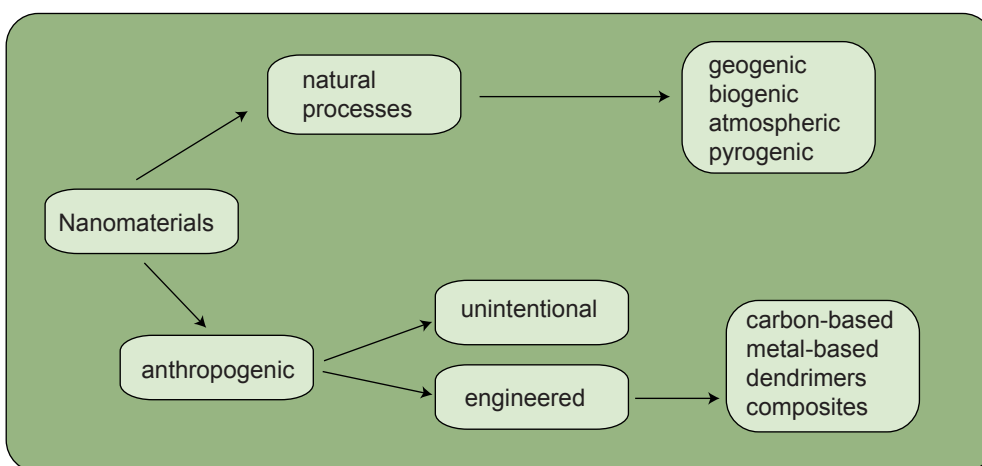


Figure 1. The classification of nanomaterials according to the method of production.

2.2.1

Carbon-based nanomaterials

Fullerenes

Fullerenes are carbon molecules, in the form of a hollow sphere, ellipsoid or tube. The C₆₀ fullerene is the best known fullerene and the most stable. It is also known as the buckminsterfullerene or buckyball. The molecular structure consists of a hollow sphere where carbon atoms are positioned at the vertices of a regular truncated icosahedrons structure (Kroto *et al*, 1985). Fullerenes are also found with 70 and 76 carbon atoms (Ju-Nam and Lead, 2008).



Fullerene C60

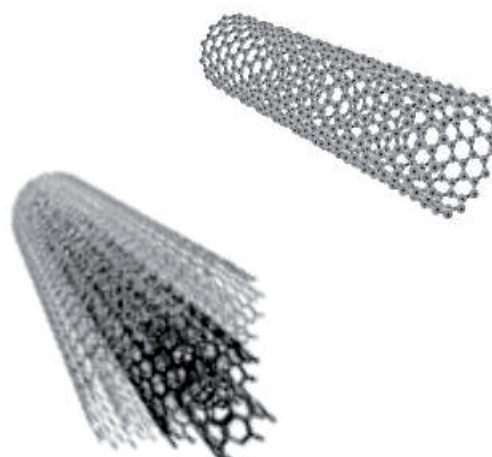
Carbon Nanotubes (CNT)

Apart from the spherical allotropes, fullerenes can also be constructed in cylindrical forms known as carbon nanotubes (CNTs). These fullerene derivatives were first pro-

duced in 1991 using arc-discharge evaporation (Iijima, 1991). They can be synthesized under defined conditions that can control the size and diameter of the tubes either from graphite using arc discharge or laser ablation, or from carbon-containing gas using chemical vapour deposition (Klaine *et al.*, 2008).

The interest in production, research and development of CNTs originate from their unique properties. These include high tensile strength, high electric and thermal conductivity, lightweight, high surface area to mass, advantages in hydrogen storing and catalyzing. Their tensile strength is 100 times greater than that of steel, while weighing only a sixth of steel. Their thermal conductivity exceeds that of diamonds (Lekas, 2005). CNTs are used in plastics, catalysts, battery and fuel cell electrodes, supercapacitors, water purification systems, orthopedic implants, conductive coatings, adhesives and composites, sensors, and components in the electronics, aircraft, aerospace, and automotive industries (Klaine *et al.*, 2008).

CNTs have two main forms: the single walled (SWCNT) and the multi walled (MWCNT). The first is a single layer graphene sheet rolled up in a cylindrical shape, with a diameter approximately of 1 nm and of varying length. The latter consists of two or more concentric layers with various lengths and diameter (Cao, 2004). CNTs are identified as the most commercially significant example of nanomaterials with two dimensions (BSI, 2007).



Carbon nanotubes: single walled (right) and multiwalled (left) structure.

Carbon Black

Natural and anthropogenic combustion processes emit a variety of particles. Of these the so-called “ultra fine” particles are compatible with nanoparticle definitions. Generally the term “soot” refers to the nanoparticle fraction of the black carbon (BC) continuum. These are produced by incomplete combustion of fossil fuels and are emitted into the atmosphere. Carbon black is an industrial use of soot used in applications such as fillers in rubber compounds, primarily in car tyres. The particle size for carbon black ranges between 20-300nm (Nowack and Bucheli, 2007).

2.2.2

Metal-based nanomaterials

Metal Oxide

Metal oxide nanoparticles have been widely used in various applications. Zinc oxide (ZnO) and titanium dioxide (TiO₂) are used in applications such as sunscreens,

cosmetics and bottle coatings because of their UV blocking ability and the visible transparency of nanoparticulate forms (Sass, 2007). Zinc oxide is a direct band gap semiconductor, which has potentially a wide range of applications (Ju-Nam and Lead, 2008).

Oxide-based nanotubes, for example titanium oxide, are also investigated for applications in catalysis, photo-catalysis, and energy storage. Shortly after the finding of CNTs, inorganic nanotubes and inorganic fullerene-like materials were discovered. These have excellent lubricating properties, resistance to shockwave impact, catalytic reactivity, and high capacity for lithium and hydrogen storage, which suggest a range of promising applications (The Royal Society and The Royal Academy of Engineering, 2004).

Cerium dioxide (CeO_2) has been investigated for its unique properties and multiple applications such as acting as three-way catalysts in vehicle emission-control systems. The most advanced properties are shown at a nanoparticulate size of less than 10nm. These exquisite properties are size dependant and would show significant quantum size effects. Because of this the development of methodologies that can get monodispersed ceria nanoparticles with well-controlled sizes is the main focus of the industry (Xu *et al.*, 2008). CeO_2 has been used as a fuel additive for increasing fuel efficiency. This is a potential concern in how diesel exhausts can disperse these nanoparticles widely in the environment (Ju-Nam and Lead, 2008).

Metal oxides can be used as the cathode in Li-ion batteries. One of the most successful applications has been the commercialization of batteries with nanometer-sized lithium iron phosphate (LiFePO_4). This cathode improves the electrical conductivity as well as facilitates the transport of lithium-ions into and out of the domains. Other potential nanoscale materials for Li-ion batteries include V_2O_5 , MnO_2 , Co_3O_4 and CuV_2O_6 (Nanda, 2008).

Elemental metal

By far the greatest number of consumer applications which use nanomaterials involve nanosilver. Consumer products include wound dressings, socks and other textiles, air filters, washing machines, and baby products. Silver can be either metallic silver NPs or electrochemically generated ionic silver. The antibacterial activity of silver is related to the toxicity of the dissolved cation more than to the high surface to area ratio (Klaine *et al.*, 2008). Because of their toxicity and the very potential release to the environment these are perhaps one of the most worrying NPs (Ju-Nam and Lead, 2008). Elemental gold has been used especially in medical applications. New applications with nanoparticulate gold include its use in electronics, films and as catalysts (Ju-Nam and Lead, 2008).

Zero-valent metals are typically made by the reduction of solutions of metal salts. Nanoparticulate zero-valent iron has been used for the remediation of contaminated groundwater. Research has shown that they are very effective in the transformation and detoxifying of a variety of common contaminants. These environmental contaminants include chlorinated organic solvents, organochlorine pesticides, PCBs and the dechlorination of chlorinated ethenes (Lien and Zhang, 2001; Zhang, 2003).

Quantum dots

Quantum dots or semiconductor dots based on e.g. CdS, CdSe, CdTe, InP and ZnSe, have a reactive core made up of metals or semiconductors surrounded by a protective shell (Ju-Nam and Lead, 2008; Klaine *et al.*, 2008). Quantum dots are assemblies of metal, metalloid or metal oxide with unique electronic, optical, magnetic and catalytic properties. They are sometimes referred to as artificial atoms

and are not considered as solid structure or a single molecular entity. They are most often manufactured via wet chemical colloid processes. Most research is involved in semiconductor quantum dots. Their quantum effects include the fact that the light they emit can be adjusted to the desired wavelength by altering the particle size by carefully controlling the growth and nucleation processes (Aitken *et al.*, 2006). They have roused interest in their potential applications, but raise concerns as they are inherently toxic.

2.2.3

Dendrimers

Dendrimers are multifunctional polymers whose size, topology, flexibility and molecular weight can be controlled. They can be used for many applications in a variety of fields from biology, material science, and surface modification to enantio selective catalysis. Examples include macrocapsules, nanolatex, coloured glasses, DNA transfecting agents and therapeutic agents for drug delivery (Klaine *et al.*, 2008).

2.2.4

Composites

Composites are materials that combine one or more separate components of nanomaterials, and are designed to display as a whole the best properties of each of the components (The Royal Society and The Royal Academy of Engineering, 2004). A Finnish innovation is a carbon nanotube enhanced epoxy, Hybtonite®. It is used for example in windmill blades and increases their performance due to low blade weight of only 50-60% of the weight of traditional blades (Kajander and Koponen, 2008). The composite has also been used in sports equipment. Nanoclays are used as additives to enhance the mechanical, thermal, barrier or flame-retardant properties of various products and materials (EPA, 2007)

2.3

Physical characterization

The principle features that are at the foundation of the major differences between the properties at the nanoscale compared to larger materials are the increased surface to volume ratio and quantum effects. These can cause a change or enhance, for example, the strength, reactivity and electrical characteristics of properties (The Royal Society and The Royal Academy of Engineering, 2004). Considering the surface area, when the particle size is 30 nm the particle has 5% of atoms on its surface, 10 nm has 25% of its atom and at 3 nm 50% of its atoms on the surface (The Royal Society and The Royal Academy of Engineering, 2004). As the particle size decreases the overall surface area increases, until reaching a small enough size where the surface molecules dominate (FAO/WHO, 2009). Growth and catalytic chemical reactions occur at surfaces, which means that a given mass of nanoparticle form will be much more reactive than the same mass made up of larger particles (The Royal Society and The Royal Academy of Engineering, 2004).

Quantum effects can affect the optical, electrical and magnetic behaviour of materials (The Royal Society and The Royal Academy of Engineering, 2004). This is especially shown in the quantum dots, which are made of semiconductor material at the core and high band gap materials as a shell. When the diameter of the core decreases it becomes so small that quantum mechanics step in and electron energy levels are not continuous but discrete. These discrete energy levels cause a situation

called quantum confinement, and the semiconductor, instead of behaving like bulk material, is called a quantum dot. The situation has large impacts on the absorptive and emissive behaviour of the semiconductor material (Evident Technologies, 2008). The nanosizing of bioactive substances is also claimed to give greater uptake, absorption and bioavailability within the body compared to the larger equivalents (FAO/WHO, 2009). This will have implications for both applications and also for environmental and health effects.

2.4

Chemical properties

Nanoparticles exhibit a range of qualities and features that are not present in the larger, molecular or atomical scale. The proportion of atoms on the surface versus the interior is higher for nanomaterials. One of the most important features is this high surface per unit mass, resulting in high surface energy and reactivity. If the surface is not protected by other molecules, so-called capping agents, interactions will occur between molecules that will lead to the reduction of this surface energy. Most often these interactions lead to aggregation (Ju-Nam and Lead, 2008). These capping agents generally work by either charge or steric stabilization. Capping agents are integral components of most nanoparticles, and chemistry needs to be taken into account when describing the nanomaterials.

At the lower end of the nanoscale (1-10nm), unusual chemical and physical properties occur. The quantum effects take place and the NPs exhibit properties that are different from the molecular scale. The unique reactivity is associated with particles with diameters less than 10 nm. For example, Mn^{2+} oxidation rates were two orders faster with hemanite particles with 7-nm diameter on average compared to particles with a diameter of 37nm on average even when the rate was normalized to surface area. (Madden *et al.*, 2006, Madden and Hochella, 2005).

The special properties of the engineered NPs raise concern as normal assumptions of chemical reactivity and behaviour may not apply with regard to NPs. The special features can also lead to the exhibition of toxic effects that have not been seen before.

2.5

Manufacturing of nanomaterials

Nanomaterials can be manufactured via two strategies (Figure 2). One is the synthetic route using a bottom up strategy. They can also be formed from larger macromolecules via various techniques. Bottom up strategies are more common in the synthesis of NMs. NPs are formed by homogenous nucleation from liquid or vapour, or by heterogenous nucleation on substances. NMs can also be synthesized by confining chemical reaction in a small place (Gao, 2004).

In the manufacturing of nanomaterial there are several factors needed to be considered. The manufactured NMs should be ideally identical in particle size, shape, morphology, chemical composition and dispersed individually so no agglomerations occur (Gao, 2004). These are the components that are difficult to control.

The more convenient method of producing nanoparticles on a commercial scale is the bottom up approach. In this the nanoparticles are "grown" from simple molecules. The size of the particle can be controlled in various ways: limiting concentration, functionalizing the surface of the particle, or using a micelle to template the growth. This approach relies on the principle of supersaturation to control particle size (Christian *et al.*, 2008).

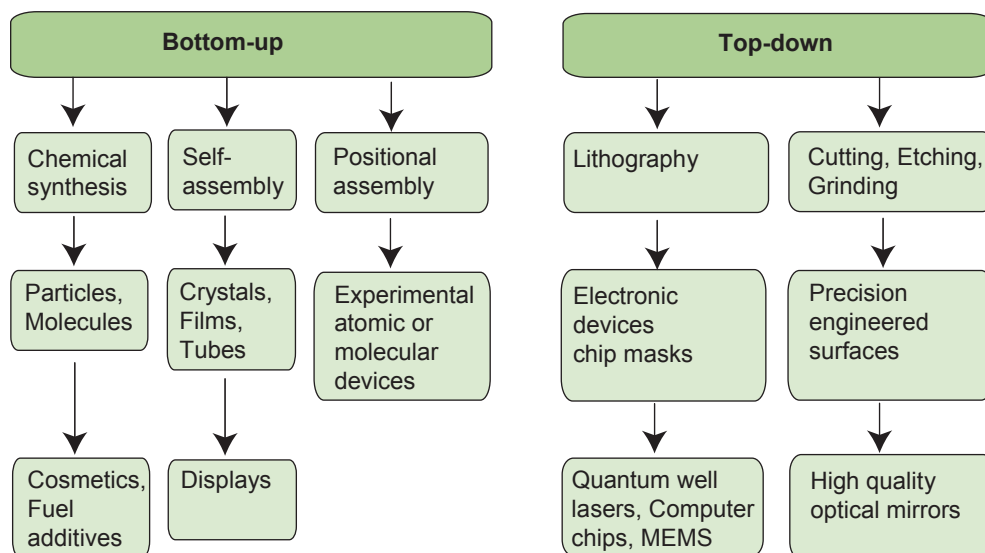


Figure 2. The mechanisms of manufacturing of nanomaterials using bottom-up and top-down techniques (The Royal Society and The Royal Academy of Engineering, 2004). MEMS= mechanical moving devices.

For a reliable environmental exposure assessment to be made estimations of the use and production of NMs should be presented. In the current situation such figures are unattainable Schmidt *et al.*, (2008) produced such numbers for Switzerland via questionnaires to companies. In April of 2008 the European Parliament called upon the Commission to review all relevant legislation within two years regarding the NMs to ensure the safety of applications and to compile an inventory by June 2011 of the different types and uses of NMs on the European market (INI/2008/2208).

Currently the majority of manufacturing and use of NMs occurs in the United States (49%), Europe is second with a 30% global share. Within Europe one-third is located in the United Kingdom (Aitken *et al.*, 2006).

2.6

Characterization techniques

To be able to study the impacts of the various properties of nanomaterials, it is essential that there are analytical methods for quantifying the concentrations and changes. To be able to quantify the concentrations and changes in the physical form of both natural and manufactured NPs a number of parameters need to be measured. Besides the normal chemical characteristics size, size distribution, specific surface area and shape should be described (Ju-Nam and Lead, 2008). As with the classification of NMs the characterization of NMs is not a straightforward issue, and there is debate over which characteristics and which methods should be used.

In order to assess the environmental effects of various NMs it is of fundamental importance to have analytical methods that are capable of identifying the material in question. Before the effects, fate and an environmental exposure assessment can be established, it is essential that the proper analytical methods for the determination of the concentration, particle size, and other properties are done. When TiO₂, ZnO and quantum dots were analyzed for particle size by different techniques in well defined conditions it was concluded that the size could not be determined explicitly (Domingos *et al.*, 2009b). Therefore it is also essential that the characterization methods are known. The organization for Economic Co-operation and Development (OECD) has a working party gathering information on a set of reference materials to support the

ecotoxicological studies of NMs (OECD/WPMN, 2008). Table 1 demonstrates some of the analytical methods commonly used in the characterization of NMs and their abbreviations and parameters looked at.

The rapid development of the nanotechnology industry has outpaced the ability of the scientific community's ability to monitor their presence. There is a lack of technical requirements for the detection and monitoring of nanoparticles. There is plenty of discussion about the characterization of nanomaterials in scientific literature but very little actual information about it. There is debate over what factors are considered key factors.

A review of published literature that consisted of 482 toxicity studies showed that while information on the chemical composition was given for all 965 NMs, only 66% of the studies had information about particle size and 16% presented measurements of surface areas. (Hansen *et al.*, 2007). The results from the NanoImpactNet (www.nanoimpactnet.eu), a multidisciplinary European network of experts in the area of nanosciences, a two-day workshop with 42 researches studying the strategies for the NM exposure, hazard and risk are reviewed in Stone *et al.*, (2009). The article highlights some of the key thoughts that resulted from the workshop. Three questions were discussed in the workshop. The first question regarded the main properties characterized for NMs used in environmental and ecotoxicological studies. All groups formed by the participants agreed upon six main priorities which are required for studies. These are aggregation/agglomeration/dispersability, size, dissolution, surface area, surface charge and surface composition/surface chemistry. These features were decided by acknowledging the importance of composition information. The workshop also concluded that the characterization should be done in the test system itself.

The second question addressed the development of reference materials for the use of ecotoxicological and environmental tests. The development of test materials was regarded as a priority, and in this context the materials regarded as being most useful were TiO₂, polystyrene beads labelled with fluorescent dyes, and Ag. The third question addressed was about the possibility of grouping different NMs into groups for consideration in environmental studies. For this question no consensus was reached.

In the question regarding the appropriate characterization methods, several issues were raised during the workshop. Firstly, trying to obtain a list of a few most important features, there is the possibility of overlooking characteristics that may become important in evaluating the risk of NMs. On the other hand, the demand for so much characterization can lead to a "paralysis of analysis" scenario where the relevant information is overlooked (Hansen *et al.*, 2008b in Stone *et al.*, 2009). It was concluded the field of nanoecotoxicology is in its infancy. The need to expand the database on the fate, exposure and effects with high quality studies is essential. These studies may however not always have a complete list of characteristics available.

At the moment there are no techniques that enable the measuring of NMs directly from the environment. Therefore sampling is an essential part in the evaluation of the amounts of engineered NPs from the environment. The characterization of NMs from environmental samples has proven to be a great challenge. As said in 2.3 and 2.4 there are several physical and chemical properties that affect their behaviour in the environment. Usually one analytical method can only be used to measure one characteristic, and therefore several different analytical methods should be applied to gather data for several characteristics. The characterization of NPs in biological matrices is more complex from an analytical point of view. In particular, there is a lack of methods for *in situ* characterization and for the detection of nanodelivery systems (FAO/WHO, 2009).

Table I. Analytical methods used for the characterization of nanomaterials. Collected from Wigginton, *et al.*, 2007; Hassellöv *et al.*, 2008; Hoyt, 2009; Tiede *et al.*, 2009; Sillanpää *et al.*, 2010.

Characteristic	Analytical method		Parameters looked at
Particle imaging			
	TEM*	Transmission electron microscopy	size, shape; state of aggregation,
	SEM*	Scanning electron microscopy	size, shape, state of aggregation topography, elemental composition in combination with other techniques
	ESEM	Environmental SEM	as SEM above
	STM	Scanning tunnel microscopy	chemical composition (some cases)
	AFM	Atomic force microscopy	size, shape, morphology, state of aggregation
Physical properties			
	DLS	Dynamic light scatter size of particle	particle size distribution
		Filtration Centrifugation	size fractionation
	FCS	Fluorescence correlation spectroscopy	size distribution
	FFF	Field flow fractionation	particle size distribution
	XRD*	X-ray diffraction	crystal structure, size
	BET*	Brunauer Emmett Teller method	surface area per unit mass and porosity
	SEC	size exclusion chromatography	size distribution
Chemical composition			
	ICP-MS	Inductively coupled - mass spectrometry	element composition, mass
	ICP-OES	Inductively coupled -optic emission spectrometry	element composition, mass
	EDS*	X-ray energy dispersive spectroscopy	element composition
	LC-MS	Liquid chromatography – mass spectrometry	fullerene structure
*) technique can be applied only for dried samples			

2.7

Potential risks and benefits of nanotechnology

It is said that nanotechnology is going to change the world and the way we live. It will create new scientific applications which are smaller, faster, stronger, safer and more reliable. A potential application lies in cheap and clean energy to meet the world's energy demand. It will provide affordable clean water through water purification. In medicine small nanodevices could be used to repair human tissue and enhance drug delivery. The technology can also be used in pollution prevention and in materials science in the development of new improved materials that are stronger and yet lighter, and more durable.

The German Federal Environment Agency, Umweltbundesamt, (UBA) asserted that nanotechnology will greatly influence industry and society in the coming decades. Nanotechnology has the potential to fundamentally change whole technological fields. In the opinion of many experts nanotechnology not only has the potential for economic development but also improvements are expected in environmental and health protection, for example an increase in resource efficiency (Becker *et al.*, 2009).

Potential benefits from the use of nanotechnologies is expected from the saving of raw materials due to miniaturization, the saving of energy due to weight reduction or functional optimization, improving the cleaning performance of filter systems, reducing or replacing hazardous substances, protecting the environment with the use of nanoscale catalysts, and being applied in health protection (Becker *et al.*, 2009). Nanomaterials will also be employed in food-packaging materials, as food additives, modifying texture and taste for example, in nutrients, and in agrochemicals where they will provide innovative routes to deliver pesticides to plants. The potential of reduction of use of some agrochemicals and the better ability to control the application and dosage of active ingredients in the field is a driving force for the industry (FAO/WHO, 2009). Food products made with nanotechnology in the future will have less salt, fat and sugar content. Nanofood with new flavours and texture and high vitamin and nutrient contents can improve the health of humans. However there is concern that nanofood might be full of additives. There is no equipment to trace the nano-additives in food (Kukkonen, 2010).

The Project on Emerging Nanotechnologies (<http://www.nanotechproject.org>) was established in 2005 as partnership between the Woodrow Wilson International Center for Scholars and the Pew Charitable Trusts. The project holds an online inventory of consumer products that are based on nanotechnology. The first inventory was released in March of 2006. Since the first release to the latest of August 2009, the number of consumer products has risen 379%, from 212 to 1015. Within the product categories the greatest increase has occurred in products related to health and fitness and within this subcategory the greatest three products are related to personal care, clothing, and cosmetics. Nanomaterials are applied for example in sunscreens and cosmetics; they are utilized in wound dressings and enhanced textiles. Composites are used for enhancing conductivity in fuel cells and batteries, and they also serve as catalysts. They are also used in medicine and diagnostics, and several internal circuit applications. They are already been used for the remediation of groundwater from pollutants such as chlorinated hydrocarbons (The Royal Society and The Royal Academy of Engineering, 2004). The field of nanotechnology is relatively new and the list of potential applications is exhaustive. Table 2 illustrates applications where NMs are used and the function of the NM in the application.

Table 2. List of some nanomaterials used in applications and their functions. (Zhang, 2003; The Royal Society and The Royal Academy of Engineering, 2004; EPA, 2007; Nowack and Bucheli, 2007; Sass, 2007; Nanda, 2008; Klaine et al, 2008; FAO/WHO, 2009; Gao and Xu, 2009)

NM	Application	Functions
Ag	textiles, wound dressings	antimicrobial purposes
Ag	food contact surfaces, packing material	antimicrobial, antiodourant
Au	medicine	markers, rapid biological tests
Carbon Black	rubbers, pigments	filler
CeO ₂	emission control system	catalyst
CeO ₂	fuel additive	optimization of combustion
CNTs	flat screens	sensorics, electronics
CNTs	polymer composites	control/enhance conductivity
CNTs	composites	enhance mechanical properties
CNTs	components	electronics, aircraft, automobile industries
Dendrimers	drug delivery	nanoscale carrier
Fe ⁰	remediation of polluted waters	transformation of toxicants
Fullerenes	solar cells	higher power conversion efficiency
Li	batteries	improve electrical conductivity
Nanoclays	additive	enhance mechanical, thermal barrier, flame retardant properties
Polystyrene	medicine, diagnostics	carrier
Quantum dots	information technology molecular biology	semiconductor probes for imaging and sensing
Se, Ca, Fe	green tea, other food matter	health supplement (claimed)
TiO ₂	water treatment applications	photocatalyst
TiO ₂	windows	self-clean
ZnO and TiO ₂	cosmetics, sunscreen	transparent UV- blocker
ZnO and TiO ₂	paints	additive

3 Environmental fate of nanomaterials

The study of the environmental fate of engineered NMs in the environment is still in its early stages. Research is no way comprehensive and the need for more research is imperative. This section aims to give some thought to aspects of the environmental fate and behaviour of NMs. NMs released into the environment are affected by all the abiotic and biotic factors in the surrounding media. The fate will also be dependent on the form in which the NM is released into the environment. It is not known exactly how NMs behave in the environment. To some extent NMs may behave in the environment similarly to colloids. Colloids are chemical mixtures in which one substance is dispersed throughout another. Their chemistry is complex and there is no precise study on how exactly all the various factors affect the various NMs. Most research seems to be involved in looking at a few chosen factors with the NMs. This makes it very difficult to perform exposure assessments. The following section will cover a few characteristics that can affect the behaviour of nanomaterials in the environment. Given the diverse range and variety of NMs, generalizations should be made with caution.

3.1

Characteristics affecting behaviour of nanomaterials

For most chemicals the fate and transport can be determined by a few characteristics, and most models are based on these. In the case with NMs, their unique features can make them differ from their molecular counterparts (Mackay and Henry *et al.*, 2009). Particles below the 100nm diameter have a settling velocity corresponding with the Brownian motion, which is the random movement of small particles suspended in a fluid resulting from the incessant bombardment of the molecules of suspending medium against the particle. The resulting systems are stable systems called sols and they can appear in either liquid (hydrosol) or gases like the atmosphere (aerosol) (Mackay and Henry *et al.*, 2009).

The principal considerations associated with the release of NMs are how the preparation size will alter the material's transport, fate and final exposure to non-target receptors (Mackay and Henry *et al.*, 2009). Behaviour will partly be the function of surface chemistry, the composition of the nanomaterials, the presence of coatings (capping agents), dissolution, and the presence of any readily soluble substances in preparation. Charge can be affected by the pH of the surrounding media. Charge heterogeneity is an important consideration as well. Surface charge screenings on particles can be altered by H⁺ concentration in a predictable manner (Handy *et al.*, 2008a). A study from Choi *et al.*, (2008) showed that the particle size plays an important role in silver toxicity. The authors looked at the cell growth inhibition to nitrifying bacteria and observed the correlation of inhibition with the particle fraction of less than 5 nm. The mechanism leading to inhibition was mediated by intracellular reactive oxygen species (ROS).

Emission of nanomaterials

The sources of NMs can be divided into three broad categories, which are related to their characterization. Nanomaterials enter the environment through intentional release and unintentional release, and they occur naturally (look at fig 1, page 13). For this report the atmosphere will not be included as engineered NMs are not expected to be released intentionally into the atmosphere. These sources can be further categorized into point sources (land fills, waste water treatment plants, production facilities) and non-point sources (wear of materials applied with NMs) (Nowack and Bucheli, 2007). The main identified sources of ENMs are production facilities, production processes, wastewater treatment plants and accidents during transport. Intentional release includes the case of zero valent iron for remediation (Farré, 2008; Nowack and Bucheli, 2007). Figure 3 illustrates these emissions and the routes of NMs.

The cross-cutting nature of nanotechnology entails that technologies used for one sector will gradually find their way into other sectors. There is also a certain degree of overlap in the food, medicine and cosmetic sectors. The concept of nanodelivery systems seem to have originated in targeted drug delivery, but it also has potential to alter the distribution of substances in the body (FAO/WHO, 2009). Already a few known studies have established that NMs are released into the environment through wear and tear, and this leads to potential exposure for both people and the environment. The following paragraphs will describe two case studies where NMs have been shown to have been released into the environment.

Nanosilver is being used in textiles because of its antimicrobial quality. This quality is based on the slow release of Ag^+ ions that are one of the most toxic metals for microorganisms. It has not been established whether the effectiveness of nanosilver is based on only the toxicity of the metal cation or whether it represents the toxic effects of the NMs itself. Geranio *et al.*, (2009) investigated the amount of silver released during washing from nine fabrics with different ways of silver incorporated onto the fibers. The effects of pH, surfactants and oxidizing agents were investigated. Eight

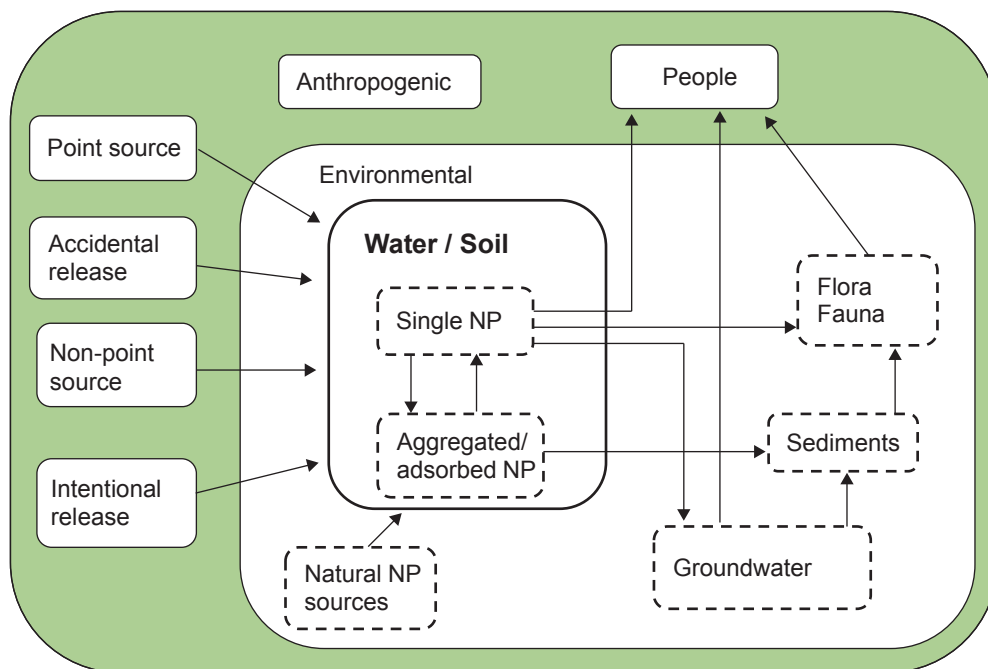


Figure 3. Nanoparticle pathways in the soil and aquatic environment. Modified for the purpose of this report from Nowack and Bucheli, (2007).

textiles were incorporated with nanosilver whereas one used bulk material. The research showed that the dissolution of silver NPs decrease as pH increases. In normal washing conditions at pH 10 the solubility was approximately a tenth of what it was at pH 7. For most textiles a significant release of Ag⁺ was only detected after the addition of oxidants. The amount and size distribution of released Ag varied in different products. The percentage of silver released during the washing cycle varied from 1 to 45% depending on the product. The amount of released Ag compared to textile weight was 0.3-377 µg/g which is slightly higher than in a similar study from Benn and Westerhoff (2008). The majority of the released Ag was found at the particulate fraction (>450nm), indicating a dominant role of mechanical stress. The research showed that during the washing cycle, the synergistic effects of chemical agents and mechanical stress may enhance the release from a textile.

Titanium dioxide (TiO₂) is being used in exterior paints as whitening pigments, and some of this TiO₂ is found in the nanoscale. A study from Kaegi *et al.*, 2008 examined the release TiO₂ particles from the exterior paints to the discharge into surface waters. The study revealed that synthetic TiO₂ particles between the size of 20-300 nm are detached from facade paints by natural weather conditions. The particles are released into facade run off and enter into natural waters. The concentration of TiO₂ in runoff water was estimated as 13.4 µg/L (Kaegi *et al.*, 2008). This is the first step in the environmental assessment of released NPs in environmental samples.

3.3

Environmental fate and transport of nanomaterials

The environmental fate and transport of NMs fall into three major categories: the behaviour in aqueous solutions, behaviour in porous media, and behaviour in the atmosphere. As previously mentioned, because the atmosphere and the study of aerosols are its own science, they will not be included in this report. This report will focus on the fate and transport of NMs in **aqueous solutions** and in **porous media** (soil and sediment). The behaviour in these media depends on chemical and physical considerations that are different for nanosized and bulk material. The environmental stability is not dependant on redox-type reactions, but more on physisorption properties, which leads them to interact with environmental constituents at low energies (Mackay and Henry, 2009).

Water

To understand the behaviour of NMs in the aquatic environment it is essential to study their interactions with abiotic and biotic factors of the environment. To understand the fate of NMs one must take into account their interactions with colloids and other organic material and combine this with a range of physicochemical properties such as pH, salinity, ionic strength and type and concentrations of cations. Information about these kinds of interactions related to engineered NMs is scarce (Christian *et al.*, 2008).

In the aquatic medium there are differences between fresh water and sea water and other water bodies depending on, for example, their salinity. A stable dispersion of NPs in a liquid is called a colloidal system or colloidal dispersion. Colloids are not solutions, and nanoparticles do not dissolve but rather are dispersed in the medium (Handy *et al.*, 2008a). In colloid chemistry a “stabilized” dispersion describes a liquid where particles may collide but do not stick together. The colloidal dispersion is thermodynamically unstable and will always tend to aggregate, however slowly. Processes important for the separation of colloidal dispersion are mainly particle collisions, and attachment that results in aggregation alongside settling.

How nanomaterials will travel and behave in natural waters such as groundwater, rivers, lakes and seawater is not well understood. Studies have dealt with the aggregation of NPs in simpler aqueous solutions, looking at ionic strength and various pH levels in the size of the aggregates (Domingos *et al.*, 2009a, French *et al.*, 2009, Saleh *et al.*, 2008) Studies have also dealt with the interactions between NPs and natural organic matter (NOM) (Zhang *et al.*, 2009). These studies have provided a mechanistic understanding that is important in predicting behaviour. It is the combined effects of all the characteristics in natural waters that affects the aggregation and sedimentation of NMs. This affects the bioavailability of the NM and therefore is essential for the evaluation of the exposure. Keller *et al.*, (2010) studied the factors that affect the fate and transport of metal NPs in several natural water matrices. These NPs were CeO₂, TiO₂ and ZnO. In conditions of seawater with low total organic carbon (TOC) and high ionic strength (IS) the rate of sedimentation was very high for all three NPs. This also depended on the concentration of the NPs. With higher initial concentrations the faster is the decrease in the concentrations of suspended NPs. With environmental conditions of fresh water with high TOC and low ionic strength a completely different behaviour occurs. The size of the aggregates remained stable at approximately 300nm for all three NPs, and particle concentration had no effect on the aggregation rate.

Keller *et al.*, (2010) suggest that metal oxide NPs entering sea water are removed from the water column in a few hours. In freshwater, on the other hand, stable dispersions of these metal oxide NPs with low sedimentation rates would occur and affect animals in the water column. In a few days these NPs would sediment out and affect benthic organisms.

Colloidal fraction is a generic name for particles in the range of 1nm-1µm, and thus NMs are colloids in that sense (Fig 4). In aquatic systems colloids consist of macromolecular organic materials, such as humic and fulvic acids, proteins, peptides, also including inorganic species such as hydrous iron and manganese oxides. Their increased surface area to volume ratio makes them important binding phases for pollutants. They also have questionable features that are important such as high surface energy, quantum confinement and conformational behaviour (Kleine *et al.*, 2008). The surface properties are one of most important factors that determine the stability and mobility of NPs as colloids in suspension, and the aggregation and deposition in aquatic systems. The stability of these colloid systems then controls their mobility in aquatic systems. (Navarro *et al.*, 2008)

When released into suspension, buoyancy suspends NMs in the fluid. Relatively weak van der Waals forces will cause the NPs to be attracted to one another and other environmental constituents. The term physisorption refers to adsorption as a consequence of this force. Unless this physisorption is inhibited nanoparticles will tend to agglomerate. As the size of the agglomerates increases this will reduce the buoyancy and the particles will settle. Nanoparticles can form suspensions and can be transported through the environment. The stability of nanoparticles depends on the physical and chemical properties of the particles themselves and the environment (Mackay and Henry, 2009).

There are some fundamental differences between the physico-chemistry of various aquatic habitats that will likely affect the behaviour of NPs. Some NPs can aggregate in the presence of Ca²⁺. This leads to fish living in high Ca²⁺ (marine fish, fish living in hard waters, benthic species living in sediment interface) being more likely to be exposed to aggregates of NPs rather than free NPs (Handy *et al.*, 2008a).

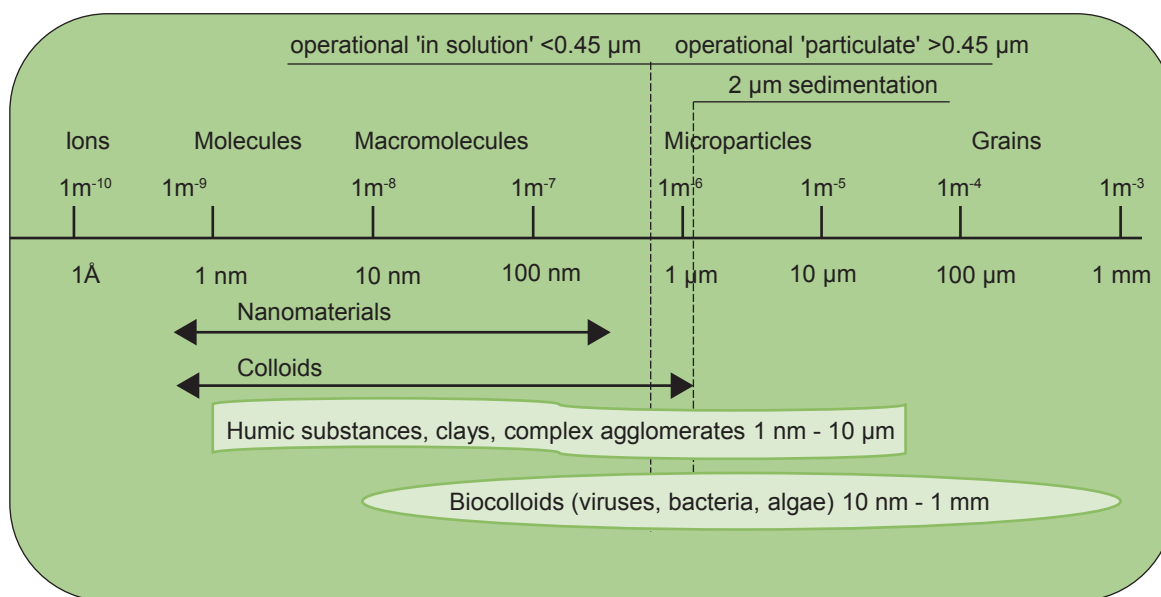


Figure 4. Size domains and definitions in different size classes relevant for nanoparticles. Modified from Christian *et al.*, 2008 and Nowack and Bucheli, 2007

Wastewater and sludge

There only a few documented findings of nanomaterials in wastewater or sludge, but very recently fullerenes and silver sulphide nanoparticles have been detected in these matrices (Farré *et al.*, 2010; Kim *et al.*, 2010). With a very sophisticated analytical instrumentation fullerenes has been detected in the suspended solid of wastewater effluents (Farré *et al.*, 2010). Twelve samples out of 22 Spanish wastewater effluents contained at least two compounds of the three analytists (C_{60} and C_{70} fullerenes, and N-methylfulleropyrrolidine C_{60}), many of them at the $\mu\text{g/L}$ level. Silver sulphide nanoparticles may be present in sewage sludge as a result of *in situ* reaction (Kim *et al.*, 2010). Under anaerobic conditions reduced sulphur can react with silver nanoparticles or soluble silver species.

In a simulation study of wastewater treatment, it was shown that the particles' surface functionality had a fundamental effect on the removal of SiO_2 -nanoparticles during flocculation (Jarvie *et al.*, 2009). The silica surface-functionalized particles would sediment into the sewage sludge, while the uncoated particle would stay in the effluent.

Sediment

A study by Bradford *et al.*, (2009) looked at the impact of silver nanoparticles on the genetic diversity of natural assemblages of bacteria on estuarine sediments. A greater microcosm was created where the parameters were gathered. The research also examined the metal and nutrient concentrations. Three different concentrations of silver were used. To achieve the various final concentrations the experimental tanks were given daily doses if 1/20th of the concentration for a time period of 20 days. After dosing, the tanks were left for another 10 days. Water samples and sediment samples were taken to establish the concentration of the silver within. It was shown that there was a steady increase in Ag concentrations over the initial 20 days for the group with the greatest final concentration of $1000\mu\text{g/L}$; this was followed by a decline after the dosing had stopped. On the other hand the sediment samples increased their Ag concentration. According to the measurements the Ag-nanoparticles were gradually transported out of the aqueous phase onto the sediment. The Ag nanoparticles

were found at the surface of the sediment in the top surface layer of approximately 3mm. Ag was also found at the surface of the sediments in the test tanks with a final concentrations of 25µg/L but this was at the end of the experiment. While the silver NPs accumulated, no impacts were observed with the overall abundance of the prokaryotes of the estuary water.

Soil

Soil colloids have been studied for their relevance for soil formation. Soil colloids and other porous media can facilitate the movement of contaminants in soils and other porous media. Darlington *et al.*, (2008) studied the properties of aluminium nanoparticles in different solutions, and the transport of these nanoparticles was investigated in soil and sand matrices. The transport of aluminium was shown to be inversely related to the size of the agglomerated particles. The agglomerate size can increase with time and affect transport, depending on the ionic strength of the solution in which the particles are suspended. Solutions that mimic surface waters in ionic strength aluminium nanoparticles will rapidly form micro-sized agglomerates and restrict transport. It was also suggested by the authors that the surface charges of the particles and soil could be the dominant physicochemical characteristic governing the transport of nanoparticle agglomerates at size ranges not subjected to filtration.

Interactions and stability

Interactions between NMs and organic toxic compounds can both potentially alleviate or amplify the toxicity of that compound. Baun *et al.*, (2008) have shown that the toxicity of certain organic compounds on *Daphnia* and algae have been increased in the presence of fullerenes in situations where the influence of the pollutant is known and the interaction between the nanoparticles and the environment alone is known. When both are present in the environment Nowack and Bucheli (2007) propose the following scenarios. The NP can either adsorb or absorb the pollutant, which leads to the reduction of the free concentration of the pollutant. If the adsorbed pollutants are taken into the cells alongside the nanoparticles the toxic effects created could be caused either by the nanoparticle, the pollutant, or the synergistic effects. A possibility of no toxic effect could be because the adsorbed pollutant might no longer be bio-available for the organism, and the nanoparticle itself might not be toxic (Nowack and Bucheli, 2007). At present there is no information on how permanent these aggregates are over long periods of time. It is not known whether it is possible that aggregates could change particle size due to chemical reactions or microbial activity.

It is difficult to differentiate between these processes of adsorption and absorption. Nanoparticles have also been used for the sorption of a variety of compounds. Carbon nanotubes have been utilized for the sorption of various kinds of hydrocarbons and divalent cations from water. The sorption mechanism is mainly attributed to the interaction between the surface functional group of the CNT and the metal. The sorption capacities are increased with oxidation of the CNT with NaOCl, HNO₃ and KMnO₄. The maximum ion sorption of the raw and oxidized CNTs follow roughly this order Pb²⁺ > Ni²⁺ > Zn²⁺ > Cu²⁺ > Cd²⁺ (Rao *et al.*, 2007).

In conclusion, it has been shown, in both laboratory and field studies, that NM interact with each other and other environmental constituents and this affects their fate and transport. The transport behaviour is difficult to model precisely. Variables such as pH, ionic strength, presence of dissolved organic material, and the organic carbon content and grain size of the soil strongly affect the migration and disposition of NMs. Consequently the fate and transport should be taken into account on a case-by-case basis.

Monitoring of nanomaterials in the environment

The presence and changes of NMs in the environmental compartments is an analytical challenge. Currently there are very few analytical methods to determine NMs from the environment. Many of the techniques, e.g. EM methods (except ESEM) mentioned in Table 1, require sample drying, which may lead to fundamental alterations of the sample (Tiede *et al.*, 2009). In laboratory experiments the changes of the samples due to drying artefacts, dissolution and aggregation can be controlled and partly avoided. However, environmental samples from complex matrices, and even natural waters, are prone to artefact formation during pre-treatment of the samples. Consequently, there are no quantified data on actual, measured concentrations of NMs in the environment. Even though there has been significant progress, reliable methods for the determination of NM identity, concentrations and characteristics in complex environmental matrices are not available.

Consequently, it is vital that monitoring data becomes available so as to identify adverse effects early. The need for monitoring is expected to increase in the future: not only to assess environmental exposure but to determine whether emissions are in compliance with various regulations such as the Water Framework Directive (WFD) (Baun *et al.*, 2009).

Due to some hazardous properties of functionalized carbon nanotubes, nano silver and zinc oxide, the inclusion of these into priority substances of the WFD has been considered (Baun *et al.*, 2009). In the WFD the environmental quality standards should be derived. However, as Baun *et al.* (2009) stated, it may well be impossible at the moment to set limit values for NMs due to a lack of data on ecotoxicity, degradation and bioaccumulation, as well as on valid test systems,

Baun *et al.*, (2009) concluded that due the uncertainty about the fate and effects on ENPs it may prove wise to follow the preventive/proactive principle of WDF and to reduce the release of NMs to aquatic environment even now.

4 Environmental exposure assessment

The increasing use and production of NMs will undoubtedly lead to environmental exposure from multiple potential sources (Baun *et al.*, 2009). In principle the exposure assessment of NMs is similar to the assessment of conventional chemicals. Two elements are essential: hazard, which is the intrinsic property of the substance, and exposure, which is a necessity for a risk to become real. Due to the special features of the NMs, exposure to nano-sized material in environmental conditions is difficult to attest. However, it is essential that NMs are not expected to behave like their bulk counterparts until it is proven so. Chemical identity must be known for NMs as for any other material. But this may not be enough. The characterization of NMs for exposure assessment should perhaps be extended beyond the pure chemical basis of the material. A few examples from the literature do just that.

In a study from Hansen *et al.*, (2008a) the location of the NP in the consumer product was investigated. The location of the NP is crucial for the determination of the potential exposure pathways of the NP. The NMs are divided according to location into three groups with several subcategories. The three main groups are a) nanomaterials in bulk, b) nanomaterials on the surface and c) as particles. The authors then applied the categorization network for the 580 consumer products on the Woodrow Wilson inventory for the Project on Emerging Nanotechnologies (information from the 2007 inventory) into these categories and subcategories. They were able to categorize approximately about 75% of the products on the inventory. The greatest number of products had NMs as particles and of these the largest amount was found suspended in liquid (37%). This was followed with NMs bound to surface (19%) and suspended in solids (13%) The data can be found in figure 5.

A combined table with the comparison between the location and the type of the nanomaterials being used was compiled (Table 3). Only the most common nanomaterials were taken into the table. None of these were found in bulk. The original data with a larger number of substances is found in Hansen *et al.*, (2008a).

Table 3. Comparison between the location and type of nanomaterial. Modified from Hansen *et al.*, (2008a).

Nanomaterial	Surface		Particles				
	Surface. structure	Structured films	Surface bound	Suspended in liquids	Suspended in solids	Airborne	Unclassifiable
Ag	1		53	33	28	1	19
ZnO			3	26		1	1
TiO ₂			9	12		1	2
CNT			3		13		
SiO ₂		1		7	7		

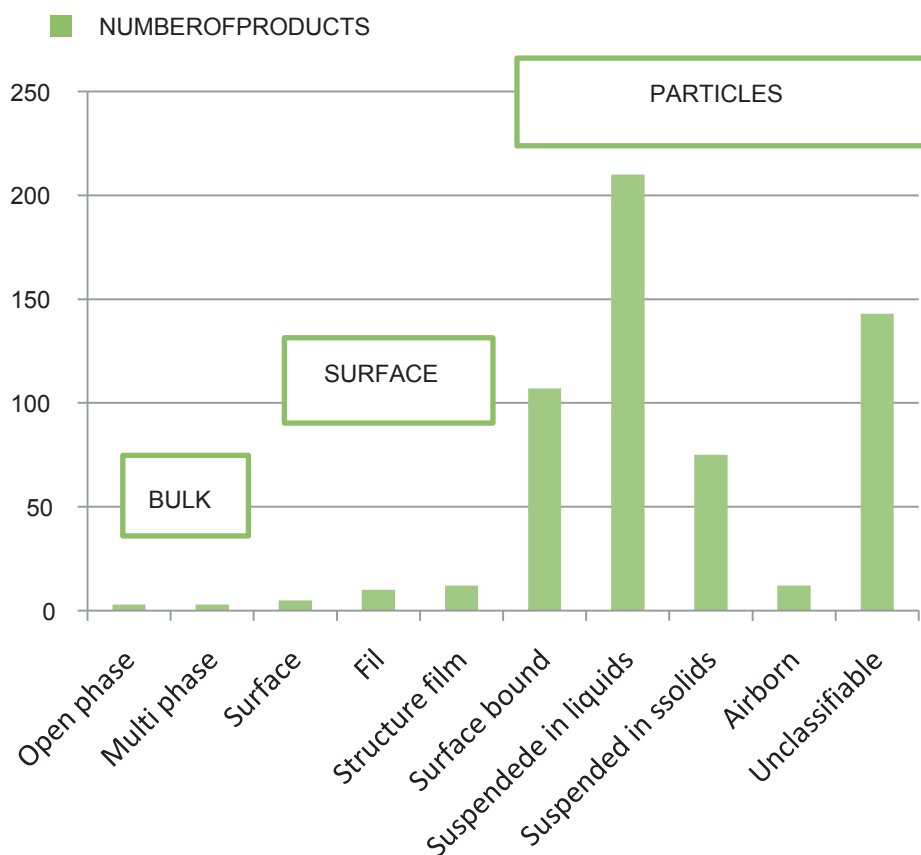


Figure 5. Distribution of products into various categories of nanomaterials (modified from Hansen *et al.*, 2008a).

From these data three groups of possible exposure can be determined: NMs expected to cause exposure, NMs possible to cause exposure, and NMs not expected to cause exposure. NMs possible to cause exposure come from the wear and tear of the product.

A survey published by the Danish Environmental Protection Agency (Stuer-Lauridsen *et al.*, 2007) looked at the products which use nanomaterials in the Danish market and produced a similar categorization for the products according to the location of the nanomaterial. The survey found 243 products based on nanomaterials in the Danish consumer market. Of these 243 products, only in 41 products were the nanomaterials identified, leaving the great majority (83%) of nanomaterials unidentifiable. There is no legal requirement for producers or importers of these products to declare the contents of the nanomaterials. Of the known nanomaterials half were found in cosmetic products, followed by textiles and home appliances. The categorization of the Danish products results in a similar outcome to the categorization of the Hansen *et al.* (2008a) of products based on the Woodrow Wilson inventory. In product categories the greatest number of products were found in the personal care and sports equipment category. Within this category the greatest category by far is for cosmetics again, followed by textiles and sports equipment. The second largest category is home and garden and within this category the greatest number of products are cleaning aids. In electronics and computers group the greatest number of products is found as displays. These displays can be for mobile phones, videos and televisions. The products were also categorized according to the type of nanomaterials found in the products. The great majority (63%) of products in the Danish market fall in the category of 'nanoparticles suspended in liquid'. The second largest group

is 'Nanoparticles encapsulated in solid materials', followed by 'film in nanometer thickness'. The results are found in the table 4 below.

The research so far has focused on the consumer products and markets. It should also be remembered that potential exposure also lies in the manufacturing of these nanomaterials. Occupational exposure also arises from the use of nanosized agrochemicals, and there is concern about the workers. Agrochemicals potentially contaminate agri-food products (FAO/WHO, 2009). Environmental exposure through contamination from the use and disposal of consumer products arise from several possible routes. Boxall *et al.*, (2007) identified these routes. The main identified routes and materials include cosmetic and personal care products (TiO₂, ZnO, C₆₀, Fe₂O₃, Ag, Cu, Au), catalysts lubricants and fuel additives (CeO₂, Pt, MoS₃), paints and coatings (TiO₂, SiO₂, Ag, QDs), water treatment and environmental remediation (Fe, Fe-Pd, polyurethane), agrochemicals (SiO₂ and others), food packaging (Ag, Clay, TiO₂, TiN) and nanomedicine and carriers (Ag, Fe, magnetic ENMs).

Environmental exposure will vary according to the conditions. These conditions include how the NMs are handled in the work place, how NMs partition to various phases in the environment, the mobility of NMs in each and their persistence, and the magnitude of their source (Nowack and Bucheli, 2007). As stated before, information on this kind of data is not available. Additionally, as pointed out, the location of the NM in the product is essential to the potential exposure of that NM. A general lack of information about the kinds of NMs used how they are used, and in which concentrations hampers full-scale quantitative exposure assessment. Not even regulators have access to the information needed to carry out realistic exposure assessment (Hansen *et al.*, 2007). When NMs are used in the food chain, a drawback is the increased packaging complexity, waste and whether the material is difficult to recycle (Kukkonen, 2010).

Table 4. Products in the Danish market categorized according to the location of the nanomaterial in the product and product category according to Stuer-Lauridsen *et al.*, 2007.

	Appliances	Other uses	Electronics and computers	Automotives	Home and Garden	Personal care and sports equipment	Total
NPs suspended in liquids		3		24	58	69	154
NPs encapsulated in solid materials					5	30	35
Film in nm thickness			1		1	20	22
Surface-bound NMs	4		1	1	3	10	19
Nanostructured films			8				8
Not categorized						5	5
Total							243

A few attempts have been made to model the exposure as a part of life cycle assessment. These models presume that normal exposure assessment is valid for NMs. However, there is very little information regarding the exposure to underpin such a conclusion, because of the lack of data concerning NMs in the environment. Depending on the model and input data, the predicted concentrations may vary considerably from study to study.

A study from Müller and Nowack, (2008) attempted to model the release of certain NPs (nano Ag, nano TiO and CNTs) into the environment by using a substance flow

analysis from products in to air, soil and water. For nano-TiO₂ in water, concentrations of 0.7 – 16 µg/L were predicted. The authors also included a risk assessment by calculating risk quotients for each NM (see chapter 6.2). Gottschalk *et al.*, (2009) calculated PEC concentrations for TiO₂, ZnO, Ag, CNT and fullerenes using a probabilistic material flow analysis. The most frequent values in surface waters ranged from 0.003 ng/L for fullerenes to 21 ng/L for TiO₂, while in the wastewater treatment plant effluents concentrations were 4 ng/L and 4 µg/L, respectively. The authors concluded, that, based on these modelled concentrations and existing ecotoxicological data, nano-Ag in surface waters, nano-Ag, nano-TiO₂ and nano-ZnO in wastewater effluents may pose a risk to aquatic organisms.

In the light of the current information it can be concluded that NMs are released into the environment resulting in the exposure of flora and fauna. The increasing use of NMs in consumer products will likely cause nanomaterials to end up in wastewater treatment plants through wear and tear of products, as has been shown. How different NMs behave in wastewater treatment plants has not been studied extensively. The expected end points for nanomaterials in the environment are aquatic environments and they are likely to end up in sediments.

5 Environmental effects assessment

5.1

Environmental effects

In addition to their own effects, NMs can play an important role by serving as carriers of other harmful substances. This would have an effect on bioavailability, persistence and mobility interactions. Evidence about the persistence of NMs is only being recognized as one of the key factor in environmental effects assessment. The challenge in analyzing environmental concentrations is still waiting for reliable methods and analytical tools. There is a demand for analytical methods to be developed if possible.

The testing of the chemical safety of NMs is similar to the risk assessment of conventional chemicals. In order to distinguish the effects of NMs from the conventional and soluble chemicals, exposure to the nano-formed chemical should be verified. However, when looking at the environmental impacts, in our view, the tests should encompass the issue of toxicity on a broader scale. This scale should look at the synergistic effects, issues with bioavailability and NMs as carriers of other toxins and as a possible source of soluble forms of the constituents for example. These all will have an influence on the possible effects of that nanomaterial. The safety of NMs has been studied in several laboratories using well-known toxicity and ecotoxicity methods. So far these methods have not been designed specifically for NMs, but existing protocols have been used with – and, unfortunately, also without - extra procedures to disperse the NM into the test medium. The true size of particles in suspension may be very different from that notified for the chemical (Adams *et al.*, 2006). Currently there is no general agreement on what metrics in dosing should be used. The number of particles per unit weight of the material or surface area per units per millilitre may prove to be better descriptors than the conventional mg/L or mmol/L units. (Clough, 2009).

The results of toxicity tests using various parameters as end-points for C₆₀ and TiO₂ are collected in Table 5 A and B, respectively. Reports with no information about the size of the particles or the pre-treatment to disperse the material were not considered. When interpreting laboratory test results for the assessment of environmental effects, one should pay attention to the possible difference in material composition and other NM properties which may be changed under environmental conditions.

A study from Hansen *et al.* (2007), where over 400 articles were identified and analyzed as relevant for nanomaterials /nanoparticle and toxicity, showed two major general findings. Firstly most of the 428 reviewed studies revealed adverse effects on tested animals or cell lines. Secondly there was a serious lack of characterization of the NP tested. This lack impedes the potential to identify the causality between the observed hazards with the special chemical or physical properties. Examples in table 5 demonstrate the diversity of methods and measured end-points used in the ecotoxicity studies. They also clearly show how difficult it may be to make accurate conclusions of the potential to cause environmental impacts.

Table 5 A. Ecotoxicity tests results compiled from studies with conventional one-organism laboratory tests for C_{60} . Test condition, preparation of the samples and characterization of the nano-scale substance differ from study to study.

Test species	End-point, exposure time, concentration range	Pretreatment of NMs particle size	Effects	Reference
Microbes				
<i>Pseudomonas putida</i>	membrane lipid composition, phase behaviour, 14 h, 0.01 and 0.5 mg/L	stirring overnight, THF evaporated, filtration 0.22µm, 50 – 200 nm	increased phase transition temperature and increased membrane fluidity, decreased viability at 0.5 mg/L	Fang et al., 2007
<i>Bacillus subtilis</i>	membrane lipid composition, phase behaviour, 14 h, 0.01 and 0.75 mg/L	stirring overnight, THF evaporated, filtration 0.22µm, 50 – 200 nm	decrease transition temperature and increased membrane fluidity, decreased viability at 0.75 mg/L	Fang et al., 2007
Green algae				
<i>Pseudokirchneriella subcapitata</i>	growth inhibition/ mixture toxicity of C_{60} and organic compounds, 72 h	stirring for 4 months, aggregated particles > 200nm	increase in phenanthrene toxicity, decrease in PCP toxicity, no effect with methyl parathion or atrazine	Baun et al., 2008
Aquatic invertebrates				
<i>Daphnia magna</i>	acute toxicity and accumulation / mixture toxicity of C_{60} and organic compounds, 72h	stirring for 4 months, aggregates > 200 nm	marked increase in phenanthrene toxicity, decrease in PCP toxicity, no effect with methyl parathion or atrazine; some accumulation of phenanthrene followed by fast clearance	Baun et al., 2008
<i>Daphnia magna</i>	acute toxicity, 48 h, max conc 22.5 mg/L; mortality and reproduction 21 d, max conc 5 mg/L; uptake at 30 mg/L, 5 d	stirring for 2 months, 10-200 nm aggregates	acute toxicity not observed; increased mortality and decreased reproduction during 21 d; maximum uptake after 48 h	Oberdörster et al., 2006
<i>Hyalella azteca</i>	mortality, 48 and 96 h, max conc 7 mg/L	stirring for 2 months, 10-200 nm aggregates	no effects via water exposure or food intake	Oberdörster et al., 2006
Marine copepod	mortality, 96 h, 22.5 mg/L	stirring for 2 months, 10-200 nm aggregates	no significant effects	
Fish				
Fathead minnow	acute toxicity, biomarkers, 96 h, 0.5 mg/L	stirring for 2 months, 10-200 nm aggregates	no mortality, indication of suppressed lipid metabolism	Oberdörster et al., 2006
<i>Pimephales promelas</i>	acute toxicity, biomarkers, 48 and 96 h, 0.5 and 1 mg/L	stirring for 2 months, 10-200 nm aggregates	no mortality, no effects in the biomarkers used	Oberdörster et al., 2006

Table 5 B. Ecotoxicity tests compiled from studies with conventional one-organism laboratory tests for TiO₂. Test condition, preparation of the samples and characterization of the nano-scale substance differ from study to study.

Test species	End-point, exposure time, concentration range	Pre-treatment of NMs particle size	Effects	Reference
Microbes				
<i>Escherichia coli</i>	growth inhibition, 14 – 20 h, 10 mg/L – 5 g/L	shaking; mean particle size 330 nm	15 % inhibition at 0.5 g/L 72 % at 5 g/L	Adams et al., 2006
<i>Bacillus subtilis</i>	growth inhibition, 14 – 20 h, 10 mg/L – 5 g/L	shaking; mean particle size 330 nm	75 % inhibition at 1 g/L 99 % at 5 g/L	Adams et al., 2006
Microbial communities in biofilm (24 d biofilm growth) and in free-living suspension	cell membrane integrity 48 h, reactive oxygen species (ROS) 4 h, initial concentration 5.3 mg/L	sonication; primary particles 10 and 20 nm, agglomerates < 1µm	significant membrane damage in both test systems slighter effect on biofilm ROS production increased when exposure under light, no effect in dark	Battin et al., 2009
Green algae				
<i>Pseudokirchneriella subcapitata</i>	growth inhibition, 96 h	stirring for 30 min; nominal size 10 nm	25 % inhibition at 1 – 2 mg/L	Hall et al., 2009
<i>Desmodesmus subcapitatus</i>	growth inhibition, 72 h, 12.5 – 50 mg/L, irradiation as pre-treatment	pre-cleaning, sonication, nominal sizes 25 and 100 nm	EC50 44 mg/L for 25 nm particles, EC50 > 50 mg/L for 100 nm particles no additional effect of pre-illumination	Hund-Rinke and Simon, 2006
Aquatic invertebrates				
<i>Daphnia pulex</i>	survival, 48 h, conc not specified	stirring for 30 min; nominal size 10 nm	LC50 6.5 – 13 mg/L	Hall et al., 2009
<i>Ceriodaphnia dubia</i>	survival, 48 h, conc not specified	stirring for 30 min, nominal size 10 nm	LC 3.0 – 15.9 mg/L	Hall et al., 2009
<i>Ceriodaphnia dubia</i>	chronic toxicity, 7 d, conc not specified	stirring for 30 min; nominal size 10 nm	25 % inhibition at 2.5 – 26.4 mg/L	
<i>Daphnia magna</i>	survival, 48 h, 1- 3 mg/L	pre-cleaning, sonication, irradiation; nominal sizes 25 and 100 nm		Hund-Rinke and Simon, 2006
Fish				
Fathead minnow	acute toxicity, 48 and 96 h, conc not specified	stirring for 30 min; nominal size 10 nm	LC50 500 mg/L (48 h) > 1 g/L (96 h)	Hall et al., 2009
Fathead minnow	chronic toxicity, 7 d, conc not specified	stirring for 30 min; nominal size 10 nm	25 % effect at 342 – 597 mg/L	Hall et al., 2009
Rainbow trout	survival, physiological and biochemical parameters, 14 d, 0.1- 0.5 – 1.0 mg/L	6 h sonication of stock solution, 30 min sonication prior dosing; 24 nm	no mortality, gill injury, oxidative stress observed	Federici et al., 2007
Fish cells <i>in vitro</i> (RTG-2, rainbow trout gonad cells)	genotoxic and cytotoxic potential, biochemical parameters; 4 – 48 h at 1.5 – 50 mg/l depending on the test, UVA irradiation as pretreatment	stock solution sonicated for 12 h plus 5 min at high energy and centrifuged; 11.8 – 38.5 nm	some genotoxic and cytotoxic effects in combination with UVA at the highest concentration of 50 mg/l	Vevers and Jha, 2008

A lot of research has been carried out in the field of nanoecotoxicology, but studies are fragmented and often contradictory. Working with these materials is difficult, standard toxicology protocols are often unsuitable for these materials. Also the quality of many studies is debatable. There is a lack of research that is environmentally relevant and models real life concentrations and situations. It can be concluded that the current state of knowledge does not permit reliable prediction of the toxicological characteristics of any given ENM from data of another engineered nanomaterial or from a consideration of the characteristics of the NM itself (FAO/WHO, 2009).

Nanosilver deserves special attention, not only because it is widely used in various applications, but also because of the severe toxicity of silver to many species. Silver is very toxic to bacteria, plants, plankton organisms and fish, but it is not especially toxic to mammals. The route of exposure seems to be of importance, and dietary exposure seems to result in significantly higher toxicity than anticipated (Luoma, 2008). However, no effects were found in a study of nanosilver on the genetic diversity of natural assemblages of bacteria on estuarine sediments (Bradford *et al.*, 2009). Typically the ionic form of silver is biologically available and effective, while the ambient conditions (particulate matter, oxygen, chloride, sulfides) determine the solubility (Luoma, 2008). Although the effects of nanosilver may be mainly caused by the soluble form released from the particles, the nano-form has also been shown to be taken up by fish embryos, for example (Lee *et al.*, 2007 ref in Luoma, 2008). Nanosilver has also been found to greatly elevate the critical oxygen tension of European perch (*Perca fluviatilis*) at a concentration of 300 µg/L. The elevation in the critical oxygen tension reduces the ability of the perch to extract oxygen from the water during progressive oxygen depletion (Bilberg *et al.*, 2010). Obviously, thorough investigation of environmental effects and risk assessment including mass loadings of silver nanomaterials will be necessary for at least some products (Luoma, 2008).

5.2

Health effects

The human safety of NMs has been investigated intensively in recent years. To a great extent the same problems apply for assessment of the health effects on humans as on other organisms, namely, characterization of the substance under investigation, verification of exposure, basis for metrics to be used, and the large number of different ENMs. Cell culture and other *in vitro* screening methods are extensively used in assessing the adverse effects on humans. The extrapolation problems of the results to an *in vivo* situation has led to a suggestion of three different levels of doses – administered, delivered, and cellular dose (ref. Teeguarden in Dhawan *et al.*, 2009). In contrast to simple aquatic organisms like unicellular algae exposed to the “administered” dose, the issue of dose and dose-response relationship in humans is far more complex.

Since larger amounts of NMs are handled in working environments than elsewhere in society, toxicological studies have mainly focused on occupational health and especially on exposure via the respiratory tract. The main possible uptake routes are lungs, skin and gut. The nasal epithelium has also been considered. Transport of NPs through healthy skin should not be very likely; however, 7nm quantum dots may enter the dermis (Ryman-Rasmussen *et al.*, 2006 cited in SCENIHR, 2007). Attention has been paid to the distribution of NPs in human models after administration via different routes. There is evidence of the translocation of manganese oxide into the olfactory bundle and brain after inhalation (Oberdörster *et al.*, 2004, Elder *et al.*, 2006 in Savolainen *et al.*, 2010). No straightforward results have been gained in studies of TiO₂ distribution after dermal administration. This route is of importance since TiO₂ is a common constituent in sun screen lotions, and a large number of individuals are so exposed.

The particle diameter is an important parameter determining the exposed compartment of the respiratory system. NPs may behave differently from the larger fine and coarse particles which are normally not absorbed from the respiratory tract (Oberdörster *et al.*, 2005). Larger particles can also cause effects in some cases, for example at very high exposures in coalminers and workers exposed to quartz dust (SCENIHR, 2007). There are several observations on the more toxic effects of NMs compared to the conventional form of the same chemical, for example inflammation caused by TiO₂ (Pylkkänen *et al.*, 2007 cited in Savolainen *et al.*, 2010). This information calls for precautionary measures in personnel protection and safety in industrial processes using NMs.

CNTs have been shown to cause respiratory toxicity in rodents. MWCNTs and ground CNTs were administered intratracheally and they both induced fibrosis and inflammation (Muller *et al.*, 2005). The research found that CNTs are not rapidly cleared from the lungs. After 60 days of exposure 81% of MWCNTs and 36% of ground CNTs were recovered. Both materials produced an inflammatory and a fibrotic response, and both responses were dose-dependent. MWCNTs and ground CNTs also induced the accumulation of both neutrophils and eosinophils, indicating an inflammatory effect. MWCNTs also induce the formation of bronchial granulomas developing around focal aggregates of MWCNT. Ground CNTs were better dispersed and did not form large granulomas (Muller *et al.*, 2005). Lam *et al.*, (2004) found that a single dose of 5 mg/kg caused fatalities in mice. The study showed that CNT products induced dose-dependent lung lesions that were mainly characterized by interstitial granulomas. A review of a larger amount of data concerning the pulmonary toxicity of manufactured carbon nanotubes concludes that CNTs are capable of inducing inflammation, epithelial granulomas, fibrosis, and biochemical toxicity changes that could damage pulmonary functions (Lam *et al.*, 2006). Certain types of carbon nanotubes could produce the same kinds of morphological changes as induced by crocidolite asbestos. Moreover, the studies have shown that these CNTs not only induce mesothelioma, the incurable carcinoma induced by crocidolite asbestos, but carbon nanotubes have a comparable potential to asbestos in causing disease (Kane and Hurt, 2008 in Savolainen *et al.*, 2010). On the basis of these studies a precautionary principle should be applied when dealing with the health and safety of carbon nanotubes. Adequate safety measures should be employed, and human exposure to CNTs via inhalation should be minimized.

In order to assess health impacts and to set occupational exposure limits, there should be a means of distinguishing between the exposure to background ultrafine particles and to nanoparticles. So far this has been technically too challenging (Savolainen *et al.*, 2010).

6 Risk analysis and oversights

6.1

Legislation and recommendations

The current legislation regulating nanomaterials within the European Union is the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH), which came into force 1st June 2007. The registration applies to all substances manufactured in or imported into the Community in quantities of 1 tonne or more per registrant per year. Registrants of the same substance will form a Substance Information Exchange Forum (SIEF) in order to avoid duplication of studies and to agree on the classification and labelling of the substance. How NMs should be treated in this legislation is a cause of ongoing debate. Problems arise from the minimum of 1 tonne per year quantity but another problem comes from the classification of NMs. According to Milmo (2009), confusion over the classification of NMs has led to two groups of companies using different criteria to submit data on carbon nanotubes. Separate SIEFs are formed to deal with CNTs. One group is setting up a SIEF registering CNTs as distinct chemicals with their own safety profile. Another greater group of producers and importers are planning to register CNTs as a form of bulk graphene so that they will not require their own registration dossier (Milmo, 2009).

In close co-operation with the CARACAL subgroup on nanomaterials ("CASG Nano", composed of Member States and stakeholder experts) the Commission is preparing advice on how to manage nanomaterials in accordance with REACH and the CLP Regulation. Currently two papers have been produced. However, with the current registration deadlines, CNTs may not be registered with safety data until 2018. Nevertheless, some steps have been taken as in November of 2009 the Council of the European Union and the European Parliament approved an updated set of regulations on cosmetic products, and they include a requirement that cosmetics containing nanoscale ingredients have that information on their labels. (PE-CONS 3623/09). The United States Environmental Protection Agency (US EPA) has refused to consider nanomaterials as new substances unless they have a new molecular structure, and therefore most materials are not regulated (Davies, 2009).

The EC has already arranged its first conference on the potential risks associated with nanoscience and nanotechnology. In 2006 the EC's scientific committee on emerging and newly identified health risks (SCENIHR) issued an opinion on the matter (10 March 2006). Currently there are three other opinions relating to NMs produced by the SCENIHR. The latest was produced 19 January 2009 and concerns the risk assessment of products of nanotechnologies. The opinion concludes that while risk assessment methodologies for the evaluation of potential risks that are used for conventional materials are applicable for NMs, specific aspects related to NMs still require further development. This situation will remain stagnant until there is sufficient scientific information available to characterize the harmful effects of NMs (both environment and human). The methodology for both exposure estimations and hazard identifica-

tion needs to be further developed, validated, and standardized. The highest risk, and thus also concern, is deemed to be associated with the presence and occurrence of free insoluble NPs either in a liquid dispersion or airborne dusts (SCENIHR, 2009).

To evaluate the member countries' regulatory challenges as regards safety on NM, the OECD's Chemicals Committee (CC) decided to consider them in some detail. The CC held a Workshop, and out of this emerged a Working Party on Manufactured Nanomaterials (WPMN), which was established 14th September 2006. The aim of the WPMN is to help member parties efficiently and effectively address the safety challenges of NMs. In 2008 the WPMN identified 14 representative NMs for testing. These NMs will sooner or later enter the market. The list includes Ag NPs, Fe NPs, TiO₂, Al₂O₃, CeO₂, ZnO, SiO₂, nanoclays, carbon black, fullerenes, SWCNTs, MWCNTs, polystyrene and dendrimers. The working party will gather information for inclusion on a set of reference materials to support the measurement, toxicology and risk assessment of NMs. (OECD/WPMN, 2008).

Additionally, the European Union is funding research programmes in the field of nanotechnology and the NMs. Within the current 7th Framework Programme (FP) a search with the term "nano" brings up 299 projects. The search term "nanotechnology" 294, "nanomaterials" 61 and "nanoparticles" 120 research programmes.

Even though research in the field of the safety of nanotechnology is being carried out, and the legislation exists, the actual tools how to deal with NMs seem to be scarce. There are already great gaps in the oversight of current nanotechnologies. A starting point for any oversight system is the ability to identify the risks and assess the likelihood and magnitude of that risk. To make risk assessments requires scientific knowledge and data about the technology and its products. The lack of an adequate scientific framework prevents researchers from knowing what data to collect (Davies, 2009). This report has already shown the problems with regard to which aspects are the most important in determining the toxicity. When looking at the whole picture the situation becomes more complex. Without this kind of data we cannot develop and test hypotheses regarding the potential impacts of NMs.

However, as already in the first generation on nanotechnologies there are significant gaps in oversight, what will happen with future generations of nanotechnologies when oversight is already lagging behind. Future oversight will probably have to focus on products instead of materials, because the material might have different impacts depending on how it is incorporated into the product (Davies, 2009). Questions to be answered for the future will also concern the acceptance of risks. What will be tolerated for the sake of this new technology? As a new technology, should caution and the precautionary principle be applied?

As nanotechnology is a relatively new technology the science is evolving and it is difficult to keep up with the pace. New technology is often beset with conflicting thoughts and opinions. Various authors have suggested different classification systems for NMs. It seems clear that nanomaterials should not only be looked at from a chemical and physical point of view, as that may not be the best choice. It is clear that legislation is not currently commensurate with the demands of nanotechnology. Until now, material in the nanoform has been treated as its larger chemically identical counterparts. This is very contradictory, as the novel, unique properties of the NMs are a direct consequence of their size, as is the fact that they behave differently than their larger counterparts.

Risk analysis and classification methods

There are some discrepancies between the definitions regarding aspects of risk. For the scope of this report the following definitions will be used. Risk analysis will include risk assessment, risk communication, and risk management. Risk assessment consists of exposure assessment, effects assessment, and risk characterization. The quantitative risk characterization is carried out by comparing the Predicted Environmental Concentration (PEC) to the Predicted No Effect Concentration (PNEC) (Fig. 6). This will produce a risk quotient (RQ).

At the moment there is no general agreement whether the environmental risks of NMs can be assessed by modelling using the common properties of certain groups of NMs. There might be characteristics of NMs which make classification possible and a rough estimate of risks characteristic to those classes. However, the characterization techniques are still being developed and we do not know whether there are properties of nanostructured material that could describe the potential hazard on a general level. At the same time with research on modelling, extensive research on the behaviour and effects of individual NMs on living organisms is necessary to form a sound basis for classification.

Nanomaterials can also be characterized on the basis of potential risks using mathematical models. Tervonen *et al.*, (2009) used the clustering of nanomaterial into risk categories in the context of multi-criteria decision analysis (MCDA). The method used as foundation for this task was the stochastic multicriteria acceptability analysis (SMAA-TRI), which allows uncertainty parameters in the model. The purpose of this classification system is to group NMs in risk classes for screening level risk assessments. The authors simulated the model by C_{60} , MWCNT, CdSe (Quantum dots), Ag NP (silver nanoparticle) and Al NP (aluminium nanoparticle) resulting in quantitative risk values based on limited and variable data. It was concluded that available data was too imprecise to make definite decisions about the risk of the individual NMs; however, preliminary classifications could be done. According to this risk categorization, the materials were awarded the highest indices for the following risk groups: C_{60} - medium risk; MWCNT - medium risk; CdSe - high risk; Ag NP - medium risk; and Al NP - low risk and very low risk.

A study from Mueller and Nowack, (2008) attempted to model the exposure of certain NPs (nano Ag, nano TiO_2 and CNTs) in the environment. The authors also included a risk assessment by calculating risk quotients for each NM by rough estimations of PEC and PNEC values. According to this estimation nano TiO_2 may pose a risk to water organisms, nano-Ag poses little or no risk for both soil and water organisms, and CNTs also pose little or no risk for water and air organisms. Models like this may lead to confusion. There are several issues that must be taken into account when looking at the results from this model. The estimations and modelled results are as good as the raw data is. In the case of NMs the raw data is inadequate, and estimations and uncertainties are used instead. The case of NP-silver in this model needs to be explained. The model looks at the risk of nano-silver. The toxicity mechanism of nano-silver is not evaluated and *per se* is much less toxic than ionic silver. The release of silver in the form of nanoparticles is of inferior importance compared to the release of ionic Ag from the nanoparticles. The results for the toxicity of silver from this model contradicts the toxicity of silver according Luoma (2008), where it was concluded that silver is toxic for water organisms (see chapter 5, p 37). This example is reminiscent of the risk assessment of pure chemicals in laboratory conditions which do not take into account the transformation of the chemical during metabolism or in the environment.

The first step in environmental risk assessment is environmental exposure assessment. In the case of nanomaterials used in products, the first challenge is to identify the chemical substance and its concentration used in the product. Herein lies the first problem. The information regarding these is scarce and currently based on voluntary information provided by the industries. The next step in environment risk assessment would be effects assessment. This was dealt with in section 5 and it can be concluded that studies are fragmented and often contradictory. This all leads to exposure scenarios that are very theoretical. Exposure assessment is critical for risk assessment. For an ideal assessment the exposure information should cover the product's whole life cycle from production, application and discharge.

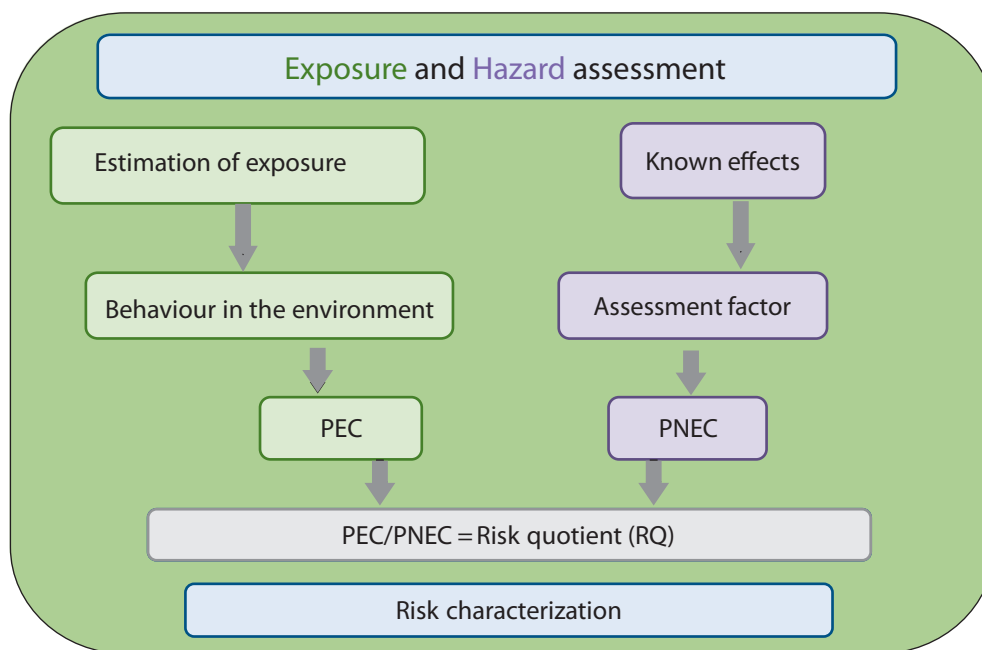


Figure 6. Risk characterization. Risk quotients are derived from PEC (Predicted Environmental Concentration) and PNEC (Predicted No Effect Concentration)

6.3

Risk perception and risk management

Nanotechnology first got attention in 2003 when it collided with the public for the first time. The term “nano” got the short end of the straw at that point in time. Michael Crichton published the bestseller *Prey* in November 2002. It tapped into existing fear of the potential new technologies where nanoscaled robots end up turning against their creators. In 2003 the Canadian environmental organization ETC produced a report called *The Big Down*. The report warns of the mass production of self-replicating nanomachinery, whose risks are incalculable. British MEP Caroline Lucas proposed a ban on products using nanotechnology. Even Prince Charles was concerned (Rantanen, 2005). Most of this concern was labelled as hysteria but the concerns were heard. In June of 2003 The Royal Society and The Royal Academy of Engineering launched its nanotechnology study and the European Parliament hosted the first seminar regarding Nanotechnology.

However the initial concern in 2003 did awake the great public, and nanotechnology is thought to be a promising new industry with a huge potential. Nanotechnology is breaking the tradition of a fear of new technologies (Kinnarinen, 2008). According

to Kinnarinen (2008), behaviourists are in awe as in the first time in history a new technology is being met without concerning scenarios. According to the article, the new technology is met with great optimism in technology according to Elizabeth Corley, Associate Professor of School of Public Affairs at Arizona State University.

However the tables seemed to have turned. It is claimed that the term “nano” is being dropped from fear of consumer recoil. It is becoming difficult to find reliable information about products that contains nanomaterials. According to Dr Andrew Maynard, chief science advisor in the Project of Emerging Nanotechnologies at the Woodrow Wilson Center, some companies have dropped the nano claim while still using nanotechnology. This could be an indication that nanotechnology is going underground. (EurActiv, 2009). A summary report of the completion of the EC’s Action Plan ANEC and BEUC established an inventory of the products using nanotechnology in the European Market. The first short inventory was produced in June 2009 and a long, updated version in November 2009. It was noticed that some products initially promoted as including nanotechnology abandoned those claims for the latter inventory. This could be caused by a change in the perception of market advantages or fears of negative public perceptions. (EC summary report for Nanosciences and nanotechnologies: An Action Plan for Europe 2005-2009).

As nanotechnology increases it is certain that the term “nano” will become a more common word for the public and in the media. Past experiences have shown that unaddressed public concerns have turned into consumer fears. Several consumer studies have been conducted, mostly in the USA and a few in Europe. On a very general level the surveys found a very low level of awareness, and positive or neutral attitudes about the relative benefits and risks concerning nanotechnology (FAO/WHO, 2009).

A summary report of the completion of the European Commission’s ‘Nanosciences and nanotechnologies (An Action Plan for Europe 2005-2009) highlighted a few important issues for consideration. These include: close the knowledge gap, update test methods and guidelines on harmful properties and exposure, identify products in the market place, consider incentives, and strengthen international cooperation. The first issues have already been addressed in this report and they cannot be emphasized more. Without enough scientific knowledge, risk assessments are impossible to make. One of the problems has been the lack of data from the companies whose products use nanomaterials. The EC summary report suggests that a mandatory registration might need to be considered.

7 Nanotechnology and nanomaterials in life cycle assessment

Life cycle assessment (LCA) quantifies all resources consumed, emissions, and the associated environmental and health impacts connected with the goods and services within its full life cycle (European Commission, ILCD handbook, 2010). The aim is to make comparisons between products or services so as to be able to choose between them. The procedure has been published as international standards aiming for a structured and comprehensive method (ISO 14040; ISO 14044). According to these standards, the life cycle assessment is carried out in 4 distinct phases: goal and scope, life cycle inventory, life cycle assessment, and interpretation. The applicability of LCA methods to nanomaterials has been a cause of debate. A workshop comprised of international experts from the field of both nanotechnology and LCA have concluded that the ISO framework is fully suitable for all stages of the life cycle of nanotechnology and nanoproductions (Klöpffer, 2007).

Despite the fact that nanotechnology is often described as a future technology, few realize that NMs are already being used in a wide variety of consumer products. The estimations of NM used in various applications are increasing. This will indisputably lead to increased exposure to both the environment and humans alike. Very few producers/distributors provide information about the content of the NMs in their products (Hansen *et al.*, 2008a). For example, sunscreens may contain up to 10 % of nano TiO₂ at the moment of production. Li-batteries conventionally use carbonaceous materials in the cathode as 6 wt. %. With CNTs this is reduced to 0.1 wt.% (Nanda, 2008).

Large scale use of NMs may lead to high degree of eco-efficiency, although NMs are not *per se* environmental friendly. Results of LCA comparisons reveal that nanotechnological applications do not exclusively offer environmental-friendly solutions (Steinfeldt *et al.*, 2007). Therefore, a case-wise analysis is necessary (Becker *et al.*, 2009). Use of NMs may reduce the exploitation of natural resources by decreasing the amount of material and use of energy. Energy may be saved during the production of smaller, lighter and more durable items. As a result the energy needed for transport per unit will also decrease. Concerning the production stage, energy savings of almost 50 % were calculated in the manufacturing of styrene using nano-fibers, and considering all emissions in surface coating industry very high eco-efficiency could be concluded (Steinfeldt *et al.* 2007). In other cases (lighting industry and displays) the material and energy savings are more uncertain (Steinfeldt *et al.*, 2007). Manufacturing the nano-sized material may need a lot of energy as does the concentration and purification of rare elements.

Even though nanotechnology has been promoted as a technology that can provide applications to decrease energy consumptions, alternate opinions are also present. Energy consumption should not only be looked at in terms of the electricity use of the device but the energy consumption of the manufacturing process should be considered. High-tech gadgets are produced by means of extremely material- and energy-intensive manufacturing process (De Decker, 2009). Reports from the International

Energy Association and the British Energy Saving Trust both estimate that energy consumption for electric devices (computers, cell phones, flat screen TVs, iPods etc.) will double within ten years and triple within 20 years. Here lies the paradox: even though technology becomes more energy efficient, the energy consumption increases (De Decker, 2009).

It is hard to obtain reliable data and up-to-date figures on energy consumed during the production phase. A life cycle analysis of a high-tech product is very complex and can take years. The manufacturing of carbon nanotubes and single walled nanotubes requires 20 000-50 000 MJ per kilogram of material. Recycling does not work for NMs because all the energy is concentrated on the manufacturing process, and so many of the large-scale applications proposed for CNTs cannot be possible purely because of energy requirements (De Decker, 2009).

Nowack (2009) presented a list of open questions waiting for answers before reliable LCA will be possible:

- how and in what quantities will synthetic NMs from products be released in the surroundings
- what level of contamination is to be expected in natural waters or soil
- analytical methods capable of detecting low levels of NMs
- the effects on the biota caused by these low concentrations

LCA meets several challenges when dealing with NMs and safety issues e.g. regarding SWCNTs and so it is important to understand the purity of the material and uniformity as well as functionality and characteristics in the end-use application. SWCNTs may contain only 10 % by mass of actual nanotubes (Seager and Linkov, 2008). At the moment it is not known whether toxicity assessment can be based on mass concentrations or should surface properties, functionalization, interaction with environmental media and microbial activity be taken into account in a way not described in terms of mass or volume concentrations. Compared to conventional chemicals with relative stability or with hundreds of different formulations, even SWCNTs may entail thousands or tens of thousands of different varieties with typical (eco)toxicological dose-response relationships. In the final application the relationship between SWCNT content and functionality may be dependent on the synthesis and purification method. This leads to uncertainties in the life cycle inventories based on mass.

Reuse, recycling and waste management of NM-containing products may not be straightforward. The life cycle assessment (LCA) should also take into account the end-of-life analysis. So far the life cycle stages that have been assessed include extraction, production and use phases, while little attention has been paid to the end-of-life stage (Bauer *et al.*, 2008). Olapiriyakul and Caudill (2009) showed that the energy required to recycle from lithium-ion batteries was higher for batteries with nano-metal than for similar conventional ones. This example provides an instance where the nano-form has effects for the LCA even after the actual product has already been used.

The study of the environmental effects of NMs is still in the early stages. The situation is characterized by a general lack of data. Additionally, the number of NMs in all of their various forms is huge, and therefore their applications are wide-ranging. Consequently, it is unfortunate that any comprehensive advice that would be easily and widely applicable is not possible to present. The following box/table represents general issues that should be taken into consideration when applying LCA to nanomaterials. It is recommended to bear in mind that not all issues are appropriate for all cases and common sense should be applied. Also the goal and scope of the LCA will determine the issues to be looked at. Naturally a cradle-to-grave LCA would be recommended.

Table 6. Summary of published life cycle assessments on various nanomaterials/nanoproducts.

Study	Product	Assessment type	Impacts assessed	Outcome
Healy <i>et al.</i> , 2008.	single walled carbon nanotube processes	LCI for materials and energy	Acidification, eutrophication, land use, mineral depletion, ecotoxicity, ozone layer depletion, and carcinogens, as well as organic and inorganic oxides, respiratory organics (SimaPro- software).	Life cycle impacts dominated by energy, of processes HiPco process lowest environmental load, CVD 2.4 times that and arc ablation 5.8 of HiPco process
Joshi, 2008.	Silicate biopolymer nanocomposite	Environmental sustainability, cradle-to-gate, comparison between	Energy requirements, global warming potential, environmental burden (CO ₂ , CO, SO _x , NO _x emissions, particulate matter, BOD, COD, nitrates and sulphates to water)	Biopolymers can potentially lower energy requirements and global warming potential, per kilogram basis environmental burden worse for nanoclays than natural fibres on most dimensions
Khanna <i>et al.</i> , 2008.	Carbon nanofibre production	Cradle-to-gate	Energy requirements, global warming potential, human toxicity potential, ozone layer depletion potential, photochemical oxidation potential, eutrophication and acidification potential, freshwater and terrestrial ecotoxicity potential.	On a per mass basis life cycle energy requirements for producing CNFs is 13-50 times greater compared to primary aluminium production, CNF greater life cycle environmental impact in all impact categories.
Krishnan <i>et al.</i> , 2008.	Semiconductor microprocessor	Hybrid LCI	Energy requirements, global warming potential	Total primary energy required upstream and device manufacturing 14 100 MJ/wafer
Kushnir and Sanden, 2008.	Carbon nanotube and fullerene synthesis	Cradle-to-gate cumulative energy requirements for life cycle.	Energy requirements	2-100 times more energy intensive than aluminium
Lloyd and Lave, 2003.	Nanocomposite automobile panelling	EIO-LCA	Non-renewable energy use, global warming potential, toxic releases, cost	Cost higher of nanocomposite, potential in reducing energy use and environmental discharges
Lloyd <i>et al.</i> , 2005.	Nanoscale platinum-group metals in automobile catalysts	EIO-LCA, GaBi software	Non-renewable energy use, resources use, global warming potential, toxic releases, cost-effectiveness	Potential in reducing energy, improving environmental quality and contributing to sustainable resource usage.
Olapiriyakul and Caudil, 2009.	NM containing Li-ion batteries	Thermodynamic analysis during EOL stage	Energy utilization and global warming potential during EOL processing stage	Increase in melting temperatures results in increased energy consumption and higher levels of carbon dioxide emissions.
Osterwalder <i>et al.</i> , 2006.	Production of oxide nanoparticles	LCI, cradle-to-gate	Energy requirements and global warming potential between wet and dry processes	Energy requirements rationalized by different production classes and complexity.
Roes <i>et al.</i> , 2007.	Polypropene layered silicate nanocomposite	Prospective LCA and LCC comparison between conventional and NM	(SimaPro), non-renewable energy use, global warming potential, abiotic depletion, ozone layer depletion, photochemical oxidant formation, acidification, eutrophication	the production of nanoclays and their incorporation in nanocomposites have an impact on the environment that may be compensated for if the weight reduction resulting from the use of nanocomposites is large enough.

BOD, biological oxygen demand; COD, chemical oxygen demand; HiPco, high-pressure carbon monoxide; CVD, chemical vapour deposition; EIO-LCA, Economic Input – Output; EOL, end of life; assessment type, (impacts assessed) and outcome stated as in referred studies.

Questions to be addressed when doing LCA for products containing NMs	
Production phase	
	<ul style="list-style-type: none"> • manufacturing process of NMs; energy efficiency, discharges to environment,
	<ul style="list-style-type: none"> • environmental fate of released materials, occupational health
	<ul style="list-style-type: none"> • sustainable use of natural resources, especially when trace elements exploited
	<ul style="list-style-type: none"> • characteristics of the NM itself: safety data of the substance, occupational health, public health, environmental safety
	<ul style="list-style-type: none"> • compare production using NMs with conventional material, and use the best and least harmful technology
Use phase	
	<ul style="list-style-type: none"> • energy use and emissions, consider potential to climate change during the whole life time of the product
	<ul style="list-style-type: none"> • environmental effects due to wear and tear of NMs
	<ul style="list-style-type: none"> • sustainable consumption; life time of the product compared to conventional products
	<ul style="list-style-type: none"> • compare conventional products with NMs/NT (when possible) using relevant units
	<ul style="list-style-type: none"> • societal impacts (risk/benefit assessment, public opinion)
Waste management	
	<ul style="list-style-type: none"> • recycling of nanomaterial-containing components, and the NM itself
	<ul style="list-style-type: none"> • recovery of energy
	<ul style="list-style-type: none"> • properties of the landfill waste e.g. leaching of materials

Currently, there are few LCA studies related to nanomaterials. Many studies have focused on the cradle-to-gate -assessments, thus excluding the application and disposal stages. No LCA study on nanomaterials according to the standardized methodology is available so far (Bauer *et al.*, 2008). Studies have so far concerned only certain aspects of the use of nanomaterials and LCA. Table 6 summarizes the current LCA studies done with nanomaterials. This is not claimed to be an exhaustive list, but merely the summary of relevant studies that were found in scientific journals up to this date.

These analyses are not full LCAs but can give information about potential benefits and disadvantages related to the use of NMs. Limitations come from obtaining comprehensive, high-quality data for carrying out rigorous LCAs, especially in the field of new emerging technologies (Joshi, 2008). A comparison between various synthesis routes concluded that the product itself determines the method of synthesis; Simple compositions often require less complex routes and materials than novel preparations (Osterwalder *et al.*, 2006). When estimates of production processes come from internal private industries, there is a lack of transparency and independent variability in the data (Joshi, 2008). When costs are compared, new technologies, and market prices will have an effect on the outcome.

Steinfeldt *et al.*, (2010) have researched the environmental and sustainability opportunities and risks associated with nanotechnology. The focus was placed on the potential environmental relief provided by nanotechnology products and processes. The study was conducted with the modelling of individual case studies with the LCA software Umberto. The chosen nanotechnology applications were: manufacture of solderable surface finishes on printed circuit boards by means of nanotechnology, MWCNT application for foils in the semiconductor industry, lithium batteries for energy storage, and Ultradur® High Speed plastic. The results show that these applications cannot be intrinsically nor exclusively associated with the potential for a large degree of environmental relief.

As previous sections have shown, there is a lack of reliable data concerning several properties related to NMs. Until a reasonable amount of environmentally relevant data is available, the environmental impact assessment of NMs is inadequate. At the moment there seems not to be enough data to generalize the environmental effects of NMs (Steinfeldt, *et al.*, 2007). Systematic investigations on the whole life-cycle of NMs will be a challenge to LCA assessors. There seems to be no consensus on the optimal framework of nano-management systems and how to use the sustainable engineering frameworks both as proactive and nano-specific (Greenberg, 2006).

The nanotechnology is based on the fact that NMs possess novel properties that differ from the properties seen in the bulk material. The NNI definition for nanotechnology includes the fact that the properties are different from those seen in material in bulk. The unique properties encompassed with NMs have been misapprehended in legislation, the LCA and some ecotoxicological studies. There is on-going research in this area (e.g. NTs as a case study in PROSUITE, an EU-funded project 2009-2013) producing new information, hopefully also methodological improvements to cope with NTs.

OECD organized a conference in July, 2009 (Møller Christensen, 2010) summing up six general recommendations for the LCA of NTs:

- comparative assessment of the up-to-date non-nano applications with the nano
- scarce materials like indium, cerium and lithium, taking the net consumption and recycling options into account
- energy consumption in manufacturing the NMs as well as during deposition and recycling
- consider emissions of toxic chemicals during manufacturing and the whole life span of the products
- inventories of the loss of NMs throughout the life cycle
- careful and honest assessment and interpretation of health and safety data

It seemed impossible to make a comprehensive list of key issues, but obviously LCA would be most helpful in comparing non-nano and nanotechnologies. Without doubt this is a relevant starting point, whenever there is a conventional technology comparable to NTs. As nanotechnological innovations produce novel materials and products, comparisons will be impossible. Current knowledge on the behaviour of NMs in the environment, and the common tendency to aggregate, suggest that at least the energy in manufacturing the materials in nanoform will be lost to a high extent. This does not exclude the recyclability of the elements themselves.

REFERENCES

- Adams, L.K., Lyon, D.Y. & Alvarez, P.J.J., 2006. Comparative eco-toxicity of nanoscale TiO₂, SiO₂ and Zn water suspensions. *Water Res.*, 40, 3527-3532.
- Aitken, R.J., Chaudry, M.Q., Boxal, A.B.A. & Hull, M., 2006. Manufacture and use of nanomaterials: current status in the UK and global trends. *Occup. Med.*, 56, 300-306.
- BEUC & ANEC, 2009. Nanotechnology: Small is beautiful but is it safe? ANEC and BEUC leaflet on nanotechnology and nanomaterials, 2009.
- Battin, T.J., von der Kammer, F., Weillhartner, A., Ottofuelling, S. & Hofman, T., 2009. Nanostructured TiO₂. Transport behavior and effects on aquatic microbial communities under environmental conditions. *Environ. Sci. Technol.*, 43, 8098-8104.
- Bauer, C., Buchgeister, J., Hischier, R., Poganietz, R., Schebek, L. & Warsen, J., 2008. Towards a framework for life cycle thinking in the assessment of nanotechnology. *J. Clean. Prod.*, 16, 910-926.
- Baun, A., Hartmann, N.N., Grieger, K. & Kusk, K.O., 2008. Ecotoxicity of engineered nanoparticles to aquatic invertebrates: a brief review and recommendations for future toxicity testing. *Ecotoxicology*, 17, 387-395.
- Baun, A., Hartmann, N.B., Grieger, K.D. & Hansen, S.F., 2009. Setting limits for engineered nanoparticles in European surface waters - are current approaches appropriate. *J. Environ. Monitor.*, 11, 1774-1781.
- Becker, H., Dubbert, W., Schwin, K. & Völker, D., 2009. Nanotechnik für Mensch und Umwelt, Chancen fördern und Risiken mindern. Deutschland: Umweltsbundesamt (UBA). http://www.umweltbundesamt.de/uba-info-medien/mysql_medien.php?enfrage=Kennnummer&Suchwort=3765.
- Benn, T. M. & Westerhoff, P., 2008. Nanoparticle silver released into water from commercially available sock fabrics. *Environ. Sci. Technol.*, 42, 4133-4139.
- Bilberg, K., Malte, H., Wang, T. & Baatrup, T., 2010. Silver nanoparticles and silver nitrate cause respiratory stress in Eurasian perch (*Perca fluviatilis*). *Aqua. Toxicol.*, 93, 159-165.
- Boxall, A.B.A., Chaudry, Q., Sinclair, C., Jones, A., Aitken, R., Jefferson, B. & Watts, C., 2007. Current and future predicted environmental exposure to engineered nanoparticles. San Hutton, York, UK . Central Science Laboratory. http://randd.defra.gov.uk/Document.aspx?Document=CB01098_6270_FRP.pdf
- Bradford, A., Handy, R.D., Readman, J.W., Atfield, A. & Muhling, M., 2009. Impact on Silver nanoparticle contamination on the genetic diversity of Natural Bacterarial Assemblages in Estuarine Sediments. *Environ. Sci. Technol.*, 43, 4530-4536.
- BSI (British Standards Institution), 2007. Nanotechnologies - Part 1: good practice guide for specifying manufactured nanomaterials. London: British Standadrs Institution.
- Cao, G., 2004. Nanostructures & Nanomaterials: Synthesis, Properties and Applications. London: Imperial College Press.
- Choi, O., Deng, K.K., Kim, Y., Ross Jr, L., Surampalli, Y. & Hu, Y., 2008. The inhibitory effects of silver nanoparticles, silver ions, and silver chloride colloids on microbial growth. *Water Res.*, 42, 3066-3074.
- Christian, P., Von der Kammer, F., Baalousha, M. & Hofmann, Th., 2008. Nanoparticles: structure, properties, preparation and behaviour in environmental media. *Ecotoxicology*, 17, 326-343.
- Clough, S.R. 2009. The Potential Ecological Hazard of Nanomaterials. In: Sellers, K., Mackay, C., Bergeson, L.L., Clough, S.R., Hoyt, M., Chen, J. and Hamblen, J., (eds.). *Nanotechnology and the Environment*. Boca raton: CRC Press. Pp. 169-192.
- Darlington, T.K., Neigh, A.M., Spencer, M.T., Nguyen, O.T. & Oldenburg, S.J., 2008. Nanoparticle characteristics affecting environmental fate and transport through soil. *Environ. Toxicol. Chem.*, 28, 1191-1199.
- Davies, J.C., 2009. Oversight of next generation nanotechnology. <http://www.nanotechproject.org/publications/archive/pen18/>.
- De Decker, K., 2009. The monster footprint of digital technology. *Low Tech magazine*, 16 June 2009. <http://www.lowtechmagazine.com/2009/06/embodied-energy-of-digital-technology.html> [Accessed 21.4.2010].
- Domingos, R.F., Tufenkji, N. & Wilkinson, K. J., 2009a. Aggregation of titanium dioxide nanoparticles: role of a fulvic acid. *Environ. Sci. Technol.* 43(5), 1284-1286.
- Domingos, R.F., Baalousha, M.A., Ju-Nam, Y., Reid, M.M., Tufenkji, N., Lead, J.R., Leppard, G.G. & Wilkinson, K.J., 2009b. Characterizing manufactured nanoparticles in the environment: multimethod determination of particle sizes. *Environ. Sci. Technol.*, 43, 7277-7284.
- Dwahan, A., Sharma, V. & Parmar, D., 2009. Nanomaterials: a challenge for toxicologist. *Nanotoxicology*, 3(1), 1-9.
- EC summary report for Nanosciences and nanotechnologies: An Action Plan for Europe 2005-2009. http://ec.europa.eu/nanotechnology/index_en.html
- EPA (United States Environmental Protection Agency), 2007. Nanotechnology White Paper. EPA 100/B-07/001 February, 2007. <http://www.epa.gov/osa/pdfs/nanotech/epa-nanotechnology-whitepaper-0207.pdf>
- EurActiv, 2009. Nanotech claims "dropped" for fear of consumer recoil. *EurActiv.com*, 15 June 2009. <http://www.euractiv.com/en/science/nanotech-claims-dropped-fear-consumer-recoil/article-183183> [Accessed 15 March 2010].
- European Commission, 2010. ILCD Handbook. <http://lct.jrc.ec.europa.eu/publications>

- Evident Technologies, 2008. How quantum dots works. <http://www.evidenttech.com/quantum-dots-explained/how-quantum-dots-work.html> [Accessed 10 June 2010].
- Fang, J., Lyon, D.Y., Wiesner, M.R., Dong, Y. & Alvarez, P.J.J., 2007. Effect of a fullerene Water Suspension on Bacterial Phospholipids and Membrane Phase Behavior. *Environ. Sci. Technol.*, 41, 2636-2642.
- FAO/ WHO (Food and Agriculture of the United Nations/ World Health Organization), 2009. FAO/ WHO Expert meeting on the Application of Nanotechnologies in the Food and Agricultural Sectors: Potential Food Safety Implications. Meeting Report. Rome. http://www.fao.org/ag/agn/agns/files/FAO_WHO_Nano_Expert_Meeting_Report_Final.pdf
- Farré, M., Gajda-Schranz, K., Kantiani, L. & Barcelo, D., 2009. Ecotoxicity and analysis of nanomaterials in the aquatic environment. *Anal. Bioanal. Chem.*, 393, 81-95.
- Farré, M., Pérez, S., Gajda-Schranz, K., Osorio, V., Kantiani, L., Ginebreda, A. & Barceló, D., 2010. First determination of C₆₀ and C₇₀ fullerenes and N-methylfulleropyrrolidine C₆₀ on the suspended material of wastewater effluents by liquid chromatography hybrid quadrupole linear ion trap tandem mass spectrometry. *J. Hydrology* 383, 44 – 51.
- Federici, G., Shaw, B.J. & Handy, R.D., 2007. Toxicity of titanium oxide nanoparticles to rainbow trout (*Oncorhynchus mykiss*): Gill injury, oxidative stress, and other physiological effects. *Aquat. Toxicol.*, 84, 415-430.
- French, R.A., Jacobson, A.R., Kim, B., Isley, S.L., Penn, R.L. & Baveye, P.C., 2009. Influence of ionic strength, pH and cation valence on aggregation kinetics of titanium dioxide nanoparticles. *Environ. Sci. Technol.*, 43(5), 1354-1359.
- Gao, J. & Xu, B., 2009. Applications of nanomaterials inside cells. *Nano Today* 4, 37-51.
- Geranio, L., Heuberger, M. & Nowack, B., 2009. The Behaviour of Silver Nanotextiles during Washing. *Environ. Sci. Technol.*, 43, 8113-8118.
- Gottschalk, F., Sonderer, T., Scholz, R.W. & Nowack, B., 2009. Modeled Environmental Concentrations of Engineered Nanomaterials (TiO₂, ZnO, Ag, CNT, Fullerenes) for Different Regions. *Environ. Sci. Technol.* 43, 9216-9222.
- Greenberg, M.R., 2006. Gap Analyses of Environmental Management Frameworks for Nanotechnology. Proceedings of the 2006 Systems and Information.
- Hall, S., Bradkey, T., Moore, J.T., Kuykindall, T. & Minella, T., 2009. Acute and chronic toxicity of nano-scale TiO₂ particles to freshwater fish, cladocerans, and green algae, and effects of organic and inorganic substrate on TiO₂ toxicity. *Nanotoxicology*, 3(2), 91-97.
- Handy, R.D., von der Kammer, F., Lead, J.R., Hassellöv, M., Owen, R. & Crane, M., 2008a. The ecotoxicity and chemistry of manufactured nanomaterials. *Ecotoxicology*, 17(4), 287-314.
- Handy, R.D., Henry, T.B., Scown, T.M., Johnston, B.D. & Tyler, C.R., 2008b. Manufactured nanoparticles: their uptake and effects on fish - a mechanistic analysis. *Ecotoxicology*, 17, 396-409.
- Hansen, S.F., Larsen, B.H., Olsen, S.I. & Baun, A., 2007. Categorization framework to aid hazard identification of nanomaterials. *Nanotoxicology*, 1, 243-50.
- Hansen, S.F., Mickelson, E.S., Kamper, A., Borling, B., Stuer-Lauridsen, F. & Baun, A., 2008a. Categorization framework to aid exposure assessment of nanomaterials in consumer products. *Ecotoxicology*, 17, 438-445.
- Hansen, S.F., Maynard, A., Baun, A. & Tickner, J.A., 2008b. Late lessons from early warnings for nanotechnology. *Nat. Nanotechnol.*, 3, 444-447.
- Hassellöv M., Readman J.W., Ranville J.F. & Tiede K., 2008. Nanoparticle analysis and characterization methodologies in environmental risk assessment of engineered nanoparticles. *Ecotoxicology* 17, 344-361.
- Hoyt, M. 2009. Analyses of Nanoparticles in the Environment. In: Sellers, K., Mackay, C., Bergeson, L.L., Clough, S.R., Hoyt, M., Chen, J. and Hamblen, J., (eds.). *Nanotechnology and the Environment*. Boca Raton: CRC Press. Pp. 99-122.
- Healy, M.L., Dahlben, L.J. & Isaacs, J.A., 2008. Environmental Assessment of Single-Walled Carbon Nanotube Processes. *J. Ind. Ecol.*, 12, 376-393.
- Hund-Rinke, K. & Simon, M., 2006. Ecotoxic effect of photocatalytic active nanoparticles (TiO₂) on algae and daphnids. *Environ. Sci. & Pollut. Res.*, 13(4), 225-232.
- Iijima, S., 1991. Helical microtubules of graphite carbon. *Nature*, 354, 56-58.
- ISO 14040:2006. Environmental management – Life cycle assessment – Principles and framework. International Organization for Standardization, Geneva.
- ISO 14044:2006. Environmental management – Life cycle assessment – Requirements and guidelines International Organization for Standardization, Geneva.
- Jarvie, P.H., Al-Obaidi, H., King, S.M., Bowes, M.J., Lawrence, M.J., Drake, A.F., Green, M.A. & Dobson, P.J., 2009. Fate of silica nanoparticle in simulated primary wastewater treatment. *Environ.Sci.Technol.* 42, 8622-8628.
- Joshi, S., 2008. Can Nanotechnology Improve the Sustainability of Biobased products? The Case of Layered Silicate Biopolymer Nanocomposites. *J. Ind. Ecol.*, 12(3), 474-489.
- Ju-Nam, Y. & Lead, J.R., 2008. Manufactured nanoparticles: An overview of their chemistry, interactions and potential environmental implications. *Sci. Total. Environ.*, 400, 396-414.
- Kaegi, R., Ulrich, A., Sinnet, B., Vonbank, R., Wichser, A., Zuleeg, S., Simmler, H., Brunner, S., Vonmont, H., Burkhardt, M. & Bolliger, M., 2008. Synthetic TiO₂ nanoparticle emission from the exterior facade into the aquatic environment. *Environ. Pollut.*, 156, 233-239.

- Kajander, J. and Koponen, P., 2008. Nanotechnology in Finnish industry 2008 –Survey Results. [online] Spinverse Consulting. Helsinki. Available at: http://akseli.tekes.fi/opencms/opencms/OhjelmaPor-taali/ohjelmat/NANO/fi/Dokumenttiarkisto/Viestinta_ja_aktivointi/Julkaisut/NIFI2008_presentation.pdf [Accessed at 10 February 2010].
- Keller, A.A., Wanf, H., Zhou, D., Lenihan, H.S., Cherr, G., Cardinale, B.J., Miller, R. & Ji, Z., 2010. Stability and Aggregation of Metal Oxide Nanoparticles in Natural Aqueous Matrices. *Environ. Sci. Technol.*, 44, 1962-1967.
- Khanna, V., Bakshi, B.R. & Lee, L.J., 2008. Carbon Nanofiber Production Life Cycle Energy Consumption and Environmental Impact. *J. Ind. Ecol.*, 12(3), 394-410.
- Kim, B., Park, C - S., Murayama, M. & Hochella Jr, M.F., 2010. Discovery and characterization of silver sulphide nanoparticles in final sewage sludge products. *Environ. Sci. Technol.* 44, 7509 – 7514.
- Kinnarinen, T, 2008. Nano murtaa pelon pitkän perinteen. *Tiede*, 4.2.2008. http://www.tiede.fi/artikkeliki/860/nano_murtaa_pelon_pitkan_perinteen#860.
- Klaine, S.J., Alvarez, P.J.J., Batley, G.E., Fernandes, T.F., Handy, R.D., Lyon, D.Y., Mahendra, S., McLaughlin, M.J. & Lead, J.R., 2008. Nanomaterials in the environment: Behaviour, fate, bioavailability and effects. *Environ Toxicol Chem.*, 9, 1825-1851.
- Klöppfer, W., 2006. Nanotechnology and Life Cycle Assessment. Synthesis of Results Obtained at a Workshop Washington DC, 2-3 October 2006. http://www.nanotechproject.org/file_download/files/NanoLCA_3.07.pdf.
- Krishnan, N., Boyd, S., Somani, A., Raoux, S., Clark, D. & Dornfeld, D., 2008. A Hybrid Life Cycle Inventory of Nano-Scale Semiconductor manufacturing. *Environ. Sci. Technol.*, 42, 3069-3075.
- Kroto, H.W., Heath, J.R., O'Brian, S.C., Curl, R.F. & Smalley, R.E., 1985. C60: Buckminsterfullerene. *Nature*, 318, 162-163.
- Kukkonen, L., 2010. Nanomaterials in the food chain. HENVI Science Day 2010: Man made Substances and Environment - Multidisciplinary Research on Risks and Future Possibilities. <http://www.helsinki.fi/henvi/research/presentations10/ScienceDay2010/kukkonenLiv.pdf>
- Kushnir, D. & Sanden, B.J., 2008. Energy Requirements of Carbon Nanoparticle Production. *J. Ind. Ecol.*, 12(3), 360-375.
- Lam, C., James, J.T., McCluskey, R. & Hunter, R.L. 2004. Pulmonary toxicity of Single-Wall Carbon Nanotubes in Mice after 7 and 90 Days after Intratracheal Instillation. *Toxicol. Sci.*, 77, 126-134.
- Lam, C., James, J.T., McCluskey, R., Arepalli, S. & Hunter, R.L., 2006. A Review of Carbon Nanotube Toxicity and Assessment of Potential Occupational and Environmental Health Risks. *Crit. Rev. Toxicol.*, 36, 189-217.
- Lekas, D., 2005. Analysis of nanotechnology from an industrial ecology perspective. Part II: Substance flow analysis of carbon nanotubes. Revised Draft - November 2005. http://www.nanotechproject.org/publications/archive/analysis_nanotechnology_from_an/
- Lien, H. & Zhang, W., 2001. Nanoscale iron particles for complete reduction of chlorinated ethenes. *Colloid. Surface*, 191, 97-105.
- Lloyd, S. M., Lave, L.B. and Matthews, H.S., 2005. Life Cycle Benefits of Using Nanotechnology To Stabilize Platinum-Group Metal Particles in Automotive Catalysts. *Environ. Sci. Technol.*, 39, 1384-1392.
- Lloyd, S.M. & Lave, L.B., 2003. Life Cycle Economic and Environmental Implications of Using Nanocomposites in Automobiles. *Environ. Sci. Technol.*, 37, 3458-3466.
- Luoma, S.N., 2008. Silver nanotechnologies and the environment: old problems or new challenges. <http://www.nanotechproject.org/publications/archive/silver/>.
- Lux Research., 2006. The nanotech report, 4th ed. http://www.luxresearchinc.com/pdf/TNR4_TOC.pdf
- Lux Research., 2008. Nanomaterials State of the Market Q3 2008: Stealth Success, Broad Impact. <https://portal.luxresearchinc.com/research/document/excerpt/3735> [The full contents are available to clients of the Lux Research Nanomaterials Intelligence service].
- Mackay, C.E. & Henry, K.M. 2009. In Sellers, J. et al, ed. *Nanotechnology and the Environment*. Boca Raton: CRC Press Taylor & Francis. Chapter 7.
- Madden, A.S. & Hochella Jr, M.F., 2005. A test of geochemical reactivity as a function of mineral size: Manganese oxidation promoted by hematite nanoparticles. *Geochem. Cosmochim. Acta.*, 69, 389-398.
- Madden, A.S., Hochella Jr, M.F. & Luxton, T.B., 2006. Insights for size-dependant reactivity of hematite nanomineral surfaces through Cu²⁺ sorption. *Geochem. Cosmochim. Acta.* 70, 4095-4104.
- Milmo, S. 2009. Nanomaterials cause classification headache for REACH, *Chemistry World*, 15 June 2009. <http://www.rsc.org/chemistryworld/News/2009/June/16060901.asp>.
- Muller, J., Huaux, F., Moreau, N., Misson, P., Heilier, J.-F., Delos, M., Arras, M., Fonseca, A., Nagy, J.B. & Lison, D., 2005. Respiratory toxicity of multi-walled carbon nanotubes. *Toxicol. Appl. Pharmacol.*, 207, 221-231.
- Mueller, N.C. & Nowack, B., 2008. Exposure Modelling of Engineered nanoparticles in the Environment. *Environ. Sci. Technol.*, 42, 4447-4453.
- Møller Christensen, F., 2010. Reflections from an OECD workshop on environmental benefits of nanotechnology. General issues to consider when doing LCA on nanotechnology-facilitated applications. *Int. J. Life Cycle Assess.*, 15, 137-138.
- Nanda, J. 2008. Nanomaterials for energy storage and conversion, *Auto Focus Asia*, 3/2008. http://www.autofocusasia.com/production_manufacturing/nanotechnology_for_automotives.htm.
- Nanotechnology facts and figures. *Nature Nanotechnology*, Evident Technologies, 2008. How quantum dots work. <http://www.evidenttech.com/quantum-dots-explained/how-quantum-dots-work.html> [Accessed 10 June 2010].

- Navarro, E., Baun, A., Behra, R., Hartmann, N.B., Filser, J., Miao, A., Quiq, A., Santschi, P.H. & Sigg, A., 2008. Environmental behaviour and ecotoxicity of engineered nanoparticles to algae, plants and fung. *Ecotoxicology*, 17, 372-386.
- Nowack, B. & Bucheli, T.D., 2007. Occurance, behavior and effects of nanoparticles in the environment. *Environ. Pollut.*, 150, 5-22.
- Nowack, B., 2009. Is anything out there? What life cycle perspectives of nano-products can tell us about nanoparticles in the environment. *Nano Today*, 4, 11-12.
- Oberdörster, E., Zhu, S., Blickney, T.M., McClellan-Green, P. & Haasch, M.L. 2006. Ecotoxicology of carbon based-based engineered nanoparticles: Effects of fullerene (C₆₀) on aquatic organisms. *Carbon*, 44, 1112-1120.
- OECD, 2008. Working Party on manufactured nanomaterials. List of manufactured nanomaterials and a list of endpoints for phase one of the OECD testing programme. Series on the safety of manufactured nanomaterials (Number 6). Paris. [http://appliance.oecd.org/olis/2008doc.nsf/linkto/env-jm-mono\(2008\)13-rev](http://appliance.oecd.org/olis/2008doc.nsf/linkto/env-jm-mono(2008)13-rev)
- Olapiriyakal, S. & Caudil, R.J., 2009. Thermodynamic analysis to assess the environmental impact of end of life recovery processing for nanotechnology products. *Environ. Sci. Technol.*, 43, 8140-8146.
- Osterwalder, N., Capello, C., Hungerbühler, K. & Stark, W.J., 2006. Energy consumption during nanoparticle production: How economic is dry synthesis. *J. Nanopart. Res.*, 8, 1-9.
- Pylkkänen, L., Alenius, H., Tuomi, T. and Savolainen, K., 2007. The effect of nanoparticles on the expression of mRNA and proteins of chemokines and cytokines in inflammatory cells in the lungs. In: *Proceedings of the Sixth Princess Chulabhorn International Science Congress: November 25-29, 2007: Bangkok, Thailand*. Pp. 237-241.
- Rantanen, K., 2005. Nanotekniikkaa turha pelätä. *Tiede*, 23.3.2005 http://www.tiede.fi/artikkeli/47/nanotekniikkaa_on_turha_pelata#47.
- Rao, G., Lu, C. & Su, F., 2007. Sorption of divalent metal ions from aqueous solution by carbon nanotubes: A review. *Sep. Purif. Technol.*, 58(1), 224-231.
- Roco, M.C., 2004. Nanoscale Science and Engineering: Unifying and Transforming Tools. *AIChE Journal*, 5, 890-897.
- Roco, M.C., 2007. National Nanotechnology Initiative - Past, Present Future. In: Goddard, W.A., Brenner, D.W., Lyshevski, S.E. and Iafrate, G.J., (eds.). *Handbook of Nanoscience, Engineering, and Technology*. Boca Raton: CRC Press. Pp. 3.1-3.26.
- Roes, A.L., Marsili, E., Nieuwlaar, E. & Patel, M.K., 2007. Environmental and Cost Assessment of a Polypropylene Nanocomposite. *J. Polym. Environ.*, 15, 212-226.
- The Royal Society and The Royal Academy of Engineers, 2004. *Nanosciences and nanotechnologies: opportunities and uncertainties*. London. <http://www.nanotec.org.uk/finalReport.htm>
- Saleh, N., Kim, H-J., Phenrat, T., Matyjaszewski, K., Tilton, R.D. & Lowry, G.W., 2008. Ionic strength and composition affect the mobility of surface-modified Fe₀ nanoparticles in
- Sass, J., 2007. *Nanotechnology's invisible threat: Small science, big consequences*. New York: Natural Resources Defence Council. <http://www.nrdc.org/health/science/nano/nano.pdf>
- Savolainen, K., Alenius, H., Norppa, H., Pylkkänen, L., Tuomi, T. & Kasper, G., 2010. Risk assessment of engineered nanomaterials and nanotechnologies – A review. *Toxicology* 269, 92-104.
- Savolainen, K., 2009. Engineered nanomaterials. *Afr Newsletter on Occup Health and Safety*, 19, 67-69.
- Scenhir (Scientific Committee on Newly Identified Health Risks), 2007. *Opinion on the scientific aspects of the existing and proposed definitions relating to products of nanoscience and nanotechnologies*. Brussels: European Commission. http://ec.europa.eu/health/ph_risk/committees/04_scenihir/docs/scenihir_o_012.pdf
- Scenihir (Scientific Committee on Emerging and Newly Identified Health Risks), 2009. *Risk Assessment of products of nanotechnologies*. Brussels: European Commission. http://ec.europa.eu/health/ph_risk/committees/04_scenihir/docs/scenihir_o_023.pdf
- Schmidt, K., 2007. *Nanofrontiers: Visions for the Future of Nanotechnology*. http://www.nanotechproject.org/publications/archive/nanofrontiers_visions_for_future/
- Schmidt, K., Danuser, B. & Riediker, M., 2008. *Swiss Nano-Inventory: An Assessment of the usage of nanoparticles in Swiss Industry*. Final Report. http://www.suva.ch/ist_nanoinventory.pdf
- Seager, T. & Linkov, I., 2008. Coupling Multicriteria Decision Analysis and Life Cycle Assessment for Nanomaterials. *J. Ind. Ecol.*, 12, 282-285.
- Sillanpää, M., Sainio, P. & Haapala, H. 2010. Determination of manufactured nanoparticles in environmental samples. *Reports of the Finnish Environment Institute 13/2010*. (in Finnish).
- Steinfeldt, M., von Gleich, A., Petschow, U. & Haum, R., 2007. *Nanotechnologies, Hazards and Resource Efficiency*. Berlin: Springer.
- Steinfeldt, M., von Gleich, A., Petschow, U., Pade, C. & Sprenger, R., 2010. *Environmental Relief Effects through Nanotechnological Processes and Products – summary*. Umweltbundesamt. 33/2010. http://www.umweltbundesamt.de/uba-info-medien-e/mysql_medien.php?anfrage=Kennnummer&Suchwort=3777.
- Stolpe, B. & Hassellöv, M., 2007. Changes in size distribution of fresh water nanoscale colloidal matter and associated elements on mixing with seawater. *Geochim. Cosmochim. Acta*, 71, 3292-3301.
- Stone, V., Nowack, B., Baun, A., van den Brink, N., von der Kammer, F., Dusinksa, M., Handy, R., Hankin, S., Hassellöv, M., Joner, E. & Fernandes, T.F., 2009. *Nanomaterials for environmental studies: Classification, reference material issues and strategies for physico-chemical characterization*. *Sci. Total Environ.*, 408(7), 1745-1754.

- Stuer-Lauridsen, F., Kamper, A., Borling, P., Petersen, G.I., Hansen S.F. and Baun, A., 2007. Survey of nanotechnological consumer products. <http://www2.mst.dk/Udgiv/publications/2007/978-87-7052-536-7/pdf/978-87-7052-537-4.pdf>
- Taniguchi, N., 1974. On the Basic Concept of 'Nano-Technology'. Proc. Intl. Conf. Prod. Eng. Tokyo, Part II, Japan Society of Precision Engineering.
- Tiede K., Hassellöv M., Breitbarth E., Chaudhry Q. & Boxall A.B.A., 2009. Considerations for environmental fate and ecotoxicity testing to support environmental risk assessments for engineered nanoparticles. *J.Chromatogr. A* 1216, 503-509.
- Tervonen, T., Linkov, I., Figueira, J.R., Steevens, J., Chappel, M. & Merad, M., 2009. Risk-based classification systems of nanomaterials. *J. Nanopart. Res.*, 11, 757-766.
- University of Jyväskylä, Nanoscience Center. Nano Business born in NSC. https://www.jyu.fi/science/muut_yksikot/nsc/en/collaboration/industrial%20cooperation/spinoff/business/?searchterm=hybtonite [Accessed 25 March 2010].
- Vevers, W.F. & Jha, A.N., 2009. Genotoxic and cytotoxic potential of titanium TiO₂ nanoparticles on fish cells in vitro. *Ecotoxicology*, 17, 410-420.
- Wigginton N.S., Haus K.L. & Hochella Jr, M.F., 2007. Aquatic environmental nanoparticles. *Journal of Environmental Monitoring* 9, 1306-1316.
- Xu, J., Li, G. & Li, L., 2008. CeO₂ nanocrystals: Seed-mediated synthesis and size control. *Mater. Res. Bull.*, 43, 990-995.
- Zhang, W., 2003. Nanoscale iron particles for environmental remediation: An overview. *J. Nanopart. Res.*, 5, 323-332.
- Zhang, Y., Chen, Y., Westerhoff, P. & Crittenden, J., 2009. Impact of natural organic matter and divalent cations on the stability of aqueous nanoparticles. *Water Res.*, 43(17), 4249-4257.

DOCUMENTATION PAGE

<i>Publisher</i>	Finnish Environment Institute (SYKE)			<i>Date</i> November 2010
<i>Author(s)</i>	Meri Tuominen and Eija Schultz			
<i>Title of publication</i>	Environmental aspects related to nanomaterials			
<i>Publication series and number</i>	The Finnish Environment 26/2010			
<i>Theme of publication</i>	Environmental protection			
<i>Parts of publication/ other project publications</i>				
<i>Abstract</i>	<p>The report sets out some basic knowledge of nanomaterials and their characteristics, general information about what is known of their environmental effects, and describes the special features, which are encountered when analysing or testing of nanomaterials. The material for this report has been assembled from the recent scientific publications and reports and summaries of various expert bodies. This publication is one result of the second work package of the FINLCA -project (Life Cycle Assessment Framework and Tools for Finnish Companies).</p> <p>Nanomaterials are manufactured in increasing volumes and used in more and more novel applications. Therefore, it is expected that some of them may be released into the environment during the production of nanomaterials, manufacturing of consumer products, or their use or disposal of waste. Chemical and physical properties of the engineered nanomaterials are substantially different from those of the bulk materials. Consequently, there are considerable challenges for analytical, as well as risk and safety assessment methodology. In order to give evidence as the cause of an effect, it is important to verify the presence of the material in nanosize during the experimental set-ups, and also in the environment. Generally speaking, for example in aquatic environment, most of the nanoparticles tend to form aggregates, a phenomenon resulting in drastic decrease of the nanosized particles. Nevertheless, at least some nanoparticles has been demonstrated in laboratory tests to cause adverse effects on organisms. A lot of more data and research is needed to make final conclusions of the environmental fate and effects of nanomaterials.</p> <p>Life cycle assessment procedures take a broader view to environmental impacts than is generally the case in safety assessment of chemicals. The use of energy and raw materials, or waste recycling and management should be considered. On the basis of the current knowledge, generalizations applying to a large group of nanomaterials or nanotechnologies are not justified, and environmental impacts need to be evaluated on a case by case approach.</p>			
<i>Keywords</i>	nanomaterials, environmental effects, environmental fate, risk assessment, life cycle assessment			
<i>Financier/ commissioner</i>				
	ISBN	ISBN 978-952-11-3813-3 (PDF)	ISSN	ISSN 1796-1637 (online)
	<i>No. of pages</i> 56	<i>Language</i> English	<i>Restrictions</i> Public	<i>Price (incl. tax 8 %)</i>
<i>For sale at/ distributor</i>				
<i>Financier of publication</i>	Finnish Environment Institute (SYKE) P.O.Box 140, FI-00251 Helsinki, Finland Tel. +358 20 610 123, fax +358 20 490 2190 Email: neuvonta.syke@ymparisto.fi, www.environment.fi/syke			
<i>Printing place and year</i>				

KUVAILEHTI

<i>Julkaisija</i>	Suomen ympäristökeskus (SYKE)			<i>Julkaisu-aika</i> Marraskuu 2010
<i>Tekijä(t)</i>	Meri Tuominen ja Eija Schultz			
<i>Julkaisun nimi</i>	Environmental aspects related to nanomaterials (Kirjallisuuskatsaus nanomateriaalien vaikutuksesta ympäristöön)			
<i>Julkaisusarjan nimi ja numero</i>	Suomen ympäristö 26/2010			
<i>Julkaisun teema</i>	Ympäristönsuojelu			
<i>Julkaisun osat/ muut saman projektin tuottamat julkaisut</i>				
<i>Tiivistelmä</i>	<p>Raportissa esitetään joitakin perusasioita nanomateriaaleista ja niiden ominaisuuksista, kerrotaan yleisesti, mitä niiden ympäristövaikutuksista tiedetään sekä kuvataan niitä erityispiirteitä, joita nanomateriaalien analysoinnissa ja ympäristövaikutusten tutkimuksessa kohdataan. Aineisto on koottu uusimmista tieteellisistä julkaisuista ja eri asiantuntijatahojen yhteenvedoista. Tämä julkaisu on yksi FINLCA -projektin (Elinkaarimetodiikkojen foorumi yritysten päätöksenteon tueksi) toisen työpaketin tuloksista.</p> <p>Nanomateriaaleja valmistetaan ja käytetään yhä enemmän ja yhä useampiin tarkoituksiin, joten on odotettavissa, että niitä joutuu myös ympäristöön itse nanomateriaalien valmistuksen, tuotteiden valmistuksen, niiden käytön tai jätteiden käsittelyn aikana. Teollisesti valmistettujen nanomateriaalien kemialliset ja fysikaaliset ominaisuudet poikkeavat oleellisesti niin sanottujen tavanomaisten aineiden ominaisuuksista. Näistä uusista ominaisuuksista seuraa suuria haasteita analytiikalle ja siten myös riskien ja turvallisuuden arvioinnille. Jotta vaikutusten voidaan osoittaa johtuvan juuri nanokokoisesta materiaalista, on kyettävä varmistamaan näiden säilyminen testiolosuhteissa ja myös ympäristössä. Yleisesti voidaan sanoa, että esimerkiksi vesiympäristössä useimmilla nanohiukkasilla on taipumus muodostaa aggregaatteja jolloin alkuperäisen kokoisia hiukkasia on huomattavasti vähemmän tai ei lainkaan. Ainakin joillakin nanohiukkasilla on osoitettu olevan laboratorioskokeissa haitallisia vaikutuksia eliöihin. Lopullisten päätelmien tekemistä varten tarvitaan tutkimustietoa vielä paljon nykyistä enemmän.</p> <p>Elinkaaritarkasteluissa nanomateriaalien ja nanoteknologian ympäristövaikutuksia arvioidaan laajemmin kuin kemikaalien riskinarvioinnissa. Nykyisen tiedon pohjalta ei voida tehdä yleistyksiä, joten energian ja raaka-aineiden käytön, tai jätteiden kierrätettävyyden tai käsittelyn merkitys kestävän kulutuksen kannalta tulee arvioida kussakin tapauksessa erikseen.</p>			
<i>Asiasanat</i>	nanomateriaalit, ympäristövaikutukset, ympäristökohtalo, riskinarviointi, elinkaariarviointi			
<i>Rahoittaja/ toimeksiantaja</i>				
	ISBN	ISBN 978-952-11-3813-3 (PDF)	ISSN	ISSN 1796-1637 (verkkokj.)
	<i>Sivuja</i> 56	<i>Kieli</i> Englanti	<i>Luottamuksellisuus</i> julkinen	<i>Hinta (sis.alv 8 %)</i>
<i>Julkaisun myynti/ jakaja</i>				
<i>Julkaisun kustantaja</i>	Suomen ympäristökeskus (SYKE) PL 140, 00251 HELSINKI Puh. 020 610 123 Sähköposti: neuvonta.syke@ymparisto.fi , www.ymparisto.fi/syke			
<i>Painopaikka ja -aika</i>				

PRESENTATIONSBLAD

Utgivare	Finlands miljöcentral (SYKE)			Datum November 2010
Författare	Meri Tuominen och Eija Schultz			
Publikationens titel	Environmental aspects related to nanomaterials (Miljöaspekter av nanomaterial – En litteraturestudie)			
Publikationsserie och nummer	Miljön i Finland 26/2010			
Publikationens tema	Miljövård			
Publikationens delar/ andra publikationer inom samma projekt				
Sammandrag	<p>Rapporten innehåller grundläggande information om nanomaterial och deras egenskaper samt allmänt om vad man vet om nanomaterials inverkan på miljön. Dessutom beskrivs de särdrag som påträffas under analys av nanomaterial och bedömning av deras miljökonsekvenser. Materialet har sammanställts utgående från de senaste vetenskapliga publikationerna och olika expertorgans sammanfattningar. Denna publikation är en del av FINLCA projektets (Forum för livscykelmetoder som stöd för beslutsfattandet inom företagen) andra arbetspakets resultat.</p> <p>Nanomaterial tillverkas i ökande volym och de används inom allt fler användningsområden. Därför är det troligt att de också hamnar i miljön under produktionen av själva nanomaterialet, under tillverkningen av produkter som innehåller nanomaterial, under användning av dessa produkter eller vid avfallshanteringen. De kemiska och fysikaliska egenskaperna hos de industriellt tillverkade nanomaterialen skiljer sig väsentligt från de så kallade konventionella ämnenas egenskaper. Dessa nya egenskaper orsakar stora utmaningar för analysmetoderna och därmed också för risk- och säkerhetsbedömningar. För att kunna påvisa att effekterna beror på material i nanostorlek, måste man kunna säkerställa deras beständighet både i testförhållanden och även i miljön. En generell slutsats till exempel är att de flesta nanopartiklar tenderar att bilda aggregat i vattenmiljö, vilket resulterar i att mängden av partiklarna i ursprunglig storlek är mycket mindre eller finns inte alls. Åtminstone vissa nanopartiklar kan orsaka skadliga effekter på testorganismer under laboratorieförsök. För att dra definitiva slutsatser behövs mycket mera forskning. Miljöeffekterna bedöms mera omfattande under livscykelanalys för nanomaterial och nanoteknik än vid kemiska riskbedömningar.</p> <p>På grund av bristen i nuvarande kunskaper kan man inte göra generaliseringar. Därför bör användning av energi och råvaror samt återvinning eller behandling av avfall utvärderas separat i varje enskilt fall för att klargöra dessa faktorerers betydelse för hållbar konsumtion.</p>			
Nyckelord	nanomaterial, miljöeffekter, beteende i miljön, riskbedömning, livscykelbedömning			
Finansiär/ uppdragsgivare				
	ISBN	ISBN 978-952-11-3813-3 (PDF)	ISSN	ISSN 1796-1637 (online)
	Sidantal 56	Språk Engelska	Offentlighet Offentlig	Pris (inneh. moms 8 %)
Beställningar/ distribution				
Förläggare	Finlands miljöcentral (SYKE) PB 140, 00251 Helsingfors Tfn. +358 20 610 123 Epost: neuvonta.syke@ymparisto.fi, www.miljo.fi/syke			
Tryckeri/tryckningsort och -år				

Nanomaterials and nanotechnologies offer great opportunities for almost all sectors of society. New materials and applications are invented all the time. Benefits are obvious in many cases, such as enhanced energy use, improved electronic devices, lighter products, higher hygiene level, or increased storage time. The motive for manufacturing nanomaterials lies in the chemical and physical characteristics, which are different from material in bulk. Due to these new properties environmental effects assessment is challenging. We are only at the beginning of understanding how nanomaterials will behave in actual environmental conditions.

