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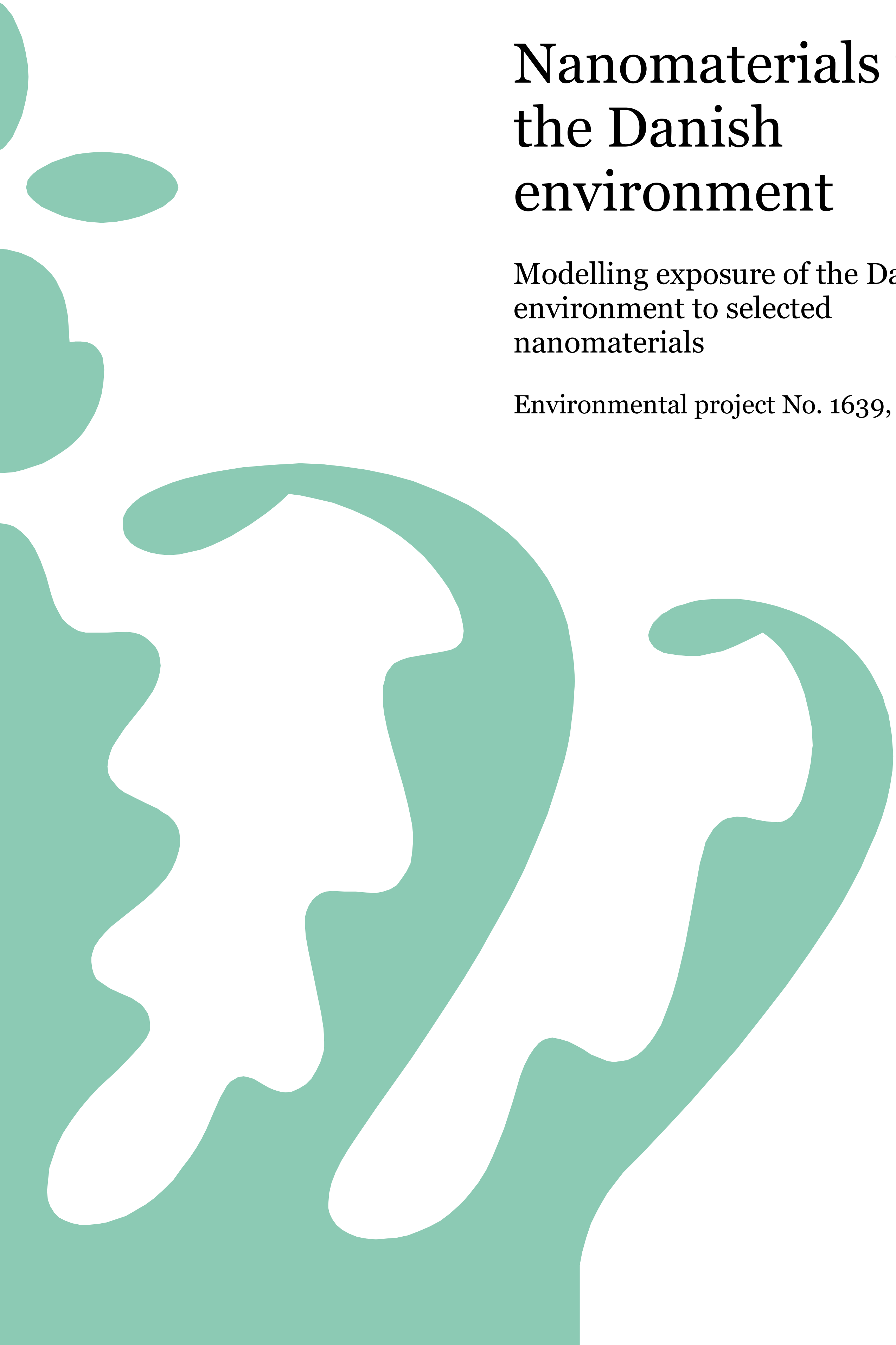
Nanomaterials in the Danish environment

Modelling exposure of the Danish environment to selected nanomaterials

Environmental project No. 1639, 2015



Title:

Environmental Exposure to Nanomaterials in Denmark.

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Foreword

This report on environmental dispersion and fate modelling and subsequent assessment of the exposure of the Danish environment to engineered nanomaterials (ENM) is part the project "Nanomaterials – Occurrence and effects in the Danish Environment" ("NanoDEN").

The project was commissioned by the Danish EPA in December 2012 and will run until mid 2015. It aims to increase the knowledge and understanding related to the occurrence of ENMs and the risks posed by these to humans and the environment in Denmark.

This report forms part of a series of projects regarding nanomaterials in Denmark ("Better control of nano") under the Danish finance law 2012-15."

The NanoDEN project provides the following main reports addressing 10 selected engineered nanomaterials:

- Report 1: A report on new knowledge about the fate and behaviour of nanomaterials in the environment;
- **Report 2:** The current report on environmental dispersion and fate modelling and subsequent assessment of the exposure of the Danish environment to nanomaterials;
- Report 3: A report on environmental effects of nanomaterials;
- Report 4: A final report summarising the main results and conclusions from the preceding reports and presenting the overall environmental risk assessment for the selected ENMs under Danish conditions.

The results on environmental fate and dispersion of ENMs provided in this report 2 is based on modelling input knowledge collected, quantified and evaluated in its Annex I. Such model input covers e.g. the annual release volume of the nanosized material from wastewater treatment and solid waste, industrial processes and from diffusive life cycle based wide dispersive use, disposal and recycling of nanomaterial containing products. A comprehensive collection of all the results is given in Annex II. The report itself is, however, designed so that it can be read without the need to consult all the details in Annex I and II.

The NanoDEN project team includes different partners with participation of COWI A/S (lead institution), the Technical University of Denmark (DTU Environment) and the Swiss Nano Modelling Consortium (SNMC). SNMC is the lead institution for the current sub-project and report.

The Steering Committee established for the NanoDEN project involves the following participants:

- Flemming Ingerslev, Danish EPA (Chairman and project responsible)
- Katrine Bom, Danish EPA
- Jørgen Larsen, Danish EPA
- Jesper Kjølholt, COWI (project manager)
- Anders Baun, DTU
- Fadri Gottschalk, SNMC
- Bernd Nowack, SNMC

Abbreviations and acronyms

Ag	Silver
Ag_2S	Silver sulphide.
CB	Carbon black
CeO2	Cerium oxide
CNT	Carbon nanotube
$CuCO_3$	Copper carbonate
Dm/dt	Changes in mass (m) over time (t), t equals one year in this report
DNAPL	Dense Non-aqueous Phase Liquid
ENHRES	Engineered Nanoparticles – Review of Health and Environmental Safety
ENM	Engineered nanomaterial
EPA	Danish Environmental Protection Agency
ERC	Environmental release categories
MC	Monte Carlo
MFA	Material flow analysis
MS	Mass spectrometry
NanoDEN	Nanomaterials – Occurrence and effects in the Danish Environment
PD	Probability distributions
PDF	Probability density functions
PEC	Predicted environmental concentrations
PMC	Production manufacturing and consumption
PMFA	Probabilistic material flow analysis
PNEC	Predicted no-effect concentrations
QD	Quantum dot
STP	Sewage treatment plants
TiO_2	Titanium dioxide
WIP	Waste incineration plants
ZnO	Zinc oxide
ZVI	Zero-valent iron

Extended summary

Background and Objective

In the context of the Agreement "Better Control of Nanomaterials" ("Bedre styr på nanomaterialer"), the Danish EPA has commissioned a series of projects aiming at investigating and presenting new knowledge regarding engineered nanomaterials (ENMs) in products on the Danish market. Besides such current nanomaterial use the aim of such project is to assess the possible associated exposure and risks to consumers and the environment.

The NanoDEN project has the overall and main objective of assessing whether those nanomaterials pose a risk to the Danish environment.

Subprojects 2-4 of this project have the purpose of providing insights into the environmental dispersion and fate with subsequent exposure of the Danish environment to ENM.
These subprojects cover the following work steps: subproject 2 is focused on method development-establishment of scenarios for nanomaterials in the environment, subproject 3 maps the environmental release from a diffusive source system and subproject 4 performs the computer based environmental concentration simulations.

This modelling work bases on a comprehensive model input data collection and preparation presented and developed in its Annex I. The Annex II of this report contains a comprehensive and detailed overview of the results based on all the modelled probability distributions that reflect in each case the complete model output.

Definition and selection of nanomaterials

In the context of the NanoDEN project as a whole (see also Report 1), the ENM is defined as manufactured material with one or more external dimensions between 1 and 100 nm. Such materials are used in applications due to their novel properties that result from its small size and other engineered material characteristics. Insofar ENMs may be considered as part of a large field of nanomaterials that may also be produced from natural, anthropogenic (incidental) and engineered (intentional) processes.

The NanoDEN project studies ENMs, since this is a relevant group of nanomaterials from a regulatory perspective. The following materials have been selected:

- Silver (Ag)
- Titanium Dioxide (TiO_2) (rutile and anatase)
- Zinc Oxide (ZnO)
- Carbon Nanotubes (CNTs)
- Copper carbonate ($CuCO_3$)
- Zero Valent Iron (ZVI)
- Cerium Oxide (CeO_2)
- Carbon Black (CB)
- Quantum Dots (QDs)

The selection follows as much as possible current or future expected production and use quantities for Denmark leading to significant applications in relevant consumer products, industrial processes, environmental remediation processes etc.

Environmental exposure model

This report presented mass transfer and predicted environmental concentrations for selected nanomaterials provided by a modelling study. The basis for such results was a comprehensive search on the manufacturing processes and the total content of the nanomaterials in mixtures and articles for end-applications in Denmark. The data fed into the modelling of total releases of nanomaterials to the environment in Denmark and the dispersion and fate of the substances in this environment are presented in detail in Annex I (separate volume).

As part of the modelling, total releases of the substances to the different environmental compartments from industrial processes, solid waste and wastewater treatment and diffuse emission from wide dispersive uses were estimated and compared to each other. The comparison of the different sources of releases for each nanomaterial and nanomaterials in general and discussion of their significance were also focussed on in this report.

The model used was derived from a model of the flows and fate of nanomaterials in the EU and in Switzerland developed by the Swiss Nano Modelling Consortium (SNMC). The modelling approach was to estimate the release of nanomaterials from the technosphere in different environmental compartments by summing such release over the complete lifecycle of the investigated material, including production of the nanomaterial, formulation and industrial processes, private or professional applications and waste treatment. The basic inputs were quantities of nanomaterials used for industrial processes and the total content of nanomaterials in imported mixtures and articles. The flow of the nanomaterials through a series of compartments/processes of the technosphere was determined by a series of transfer coefficients which, for example, described the percentages of nanomaterials directed to sewage treatment plants (STPs) that are eliminated by the treatment process or released into the air, soil, landfill or surface water. In addition to the unintentional releases to the environment, intentional releases may take place for some nanomaterials, such as via the use of nano-zerovalent iron (nano-ZVI) in the remediation of polluted soils and groundwater. For nano-ZVI the report did not provide the total probabilistic model[1], but was rather restricted to one unique significant use for soil remediation by giving only rough estimations of the expected environmental exposure.

For four of the nanomaterials addressed by this study, a detailed analysis for the EU and Switzerland was published in 2014 (Sun et al., 2014). These were nano–titanium dioxide (nano-TiO_2), nano–zinc oxide (nano-ZnO), nanosilver particles (AgNPs) and carbon nanotubes (CNTs). In relation to these nanomaterials, the Swiss data on import in mixtures and articles were partially used as a first estimate for the use in Denmark (on a *per capita* basis), and the transfer coefficients developed to describe the Swiss situation was also partially applied to Denmark, considering that the differences between the two countries with regard to the use of the mixtures and articles and waste treatment processes are small compared to the uncertainties on the use of data and transfer coefficients. However, a critical evaluation of the Swiss data was performed, and the report updated outdated data by replacing them with new findings. The details were given for each case and each nanomaterial.

For the other substances addressed by the study, data on uses and transfer coefficients were completely collected as part of this study. These substances were nano-copper (nano-CuCo3, nano-CuO, nano-Cu), nano-ZVI, nano–cerium dioxide (nano-CeO2), quantum dots (various substances) and carbon black.

The probabilistic, stochastic approach[2]

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[1] The probabilistic approach computes for all model input and output data probability distributions (probability density functions) instead of single numbers. These distributions reflect the probability of occurring of all the data values computed and show at the same time their total possible spectrum.

[2] The term stochastic (random) process stands for the computing procedure that produces random numbers used to form the probability distributions (probability density functions) of the model input and output data.

The data collected were not fed into the model by means of single deterministic values, but instead by computing probability distributions based on the data. For missing knowledge, assumptive information based on expert indications had to be used. The details on the distributions computed were given for each data case and each material. Thus, the model used was based on probabilistic nanomaterial production and use parameters, as well as release and mass transfer coefficients at all stages of the nanomaterial lifecycle. One type of parameter reflected tonnes or kilogrammes of use or release of nanomaterial each year. The second type represented transfer coefficients which indicated the percentage of the nanomaterial going into a further compartment (nanoproducts, natural or technical environments), or being dissolved/eliminated or finally deposited. This means that the probabilistic lifecycle-based (from the cradle to the grave) nanomaterial mass transport model tracked the engineered nanomaterial (ENM) mass transport as far as possible through all environmental release pathways of the target nanosized materials, as well as their transport flows between several technical and natural compartments. The stochastic model combined a large number of scenarios (100,000) for each mass transfer and mimicked such a complex system of engineered nanomaterial transport and fate. The ENM total input, output and deposition/transformation was balanced at each lifecycle stage of ENM and ENM-containing products. Chapters 2 and 4 give the mathematical details.

Nanomaterial sources

None of the selected nanomaterials are manufactured in Denmark. Information on the use of nanomaterials for formulation processes was obtained from companies involved in the manufacture of pigments, paints and varnishes (including antifouling paints), plastics and cosmetics.

As a general trend (with a few exceptions), companies in the chemicals sector have moved production to Eastern Europe or Asia over the past few decades, and the activities in Denmark are limited mainly to research and some formulation of chemical products into ready-to-use products. For example, in the paint sector, most of the production takes place abroad but, in particular, speciality paints are still produced by a number of small and medium-sized companies. A request via the trade organisation DFL only revealed one company using nanomaterials, but from other surveys, it is known that nanomaterials are used at least by a few of the companies. For confidentiality reasons, details on the use of nanomaterials for different formulation processes cannot be published.

Industrial point sources with direct discharges to surface water in Denmark mainly include industries in the food and feed sector, airports, wastewater treatments plants, shipyards, landfills/deposits and power plants. The study only identified one company using the nanomaterials addressed in the study with direct discharge to the aquatic environments, and probably only a few companies using the nanomaterials concerned discharge treated wastewater directly to surface water. More commonly, the pretreated wastewater is directed to municipal STPs for further treatment.

Both for production of pigments and production of paints and varnishes (according to the obtained information), the nanomaterials are imported as pastes, and dust does not seem to be an issue when the nanomaterials are applied in the formulation processes. Of the nanomaterials addressed by the study, the use of nano-TiO_2 (both photostable and photocatalytic), nano-CeO_2 and carbon black has been confirmed. Wastewater is generated from the cleaning of tanks and other production equipment. The first step in wastewater treatment at all sites is an on-site precipitation/flocculation where the majority of the nanomaterial in the wastewater is precipitated and ends up in a sludge/filter cake which is disposed of for off-site incineration or gasification. The pretreated wastewater is either directed to municipal wastewater plants or further treated at the manufacturing site. Direct releases to the air were considered insignificant. The transfer coefficients were derived by combining information from Danish manufacturers with sector-specific transfer coefficients from the OECD Emission Scenario Document for the sector.

Other ongoing surveys on the use of nanomaterials in Denmark have indicated the possible use of TiO_2, ZnO and CB in medical devices produced in Denmark. According to information obtained in this study, pigment grade (not nano) TiO and ZnO are used as pigments in Danish-produced medical devices, but nano-TiO_2 and nano-ZnO are not used. CB is used as pigment in the manufacture of some medical devices, in common with its use as pigment for many other applications. No specific data on the releases of CB from the plastics industry was obtained, but transfer coefficients were derived from the OECD Emission Scenario Documents for the sector.

According to information obtained in other ongoing surveys, in general, Danish-produced sunscreens for the Danish market do not contain nano-TiO_2 as UV-filters, but nano-TiO_2 may be added to other cosmetic products for sun protection. It was not possible to obtain quantitative data for the use of nano-TiO_2 in Danish production, but some information on potential quantities and the handling of the substances during production was obtained from previous surveys. Nano-ZnO is currently not included on the list of approved UV filters for cosmetics in the EU and Denmark, but pigmentary-grade ZnO may be used. Transfer coefficients were estimated from OECD Emission Scenario Documents.

Sewage treatment plants

STPs are considered one of the main sources of release of some of the nanomaterials studied. However, no specific and empirical data on actual discharges of nanomaterials to the Danish municipal sewer system or on the releases from these STPs are available. Therefore, assumptive information and general data available for transfer coefficients were used to calculate the quantities discharged to the sewer system from manufacturing processes, from the use of the materials in mixtures and articles and from waste handling. Furthermore, the report provided transfer coefficients for the treatment processes within the STPs and coefficients for the quantities discharged directly to surface water from overflows due to heavy rain and from separate storm water sewer systems. The model input parameter details for each material are given in Annex I.

Sources and environmental exposure to ENMs – Case studies

Titanium dioxide (nano-TiO_2)

The use of nano-TiO_2 was divided into two groups of applications in this study: the photostable TiO_2 and other applications (mainly used as UV absorbers) and the photocatalytic TiO_2 group. The anatase crystal form of TiO_2 is a more efficient photocatalyst than the rutile form of TiO_2. As a consequence, most photocatalytic consumer products contain nanosized anatase TiO_2. However, mixtures of both crystal forms are often used, and the two groups of applications do not fully reflect a division between the two crystal forms. The Swiss study did not differentiate between these groups, and for the present study, the application areas of the Swiss study were allocated to the two groups based on what was considered to be the main application within each area. As an example, paint was allocated to the photocatalytic TiO_2 group, even though some paints may contain TiO_2 as an UV absorber.

A: Photostable nano-TiO_2 and other applications

The main applications listed in the Swiss study were cosmetics, cleaning agents, plastics and consumer electronics. Based on the mean values of the nanomaterial mass in the different product categories, cosmetics accounted for more than half of the total consumption. Considering that the major part of this is released directly to the environment or STPs, this application is likely the major source of nano-TiO_2 in the environment. Its use in sunscreens in Denmark may likely be lower than the EU average, as the Nordic ecolabel (the Swan) does not allow the use of TiO_2 in sunscreens. As exact quantitative data on the consumption are not available, the data derived from the Swiss study were used as a worst case estimate. A number of other applications were included in the Swiss study, with a consumption ranging from zero to a few percent of the total. Photostable nano-TiO_2 is used in Denmark for production of pigments, cosmetics and possibly paints. An ongoing survey has indicated that the use of TiO_2 for the production of sunscreens in Denmark has decreased in recent years, but nano-TiO_2 may be used in other types of cosmetics. In the absence of newer quantitative data, information from a previous study was used as a best estimate for the quantities used in the cosmetics industry.

According to earlier findings (Gottschalk et al., 2009; Sun et al., 2014), amongst all metallic nanosized materials studied for Denmark, the highest aquatic exposure was modelled for nano-TiO_2. This was seen here, although we modelled a higher nano-TiO_2 elimination in STPs by following new measurement data that predicted greater elimination of such ENM from the STP water phase. Thus, our results revealed some aquatic relevance for such nano-TiO_2. One limit of our model, however, was that although the aggregation research has progressed (Praetorius et al., 2012), we had to assume for the target that large regional aquatic Danish system probability distributions were spread out over the total possible spectrum of immediate aggregation/sedimentation and no sedimentation at all. Downsizing such a broad spectrum would be crucial for improving the exposure model.

The STP effluents showed the highest concentrations of a few to almost 100 µg/l (modal value around 13 µg/l). The fresh water equivalents reached at most 0.1 µg/l (worst case scenario), while those for seawater were almost completely in pg/l concentrations. Soils and sediments were the most significant nano-TiO_2 sinks, with approximate expected concentrations (most frequent results) for 2020 of 3 mg/kg in sludge treated soils and a few tenths of µg/kg in non-sludge-based fertilised soils. In sediments (fresh water and marine water), 2.4 and 0.8 mg/kg were modelled. The air concentrations were marginal, as is the case with almost all studied ENMs, and showed values in the range of pg/m^3. This mostly reflected very small direct emissions into the air from nanoproduct uses and almost complete nanomaterial removal in waste incineration plants. Since these findings apply to almost all nanomaterials studied, we do not discuss the air exposure any more in this summary.

To conclude, we may state that a precise understanding is above all needed concerning fate and behaviour of photostable and other nano-TiO_2 in STPs, soils and water. Second, quantitative information on real Danish ENM use quantities, which by far represent the most important parameter for environmental exposure assessment, is needed as well. This need for use quantity amount applies to all the nanomaterials mentioned in the sections below, and is therefore not repeated for the other ENMs.

B: Photocatalytic nano-TiO_2

In photocatalytic nano-TiO_2, UV and visible light can induce catalytic activity. Via the photocatalytic effect, reactive oxygen species are formed, which can decompose organic substances and bacteria on illuminated surfaces to achieve self-cleaning/antibacterial effects. Main applications from the Swiss study were paints, coatings and water and air treatment, with construction materials (self-cleaning surfaces with TiO_2) and wastewater treatment as likely smaller applications. Photocatalytic TiO_2 is used in the Danish production of paints with antibacterial self-cleaning effects.

To our knowledge, this report presents the first study specifically focussed on photocatalytic nano-TiO_2. The photocatalytic nano-TiO_2 water load did not add too much (one-tenth) to the total nano-TiO_2 aquatic load. The concentrations for surface waters were at most in the pg/l ranges comparable to those for nano-ZnO (please see the next section). Hence, depending on the type on ENM applications, the nano-TiO_2 aquatic relevancy may vary significantly. For risk assessment and toxicology studies, it will be important to distinguish these two material categories of the same compound in the future. Relatively small PECs have also been modelled for sediments, and concentrations of approximately 200 µg/kg (freshwater sediment) and 60 µg/kg (seawater sediment) have been predicted (modal values) for 2020. In soils fertilised with STP sludge, the model revealed about 350 µg/kg (modal values) for 2020.

Most photocatalytic nano-TiO_2 ends up in recycling and landfill plants, as also seen in several other ENMs. Hence, we should study the fate and behaviour of ENMs in such plants in detail.

Zinc oxide (nano-ZnO)
The major application of nano-ZnO in the Swiss study, accounting for more than half of the consumption, was as a UV filter in sunscreens. However, nano-ZnO is not included in the list of UV filters allowed in cosmetic products in the EU and Denmark. The pigmentary grades of ZnO still allow it to be used as a white pigment, but it is not considered a nanomaterial. For the modelling, the consumption data from the Swiss study were used as worst case estimates, but could be reconsidered if the modelling results indicated an environmental risk. The only other potential major application from the Swiss study was the use of nano-ZnO in paint. No actual use of nano-ZnO for production processes in Denmark was identified.

The nano-ZnO case study did not show any significant loads or concentrations, either in waters or in soils. The freshwater PECs were mainly in pg/l to some ngl/l dimensions; the marine water PECs were smaller by a factor 10 smaller, and all exhibited pg/l concentrations. Soils and sediments represented the final sinks; however, they exhibited very low quantities of nano-ZnO load. In 2020, a few hundred ng/kg are predicted in soils, and a few hundred μg/kg in sediments. These values are much lower than, for example, the predicted few mg/kg concentrations for photostable nano-TiO_2.

Silver (nano-Ag)
Nanosilver may have various applications, including as antimicrobial agents in textiles, cleaning agents, paints, cosmetics and hygienic surfaces (e.g. kitchenware and medtech). No actual use of nanosilver in production processes in Denmark was identified, and the model parameters were all derived from the Swiss study. In some types of applications, the AgNP is dispersed in a mixture (e.g. paint or printing colours), whereas in others it may be adsorbed to a surface (e.g. in textiles) or embedded in a polymer matrix, as in hygienic surfaces of kitchenware and equipment for food storage. In general, limited information on the quantities used for the different applications exist, and the Swiss data indicate more than 10 application areas, which may be among the main areas.

Very low nano-Ag use volumes and an efficient removal of such silver during sewage treatment, as well as the highly efficient removal in waste incineration (as is the case for all nanomaterials) leads to consistently low environmental release quantities in this case. The greatest part of the target nano-Ag reaching STPs is converted into silver sulphide (Ag_2S). The nano-Ag freshwater and seawater concentrations are in pg/l levels if not almost zero for a large number of the probabilistic Monte Carlo (MC)[3] computer simulation scenarios. The terrestrial concentrations were even lower than those for nano-ZnO, which means that they were almost completely transformed into non-nanomaterial forms during sewage treatment.

Carbon nanotubes (CNTs)
The main applications of CNTs are as a composite and polymer additive and as a component of batteries. End applications include flat panel displays, super composite fibres, conductive plastics, field storage batteries, micro-electronics based on semiconductors and other conductive material. Figures on the potential consumption with end uses were derived from the Swiss study. The Danish Plastics Federation did not hold any information on the use of CNTs in the Danish plastics industry, but the possibility that they are used cannot be excluded. Some R&D on the use of CNT has been undertaken in Denmark; among these is the NANOPLAST project titled 'Nano-technological materials and products in the plastics industry: Exposure assessment and toxicological properties'. No attempt was made to estimate the potential releases of CNTs from R&D in Denmark.

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[3] Monte Carlo (MC) computer simulations that are also called computer experiments are computational routines that repeat random sampling a large number of times (in our report e.g. 100,000 times) in order to produce numerical results.

Very low volumes of CNTs (a few tonnes annually) were modelled in the CNT flow charts, which showed a high mass fraction (up to 90 95%), ending up in recycling, waste incineration and landfilling processes. The results from such findings roughly showed a fully marginal environmental exposure to such carbon. This applied to aquatic and terrestrial environments. CNT concentrations in natural waters only reached pg/l levels (freshwater); in marine water, the model also revealed some fg/l concentrations. In 2020, we do not expect, for example, much more than a few µg/kg in freshwater sediment concentrations. Up to 2020, the concentrations in soils will not significantly contribute to the total carbon already there.

Copper (nano-$CuCO_3$*, nano-CuO and nano-Cu)*
Nano-copper was not included in the Swiss study. Three different applications of nanocopper were considered here. Of these, the use of micronised particles of copper carbonate ($CuCO_3$) for wood preservatives was considered to potentially account for the major portion. Micronised $CuCO_3$ is not intentionally a nanomaterial, but would probably fall within the definition with the current particle size distribution. Manufacturers are trying to optimise the grinding process in order to have fewer particles below 100 nm, and in the future, micronised $CuCO_3$ may possibly fall outside the definition of nanomaterials. Micronised copper carbonate is not currently marketed in Denmark, but in the United States, the market penetration of micronised copper technology is about 75–80%. It is expected that in the next few years, micronised $CuCO_3$ may substitute for a significant part of the $CuCO_3$ used for wood treatment in Denmark today. Copper carbonate is used for the production of pressure-impregnated wood in Denmark, and micronised $CuCO_3$ may already be present in imported treated wood. The use and release of $CuCO_3$ was modelled for a scenario of a future situation where the micronised $CuCO_3$ has substituted the $CuCO_3$ used today. The modelling was complicated by the uncertainty related to the actual presence of nanoparticles in the treated wood and the rates of release from the wood. Nano-CuO may be used for various applications discussed in the report, but no attempt was made to estimate the total quantities in imported mixtures and articles. Copper oxides are widely used for antifouling paints, and such paints have been described in the literature as a potential application area for nano-CuO. According to a manufacturer and an importer of copper-based antifouling paints, however, these paints do not contain copper oxides in the nano-form; moreover, it would not be an advantage, but in fact more expensive, to use nano-CuO for this application.

The nanocopper (nano-$CuCO_3$) case model showed results that completely varied from all other findings concerning the target metallic nanomaterials. The use in wood impregnation strongly leads to a high mass transfer of such nanomaterial into waste flows (waste incineration, recycling and landfilling). Here, however, we must emphasise again that our model stopped at the last two mentioned plants by assuming zero environmental release from those compartments. Thus, in order to give an example, no water was assumed to percolate through these systems and leach out the nanosized potential contaminants. For Danish standards of those infrastructures, these seem to be realistic model conditions. Definitive scientific evidence on these questions, however, has not yet been collected (Mueller et al., 2013). The greatest portion of nano-copper environmental release (approx. 98%) covers direct discharge from the impregnated wood into soils. This occurs via soil contact of such woods under the ground, as well as via air deposition. Most of the 100,000 Monte Carlo computer model scenarios revealed concentrations of a few ng/l (freshwater) and equivalent values in pg/l levels in marine water. Some exposure in soils cannot be excluded for 2020, as the high exposure scenarios showed values up to approximately 200 µg/kg of soil. However, such values reflect our worst case exposure model, which assumed a high micronised fraction of the total nanocopper used in wood impregnation.

This report underlined that in the future, new or further nano-copper carbonate applications combined with a high micronised material market penetration and higher environmental release could make reassessment of the environmental exposure necessary.

Zerovalent iron (nano-ZVI)
Zerovalent iron can be used for in situ remediation of contaminated soils and groundwater. Zerovalent iron fillings or iron sponges (not at a nanosize) have been used for at least four full-scale remediation projects in Denmark. Moreover, nano-ZVI was recently used for a pilot study in Denmark. Based on the experience from the pilot study, a scenario for full-size remediation using nano-ZVI was studied.

In the nano-ZVI case study, we focussed on local scenarios, since currently, this nanomaterial is not expected to be used in a variety of different applications. Although medical applications have been mentioned in the literature, it is the application in soil (and groundwater) remediation that seems currently the only relevant one. Such remediation is a local event due to the high, rapid reactivity of the used nano-ZVI. Our hypothetical worst-case (no iron degradation after being discharged to soils) nano-ZVI computations showed some hundred µg/kg in soil, which did not represent a significant amount when compared to the naturally occurring iron concentrations of some g/kg.

Cerium dioxide (nano-CeO_2)
Nano-CeO_2 was not included in the Swiss study, but data were derived from a survey of the use of nanomaterials in the EU. The main uses in the EU were estimated to be diesel fuel additives, automotive catalyst converters, glass polishing and paint and coatings. For each of these applications, transfer coefficients were estimated. The use of nano-CeO as a UV filter in wood oil manufactured in Denmark was confirmed.

The modelled nano-CeO_2 Danish use volumes were relatively low with modal values of around 5 tonnes annually. The results showed load values of such cerium into the natural environment which do not exceed half a tonne per year. Such environmental discharge mostly occurred via STP sludge fertilisation and some air emissions. However, these releases were in very low quantities not reaching t/a amounts in any single case.

The nano-CeO_2 water and marine water concentrations were at pg/l levels; some fg/l Monte Carlo scenarios were also modelled. In 2020, for non-STP-sludge-fertilised soil areas (modal values), concentrations of about a few hundred ng/kg expected, while they will be a few µg/kg for STP-sludge-treated soils.

Quantum dots
Quantum dots were not included in the Swiss study, but data were derived from a survey of the use of nanomaterials in the EU. Quantum dots are semiconductor materials of metals such as Cd and Zn which range from 2 to 10 nm in diameter. Applications of quantum dots in products and commodities include semiconductors transistors, solar cells, light-emitting devices (e.g. LEDs), diode lasers and medical imaging devices. No information on the use of quantum dots for manufacturing in Denmark has been found, but such a use cannot be excluded.

The current Danish quantum dots use volumes are most likely below half a tonne per year. The modelled environmental concentrations in air and surface waters were so small that a detailed evaluation of their probability distributions was not performed. The results mostly reflected values lower than some fg/l (water) or fg/m^3 (air). A few µg/kg were expected for sediments in 2020 (freshwater) and even lower values for marine water equivalents. In this report, such low values do not have any comparable results amongst the other nanomaterials studied.

Carbon black
Carbon black is elemental carbon in the form of an extremely fine black powder, and is widely used as a black pigment. The primary particles of carbon black meet the definition of nanomaterials. During the production process, however, the primary particles form larger aggregates, and further along, agglomerates of 1–100 mm in diameter which consist of hundreds to thousands of adhering

aggregates may be formed. Although the aggregation which spontaneously occurs in manufacturing processes produces unbreakable aggregates of an average size that is generally over 100 nm, carbon black can include a limited fraction of materials that are smaller than this, that is, nanoscale materials. Carbon black was not included in the Swiss study. On a global scale, 90% of the carbon black is used in the rubber industry as a reinforcing filler in a variety of products, with tyres as the major application area. In Denmark, the use of carbon black as a black pigment in the manufacture of inks, paints, plastics, cosmetics and textiles has been identified.

The carbon black model shows the highest exposure results in this report for all natural compartments. We modelled much higher use amounts (kt per year levels instead of t per year). Furthermore, such amounts are mainly used in rubber component mixtures, which represent an ideal basis for significant material (of all kinds) release due to permanent material degradation processes (wear and tear). However, our model assumed that the whole released fraction of carbon black would occur as nanosized material. Such model conditions certainly represent the results for a conservative exposure (and risk) assessment. Thus, we have to state that such carbon may also be released as a part of non-nanoparticulated material components belonging to the initial mixture material source. Insofar as this is the case, the actual carbon black nanoparticulated exposure concentrations could be lower. Finally, the distinction between engineered and naturally occurring carbon black (e.g. from combustion sources) is in practice almost impossible. Nevertheless, some attention should be given to the possible negative effects on the environment and risks of the target carbon black.

Conclusions regarding ENM sources and environmental exposure
No particularly high Danish nanomaterial production/use (incl. environmental release) was observed. However, it was found very difficult to obtain Danish specific data on nanomaterial production, import and application types and amounts. Hence, our model partially for some substances also bases on nanomaterial use knowledge gathered for general European contexts. Specific, Danish data are used regarding e.g. geographic conditions and general environmental management of wastewater and solid waste etc.

Most of the modelled case studies revealed only a small annual discharge into the natural environment of some tonnes. In a few cases (e.g. nano-Ag, CNT, nano-CeO_2) such discharge does not reach (even for the high release scenarios) tonnes per year levels. These findings on the total environmental discharge are in line with other European results. However, for several nanomaterials (nano-$CuCO_3$, nano-CeO_2, nano-ZVI, quantum dots, carbon black) we present to our knowledge the first comprehensive study.

Noteworthy environmental discharge and exposure has above all been modelled for photostable and other nano-TiO_2 and carbon black (CB) (aquatic and terrestrial environment) as well as for nano-copper carbonate in soils. In these cases a particular attention on possible environmental effects and risks will be given in report 3 and 4.

Although our model clearly reveals the concentration limits that exclude unrealistic (or not to be expected) concentrations, we have to explicitly emphasize the limitations in interpreting the results. Future exposures may be considerably higher as production and use of the nanomaterials investigated increases. As long as the companies involved are reluctant to provide their current (and anticipated) quantities of nanomaterials used and engineered it is almost impossible to point to the specific ENMs that have particular potential for high environmental release and exposure. As long as such a data-base is lacking, such a forecast remains purely in the realm of speculation. The increased electrification of mobility could lead to an increased use of ENM, for example in batteries (e.g. QD and CNT). The expectations for CNTs are huge, and are anticipated in a large number of applications (polymer composites, consumer electronics, textiles, etc.); however, currently commercially relevant use does not seem to be occurring. The 100% market penetration of the use of nano-$CUCO_3$ in wood treatment, or nanosized CeO_2 as a fuel additive, may lead to scenarios with environmental relevance. Finally, we must underline that transparency with respect to volumes of nanomaterial production and use on the part of industry would help considerably in making the exposure modelling more precise. Hence, there is a need for a better understanding and more empirical data regarding Danish nanomaterial use and import quantities, and this by far represents the most important factor necessary for the updating of this kind of environmental exposure assessment.

The novelty of the modelling work presented here is based on several pillars with various novelty factors that range from new model input data and geometry to the new substances studied. First, the model benefitted from the NanoDEN project report 1 (Environmental fate and behaviour of nanomaterials) that collected and evaluated the newest scientific evidence on a series of environmental fate and behaviour parameters. This evaluation showed that the current database for incorporating, for example, photochemical degradation, oxidation, reduction, adsorption, desorption and biotransformation in detail into the generic mass transfer model is too thin. However, it also shows that some progress has been made and that we cannot exclude the possibility that this knowledge may become available in the near future. Nevertheless, new data on the dissolution and aggregation/agglomeration (leading to sedimentation) of engineered nanomaterials could be used to feed the model. Dissolution for some metals (e.g. Ag, $CeO2$ or ZnO) is seen upon contact with water and this may occur during the nanoproduct consumption process when they are released into waste water from a variety of uses (e.g. in cosmetics, textiles, paints, coatings, food, cleaning agents etc.) , or during the subsequent treatment of the nanomaterials in sewage treatment plants.

Knowledge about sedimentation is crucial for estimating the residence time of the nanomaterials in water, including sewage treatment waters, as well as their subsequent discharge into sediments and sewage treatment sludges. Similarly, it is important to know about the residence time of nanomaterials in air, and about their discharge into soils and water. Regarding the residence time of nanomaterials in water, the report 1 confirmed that currently accurate scientific information is missing, and that a large spectrum of materials with either immediate or almost no sedimentation (water-sediment transport) has to be expected. However, in the context of nano-TiO_2 and nano-ZnO in sewage treatment processes, our model, based on clearly improved parameters, shows a much higher removal from the water phase compared to earlier and comparable studies focused on Swiss or European geographies. Regarding air residence time, we currently have to base our parameters on knowledge about ultrafine particles. However, due to consistently low air release such roughness in our model does not show a significant impact on the results. Further points of relevance for our model are that, as far as possible, we collected the newest (as well as the first Danish specific) information for the usage quantities of engineered nanomaterials. Our model is also the first to be applied to the complete life cycle data of the nanoproducts considered. Both models' parameters highly determine the engineered nanomaterial release into the environment. Finally, to the best of our knowledge such comprehensive data collection and subsequent modelling for the nanosized substances $CUCO3$, ZVI, $CeO2$, CB, QDs, occurred for the first time. The same applied for all target engineered nanomaterial in all studied marine environments (water and sediments).

Dansk sammendrag

Baggrund og formål
Under hovedoverskriften "Bedre styr på nanomaterialer" har Miljøstyrelsen iværksat en række projekter, der har til formål at undersøge og generere ny viden om industrielt fremstillede nanomaterialer (ENM) i produkter på det danske marked. Et af disse projekter er det såkaldte NanoDEN-projekt, som denne rapport udgør en del af, og hvis overordnede formål er at vurdere, hvorvidt (udvalgte) nanomaterialer udgør en risiko for det danske miljø.

Delprojekt 2, 3 og 4 af NanoDEN-projektet, som afrapporteres her, har til formål at give indsigt i den miljømæssige spredning samt efterfølgende eksponering af det danske miljø for ENM. Disse tre delprojekter omfatter følgende: Delprojekt 2 har fokus på metodeudvikling og etablering af scenarier for nanomaterialer i miljøet, i delprojekt 3 kortlægges de miljømæssige udslip fra diffuse kilder og i delprojekt 4 udføres computerbaserede simuleringer af nanomaterialers koncentrationer i miljøet.

Definition og udvælgelse af nanomaterialer
I forbindelse med denne rapport defineres nanomaterialer som fremstillede materialer med en eller flere eksterne dimensioner på mellem 1 og 100 nm, og som anvendes i produkter eller artikler på grund af de nye egenskaber der opnås som følge af nanomaterialernes lille størrelse og andre manipulerede egenskaber. Følgende nanomaterialer er blevet udvalgt som casestudier:

- Sølv (Ag)
- Titaniumdioxid (TiO_2) (rutil og anatase krystalstrukturer)
- Zinkoxid (ZnO)
- Kulstof-nanorør (CNT)
- Kobbercarbonat ($CuCO_3$)
- Nano-skala nulvalent jern (nZVI)
- Ceriumdioxid (CeO_2)
- Carbon black (CB)
- Kvantepunkter (QDs)

Udvælgelsen er baseret på de forventede produktions- og anvendelsesmængder af ENM i Danmark samt deres anvendelse i relevante forbrugerprodukter, industrielle processer og miljøoprensningsprocesser. Disse materialer er anvendt til at illustrere og fremhæve forskelle og ligheder i miljøprocessernes betydning for skæbne og opførsel for forskellige materialetyper.

Miljømæssig eksponeringsmodel
I denne rapport rapporteres massestrømme og forventede miljømæssige koncentrationer for udvalgte nanomaterialer på basis af en modelbaseret undersøgelse. Grundlaget for resultaterne har været en omfattende søgning for data om fremstillingsprocesser og indhold af de udvalgte nanomaterialer i blandinger og artikler til brug for anvendelser i Danmark. De detaljerede data, der har været benyttet ved modelleringen af det samlede udslip af nanomaterialer til miljøet i Danmark og spredningen og skæbne af stofferne i miljøet, kan findes i bilag I (separat bilagsrapport).

Som en del af modelarbejdet er de samlede udslip af stofferne til forskellige delmiljøer fra punktkilder som industrielle processer, affald og spildevandsbehandling samt diffuse emissioner fra diverse anvendelser beregnet og sammenlignet med hinanden. Desuden er de forskellige kilder til udslip for hvert af de udvalgte nanomaterialer og nanomaterialer i almindelighed og deres relative betydning også behandlet i denne rapport.

Den anvendte model er udviklet på basis af en model for massestrømme og skæbne af nanomaterialer i EU og i Schweiz, som er udviklet af en schweizisk forskergruppe, "The Nano Modelling Consortium" (SNMC). Modellen estimerer frigivelsen af nanomaterialer fra teknosfæren til forskellige delmiljøer som summen af frigivelse over hele livscyklus af de undersøgte nanomaterialer, herunder produktion og formulering af nanomaterialer samt andre industrielle (downstream) processer, privat og professionel anvendelse af materialerne samt behandling/bortskaffelse af affald. De grundlæggende input har været de mængder af nanomaterialer, der anvendes til industrielle processer, samt det totale indhold af nanomaterialer i importerede blandinger og artikler. Flow'et af nanomaterialer gennem forskellige trin og processer i teknosfæren er blevet bestemt ved en række overførselskoefficienter, som for eksempel procentdelen af de nanomaterialer, der ledes til renseanlæg, som nedbrydes ved behandlingsprocessen eller afgives til luften, jorden eller overfladevand eller deponeres. Ud over de utilsigtede udslip til miljøet, kan forsætlige tilførsler forekomme for nogle nanomaterialer, så som ved brug af nul-valent nanojern (nano-ZVI) til rensning af forurenet grundvand. Hvad angår nano-ZVI giver rapporten ikke en samlet probabilistisk model, men begrænser sig til én unik, væsentlig anvendelse, nemlig til rensning af jord, og giver kun grove skøn over den forventede eksponering af miljøet.

For fire af de nanomaterialer, som denne undersøgelse omfatter, er en detaljeret analyse for EU og Schweiz offentliggjort i 2014 (Sun et al., 2014). De fire materialer var nano-titaniumdioxid (nano-TiO2), nano-zinkoxid (nano-ZnO), nanosølvpartikler indlejret i fibre (AgNPs) og nano-kulstofrør (CNT). For disse nanomaterialer er de schweiziske data om import i blandinger og artikler blevet benyttet som et første estimat for anvendelsen i Danmark (på per capita-grundlag), og overførselskoefficienter udviklet til at beskrive den schweiziske situationen også delvist blevet benyttet for Danmark, hvilket kan retfærdiggøres med, at forskellene mellem de to lande både med hensyn til anvendelsen af nanomaterialerne og de efterfølgende affaldsbehandlingsprocesser er små i forhold til de usikkerheder, der i øvrigt er mht. data og overførselskoefficienter. Dog er der gennemført en kritisk vurdering af de schweiziske data, og rapporten er i øvrigt blevet opdateret på en række punkter med nye informationer og data.

For de øvrige nanomaterialer omfattet af undersøgelsen er data om anvendelser og overførselskoefficienter blevet indsamlet fra grunden. Disse materialer er nano-kobber (nano-CuCo3, nano-CuO, nano-Cu), nano-ZVI, nano-cerium dioxid (nano-CeO2), quantum dots (forskellige stoffer) og carbon black.

Den probabilistiske, stokastiske tilgang
De indsamlede data blev ikke indlagt i modellen i form af enkelte, deterministiske værdier, men i stedet er der beregnet sandsynlighedsfordelinger baseret på dataene. I tilfælde af manglende eksakt viden blev estimater baseret på ekspertvurderinger benyttet som input til modellen. Således er den anvendte model baseret på probabilistisk bestemte parametre for produktion og anvendelse af nanomaterialerne samt frigivelses- og massestrømskoefficienter for alle stadier af nanomaterialernes livscyklus. En type parameter afspejlede det antal tons eller kilogram nanomateriale, der blev anvendt eller frigivet hvert år. En anden type repræsenterede overførselskoefficienter, som indikerer den procentdel af et nanomateriale, som overføres til et andet compartment (produkter, naturlige eller tekniske miljøer), eller opløses / fjernes eller slutdeponeres. Det vil sige, at den probabilistiske livscyklus-baserede massetransportmodel fulgte massetransporten af industrielt fremstillede nanomaterialer (ENM) så langt som muligt gennem alle frigivelsesveje til miljøet samt transportstrømmene mellem flere forskellige tekniske og naturlige delmiljøer. Den stokastiske model kombinerede en lang række scenarier (100.000) for

hver massetransport og simulerede et komplekst system af nanomaterialers transport og skæbne. Det samlede input, output og deponering/transformation blev afbalanceret på hver livscyklusfase af ENM og ENM-holdige produkter. Kapitel 2 og 4.1 giver de matematiske detaljer.

Kilder til nanomaterialer i miljøet
Ingen af de udvalgte nanomaterialer fremstilles i Danmark. Oplysninger om anvendelsen af nanomaterialer i diverse formuleringsprocesser er indhentet ved kontakt til virksomheder, der fremstiller pigmenter, maling (herunder bundmalinger) og lak samt plast og kosmetik.

Som en generel tendens (med få undtagelser), har virksomheder i den kemiske sektor gennem de seneste årtier flyttet væsentlige dele af produktionen til Østeuropa eller Asien, og aktiviteterne i Danmark er begrænset primært til forskning og formulering af kemiske produkter i brugsklare produkter. For eksempel finder det meste af produktionen af maling o.lign. sted i udlandet, men visse specialmalinger produceres stadig lokalt af en række små og mellemstore danske virksomheder. En henvendelse til brancheorganisationen DFL identificerede kun en enkelt virksomhed, der anvendte nanomaterialer, men fra andre undersøgelser vides det, at nanomaterialer anvendes af i hvert fald et mindre antal virksomheder. Af fortrolighedshensyn kan konkrete oplysninger om anvendelsen af nanomaterialer til forskellige formuleringsprocesser ikke offentliggøres.

Industrielle punktkilder, der udleder spildevand direkte til overfladevand i Danmark, omfatter hovedsagelig industrier inden for fødevare- og fodersektoren, lufthavne, renseanlæg, skibsværfter, lossepladser/deponier og kraftværker. Undersøgelsen identificerede kun én virksomhed med direkte udledning til vandmiljøet af de nanomaterialer, der er omfattet af denne rapport, og sandsynligvis er der kun få virksomheder, der anvender de pågældende materialer, der udleder renset spildevand direkte til overfladevand. Mere almindeligt ses det, at det forbehandlede spildevand bliver ledet til et kommunalt renseanlæg mhp. videre behandling.

Både til produktion af pigmenter og produktion af maling og lak importeres nanomaterialer som pastaer, og støv synes ikke at være et problem når nanomaterialer anvendes i formuleringsprocesser. For de undersøgte nanomaterialer er brugen af nano-TiO2 (både fotostabilt og fotokatalytisk), nano-CeO2 og carbon black blevet bekræftet. Spildevand fremkommer ved rensning af tanke og andet produktionsudstyr. Det første skridt i spildevandsrensningen var på alle lokaliteter en on-site udfældning/flokkulering resulterende i, at størstedelen af nanomaterialet i spildevandet udfældes og ender i slam/filterkage, der bortskaffes til off-site forbrænding eller forgasning. Det forbehandlede spildevand ledes enten til kommunale renseanlæg eller behandles yderligere på produktionsstedet. Direkte udledning til luften anses for ubetydelig. Overførselskoefficienter blev beregnet ved at kombinere oplysninger fra danske producenter med sektorspecifikke overførselskoefficienter fra OECD's såkaldte Emission Scenario Documents for den pågældende sektor.

Andre igangværende kortlægninger af anvendelsen af nanomaterialer i Danmark har indikeret at TiO2, ZnO og CB anvendes i medicinsk udstyr, der er fremstillet i Danmark. Ifølge oplysninger indhentet i denne undersøgelse anvendes TiO_2 og ZnO (ikke nano) som pigmenter i danskproduceret medicinsk udstyr, mens nano-TiO2 og nano-ZnO ikke anvendes. CB anvendes som pigment ved fremstilling af medicinske apparater og også som pigment ved mange andre applikationer. Der er ikke tilvejebragt specifikke data om udledninger af CB fra plastindustrien, så overførselskoefficienterne er beregnet ud fra OECD Emission Scenario Documents for sektoren.

Ifølge oplysninger fra de andre igangværende undersøgelser indeholder dansk-producerede solcremer til det danske marked generelt ikke nano-TiO2 som UV-filtre, men nano-TiO2 tilsættes andre kosmetiske produkter med henblik på solbeskyttelse. Det har ikke været muligt at få kvantitative data vedrørende brugen af nano-TiO2 i dansk produktion, men nogle oplysninger om potentielle mængder og håndteringen af nanomaterialerne under produktionen er indhentet fra tidligere undersøgelser. Nano-ZnO er i øjeblikket ikke opført på listen over godkendte UV-filtre til kosmetik i EU og Danmark, men pigment-grade ZnO kan anvendes. Overførselskoefficienter blev estimeret ud fra OECD Emission Scenario Documents.

Renseanlæg
Renseanlæg betragtes som en af de vigtigste kilder til frigivelse af nogle af de undersøgte nanomaterialer til miljøet. Der er dog ikke identificeret specifikke empiriske data om de faktiske udledninger af nanomaterialer til kommunale kloaksystemer eller om udledninger fra renseanlæg til vandmiljøet.

I rapporten bruges ekspertvurderinger og generelle oplysninger til at fastlægge overførselskoefficienter til beregning af de mængder, der udledes til kloaksystemet fra fremstillingsprocesser, fra brugen af materialerne i blandinger og artikler og fra affaldshåndtering. Desuden præsenterer rapporten overførselskoefficienter for både interne behandlingsprocesser på renseanlæg og koefficienter for direkte udledninger til overfladevand fra overløb som følge af kraftig regn og oversvømmelser, og fra separate regnvandsafledningssystemer. Oplysninger om de anvendte inputparametre til modellen er for hvert materiale angivet i bilag I.

Kilder til og miljømæssig eksponering af ENM - Casestudier

Titandioxid (nano-TiO_2)
Anvendelsen af nano-TiO_2 blev delt i to grupper i denne undersøgelse: en gruppe med fotostabilt TiO_2 og andre anvendelser (hovedsagelig anvendelsen som UV-absorbere), samt en gruppe med fotokatalytisk TiO_2.

Der findes to krystalstrukturformer af TiO2, anatase og rutil, hvoraf anatasestrukturen er en mere effektiv fotokatalysator end rutilstrukturen. Som følge heraf indeholder de fleste fotokatalytiske forbrugerprodukter anataseformen af nano-TiO_2. Dog bruges en blanding af begge krystalstrukturer ofte og opdelingen i de to grupper afspejler derfor ikke en fuldstændig opdeling af de to krystalstrukturer. Den schweiziske undersøgelse af Sun et al. (2014) skelnede ikke mellem disse to grupper, og derfor er de anvendelsesområder, der indgår i den schweiziske undersøgelse, fordelt mellem de to grupper ud fra, hvad der blev anset for at være den vigtigste anvendelse inden for hvert område. Eksempelvis blev maling tildelt gruppen med fotokatalytisk TiO_2, selvom nogle malinger kan indeholde TiO_2 brugt som UV-absorber.

A: Fotostabilt nano-TiO_2 og andre anvendelser
De vigtigste anvendelser, som er anført i den schweiziske undersøgelse var kosmetik, rengøringsmidler, plast og forbrugerelektronik. Baseret på gennemsnitsværdier af massen af nanomateriale i de forskellige produktkategorier, tegnede kosmetik sig for over halvdelen af det samplede forbrug. I betragtning af, at hovedparten af disse bliver frigjort direkte til miljøet eller til renseanlæg, er denne anvendelse sandsynligvis den største kilde til nano-TiO_2 i miljøet. Anvendelsen af nano-TiO_2 i solcremer i Danmark er sandsynligvis lavere end EU-gennemsnittet, eftersom det nordiske miljømærke (Svanemærket) ikke tillader brug af TiO2 i solcremer. Idet eksakte kvantitative data for forbruget ikke har været tilgængelige, er dataene fra den schweiziske undersøgelse benyttet som et "worst case" estimat. En række andre anvendelser nævnt i den schweiziske undersøgelse havde et forbrug i intervallet fra nul til nogle få procent af totalen. Fotostabilt nano-TiO_2 bruges i Danmark til produktion af pigmenter, kosmetik og eventuelt maling. En igangværende undersøgelse har vist, at brugen af TiO2 til produktion af solcremer i Danmark er faldet i de seneste år, men nano-TiO2 kan anvendes i andre typer af kosmetik. I mangel af nyere kvantitative data, blev oplysninger fra en tidligere undersøgelse anvendt som et bedste skøn for de mængder, der anvendes i kosmetikindustrien

Tidligere studier (Gottschalk et al., 2009; Sun et al., 2014) har vist, at blandt alle de metalliske nanomaterialer, der har indgået i denne undersøgelse, er den modellerede akvatiske eksponering højest for nano-TiO_2. Dette er også observeret i nærværende studie til trods for, at vi har modelleret en større eliminering af nano-TiO_2 i renseanlæggene som følge af nye måledata, der forudsagde en større eliminering af ENMs fra spildevandet fra renseanlæg. En begrænsning i den anvendte model har dog været, at selv om forskningen inden for nanomaterialers aggregering til stadighed udvikler sig, har vi for målmaterialerne måttet antage sandsynlighedsfordelinger over et bredt spektrum af umiddelbar aggregering og/eller sedimentation og ingen sedimentation overhovedet. Det vurderes at ville have stor værdi for sikkerheden i modellen, hvis dette spektrum kan begrænses.

De højeste koncentrationer, fra få µg/l op til næsten 100 µg/l (modalværdien var omkring 13 µg/l), blev fundet i spildevand fra renseanlæg. Koncentrationerne i ferskvand nåede højst 0,1 µg/l ("worst case" scenarie), mens koncentrationerne i havvand var helt nede i pg/l. Jord og sediment var de væsentligste "sinks" for nano-TiO_2, med forventede omtrentlige koncentrationer (baseret på de hyppigste forekommende resultater) for år 2020 på 3 mg/kg i jord gødet med slam og på et par tiendedele af µg/kg i jord, der ikke var blevet gødet med slam. I sedimenter (ferskvand og havvand), var de modellerede koncentrationer hhv. 2, 4 og 0,8 mg/kg. Koncentrationerne i luft var marginale, som det er tilfældet med næsten alle undersøgte ENM, og værdierne var i størrelsesordenen pg/m^3. Dette afspejler hovedsageligt meget små direkte emissioner til luft forbundet med brugen af nanoprodukter, samt en nærmest fuldstændig eliminering af nanomaterialerne i affaldsforbrændingsanlæg. Eftersom disse resultater er generelt gældende for næsten alle de nanomaterialer, der er undersøgt, vil lufteksponering ikke blive diskuteret yderligere i dette resumé.

Det må konkluderes, at der for det første mangler mere præcis viden om skæbne og opførsel af fotostabilt og andet TiO_2 i renseanlæg, jord og vand, og for det andet mangler der derudover kvantitative informationer om det reelle danske forbrug, da disse to parametre er langt de vigtigste i en miljømæssig eksponeringsvurdering. Mangel på kvantitative data gælder generelt for alle de undersøgte nanomaterialer og vil derfor ikke blive nævnt i de følgende afsnit.

B: Fotokatalytisk nano-TiO_2

UV-stråler og synligt lys kan fremkalde katalytisk aktivitet i fotokatalytisk nano-TiO_2. Via den fotokatalytiske effekt dannes reaktive iltradikaler, der kan nedbryde organiske stoffer og bakterier på belyste overflader, hvorved man kan opnå selvrensende/antibakterielle virkninger. De vigtigste anvendelser, som er anført i den schweiziske undersøgelse, var maling, overfladebehandlinger og rensning af luft og vand, hvorimod byggematerialer (selvrensende overflader med TiO_2) og spildevandrensning var angivet som mindre sandsynlige anvendelsesområder. Fotokatalytisk TiO2 bruges i den danske produktion af maling med antibakteriel, selvrensende effekt.

Så vidt vides præsenterer denne rapport den første undersøgelse, hvor der specifikt fokuseres på fotokatalytisk nano-TiO_2. Belastningen med fotokatalytisk nano-TiO_2 i vand udgør ikke meget (en tiendedel) af den samlede belastning af nano-TiO_2 i det akvatiske miljø. Koncentrationen i overfladevand var maksimalt i enheden pg/L, hvilket er sammenligneligt med koncentationen af nano-ZnO (se næste afnit). Relevansen for det akvatiske miljø af nano-TiO_2-kan derfor variere betydeligt, alt afhængigt af typen af anvendelsen af nanomaterialet. I forbindelse med fremtidige risikovurderinger og toksikologiske undersøgelser vil det derfor være vigtigt at skelne mellem disse to kategorier af TiO_2. Relativt lave miljøkoncentrationer er er også blevet modelleret for sediment, hvor koncentrationer på ca. 200 µg/kg (ferskvandssediment) og 60 µg/kg (marint sediment) (modale værdier) er blevet beregnet for år 2020. I jord gødet med spildevandsslam, er den modelberegnede koncentration på omkring 350 µg/kg (modal værdi) for år 2020. Fotokatalytisk nano-TiO2 ender hovedsageligt til genanvendelse og til deponering i affaldsdepoter, hvilket også er tilfældet for flere andre ENM. Derfor bør skæbnen og opførslen af ENM i sådanne anlæg i undersøges grundigt.

Zinkoxid (nano-ZnO)
Den største anvendelse af nano-ZnO i den schweiziske undersøgelse var som UV-filter i solcreme, og denne tegner sig for over halvdelen af forbruget. Nano-ZnO er dog ikke inkluderet på listen over de UV-filtre, der er tilladt i kosmetiske produkter i EU og Danmark. ZnO i pigmentkvalitet kan bruges som hvidt pigment, men dette betragtes ikke som et nanomateriale. Til modelleringen blev forbrugsdata fra den schweiziske undersøgelse benyttet som worst case-estimater, der dog skulle forfines, hvis resultaterne skulle pege på en miljørisiko. Den eneste anden større anvendelse af nano-ZnO identificeret i den schweiziske undersøgelse var brugen i maling. Der er ikke identificeret nogen anvendelse af nano-ZnO i produktionsprocesser i Danmark.

Casestudiet med Nano-ZnO viste ingen signifikante belastninger eller koncentrationer, hverken i vandmiljøet eller i jord. PEC i ferskvand var hovedsagelig i størrelsesordenen pg/l til nogle ng/l, mens marine koncentrationer var omkring en faktor 10 mindre, og alle i pg/l-koncentrationer. I jord og sedimenter, var de beregnede mængder af nano-ZnO meget små. I 2020 forudsiger modellen koncentrationer på et par hundrede ng/kg i jord og et par hundrede µg/kg i sedimenter. Disse værdier er meget lavere end de forudsagte koncentrationer for fotostabilt nano-TiO2, som er i mg/kg.

Sølv (nano-Ag)
Nanosølv kan have forskellige anvendelser, herunder som antimikrobielt middel i tekstiler, rengøringsmidler, maling, kosmetik og på overflader med høje hygiejnekrav (f.eks køkkenudstyr og medicoteknisk udstyr). Der er ikke identificeret nogen faktisk brug af nanosølv i produktionsprocesser i Danmark, og modellens parametre stammer derfor alle fra den schweiziske undersøgelse. Til visse typer applikationer findes nano-Ag dispergeret i en blanding (f.eks maling og trykfarver), mens det i andre findes adsorberet til en overflade (f.eks. tekstiler) eller indlejret i en polymer matrix, som f.eks. overflader af køkkenudstyr og beholdere til opbevaring af fødevarer. Generelt er der begrænsede oplysninger om de forskelige anvendelser, men de schweiziske data indikerer, at der kan være mere end 10 væsentlige anvendelsesområder.

De meget små mængder nano-Ag og den effektive fjernelse heraf ved spildevandsbehandling, samt meget effektiv fjernelse ved affaldsforbrænding resulterer i konsekvent små mængder udledninger til miljøet af dette nanomateriale. Den største del af det nano-Ag, der tilgår renseanlæg, omdannes til sølvsulfid (Ag2S). I ferskvand og havvand var koncentrationerne af nano-Ag på pg/l-niveau, og næsten nul for en række af de Monte Carlo-simulerede scenarier. Koncentrationerne i jordmiljøet var endnu lavere end for nano-ZnO, hvilket betyder, at nano-Ag omdannes næsten fuldstændigt til ikke-nano-former ved spildevandsbehandling.

Kulstofnanorør (CNT)
De vigtigste anvendelser af CNT er som kompositmateriale og polymeradditiv samt som en bestanddel af batterier. Slutanvendelser omfatter fladskærme, super komposit-fibre, elektrisk ledende plast, udendørs batterier, mikroelektronik baseret på halvledere og andet ledende materiale. Tal for det potentielle forbrug til disse anvendelsesformål blev estimeret baseret på dataene fra den schweiziske undersøgelse. Der har ikke kunnet indhentes oplysninger om brugen af CNT i den danske plastindustri, men det kan ikke udelukkes at de anvendes. Der er gennemført F&U-projekter i Danmark om anvendelser af CNT, blandt disse er et NANOPLAST-projekt med titlen "Nano-teknologiske materialer og produkter i plastindustrien: Vurdering af eksponering og toksikologiske egenskaber".

Modelberegningerne viste meget små mængder af CNT (et par tons årligt), hvoraf en stor del (op til 90 95%) går til genbrug eller ender i affaldsforbrænding og på deponeringsanlæg. Resultaterne viser, at den miljømæssige eksponering for CNT er helt marginal. Dette gælder for vandmiljø og terrestrisk miljø. CNT-koncentrationerne i naturlige vandområder var på pg/l-niveau i ferskvand og kun nogle fg/l i havvand. I 2020 forventes der ikke koncentrationer på meget mere end et par ug/kg i ferskvandssediment. Op til 2020 vil koncentrationerne af CNT i jord ikke bidrage væsentligt til den eksisternde pulje af kulstof.

Kobber (nano-CuCO3, nano-CuO og nano-Cu)
Nano-kobber indgik ikke i den schweiziske undersøgelse. Tre forskellige former af nanokobber er overvejet i dette projekt, og af disse vurderes anvendelsen af kobbercarbonat ($CuCO_3$) på mikroform til brug i træbeskyttelsesmidler potentielt at udgøre den største del. Mikro-$CuCO_3$ er ikke designet som et nanomateriale, men vil sandsynligvis falde ind under definitionen med den nuværende partikelstørrelsesfordeling. Producenterne forsøger at optimere slibeprocessen med henblik på at have færre partikler under 100 nm, og i fremtiden kan mikro-$CuCO_3$ således muligvis komme til at falde uden for definitionen på nanomaterialer. Kobbercarbonat på mikroform markedsføres i øjeblikket ikke i Danmark, men i USA udgør mikro-kobber omkring 75-80% af markedet for denne type produkter. Det forventes, at i de kommende år vil mikro-$CuCO_3$ erstatte en væsentlig del af den $CuCO_3$, der i dag anvendes til træbeskyttelse i Danmark. Kobbercarbonat anvendes til produktion af trykimprægneret træ i Danmark, og mikro-$CuCO_3$ kan allerede være til stede i importeret behandlet træ. Brugen og frigivelse af $CuCO_3$ blev modelleret for et scenarie med en fremtidig situation, hvor mikro-$CuCO_3$ har erstattet den $CuCO_3$, deranvendes i dag. Modelberegningen blev vanskeliggjort af usikkerheden om den faktiske forekomst af nanopartikler i det behandlede træ og hastigheden hvormed partiklerne frigøres fra træet. Nano-CuO kan anvendes til forskellige formål, som omtales i rapporten, men de samlede mængder i importerede blandinger og artikler er ikke estimeret. Kobberoxid er almindeligt anvendt som antibegroningsmiddel i malinger, og sådanne malinger er beskrevet i litteraturen som et potentielt anvendelsesområde for nano-CuO. Ifølge en dansk producent og importør af kobberbaserede antibegroningsmalinger indeholder disse malinger dog ikke i dag kobberoxid på nano-form.

Modelberegningerne for nanokobber (nano-$CuCO_3$) gav resultater, der var helt anderledes end for de øvrige metalliske nanomaterialer omfattet af dette projekt. Anvendelsen som træimprægneringsmiddel medfører en stor masseoverførsel i affaldsstrømme (affaldsforbrænding, genanvendelse og deponering). Det skal dog igen understreges, at vores modelkørsel stoppede ved de sidste to nævnte anlægstyper ved at antage, at de ikke giver anledning til miljømæssige udslip. Som eksempel kan nævmes, at intet vand antages at passere gennem sådanne anlæg og derfor kan der heller ikke ske nogen udvaskning. Med den standard, som de danske anlæg har, synes denne forudsætning at være realistisk. Den største andel af tilførsel af nano-kobber til miljøet (cirka. 98%) skyldes frigivelse direkte fra imprægneret træ til jord og primært ved direkte kontakt mellem træ og jord, men også via deposition fra luft. De fleste af de 100.000 udførte Monte Carlo-modelberegninger viste koncentrationer på nogle få ng/l i ferskvand og pg/l-niveauer i havvand. Derimod kan en vis eksponering af jord kan ikke udelukkes i fremtiden (2020), da højeksponeringsscenarierne viste værdier op til ca. 200 µg/kg jord. Så høje værdier forekommer dog kun ved "worst case", hvor det antages, at mikro-Cu udgør en stor del af den samlede mængde nanokobber anvendt til træimprægnering.

Det skal påpeges, at hvis der i fremtiden forekommer nye eller forøgede anvendelser af nano-$CuCO_3$ i kombination med en høj andel på mikro-form, og dermed højere afgivelse til miljøet, kan en revurdering af miljøeksponeringen blive nødvendig.

Nul-valent jern (nano-ZVI)
Nul-valent jern (ZVI) kan bruges til in situ oprensning af forurenet jord og grundvand. Nul-valent jern (ikke i nanostørrelse) er i mindst fire tilfælde blevet anvendt i fuld skala på oprydningsprojekter i Danmark. Desuden blev nano-ZVI nylig anvendt ved en pilotundersøgelse i Danmark. På baggrund af erfaringerne fra pilotundersøgelsen er et fuldskala-scenarie for oprydning med nano-ZVI blev modelleret i dette projekt.

I casen for nano-ZVI er der fokuseret på lokale jordscenarier idet dette nanomateriale ikke for øjeblikket forventes at få mange forskellige anvendelser. Selv om visse medicinske anvendelser er nævnt i litteraturen, synes anvendelsen til oprydning af forureninger i jord (og grundvand) i øjeblikket at være den eneste relevante. En sådan oprensning har lokal karakter på grund af den høje umiddelbare reaktivitet af nano-ZVI. Vores hypotetiske worst case-beregninger for nano-ZVI (ingen transformation af jern efter tilledning til jordmatricen) viste nogle hundrede ug/kg i jord, hvilket ikke kan siges at være en væsentlig koncentration i sammenligning med de naturligt forekommende koncentrationer af jern i jord (nogle g/kg jord).

Ceriumdioxid (nano-CeO2)
Da nano-CeO2 ikke indgik i den schweiziske undersøgelse blev der til dette projekt anvendt data fra en undersøgelse af anvendelsen af nanomaterialer i EU. De vigtigste anvendelser i EU blev vurderet at være som additiv til diesel, til bilkatalysatorer, glaspoleringsmidler, malinger og diverse coatninger. For hver af disse anvendelser blev der estimeret transferkoefficienter. Brugen af nano-CeO2 som UV-filter i træolier fremstillet i Danmark blev bekræftet.

De forbrugte mængder af nano-CeO2 i Danmark vurderedes at være forholdsvis små med mest sandsynlige værdier på omkring 5 tons årligt. Resultaterne af modelberegningerne viste belastningsværdier for nano-cerium i naturlige miljør, der ikke overstiger 0,5 tons om året. De væsentligste udledninger til miljøet var gennem spildevandsslam udbragt på jord samt visse luftemissioner. Disse udledninger/emissioner var alle små, dvs. var mindre end tons/år per anvendelse.

Modellerede koncentrationer af nano-CeO2 i ferskvand og i det marine miljø var på pg/l niveau og nogle koncentrationer var endda helt nede i fg/l. I 2020 forventes modalværdier for ikke-slamgødet jord at være på ca. et par hundrede ng/kg jord, mens de vil være et par µg/kg jord i slamgødet jord.

Quantum dots
For quantum dots stammede de anvendte data ligeledes grundlæggende fra en undersøgelse af anvendelsen af nanomaterialer i EU. Quantum dots er halvledermaterialer baseret på metaller såsom cadmium (Cd) og zink (Zn) med en størrelse på fra 2 til 10 nm i diameter. Anvendelser af quantum dots i produkter og forbrugsartikler omfatter halvledertransistorer, solceller, lysemitterende enheder (f.eks LEDs), diode lasere og medicinsk billedbehandlingsudstyr. Der er ikke fundet oplysninger om brugen af quantum dots i produktion i Danmark, men sådan brug kan på den anden side heller ikke udelukkes.

De nuværende danske mængder af quantum dots ligger mest sandsynligt på under 0,5 tons om året. De modelberegnede koncentrationer i luft og overfladevand var så små, at en detaljeret evaluering af deres sandsynlighedsfordelinger ikke blev udført. Resultaterne gav hovedsagelig værdier på mindre end nogle fg/l for vandmiljøer eller fg/m^3 for luft. Et par µg/kg forventes som typisk koncentration i sedimenter i 2020 (ferskvand) og endnu lavere i marine sedimenter. Der er ingen andre af undersøgte nanomaterialer i denne rapport, der er beregnet at ville forekomme i så lave koncentrationer.

Carbon black
Carbon black er elementært kulstof i form af et ekstremt fint, sort pulver, der er udbredt anvendt som sort pigment. De primære carbon black-partikler opfylder definitionen for nanomaterialer. Imidlertid kan de primære partikler allerede under fremstillingsprocessen danne større aggregater, og senere kan der dannes agglomerater på 1-100 mm i diameter bestående af hundredvis til tusindvis af sammenhæftede små aggregater. Selv om aggregeringen, der opstår spontant i fremstillingsprocesser, producerer ubrydelige aggregater af en gennemsnitsstørrelse på generelt over 100 nm, kan carbon black omfatte en begrænset andel af partikler, der er mindre end dette, altså nanoskala-partikler. På verdensplan anvendes 90% af al carbon black i gummiindustrien som

forstærkende materiale i en række forskellige produkter, hvoraf bildæk det største enkelte anvendelsesområde. I Danmark blev der identificeret anvendelse af carbon black som sort pigment til fremstilling af trykfarver, malinger, plast, kosmetik og tekstiler.

Modelberegningerne for carbon black viste de højeste eksponeringer for alle medier blandt de materialer, der er omfattet af denne rapport, dvs. værdier i kilotons om året i stedet for tons om året. Desuden koncentrerer anvendelserne sig omkring gummiblandinger, som er et ideelt udgangspunkt for betydelig materialefrigivelse til miljøet som følge af stadig materialenedbrydning ved slitage. I den anvendte model antages det, at hele den frigivne andel af carbon black vil forekomme på nanostørrelse, hvilket med sikkerhed medfører en konservativ eksponeringsvurdering da carbon black også vil kunne frigives som ikke-nanopartikulært materiale fra den oprindelige kilde og de egentlige carbon black-koncentrationer i nanostørrelse derfor kan være lavere. Endelig skal det nævnes, at det i praksis vil være næsten umuligt at skelne mellem fremstillet og naturligt forekommende carbon black (fx fra forbrændingskilder). Ikke desto mindre bør en vis opmærksomhed rettes mod de mulige negative virkninger på miljøet af bevidst fremstillet nano-carbon black.

Konklusioner vedrørende ENM-kilder og miljømæssig eksponering

Der er ikke identificeret nogen særlig dansk produktion, hvor de udvalgte ENM indgår, eller andre former for særlige danske kilder ift. afgivelse til miljøet. Det skal dog nævnes, at det har været vanskeligt at indhente konkrete oplysninger om produktion, import og anvendelse (typer og mængder) af nanomaterialer i Danmark, hvorfor den anvendte model i betydelig grad har måttet baseres på viden og data om brugen af nanomaterialer indsamlet i andre europæiske sammenhænge. Dog er der benyttet specifikke danske data vedr. geografi og forskellige overordnede samfundsmæssige forhold, f.eks. vedrørende affalds- og spildevandshåndtering.

De fleste af de modellerede scenarier for de udvalgte ENM har kun vist en ret lille årlig udledning til det naturlige miljø, dvs. nogle tons om året. I nogle få tilfælde (f.eks nano-Ag, CNT, nano-CeO2) når størrelsen af udledningerne, selv for de høje udslipsscenarier, ikke engang op på tons om året-niveauer. Disse resultater for den samlede udledning til miljøet er på linje med resultater fra andre europæiske undersøgelser. Dog er det for flere af nanomaterialerne (nano-CuCO3, nano-CeO2, nZVI, quantum dots, carbon black) første gang at en så omfattende undersøgelse præsenteres. Særlig bemærkelsesværdige resultater vedrørende nanomaterialers udledning til og eksponering af miljøet er frem for alt blevet fundet for fotostabilt og andet nano-TiO2m samt for carbon black i vand- og jordmiljøet, og for kobbercarbonat i jord.

Selvom vores model giver nogle klare afgrænsninger af eksponeringsniveauerne, der udelukker urealistiske ENM-koncentrationer, er det nødvendigt eksplicit at gøre opmærksom på grænserne for fortolkning af resultaterne. Således kan eksponering i fremtiden blive betydeligt højere end modelleret, hvis der kommer en stigende produktion og anvendelse af de undersøgte nanomaterialer. Så længe brancherne/virksomhederne er tilbageholdende med at give oplysninger om anvendelser og mængder af industrielt fremstillede nanomaterialer er det dog næsten umuligt at pege hvilke specifikke ENM, der har særligt potentiale for høje udslip til og eksponering af miljøet. Den øgede elektrificering af transportmidler kan medføre øget brug af ENM, f.eks. i batterier (fx QD, CNT). For CNT er der store forventninger til en række mulige anvendelser (polymerkompositter, forbrugerelektronik, tekstiler etc.), som dog ikke synes at have noget større kommercielt omfang i øjeblikket. Fuld gennemtrængning på markedet af nano-CuCO3 til træbeskyttelse eller nanostørrelse CeO2 som brændstofadditiv vil kunne føre til scenarier af miljømæssig betydning. Bedre forståelse af og flere empiriske data vedr. brug og importerede mængder af ENM i Danmark er den vigtigste faktor for opdatering og forbedring af modelberegningerne og deraf følgende bedre miljøeksponeringsvurdering.

Det nye ved det udførte modelleringsarbejde i dette projekt fordeler sig på flere søjler med forskellige nyhedsfacetter, der spænder fra nye modeldatainput og -geometri til nye ENM, der er undersøgt. For det første har modellen draget nytte af resultater og data fra det første delprojekt under NanoDEN (miljømæssig skæbne og opførsel af nanomaterialer), der har indsamlet og evalueret den nyeste videnskabelige viden om en række miljømæssige skæbne- og adfærdsparametre for ENM generelt og specifikt for de udvalgte materialer. Evalueringen af disse data viste, at med henblik på at kunne indarbejde bl.a. fotokemisk nedbrydning, oxidation, reduktion, adsorption, desorption og biotransformation i den generiske massetransportmodel, er den aktuelle database for tynd. Der er dog sket visse fremskridt i de seneste år, således at det ikke kan udelukkes, at sådan viden vil være tilgængelig i nærmere fremtid, og allerede nu var det muligt at fodre modellen med nye data om industrielt fremstillede nanomaterialers opløsning og aggregering/agglomerering (der fører til sedimentation). For nogle metaller (fx Ag, CeO2 eller ZnO) ses det således, at de kan gå i opløsning ved kontakt med vand, hvilket kan forekomme i løbet af et nanoprodukts brugsfase ved afgivelse til spildevand fra en bred vifte af anvendelser (kosmetik, tekstiler, maling, belægninger, mad, rengøringsmidler etc.), eller efterfølgende under materialets behandling i renseanlæg.

Viden om sedimentation er afgørende for at kunne estimere opholdstiden af nanomaterialer i vand, herunder ved spildevandsbehandling, såvel som den følgende ophobning i sedimenter og spildevandsslam (og fra luft til jord og vand). I delprojekt 1 blev det bekræftet, at der i øjeblikket mangler videnskabelig viden på dette område, og at mange af beregningerne derfor er baseret på en antagelse om øjeblikkelig eller næsten ingen sedimentation (for vand-sediment transport). Dog har modellen i forbindelse med nano-TiO2 og nano-ZnO i spildevandsbehandlingsprocesser kunnet baseres på klart forbedrede parametre, der viser meget højere fjernelse fra vandfasen, i forhold til tidligere, sammenlignelige undersøgelser foretaget på schweiziske eller europæiske geografier.

Med hensyn til opholdstid i luft er det p.t. nødvendigt at basere modellen på generel viden om ultrafine partikler, men da afgivelse til luft konsistent er lav forårsager denne "grovhed" ved modellen ikke nogen væsentlig indvirkning på resultaterne. Yderligere nyhedselementer i vores model er, at vi så vidt muligt har anvendt de nyeste oplysninger (samt de første specifikke danske data) om mængder af de industrielt fremstillede nanomaterialer samt fuldstændige livscyklusoplysninger for de vurderede nanoprodukter. Begge slags modelparametre er meget vigtige for fastlæggelsen af udlednine af ENM til miljøet. Endelig er det, så vidt vides, første gang, at der er foretaget en så omfattende dataindsamling og eksponeringsmodellering af nanoformerne af stoffer som CUCO3, ZVI, CeO2, CB og QD.

1. Introduction

1.1 Background

Engineered nanomaterials (ENMs) are expected, in the short and medium terms, to be increasingly used in an increasing and unlimited field of applications in research and industry (Mangematin and Walsh, 2012). Scientific consensus also predicts that, due to such broad use, ENMs may be released into the environment (Nowack et al., 2012). A distinct lack of knowledge faces environmental risk analysts with regard to the fates and behaviours, as well as the potential negative effects, of ENMs for organisms in the natural environment (Wiesner et al., 2006; Nowack and Bucheli, 2007; Baun et al., 2008; Gottschalk and Nowack, 2011; Grieger et al., 2012; Nowack et al., 2012).

Beyond such scientific gaps, society is faced with governmental and regulatory challenges related to nanospecific risk analyses, risk evaluation methodologies and political recommendations (Grieger et al., 2009; Grieger et al., 2010; Grieger et al., 2011; Hansen and Baun, 2012). The Danish Environmental Protection Agency (EPA) has launched several research projects and investigations focused on the emissions and fates of such materials in natural environments. These studies have covered (based on a whole-lifecycle perspective of ENMs and the products containing them), not only the materials' release into and fates in natural environments, but also relevant Danish product consummation processes, material fates and releases during waste handling and incineration, sewage treatment and recycling processes and disposal and recycling procedures. By assessing the release of ENMs and the resulting exposure concentrations in the environment and by comparing these to potentially negative (eco)toxicological effects, the probability of associated risks for the environment (and consumers) can be estimated.

Nanomaterials' release into the natural environment is expected to occur both intentionally and unintentionally throughout the lifecycle of nanomaterial production, use and disposal (Nowack and Bucheli, 2007; Koehler et al., 2008). Intentional discharge into natural media must be considered because such discharge occurs through, for example, the use of nano-zero valent iron (nano-ZVI) in the remediation of groundwater polluted with chemicals, such as chlorinated solvents (Grieger et al., 2010). Non-intentional discharge refers to discharges from, for example, wastewater treatment streams, landfill leachates and waste incineration products, all of which are likely to contain nanomaterials from nano-enabled products disposed at the end of their use phases, from accidental spills during production or the later transport of nanomaterials or from releases due to wear and tear on materials containing engineered nanomaterial (Nowack et al., 2012).

Presently, secure scientific knowledge on the environmental release, exposure concentrations and possible ecotoxicological effects of ENMs is limited (Gottschalk et al., 2013b). A recent review (Gottschalk et al., 2013b) collected and critically evaluated a dozen studies that modelled environmental concentrations for several nanomaterials (i.e., TiO_2, Ag, ZnO, CNT, fullerenes and CeO_2). This review evaluated several of the analytical contributions to such concentrations, creating a rough and early validation of the available modelled results. The major gaps and limitations found reflect difficulties in the estimation of nanomaterial production and use amounts, resulting in a very uncertain assessment of environmental release amounts. A secure validation of the modelled PECs will be difficult until trace analytical methods suitable for material detection and quantification at nanosized levels become available (von der Kammer et al., 2012). The few measurements that are currently used, which combine various filtration, spectro- and microscopic, chromatographic and other techniques, cannot be used for real-time or long-term exposure concentration monitoring.

However, as shown in Gottschalk et al. (2013b) experimental/analytical results concerning ENM release and concentrations in natural media are not completely absent. The mentioned review underlines that it has repeatedly been shown that, for example, nanoTiO_2 and/or nano-Ag may reach natural waters when used in paints (e.g., paints for house facades) (Kaegi et al., 2008; Kaegi et al., 2010). Nanosilver has been found in wastewater treatment, and its fate there (e.g., the formation of nanosulfide) is thus far understood to some extent (Kaegi et al., 2011). The same applies to, for example, certain questions concerning the survival and elimination of nanosized metals (e.g., CeO_2) in waste incineration processes (Walser et al., 2012b; Walser and Gottschalk, 2014). ENM release during the washing processes of textiles has been measured several times (Benn and Westerhoff, 2008; Geranio et al., 2009; Benn et al., 2010; Windler et al., 2012). First explorations into the release of and exposure to ENM in work areas have been undertaken as well (Methner et al., 2010; Walser et al., 2012a). Finally, a few equivalent initial and rough analytical results concerning exposure in natural environments are also available: for example, nano-CeO_2 has been found in PM_{10} filter samples (Park et al., 2008); Ti (< 700 nm) has been found in effluents of sewage treatment plants (Kiser et al., 2009); Ti (<0.45 µm filtered fraction and <0.2 µm) has been found in English rivers (Johnson et al., 2011b; Neal et al., 2011); fullerenes has been found in effluents of waste water plants (Farré et al., 2010); and others, such as nano silver (Johnson et al., 2011a; Mitrano et al., 2012) and nanoTiO_x (Westerhoff et al., 2011), have been found in other waters. Aerosol fullerenes (<0.7 µm) was measured in Mediterranean atmospheric samples (Sanchis et al., 2011), and Ti (<300 nm) and similar Ti substances have been detected in marine sediments (Luo et al., 2011), soils and biosolids (Kim et al., 2012).

Against such a background of research, the reader may not expect our report to completely fill the gap between the current state of science and the urgent and permanent demand for completely indisputable results. Such results would have to cover the (measured or modelled) environmental fate, as well as the concentrations that can be used for environmental risk purposes. Nevertheless, beyond the aim of modelling specific Danish ENM releases (and exposure concentrations), a refinement of such results, including risk estimations, may be achieved by using the most updated evidence on the physico-chemical fates and behaviour analyses for ENM in natural media.

Our efforts concerning material release, fate and exposure modelling build on various previous studies, which mostly sought to consider the complete spectrum of possible ENM applications and release volumes. However, as stated by NanoSustain, “Regrettably, some of the models are based almost exclusively on hypothetical model input values and/or they only cover a limited lifecycle perspective and product application field” (NanoSustain, 2013). In this context of hypothetical data use, this report refers to several initial studies (Boxall et al., 2007; Musee, 2010; O'Brien and Cummins, 2010; Tiede et al., 2010; Johnson et al., 2011b). To risk assessment purposes, the limitations of other contributions based on classical colloid science approaches are reflected by the missing quantifications of ENM release volumes and exposure concentrations (Arvidsson et al., 2012).

As shown among others in our overview in Report 1 (NanoDEN, 2014), some of these models base their computations regarding the environmental fate and distribution of ENMs on classical approaches of colloid science (Arvidsson et al., 2011a; Arvidsson et al., 2011b), while others are designed to model chemical fates and material transport (Blaser et al., 2008; Mueller and Nowack, 2008; Gottschalk et al., 2009; Gottschalk et al., 2010b; Gottschalk et al., 2011; Praetorius et al., 2012; Sun et al., 2014).

Several of the above-mentioned modelling studies may be seen as first attempts to overcome the limitations of purely speculative and qualitative ENM exposure estimations, representing the first quantitative knowledge on environmental concentration results. Mueller and Nowack (2008), the authors of the first work to compute a completely lifecycle-based ENM release model, provided scenario-based results (including worst-case and almost zero release estimations) for nanoAg, nanoTiO_2 and CNT in waters, soils and air. This lifecycle-based methodology was later updated through refinements to the computation of the high uncertainty at each stage of ENM transfer in such multimedia contexts. A stochastic and probabilistic methodology (Gottschalk et al., 2010a) was used in several studies, and exposure concentrations for several ENMs (i.e., nanosized Ag, ZnO, TiO_2, fullerenes and CNT) were predicted for all environmental compartments (i.e., surface waters and ground waters, sediments, soils, sewage sludge, sludge-treated soils and air) (Gottschalk et al., 2013b).

The results of these first quantitative studies reflect all of the above ENM transfers from the anthroposhere/technosphere into the natural environment, computed based on a mass flow (deposition and transformation) analysis over the entire lifecycle of the target ENMs and their products. In this report, we will perform an ENM fate analysis by following the same lifecycle approach that covers ENM release during ENM production and incorporation into products, as well as during ENM use, degradation, disposal and recycling, as shown in detail in Annex I to this report. The most prominent nanoproduct categories are paintings, cosmetics, textiles and electronics, among others. Scientific and experimental studies of the environmental release of ENMs have been undertaken and reported for a few situations (e.g., releases from the washing of nanomaterial-containing textiles, releases from the degradation of painted facades, releases from waste incineration or sewage treatment processes, etc.) (Gottschalk and Nowack, 2011).

Given the difficulties in assessing precise parameter values for most release volumes and pathways, we based all our computational work on a stochastic/probabilistic model approach (Gottschalk et al., 2010a). Such Monte Carlo computer modelling, based on stochastic procedures, allowed us to cover as the complete spectrum of possible values (as far as possible) for each stage of the mass flow, including deposition and transformation. Hence, our MC scenario results reflect computer simulation results that provided predicted environmental concentrations (PEC) probabilities by considering (throughout the model) the uncertainty of all parameters related to environmental exposure.

1.2 Modelling approach

As shown in Figure 1.1, the elemental structure/geometry of our model (recently used by Sun et al. (2014)) aims to track ENM mass transfers throughout the complete lifecycle and covers several possible emissions pathways, including releases during ENM production, during the manufacturing of ENM products, during the use and degradation of ENM products; during transfers into and behaviours of ENMs in sewage treatment plants (STP) and waste incineration plants (WIP) and during landfill and recycling processes, as well as releases to water, sediments, air and soils and releases due to transfer kinetics between environmental compartments.

The values for the model input parameter data collection and estimation are shown in detail in a comprehensive Annex to this report and were partially derived from knowledge collected in Report 1 (NanoDEN, 2014). For transparency reasons, we present all the values fed into the MC simulations. In cases where specific values for Denmark were not available, we based our input parameter estimations on the results of the most updated knowledge from a recent and similar study conducted for European and Swiss contexts (Sun et al., 2014). Some literature data (Keller et al., 2013) were also available for global estimations of the likely ENM release into natural compartments. However, these global estimations were based solely on a single market report, without the indications of uncertainty or variability necessary for our stochastic, probabilistic computations.

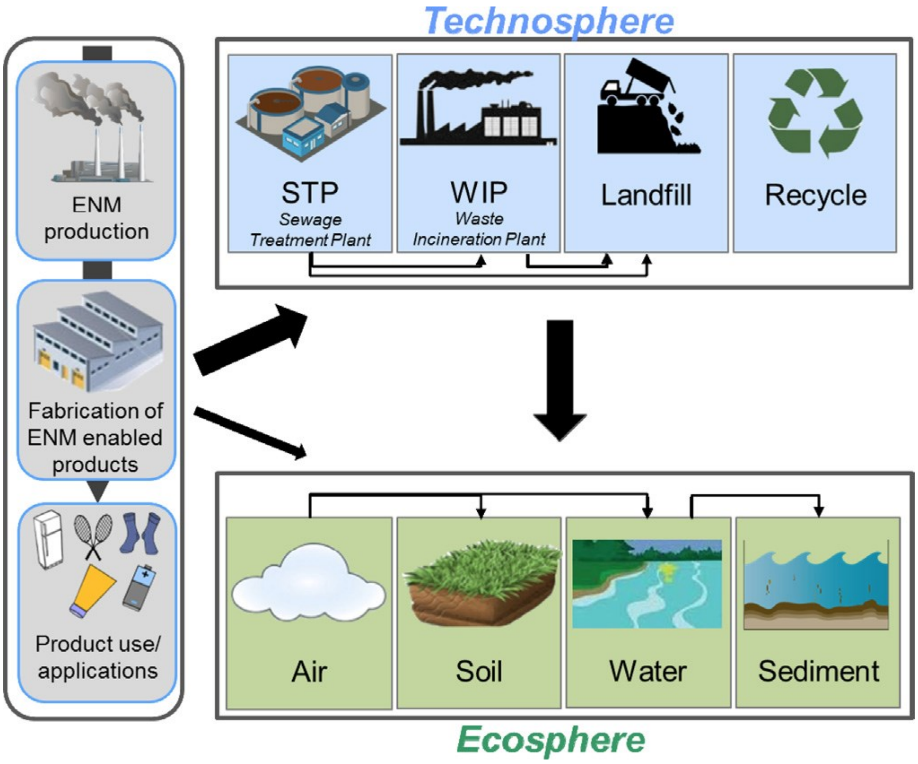


FIGURE. 1.1.
FUNDAMENTAL GEOMETRY OF THE MATERIAL-FLOW ANALYSIS TRACKING ENM MASS TRANSFERS THROUGHOUT THE COMPLETE LIFECYCLE: ENM PRODUCTION; ENM PRODUCT MANUFACTURING; ENM EMISSIONS DURING USE AND TRANSFER; THE BEHAVIOUR OF ENMS IN STPS AND WIPS RELEASES DURING LANDFILLS AND RECYCLING PROCESSES; RELEASES TO WATER, SEDIMENTS, AIR AND SOILS; AND RELEASES DUE TO TRANSFERS AMONG ENVIRONMENTAL COMPARTMENTS (SUN ET AL., 2014) (REPRINTED WITH PERMISSION, ELSEVIER, 2014).

1.3 Objectives

The main goal of NanDEN is to present the best possible answers to whether ENMs (both currently and in the near future) pose risks to the Danish environment or not. To reach such types of conclusions, we, in this report, aim to quantify the amounts of ENM that end up in natural compartments, as well as to some extents their residence times and behaviours in these compartments. We will focus our investigations on several relevant environmental matrices, such as waste, river water and sea water, urban and agricultural soils, river sediments and air. Concentrations are also presented for relevant technical compartments, such as sewage treatment sludge, municipal waste masses, the bottom ash of waste incineration processes and the fly ash from such processes.

Methodologically, our objective in this report is to adapt available methods (Gottschalk et al., 2010a) of environmental release and exposure modelling to Danish conditions. The techniques used allow for the implementation of a fully stochastic and probabilistic environmental exposure level analysis, based mainly on MC computations. Such stochastic computer simulations have been used in a series of nanomaterial case studies at different times and space levels for Swiss, European and American conditions (Gottschalk et al., 2013b; Sun et al., 2014). Our material transport model combines release quantification with an initial, very crude environmental fate analysis (see also (NanoDEN, 2014)) for the receiving of environmental compartments. This means, in the latter case, that our greatest aim is to capture, as much as possible and based on the newest available experimental knowledge, the influences of sedimentation, aggregation and dissolution behaviours of the released nanomaterial.

The following materials have been selected based on expected use and other relevance criteria in Denmark for predicting the environmental concentrations:

- Photostable and other Titanium Dioxide (TiO_2)
- Photocatalytic Titanium Dioxide (TiO_2)
- Zinc Oxide (ZnO)
- Silver (Ag)
- Carbon Nanotubes (CNTs)
- Copper carbonate ($CuCO_3$)
- Nano Zero Valent Iron (nano-ZVI)
- Cerium Oxide (CeO_2)
- Carbon Black (CB)
- Quantum Dots (QDs)

In addition to presenting the PECs, we aim to discuss the plausibility of our results by comparing them to the currently available literature data on concentrations in natural environments (Gottschalk et al., 2013b). Such literature mostly provides modelled evidence, since analytical methods are currently almost totally absent, due to the difficulties in measuring the material quantities at such small size dimensions (Nowack et al., 2012). The same difficulties are seen for detecting and quantifying the release of manufactured nanomaterials into the environment and/or into working areas.

2. Methodological framework and engineered nanomaterials

In this chapter, we discuss the selection of the studied nanomaterials and their advantages and limitations, as well as the fundamental principles of the chosen modelling method. Regarding the selection of nanomaterials, we underline the decision criteria related to, for example, the availability of knowledge data regarding the material use and production quantities expected to exist in the future in significant levels in Denmark. In addition, we focused, in our selection, on the relevancy of the expected nanomaterials in relation to toxicological and ecotoxicological aspects.

Furthermore, we address a situation of distinct knowledge gaps and uncertainty and explain why probabilistic modelling is the most appropriate way to handle it. With regard to the environmental exposure model used, we focus on the generic architecture and stochastic approach and the ways in which this approach addresses the significant uncertainties regarding quantitative knowledge of the environmental release and fate of the targeted nanosized materials.

2.1 Engineered Nanomaterials (ENM)

The selection of ENMs to be studied in this environmental exposure and risk assessment was a crucial step in the project. The selection was made with the intention of achieving the best possible representation of the overall environmental situation, with regard to the environmental release of and exposure to all nanomaterials in general. Thus, the ENM selection should, ideally, be risk-oriented (i.e., it should include considerations of possible toxicity, as well as of any significant amounts and exposure concentrations expected in the environment).

Secondly, given the challenging timeline and the very limited resources of the project, as well as the open question regarding finding sufficient data, it is important to address nanomaterials for which some use knowledge is available. This means that we could focus, at least in part, on nanomaterials that have already been subject to earlier initial studies. In such cases, our report presents new findings based on the complete adaptation of and complement to previous assessment model input data, as well as on completely revised modelling.

As a result of these considerations, the following nanosized substances were selected: two titanium dioxide (TiO_2) (rutile and anatase), zinc oxide (ZnO), silver (Ag), carbon nanotubes (CNTs), copper carbonate ($CuCO_3$), nano zero valent iron (nano-ZVI), cerium oxide (CeO_2), quantum dots (QDs) and carbon black (CB). TiO_2 was investigated in two case studies, each of which considered different material properties. The first focused on photostable and other titanium materials, and the second focused on photocatalytic titanium dioxide nanomaterials. For the generic TiO_2, ZnO, Ag and CNT nanosized substances, initial assessments were performed on European and Swiss levels (Sun et al., 2014).

Second, several selected substances were also included in a European review (ENRHES, 2009). Since we partially were contributing authors for this review, we had access to its underlying database—and, therefore, had a full overview of the fate and effect knowledge published so far. The same authorship and data situation applies to another study, which addressed some of the other selected substances (see "Survey of basic knowledge about exposure and potential environmental and health risks for selected nanomaterials" (DEPA Environmental Project No. 1370, 2011)): that is, nano-TiO_2, nano-silver, zero valent iron and CeO_2.

2.2 Material flow (release, deposition and transformation) model

2.2.1 Mathematical background and model architecture

A fundamental requirement for computing and monitoring the release of potentially toxic substances into the environment is having some knowledge of the material flow of the targeted potential toxins (Hungerbuehler et al., 1998; Scheringer, 2002). In the context of ENMs, such a material flow analysis (MFA) faces distinct knowledge gaps throughout the complete lifecycles of the targeted ENMs (Koehler et al., 2008; Nowack, 2009). Nevertheless, the need to understand ENM releases throughout the complete lifecycles of ENMs and ENM products has been widely recognized and discussed (Wiesner et al., 2006; Nowack and Bucheli, 2007; Scheringer, 2008; Som et al., 2010).

Figure 2.1 shows the basic geometrical architecture of the material flow analysis for the current project. Essentially, the figure shows the model compartments in which nanomaterials could be expected to occur, due to either production or transportation between the compartments. Moreover, it illustrates the processes that may transfer nanomaterials between those compartments. By model compartments we mean, for example, ENM production sites, the plants for ENM product manufacture, ENM-containing products, and the technical treatment centres of waste materials and waste water (e.g., waste incineration plants, sewage treatment plants and others), as well as natural compartments (e.g., surface water, soils, etc.).

The material flows shown in Figure 2.2 are estimated using the above-mentioned stochastic methodology of performing probabilistic material flows (Gottschalk et al., 2010a). Such an approach is suitable in cases of highly unknowable ENM releases and transfers throughout the entire lifecycles of ENMs and ENM products. In simple words, these stochastic computations randomly explore the possible value spectra of all model input and output scenarios, allowing us to draw probabilistic conclusions regarding the computed results. The model input value spectra only partially reflect experimental or measurement evidence. However, our model also gives us the ability to quantify missing model values based on expert knowledge and/or assumptive default parameters. This allows us to cope with missing or highly imprecise values, and the model comes into its own when such imprecision is observed for a significant number of model values.

As mentioned in the introduction, this methodology has been used on several occasions related to general environmental exposure studies (Gottschalk et al., 2009; Gottschalk et al., 2010b; Gottschalk et al., 2011; Sun et al., 2014), ENM lifecycles and releases (ModNanoTox, 2013; NanoHOUSE, 2013; NanoSustain, 2013), and nanomaterial fates in waste incineration plants (Walser and Gottschalk, 2014).

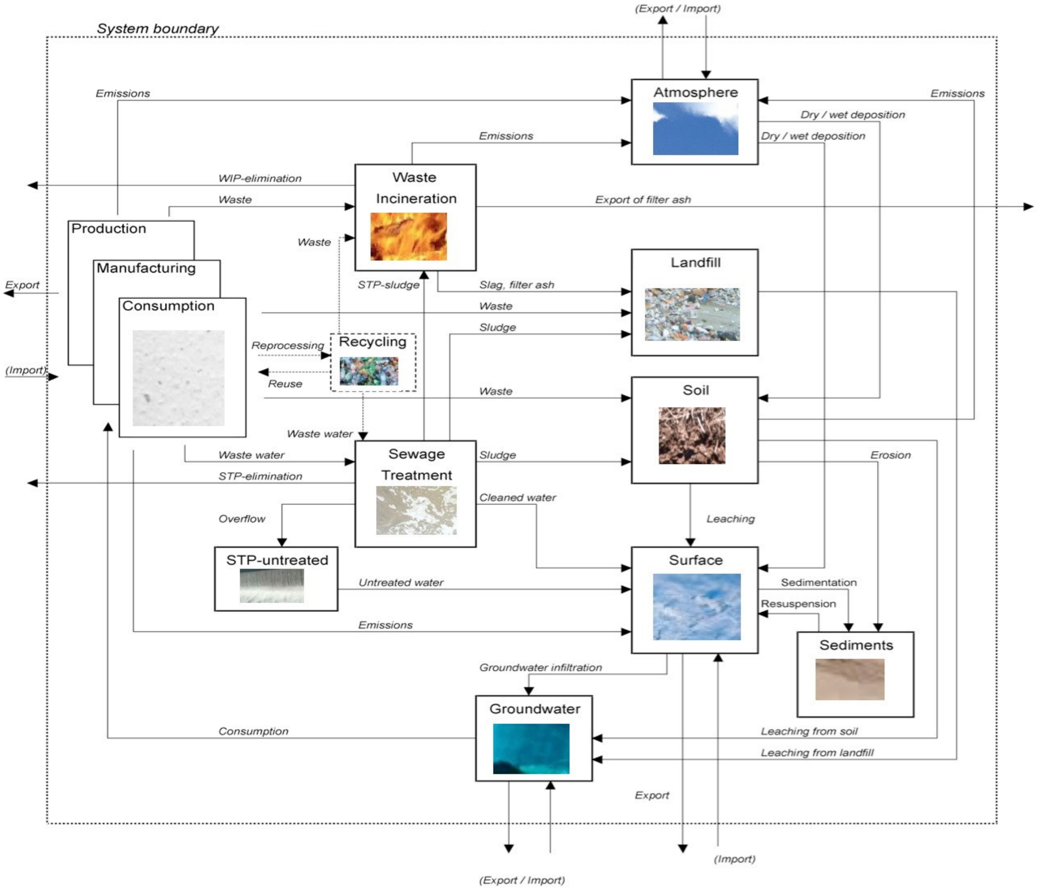


FIGURE 2.1.
ARCHITECTURE OF THE ENM FLOW ANALYSIS IN TECHNICAL AND NATURAL ENVIRONMENTS (COMPARTMENTS). THE ARROWS ILLUSTRATE NANOMATERIAL TRANSFER BETWEEN COMPARTMENTS. NOTE THAT THE PARAMETERS IN BRACKETS ARE NOT CONSIDERED, DUE TO A LACK OF KNOWLEDGE OR DUE TO INPUTS AND OUTPUTS BEING EITHER EQUAL IN SIZE AND/OR NOT QUANTIFIABLE. THE FIGURE IS PRESENTED AS SHOWN IN NANOHOUSE (2013).

From Figure 2.1, we see that our modeling includes ENM fabric production, as well as manufacturing of ENM-containing products, their consummation/application and their fates in water and in waste treatment, recycling and disposal processes, which are completed through the transfer, fates and behaviors of ENMs in and between natural media. The system boundary for this study is Denmark and the surrounding Danish territorial waters.

Our MFA mathematically reflects a linear material mass balance approach for every box/compartment illustrated. For each nanomaterial, this mass balance covers the mass inputs and outputs into/from the model compartments, as well as ENM elimination and deposition processes of these compartments. The result of the MFA is the total mass distribution of ENMs in the complete system shown in Figure 2.1.

Based on the MC computer algorithms—which are programmed in the language of statistical programming (R) (R Development Core Team, 2012), technically described in detail elsewhere (Gottschalk et al., 2010a; Walser and Gottschalk, 2014) and conceptually presented in Chapter 4.1—we capture the uncertainty and natural variability of such mass input/output analysis parameters at every stage of the target lifecycles.

In a first modelling phase, the algorithms compute values from the entire model input spectrum in the form of probability distributions (PDs). Those PDs ideally reflect measured or experimental experience. Otherwise, expert opinion is preferred over pure assumptive knowledge. However, when pure assumptions have to be made to estimate model input parameter values, we aim to cover the largest possible parameter space in order to avoid the potential of overlooking possible scenarios. This means that, in cases of total data gaps, such assumptive information is used to derive the maximum and minimum numbers that build the basis of uniform distributions.

In the following computational procedure, the MC algorithms randomly combine all possible model input values and iteratively and repeatedly solve 100,000 mass balance scenarios for the whole system. Such a high number of scenarios is necessary for a robust statistical analysis of the results. In contrast to a single scenario evaluation for extreme events on both sides of the release spectrum (which would not be technically feasible for complex material flow systems), such MC results will provide insight into the probability (i.e., density) of environmental exposure (and, finally, risk) events.

Mathematically, the method is based on matrix algebra, nestled inside iterative computing that connects ENM fabrication, transport, transformation and deposition. This has been undertaken here in its fundamental form, reflecting the constant mass transfer of steady-state conditions for one-year periods. For dynamic transfer and fate analyses of more complex systems (e.g., with time-dependent or with pulsatile or low-periodic ENM mass transfer (release) kinetics), the current data basis is too limited.

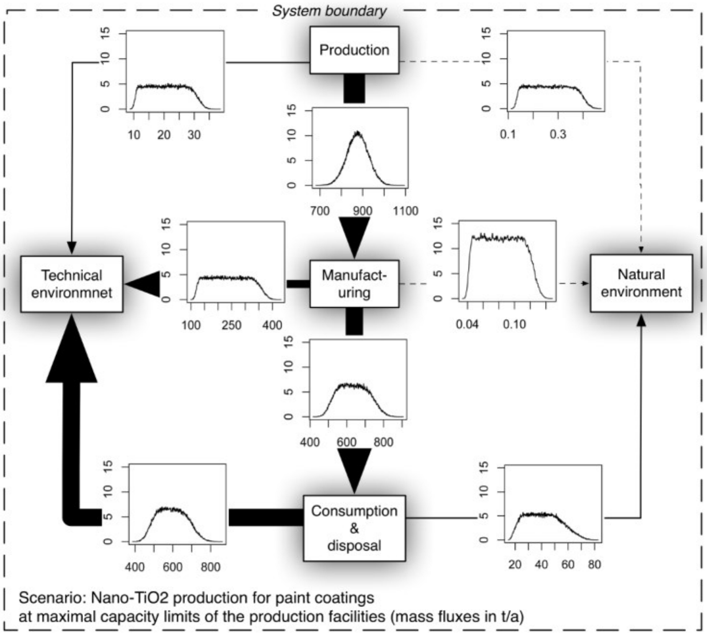


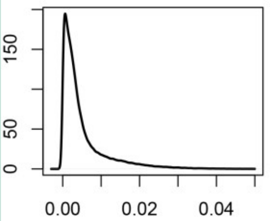
FIGURE 2.2.
EXEMPLARY MASS TRANSFER FLOWS IN EUROPE FOR NANO-TiO_2 PAINT-COATING APPLICATIONS, SHOWING THE TOTAL ENM TRANSPORT BETWEEN NATURAL AND TECHNICAL SYSTEMS, AS USED ELSEWHERE (NANOSUSTAIN, 2013).

Our model is based on constant ENM product use/consumption and does not consider totally uncertain trends in such consumption. This means that we estimate the total annual ENM release into the environment, assuming that the consumption of nanomaterials remains at the quantities currently expected. Hence, the lifetime release from the target equipment on the market is allocated to the model period of 2012. However, in the evaluation and discussion of our findings, some future ENM use trends may be considered. This seems important if we want to be able to make early predictions of critical concentrations in the environment, which may be caused unexpectedly by high ENM releases from new ENM application areas.

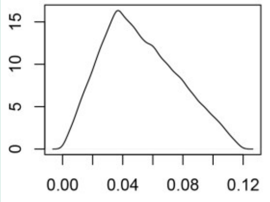
Explanatory box on probability distributions

- A probability distribution (PD) is, in our work, a method of expressing a flow of nanomaterial (i.e., input, output, elimination or deposition) in a model compartment. Since no exact value is available, such a flow is expressed as likelihood of different possible flow values (in units of, for example, tons / year) and illustrated in a PD that assigns, in simple words, probabilities to these values. Examples are shown for a first time in Figure 4.3. Chapter 4.1 discusses the generic mathematical background for the use of such PDs, which are computed in the form of probability density functions (PDFs).

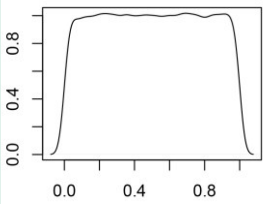
- Types of (theoretical) probability distributions used:



Exemplary log-normal (normal) probability distribution (probability density function): assigns the highest probabilities (densities) to values (without units) between zero and approx. 0.01, excluding higher values.



Exemplary triangular distribution: assigns the highest probabilities (densities) to values (without units) around 0.4, excluding values higher than 0.12.



Exemplary uniform distribution: assigns equal probabilities (densities) to all values (without units) between 0 and 1, excluding higher values..

All sorts of combinations of these forms are available if the empirical/experimental data are used for the model input or if the model results are produced. For a more detailed explanation of the use of probability distributions, please see Chapter 4.

2.2.2 Types of engineered nanomaterial (ENM) flows

Total ENM use volumes

The mass transfer model reflects a bottom-up approach that includes, as far as possible, the studied ENMs and their mass quantities, from the synthesizing process throughout the materials' lifecycles, with all their significant product application, aging and disposal processes, as well as all environmental release flows during such lifecycle stages.

This means, first, that the annual nanomaterial production/use in Denmark has to be quantified for each studied ENM. If the nanosized substances are not produced in significant amounts in Denmark, the ENM input flow into the Danish system is fully depicted by the imported use mass of the selected nanomaterials. This could involve an import to the ENM itself for further use in the manufacturing of products or an import of nanomaterial-containing products. When the ENM production/import amounts for Denmark could not be quantified due to missing information, we extrapolated from values found in global or European contexts, adjusting them in proportion to the corresponding populations to derive Danish regional quantities.

Since use and import data are extremely rare and almost completely unavailable for Denmark, the ENM use values were mostly derived from recent Swiss ENM use research (Piccinno et al., 2012; Sun et al., 2014). For ENMs not covered by these works, the use volumes were computed by combining data from Danish and international literature, as indicated in detail in each nanomaterial case study.

ENM use applications and release

In a second stage, these use quantities were allocated to so-called product categories. These categories grouped ENM products that show similarities in material lifecycle properties, as determined by identical environmental release behaviours. Consequently, all the relevant release pathways of nanomaterials to the environment had to be identified for each category during its lifecycle. The product category data were collected for Denmark and made ready for modelling purposes mostly by following the categorization presented in Sun et al. (2014). These authors used publicly available nano-product inventories, such as the Woodrow Wilson Centre inventory of the Scholars' Project on Emerging Nanotechnologies (WWI, 2012), the ANEC/BEUC Inventory (ANEC/BEUC, 2010), the so-called BUND inventory (BUND, 2011) and a summary of nanotechnology patents (Lem et al., 2012), as well as a comprehensive nanomaterial market report (Future Markets, 2011).

The quantifications of the numbers of products available on the market, which had to be allocated to the categories, as well as the shares of ENMs in particular product applications, were based on an Internet search using Google, Yahoo and EC21 (Sun et al., 2014). The obtained product ENM shares, as described in Gottschalk et al. (2009), reflect, for each category, the relative number of products per category, multiplied by the relative share of the overall distributed ENM mass of each product. From such information, minimal, modal and maximal values were computed for the shares of each product category in order to build, in most cases, triangular distributions.

In a next modelling phase and based on these identified pathway geometries for each category, the environmental release was modelled. Release occurs into natural and technical environments (e.g., via textile washing, waste incineration, or wastewater treatment) or directly into nature when consumers are, for example, swimming in natural waters or taking showers or baths after using sunscreens, etc.

The release data needed in this context refers to the release mass fraction/year of an ENM in the respective stages of life of the ENM and the products containing it. Our complete environmental release quantification basically follows the European guide by integrating the following aspects (see Chapter R.16 (ECHA, 2010)): 1. the lifecycle stage; 2. the level of containment; 3. the type of use and technical fate of a substance; 4. the dispersion of release sources; 5. the indoor or outdoor use; 6. the release potential during the service life and waste stage.

In cases for which empirical/experimental knowledge was not available, assumptions on emission quantities were used to feed the models. These assumptive model input might be derived based on the above-mentioned guidelines for chemical release, which define default parameters for release rates based on environmental release categories (ERC). Such ERCs cover a certain spectrum of material use conditions that define, for example, conservative default release factors in cases for which no other emission data are available. Part of this use-release spectrum lies above the lifecycle stages of the target substances, such as the manufacturing and formulation processes for the different matrix-mixing procedures of the studied materials. The advantage of conservative default model input data is that, in cases of a complete lack of knowledge, such use of default release values replaces, with some plausibility (due to being based on worst case release scenarios), any missing explicit knowledge and does not force us to stop the modelling work due to isolated data gaps.

The complete environmental release aims to include industrial and wide dispersive nanomaterial sources, which have to be integrated into the total nanomaterial discharge (e.g., discharge into surface water, sewage treatment effluents, air, soil, sludge treated soil and sediments). These environmental release/discharge parameters and their sources are given in detail for each nanomaterial in Annex I.

Most release factors were estimated as shown in the reference work (Sun et al., 2014) by following published release analyses concerning, for example, ENM release from paint applications and paint aging (Kaegi et al., 2008; Kaegi et al., 2010), during the washing of textiles (Geranio et al., 2009; Lorenz et al., 2012), from sewage treatment processes in STPs (Kaegi et al., 2011; Lombi et al., 2012) and during waste incineration (Walser et al., 2012b). The transfer coefficients for sewage treatment and waste incineration follow the Swiss situation, not the average European values, because the Danish waste and sewage management system (which involves, for example, extensive use of waste incineration) is more comparable with the Swiss one than the EU average situation. For ENMs not investigated in the reference studies, the transfer coefficients were derived using information from Danish and international literature, as indicated in detail for each case in the above mentioned Annex I.

ENM fate in natural compartments

Mass transfer that mimics the non-mechanistic transport and fate of ENMs in natural media covers material degradation and transformation, as well as deposition and the overall transfer between different natural compartments. Such fate analysis is, therefore, kept very simple, since the data basis is currently very thin. However, by theoretically covering the full possible spectrum of action (e.g., full or no sedimentation), we ensure that no relevant scenario is overlooked. The most important processes in this context are: i) aggregation and the subsequent deposition/sedimentation in waters and ii) some resuspension (which was considered to be very small and based on certain insignificantly low default values), iii) dissolution in different liquid media (e.g., surface waters, washing water, etc.) and iv) wet and dry deposition from air in soils and surface waters.

In order to prepare the model input probability distributions for such transfers, we focused mostly on literature studies that were able to provide wide ranges of possible transfer coefficients. Regarding deposition from air, for example, we based our model as had been done before in the reference studies (Gottschalk et al., 2009; Sun et al., 2014): that is, on probability distributions (that fully consider possible variability) for the transfer coefficients derived from the atmospheric residence-time of ultrafine particles (Anastasio and Martin, 2001).

Sediments and topsoils are modeled as final material sinks; thus, beyond some almost-zero resuspension defaults, no other ENM behaviors/fate kinetics have been considered. Detailed scenarios for the sedimentation and aggregation describing the important heteroagglomeration are given in the work of (Praetorius et al., 2012). For our results on regional/national resolutions, the range of the two extreme scenarios of full sedimentation and no sedimentation were computed as mentioned above and completed in, e.g., river studies for Switzerland (Gottschalk et al., 2011).

According to the previous works (Gottschalk et al., 2009; Sun et al., 2014), such material transformation, dissolution, degradation and incineration kinetics were modelled as mass balance transfers, ending up in virtual "elimination" compartments. Some examples show that most of nano-Ag (85%-100%) is transformed into silver sulphide during sewage treatment in STPs (Kaegi et al., 2011) whereas nano-ZnO can be transformed into other non-nano orms when undergoing the same anaerobic digestion processes in such plants (Lombi et al., 2012). Carbon-based nanomaterials is mostly burned during waste incineration (Mueller et al., 2013). All of the details are given for each ENM in the information for the individual case studies in Annex I. The reader may also consult Report 1, which presents the most up-to-date knowledge on all possible fate scenarios of the studied ENMs in natural media (NanoDEN, 2014).

2.3 Model structure and model input parameters

2.3.1 Adaptations of the Swiss/European models to Danish conditions

The adaption of the European-Swiss model approach to Danish conditions followed at four different levels. These levels are shown in Figure 2.3 and entail input parameters related to i) ENM production and use, ii) ENM release geography and mass volumes, iii) ENM fates in natural and technical compartments and iv) model geometry.

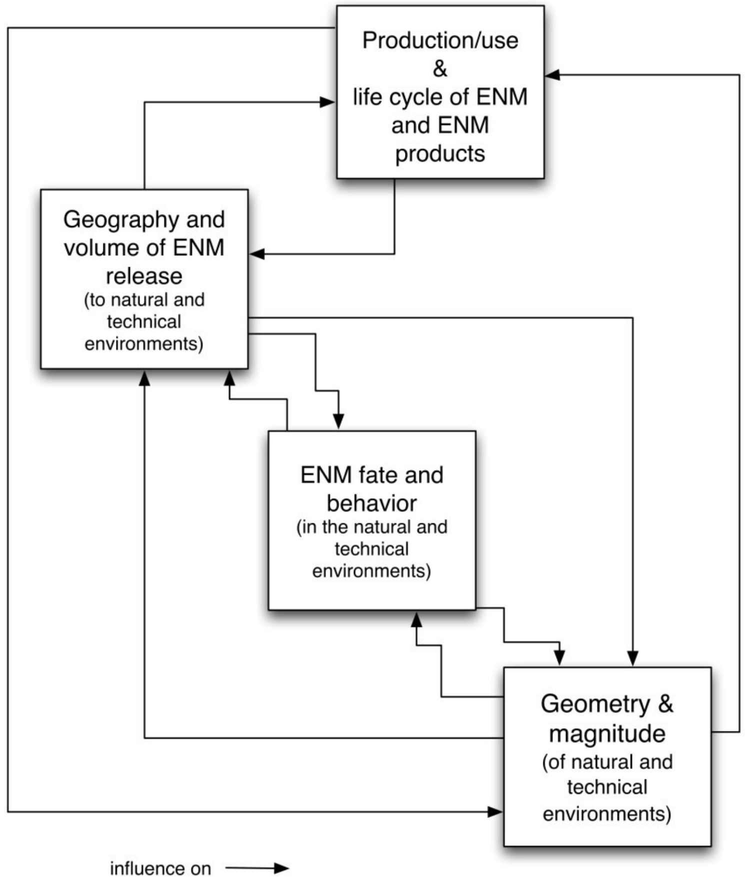


FIGURE 2.3.
MODELLING LEVELS (SWISS-DANISH ADAPTION).

ENM sources

First, information on material-based parameters such as ENM use volumes, use categories and nanomaterial release scenarios for such categories had to be collected. Where no information was available, we scaled the European-Swiss values to Danish dimensions. The details are given for each material in the corresponding chapter, as well as in the Annex I. Data on the use and handling of the studied ENMs for production processes in Denmark were collected by interviewing industrial users of the target nanomaterials in Denmark. As underlined in each case in Annex I, none of the studied ENMs are manufactured in Denmark. Hence, the total ENM use reflects nanomaterials imported for product manufacturing or material imported as nanosized ingredients of products.

Unfortunately, none of the interviewed companies had concrete information on the potential emissions of ENMs from their production sites. However, they did provide information on the procedures of handling ENMs and their generation, treatment and discharge (e.g., in waste water). Hence, the transfer coefficients for release factors were computed by combining this information on the procedures for handling ENMs and waste water treatment with the default release factors of the OECD Emission Scenario Documents for the relevant sectors and/or by using equivalent Swiss-European values from Sun et al. (2014).

Companies within the following sectors were interviewed: pigments manufacture, medical devices, paint and lacquers (including antifouling paints) and cosmetics. Information from other Danish projects were used as well(Sørensen, 2014a; Sørensen, 2014b). The project "Supplementary survey of products on the Danish market containing nanomaterials" provides a broad outline on the uses of ENM for food and feed, medical devices, cosmetics, pesticides and water treatment processes (Sørensen, 2014a). These authors contacted a large range of companies that were asked whether they would support the project in collecting data on ENM industrial use. One single firm was interested in participating. However, due to confidentiality reasons, the data on the other users of the target ENM could not be determined from these projects. Instead, information could only be collected for the application of anatase TiO_2, paints with photocatalytic TiO_2 and sunscreens (Sørensen, 2014b). Those two studies also provided quantitative values for the concentrations of the nanomaterials in different mixtures and products.

However, in 2007, certain company-specific data on the use of ENMs in Danish industries was collected and prepared for publication (Tønning and Poulsen, 2007). Unfortunately, as underlined in Annex I, the interviewed companies are more resistant today to giving concrete information, and if any information is given, it is generally considered confidential. A few figures on the use of ENMs in Danish production processes (Tønning and Poulsen, 2007) were able to be taken as best estimates when no other updated data were available.

ENM release geography

First, the data on ENM- and Danish-specific release geography, which involve information on the population of Denmark (which is crucial to measurements of ENM product consumption per capita and subsequent ENM release per capita), had to be drawn from European results and scaled to Danish dimensions. For the national resolution of our PEC calculations, the total ENM release was distributed homogeneously over Denmark. For local PEC calculations, such ENM releases were adapted to regional values in particular areas in the interior of the country (see river water results for nano-TiO_2). This process also included a consideration of the coastline dimensions and geography (coastal length), since all the largest STPs in Denmark are located at the coast. The daily water consumption (2011) per inhabitant was taken from available data from the Danish Nature Agency (2012). Moreover, processes like, for example, the annual sewage treatment sludge production, annual sludge incineration amounts and sludge volumes disposed to agricultural soils significantly influence ENM releases.

Geometry and magnitudes of the environmental and technical compartments
According to the derivation of the involved population numbers and as shown in detail elsewhere (Annex I) precise geometrical (surfaces, relevant depths and volumes) parameters for the Danish context that varied from those of other European contexts were derived for the studied environments (i.e., natural, agricultural, urban and sludge-treated soils, atmosphere, sediments and water-covered surfaces for fresh water and sea water), as well as for the geographic locations of the STPs that served as relevant point release sources. The latter was important in distinguishing between potential nanomaterial discharge volumes into sea water and fresh water. Again, the locations and effluent volumes (2011) were derived from data available from the (Danish Nature Agency, 2012). The same applied to the connection rate of waste water for industries and households to sewage treatment plants, as well as for sewage treatment plant overflows during periods of heavy rain and floods and overflows escaping STP material treatment procedures.

New aquatic parameters for the Denmark situation had to be derived for the residence time of water in rivers (from the source to the stream mouth and into the sea), the (approximate) river flow velocity and the water chemistry values on concentrations and compositions (if possible) of suspended particulate matter and on concentrations of sulphate, chloride, calcium, sodium and dissolved organic carbon for the nano-TiO_2 local scenarios.
Danish model parameters were also critically checked for waste incineration sites. This adaptation involved deriving percentages of combustible (non-combustible) waste masses incinerated, as well as the kinetics involved in burning, filtration, acid washing, wet-flue gas cleaning, the application of bottom ash (e.g., in construction works), etc. The same applied for leachate escapes to soils and waters from landfills.

ENM fates in natural and technical environments
Essentially, natural media properties do not follow the geographical borders of nations. Thus, some model adaptations were necessary in this context. For example, the Danish marine water geography had to be completely remodelled since it was not comparable to the Swiss alpine continental Europe parameters.

2.3.2 Technical compartments

Nanomaterials pass through lifecycle stages (see Figure 2.1) that integrate the following model boxes i) ENM production; ii) ENM product manufacturing; iii) ENM product consumption space; iv) STPs; v) WIPs with solid waste, bottom ash and fly ash subcompartments; vi) landfills; and vii) recycling plants.

For ENM production and ENM product manufacturing, first, two material transfers are studied: the transfer to the next lifecycle stage and the nanomaterial's release into the environment via its surroundings. Due to missing data, such release and lifecycle stage transport numbers are based on complete annual material transfers into other lifecycle stages or natural media, without any specific quantification of ENM residence times or concentrations in single nanoproducts (e.g., in worker areas, canalizations to waste water treatment, etc).

For the ENM product consumption space, beyond the ENM release and further transport into other lifecycle stages, nanomaterial dissolution upon contact with water has been considered to be an elimination process for different products. Such dissolved masses are mathematically transferred to a virtual material elimination box. The dissolution of, for example, nano-ZnO in food is predicted based on its reaction with gastric acid in the stomach, or in cosmetics, textiles, paints and filters, which can easily come into contact with water (Sun et al., 2014). For carbon-based ENMs, no dissolution or elimination was considered during the consumption phase of the products. For the lifecycle stages i) through iii), wastewater from households containing ENMs ends up in STPs or is directly released into the environment when households are not connected to STPs. Hence, in this context, one crucial parameter is the Danish connection rate of waste water to such plants.

For these STPs, the removal efficiency and the ENM fraction not removed (due to overflows caused by heavy rain and flood events or to other overflows escaping STP treatment) are crucial in the mass balance calculations. For the latter, precise and non-nano-specific data are available. Regarding the ENM removal efficiency, our parameter values are based on, for example, full-scale wastewater treatment plant measurements and on some experimental evidence from laboratory-scale activated sludge system studies. Removal here encompasses material dissolution, aggregation and transformation into other non-nano forms, into other compounds (for example, nano-Ag is transformed into Ag_2S (Kaegi et al., 2011)), or, further, into sludge material. Such remaining STP sludge is used in cement production, burnt in WIPs or deposited in sludge incineration plants. Where empirical evidence did not exist for some materials (e.g., nano-ZnO and CNT), analogies to other ENMs had to be assumed.

In the WIP lifecycle, material burning, filtration, and acid washing with and without wet-flue gas cleaning represent the pathways of ENM transport or transformation (Mueller et al., 2013). Bottom ash is normally landfilled, as seen in Switzerland, and fly ash usually passes the acid washing procedure. In Denmark, approximately 72% of ash is reused for the construction of roads, parking lots, cycling tracks, etc. (Reijnders, 2005). We modelled individual and ENM-specific elimination/transformation values for burning and acid-washing processes, as outlined elsewhere (Walser and Gottschalk, 2014).

The filter removal efficiency in WIP material treatment is not a material-specific parameter, but, rather, depends on particle size. According to others (Burtscher et al., 2001; Walser et al., 2012b), such removal efficiency (e.g., through filters, wet scrubbers, acid washing) ranges approximately and in total from 99.5 to 99.9%.

In the case of landfills, the main environmentally relevant point was to quantify the ENM fraction leaching out of them. Sun et al. (2014) assumed zero release to the environment in such cases for Swiss landfill security and infrastructure conditions, which should be comparable to Danish ones.

2.3.3 Natural compartments

The model presented in this report encompasses lifecycle stages that cover ENM residence and transfer, as well as transformation, in the following natural (and semi-natural) media: i) river water and sea water, ii) sewage treatment effluents, iii) sewage treatment sludge, iv) river sediments and sea water sediments, v) agricultural, natural and urban soils and vi) the lower layer of the atmosphere.

The concentrations computed for sludge treated soils purely reflect the STP sludge contribution on soil exposure. This provides a clearer picture on the influence of such kind of fertilization on the soil exposure. Since we do not mix exposure purely caused by STP sludge with the one observed in non-fertilized areas the total exposure in such areas may be slightly higher. In order to assess this total exposure one can add the generic agricultural soil values to the ones of the pure sludge based contribution.

In waters, partial or complete ENM dissolution, aggregation (heteroaggregation) and deposition processes may be considered and transformed into mass transfers into the elimination box (i.e., material no longer in a nanosized form) or into sediments following ENM deposition. Detailed resuspension from sediments should only be considered for local resolution results, which are focused on short-term concentration changes. In a national long-term sedimentation-based average exposure model, such resuspension was assumed to be insignificant. Partial dissolution was considered for Ag in natural waters, although a continuous dissolution was not excluded. The reason for this is that the particle form can persist long enough for ENM transfer via further ENM transport pathways (Sun et al., 2014). These authors also suggest the nanoparticles suspended in air persist only a short time before settling down on the Earth's surface due to wet and dry deposition.

Here, we follow the recommendations of such previous studies and consider ten days to be the persistence of the target material in air. Therefore, due to a very simple deposition model and given various missing, detailed information, we did not perform any mechanistic fate analyses for ENM in the air (which could include, for example, interactions with natural aerosols).

However, the air compartment is particularly challenging with regard to exposure level measurements/analytics due to the enormous background noise caused by naturally (and, incidentally, from a diffusive source field) emitted micro- and nanosized particles of the same (or different) material composition (Gottschalk et al., 2013b). Missing data for mechanistic fate analysis also applies to the soil compartment. However, following previous suggestions (Sun et al., 2014) and analogies to organic compounds, we modelled a very low ENM transfer from soils to surface waters due to erosion processes or storm events. O'Brien and Cummins (2010) found a way to derive transfer coefficients for this process in accordance to evidence for such transport (i.e., from soils to surface water) from the organic compounds' linear alkylbenzene sulphonate (LAS) levels (Kannan et al., 2007).

2.3.4 ENM production amounts

From our lifecycle perspective for the environmental release of ENM, the production of the material is elemental and influences the results over the entire remaining lifecycle path of the ENMs and the products containing them. Such basic model input covers, in our case, quantities of nanomaterial used for industrial processes and the total content of ENMs in imported mixtures and products. Unfortunately, precise values for such inputs are not available on European or global levels, and are certainly not available for particular geographical areas. In most studies, global or European figures have had to be scaled to regional results based on comparisons of populations (Gottschalk et al., 2013b) or of corresponding Gross Domestic Products (Sun et al., 2014). For our Danish-Europe scaling factors, the population-based approach is used because people's consumption capabilities do not vary too much in intra-European contexts or in contrast to US-Switzerland/Europe comparisons.

However, we must emphasize that this approach does not distinguish between production in the country and the import of nanomaterials from foreign countries. Here, we observed a need for improvement concerning precise data collection and, necessarily, and increased willingness on the part of the industry to provide relevant information. Such willingness has been seen in our work, and it confirms the conclusions of others (Piccinno et al., 2012).

In most cases, it has not been possible to calculate quantitative results for the use of ENMs in Danish production. Thus, most of the figures on such quantities (and the handling of environmental releases of ENMs from production) had to be derived from various state or ENM market development reports on estimated nanomaterial use (Nightingale et al., 2008; Schmid and Riediker, 2008; EPA, 2010; Future Markets, 2011)—and, in the best case, from materials derived from peer-reviewed surveys (Robichaud et al., 2009; Aschberger et al., 2011; Piccinno et al., 2012). The values and details of the derivations of such ENM use figures are given for each material in the Annex I report.

2.3.5 Environmental release

In our lifecycle-based approach regarding environmental release, we aim to completely cover the ENM transfer into the environment at all stages of ENM fabrication and use (see Figures 2.1-2.3). For materials for which such data were available, application-specific release coefficients could be erived from the newest available knowledge (Sun et al., 2014). An adaptation to Danish conditions was, in most cases, not necessary because most of the release fractions did not vary across geographical areas. The release factors for the Swiss situation were used for the Danish model because Danish waste management and its infrastructure had the same quality as the Swiss one, in that it focuses on extensive waste incineration and further use (e.g., ash used for the cement industry, etc.). This contrasts with EU average conditions, which are more focused on landfilling and other poorly known European end-life treatment processes of consumer and other products.

For the focal ENMs that are being studied essentially for the first time, the release coefficients were determined by combining Danish and international information from different literature. For these cases, release coefficients were derived mostly from information on procedures of handling the ENMs and of the waste incineration and waste water treatment procedures by using, for example, release factors from OECD Emission Scenario Documents of the relevant sectors. If pure assumptions were needed to cover the whole possible release spectrum (as done at each lifecycle phase), this is indicated in detail for each case in Annex I.

As illustrated in Figure 2.1 (and concretely shown in the flow chart figures in Chapters 4 and 5), the main pathways of environmental release include, for most materials, a material transfer to the aquatic environment via waste water canalisation, sewage treatment plant effluents and direct emissions during the initial lifecycle stages of ENM production, product manufacturing and product consumption.

Later (in the lifecycle), environmental release via soil, air and sediments is expected to be less frequent. Landfills feed mostly on materials from direct product disposal, including some sludge from STPs and other materials (i.e., ash) from the WIP processes. Sediments are connected to inflows (sedimentation) from waters and soils (erosion). For soils, a prominent potential flow is that of sludge deposition on agricultural soils. Hence, the most important ENM links to soils comes from sludge fertilization, wet and dry depositions from the atmosphere and certain direct and diffusive waste depositions.

ENMs in the atmosphere can mostly be traced as direct emissions from initial lifecycle stages of ENMs (e.g., manufacturing processes and consumption, alterations of products in use) and as releases (in very low rates) via the WIP treatment of nanoproducts. If not directly applied to groundwater remediation, the ENMs ending up in such waters seem to be marginal; however, for such cases, there are almost no available scientific results. This means that, for this compartment, one should base the release parameters on assumptive and very low release values. An exposure model and evaluation was not conducted for groundwater, since, currently, potential nanomaterial-based contamination of such waters is not expected. However, from a long-term perspective, which could integrate a new dimension of nanoparticle residence in surface waters and soils, such waters could also come to the attention of exposure and risk research.

3. Model input data on emissions, environmental fate and exposure

3.1 Data types and categories

Annex I fully presents all data used in this report's modelling work. This annex lists all the parameter values fed into the modelling, aiming to reflect the total ENM releases into the environment. The modelling partially reflects their dispersion and fate in Denmark's environment. We assume dispersion to occur in a completely homogeneous manner; thus, we model the fate and behaviour of ENM based on three options: potential further transport, final deposition (with no further nanomaterial transformation) or nanomaterial elimination/transformation. We describe these processes for each nanomaterial; for each case, we also provide information regarding its lifecycle stages individually.

The data collection in includes two main information types. First, the annex presents total material flow into the system. Second, it describes the fate and transport of the nanomaterial in and between a series of technical compartments/processes: production of the nanomaterial, manufacturing of mixtures and articles containing the nanomaterial for its specific consumption/application, processes of waste incineration and sewage treatment as well as recycling and landfilling of such products, and the main natural compartments of surface water (fresh and marine types), sediments (fresh and marine types), soils (agricultural, natural and urban types as well as sludge-treated soils) and air.

In this project, the model's system boundary is Denmark and the nation's surrounding territorial waters. Roughly speaking, 2012 is the year reflected by the time-dependent data values. However, the nature of the data search makes it difficult to assign a precise time allocation of all values (e.g., nanomaterial production amounts are not possible to date). An uncertainty of one to two years is not excluded due to non-specific time indications as well as the time needed to prepare the data itself.

The model assumes a steady state in nanomaterial use, consumption and release; it does not take consumption trends into account. This means that all lifetime use and environmental release from the equipment placed on the market in 2012 is allocated to the model year. The model estimates the total annual nanomaterial discharge to the environment assuming that nanomaterial use remained constant as in the case of 2012. Table 3.1 categorizes all the different types of model data collected in Annex I.

TABLE 3.1. MODEL INPUT DATA CATEGORIES AS PRESENTED AND QUANTIFIED IN DETAIL IN ANNEX I.

General data

Geographical data on:

- Population of Denmark
- Population of the EU
- Total area of Denmark

Geometry of the natural compartments:

- Surface areas
- Height
- Density
- Water-covered surface
- Sea volume

Aquatic parameters:

- Daily water consumption per inhabitant
- Water residence time in rivers
- Infrastructure data on sewage treatment plants (STP):
- STP connection rate
- Geography (fresh water or marine relevancy) of STPs

Waste handling:

- STP sludge production
- STP sludge use types and amounts
- STP overflow
- Industrial and household waste ending up in WIPs
- WIP material treatment processes
- Types, use and amounts of WIP residues
- Leachate from landfills

Nanomaterial specific data

Use and environmental release:

- Manufacturing volumes in Denmark
- Import of the substance on its own or in mixtures
- Quantities produced (annually)
- Application fields (use categories)
- Quantities used in different applications (annually)
- Percentage of produced products exported
- Release from production and use categories:
- Direct release to municipal waste water system
- Direct release to natural compartments
- Disposed of as solid waste for incineration
- Transformation during use into other forms

Environmental fate:

- Sedimentation from air
- Sedimentation in water
- Erosion (soils-water)
- Dissolution of nanomaterial upon contact with water

Waste handling:

- Nanomaterial removal efficiency in STPs
- Nanomaterial removal efficiency in WIPs

The data collected is not fed into the model by using them as single deterministic values, but by computing four different types of probability distributions based on the information collected. The details of such computations are given in each data case and for each material.

Therefore, the applied model is largely based on probabilistic production and use parameters, release and mass transfer coefficients for each model compartment. The first mentioned kind of parameters reflect tonnes or kg per year; all the other values have to be transformed into transfer coefficients that indicate the percentage of the nanomaterial flow going in each direction (e.g., released to the different environmental compartments).

The following types of probability distributions have been used:

Log-normal (normal) distributions **-** It is characteristic of the distribution that the value cannot be less than zero; in addition, at the higher end, the distribution has a long tail.

We employ log-normal (normal) distributions for ENM production and use, including material import into Denmark. The main property of such distributions is that their values cannot be less than zero; however, they are very small with some certainty, but also very high with some small probabilities at the higher end (long tail) of the distribution. Referring to Sun et al. (2014), we present the details for each nanomaterial investigated, giving the values mostly in t/y.

All other parameters of the model are transformed into a mass transfer depicted by transfer coefficients lying between zero and one. Such coefficients indicate the percentage of the ENM flow going in a particular direction or the fraction deposited or transformed in a particular area. Hence, mass transfer indicates, for example, incorporation of ENM into products, ENM products migrating through all lifecycle stages of such products, and ENM environmental release, deposition and elimination during such migration.

Triangular distributions – These distributions are used for a breakdown of the total consumption by application areas. The triangular distribution is characterised by a lower, a higher and a modal value representing the three corners of the triangle. The modal value is the top point and considered the most prevalent value. The triangle may not have two equal sides (an isosceles triangle), and the modal value may be displaced towards the lower or higher value, indicating that the highest uncertainty is in the low or high end of the range.

Again we provide the details for each material and each stage of the studied lifecycle. For triangles without two equal sides (isosceles examples), the modal number is displaced towards the lower or higher value, showing the side where higher probabilities are to be expected.

Uniform distributions **-** Uniformly distributed parameter values are needed for parameters where only the borders of the distributions have to be estimated by experts. This form of distribution has been used for a few parameters with a distinct lack of data. However, the same distribution may also be applied when the extremes are well-known from empirical evidence; however, evidence on the average or mode is missing. We have conducted the coding by using the standard R routines for uniform distributions.

Uniformly distributed model input values are computed when only the borders of the distributions can be estimated based on expert knowledge or pure assumptions. In the case of pure assumptions, we consider the largest possible spectrum. In the best case scenario, these distributions are also used when the extremes can be derived from experimental evidence without having any indication of the most prevalent values.

Empirical distributions – Empirical distributions are the most widely-used distributions. Such use is one of the model's distinctive strengths (Bornhöft et al., 2013), allowing use so far as possible with empirical evidence. This distribution also applies in cases where such evidence does not reflect any mathematical (theoretical) curves. The use is described in detail for each material and mostly covers parameters for ENM fate and behaviour in technical and natural compartments as well as parameters reflecting the use amounts (fractions) in different ENM product categories.

These distributions directly reflect varying measurement results, data collection outputs and statistical evaluation methods. Technically, in such cases, we directly compute (select) MC calculations based on boot strap techniques from the available raw values. However, to fill data gaps that represent possible values, a prior uniform distribution may be used for MC-based Bayes computations.

Empirical distributions precisely show the actual state of knowledge for these parts of the model. The main limitation of such distributions is that they basically tend to overfit the model in terms of the available data. However, the negative influence on the results of such model overfitting is regarded as small compared to using theoretical distributions without any empirical evidence. Such theoretical distributions tend towards missing data gaps and neglect of extreme events in nanotech contexts.

Particularly for environmental fate parameters (and fate and behaviour in technical compartments), it is not possible, necessary, or desirable to use theoretical distributions to calculate their inherent variability and uncertainty. These distributions have to reflect different observations, measurements, statistical evaluation methods and others. Therefore, in such cases, we preferred to model empirical distributions selecting MC computations directly from the available raw data. Such distributions more precisely show the actual state of knowledge for these parts of the model.

3.2 Data collection

Data derived from Swiss studies

Very limited quantitative information is available regarding the total content of nanomaterials in mixtures and articles imported to Denmark. For modelling purposes, for nanomaterials where data on the global consumption or EU consumption are available, we estimated the potential consumption in Denmark on the basis of the EU consumption data assuming the same per capita consumption in Denmark as in the EU. These data have mainly been derived from two recent Swiss studies (Piccinno et al., 2012; Sun et al., 2014). Also, application-specific transfer coefficients partially have been derived from Sun et al. (2014). The study partially uses different coefficients for the model of the Swiss and EU average situation. We applied the transfer coefficients for the Swiss situation to the Danish context; the Danish waste management system, with its extensive use of waste incineration, is more comparable to the Swiss system than the EU average. For nanomaterials not covered by the reference Swiss study, the transfer coefficients have been derived by combining information from Danish and international literature.

Collection of information on industrial point sources of nanomaterials in Denmark

We collected information on the use and handling of the nanomaterials for production processes in Denmark and the potential releases to the environment by interviewing industrial users. None of the contacted companies had specific information on the releases of the nanomaterials from the production sites, but they provided information about the procedures used for handling the nanomaterials and the generation, treatment and discharge of waste water. We derived transfer coefficients (emission factors) by combining the information on procedures for nanomaterial handling and the waste water treatment with default emission factors from OECD emission scenario documents for the relevant sectors.

Users within the following sectors have been contacted: paint and lacquers (including antifouling paints), pigments manufacture, medical devices and cosmetics. The project has run in parallel with two other nanomaterial studies and has coordinated with these studies. As part of the project entitled, "Supplementary Survey of Products on the Danish Market Containing Nanomaterials", a broad survey was undertaken regarding the use of nanomaterials in food and feed, cosmetics, pesticides, medical devices and for water treatment (Sørensen et al., 2014a). For this survey, a large number of potential nanomaterial users in Denmark were contacted, and as part of the request, the users were asked if they would participate in data collection regarding industrial uses of such substances. Only one company was interested in participating, and it was identified and interviewed. For confidentiality reasons, information on other users of nanomaterials could not be shared between the projects. As part of a survey on the use of anatase TiO_2, a questionnaire was sent to potential manufacturers of paints with photocatalytic TiO_2 and to manufacturers of sunscreens (Sørensen, 2014b). Two manufacturers identified were subsequently contacted. In addition, a request was directed to manufacturers of paints, inks and adhesives via the DFL trade organisation. Only one company responded and was later interviewed. In addition, direct contact has been established with a few companies that potentially use nanomaterials.

Contrary to the situation a few years ago, where company-specific information on the use of nanomaterials in the Danish industry could be reported (Tønning and Poulsen, 2007), the companies are more reluctant today to provide such information; in general, the information is considered confidential. For this reason, several processes have been grouped by their description, and consumption figures are indicated as ranges.

Data derived from other studies in Denmark

Information on the potential uses of nanomaterials in Denmark has been derived from two studies undertaken in parallel with this study (Sørensen, 2014a; Sørensen, 2014b). The two studies provide quantitative information on the concentration of the nanomaterials in different mixtures and articles, but no consumption figures. Some figures on the use of nanomaterials in production processes in Denmark (Tønning and Poulsen, 2007) have been used as best estimates when updated information was unavailable.

4. Guide to understanding the results

4.1 Guide for reading the model results

The purpose of this chapter is to provide readers with an overview on how to read and interpret the results. Ideally, this guideline will allow the reader to interpret the results without having to go through the details of the model methodology presented in chapter 2 and model input data collection/preparation introduced in chapter 3.

In particular, this chapter points out that the reader should not expect definitive results in this report. The results of all computer-based simulations, as well as the model input data used to feed those simulations, are computed by means of probability distributions (probability density functions). The use of such distributions is necessary and appropriate if precise knowledge is lacking, and if there are data gaps and observed variations in use, and when the release and fate of engineered nanomaterial into the environment have to be assessed quantitatively.

In our work this uncertainty regarding the model parameters are computed by combining (summing) the knowledge imprecision (and gaps) with the natural variability of the parameters. This can be done without discriminating between them, since the current data situation would not allow us to make such a distinction. Thus, the total model output value spectrum reflects the spread of both types of data. In cases where the data gaps are absolute expert assumptions have been used as indicated in detail in Annex I, where the data-base used has been listed and commented on.

4.1.1 Material flows and environmental release

Engineered nanomaterial mass transport architecture
Here, we lead the reader through probabilistic lifecycle-based mass transport modelling for ENMs. Our lifecycle perspective tracks ENM mass transfer, considering, as far as possible, all environmental release pathways of the target nanosized materials, as well as their transport flows between several technical and natural compartments. This means that we pursue, as far as possible, what happens to ENMs and their products and applications, whether produced in Denmark or imported from abroad.

Figure 4.1 shows the complete nanomaterial tracking modelled in this report, including all staging points (in both technical and natural compartments) of the investigated nanosized substances. The material life stages (on the left side) in technical plants cover the ENM production itself and/or the import of produced ENMs from outside the country. The same applies to processes of incorporating such ENMs into products that reflect the manufacturing of ENM-containing products and the use/consumption of those nanoproducts.

First, direct releases from these three initial lifecycle stages (i.e., production, manufacturing and consumption (PMC)) to air, waters and soils are pursued. Such releases may occur, for example, due to uncontrolled emissions (as aerosols or in liquid form) during ENM production, from nanoproduct manufacturing plants or from the material degradation of product use (such as, for example, textile weathering).

Second, from these initial stages, all technical compartments (in the middle of the figure), including WIPs, STPs, landfills and recycling processes, may be reached by the ENMs, thus forming the next point on the materials' life journeys. STPs may be reached as a result of uncontrolled release (in liquid form) during production and product manufacture or when ENMs are incorporated into, for example, cosmetics, which end up in the water treatment system. ENMs may reach WIPs as part of waste streams containing ENM products (such as, for example, when ENMs occur in a textile matrix) and are, thus, automatically captured by the incineration path of waste management. Alternative transport paths for ENM waste mass transfer include, for example, electronic products or plastic composites, which may end up in landfilling and recycling processes. ENMs' fates in these processes (i.e., landfilling and recycling) were not studied due to a lack of data. Thus, the model was stopped at these two lifecycle stages, and no ENM draining away or ENM aerosol emissions were considered for landfills and recycling plants. What happens to the nanomaterial that annually reach recycling and landfill plants was not pursued further. Theoretically, such masses could be attributed to the elimination/degradation, deposition or recirculation (in the recycling case) of nanomaterials. However, we assume that no nanomaterial degradation in these compartments is harmless, to the extent that this modelling procedure leads to conservative exposure concentration and risk estimations.

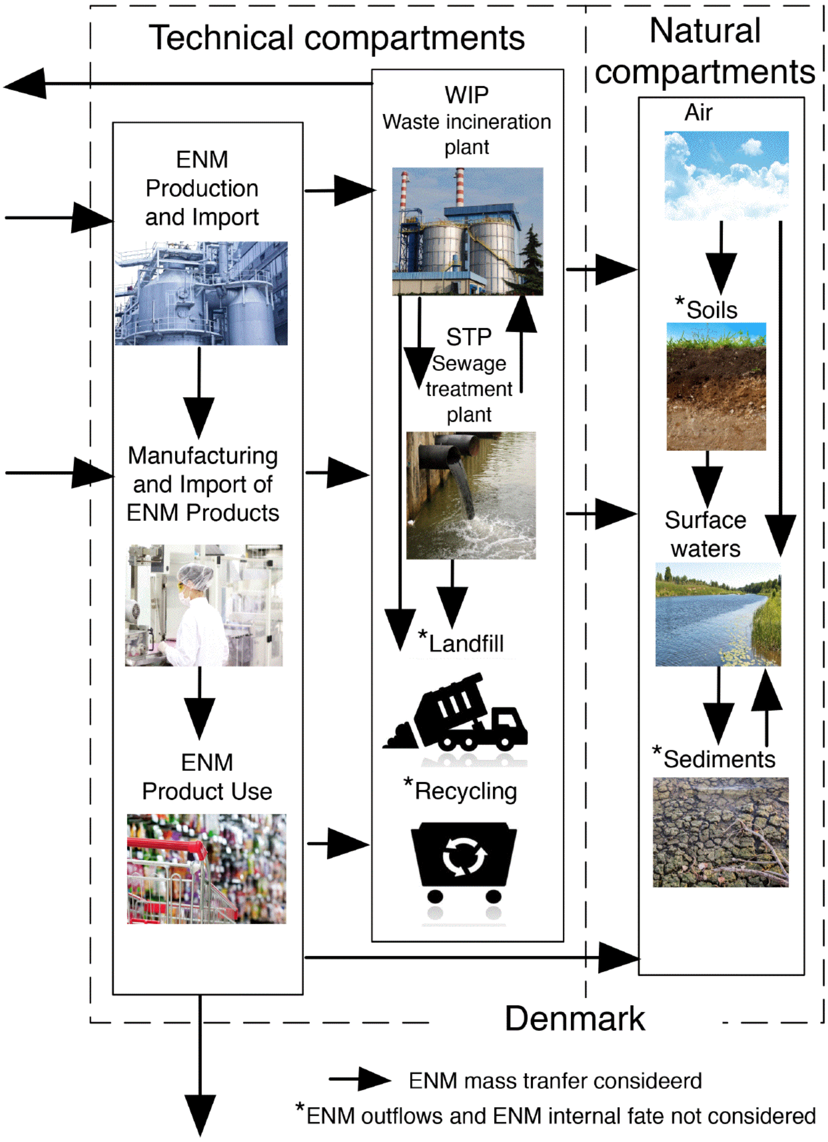


FIGURE 4.1.
MATERIAL-FLOW ANALYSIS FRAMEWORK TRACKING THE TARGETED ENMS' MASS TRANSPORT THROUGHOUT THEIR COMPLETE LIFECYCLES: I) ENM PRODUCTION; II) ENM PRODUCT MANUFACTURE OR THE IMPORT OF ENMS AND THEIR PRODUCTS; III) ENM EMISSIONS DURING THE USE OF SUCH PRODUCTS, AS WELL AS DURING NANOMATERIAL PRODUCTION AND NANOPRODUCT MANUFACTURING PROCESSES; IV) MASS TRANSFERS AROUND (I.E., THROUGH INFLOWS, OUTFLOWS AND INTERNAL MASS TRANSFERS) STPS, WIPS, LANDFILLS AND RECYCLING PROCESSES (ONLY INFLOWS), AS WELL AS RELEASES TO WATER, SEDIMENTS, AIR AND SOILS AND SEVERAL MASS TRANSFERS BETWEEN THESE ENVIRONMENTAL COMPARTMENTS.[4]

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[4] Licensed photos from http://www.123rf.com.

If engineered nanomaterial ends up in the incineration processes of waste incineration plants, only a very low amount (largely promille dimensions or less) is expected to be emitted into the air. The ENM is mostly removed from the flue gas and transferred to the solid incineration residues of slag and fly ash, which may be reused in, for example, cement production. Such cement use thus reflects a modelled recycling process for the purposes of our report. The model tracks and quantifies the amount of ENM reaching the general waste mass and its residues following the incineration process, such as fly ash and bottom ash (i.e., boiler slag). For metallic nanosized particles, we considered Walser and Gottschalk's (2014) WIP model based on measurements for CeO_2, which confirms earlier evidence of almost no environmental release from such plants. These authors assume that around 99% of the nanoparticles are finally deposited in the fly ash and slag. This subsystem is shown in detail in the nano-ZnO case study (Annex I).

With regard to the fate of ENMs in STP material treatment, the newest scientific evidence was used to quantify overflows and nanomaterial elimination efficiency, including, for example, aggregation and sedimentation in the sewage treatment water, resulting in ENMs ending up in sewage sludge. Such sludge was used and modelled as an ENM-containing mass, used either for soil fertilization or for incineration in WIPs. The model stopped again after ENM entered such sludge and assumed no further degradation of the STP residue. In some European regions, STP sludge is landfilled; however, this was not assumed for Denmark. The non-eliminated part of the ENMs in the STP treatments were considered to be mass flows of wastewater effluents into surface waters.

Third, mass transports between natural compartments (right hand side of the figure) are reflected by dry and wet depositions from the air into soils and waters. For the surface water compartments, we distinguished between fresh and marine water and considered, for both compartments, the ENM aggregation and sedimentation (which represent removal paths of ENM from the water into sediments). A certain almost-zero reflux (i.e., sediment–water transfer) in the form of ENM resuspension is also considered in both cases. Erosion processes of soils may also lead to some marginal mass transfers to water compartments. Internal ENM fates in sediments and soils were not studied, and the model stopped by assuming homogeneous ENM distributions in such compartments, modelled as final sinks without any ENM degradation. Hence, the ENM amounts (and concentrations) predicted for soils and sediments must be interpreted as conservative exposure scenarios.

Finally, quantitative information to complement the model with nanomaterial return flows into the PMC processes (right side to the left side in the figure), due to, for example, bioaccumulation in plants and humans/animals or due to drinking water treatments, is currently almost completely missing and, therefore, was not quantified.

Modelling stochastic[5] *mass transport*

The stochastic mass transport model approach combines a large number of scenarios (e.g., 100,000) for each mass transfer in a complex system of ENM transports. Such transports include, as shown in a simplified example in Figure 4.2, mass inflows and outflows from a particular compartment (i.e., box) as well as internal flows (i.e., flows inside a particular box) into the deposition or nanomaterial degradation processes (i.e., flows (1-1), (2-2)[6]). The example shows the mass transfer scenarios for only two initial compartments (for example, a factory (box 1) and a lake (box 3)) and two others (boxes 3 and 4), which are not shown in detail.

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[5] The term "stochastic" means, in simple terms, "non-deterministic" (i.e., "random"). Thus, the values used in our modelling were not reflected by single values for single model parameters, but instead always by a range of possible values, computed in so-called probability distributions (for these distributions, see Chapters 2 and 4). Hence, the stochastic (or random) process—that is, the probabilistic counterpart to the deterministic process—represents the computation of possible random values that represent the evolution of our environmental exposure system.

[6] Flow (1-2) stands for a nanomaterial flow from, for example, compartment 1 to compartment 2. Flows (1-1) and (2-2) represent internal flows inside a target box (1 or 2), which reflect nanomaterial deposition or nanomaterial degradation/elimination.

A scenario represents, therefore, the particular material mass fraction transferred from one to another and including flows inside the boxes. Each possible scenario at each stage of the nanomaterial lifecycle is randomly combined with all other life stage scenarios by exploring the full value spectrum at all material life stages.

The total input, output and deposition/degradation (including ENM generation) in each compartment is balanced for the whole nanomaterial lifecycle-based transport. This means that the transfer, production or deposition of nanomaterials can be calculated for each of the 100,000 simulations shown (in an exemplary manner) in the figure below. This figure covers the following mass transfer scenarios: scenario 1 (1-2) (which connects compartment 1 and 2) is combined, for example, with scenario 2 (1-1), scenario 100,000 (2-2), scenario 2 (2-3), scenario 1 (2-1) and scenario 100,000 (1-4).

This kind of random (Monte Carlo based) mass transport scenario linking is performed 100,000 times by always keeping a mass balance. The scenario factors are computed as values between 0 and 1 and reflect the mass fraction transferred from one stage to another. They follow the probability density distributions (see also Figures 4.3 and 4.4) produced based on empirical evidence or assumptive knowledge. Lifecycle stages (called compartments or boxes) may be represented by different nanoproducts or technical or natural compartments. Having a mass balance means that the scenarios belonging together add up to one, which applies in the above example for the flows (1-1), (1-2) and (1-4) as well as for (2-1), (2-2) and (2-3).

Example of a stochastic ENM mass transport model
In order to illustrate how we quantify ENM mass transport, a simple artificial mass transport example is given in Figure 4.3. This example is shown to help the reader interpret the flow chart results and is not based on real data. The number values are in tons per year, and we see a total annual mass input into the system of approximately 100 tons on average (shown in the PMC box on the left side of the figure). We see an arbitrary case with five nanomaterial lifecycle stages. This case tracks the annual ENM mass transfer throughout the ENMs' production, manufacturing and consumption (PMC) through two technical and two natural compartments (which are not further described).

The curves and values show the mass transport between the compartments, and the ones inside the compartments represent material mass that no longer leaves the corresponding lifecycle stage due to final nanomaterial deposition or degradation (i.e., the compartment acts as a sink). Such final elimination can occur due to dissolution reactions, to aggregation and sedimentation processes in liquids or to other ENM behaviours (explained in each case).

Panel A depicts the complete computer simulation output in the form of probability distributions (probability density functions). In B and C, we see single values extracted from the distributions in panel A. In panel B (and in panel A), the blue values belong to a single simulation (out of 100,000 Monte Carlo computer simulations) that precisely reflects mass balance. Thus, what we see is a single, but complete, mass transport scenario for a whole lifecycle study of the ENM. In total (as mentioned), we produced 100,000 such scenarios. Such a large quantity of scenarios is needed in order to present and study the general model output tendency when faced with a distinctive scarcity and uncertainty of model input parameters. In contrast, panel C shows approximately the most frequently computed (red) values (modal values) for each mass transfer, without keeping an exact mass balance for the whole system. These modes only roughly reflect mass balance, since they do not belong to an individual mass transport simulation (as shown in B). Rather, they show the most probable values at particular points across the entire mass balance system.

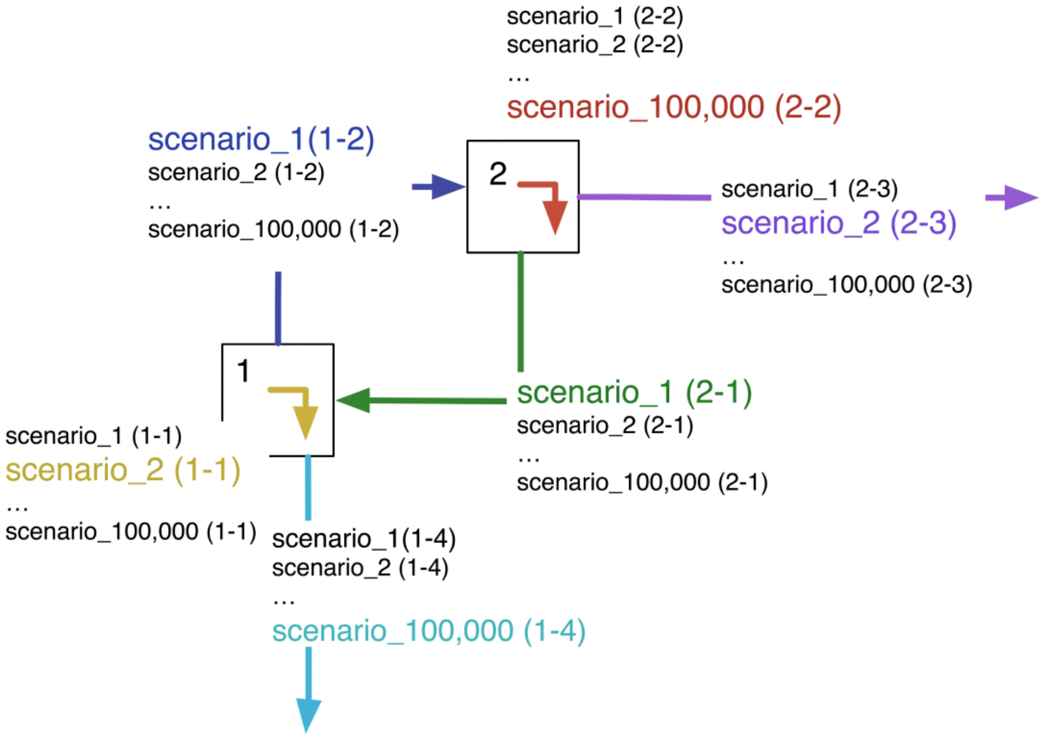


FIGURE 4.2.
A STOCHASTIC MASS TRANSPORT MODEL APPROACH THAT COMBINES A LARGE NUMBER OF SCENARIOS (E.G., 100,000) FOR EACH MASS TRANSFER. THIS EXAMPLE SHOWS MASS TRANSFER SCENARIOS FOR TWO COMPARTMENTS.

These values thus best show which nanomaterial immissions/emissions are to be expected for each individually studied compartment. The term “best” means that the model most frequently produced values in the close vicinity of the mode. The mode itself was not necessarily produced by the model, since it does not represent a single, linearly dependent mass transport simulation scenario.

Hence, these results depict, for each case the most probable figures produced by the stochastic model across a large number of computer simulations. These figures should not be interpreted as precise values; instead, as noted, they should be interpreted as the values with the highest probabilities in a general and holistic tendency analysis. In this context, the term “tendency” means that our model produces a complete picture of all possible flows by additionally assigning probabilities to all the model output scenarios. What we see below in Figure 5.1, for example, are the most probable outputs, illustrated in their totality for a nano-TiO_2 study.

There is no doubt that the precision of these tendency results stands and falls with the precision of the data (see the parameter values prepared in Annex I) fed into the model. However, in contrast to single deterministic scenario modelling, the stochastic procedure is relatively robust to individual model input errors, since it is always based on the largest currently possible spectrum of values, used in a large number of mass transport system simulations. Thus, single input changes are unlikely to cause significant changes to the overall curves.

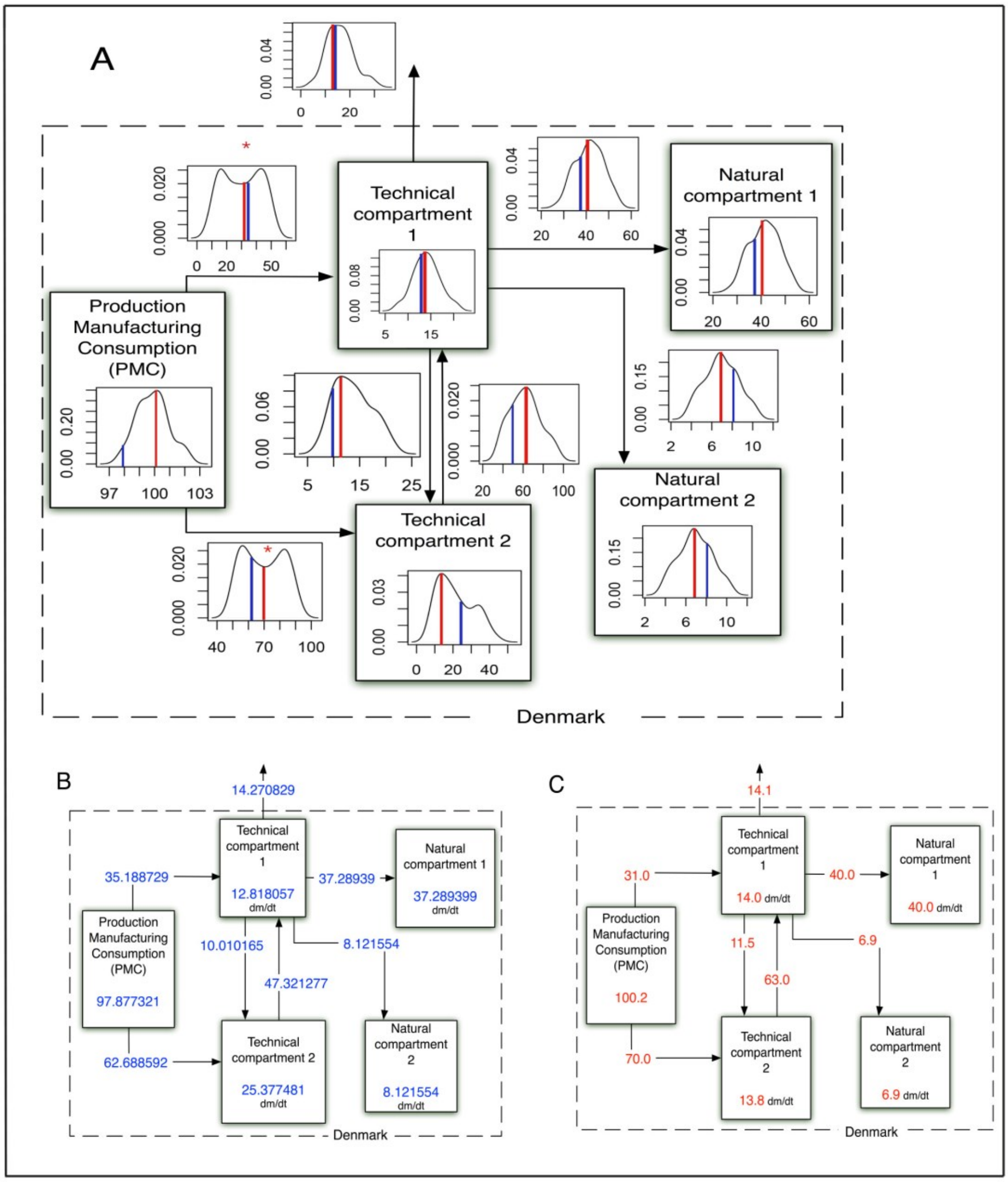


FIGURE 4.3.
A SIMPLE ARTIFICIAL EXAMPLE OF ENM MASS TRANSPORT,..

Primary ENM sources of environmental release and ENM release recipients
Based on the scheme shown in Figure 4.4, the most prominent ENM sources were visualized and quantified in order to compare them to the primary ENM recipients. This is crucial for assessing, for example, the water release relevance of particular ENMs and for contrasting such releases to those into soils or air. Such an assessment reveals important indications in the form of prominent material flow tendencies, which may show, for example, risk assessors for which future research needs to be intensified or for which measurement techniques/analytical tools need to be developed for particular materials.

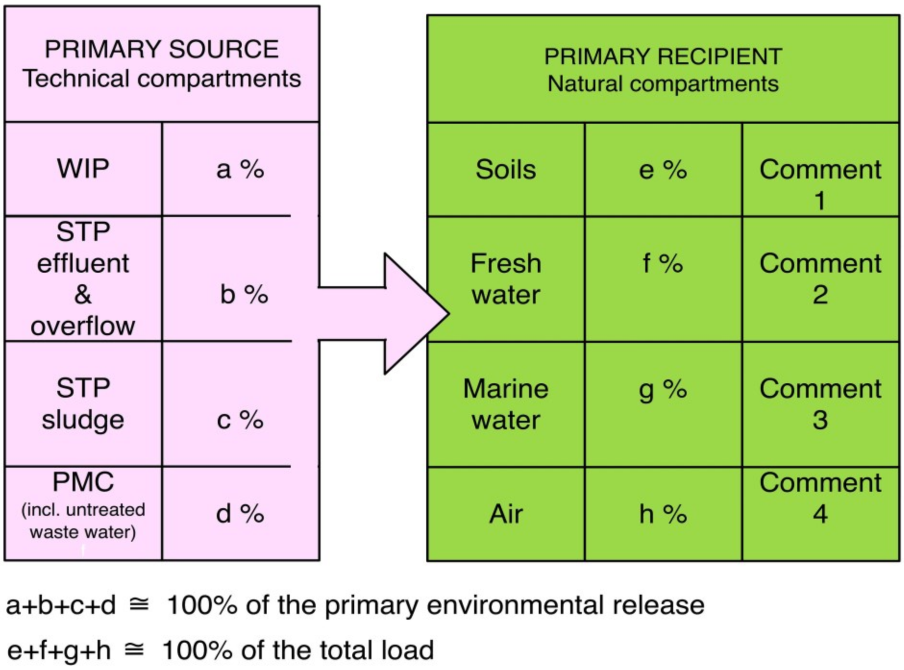


FIGURE 4.4.
COMPARISON AND SUMMARY OF THE MOST IMPORTANT SOURCES AND RECEIVERS. THE VALUES REFLECT THE MODAL VALUES (I.E., THE MOST FREQUENTLY OCCURRING VALUES).

4.1.2 Exposure concentrations in technical and natural compartments

From mass flows to predicted environmental concentrations (PEC)
In order to conduct an environmental exposure and risk assessment, it is crucial to know the environmental concentrations of potential contaminants. Risk is often derived by dividing the predicted exposure concentrations (PEC) by the predicted no-effect concentrations (PNEC). This report models the PECs by dividing homogeneously distributed ENM masses in particular compartments by the volumes or masses of corresponding compartments. As shown in Figure 4.5, two kinds of computations for deriving PECs are used.

In one situation (option I), the ENM inflows (immissions) into a compartment for a studied time period (one year) are transformed into a permanent ENM mass fraction in that compartment. Such a transformation links the inflow rates and residence times of the investigated nanomaterial in a particular compartment, such as in studies on water, air, sewage treatment sludge or waste mass and its residues.

Secondly (option II), the ENM mass inflows for a particular time period (in our case, one-year periods) contribute to the continuous, periodic increase in ENM quantities in particular compartment. This occurs for sediments and soils, for example.

For these two types of natural compartments, we forecasted concentration scenarios for the studied ENMs following a nanomaterial deposition period in sediments/soils, which began in 2000 and ended at the beginnings of the years 2014 and 2020. Zero-use amounts and release and accumulation quantities for ENMs were assumed for the time prior to the year 2000. Beyond the year 2000, a linear increase in ENM depositions was computed by scaling the annual depositions computed in this report for the year 2014.

For the actual PEC derivation we divided all of the ENM load values (i.e., 100,000) by one volume or mass number of the target compartment. From these computations, we presented the most frequent results (i.e., the modal values) and the 95% ranges, giving us a 95% probability of the modelled concentrations falling within the presented range (see also Figure 4.7).

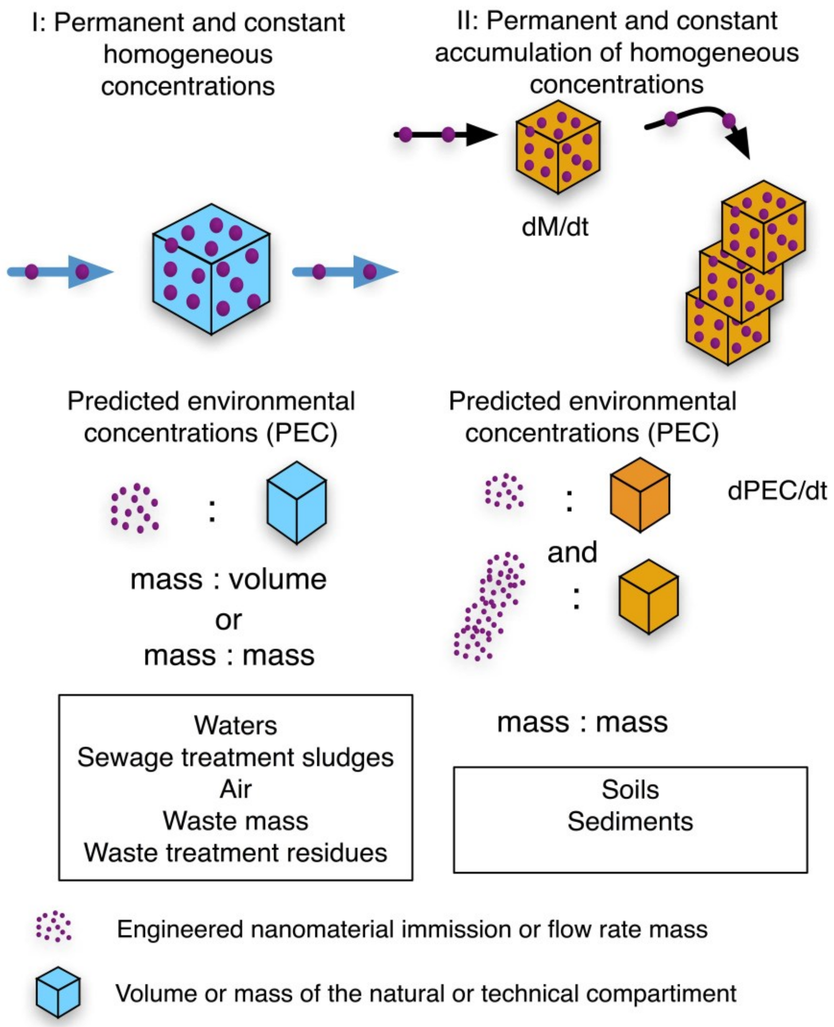


FIGURE 4.5.
TWO TYPES OF COMPUTATIONS FOR DERIVING PECS, PECS ARE COMPUTED BY DIVIDING A HOMOGENEOUSLY DISTRIBUTED ENM MASS IN A PARTICULAR COMPARTMENT BY ITS VOLUME OR MASS. OPTION I: THE ENM MASS IS DERIVED BY TRANSFORMING THE INFLOW (IMMISSION) MASS INTO A PERMANENT ENM MASS FRACTION FOR THE CONCERNED COMPARTMENT (E.G., WATER, AIR, SEWAGE TREATMENT SLUDGE OR WASTE MASS AND ITS RESIDUES). OPTION II: THE ENM MASS INFLOW CONTRIBUTES TO THE CONTINUOUS INCREASE OF THE ENM MASS IN A PARTICULAR COMPARTMENT (E.G., SOILS AND SEDIMENTS).

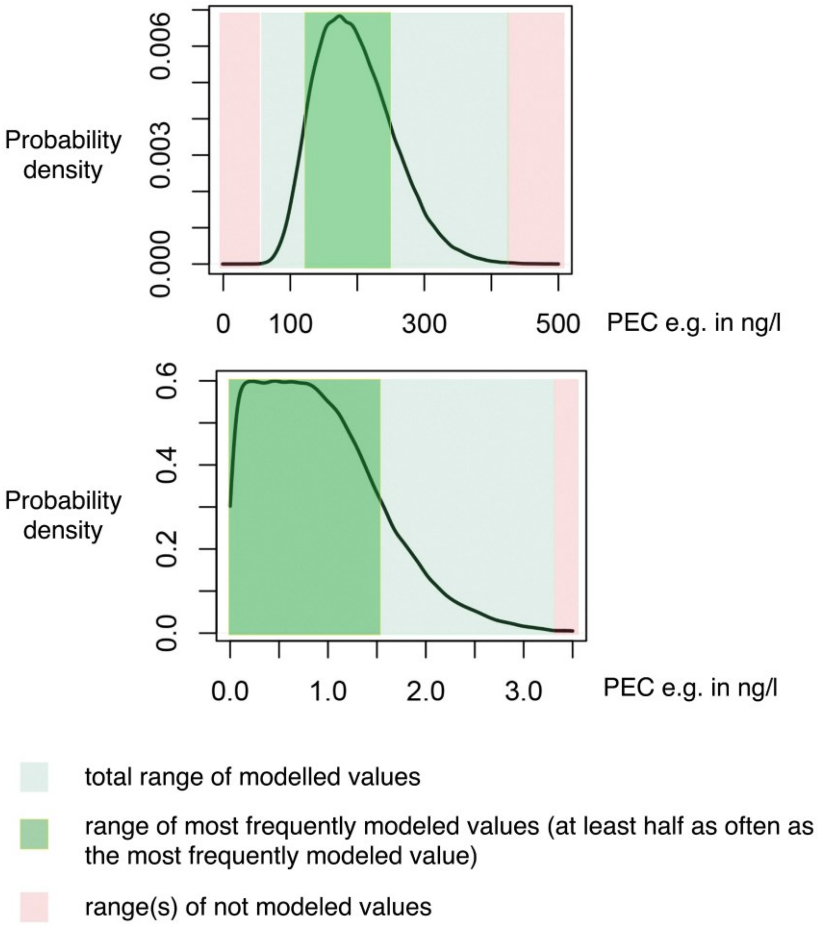


FIGURE 4.6.
SIMPLIFIED SCHEME FOR INTERPRETING THE PROBABILITY DENSITY FUNCTION CURVES OF THE PECS OF A DIDACTIC CASE. FOR EXAMPLE, IN THE LOWER FIGURE, THE MODELLED VALUES HIGHER THAN 1.5 NG/L (LIME-COLOURED AREA WITH A DENSITY OF 0.3 AND SMALLER) WERE MODELLED LESS THAN HALF AS OFTEN AS (AND EVEN MORE RARELY THAN) THE VALUES BETWEEN (ALMOST) 0 AND 1 NG/L (WITH DENSITIES AROUND 0.6). THE INTEGRAL OVER THE ENTIRE GREEN SPACE IS EQUAL TO ONE. THE RED (ZERO PROBABILITY) AREAS REPRESENT VALUE RANGES FOR WHICH OUR MODEL DID NOT PRODUCE ANY RESULTS.

Interpretation of probability density function curves
In Figure 4.6 (and Figure 4.7), we show a simplified scheme for interpreting the probability density function curves. In simple terms, these density functions reflect the relative likelihoods of particular modelled values. For the reader, this means that the functions show, for example, how often a particular value (and its surrounding values) were produced in the stochastic model. In the figure legend, a concrete interpretation example is given. In addition, by showing which concentration values may be expected, the model also provides some evidence concerning which values can be excluded. The red (zero probability) areas represent concentrations that our model did not produce in any simulation rounds. However, the integral over the entire (green) space is equal to one, and the modelled probabilities for finding PECs in the red areas is zero; thus, we cannot definitely exclude the possibility of the existence of higher (red) PECs in the future. The extremes of the model's output are highly limited and are determined by the data used to feed the model and to run the computer simulations.

We cannot claim that these curves perfectly reflect a realistic picture of the environmental exposure concentrations. If the model input data are changed, the results will change as well, to a certain extent. Thus (beyond architectural inadequacies, which cannot be completely excluded, but are neglected here), the interpretation of the results is always a conditional one: that is, “based on the currently available data, our model shows...”

However, despite these reservations, it is important to note that this national ENM report is based on what likely represents the most meticulously calculated data currently available. It follows the traditional bottom-up approach of previous works, seeking to provide a comprehensive view of nanoproduct use and subsequent environmental release during the whole life period of the ENMs and their products (Gottschalk et al., 2013b; Sun et al., 2014). In particular, the Sun et al. (2014) study has helped us to fill and improve Danish-specific data gaps in several places (see the sources of model input data in Annex I). In addition to collecting new data specific to Denmark, our study also distinguishes, for the first time, between photostable and photocatalytic TiO_2 (for example) and uses the newest evidence on ENM elimination in crucial material treatment processes in STPs and WIPs.

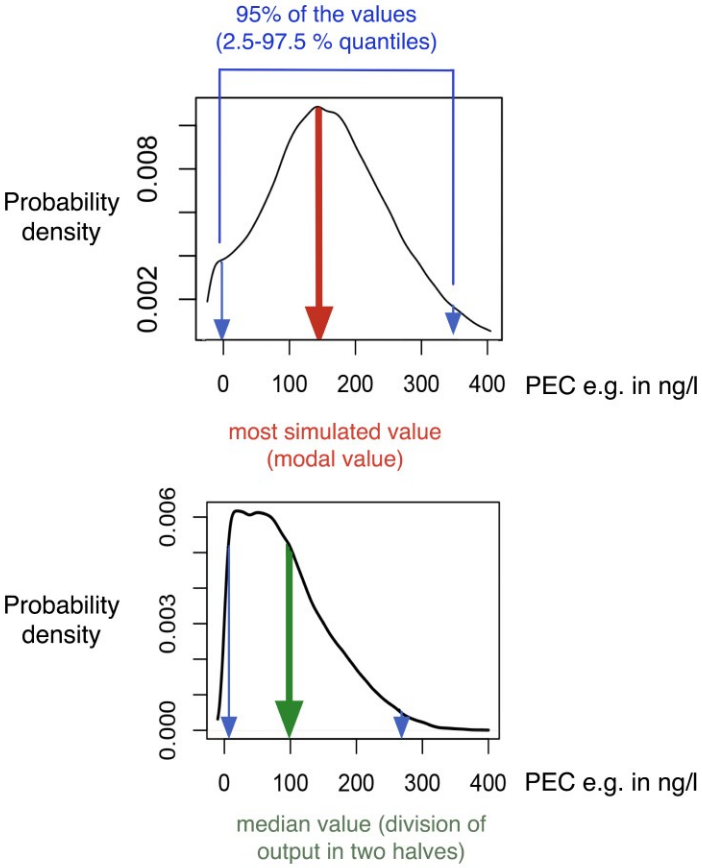


FIGURE 4.7.
EXEMPLARY PROBABILITY DENSITY CURVES OF PREDICTED ENVIRONMENTAL CONCENTRATIONS (PEC). THE 2.5 % AND 97.5 % QUANTILES FRAME THE 95% RANGES THAT ILLUSTRATE A 95% PROBABILITY OF THE PECS PRODUCED FALLING WITHIN THIS SPREAD. THE MOST FREQUENT VALUE (MODAL VALUES) REFLECT THE MOST PROBABLE EXPOSURE CONCENTRATIONS. IN A FEW CASES WITH INCONCLUSIVE, BIPOLAR OR PLURIPOLAR (SEE LOWER FIGURE FOR A BIPOLAR CASE) CURVES THE MODAL VALUES WERE REPLACED BY THE MEDIAN ONES.

5. Substance-specific model results and discussion

The modelling results for all the selected nanomaterials are presented in this chapter. The specific section for each nanomaterial contains three key figures. The first figure contains the complete ENM mass transfer system (e.g. Figure 5.1). A second figure gives an overview of all the ENM sources and receivers (e.g. Figure 5.2), and in the third figure, two tables present the modelled PEC-values (e.g. Tables 5.1 and 5.2). Finally, a summary box provides the main findings for each nanomaterial.

5.1 Photostable nano titanium dioxide (TiO_2)

5.1.1 Material flows and environmental release

Mass flows

The annual use volumes of photostable nano-TiO_2 in different products and applications are modelled at approx. 190 t/year (modal value). However, the probability distributions (see Annex I) for such material use show a range of very likely values from 100 to 300 t/year and a total use volume spectrum ranging from a few tonnes per year to almost 400 t/year.

With a semicircle, Figure 5.1 illustrates the most prominent flows by far: production, manufacturing, consumption (PMC), sewage treatment, waste incineration (STP, WIP) and recycling plants. The circle remains unclosed because we stopped the model after nanosized TiO_2 enters nanoproduct recycling plants. Although almost half of the mass ends up in these plants, there is no data basis to study and model the behaviour of such materials inside these systems. As shown in Figure 5.1, the most frequently-modelled value (modal value) was around 60 t of nanomaterial ending up in recycling processes. In considering the whole PD (not shown here), we cannot exclude that up to 200 t or more ends up in these processes annually. One-third goes into sewage sludge fertilization flows, representing about 70% of the total environmental release (see Figure 5.3). Here, our model stops again by ignoring the environmental fate of such fertilizers and soils and by assuming a conservative exposure concentration of zero nanomaterial degradation.

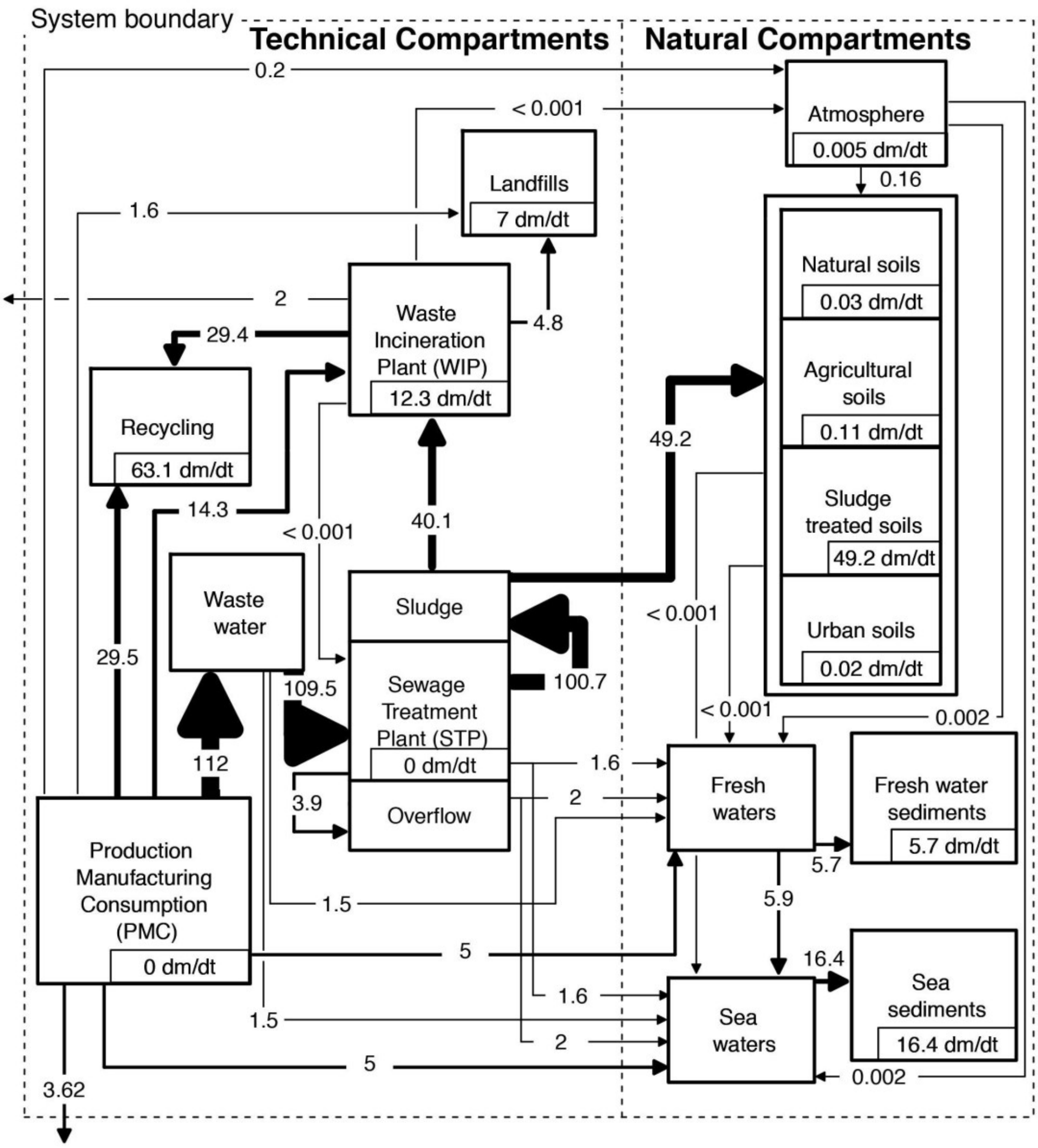


FIGURE 5.1.

MASS FLOW SYSTEM OF PHOTOSTABLE AND OTHER NANO-TiO_2 WITH ROUNDED MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) IN T/A. BOXES SHOW ACCUMULATION OR TRANSFORMATION MASS. THESE MODES, EXTRACTED FROM THE MONTE CARLO SIMULATIONS, REPRESENT HIGH PROBABILITY RESULTS AT DIFFERENT STAGES OF THE MODEL WITHOUT PRECISELY ILLUSTRATING HOLISTIC MASS-BALANCE IN THE FIGURE.

A small part (approx. 10% of the mass, at most 20-25%) reaches the aquatic environment, ending up in sediments. The amount released into the air is insignificantly small. Direct release into the aquatic environment also seems minimal (a few tons annually), and the amount released into soils is assumed to be almost zero.

In the WIP model, we see almost no environmental release from such plants, as suggested other researchers (Walser et al., 2012b). Most nano-TiO_2 is ultimately found in the fly ash and slag. However, due to current severe analytic limitations, a distinction between internal (WIP) deposition and elimination/transformation (12 t/a) is not possible. Nonetheless, it is thus far irrelevant for a general environmental release assessment that confirms almost zero emissions into the atmosphere.

There exists a clear contrast between technical environments with values partially in the range of a few hundred tons, and loads into natural environments with a frame of around 15 tons. However, if we compare the loads into the aquatic environment to the ones of other nanometals studied in this work (photocatalytic nano-TiO_2, ZnO, Ag, CeO_2 $CuCo_3$ and QDs), we see that the results are much larger for the substance category "photostable and other nano-TiO_2." The differences reach approx. and very roughly a factor of a thousand when compared to the cases of nano-Ag and CeO_2; in addition, they are somehow around a factor of 10-100 for the comparison with ZnO, copper carbonate and photocatalytic nano-TiO_2. These figures clearly could indicate some higher aquatic relevancy for this nano-TiO_2 material compared to the other one. Ultimately, it demonstrates a need for research regarding its fate in water, which is mostly determined by its aggregation/sedimentation behaviour.

In comparing the modal mass flow values in Figure 5.2 with the whole distributions of these flows, uncertainties in the data become apparent. We see that the higher end of the probability distributions may be by a factor 3-4 higher and the lower one has some probability around (if not almost) zero. Based on the used data, this information illustrates that our model explores all possible scenarios without excluding very low and very high release into the environment.

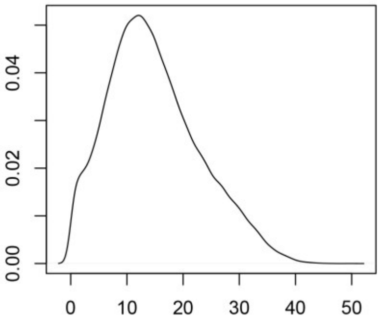
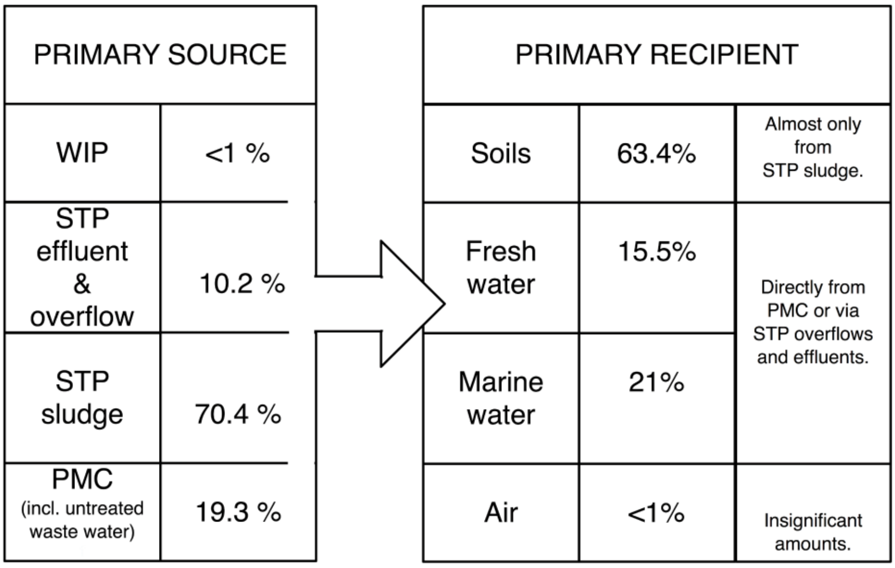


FIGURE 5.2.
PROBABILITY DISTRIBUTION (PROBABILITY DENSITY FUNCTION) OF ANNUAL DISCHARGE IN T/A OF PHOTOSTABLE AND OTHER TiO_2 INTO DANISH FRESH WATERS.

ENM sources of environmental release and its recipients

Figure 5.3 illustrates a relative picture summarizing the total environmental release of photostable and other nano-TiO_2. Relative means that the summary fractionates the environmental release amounts that only represent a fraction of the total mass transfer volume seen for photostable and other nano-TiO_2 during a one-year period in Denmark. In this case, the total environmental release (named primary sources in Figure 5.3) based mass transfer covers about 30% of the total mass mentioned. The rest is hold back by different waste treatments and waste water treatment processes. Around four-fifths of such environmentally relevant nano-TiO_2 ends up in STP sludge, and subsequently, in soils treated with this type of sludge as a consequence of the high photostable and other nano-TiO_2 used in cosmetic products and cleaning agents (approx. 66% modal value). For environmental release via STP liquids, 10% of the total release has been modelled. Thus, if we correctly understand the fate of nano-TiO_2 in STPs, then most (about 80%) of the questions regarding environmental emissions and exposure are resolved for this material. Of course, these findings reflect the current nanomaterial product market and its application field, which could change with new environmental release dynamics caused by novel ENM applications and products.



PRIMARY SOURCE	
WIP	<1 %
STP effluent & overflow	10.2 %
STP sludge	70.4 %
PMC (incl. untreated waste water)	19.3 %

PRIMARY RECIPIENT		
Soils	63.4%	Almost only from STP sludge.
Fresh water	15.5%	Directly from PMC or via STP overflows and effluents.
Marine water	21%	
Air	<1%	Insignificant amounts.

FIGURE 5.3.
OVERVIEW OF THE MOST IMPORTANT PHOTOSTABLE AND OTHER NANO-TiO_2 SOURCES AND RECEIVERS. THE PERCENTAGES REFLECT MODAL RESULTS (THE MOST FREQUENTLY MODELLED VALUES).

5.1.2 Exposure concentrations in technical compartments

Table 5.1 summarizes the modelled predicted environmental concentrations (PEC), which are comprehensively shown in Annex II. The results are presented as the most frequently modelled values. Lower and upper limits are covered by a 95% range depicting the 95% probability of the PECs modelled falling within this span.

We investigated the concentrations in several technical compartments: sewage treatment sludge, waste mass and its residues bottom ash and fly ash. We have modelled concentrations in the mg/kg range in all cases with modal numbers at around 15 mg/kg for waste mass and 770 mg/kg in sewage sludge. This model strongly reflects the prominent nano-TiO_2 mass flow captured by water treatment, which is more than twice as high as the one into waste management (incl. recycling).

The waste mass results correlate to earlier findings focused on a complete nano-TiO_2 spectrum (Sun et al., 2014). Although based on different models and data, the same applies for the bottom and fly ash values (approx. 30 and 170 mg/kg), which corresponded well to 120 ad 150 mg/kg in the 2014 reference study, confirming that almost all incinerated nano-TiO_2 is captured in these waste residues.

The sewage sludge findings, however, differ if compared to the aformentioned study at about a factor of 5 times higher. This difference results from our improved model of nano-TiO_2 absorption in treated sludge based on new nanospecific evidence, which does not have to rely on data valid for material mostly in size dimensions larger than 100 nm. Our nano-TiO_2 concentrations are greater than those of all other materials studied in this report, except those of carbon black, which represent a totally different kind of nanomaterial compound with much higher use volumes.

By evaluating the probability distribution spread and shape of all these predictions, we see that the higher end of the distributions are often about a factor of 2-3 times greater than the modes and the lower distribution ends, in all cases and with some probability, very small if not almost zero (see e.g. Figure 5.4). This distribution shows that we cannot exclude twice as high and higher concentrations (compared to modal values) based on the current data situation in a high concentration scenario (out of a total of 100,000 Monte Carlo modelling scenarios). On the other side, the model also shows some probability for very small, almost zero, concentrations. For more details on the modelled PDs of the PEC results, please see Annex II.

Compared to the natural surface water system, the sewage treatment effluent concentrations that represent values in non-diluted water are approx. 4000 times higher. The whole PEC range of the STP effluent lies in µg/l - dimensions. Thus, based on the data used, our model excludes lower values in ng/l areas for this compartment, aligning with earlier studies (Sun et al., 2014).

TABLE 5-1

PREDICTED ENVIRONMENTAL CONCENTRATIONS (PEC) FOR PHOTOSTABLE AND OTHER NANO-TiO_2 IN DIFFERENT TECHNICAL AND NATURAL COMPARTMENTS, AS MODELLED FROM COMPUTER-BASED STOCHASTIC SIMULATIONS ON NANO-TiO_2 RELEASE TO, AND SCENARIOS FOR, FATE/RESIDENCE TIME IN THOSE COMPARTMENTS. THE RESULTS ARE SHOWN AS MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) AND AS LOWER AND UPPER LIMITS CONSIDERED BY 95% RANGES THAT ALSO ILLUSTRATE A 95% PROBABILITY OF THE PECS PRODUCED FALLING WITHIN THEM. FOR SOILS AND SEDIMENTS, AN ANNUAL INCREASE OF PECS IS GIVEN.

Compartments (sources)	**Concentrations**				
	Unit	Mode	95% range		
Technical compartments					
Sewage treatment effluent	µg/l	12.6	3.4	-	91.9
Sewage treatment sludge	mg/kg	774.8	68.7	-	1478
Waste mass incinerated	mg/kg	15.0	1.4	-	32.1
Bottom ash of waste incineration	mg/kg	33.0	3.4	-	87.6
Fly ash of waste incineration	mg/kg	169.0	16.9	-	432.9
Natural compartments					
Surface water (fresh water)	µg/l	0.003	5.7E-04	-	0.1

Compartments (sources)	Concentrations				
Sea water	µg/l	3.2E-04	4.0E-05	-	0.001
Sediments (fresh water)	µg/kg	180.3	31.1	-	4292
Sediments (sea water)	µg/kg	60.1	7.6	-	195.3
Agricultural soils	µg/kg	0.013	0.002	-	0.1
Natural soils	µg/kg	0.028	0.004	-	0.2
Urban soils	µg/kg	0.051	0.006	-	0.2
Sludge treated soils	µg/kg	204.9	19.9	-	472.6
Air	µg/m3	1.1E-04	1.3E-05	-	4.9E-04

5.1.3 Exposure concentrations in natural systems

We predicted concentrations for surface waters (fresh water, sea water), sewage treatment effluents, air, different soil types (agricultural, natural, urban and sludge-treated soils) and sediments (fresh water and sea water sediments). As was done for technical compartments, the results are summarized in (Table 5.1) and comprehensively listed based on probability density functions in Annex II.

For soil and sediment values, we present the annual concentration increase given a conservative scenario of no engineered nanomaterial transformation/degradation in such compartments. All non-fertilized soils (with sewage sludge) depict results in the ng/kg range, similar to previous studies on a Swiss and European level (Sun et al., 2014). The sludge-treated soil concentration increase[7] ranges from some twenty to a few hundred µg/kg.
The sludge-treated soil concentration increase reported in 2014 showed slightly higher values (in some mg/kg dimensions) for Europe, although modelling lower absorption of sludge in wastewater treatment plants. Because the Danish calculations are based on newer data regarding the crucial removal of nano-TiO_2 in sewage treatment processes and because our model involves a smaller fertilized soil area with geographical size and sludge volumes that could be estimated in more detail, the latter results may be considered more precise.

The fresh water compartment concentrations – at most in a few ng/l-dimensions – are smaller by approx. a factor of 180 times smaller than comparable European values for fresh water. This figure reflects the immense Danish national water quantity, the higher removal efficiency for sewage water treatment plants and the high fraction (97%) of households connected to them. Based on our model, input concentrations in µg/l dimensions can be excluded. Nevertheless, the PECs were a bit lower than the ones in the reference study. For photostable and other nano-TiO_2, we confirm a clear tendency – seen also for nano-TiO_2 on the European and Swiss levels – showing the highest aquatic (fresh water) exposure values for such nano-TiO_2. This comparison works for photostable and other nano-TiO_2 when contrasted to other metallic nanomaterials, e.g. Ag, ZnO, that in our report are complemented by studies on photocatalytic nano-TiO_2, CeO_2, QD and copper carbonate.

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[7] In our report this concentration increase only focuses on the purely STP sludge contribution on soil exposure. This focus directly reflects the influence of such kind of fertilization on the soil exposure. In order to assess the total exposure one can add the generic agricultural soil concentrations to the ones of the sludge based contribution.

Furthermore, to our knowledge, we present the first marine water results for engineered nanosized substances. Roughly speaking, these marine concentrations are smaller by a factor of 10 than our fresh water model output. This finding shows ongoing sedimentation and larger water volumes compared to the fresh water compartment.

With about 13 µg/l (modal value), the sewage treatment effluents absolutely correlate when compared to the recent European values. The results do not differ even though we base our sewage treatment model on new evidence for nano-TiO_2 removed from wastewater treated and settled in sewage sludge. This finding can be explained by the lower precision in European estimations of water treatment infrastructure and inventory data when compared to the Danish situation.

The annual increase in the freshwater sediment concentrations of about 180 µg/kg sediment is approx. 10 times smaller (and in line with the water results comparison) than the European estimations. As seen above, this difference confirms the improved engineered nanomaterial removal modelling for water values in sewage treatment. The equivalent marine water sediment results – again to our knowledge the first values of this kind – correlate well with our fresh water ones and show a modal concentration increase of approx. 60 µg/kg sediment. Also with regard to the sediments, the values for photostable and other nano-TiO_2 are the highest among all our metallic engineered nanomaterial and CNTs. The ones for CB are significantly higher due to much greater use and release volumes.

The atmospheric exposure calculations confirm everything modelled up until now and show negligible small nano-TiO_2 exposure concentrations due to very low emission volumes and a short residence time in air.

Table 5.2 forecasts concentrations for photostable and other nano-TiO_2 after an engineered nanomaterial deposition period in soils beginning in 2000 and ending at the beginning of the years 2014 and 2020. For non-fertilized (no sewage sludge fertilizer) soil areas, our model suggests mode values around 80-330 ng/kg in 2014. The predictions for 2020 are approx. twice as high.

The sludge-treated soil predictions of 1.4 mg/kg (modal value) for 2014 correlate very well to US modal results of 0.5 mg/kg in 2009 for the year 2012 (Gottschalk et al., 2009). We observe the same accordance for fresh water sediment predictions: our 2014 values of about 1 mg/kg may be compared to the approx. 0.6 mg/kg US modal results presented in 2009 for the year 2012. According to the soil results, our predictions for 2020 are twice as high. For soil as well as sediments, the probability distributions for the year 2020 show a much wider spectrum, which of course relates to more uncertainty in the forecast (see Figure 5.4). To understand the large spectrum of the model input parameter values used, Figure 5.4 shows that both forecasts come with some significant certainty with values ranging from almost zero to concentrations of a few mg/kg soil. “Significant certainty” means that the densities are not lower than half of the highest density (see also Figure 4.6). Here, we should also mention that we do not know whether these concentrations continue to be in the form of ENM after they are incorporated into soil. The model simply stops at this point by assuming no ENM transformation since data for ENM fate and behaviour is completely lacking. Thus, it is within this context that Figure 5.4 illustrates conservative PECs in a worst-case model.

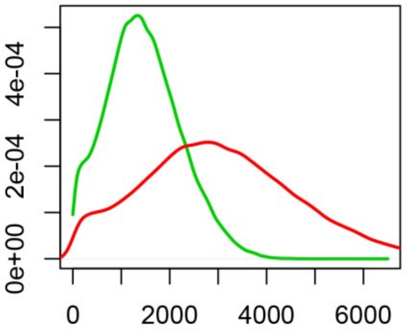

FIGURE 5.4.
PREDICTED CONCENTRATIONS (X –AXIS µG/KG SOIL) IN SLUDGE-TREATED SOILS FOR PHOTOSTABLE AND OTHER NANO-TiO_2 IN 2014 (GREEN CURVE) AND 2020.

TABLE 5-2
PREDICTED ENVIRONMENTAL CONCENTRATIONS (PEC) FOR PHOTOSTABLE AND OTHER NANO-TiO_2 IN SEDIMENTS AND SOILS MODELLED FROM COMPUTER-BASED STOCHASTIC SIMULATIONS ON NANO-TiO_2 RELEASE TO THOSE COMPARTMENTS. THE PREDICTIONS ARE SHOWN AS MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) AND AS LOWER AND UPPER LIMITS CONSIDERED BY 95% RANGES THAT ILLUSTRATE A 95% PROBABILITY OF THE MODELLED PECS FALLING WITHIN THIS RANGE. THE PEC VALUES REFLECT NANO-TIO_2 CONCENTRATIONS AFTER BEING DEPOSITED IN SEDIMENTS AND SOILS UNTIL THE BEGINNING OF THE YEARS 2014 AND 2020. ALL THE CURVES ARE SHOWN IN ANNEX II OF THIS REPORT.

Compartments	**Concentrations**				
	Unit	Mode	95% range		
Prediction for 2014					
Sediments (fresh water)	µg/kg	1172	202.4	-	27900
Sediments (sea water)	µg/kg	390.7	49.1	-	1269
Agricultural soils	µg/kg	0.085	0.010	-	0.390
Natural soils	µg/kg	0.183	0.024	-	1.1
Urban soils	µg/kg	0.331	0.039	-	1.5
Sludge treated soils	µg/kg	1332	129.4	-	3072
Prediction for 2020					
Sediments (fresh water)	µg/kg	2447	422.7	-	58252
Sediments (sea water)	µg/kg	815.7	102.5	-	2650
Agricultural soils	µg/kg	0.2	0.021	-	0.8
Natural soils	µg/kg	0.4	0.1	-	2.2
Urban soils	µg/kg	0.7	0.1	-	3.2
Sludge treated soils	µg/kg	2781	270.1	-	6414

5.1.4 Discussion and conclusions

In summary, our study confirms earlier research findings (Gottschalk et al., 2009; Sun et al., 2014). In Denmark, the highest aquatic exposure is for nano-TiO_2 compared to other metallic nanosized materials. This study output is remarkable because we have improved upon other studies; in this research, the nano-TiO_2 elimination in sewage treatment was based entirely upon nanomaterial specific data, which predicts a much higher elimination of such ENM from the water phase.

The results showed some aquatic relevancy for this nano-TiO_2 material and indicated a need for research regarding its fate in water. Aggregation research has made some progress (Praetorius et al., 2012); however, we had to assume probability distributions spread out over the total possible spectrum of immediate aggregation/sedimentation and no sedimentation at all based on currently available data. Downsizing this spectrum would be an important step in improving the environmental exposure assessment.

Although we see clear high-end PEC limits that exclude non-realistic (not to expect) high concentrations for all compartments, we have to explicitly underscore the limits of interpretation of these results. Future PECs may be considerably higher with the increasing production and use of the investigated nano-TiO_2. On the other hand, improved and newly available release measurements could also shift the release values and subsequent PEC results to even lower dimensions by significantly altering the model input. Finally, we must point out that transparency with respect to nano-TiO_2 production and use volumes on the part of industry would make such exposure modelling more precise. These two general points of conclusion apply to all examined substances, and are therefore not repeated in each of the following cases.

Summary

- In line with European studies and compared to other metallic nanomaterials also for Denmark the currently highest (compared to the other ENM investigated in this report) aquatic exposure is assumed for photostable and other nano-TiO_2.

- The non-diluted effluent from sewage treatment plants shows the highest concentrations in the range of a few to almost one hundred µg/l (modal value around 13 µg/l). This correlates well with European modal values of 16 µg/l (Sun et al., 2014) that are half as high as the Swiss equivalents

- The fresh water concentrations reach at most one tenth of a µg/l, (worst case scenarios) the ones in marine water are smaller and almost completely in pg/l dimensions.

- The air results show marginal concentrations in pg/m^3 ranges and reflect very small emissions into the air and almost complete nanomaterial removal in waste incineration plants.

- Soils and sediments represent the most significant nanomaterial sinks with approx. expected concentrations (most frequent results) for 2020 of 2.4 and 0.8 mg/kg in sediments (fresh water and marine water), 3 mg in sludge treated soils and a few tenths µg/kg in non-sludge based fertilized soils.

- The fate in soils and sediments is not considered, the report assumes a conservative scenario of no engineered nanomaterial degradation in such environments.

- A better understanding and empirical data is needed for:
  - Fate and behaviour of photostable and other nano-TiO_2. in sewage treatment plants, soils and water;
  - Knowledge on real Danish ENM use quantities that by far represents the most important factor for updating the environmental exposure assessment.

5.2 Photocatalytic titanium dioxide (TiO2)

Similar to the previous section, we present mass transfer and predicted environmental concentrations, this time for photostable nanosized titanium dioxide. We investigated the concentrations in sewage treatment sludge, waste mass and its residues bottom ash and fly ash; we also predicted concentrations for surface waters (fresh water, sea water), sewage treatment effluents, air, different soil types (agricultural, natural, urban and sludge-treated soils) and sediments (fresh water and sea water sediments).

The results are summarized in Table 5.3 and comprehensively listed and shown based on probability density functions in Annex II.

5.2.1 Material flows and environmental release

Mass flows

To our knowledge, this report presents the first study that distinguishes photostable from photocatalytic nano-TiO_2. Roughly speaking, we see in Figure 5.5 that the photocatalytic part of the TiO_2 nanomaterial mass flows are much smaller than the photostable titanium equivalents, in some cases up to a factor of around 10 time smaller (when comparing modal values). Basically, this finding reflects the much lower use volumes of approx. 45 t annually (modal value) that are approx. a factor of 4 times smaller than the modal ones for photostable nano-TiO2. In contrast to the previous case study on photostable nano-TiO_2, we see new dominant mass transports. The transfer (incomplete) circle of production, manufacturing, consumption (PMC), waste incineration (WIP), recycling plants and landfills dominates (shows a higher mass transport total) that of PMC, waste water, sewage treatment plants (STP) and aquatic as well as terrestrial environments. In the previous case on photostable titanium, we observed the reverse situation. Compared to the mass transport into waste, landfilling and recycling processes, the relative photocatalytic nano- TiO_2 water relevancy – reflected by mass transport into waste water and sewage treatment processes – is lower than that of the photostable nano-titanium model. This distinction results primarily from a prominent water relevant use of photostable nano-TiO_2 in cosmetics that was not significant in the photocatalytic nanomaterial application field. Annex I of this report provides an overview of all nano-TiO_2 applications. The annual load of this nanosized photocatalytic TiO_2 into the aquatic compartments is approx. 10 times lower (than the equivalent one for photostable nano-TiO_2) and does not exceed one tonne annually (modal values). The annual load into the terrestrial environment is higher at about 6 t/a. The emissions into the air of about 1 t/a are, however, about five times higher those of photostable nano-TiO2 and higher than most of the studied nanomaterials in this report. This finding reflects the main use of such TiO_2 in paints and coatings where some air emissions cannot be avoided. Nevertheless, when considering the current nanomaterial use volumes of such titanium material, the ENM emissions into the air compartment are insignificant, as observed in most (if not all) other studies in this report.

Here, we also must mention that we actually do not know whether the modelled ENM load into landfills, recycling plants, soils and sediments continues in the form of ENM after ending up there. The model stops at this point. First assumptions expect only very reduced nanomaterial feedback-flows into productive and consumption processes (Caballero-Guzman et al., 2014). For soils and sediments, we assume no ENM transformation because data for the ENM fate and behaviour is completely missing. For landfills and recycling plants, our model simply reflects the total annual load without any further indications on nanomaterial fate and behaviour in these plants. For further indications on such model properties, please see chapter 4.1 and detailed explanations on our first case study on photostable and other nano-TiO2.

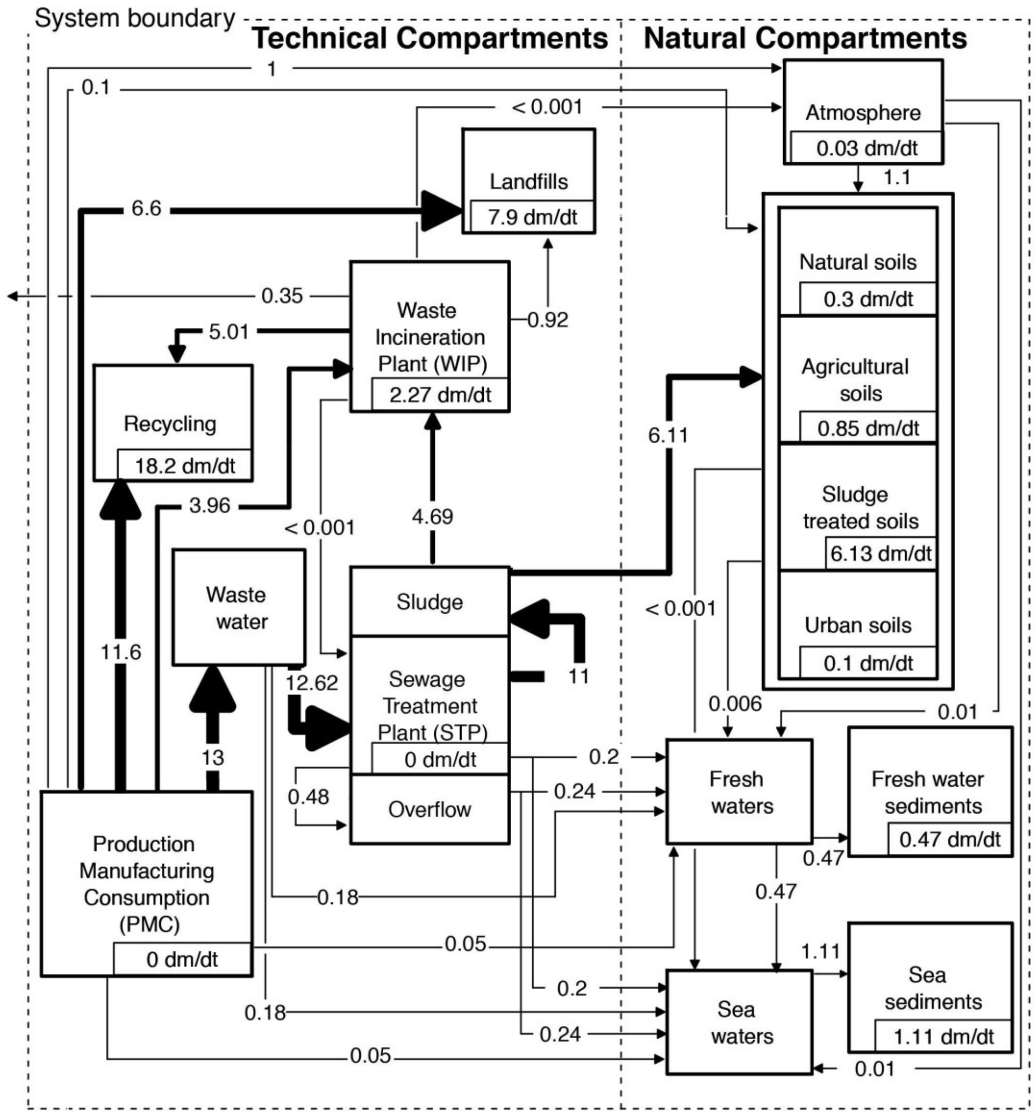

FIGURE 5.5.
MASS FLOW SYSTEM OF PHOTOCATALYTIC NANO-TiO$_2$ WITH ROUNDED MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) IN T/A. BOXES SHOW ACCUMULATION OR TRANSFORMATION MASS. THESE MODES, EXTRACTED FROM THE MONTE CARLO SIMULATIONS, REPRESENT HIGH PROBABILITY RESULTS AT DIFFERENT STAGES OF THE MODEL WITHOUT PRECISELY ILLUSTRATING HOLISTIC MASS-BALANCE IN THE FIGURE.

ENM sources of environmental release and its recipients

The overview in Figure 5.6 regarding the environmental release of photocatalytic nano-TiO$_2$ opposes the total for the most relevant ENM release sources to their primary recipients. As is also the case for the photostable nano-TiO$_2$, we see that the ENM fate in sewage treatment is the most prominent factor (80%) influencing the environmental release of such material. Therefore, our findings in the first case study are confirmed: understanding the fate of such ENM in STPs answers most open points regarding environmental emissions and exposure. However, for the photocatalytic material, the contribution from the PMC compartment is slightly higher, in this case, about 20% of the total environmental release. Most ENM ends up in soils after treatment with STP sludge; as an alternative pathway, a smaller portion (approx. 6 times smaller) comes into soils from PMC-based emissions via air deposition. This finding confirms the remark made above that photocatalytic nano-TiO$_2$ use in various types of paints and coatings my also lead to some nanomaterial release into soils via air deposition. Although the release paths show slightly higher relevancy in the PMC compartment for photocatalytic nano- TiO_2 use, the distribution of such ENM in the natural environment is not distinguishable from the one for photostable TiO_2. The results on ENM recipients here show that about 80% ends up in soils while the rest reaches the aquatic environment. The potential air contamination again seems to be insignificant for the current ENM use amounts and fields of application.

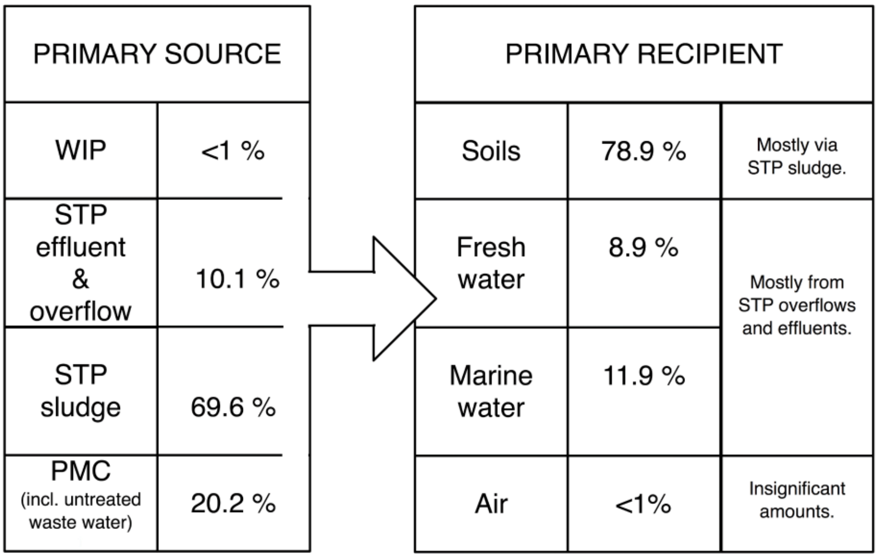

FIGURE 5.6.
OVERVIEW OF THE MOST IMPORTANT PHOTOCATALYTIC NANO-TiO_2 SOURCES AND RECEIVERS. THE PERCENTAGES REFLECT MODAL RESULTS (THE MOST FREQUENTLY MODELLED VALUES).

5.2.2 Exposure concentrations in technical compartments

The concentration results for photocatalytic nano-TiO_2 in technical compartments (see Table 5.3) do not greatly differ from the model results for photostable and other nano-TiO_2, which completely aligned with earlier studies (Sun et al., 2014). For waste and ash materials, we again see concentrations in the mg/kg range that have been modelled in all cases with modal numbers around 5 times smaller than the ones for photostable TiO_2. In addition, the model computes approx. 3 mg/kg in waste mass and 6 mg/kg in bottom ash (30 mg/kg in fly ash).

The STP effluents for such photocatalytic nano-TiO_2 show concentrations with modal results around 1.6 µg/l, confirming the smaller (10 times) aquatic relevancy (and PECs) explained above. This finding means that the photocatalytic nano-TiO_2 fraction contributes about one-tenth, at most, of the total load of nano-TiO_2 into such technical compartments.

TABLE 5.3

PREDICTED ENVIRONMENTAL CONCENTRATIONS (PEC) FOR PHOTOCATALYTIC NANO-TiO_2 IN DIFFERENT TECHNICAL AND NATURAL COMPARTMENTS, AS MODELLED FROM COMPUTER-BASED STOCHASTIC SIMULATIONS ON NANO-TIO_2 RELEASE TO, AND SCENARIOS FOR, FATE/RESIDENCE TIME IN THOSE COMPARTMENTS. THE RESULTS ARE SHOWN AS MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) AND AS LOWER AND UPPER LIMITS CONSIDERED BY 95% RANGES THAT ALSO ILLUSTRATE A 95% PROBABILITY OF THE PECS PRODUCED FALLING WITHIN THEM. FOR SOILS AND SEDIMENTS, AN ANNUAL INCREASE OF PECS IS GIVEN.

Technical compartments					
Sewage treatment effluent	µg/l	1.6	0.4	-	14.3
Sewage treatment sludge	mg/kg	84.6	9.3	-	232.4
Waste mass incinerated	mg/kg	2.8	0.3	-	6.8
Bottom ash of waste incineration	mg/kg	6.0	0.7	-	18.3
Fly ash of waste incineration	mg/kg	29.7	3.3	-	90.4
Natural compartments					
Surface water (fresh water)	µg/l	2.7E-04	4.7E-05	-	0.007
Sea water	µg/l	2.2E-05	3.6E-06	-	9.9E-05
Sediments (fresh water)	µg/kg	14.2	2.6	-	401
Sediments (sea water)	µg/kg	4.1	0.7	-	18.5
Agricultural soils	µg/kg	0.1	0.011	-	0.3
Natural soils	µg/kg	0.2	0.027	-	0.7
Urban soils	µg/kg	0.4	0.044	-	1.0
Sludge treated soils	µg/kg	25.5	2.7	-	73.4
Air	µg/m3	7.3E-04	7.7E-05	-	0.002

5.2.3 Exposure concentrations in natural compartments

The photocatalytic nano-TiO_2 aquatic PECs for fresh and marine water as well as their sediments are with no exception much smaller than the ones for photostable nano-TiO_2, by a factor 10 on average. Such a factor is composed of the difference in the generic ENM use volumes (factor 4) and the relative smaller water relevancy (remaining factor) reflected by the main ENM applications of photocatalytic nano-TiO_2 in coatings, paints and use in cement. The fresh water PEC values are mostly in pg/l to ng/l dimensions and confirm our previous nano-TiO_2 results. Marine water PECs seem to be marginal, with all values in pg/l concentrations. This finding simply means that the photocatalytic contribution to the total nano-TiO_2 aquatic PECs is very low, not to say insignificant. Hence, our above-modelled photostable PEC values for surface waters more or less reflect the generic Danish nano-TiO_2 PECs that were compared to the above-mentioned European studies (Sun et al., 2014).

The same small PECs have been modelled for sediments where we computed some µg/kg annual augmentation that could lead to approx. 200 µg /kg (fresh water sediment) and 60 µg /kg (sea water sediment) concentrations (modal values) in 2020 (see Table 5.4). Taken together, the total nano-TiO_2 (photocatalytic and photostable nanomaterial) annual PEC augmentation leads to approx. 2.6 mg/kg (fresh water sediment) and 0.9 mg/kg (sea water sediment) concentrations in 2020. The fresh water sediment results are much smaller than the ones presented by others for Europe. However, as emphasized above, we could update our STP removal of nano-TiO_2 by considering new scientific data that suggests a much better removal of nano-TiO_2 from the water phase. For marine water PECs, we do not have any means of comparison, because to our knowledge, we present the first results of this kind.

For our soil PECs, the model reveals a current annual augmentation of about 25 µg/kg for the ones fertilized with STP sludge. Such fertilization could lead to PEC values of about 350 µg/kg (modal values) until 2020. Again, such PEC values may be seen as an additional load to the one of photostable nano-TiO_2, which is approx. ten times higher. Taken together (photocatalytic and photostable nano-TiO_2), such concentrations could reach approx. 3 mg/kg in 2020.

TABLE 5.4.

PREDICTED ENVIRONMENTAL CONCENTRATIONS (PEC) FOR PHOTOCATALYTIC NANO-TiO_2 IN SEDIMENTS AND SOILS MODELLED FROM COMPUTER-BASED STOCHASTIC SIMULATIONS ON NANO-TiO_2 RELEASE TO THOSE COMPARTMENTS. THE PREDICTIONS ARE SHOWN AS MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) AND AS LOWER AND UPPER LIMITS CONSIDERED BY 95% RANGES THAT ILLUSTRATE A 95% PROBABILITY OF THE MODELLED PECS FALLING WITHIN THIS RANGE. THE PEC VALUES REFLECT NANO-TIO_2 CONCENTRATIONS AFTER BEING DEPOSITED IN SEDIMENTS AND SOILS UNTIL THE BEGINNING OF THE YEARS 2014 AND 2020. ALL THE CURVES ARE SHOWN IN ANNEX II OF THIS REPORT.

Compartments	**Concentrations**		
	Unit	Mode	95% range
Prediction for 2014			
Sediments (fresh water)	µg/kg	92.3	17.0 - 2607
Sediments (sea water)	µg/kg	26.5	4.3 - 119.9
Agricultural soils	µg/kg	0.7	0.1 - 1.7
Natural soils	µg/kg	1.5	0.2 - 4.9
Urban soils	µg/kg	2.7	0.3 - 6.7
Sludge treated soils	µg/kg	165.8	17.4 - 476.9
Prediction for 2020			
Sediments (fresh water)	µg/kg	192.6	35.4 - 5444
Sediments (sea water)	µg/kg	55.3	9.1 - 250.4
Agricultural soils	µg/kg	1.4	0.2 - 3.6
Natural soils	µg/kg	3.2	0.4 - 10.1
Urban soils	µg/kg	5.6	0.6 - 14.0
Sludge treated soils	µg/kg	346.2	36.4 - 995.7

5.2.4 Discussion and conclusions

So far as we know, this report is the first specifically focused on photocatalytic nano-TiO_2. Therefore, it is not possible to compare our results to other studies. The same also applies to all the results in marine environments where we currently do not have any equivalent reference studies. Nevertheless, our comparison of the Danish fresh water results of photostable and other engineered nanomaterial TiO_2 shows high plausibility when compared to similar studies on European levels (Gottschalk et al., 2009; Sun et al., 2014). Such plausibility could even be higher in our case due the consideration of new scientific evidence of much higher nano-TiO_2 removal in STP processes.

Despite new insights on the elimination of nano-TiO_2 before entering the aquatic environment, for Denmark, the highest aquatic exposure was modelled for photostable and other engineered nano-TiO_2 when compared to other metallic nanosized materials studied so far. However, in isolation, the water photocatalytic nano-TiO_2 results do not add much (one-tenth) to such high exposure. The photocatalytic nano-TiO_2 PECs for surface waters are, at the most, in a similar pg/l range as the ones for nano-ZnO (please see next chapter); there, the total load into the aquatic environment is very low due to the almost complete elimination of nano-Zno in the STP process. Therefore, this report primarily concludes that distinguishing two different categories of nano-TiO_2 depends on the type of ENM applications; the nano-TiO_2 aquatic relevancy may vary greatly.

For risk assessment and toxicology studies, it will be important to have the possibility to compare the photocatalytic nano-TiO_2-specific results to equivalent ones in the ecotoxicological field. Accordingly, toxic endpoints have to be derived for such photocatalytic nanomaterial types. However, the photocatalytic TiO_2-specific collection of data and its distinction from the photostable counterpart data remains difficult because clear indications on material properties (photocatalytic versus photostable) are largely absent for nanoproducts (and its applications).

Summary

- Contrary to photostable nano-TiO_2, the relative mass transfer of photocatalytic nano-TiO_2 into waste, recycling and landfilling processes is probably higher than that into the aquatic and terrestrial environments (compared to other transport pathways of the same material).

- In the case of photocatalytic TiO_2 nanomaterial, the engineered nanomaterial's fate and behaviour in waste, recycling, landfilling and sewage treatment processes covers approx. 90% of the total annual ENM mass movement in Denmark.

- Currently, the Danish environmental release of photocatalytic TiO_2 nanomaterial seems not to be too critical: the terrestrial compartments receive about 6 tonnes, while aquatic environments receive, at the most, one tonne annually (modal values).

  Compared to photostable and other nano-TiO_2 and based on current predictions of the use amounts of photocatalytic nano-TiO_2, its aquatic exposure relevance is much lower (approx. by a factor of 10).

- The fate and behaviour of photocatalytic nano-TiO_2 in recycling and landfill plants should be studied because a significant mass of that material ends up in such plants.

- For general summary points on the assessment of Danish ENM use quantities, please the summary box on photostable and other nano-TiO_2.

5.3 Zinc oxide (ZnO)

This chapter presents nano-zinc oxide mass transport results and predicted environmental concentrations. As done above for different types of nanosized titanium dioxide, PECs are computed for sewage treatment sludge, waste mass and its residues bottom ash and fly ash, surface waters (fresh water, sea water), sewage treatment effluents, air, soils (agricultural, natural, urban and sludge-treated soils) and sediments (fresh water and sea water sediments).

The nano-ZnO PECs are summarized in Table 5.5 and fully shown based on probability density functions in Annex II.

5.3.1 Material flows and environmental release

Mass flows

Figure 5.7 illustrates the Danish mass transfer system for nano-ZnO, revealing a comprehensive overview of all mass transport based on current modal values in tonnes (most frequently modelled values) during a one-year period.

It is noticeable that two-thirds of ZNO-based nanomaterial finds its way into STP, mostly ending up as sewage treatment sludge. However, based on new evidence for its fate in such sludge, we see that this nanomaterial transport then stops at this stage of our flow chart system. New insights (Lombi et al., 2012) into the fate and behaviour of nano-Zno during anaerobic digestion in wastewater and sewage sludge post-treatment processes demonstrate that, after those treatments, the target nanoparticles are fully transformed into non-nanomaterial forms. Hence, the fertilization flow bringing this kind of ENM into soils is completely missing in this case, and the ENM load for soils is considerably smaller than the ones for the previous titanium case studies. Since most (two-thirds) of such nanosized ZnO ends up in such STP-based elimination, the remaining nano-ZnO load into terrestrial and aquatic compartments is modelled at a very low level that reaches a few tonnes per year at most in the aquatic case and does not exceed one tonne of discharge into soils.

The latter conclusion also applies to air emissions, where we see marginal values in much the same order of magnitude (lower than one tonne annually) as the ones of the photostable nanosized titanium. Such low air emissions results from the high use amount (approx. 80% modal value) in cosmetics for this kind of ENM, which does not lead to significant release into air.

In addition to low air emissions, we see relatively high quantities ending up in recycling and landfilling processes, mostly from their use in paints, consumer electronics, plastics and others. However, also in the case of nano-ZnO, we are faced with a knowledge gap regarding the following question: does the modelled ENM load into landfills and recycling plants (nearly one-third of the total mass transport mass) continue to be in the form of ENM after they end up there? The model stops at this point and assumes a total annual load without any further indications on nanomaterial fate and behaviour in these compartments. Consistent with the modelling procedure for the other nanomaterials, however, we assume that no significant amounts of ENM should leave such systems (no leaching out process), thus leading to zero environmental release. For nano-ZnO in soils and sediments, we again consider a scenario of no elimination and transformation; thus, in these cases, we also model the highest possible PECs for nano-ZnO in order to reach a conservative environmental risk assessment.

Furthermore, for nano-ZnO in the PMC box, the model considers an annual elimination of 2.5 t (modal values), reflecting its use in products like paints, cosmetics, textiles and filters where it easily comes into contact with water and is assumed to dissolve. Such dissolution may compose up to 10% of the nanomaterial mass in such applications.

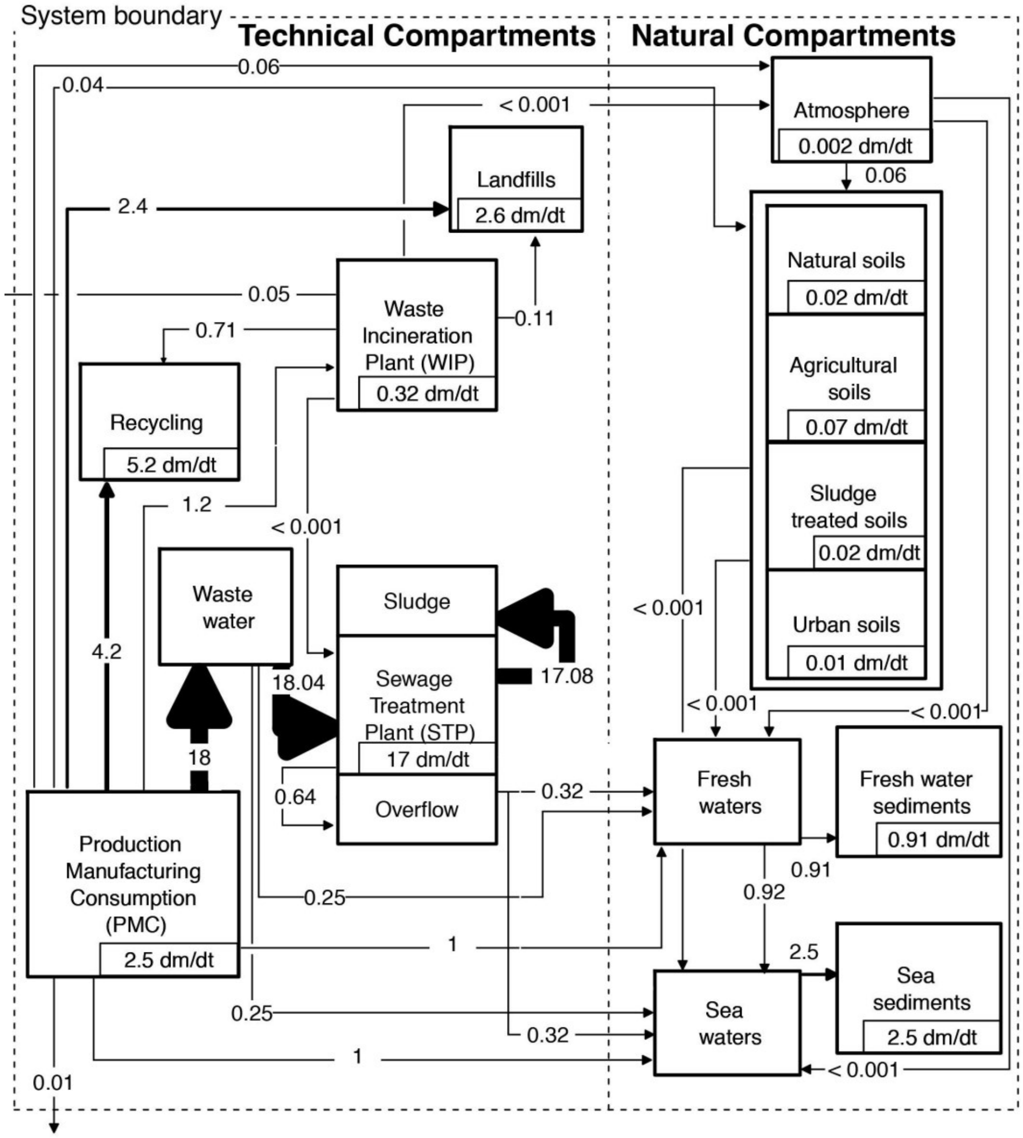

FIGURE 5.7.
MASS FLOW SYSTEM OF ENGINEERED NANOMATERIAL (ZnO) WITH ROUNDED MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) IN T/A. BOXES SHOW ACCUMULATION OR TRANSFORMATION MASS. THESE MODES, EXTRACTED FROM THE MONTE CARLO SIMULATIONS, REPRESENT HIGH PROBABILITY RESULTS AT DIFFERENT STAGES OF THE MODEL WITHOUT PRECISELY ILLUSTRATING HOLISTIC MASS-BALANCE IN THE FIGURE.

ENM sources of environmental release and its recipients

Figure 5.8 complements the flow chart system in Figure 5.7 by giving an overview of the most important nano-ZnO sources for environmental release and the receiver compartments for the released nanomaterial. The percentages reflect modal values extracted from our computer-based mass transfer simulations. What we learn from this overview is that most of the released nano-ZnO comes from the PMC compartment and that the sewage treatment process eliminates most nano-ZnO from the environmentally relevant mass transport system. The 82.5% mass coming from the PMC again highlights the dominant use of such ENM in cosmetic products (approx. modal value of 80%). As a consequence, most of the environmental flows, which are a few tonnes at most, bring such ENM into the aquatic environment (approx. 98%). The approximate 17% of released nanomaterial that has its origin in STPs has to be fully allocated to the overflow of such sewage treatment facilities. Significant air and soil contamination cannot be anticipated based on the current use volumes and types of nano-ZnO product applications. A complete overview of such applications is given in Annex I of this report.

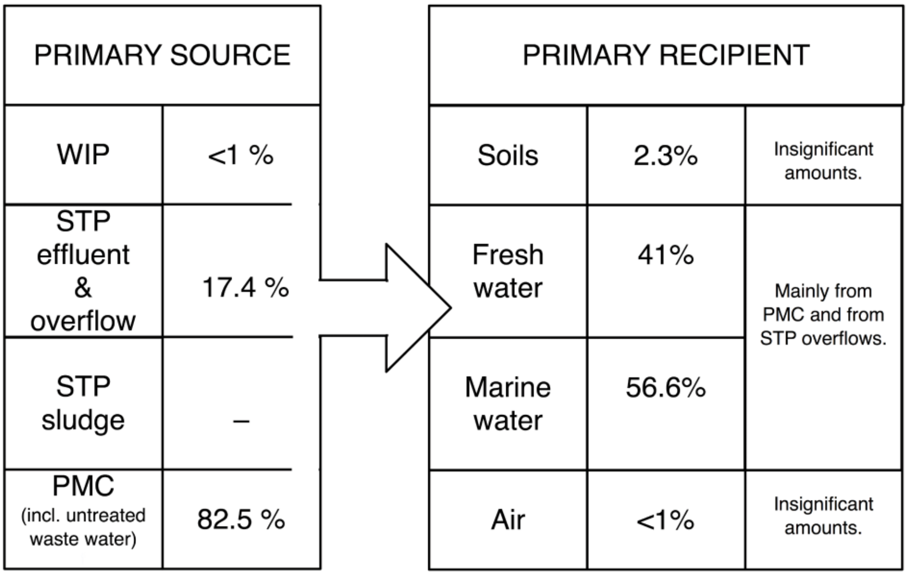

FIGURE 5.8.
OVERVIEW OF THE MOST IMPORTANT NANO-ZnO SOURCES AND RECEIVERS. THE PERCENTAGES REFLECT MODAL RESULTS (THE MOST FREQUENTLY MODELLED VALUES).

5.3.2 Exposure concentrations in technical compartments

Remarkable in this case study is that our model predicts almost zero nano-ZnO concentrations (see Table 5.5) in sewage treatment effluents and sewage treatment sludge. This finding reflects the non-accuring environmental release of such anno-ZnO from such plants, as recently demonstrated by other researchers (Lombi et al., 2012). These authors experimented on the fate and behaviour of nano-ZnO particles during anaerobic digestion in wastewater and during post-sewage treatment processes, finding that after such material treatment, the investigated particles were almost fully transformed into non-nanomaterial forms.

The waste mass and ash materials show concentrations far below what we have seen in the two previous nanoszied titanium dioxide cases. Almost all values (waste and bottom ash) are in the µg/kg range in contrast to the nanoszied titanium dioxide mg/kg dimensions. This figure also applies to the comparison to photocatalytic nanosized titanium, which has similar use volumes to the nano-ZnO case. Such concentration differences (approx. factor of 10) are caused by the nan-ZnO application fields, which considerably differ when compared to the photocatalytoc nanosized titanium. Nano-ZnO is primarily used in cosmetics that do not show the same waste incineration relevancy as those of the photocatalytic TiO_2 material (paints, coatings construction materials).

TABLE 5.5.

PREDICTED ENVIRONMENTAL CONCENTRATIONS (PEC) FOR NANO-ZnO IN DIFFERENT TECHNICAL AND NATURAL COMPARTMENTS, AS MODELLED FROM COMPUTER-BASED STOCHASTIC SIMULATIONS ON NANO-ZnO RELEASE TO, AND SCENARIOS FOR, FATE/RESIDENCE TIME IN THOSE COMPARTMENTS. THE RESULTS ARE SHOWN AS MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) AND AS LOWER AND UPPER LIMITS CONSIDERED BY 95% RANGES THAT ALSO ILLUSTRATE A 95% PROBABILITY OF THE PECS PRODUCED FALLING WITHIN THEM. FOR SOILS AND SEDIMENTS, AN ANNUAL INCREASE OF PECS IS GIVEN.

Compartments (sources)	**Concentrations**		
	Unit	Mode	95% range
Technical compartments			
Sewage treatment effluent	µg/l	≈0	
Sewage treatment sludge	mg/kg	Almost no ZnO remaining in its initial nanoform.	
Waste mass incinerated	mg/kg	0.3	0.04 - 1.5
Bottom ash of waste incineration	mg/kg	0.7	0.1 - 3.9
Fly ash of waste incineration	mg/kg	3.6	0.5 - 19.2
Natural compartments			
Surface water (fresh water)	µg/l	4.5E-04	8.6E-05 - 0.013
Sea water	µg/l	4.1E-05	5.6E-06 - 1.8E-04
Sediments (fresh water)	µg/kg	25.2	4.5 - 734.6
Sediments (sea water)	µg/kg	7.6	0.9 - 33.8
Agricultural soils	µg/kg	0.008	0.001 - 0.1
Natural soils	µg/kg	0.017	0.003 - 0.1
Urban soils	µg/kg	0.031	0.005 - 0.2
Sludge treated soils	µg/kg	Almost no ZnO remaining in its initial nanoform.	
Air	µg/m3	3.6E-05	5.2E-06 - 2.3E-04

5.3.3 Exposure concentrations in natural compartments

The aquatic PECs (modal values) for waters and sediments (Table 5.5) show almost identical low magnitudes to those of photocatalytic nano-TiO_2. This basically goes hand in hand with similar total annual use volumes of these two nanomaterial types. Here, it is striking that the model shows very low values in pg/l levels with high probability for surface waters (fresh water and marine water). These low values are a direct consequence of the above-mentioned almost complete removal of nano-ZnO during the sewage treatment process. Such removal leads to aquatic release that is almost entirely determined by direct discharge from the nanoproducts, such as those used in cosmetics. If, for example, Monte Carlo-based scenarios for low cosmetic use are combined with the zero release from water treatment, then the total nano-ZnO discharge into surface water is nearly zero and finds its way into high probabilities. These probability distributions are fully shown in Annex II of this report. Figure 5.9 illustrates one example for a density curve of the predicted environmental concentrations in fresh water.

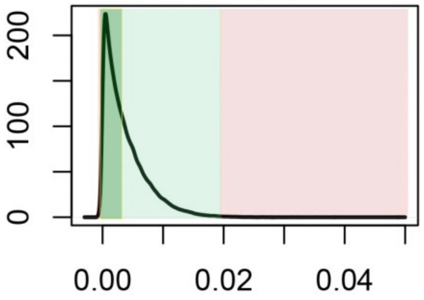

FIGURE 5.9.
PROBABILITY DENSITY CURVE OF THE PREDICTED ENVIRONMENTAL CONCENTRATIONS (PEC) IN µG/L (X-AXIS) OF NANO-ZnO IN SURFACE WATERS (FRESH WATER). CURVE INTERPRETATION, GREEN: TOTAL SPECTRUM OF PEC VALUES; DARK GREEN: RANGE OF MOST-FREQUENTLY MODELLED PECS (AT LEAST HALF AS OFTEN AS THE MOST FREQUENTLY MODELLED VALUE); RED: NOT MODELLED/EXPECTED VALUES FOR PECS.

In contrast to the nanotitanium cases, the model for nano-ZnO fails to lead to any significant load or concentration in soils. Even our predictions for 2020 (Table 5.6) covering about 20 years of nanomaterial deposition into soils, combined with no subsequent transformation or other elimination from such environments, show modal concentrations in ng/kg levels at the most. Such values appear low in comparison to some µg/kg in the photocatalytic nanotitanium dioxide case. The reason for such marginal soil concentrations is again the full removal of nano-Zno in STP sludge, which would be the most important source of fertilization for some agricultural soil areas. Second, the low soil relevancy is a consequence of an insignificant direct discharge into terrestrial environments of the main product category of cosmetics, which accounts for four-fifths of nano-Zno use and has significantly negative impacts, such as soil release volume.

TABLE 5.6.
PREDICTED ENVIRONMENTAL CONCENTRATIONS (PEC) FOR NANO-ZnO IN SEDIMENTS AND SOILS MODELLED FROM COMPUTER-BASED STOCHASTIC SIMULATIONS ON NANO-ZnO. RELEASE TO THOSE COMPARTMENTS. THE PREDICTIONS ARE SHOWN AS MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) AND AS LOWER AND UPPER LIMITS CONSIDERED BY 95% RANGES THAT ILLUSTRATE A 95% PROBABILITY OF THE MODELLED PECS FALLING WITHIN THIS RANGE. THE PEC VALUES REFLECT NANO-TIO_2 CONCENTRATIONS AFTER BEING DEPOSITED IN SEDIMENTS AND SOILS UNTIL THE BEGINNING OF THE YEARS 2014 AND 2020. ALL THE CURVES ARE SHOWN IN ANNEX II OF THIS REPORT.

Compartments	**Concentrations**				
	Unit	Mode	95% range		
Prediction for 2014					
Sediments (fresh water)	µg/kg	163.8	29.6	-	4775
Sediments (sea water)	µg/kg	49.4	6.1	-	219.9
Agricultural soils	µg/kg	0.052	0.008	-	0.347
Natural soils	µg/kg	0.122	0.018	-	0.9
Urban soils	µg/kg	0.2	0.030	-	1.3
Sludge treated soils	µg/kg	Almost no ZnO remaining in its initial nanoform.			
Prediction for 2020					
Sediments (fresh water)	µg/kg	342.1	61.7	-	9969
Sediments (sea water)	µg/kg	103.0	12.8	-	459.1
Agricultural soils	µg/kg	0.1	0.016	-	0.7
Natural soils	µg/kg	0.2	0.038	-	2.0
Urban soils	µg/kg	0.4	0.1	-	2.8
Sludge treated soils	µg/kg	Almost no ZnO remaining in its initial nanoform.			

5.3.4 Discussion and conclusions

In sum, our nano-Zno study for Denmark is fully in line with earlier modelling results for natural and urban soils as well as air exposure concentrations (Gottschalk et al., 2009; Sun et al., 2014). The same high correlation applies for the concentrations of nano-ZnO modelled in waste mass and waste incineration ash-based residues.

However, this consensus does not apply for the aquatic results (surface waters, sediments). The crucial parameters around ZnO nanomaterial fate and elimination in sewage treatment plant processes in this Danish work has been significantly improved compared to the aforementioned reference studies. An almost complete nano-ZnO removal in these plants leads only to marginal PEC values in waters and sediments for ZnO-engineered nanomaterial. The results on STP sludge and soils treated with such sludge have to be considered to be almost zero because no nano-Zno maintains it initial nanoform after such sewage treatment processes.

All in all, our results indicate a low generic environmental relevancy for nano-ZnO. However, we must again point out that these values may change in the future with new and other types of nano-ZnO applications. These emerging nano-ZnO applications could cover completely new nanomaterial emission paths and release volumes that could considerably change the environmental exposure of such nanosized zinc.

Summary

- The model for nano-ZnO shows no significant load or concentrations in waters or in soils.
- Most of the target nano-ZnO is transformed into other non-nanoparticle forms during sewage treatment processes. The investigated nano-ZnO mostly converts to sulfides during these treatments.
- The fresh water and marine water concentrations are mostly in pg/l to some ngl/l concentrations; the latter ones are by a factor of 10 times smaller and completely in pg/l levels.
- The air results show marginal concentrations as in the case of the previous TiO_2-based studies in some pg/m^3 ranges. This again reflects the insignificance of air emissions and the almost complete nano-ZnO removal in waste incineration processes.
- Soils and sediments represent the final nanomaterial, however with very low quantities of nano-ZnO. For 2020, a few hundred ng/kg are expected in soils and the same amount in µg/kg in sediments, which is much lower than the expected few mg/kg for photostable nano-TiO_2.
- This report indicates a low generic environmental relevance for nano-ZnO. However, it points out that changes in future nano-ZnO applications and use volumes could lead to much higher environmental exposure to such ZnO.
- For general summary points on the assessment of Danish ENM use quantities, please see the summary box on photostable and other nano-TiO_2.

5.4 Silver (AgNP)

This chapter contains the nano-Ag mass transfer model results and predicted environmental concentrations. We present the modelled concentrations for sewage treatment sludge, waste mass and its residues bottom ash and fly ash, surface waters (fresh water, sea water), sewage treatment effluents, air, soils (agricultural, natural, urban and sludge-treated soils) and sediments (fresh water and sea water sediments).

All PECs are summarized in Table 5.7 and fully shown by means of probability density functions in Annex II.

5.4.1 Material flows and environmental release

Mass flows
The flow chart system in Figure 5.10 considerably differs from all others shown in the chapters proceeding this report. Everywhere in the system, we observe much smaller mass data, which can be interpreted as indicating almost no nanosilver being used on a large commercial scale. Based on such small amounts, it is difficult to make out the most dominant mass transfers in this system. There is no doubt that approx. one-fourth (0.2 tonnes modal value) ends up in STP treatment where most (85%-100%) of the nano-Ag was shown to be transformed into silver sulphide Ag_2S (Kaegi et al., 2011). Thus, at most, 15% of the initial nano-Ag entering into STP via wastewater survives the sewage treatment process.

About twice as much (modal value) enters into recycling processes and is lost in our model, since we do not have any data that would allow modelling the fate and behaviour of this context. The remaining quarter is covered by diffusive direct release from the PMC compartment into different directions (aquatic, air, landfills and soils).

Additionally, in the PMC box, we see that dissolution processes in contact with liquids during the use phase leads to some nanomaterial elimination at the beginning of the product life cycles. Such dissolution upon contact with water during the use phase was modelled as material elimination, as indicated elsewhere (Sun et al., 2014). This dissolution may occur in the product use categories of textiles, cleaning agents, paints and cosmetics. Again, Annex I of this report provides detailed information regarding all parameters used on such categories, among all other model input parameters.

The input mass flows into incineration and potential outflows are far below one t per year, which makes it difficult to evaluate these numbers beyond saying that such mass transfer is modelled at insignificant, low levels. The same applies for all environmental release mass transport into the terrestrial and aquatic environments.

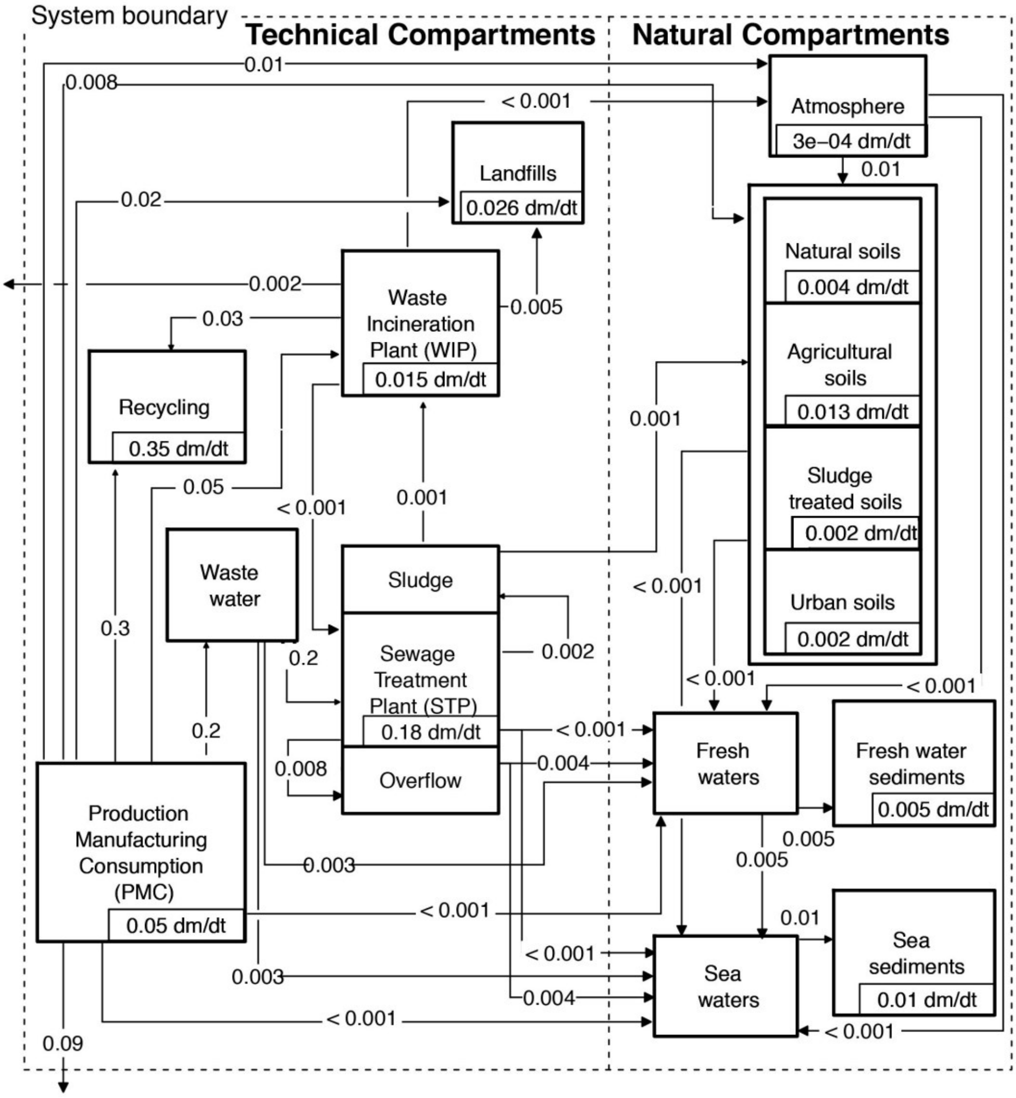

FIGURE 5.10.
MASS FLOW SYSTEM OF ENGINEERED NANOMATERIAL SILVER WITH ROUNDED MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) IN T/A. BOXES SHOW ACCUMULATION OR TRANSFORMATION MASS. THESE MODES, EXTRACTED FROM THE MONTE CARLO SIMULATIONS, REPRESENT HIGH PROBABILITY RESULTS AT DIFFERENT STAGES OF THE MODEL WITHOUT PRECISELY ILLUSTRATING HOLISTIC MASS-BALANCE IN THE FIGURE.

ENM sources of environmental release and its recipients

Despite the small values seen above for almost all nano-Ag mass-transport pathways, the relative evaluation of the origin and destination of such material may be of importance; such an evaluation is independent of the total nanomaterial volume transferred in a particular system. This evaluation may also be consulted later for future larger-use volumes of nanosilver application. Figure 5.11 provides an overview of the environmental release percentages of nano-Ag compared to those of the primary natural recipients (natural compartments) of such silver. Accordingly, three-quarters come from the PMC compartment, including nanomaterial production, manufacturing and consumption. For Denmark, we could not identify any nanoproduct manufacturing processes; therefore, such release comes entirely from the use of nanoproducts that could be allocated to textiles, cleaning agents, paints, cosmetics and consumer electronics, among others. The remaining quarter of nanosilver passes the STP treatment mostly via STP overflow. Besides untreated wastewater, such overflows are the most important sources of nanosilver in the aquatic environment. The latter represents the greater part of the fraction coming directly from the PMC compartment. The nearly equal and complete distribution among natural nanosilver soils and waters shows that there are also some product categories directly discharging some nanosilver release into soils (in addition to STP sludge fertilization). This phenomenon may occur via paints degradation or air transport, for example, and compose about 3% of the total use fraction.

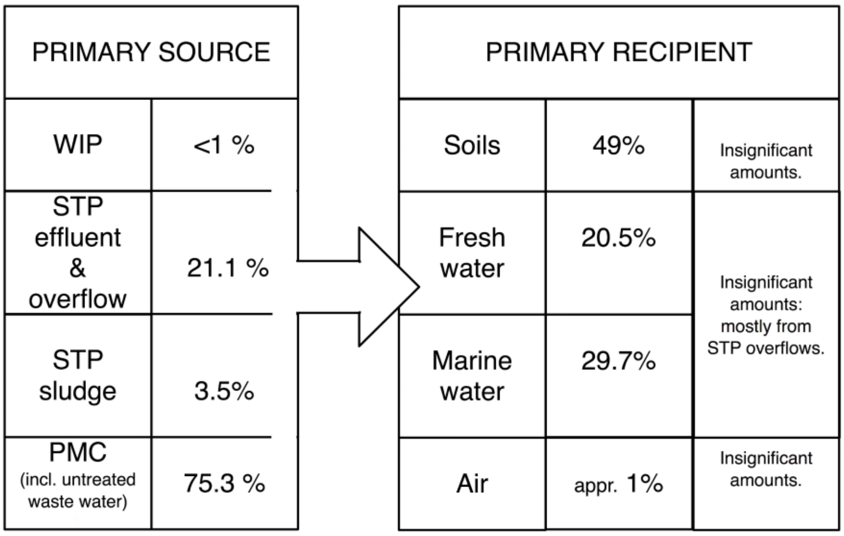

FIGURE 5.11.
OVERVIEW OF THE MOST IMPORTANT NANO-Ag SOURCES AND RECEIVERS. THE PERCENTAGES REFLECT MODAL RESULTS (THE MOST FREQUENTLY MODELLED VALUES).

5.4.2 Exposure concentrations in technical compartments

The concentrations predicted for STP effluents are (modal value) around 0.5 ng/l (Table 5.7). This figure is about 25,000 times lower than the ones for photostable nano-TiO_2. In addition to the much lower use and release quantities, it also shows that most of the silver is kept back in the sewage treatment process and transformed during the anaerobic phase into sulphide (Kaegi et al., 2011). Hence, in the nano-Ag study, the STP overflow is much more prominent as a nanomaterial source than the STP effluent itself. As a result of the same sulfidation and material transformation (and of the much lower use volumes), the STP sludge concentrations with approx. 80 µg/kg sludge are again about more than 10,000 times lower than the photostable nano-TiO_2 results. A similar picture can be drawn for the waste mass and waste residues (ashes). In contrast to mg/kg concentrations modelled for nano-TiO_2 and nano-ZnO materials, the concentrations of nano-Ag are all in a µg/kg level (15 and 170 µg/kg range, waste mass and fly ash of waste incineration). These results confirm the low nanosilver mass flows into waste management processes (Figure 5.10), as documented by previous research (Sun et al., 2014).

TABLE 5.7.

PREDICTED ENVIRONMENTAL CONCENTRATIONS (PEC) FOR NANO-Ag IN DIFFERENT TECHNICAL AND NATURAL COMPARTMENTS, AS MODELLED FROM COMPUTER-BASED STOCHASTIC SIMULATIONS ON NANO-Ag RELEASE TO, AND SCENARIOS FOR, FATE/RESIDENCE TIME IN THOSE COMPARTMENTS. THE RESULTS ARE SHOWN AS MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) AND AS LOWER AND UPPER LIMITS CONSIDERED BY 95% RANGES THAT ALSO ILLUSTRATE A 95% PROBABILITY OF THE PECS PRODUCED FALLING WITHIN THEM. FOR SOILS AND SEDIMENTS, AN ANNUAL INCREASE OF PECS IS GIVEN.

Compartments (sources)	**Concentrations**				
	Unit	Mode *median	95% range		
Technical compartments					
Sewage treatment effluent	ng/l	0.5	0.012	-	58.6
Sewage treatment sludge*	µg/kg	82.1	4.2	-	254.2
Waste mass incinerated	µg/kg	15.3	10.1	-	23.4
Bottom ash of waste incineration	µg/kg	34.9	20.9	-	65.7
Fly ash of waste incineration	µg/kg	174.0	103.2	-	326.6
Natural compartments					
Surface water (fresh water)*	ng/l	0.015	≈0	-	0.044
Sea water	ng/l	2.5E-04	≈0	-	5.8E-04
Sediments (fresh water)*	µg/kg	0.8	≈0	-	2.4
Sediments (sea water)	µg/kg	0.046	≈0	-	0.1
Agricultural soils	ng/kg	1.6	0.9	-	3.2
Natural soils	ng/kg	3.7	2.0	-	9.3
Urban soils	ng/kg	6.1	3.5	-	12.5
Sludge treated soils*	ng/kg	25.7	3.0	-	81.6
Air	ng/m3	0.007	0.004	-	0.011

*inconclusive, bipolar (or pluripolar) results or insignifact difference between mode and median

5.4.3 Exposure concentrations in natural compartments

In the nanosilver study it is noteworthy that, for example, a large number of the fresh water PECs are practically zero, as provided by the Monte Carlo-based computer simulations (Figure 5.12). These very small values are only rudimentarily recognized by the graphical resolution needed to show the whole spectrum of fresh water concentrations in Figure 5.12 A. Almost all modelled values with high densities (probabilities) lie between zero and 30 pg/l. The model excludes PECs above 60 pg/l when based on the current estimated nanosilver use quantities. Figure 5.12 b shows the marine results that have a much thinner spectrum, completely at pg/l and lower levels. In this case, the almost zero values are recognized in detail by the graphical resolution that shows a much thinner spectrum of concentrations than the one in Figure 5.12 A. Thus, this figure also shows, in detail, the densities (probabilities) of the almost zero concentrations.

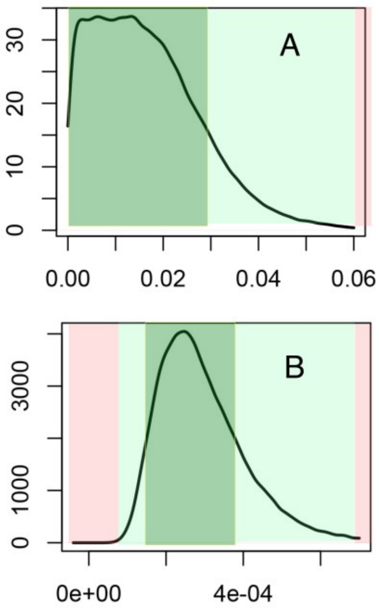

FIGURE 5.12.
PROBABILITY DENSITY CURVE OF THE PREDICTED ENVIRONMENTAL CONCENTRATIONS (PEC) IN NG/L (X-AXIS) OF NANO-Ag IN SURFACE WATERS (A: FRESH WATER, B: MARINE WATER). CURVE INTERPRETATION, GREEN: TOTAL SPECTRUM OF PEC VALUES; DARK GREEN: RANGE OF MOST FREQUENTLY MODELLED PECS (AT LEAST HALF AS OFTEN AS THE MOST FREQUENTLY MODELLED VALUE); RED: NOT MODELLED/EXPECTED VALUES FOR PECS.

From such results, we learn that the contribution of nano-Ag to the total silver contamination in Danish surface water is marginally low at current use and release amounts. Consequently, the same low contribution to the total silver contamination can also be seen for PECs in all sediments where we will have only a few µg/kg sediment of nano-Ag, even in 2020 (Table 5.8). This trend is seen for fresh water sediments and is about 20 times less than what has been predicted for photostable nano-TiO_2.

Regarding the soil concentrations, we may state that those for non-fertilized soils are in a similar range as the nano-ZnO ones and show annual concentration increases of a few ng/kg soil. Such increases in sludge-treated soils are a bit higher, with modal values around 25 ng/kg soil. The annual augmentations will lead to a maximum environmental concentration of about 1 µg/kg soil (in worst case MC scenarios) in sewage-sludge fertilized areas in 2020. All of these results follow very similar magnitudes to earlier findings presented for European contexts (Sun et al., 2014).

TABLE 5.8.

PREDICTED ENVIRONMENTAL CONCENTRATIONS (PEC) FOR NANO-Ag IN SEDIMENTS AND SOILS MODELLED FROM COMPUTER-BASED STOCHASTIC SIMULATIONS ON NANO-Ag RELEASE TO THOSE COMPARTMENTS. THE PREDICTIONS ARE SHOWN AS MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) AND AS LOWER AND UPPER LIMITS CONSIDERED BY 95% RANGES THAT ILLUSTRATE A 95% PROBABILITY OF THE MODELLED PECS FALLING WITHIN THIS RANGE. THE PEC VALUES REFLECT NANO-TIO_2 CONCENTRATIONS AFTER BEING DEPOSITED IN SEDIMENTS AND SOILS UNTIL THE BEGINNING OF THE YEARS 2014 AND 2020. ALL THE CURVES ARE SHOWN IN ANNEX II OF THIS REPORT.

Compartments	**Concentrations**		
	Unit	Mode *median	95% range
Prediction for 2014			
Sediments (fresh water)*	µg/kg	5.4	≈0 - 15.9
Sediments (sea water)	µg/kg	0.3	≈0 - 0.7
Agricultural soils	ng/kg	10.3	5.9 - 20.9
Natural soils	ng/kg	23.9	13.0 - 60.6
Urban soils	ng/kg	39.9	22.9 - 81.0
Sludge treated soils*	ng/kg	167.3	19.5 - 530.3
Prediction for 2020			
Sediments (fresh water)*	µg/kg	11.4	≈0 - 33.2
Sediments (sea water)	µg/kg	0.6	≈0 - 1.5
Agricultural soils	ng/kg	21.4	12.3 - 43.6
Natural soils	ng/kg	49.8	27.1 - 126.6
Urban soils	ng/kg	83.2	47.7 - 169.1
Sludge treated soils*	ng/kg	349.4	40.8 - 1107

*inconclusive, bipolar (or pluripolar) results or insignifact difference between mode and median

5.4.4 Discussion and conclusions

A combination of the relatively low use volumes of nano-Ag and the efficient removal of such nanosized metals during the sewage treatment process (as well as the removal in waste incineration as is the case for most nanomaterials) leads to consistently low release quantities of such silver into the natural environment. The current amount of nano-Ag in products and its release from such use appears marginal. Meanwhile, the aforementioned STP process transforms potentially toxic nano-Ag into less toxic silver sulfide compounds. Nevertheless, and as emphasized elsewhere (Nowack, 2010), for the aquatic exposure context, we cannot exclude the possibility that future surface modifications and new coatings will make engineered nanosilver more mobile and resistant to Ag_2S formation. Also, a transformation back into other silver forms may also be possible (Nowack, 2010). Finally, we should also keep in mind that, though the silver release and exposure in nanoform is currently small, it still contributes to the total silver release and exposure in the water and soil environments. Knowing the general toxicity of silver, the risk assessment should focus on the general silver concentrations in such compartments, which may be a few magnitudes higher than the ones for the corresponding engineered nanoparticles (Sun et al., 2014).

Summary

- The modelled nano-Ag annual use volumes are almost all below one tonne. Such low amounts probably do not stand for large-scale commercialization of such nanomaterial.

- The model for nano-Ag shows a low annual load that does not exceed the tonnes-per-year level for waters or for soils.

- During sewage treatment, most of the target nano-Ag is converted into silver sulfide (Ag_2S), a much less toxic compound.

- All modelled nano-Ag fresh water and marine water concentrations are in pg/l concentration levels, if not almost zero.

- The terrestrial concentrations modelled were even lower than the ones for nano-ZnO, which is also transformed into other non- nanoparticle forms during sewage treatment processes.

- Although the aquatic concentrations are marginal, they contribute to the total silver exposure concentrations in waters and soils, which are a few magnitudes higher.

- As seen for all other nanometals investigated in the previous chapters, the modelled air concentrations confirm marginal concentrations in some pg/m^3 ranges, insignificant air emissions and the almost complete removal of such substances in the waste incineration processes.

- This report indicates a low general environmental relevancy for nano-Ag. However, it points out the possibility of new types of nano-Ag surface modifications and higher use volumes that could change the environmental exposure situation in the future.

- For general summary points on the assessment of Danish ENM use quantities, please see the summary box on photostable and other nano-TiO_2.

5.5 Carbon nanotubes (CNT)

In this chapter, we provide this report's first results for carbon-based (non-metallic) nanomaterials: carbon nanotubes (CNT). We again show the mass transport and modelled concentrations for sewage treatment sludge, waste mass and its residues bottom ash and fly ash, surface waters (fresh water, sea water), sewage treatment effluents, air, soils (agricultural, natural, urban and sludge-treated soils) and sediments (fresh water and sea water sediments).

Table 5.9 summarizes all PECs, and Annex II illustrates them fully by means of probability density functions.

5.5.1 Material flows and environmental release

As depicted in Figure 5.13, the carbon nanotube flows, including accumulation or transformation, show that this carbon nanomaterial reveals a strong tendency towards mass movement into non-aquatic areas, including waste incineration, recycling plants and landfills. This tendency directly reflects the nanomaterial's use mostly in products and applications that do not lead to significant nanomaterial discharge to aquatic areas. More than 90% (modal values) of the target CNT is used in polymer composites, consumer electronics and the energy sector with no affinity for material release into surface water. The uses (e.g., paints, textiles) that would lead to some aquatic relevancy compose 10% of total CNT use, at most. Another point that attracts attention is the total modal mass transfer, which probably does not exceed 10 tonnes (modal values) annually. This point again supports the impression that large-scale commercialization can be excluded for such CNT, as we could also assume for nanosilver.

There is no Danish information available for current domestic nanomaterial production processes, including CNT product manufacturing. Roughly speaking, less than 5% of the CNT transported in the target Danish system finds its way into natural environments. Via nanoproducts, almost half of the CNT mass goes into recycling treatment where we stop our model due to a lack of knowledge regarding the fate and behaviour of ENM in such processes; approximately one-thirds go into the waste incineration process where it is mostly eliminated. The remaining small release portion (approx. 5%) may be attributed to diffusive mass transport into soils and surface waters, mostly directly from nanoproduct use (see also Figure 5.14). This process mainly occurs through product alteration as well as the wear and tear processes of polymer composites, paints and textiles, among others. However, these diffusive release values are so small that most of them are below a t/year level. These findings align with mass transfer studies on the continental level (Sun et al., 2014). However, in this case, it should be particularly noted that we have to be careful in evaluating the initial model because the use amounts reflect applications more in a research and development context than in a large-scale commercialization arena. New developments for the target material, its products and product manufacturing processes—or a reduction in the costs of such processes and developments—could lead to much larger use and environmental release volumes, necessitating a new release and exposure assessment.

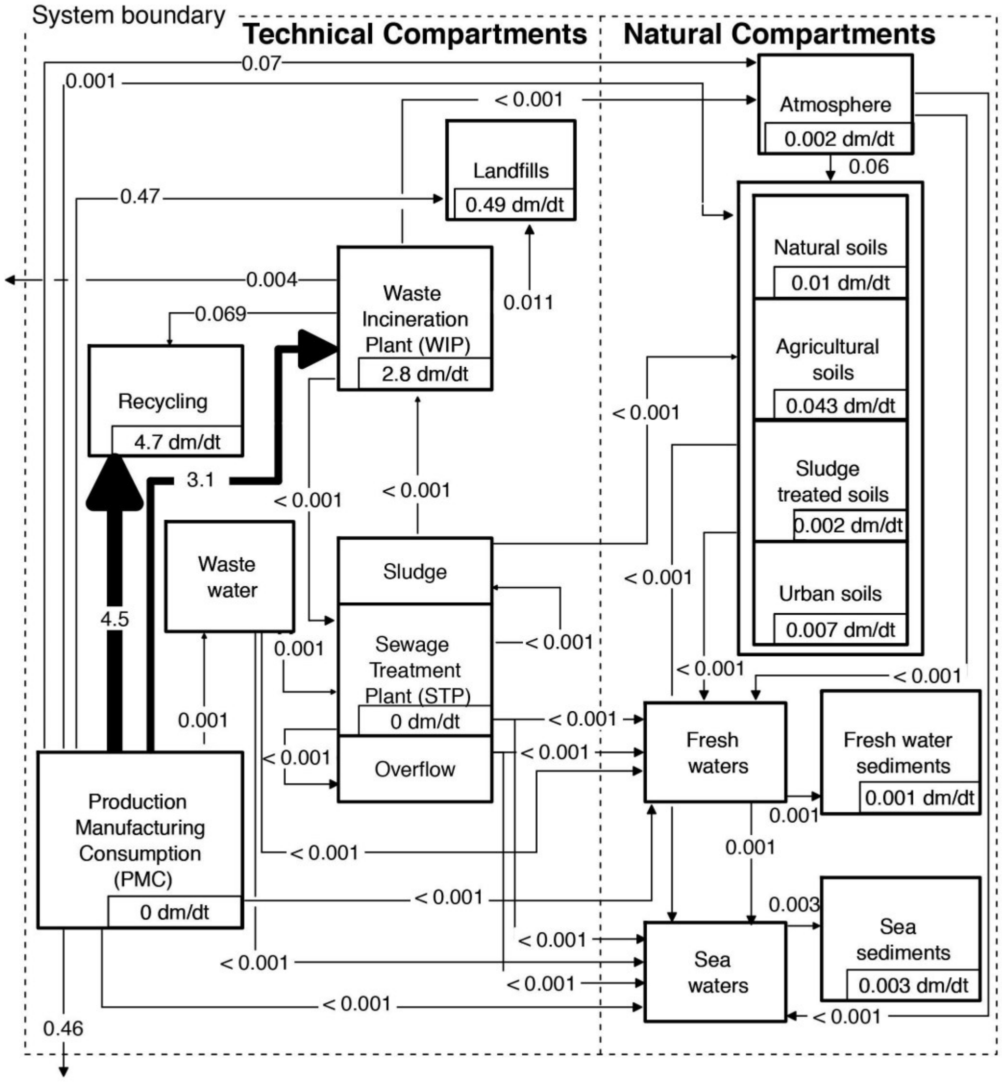

FIGURE 5.13.
MASS FLOW SYSTEM OF CNT WITH ROUNDED MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) IN T/A. BOXES SHOW ACCUMULATION OR TRANSFORMATION MASS. THESE MODES, EXTRACTED FROM THE MONTE CARLO SIMULATIONS, REPRESENT HIGH PROBABILITY RESULTS AT DIFFERENT STAGES OF THE MODEL WITHOUT PRECISELY ILLUSTRATING HOLISTIC MASS-BALANCE IN THE FIGURE.

ENM sources of environmental release and its recipients

As noted, only a marginal portion of in-use CNT finds its way into nature (approx. 5%). This 5% environmental release almost exclusively occurs from direct nanoproduct use (99%), as shown in Figure 5.14. This small material fraction reflects diffusive mass transport mostly into soils (approx. 90% based on the computations of modal values). The rest is equally distributed to fresh and marine waters and air. This release mainly occurs via product alteration (polymer composites, paints, textiles) as well as wear and tear processes that lead to some small emissions into air following dry or wet deposition from the air into the ground and water. However, as stated above, the single release values are so small that it is difficult to provide a single detailed value evaluation. We limit ourselves to giving this general presentation of the environmental release situation. Nevertheless, a full overview on all use product categories is given in Annex I of this report.

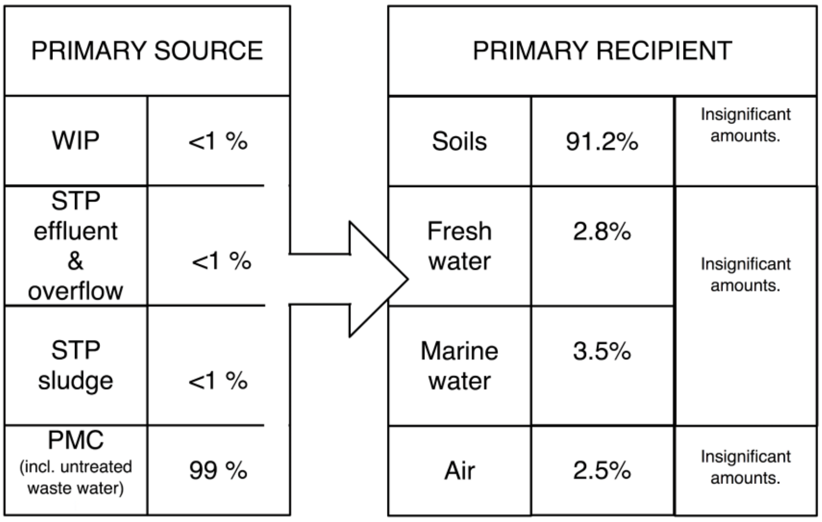

FIGURE 5.14.
OVERVIEW OF THE MOST IMPORTANT CNT SOURCES AND RECEIVERS. THE PERCENTAGES REFLECT MODAL RESULTS (THE MOST FREQUENTLY MODELLED VALUES).

5.5.2 Exposure concentrations in technical compartments

The predicted concentration (Table 5.9) in Danish waste mass and the ash based residues from the waste incineration process show concentrations that may reach for some Monte Carlo scenarios mg/kg dimensions. This is fully in line with results recently modelled for Europe (Sun et al., 2014). Nevertheless, since we could base our model on a smaller geographical system with access to specific Danish data (around precise annual waste volumes), the results presented here could be interpreted as an improvement of the values in the previously-mentioned reference work. The same improvement may be seen for PECs in the other main technical compartment (STP effluent), where we could use more specific data in the Danish context compared to European average values on the STP infrastructure, such as the STP connection rate of households and wastewater production per head. Based on our predictions, the STP effluents contain a few tenths ng/l CNT, which fully aligns with the magnitudes reported in the above-mentioned study, which indicates values that are approx. a factor of 10 times higher. At most, such ng/l values may compare to the low exposure concentrations of nanosilver; they are much lower than those µg/l levels of other metallic nanoparticles studied in this report so far. This finding confirms that the low exposure for CNT already has occurred at the beginning of the dilution when it passes from the STP effluent into the natural water system. Thus, the subsequent concentrations in natural water are again much lower, and in the case of CNTs, completely in pg/l dimensions (as reported below). For marine water, the computer model also partially produced some f[8]g/l values.

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[8] 1fg= 10^{-15} g

TABLE 5.9.

PREDICTED ENVIRONMENTAL CONCENTRATIONS (PEC) FOR CNT IN DIFFERENT TECHNICAL AND NATURAL COMPARTMENTS, AS MODELLED FROM COMPUTER-BASED STOCHASTIC SIMULATIONS ON CNT RELEASE TO, AND SCENARIOS FOR, FATE/RESIDENCE TIME IN THOSE COMPARTMENTS. THE RESULTS ARE SHOWN AS MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) AND AS LOWER AND UPPER LIMITS CONSIDERED BY 95% RANGES THAT ALSO ILLUSTRATE A 95% PROBABILITY OF THE PECS PRODUCED FALLING WITHIN THEM. FOR SOILS AND SEDIMENTS, AN ANNUAL INCREASE OF PECS IS GIVEN.

Compartments (sources)	**Concentrations**		
	Unit	Mode	95% range
Technical compartments			
Sewage treatment effluent	ng/l	0.3	0.1 - 3.5
Sewage treatment sludge	µg/kg	7.6	2.7 - 61.6
Waste mass incinerated	µg/kg	802	435.9 - 1317
Bottom ash of waste incineration	µg/kg	75.7	26.5 - 710.9
Fly ash of waste incineration	µg/kg	325.6	87.9 - 4774
Natural compartments			
Surface water (fresh water)	ng/l	0.001	1.8E-04 - 0.015
Sea water	ng/l	4.9E-05	2.2E-05 - 2.0E-04
Sediments (fresh water)	µg/kg	0.1	0.011 - 0.9
Sediments (sea water)	µg/kg	0.009	0.004 - 0.038
Agricultural soils	ng/kg	5.3	2.8 - 11.5
Natural soils	ng/kg	12.7	6.3 - 33.1
Urban soils	ng/kg	20.6	11.0 - 44.8
Sludge treated soils	ng/kg	9.2	4.6 - 27.4
Air	ng/m3	0.042	0.022 - 0.091

5.5.3 Exposure concentrations in natural compartments

Not surprisingly, 95% of CNT ends up in technical compartments (see also Figure 5.13). The predicted concentrations in technical receiver media (waste mass and other waste management residues, such as fly and bottom ash) are much higher than the ones in natural compartments. Such comparison only works if we simply compare mass units with mass units and ignore the fact that we are dealing with quite different media types. Therefore, we may generalize that all the PECs for natural waters are reported in mass units (pg/l or fg/l) usually not applied to other substances in aquatic compartments or to CNT itself (in this study) for concentrations in the technical compartments. Thus, as noted, CNT concentrations in natural waters are completely in pg/l dimensions (fresh water); for marine water, the model also produced some fg/l values. This finding is only roughly in line with earlier models (Sun et al., 2014) that show PECs (modal values) approx.

200 times higher for fresh water. Such differences may be explained by the high Danish water volume, which leads to a much higher dilution effect; another contributing factor could be the general model input knowledge, which has improved compared to the one of a few years ago. This data quality difference particularly applies to the highly influential parameters around the STP infrastructure mentioned above. The marine water results are approx. a factor of 10 lower. Again, such a factor first reflects aggregation and sedimentation in freshwater, which continues in the marine compartment; second, it indicates a greater sea water volume (compared to fresh water) that automatically leads to higher dilution.

The sediment (fresh and marine water) PECs are very low; in dimensions modelled for nanosilver, they also display very low exposure concentrations in the aquatic environment. Even by 2020, we do not expect much more than a few µg/kg of fresh water sediment concentrations. Those for marine sediments will remain in a ng/kg range until 2020 (Table 5.10) based on current CNT use amounts.

The soil results for 2020 show a few hundred ng/kg soil for urban areas at the most. The results for natural and agricultural areas are a bit lower due to varying soil depths and the subsequent varying volumes for potential soil contamination. The STP sludge-based soil fertilization has negligible importance in this case, since almost no CNT ends up in such sludge.

TABLE 5.10.

PREDICTED ENVIRONMENTAL CONCENTRATIONS (PEC) FOR CNT IN SEDIMENTS AND SOILS MODELLED FROM COMPUTER-BASED STOCHASTIC SIMULATIONS ON CNT RELEASE TO THOSE COMPARTMENTS. THE PREDICTIONS ARE SHOWN AS MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) AND AS LOWER AND UPPER LIMITS CONSIDERED BY 95% RANGES THAT ILLUSTRATE A 95% PROBABILITY OF THE MODELLED PECS FALLING WITHIN THIS RANGE. THE PEC VALUES REFLECT NANO-TIO$_2$ CONCENTRATIONS AFTER BEING DEPOSITED IN SEDIMENTS AND SOILS UNTIL THE BEGINNING OF THE YEARS 2014 AND 2020. ALL THE CURVES ARE SHOWN IN ANNEX II OF THIS REPORT.

Compartments	**Concentrations**		
	Unit	Mode	95% range
Prediction for 2014			
Sediments (fresh water)	µg/kg	0.5	0.1 - 5.6
Sediments (sea water)	µg/kg	0.1	0.0 - 0.2
Agricultural soils	ng/kg	34.5	18.3 - 75.1
Natural soils	ng/kg	82.5	41.0 - 215.1
Urban soils	ng/kg	133.8	71.2 - 291.2
Sludge treated soils	ng/kg	59.8	30.1 - 177.9
Prediction for 2020			
Sediments (fresh water)	µg/kg	1.0	0.1 - 11.6
Sediments (sea water)	µg/kg	0.1	0.1 - 0.5
Agricultural soils	ng/kg	72.0	38.3 - 156.7
Natural soils	ng/kg	172.3	85.5 - 449.1
Urban soils	ng/kg	279.3	148.6 - 608.0
Sludge treated soils	ng/kg	124.8	62.9 - 371.5

5.5.4 Discussion and conclusions

Low CNT use volumes (a few tonnes annually) and a high mass fraction (up to 90-95%) results in a kind of one-way transport subsystem into recycling, waste incineration and landfilling processes. Generally speaking, this leads to marginal environmental exposure to carbon material for aquatic and terrestrial environments.

For this nanomaterial, it can be affirmed (see similar results (Gottschalk et al., 2013a) that critical exposure scenarios for all environmental compartments can probably be excluded when considering the current use amounts. However, the CNT case has to be monitored with particular attention because we currently only model exposure that reflects nearly no commercial use, and a great deal of mass is only used for research and development of new products. The environmental release and exposure situation could completely change following a breakthrough in the research and marketing of new applications and subsequent large-scale commercialization of such products.

Summary

- The estimated CNT use volumes do not reflect large-scale commercialization of CNT-based products and applications.
- Most (approx. 95%) of CNT ends up in technical compartments, such as waste mass and waste incineration residues, recycling plants and landfills.
- The CNT in natural waters only reaches pg/l concentration levels (fresh water); in marine water, the model also produced some fg/l values.
- Until 2020, we do not expect much more than a few µg/kg of fresh water sediment concentrations; the marine concentrations are even a little lower.
- Until 2020, the concentrations in soils will not significantly augment the carbon mass already there. The STP sludge-based soil fertilized has almost no impact in that context, since almost no CNT ends up in such sludge.
- The modelled air concentrations do not differ from the ones for metals in the previous chapter, and they show some marginal concentrations in pg/m^3 levels.
- This report indicates nearly no environmental relevance for CNT. However, it points out that a breakthrough in the market is possible, which would lead to new, much higher use quantities and subsequent environmental releases.

5.6 Nano-copper carbonate

In this report, we provide, to our knowledge, the first environmental exposure study on nano-copper carbonate. We present Danish mass transfer computer simulation results as well as predicted environmental concentrations that are modelled for the compartments seen in the previous chapters: sewage treatment sludge, waste mass and its residues bottom ash and fly ash, surface waters (fresh water, sea water), sewage treatment effluents, air, soils (agricultural, natural, urban and sludge-treated soils) and sediments (fresh water and sea water sediments).

All PECs are summarized in the Tables 5.11 (and 5.12) and fully shown by means of probability density functions in Annex II of this report.

5.6.1 Material flows and environmental release

Mass flows

Figure 5.15 provides an overview of the Danish mass transfer system for nano-copper carbonate in and between the main technical and natural compartments. First, the modal values shown reveal a very low water relevancy of such ENM. The annual environmental release of nano-copper carbonate into the aquatic environment probably does not exceed 1% of the total annual nano-copper carbonate mass transfer volume. A very large portion (approx. 70%) of the annual nano-copper carbonate mass ends up in technical treatment processes for nanomaterial-containing products, such as recycling, waste incineration and landfilling.

We anticipated that the nano-copper carbonate impregnated wood would mostly be disposed of by landfill due to regulatory aims and pressure. The remaining portion, almost 30%, will end up in soils, mostly as a consequence of altering and weathering processes of nano-copper carbonate-treated wood outdoor surfaces, including underground surfaces. Such discharge occurs throughout the entire life cycle of impregnated wood. Nevertheless, the model uses such release estimations in its annual mass balance, and in this way, also covers the highest possible release spectrum into soils. Most of such release is assumed to occur directly from wood below ground; the rest occurs via air transport and deposition on the ground.

Due to the marginal discharge of nano-copper carbonate into the sewage treatment processes, STP sludge fertilization plays almost no role in the total soil discharge of copper in this context. Approximately 1% of this soil exposure comes from this fertilizer (see also Figure 5.16).

Regarding the release during wood pressure impregnation in Denmark, the model assumes that impregnation takes place in closed systems without any losses (less than 1%) of the material to its surroundings, with subsequent discharge to waste water. Such (small) releases could be caused by leakages in the collection systems or by working clothes washing or from cleaning of filters.

As seen for all studied metals in this report, in the WIP model, almost no emissions from such plants occur, aligning with other research (Walser et al., 2012b). A large part of the target nano-copper ends up in the fly ash and slag and is captured by the recycling processes of these recipients. However, due to distinct analytic limitations for a certain volume (2 t/a) of copper-carbonate, its fate in such plants remains to be researched. For such amounts, a distinction between internal (WIP) deposition or elimination/transformation is not possible, as seen in detail for other metals (nano-CeO2) (Walser and Gottschalk, 2014). However, thus far this distinction has not been crucial because the model of WIP emissions displays almost zero emissions into the air for all possible MC scenarios.

In summary, risk research for nano-copper carbonate should focus on the nanomaterial fate in soils, landfills and recycling processes, including its primary use for wood treatment. The mass transfer chart shown may, however, significantly change as new types of copper nanomaterial emerge; this has to be expressed explicitly in such a single application situation.

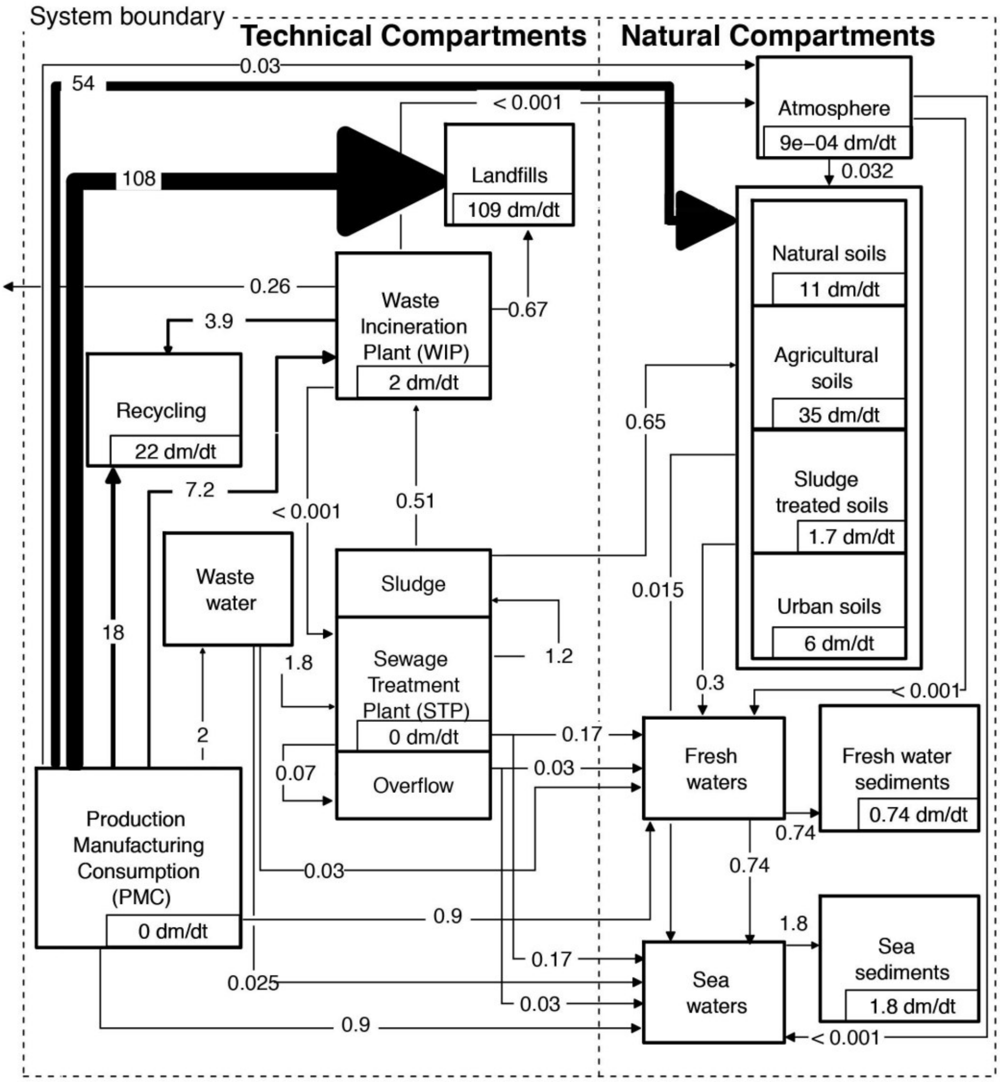

FIGURE 5.15.
MASS FLOW SYSTEM OF NANO-COPPER CARBONATE WITH ROUNDED MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) IN T/A. BOXES SHOW ACCUMULATION OR TRANSFORMATION MASS. THESE MODES, EXTRACTED FROM THE MONTE CARLO SIMULATIONS, REPRESENT HIGH PROBABILITY RESULTS AT DIFFERENT STAGES OF THE MODEL WITHOUT PRECISELY ILLUSTRATING HOLISTIC MASS-BALANCE IN THE FIGURE.

ENM sources of environmental release and its recipients
Figure 5.16 presents a relative overview that summarizes the total environmental release of copper carbonate nanomaterial into the natural environment. Relative means that it fractionates the environmental release amounts, only representing a segment of the total mass transfer volume seen during a one-year period in Denmark. Thus, in the copper case, such environmental release-based mass transfer covers approx. 30 % of the total mass mentioned. This 30% is allocated to the primary sources. What we see from the comparison of the most prominent ENM release sources and their primary recipients is that, in the nano-copper carbonate case, the release into the environment occurs almost exclusively via the PMC (approx. 98%). This confirms the finding that use for impregnating wood surfaces does not lead to significant ENM discharge via waste water treatment or waste incineration. Because the water treatment receives almost no nano-copper carbonate, the waste incineration plants do not emit that kind of copper at all.

These findings are confirmed on the other side of the overview by very small percentage amounts for surface waters and air as primary ENM recipients. The rest (above 90%, modal value) will remain in underground wood use or be deposited into soils. Such soil release occurs during the whole lifecycle (approx. 30 years) of impregnated wood. The model, however, treats such release as an annual one for mass balance percentages by covering the highest possible release spectrum for soils. The needed data – precise market penetration amounts/developments and the starting point of such nano-copper carbonate applications – for a higher model resolution based on time-based dynamics are currently unavailable.

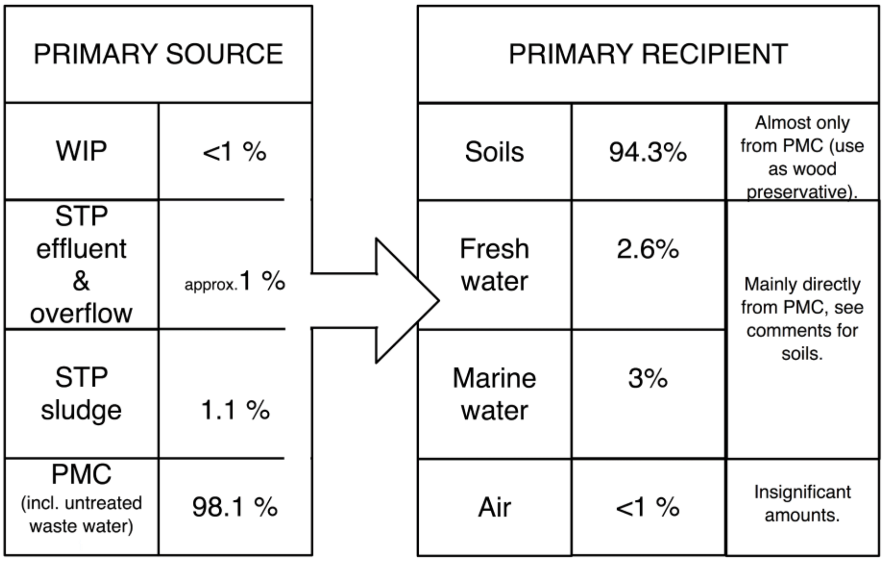

FIGURE 5.16.
OVERVIEW OF THE MOST IMPORTANT NANO-COPPER CARBONATE SOURCES AND RECEIVERS. THE PERCENTAGES REFLECT MODAL RESULTS (THE MOST FREQUENTLY MODELLED VALUES).

5.6.2 Exposure concentrations in technical compartments

The nano-copper concentrations (Table 5.11) in STP effluents and sludge as well as in waste mass and waste incineration residues (bottom and fly ash) are in similar order of magnitude as the ones in the nano-TiO_2 case studies (photocatalytic TiO_2). The STP effluent shows roughly 1.3 µg/l modal concentrations and 10 mg/kg in STP sludge (1.6 µg/l and 85 mg/kg for photocatalytic nano-TiO_2). This figure means that, for example, the copper nanomaterial STP effluent concentrations are more than 2000 times higher than those of nanosilver. However, this applies more for extremely small amounts of nanosilver reaching the aquatic environment than for high nano copper-carbonate. It should be stressed that the annual modal contribution (release into surface waters) of nano-copper carbonate to the generic copper amounts in surface water is about 2.5 tonnes annually.

As also modelled for photocatalytic nano-TiO_2, the modal values range from a few mg/kg to more than 20 mg/kg (fly ash) in all three ENM receiving waste materials. This finding again indicates that such nanosized copper-based concentrations are roughly spoken a factor 100 times higher than those of silver metal nanomaterial, for example.

TABLE 5.11.

PREDICTED ENVIRONMENTAL CONCENTRATIONS (PEC) FOR NANO-COPPER CARBONATE IN DIFFERENT TECHNICAL AND NATURAL COMPARTMENTS, AS MODELLED FROM COMPUTER-BASED STOCHASTIC SIMULATIONS ON NANO-COPPER CARBONATE RELEASE TO, AND SCENARIOS FOR, FATE/RESIDENCE TIME IN THOSE COMPARTMENTS. THE RESULTS ARE SHOWN AS MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) AND AS LOWER AND UPPER LIMITS CONSIDERED BY 95% RANGES THAT ALSO ILLUSTRATE A 95% PROBABILITY OF THE PECS PRODUCED FALLING WITHIN THEM. FOR SOILS AND SEDIMENTS, AN ANNUAL INCREASE OF PECS IS GIVEN.

Compartments (sources)	**Concentrations**		
	Unit	Mode *median	95% range
Technical compartments			
Sewage treatment effluent	µg/l	1.3	0.3 - 4.1
Sewage treatment sludge	mg/kg	9.1	5.2 - 17.2
Waste mass incinerated	mg/kg	2.0	1.3 - 3.0
Bottom ash of waste incineration	mg/kg	4.4	2.7 - 8.5
Fly ash of waste incineration	mg/kg	22.1	13.2 - 42.3
Natural compartments			
Surface water (fresh water)*	µg/l	0.002	1.2E-04 - 0.006
Sea water	µg/l	3.5E-05	2.0E-05 - 6.8E-05
Sediments (fresh water)*	µg/kg	135.9	6.7 - 321.7
Sediments (sea water)	µg/kg	6.5	3.8 - 12.8
Agricultural soils	µg/kg	4.4	2.8 - 6.3
Natural soils	µg/kg	9.3	5.9 - 19.4
Urban soils	µg/kg	17.0	10.8 - 24.4
Sludge treated soils	µg/kg	7.4	5.0 - 10.7
Air	µg/m3	2.1E-05	4.6E-06 - 3.9E-05

*inconclusive, bipolar (or pluripolar) results or insignifact difference between mode and median

5.6.3 Exposure concentrations in natural compartments

Here, we present, to our knowledge, the first PEC values for nano-copper carbonate in all main environmental compartments. Most of the 100,000 Monte Carlo computer model scenarios for fresh water concentration come to values of a few ng/l. As demonstrated in Figure 5.12 A for another case (silver nanomaterial), the model predicts almost zero results for numerous scenarios (that means with some probability; see chapter 4 for a detailed discussion of almost zero results). The same applies for the marine water concentrations where concentrations of pg/l water are predicted at most. Annex II provides detailed probability distributions.

The annual increase in freshwater sediment concentrations composes about 140 µg/kg sediment; for marine water sediments, it is about 7 µg/kg. Modelled for 2014 and proportionally scaled back to an initial use of such material in 2000 and forecasted to 2020, such annual increases would lead to PEC values of around 2 mg/kg and 0.1 mg/kg for fresh water and marine water sediments. These amounts are in similar magnitudes as those for the photocatalytic nano-TiO_2 study, and again, much higher (100-200 times) than the nanosilver ones.

For soils, we see a double-edged sword. On the one side, the non-STP sludge fertilized soil types show the highest concentrations of all nanomaterials presented so far. In 2020, we may expect copper carbonate figures ranging from 60 to 230 µg/kg, roughly speaking 300 times (modal values) larger those for high-use nanomaterial photostables and other nano-TiO_2. On the other hand, the pure STP sludge-treated results do not show any significant differences when compared to agricultural soils not-fertilized with such sludge. For their part, such purely STP sludge contribution based concentrations are approx. 30 times smaller than those for the photostable titanium case. This simply confirms the very small amounts (compared to the total release into soils) of nano-copper carbonate that ends up in such soils via sludge fertilization. Finally, this finding is also in line with the small fraction of such copper ending up in the aquatic environment (see also Figures 5.15 and 5.16).

TABLE 5.12.

PREDICTED ENVIRONMENTAL CONCENTRATIONS (PEC) FOR NANO-COPPER CARBONATE IN SEDIMENTS AND SOILS MODELLED FROM COMPUTER-BASED STOCHASTIC SIMULATIONS ON NANO-COPPER CARBONATE RELEASE TO THOSE COMPARTMENTS. THE PREDICTIONS ARE SHOWN AS MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) AND AS LOWER AND UPPER LIMITS CONSIDERED BY 95% RANGES THAT ILLUSTRATE A 95% PROBABILITY OF THE MODELLED PECS FALLING WITHIN THIS RANGE. THE PEC VALUES REFLECT NANO-TIO_2 CONCENTRATIONS AFTER BEING DEPOSITED IN SEDIMENTS AND SOILS UNTIL THE BEGINNING OF THE YEARS 2014 AND 2020. ALL THE CURVES ARE SHOWN IN ANNEX II OF THIS REPORT.

Compartments	**Concentrations**		
	Unit	Mode *median	95% range
Prediction for 2014			
Sediments (fresh water)*	µg/kg	883.7	43.4 - 2091
Sediments (sea water)	µg/kg	42.2	24.6 - 83.0
Agricultural soils	µg/kg	28.4	18.1 - 40.9
Natural soils	µg/kg	60.3	38.6 - 126.1
Urban soils	µg/kg	110.2	70.2 - 158.6
Sludge treated soils	µg/kg	48.0	32.4 - 69.5
Prediction for 2020			
Sediments (fresh water)*	µg/kg	1845	90.6 - 4366
Sediments (sea water)	µg/kg	88.0	51.4 - 173.4
Agricultural soils	µg/kg	59.3	37.8 - 85.4
Natural soils	µg/kg	126.0	80.6 - 263.3
Urban soils	µg/kg	230.2	146.5 - 331.2
Sludge treated soils	µg/kg	100.2	67.6 - 145.1

*inconclusive, bipolar (or pluripolar) results or insignifact difference between mode and median

5.6.4 Discussion and conclusions

The nano-copper case shows a flow chart system that completely varies from all other studied metals. The application for wood impregnation leads to a strong dominance of the mass transfer of such nanomaterial into the waste flows (waste incineration, recycling and landfilling). Our model stops at the last two mentioned plants by assuming no nanomaterial release from these compartments. Thus, it is assumed that no water will percolate through these waste masses in such plants to leach out the nanosized constituents. By Danish standards for infrastructure, such assumptions seem realistic. Scientific evidence on these questions is lacking (Mueller et al., 2013). However, release from waste incineration is minimal, as seen before for other nanomaterials.

Future research should focus on the fate of the copper carbonate in soils. Soil concentrations of up to a few hundred µg/kg cannot be excluded for 2020. The model used assumes no nano-copper carbonate transformation in such soils. Thus, the results presented depict a conservative exposure scenario that aims at excluding a large spectrum of possible environmental risk. Finally, the PEC results confirm the first impression given by the flow chart model of currently low aquatic relevancy for such an application of copper nanomaterial for wood treatment. However, exposure and risk assessors should keep an eye on higher market penetration because such micronized copper carbonate and new applications emerging in the future could revise the flow charts. Single-use nanomaterials particularly have to be monitored with regard to this latter point.

Summary

- The main environmental release (approx. 98%) of nano-copper
- carbonate occurs directly from the impregnated wood into soils. Underground leaching out or weathering in combination with air transport deposition is assumed.
-
- The current use type (impregnating wood) and nanomaterial environmental release amounts do not lead to significant exposure to such material in surface waters and sediments. The predicted concentrations of most of the 100,000 Monte Carlo computer model scenarios show some few ng/l levels in fresh water and equivalent values for pg/l levels in marine water.
-
- Significant future exposure of soils to nano-copper carbonate should be viewed as possible. In 2020, the high exposure scenarios do not exclude values of up to approx. 200 µg/kg soil.
-
- Research is needed into nano-copper's fate and behaviour in landfills and recycling plants since significant amounts of nano-copper seem to end up in such plants.
-
- This report points out on the possibility of future nano-copper
- carbonate applications and higher micronized material market penetration with higher environmental release volumes that would make a reassessment of the environmental exposure necessary.

5.7 Zero-valent iron (nano-ZVI)

5.7.1 Material and application

In the case of nanosized zero-valent iron (nano-ZVI), we only focus on one local scenario of soil remediation since such nanomaterial is not expected to be used in a variety of different applications that would lead to diffuse environmental release.

Although a few medical applications have been reported, it is the application in soil (and groundwater) remediation that currently seems to be the only relevant use of nano-ZVI (Mikkelsen et al., 2011). Hence, in this case study we are faced with an emerging iron-based option that can, above all other metals, be used in situ remediation of contaminated groundwater and soil to target chlorinated organic pollutants such as pesticides, solvents or inorganic anions (Mueller et al., 2012).

The nano-ZVI application for soil remediation is by nature a local event due to the high reactivity of nano-ZVI. Through oxidation, this iron reacts with its surroundings, such as air, soil components, and water, and forms iron oxides or hydroxides. In remediation, electrons released from these reactions allow the reduction of different kinds of soil or groundwater pollution. For such reactivity and transformations, see the details presented in Report 1 (NanoDEN, 2014).

In contrast to all other case studies in our report, the iron study will be local and totally focused on soil exposure. This means that the regional stochastic modelling addressing all main environmental compartments and the diffusive release from a variety of products cannot be performed for such a particularly local use of ENM. What we do in this chapter is evaluate possible soil contamination using the findings of a well-documented remediation pilot study performed in Denmark. Based on this pilot study, local scenario results for a full-size remediation using nano-ZVI are presented. As a courtesy, insights into the study applying nano-ZVI at a Danish location have been made available by Geosyntec Consultants, Inc. (Geosyntec Consultants, 2012). Additionally, we give an estimation of the total volume of nano-ZVI that may be used in Denmark, which is complemented by a discussion of the future trends or of worst case scenarios. Based on the local results, we therefore present some hypothetical computations regarding general soil exposure to such iron in Denmark. Such extrapolation from local to regional concentrations will be based on a simple model covering nano-ZVI discharge homogeneously distributed in the soil environment.

5.7.2 Use mass and exposure concentrations in nano-ZVI-treated soil

Local scenarios

As described in detail in Annex I to this report Geosyntec Consultants, Inc. and FRx Inc. conducted injection field experiments with micro- and nanosized ZVI in 2012 on behalf of the Capital Region of Denmark (Geosyntec Consultants, 2012). These injections occurred at a clean test site in Taastrup, located about 21 km west of Copenhagen. The micro- and nanosized ZVI was injected into basal clay as it is very common in Denmark.

During the experiment, more than one hundred soil samples were collected and analysed for their total iron concentration. Interestingly, several soil samples were also tested for background concentrations of iron. The results of the total iron analysis varied, with iron concentrations between 0.95% and 3.98% according to soil weight. The samples tested for background iron concentrations contained between 0.99% and 2.14% iron. Translated into the concentration units used in other cases, this would equate to values ranging from 10,000 mg/kg to 40,000 mg/kg soil. The equivalents for the background concentrations are then between 10,000 mg/kg to 21,000 mg/kg soil. However, a statistical evaluation did not reveal any difference between the background and the sample mean results.

One of the main findings was that the results showed that the concentrations of total iron naturally occurring in the soil were too high for the total iron analysis, the aim of which was to detect elevated iron concentrations due to the injection of different types of ZVI.
However, these results also confirm general knowledge of iron concentrations in soil (and water). As environmental authorities have shown regarding German conditions (Masch and Brandorff, 1997), the total iron content in soil is usually between 0.5% and 5%. Such iron in the soil mainly occurs in the form of goethite (FeOOH), hematite (Fe2O3) and iron (Fe [OH] 3).

In surface waters, the German monitoring (Masch and Brandorff, 1997) revealed iron concentrations between 0.1 mg/l and 10 mg/l. The background concentrations are around 0.5 mg iron/l to 1.0 mg iron/l. In surface water, the iron is barely dissolved and is in the form of organic iron complexes and suspended iron oxides. In the sediment, the concentrations are much higher, similar to those in the ground. The equivalent groundwater concentrations are between 0.01 mg/l and 100 mg/l. In most cases, groundwater has little organic matter, almost no oxygen and pH values below 7.5. Under such conditions the iron is present in solution as iron (II). These water values give us a further impression of the magnitude of environmental iron concentrations that may be compared to the generic soil results presented above.

The Danish iron injection study (Geosyntec Consultants, 2012) went beyond a general analysis and included a mass spectrometry (MS) reading collected for the target soil areas. In contrast to the total iron analysis, the background results of the MS reading and the one of the soil fracture sample of MS readings differed significantly. The results that fell above the maximum background reading represented the soil locations where a significant amount of iron was injected. This MS reading can be related to the concentration of iron based on some calibration curves that convert the MS reading into mass-based values (Figure 5.17).

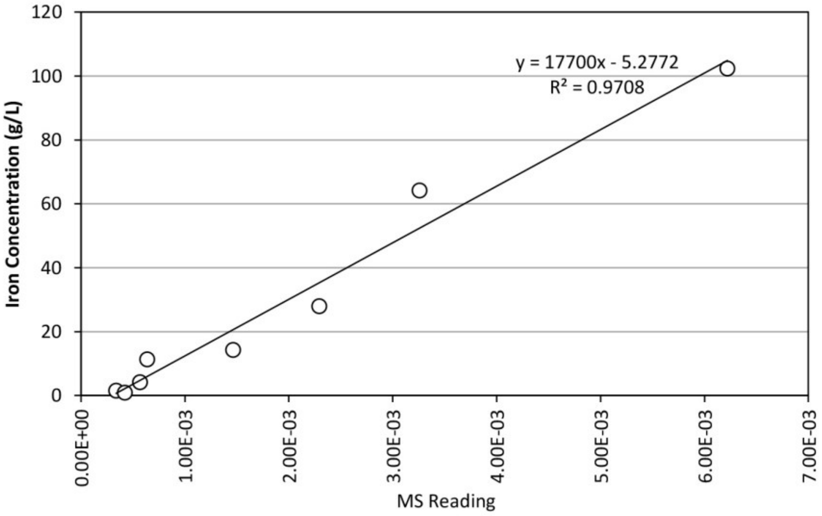

FIGURE 5.17. MASS SPECTROMETRY (MS) READING CALIBRATION CURVE FOR THE NANO-ZVI INJECTION CASE STUDY (GEOSYNTEC CONSULTANTS, 2012).

The concentrations of nano ZVI (Figure 5.17) reveal iron values up to 100 g/l. If we alternatively take the values of this study that show the absolute concentration of nano-ZVI in the injected slurry component, we would have approximately 14.2 g/l slurry. Thus, this concentration is a maximal exposure scenario that should never be reached for homogeneous distribution of nano-ZVI in Danish soil.

From the local scenario to general Danish soil exposure
Our enquiry (for details, see (Annex I)) found that currently in Denmark, mainly iron sponge or iron filings that are not nanosized and are therefore not seen as nano-ZVI have been used for soil remediation. To our knowledge, these materials have been used at four sites in Denmark. In these remediation cases, a few hundred tonnes were used and about some 1000 m^3 of soil was remediated. The potential Danish net import of nano-ZVI is estimated to be around 100 t/y. If nano-ZVI would in the future substitute iron filings or iron sponge for all in situ groundwater remediation in Denmark, we would assume such mass being distributed (and not degraded any more after such distribution) into the total soil volume by an average annual concentration increase of 20 micro/kg would be modelled. In 2020, we would have, based on the same increase model used in other nanomaterial cases, average nano-ZVI soil concentrations of 270 µ /kg soil. If we then compare this worst-case nano-ZVI scenario of 270 µ /kg to the total (natural) iron amount of 20,000 mg/kg to 40,000 mg/kg (as shown above), we see that the hypothetical nano-ZVI fraction is insignificant.

In order to get a critical nano-ZVI contribution to the iron content in soil, the hypothetical worst case computations based on the 14.2 g/l nano-ZVI in slurry mentioned above should be directly converted into soil concentrations (although this is certainly a value that cannot be reached in homogeneously distributed nano-ZVI in Danish soil). If this is done based on an average soil density of 1500 kg/m^3, then for the whole soil volume in Denmark the model reveals 9.5 g/kg soil, which would represent a significant nano-ZVI content compared to the 40 g/kg of the naturally occurring iron. However, this is certainly a value that should never be reached in the homogeneous distribution of nano-ZVI in Danish soil.

5.7.3 Discussion and conclusions

In summary, we may state that even hypothetical worst-case nano-ZVI scenarios of some hundred µg/kg soil do not represent a significant amount when compared to the natural concentrations of 20 g/kg to 40 g/kg. In order to get a significant nano-ZVI exposure to such iron, the nano-ZVI in slurry should be directly converted into soil concentrations, which currently seems unrealistic.

As discussed above and elsewhere (Mueller and Nowack, 2010), the mobility and lifetime of nano-ZVI are very limited. However, in the future, we may expect several modifications of nano-ZVI that aim at increasing the life cycle factors (NanoDEN, 2014). Mueller and Nowack (2010) predict the following types of modifications: surface-modified nano-ZVI (impact on generic reactivity), nano-ZVI on carbon support (improved mobility within the soil), bimetallic nano-ZVI (greater reactivity) and emulsified nano-ZVI (improved miscibility with Dense Nonaqueous Phase Liquid (DNAPL)). In the Danish remediation studies mentioned here, only surface-modified nano-ZVI (e.g. with surfactants) was applied. According to the nano-ZVI product specifications, a nano-ZVI suspension of stabilized nanoparticles was used. The reactive solids in this suspension were combined with water and a non-specified surfactant that limited the agglomeration of the nanoparticles. In order to maintain reactivity during and after the injection, the nano-ZVI was produced and transported to Denmark within one week prior to its use.

In conclusion, it is emphasized that in this study concerns about potential high-volume use in the future are not addressed. This, along with the long-term environmental behaviour of nano-ZVI, needs to be thoroughly researched in future work. In this context, others (Crane and Scott, 2012) emphasize the possible remobilisation of heavy metals and radionuclides over long periods.

Summary

- The use of nano zero-valent iron (nano-ZVI) in soil and groundwater remediation has led to a need for information on the environmental fate and behaviour of such iron.
- Due to the intended use of these nanoparticles, they will be discharged to the natural environment, where some reactivity is expected.
- The nano-ZVI-based remediation is a local event since it is driven by high and rapid reactivity of the nano-ZVI. For more about such reactivity and transformations, see the details in NanoDEN Report 1.
- Even hypothetical worst-case nano-ZVI scenarios of some hundred µg/kg in soil do not represent a significant amount when compared to the natural concentrations of g/kg soil concentrations.
- In order to achieve serious nano-ZVI loads in soils, such loads should reflect the same concentrations as the ones of nano-ZVI in slurry that is used for the soil remediation itself.

5.8 Nano-CeO_2

As done for previous sections, the nano-CeO_2 mass transport system and concentrations are shown for the main technical and natural compartments: sewage treatment sludge, waste mass and its residues bottom ash and fly ash, surface waters (fresh water, sea water), sewage treatment effluents, air, soils (agricultural, natural, urban and sludge-treated soils) and sediments (fresh water and sea water sediments).

All mass transport results are illustrated in Figures 5.18 and 5.19; the PECs are shown in Tables 5.13 and 5.14 and fully described by means of probability density functions in Annex II of this report.

5.8.1 Material flows and environmental release

Mass flows
The nano-CeO_2 mass transfer system depicted in Figure 5.18 includes modal values for transmission, accumulation and transformation of this engineered nanomaterial. The total annual input into the system (modal value) is about 5 tonnes. With the exception of transport into product recycling, no other transitions reach an annual mass in tonnes-per-year levels.

There is a strong dominance of mass movement into non-aquatic areas, such as waste incineration, recycling and landfilling (90% of the total mass) as well as some significant amounts into the atmosphere (approx. 6%). Hence, the non-aquatic mass transmission accounts for about 96% of the total nano-CeO_2 annual mass entering into the Danish system. The last mentioned transfer occurs in the form of air emissions from the material lifecycle phase of the PMC (production, manufacturing and consumption) box. These kinds of release are determined by the nano-CeO_2 applications, such as use in fuel additives, automotive catalysts or batteries. A very small fraction (1%) of nano-CeO_2 gets lost in the PMC box due to the dissolution process upon contact with water, which may occur if the nanomaterial is used in paint and coatings, cosmetics and other liquids. Another small portion, primarily from such paints and coatings, goes into the aquatic relevant mass transfer (approx. 4%), which includes STP inflows and direct release from the PMC compartment into waters.

Regarding air emissions, it is worth mentioning that they are as high as the ones of the high-use volume nanomaterial photostable nano-TiO_2 (approx. 40 times higher use volumes than nano-CeO_2). This may be explained by the fact that half (approx.) of all main nano-CeO_2 applications (automotive catalysts converters, fuel additives) cause some air emissions with CeO_2.

However, as seen above for the main part, the 90% ending up in recycling, landfills and waste incineration, the model assumes that all nanomaterial is removed from the system. The model stops when the ENM enters into landfills and recycling plants; in addition, the detailed model of nano-CeO_2 in waste incineration processes follows previous experimental evidence (Walser and Gottschalk, 2014). The waste incineration shows almost no release into air from such incineration (see also Annex I. Regarding recycling processes and landfills, the fate of nano-CeO_2 in such plants remains to be researched. For such mass, a distinction between internal deposition and elimination/transformation is currently impossible due to the lack of analytical evidence. However, based on Danish security standards, it seems most plausible to assume that there is no further nanomaterial release because such plants operate as closed systems.

The marginal nano-CeO_2 load into waters occurs directly from its use in paints and coatings, in glass polishing, and to a smaller extent, via STP since STP sludge catches most STP nano-CeO_2. Such sludge is incinerated (approx. 45%) or ends up as fertilizer mass (55%) in soils.

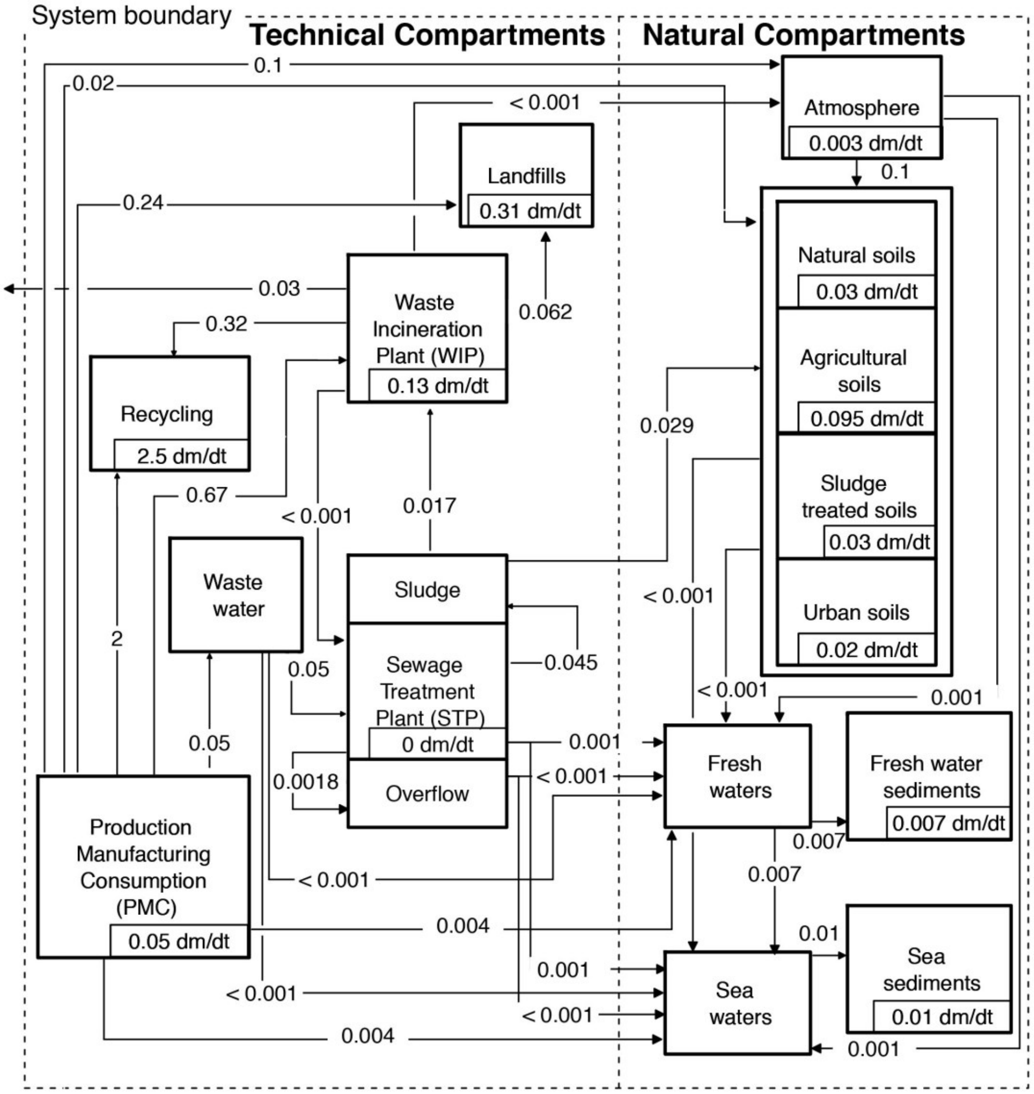

FIGURE 5.18.

MASS FLOW SYSTEM OF NANO-CeO_2 WITH ROUNDED MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) IN T/A. BOXES SHOW ACCUMULATION OR TRANSFORMATION MASS. THESE MODES, EXTRACTED FROM THE MONTE CARLO SIMULATIONS, REPRESENT HIGH PROBABILITY RESULTS AT DIFFERENT STAGES OF THE MODEL WITHOUT PRECISELY ILLUSTRATING HOLISTIC MASS-BALANCE IN THE FIGURE.

ENM sources of environmental release and its recipients

Figure 5.19 provides an overview of the total environmental release of nano-CeO_2 along with the primary recipients of such released nanomaterial. About 10% of the total mass transferred in the Danish system is caught by environmental release and here reflects the so-called primary source, which sums and fractionates this release. We see most (approx. 84%) nanomaterial mass released directly from PMC. This tendency has been explained through the nano-CeO_2 main applications (e.g., use as fuel additives/fuel-borne catalysts or for glass polishing). The use in paints and coatings and probably in some cosmetics and medicinal products (though not quantified due to missing data) also leads to some release fractions caught by the water treatment in STPs.

Soils represent the main natural recipient of nano-CeO_2, which is explained by the fact that air emissions do not show a long residence time in the air, but end up in dry and wet deposition on the ground. Research has suggested a 10-day retention in the air (Sun et al., 2014) by using data on the lifetime of ultrafine particles (Anastasio and Martin, 2001). Such air pathway emissions are complemented by some amounts ending up in the STP sludge. Taken together, these two release paths feed about 87% of the receiving mass that completely ends up in soils. The aquatic receivers currently seem to catch 12% of the released nano-CeO_2 at most. Concluding, we must again emphasize that against the backdrop of this evaluation, one must consider that the quantities released in each case are very small and never reach tonnes-per-year dimensions. However, for this material, we must also point out that it was not possible to quantify its use in medicinal products, sunscreen and make-up, which could become important and shift the percentage values in the aquatic direction.

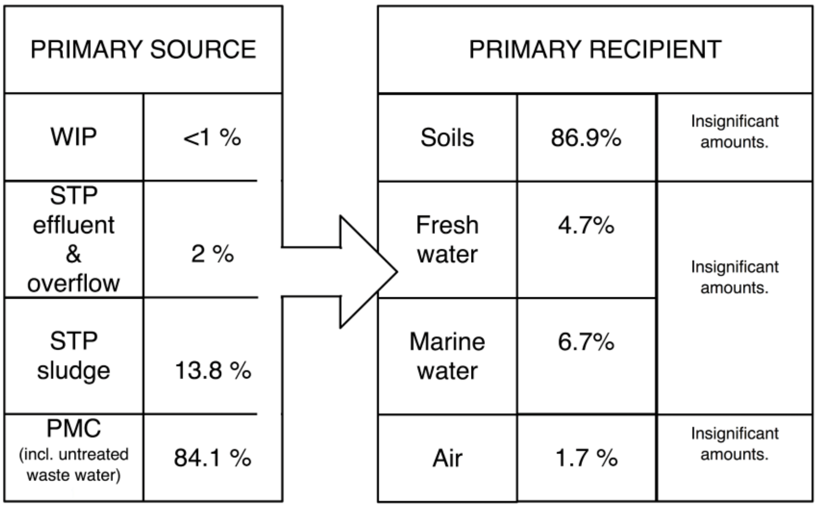

FIGURE 5.19.
OVERVIEW OF THE MOST IMPORTANT NANO-CeO_2 SOURCES AND RECEIVERS. THE PERCENTAGES REFLECT MODAL RESULTS (THE MOST FREQUENTLY MODELLED VALUES).

5.8.2 Exposure concentrations in technical compartments

The modelled PECs for nano-CeO_2 are presented here for technical compartments. A similar picture to the nano-ZnO case study is drawn for the concentrations in waste mass and waste residues (ashes). These nano-CeO_2 concentrations are all at least in a µg/kg level ranging from 180 µg/kg to 2 mg/kg e.g. for waste mass and fly ash from waste incineration. The concentrations in STP waters and sludge show modal values around 10 ng/l in STP effluent waters and about 350 µg/kg concentrations in STP sludge. This figure is for the effluent results and is roughly 20 times higher than the nano-silver results, but still about 100 times lower than the ones of copper carbonate. All in all, the model currently does not predict significant loads of such CeO_2 into non-diluted waters or into natural surface waters. The waste incineration ashes will end up in some recycling or deposition assumed to represent Danish closed systems that do not have any environmental relevance in the context of nanomaterial release.

TABLE 5.13.

PREDICTED ENVIRONMENTAL CONCENTRATIONS (PEC) FOR NANO-CeO_2 IN DIFFERENT TECHNICAL AND NATURAL COMPARTMENTS, AS MODELLED FROM COMPUTER-BASED STOCHASTIC SIMULATIONS ON NANO-CeO_2 RELEASE TO, AND SCENARIOS FOR, FATE/RESIDENCE TIME IN THOSE COMPARTMENTS. THE RESULTS ARE SHOWN AS MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) AND AS LOWER AND UPPER LIMITS CONSIDERED BY 95% RANGES THAT ALSO ILLUSTRATE A 95% PROBABILITY OF THE PECS PRODUCED FALLING WITHIN THEM. FOR SOILS AND SEDIMENTS, AN ANNUAL INCREASE OF PECS IS GIVEN.

Compartments (sources)	**Concentrations**		
	Unit	Mode *median	95% range
Technical compartments			
Sewage treatment effluent	ng/l	9.3	1.1 - 59.6
Sewage treatment sludge	µg/kg	352.3	44.1 - 2308
Waste mass incinerated	µg/kg	178.6	21.0 - 931
Bottom ash of waste incineration	µg/kg	359.0	49.7 - 2462
Fly ash of waste incineration	µg/kg	2198	243.3 - 12260
Natural compartments			
Surface water (fresh water)	ng/l	0.004	5.8E-04 - 0.1
Sea water	ng/l	2.6E-04	3.2E-05 - 0.002
Sediments (fresh water)	µg/kg	0.2	0.033 - 6.9
Sediments (sea water)	µg/kg	0.049	0.006 - 0.3
Agricultural soils	ng/kg	11.7	1.5 - 81.6
Natural soils	ng/kg	26.9	3.7 - 223.9
Urban soils	ng/kg	45.6	6.0 - 316.4
Sludge treated soils*	ng/kg	231.7	14.5 - 780.5
Air	ng/m3	0.1	0.010 - 0.6

*inconclusive, bipolar (or pluripolar) results or insignifact difference between mode and median

5.8.3 Exposure concentrations in natural compartments

In the nano-CeO_2 results, it is noteworthy that all the fresh water PECs provided by the Monte Carlo-based computer simulations at pg/l levels at the most. Even fg/l cannot be excluded. Although these extremely low values are more theoretical constructs than something measurable in nature, they show that, at the moment, we cannot expect significant surface water contamination by such material. This statement also applies to the marine water values, which are almost all in theoretical fg/l dimensions. As a consequence of low water concentrations, the model also performed small sedimentation amounts that lead to a few µg nano-CeO_2 per kg sediments (fresh water) until 2020. The ones for marine water sediments only reach µg/kg levels in a few Monte Carlo scenarios. We therefore see the same low-level magnitudes as modelled for nanosilver.

However, as we emphasized above in the context of nanomaterial aquatic release, data is currently not available on the quantification of nano-CeO_2 use in medicinal products, sunscreen and make-up, which could increase the aquatic exposure concentrations of such CeO_2.

The modelled soil concentrations are also very low compared to the copper-carbonate concentrations, and they are in similar magnitudes as the nanosilver concentrations. In 2020, we may expect (modal values) that the non-STP sludge fertilized soil areas (agricultural, natural and urban soils) will not fully reach µg nano-CeO_2 per kg soil. At the end of the second decade, only a few µg/kg are expected for STP sludge-treated soils.

The modelled marginal concentrations in air of some pg/m^3 ranges are higher than the ones for nanosilver or e.g. nano-copper carbonate and in a similar magnitude as the concentrations for the high use volume example of photostable nano-TiO_2.

TABLE 5.14.

PREDICTED ENVIRONMENTAL CONCENTRATIONS (PEC) FOR NANO-CeO_2 IN SEDIMENTS AND SOILS MODELLED FROM COMPUTER-BASED STOCHASTIC SIMULATIONS ON NANO-CeO_2 RELEASE TO THOSE COMPARTMENTS. THE PREDICTIONS ARE SHOWN AS MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) AND AS LOWER AND UPPER LIMITS CONSIDERED BY 95% RANGES THAT ILLUSTRATE A 95% PROBABILITY OF THE MODELLED PECS FALLING WITHIN THIS RANGE. THE PEC VALUES REFLECT NANO-TIO_2 CONCENTRATIONS AFTER BEING DEPOSITED IN SEDIMENTS AND SOILS UNTIL THE BEGINNING OF THE YEARS 2014 AND 2020. ALL THE CURVES ARE SHOWN IN ANNEX II OF THIS REPORT.

Compartments	**Concentrations**		
	Unit	Mode *median	95% range
Prediction for 2014			
Sediments (fresh water)	µg/kg	1.6	0.2 - 44.7
Sediments (sea water)	µg/kg	0.3	0.038 - 2.0
Agricultural soils	ng/kg	76.3	10.0 - 530.1
Natural soils	ng/kg	174.5	24.2 - 1455
Urban soils	ng/kg	296.2	38.8 - 2057
Sludge treated soils*	ng/kg	1506	94.4 - 5073
Prediction for 2020			
Sediments (fresh water)	µg/kg	3.3	0.4 - 93.2
Sediments (sea water)	µg/kg	0.7	0.1 - 4.1
Agricultural soils	ng/kg	159.4	20.9 - 1107
Natural soils	ng/kg	364.4	50.5 - 3039
Urban soils	ng/kg	618.5	80.9 - 4294
Sludge treated soils*	ng/kg	3144	197.0 - 10593

*inconclusive, bipolar (or pluripolar) results or insignifact difference between mode and median

5.8.4 Discussion and conclusions

The current nano-CeO_2 release amounts in the Danish environment and the subsequent concentrations appear throughout (water and soils) to be small and mostly lie in the range of those for nano-silver. This finding applies to current available data and could change if the use of nano-CeO_2 in medicinal products, sunscreen and make-up achieves significant amounts; then, it should be quantified and documented in future reports focused on such use.

We recognize the current research need for investigation of direct release via the use of nano-CeO_2, which may occur from applications, mainly from the fuel-borne catalysts. In the case of air emissions via waste treatment for this nanomaterial, we have more specific data than is usually the case. As reported elsewhere (Walser and Gottschalk, 2014) in an evaluation and modelling of a full-scale experiment based on real nano-CeO_2 measurements, even inert nanosized particles of that CeO_2 type are removed from the flue gas and transferred into the incineration residues.

Summary

- The nano-CeO_2 Danish use volumes seem relatively low with modal values of around 5 tonnes per year. The model shows a low annual load of cerium into the natural environment, not exceeding half a tonne annually.
- Most environmental discharge covers air emissions and STP sludge fertilizations. However, these releases are always modelled in very low quantities, not reaching t/a levels.
- Most of the nano-CeO_2 water and marine water concentrations are in pg/l concentration levels; partially, some fg/l were also computed.
- For non-STP sludge fertilized areas, the soil concentrations in 2020 are expected (modal values) to be in a few hundred ng/kg levels. A few µg/kg are expected at this time for STP sludge-treated areas.
- The air concentrations show values of some pg/m^3 and are in the same dimensions as the ones for the high use volume photostable and other TiO_2 nanomaterial.
- This report results indicate a low general environmental relevancy for nano-CeO_2. However, it underscores some types of nano-CeO_2 use (cosmetics, medicinal use, cleaning agents) that were not quantified here and could show increasing volumes in the future, subsequently changing the environmental exposure levels.
- For general indications on the assessment of Danish ENM use quantities, please see the summary box on photostable and other nano-TiO_2.

5.9 Quantum dots

In this chapter, we present mass transport charts and predict environmental concentrations of quantum dots, probably for the first time. As performed for the other nanomaterials, this study covers all the main technical and natural compartments: sewage treatment sludge, waste mass and its residues bottom ash and fly ash, surface waters (fresh water, sea water), sewage treatment effluents, air, soils (agricultural, natural, urban and sludge-treated soils) and sediments (fresh water and sea water sediments). However, due to a much lower total annual use in the Danish model (lower than one tonne per year) and consequently almost zero nanomaterial release in some cases, the concentrations were not quantified in detail for some compartments. These compartments then contain a not-quantified (nq) indication or some verbal explanation that refers to extremely low values at a lower level than some fg/l. In such cases, a qualitative discussion of currently almost not-occurring release seemed more appropriate than the presentation of theoretical values that no one will ever be able to measure in the natural environment.

The Danish mass transport is illustrated in Figure 5.20; the PECs are shown in Table 5.15 (and 5.16) and fully presented by means of probability density functions in Annex II of this report.

5.9.1 Material flows and environmental release

Mass flows

As noted in the introduction, in the Danish case study of quantum dots, we are faced with a mass transfer that most likely does not reach total mass transport of tonnes per year dimensions. This fact applies even for high use scenarios in the Monte Carlo computer simulations that, at most, reveal some hundred kilograms of use. The mass transfer overview in Figure 5.20 confirms this low use. What we see at first glance is that the majority of the quantum dot nanomaterial will end up in the waste management compartments of recycling at the end of its life cycle. An additional but much lower mass goes into waste incineration or is deposited in landfills. However, this portion composes 1% (modal values) of cases at most. The remaining hardly 10% (modal value) of the total mass material is distributed somewhat equally to the natural compartments. Due to the very low quantities, we have not conducted a quantitative distinction between the aquatic, terrestrial, or air environments. As mentioned above, such computations would just reflect theoretical or computer-produced artificial values that no one would ever be able to measure in the natural media.

The currently more or less insignificant environmental release is reflected by two main factors: 1) the current low- use volumes and 2) applications that are far away from discharging any components to the natural environment. This especially applies if recycling and landfilling processes occur at high (standard) quality and security levels as in the case in Denmark.

As shown in the Annex I, quantum dots applications in products and commodities include light emitting devices (e.g. LEDs) and diode lasers, lab use for imaging, semiconductors transistors, solar cells, medical imaging (and diagnostics/detection) instruments and some qubits in quantum computing. About 90% of the total mass is assumed to be used for light emitting devices (e.g. LEDs), as suggested elsewhere (Piccinno et al., 2012). Danish manufacturing of these application products cannot be excluded. In this report, manufacturing that would lead to some initial direct release to the surroundings (air and waste water) of the corresponding facilities could not be documented. However, due to the very low use amounts that would be covered by such uses, filling the data gap would not significantly change the environmental and exposure assessment model. A full data gap has also been detected for use amounts in semiconductors transistors, solar cells, medical imaging (and diagnostics/detection) instruments and some qubits in quantum computing. Nevertheless, the environmental release of such non-quantified use fields should not considerably differ from that in electronics where the LEDs in electronic equipment are expected to be totally disposed of for recycling. The fate of quantum dots in natural media is evaluated in detail in Annex I. For the small fraction (below 10%) that could reach the natural environment, fast degradation is expected since most of the environmental media conditions probably favour QD degradation (Blickley, 2010). Other scientific literature confirms these conclusions by referring to transformation to the core/shell structure of such nanomaterials that may occur due to changes in redox conditions, pH, and light conditions (Slaveykova and Startchev, 2009; Navarro et al., 2011).

ENM sources of environmental release and its recipients
For quantum dots, the report abstains from fractionating in detail the environmental release amounts into single sources and allocating such sources to the primary recipients. By equally distributing the very low mass of released QD to all the release paths into the natural environment (Figure 5.20), the single values become so small that a detailed evaluation of single resource and receiving percentages of primary recipients becomes a pure computer exercise without any practical relevance. As noted above, such total environmental release mass transfer embodies a total mass below tonnes-per-year levels. Secondly, as already emphasized for the small mass QD fraction that annually finds its way into nature, fast degradation is expected due to influence factors, such as the changes in redox conditions, pH, and light-based material altering.

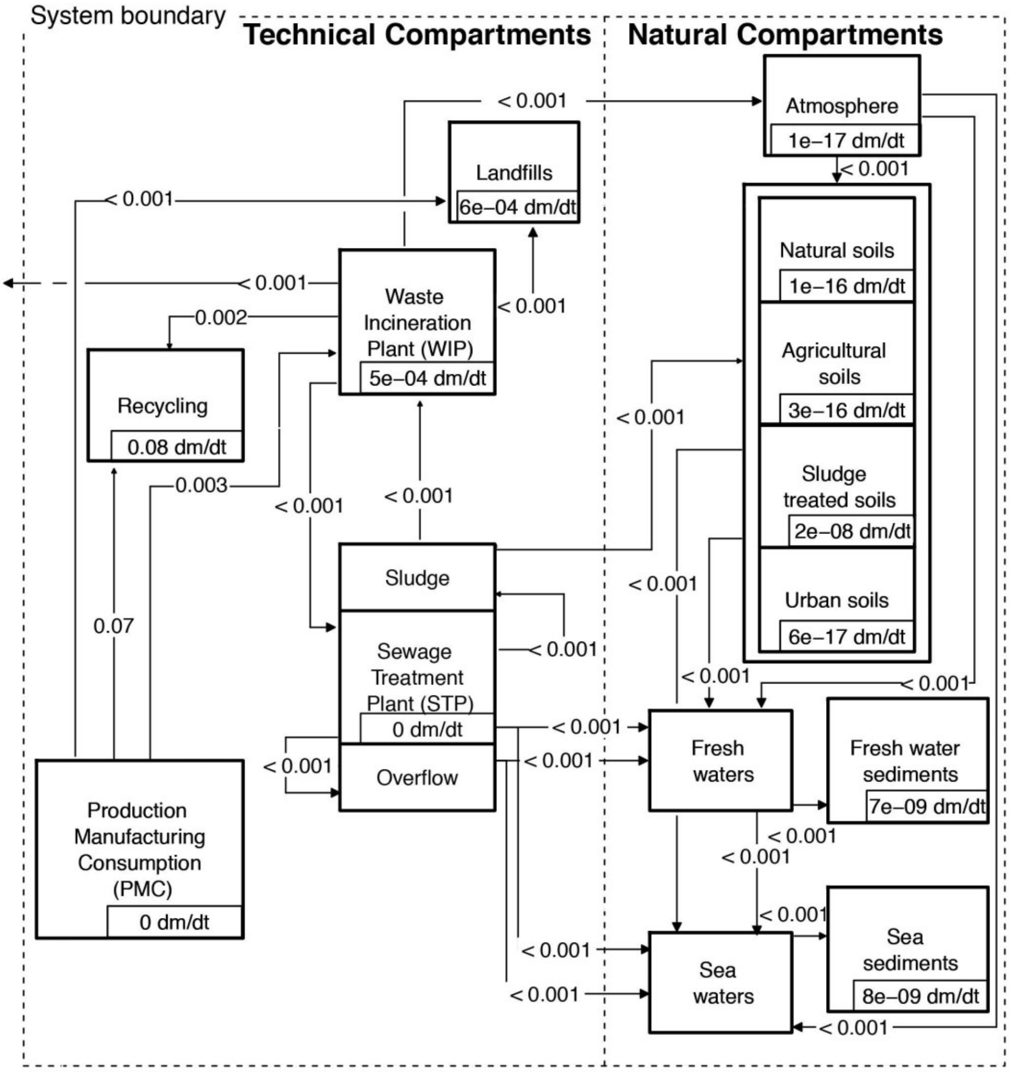

FIGURE 5.20.
MASS FLOW SYSTEM OF QUANTUM DOTS (QD) WITH ROUNDED MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) IN T/A. BOXES SHOW ACCUMULATION OR TRANSFORMATION MASS. THESE MODES, EXTRACTED FROM THE MONTE CARLO SIMULATIONS, REPRESENT HIGH PROBABILITY RESULTS AT DIFFERENT STAGES OF THE MODEL WITHOUT PRECISELY ILLUSTRATING HOLISTIC MASS-BALANCE IN THE FIGURE.

5.9.2 Exposure concentrations in technical compartments

The highest amounts of quantum dots were modelled for waste mass, slag and fly ash of waste incineration processes. The waste mass concentrations were predicted at approx. 1 µg /l waste (modal value) with minimal and maximal values around 0.1 µg /l and 4.4 µg /l (95% value range). The equivalent values for slag (bottom ash) material ranges were 0.2 µg /l and 11.4 µg /l with a modal value of about 2.2 µg /l. The fly ash results are around 10 µg /l (modal values). Such concentrations are very low compared to those of other metals studied in this report and about 300-350 times lower than the pure nano-ZnO concentrations predicted in such waste mass and waste incineration residues. The nearest case can be found in nano-Ag, which shows concentrations in the same order of magnitude but are, however, still almost 20-30 times higher.

The aquatic high exposure compartment STP effluent reveals PECs almost completely in fg/l levels. This finding explains why we limited ourselves on this water compartment and did not further quantify surface water concentrations in much higher diluted surface waters. The sewage treatment sludge concentrations per unit sludge showed values ranging from 40 pg/kg to some ng/kg (95% value range). No other metals studied revealed such low water and STP sludge exposure levels.

TABLE 5.15.

PREDICTED ENVIRONMENTAL CONCENTRATIONS (PEC) FOR QUANTUM DOTS (QD) IN DIFFERENT TECHNICAL AND NATURAL COMPARTMENTS, AS MODELLED FROM COMPUTER-BASED STOCHASTIC SIMULATIONS ON QUANTUM DOTS RELEASE TO, AND SCENARIOS FOR, FATE/RESIDENCE TIME IN THOSE COMPARTMENTS. THE RESULTS ARE SHOWN AS MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) AND AS LOWER AND UPPER LIMITS CONSIDERED BY 95% RANGES THAT ALSO ILLUSTRATE A 95% PROBABILITY OF THE PECS PRODUCED FALLING WITHIN THEM. FOR SOILS AND SEDIMENTS, AN ANNUAL INCREASE OF PECS IS GIVEN.

Compartments (sources)	Concentrations		
	Unit	Mode	95% range
Technical compartments			
Sewage treatment effluent	ng/l	3.0E-05	5.2E-06 - 0.001
Sewage treatment sludge	µg/kg	2.4E-04	3.6E-05 - 0.003
Waste mass incinerated	µg/kg	0.9	0.1 - 4.4
Bottom ash of waste incineration	µg/kg	2.2	0.2 - 11.4
Fly ash of waste incineration	µg/kg	10.3	1.0 - 56.7
Natural compartments			
Surface water (fresh water)	below fg/l		
Sea water	below fg/l		
Sediments (fresh water)	fg/l up to some pg/l		
Sediments (sea water)	fg/l/a		
Agricultural soils	nq		
Natural soils	nq		
Urban soils	nq		
Sludge treated soils	pg/kg	0.1	0.010 - 1.0
Air	nq		

5.9.3 Exposure concentrations in natural compartments

As stated above, the water concentrations were so low that a realistic quantification and evaluation of the probability distributions in a fg/l and lower levels seemed to lack meaning. Instead of evaluating theoretical computer values, we restrict ourselves in stating that, based on the current quantum dots use volumes, the aquatic (fresh water and marine water) values are most likely near zero if not almost absent. In principle, similar findings apply for sediments as well; however, due to a two-decade time period of marginal quantum dots deposition, some values could be derived. After 20 years of sedimentation, a few µg/kg sediments (fresh water) are predicted (3 µg/kg modal value). The equivalent for marine water sediments does not fully reach µg/kg concentrations in 2020. These sediment values are in similar ranges as the ones of nano-Ag, reflecting a very low use volume and aquatic release. The 20-year-deposition results for sludge-treated soils are mostly in fg/kg concentrations with a few high exposure scenarios in the Monte Carlo computer simulations in pg/kg dimensions. Besides the zero exposure case of nano-ZnO, the latter are too low to find a comparison to other nanomaterials in our report. This ZnO-based accordance is not a surprise since quantum dots are traditionally chalcogenides (selenides or sulphides) of metals, such as zinc (or cadmium). However, future cadmium-free formulations are supposed to include rare earths, such as indium and tellurium. For a detailed material description, see Annex I of this report.

TABLE 5.16.

PREDICTED ENVIRONMENTAL CONCENTRATIONS (PEC) FOR QUANTUM DOTS (QD) IN SEDIMENTS AND SOILS MODELLED FROM COMPUTER-BASED STOCHASTIC SIMULATIONS ON QUANTUM DOTS RELEASE TO THOSE COMPARTMENTS. THE PREDICTIONS ARE SHOWN AS MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) AND AS LOWER AND UPPER LIMITS CONSIDERED BY 95% RANGES THAT ILLUSTRATE A 95% PROBABILITY OF THE MODELLED PECS FALLING WITHIN THIS RANGE. THE PEC VALUES REFLECT NANO-TIO_2 CONCENTRATIONS AFTER BEING DEPOSITED IN SEDIMENTS AND SOILS UNTIL THE BEGINNING OF THE YEARS 2014 AND 2020. ALL THE CURVES ARE SHOWN IN ANNEX II OF THIS REPORT.

Compartments	**Concentrations**		
	Unit	Mode	95% range
Prediction for 2014			
Sediments (fresh water)	µg/kg	1.6	0.2 - 44.7
Sediments (sea water)	µg/kg	0.3	0.038 - 2.0
Agricultural soils	nq		
Natural soils	nq		
Urban soils	nq		
Sludge treated soils	ng/kg	4.5E-04	6.7E-05 - 0.006
Prediction for 2020			
Sediments (fresh water)	µg/kg	3.3	0.4 - 93.2
Sediments (sea water)	µg/kg	0.7	0.1 - 4.1
Agricultural soils	nq		
Natural soils	nq		
Urban soils	nq		
Sludge treated soils	ng/kg	0.001	1.4E-04 - 0.013

5.9.4 Discussion and conclusions

This report shows some use (0.5 t/at the most) of quantum dots mainly in light-emitting devices (e.g. LEDs), which do not currently lead to significant discharge of such nanomaterial into the environment. In the future, however, the use situation could change if significant use is observed for a series of promising applications in the fields of solar cells, semiconductors transistors, medical diagnostic instruments or quantum computing.

The computed environmental concentrations in air and surface waters were so small that an evaluation of their probability distributions seemed to lack practical relevance. A few µg/kg were predicted for sediments in 2020 (fresh water), and even lower values were found for marine water equivalents, which did not have any comparable results to other materials in our report.

Summary

- The quantum dots use volumes are most likely below half-a-tonne-per-year levels.
- About 90% of the total mass is assumed to be used for light emitting devices (e.g. LEDs) that mostly end up in recycling processes at the end of their lifecycles.
.
- Even for high use scenarios of the Monte Carlo computer simulations, the environmental release is marginal. The single environmental release pathway quantities are too small for detailed quantification.
- The surface water and air concentration probability distributions were not quantified and evaluated because all values were lower than fg/l (water) or fg/m^3 (air).
- After a 20-year-sedimentation period, a few µg/kg of sediment (fresh water) are predicted; the equivalents for marine water sediments do not reach µg/kg concentrations in 2020.
- The 2020 results for STP sludge-fertilized soils are just for high exposure scenarios of the Monte Carlo computer simulations in some pg/kg dimensions.
- For general indications on the assessment of Danish ENM use quantities, please see the summary box on photostable and other nano-TiO_2.

5.10 Carbon black

In this chapter, we present, to our knowledge, the first comprehensive quantitative study on mass transport and predicted environmental concentrations for carbon black. This is the second carbon-based nanomaterial studied (see also chapter 5. 6 on CNTs) in this report. As done in the other case studies, we investigated the technical compartments of sewage treatment sludge, waste mass and its residues bottom ash and fly ash, and we predicted concentrations for the natural environments of surface waters (fresh water, sea water), sewage treatment effluents, air, different soil types (agricultural, natural, urban and sludge-treated soils) and sediments (fresh water and sea water sediments).

The results are summarized in Table 5.17 and (Table 5.18) and shown based on probability density functions in Annex II.

5.10.1 Material flows and environmental release

Mass flows
Figure 5.21 shows a complete overview based on modelled modal values of the mass transport system for carbon black in Denmark. Due to an annual mass transfer and input into the system in ranges of a few thousand tonnes, we this time display these results in kt/a units. Therefore, the arrow thicknesses show the mass relations in this higher unit and cannot be compared without considering the other mass flow charts in t/a units in this report.

The first impression of high Danish mass volumes reflects a carbon black market that shows approximately 36 kt use amounts per year (modal value). Most of this mass (approx. 90% modal value) ends up in reinforcement of tires and other rubber components. The remaining portion is used in paints and varnishes, inks and some plastic components.

Because there are no explicit indications available on the distinction between import and inland production, it is difficult to make out whether these mixtures (carbon black mixed in such products) placed on the Danish market are imported or produced in Denmark. Inland formulation (100-400t) has been modelled for the mixtures in paints, lacquers, pigments, reprographic agents and different adhesives that represent only a tiny minority of 1% of the total Danish use amounts. This distinction does not influence our total mass flow system too much since we only focus on the complete inland nanomaterial mass transfer that determines the inland natural exposure to the target nanomaterials. Hence, whether or not the nanomaterial (or the transported nanoproduct) is not so crucial for later release in the system, when during formulation, we do not expect high release. The formulation-based total release of nanomaterial is modelled around 3%. Most of this small fraction of formulation mass that gets lost ends up in waste incineration where it is almost completely eliminated.

The mass transport chart shows that almost 90% (modal value) of the total black carbon used in Denmark directly goes (at the end of its lifecycle) into recycling (approx. 25 kt), waste incineration (approx. 5 kt) and landfilling (approx. 1 kt) processes. Based on complete incineration for such carbon and a model of terminal lifecycle phases for carbon black in recycling and landfilling, we may state that roughly 90% of carbon black will probably never end up in natural environments.

In the case of landfills, such final sinks are modelled in line with others, such as Sun et al. (2014), who predicted nanomaterials' zero release (leaching out of nanomaterial) in the environment for Swiss conditions. Such conditions of environmental security for landfills should be comparable to those in Denmark. Also aligned with these authors, the same zero release model is assumed for the recycling process. It is difficult to imagine that a mixture of carbon black product mixtures reused in cement mass will release some intact carbon nanoparticles.

Regarding the amounts of carbon black ending up in natural environments, we note that approx. 6-7% of the total annual transfer mass reach the surface waters, and 3-4% (modal values) find their way into soils. The aquatic path way is dominated by direct release into surface waters. Such release without any detour via STPs may come from released tire components via street water drain systems not connected to any water treatment. This and other rubber wear mainly leads to release into soils, more or less directly or via previous air transport and subsequent dry or wet (rain-based) deposition.

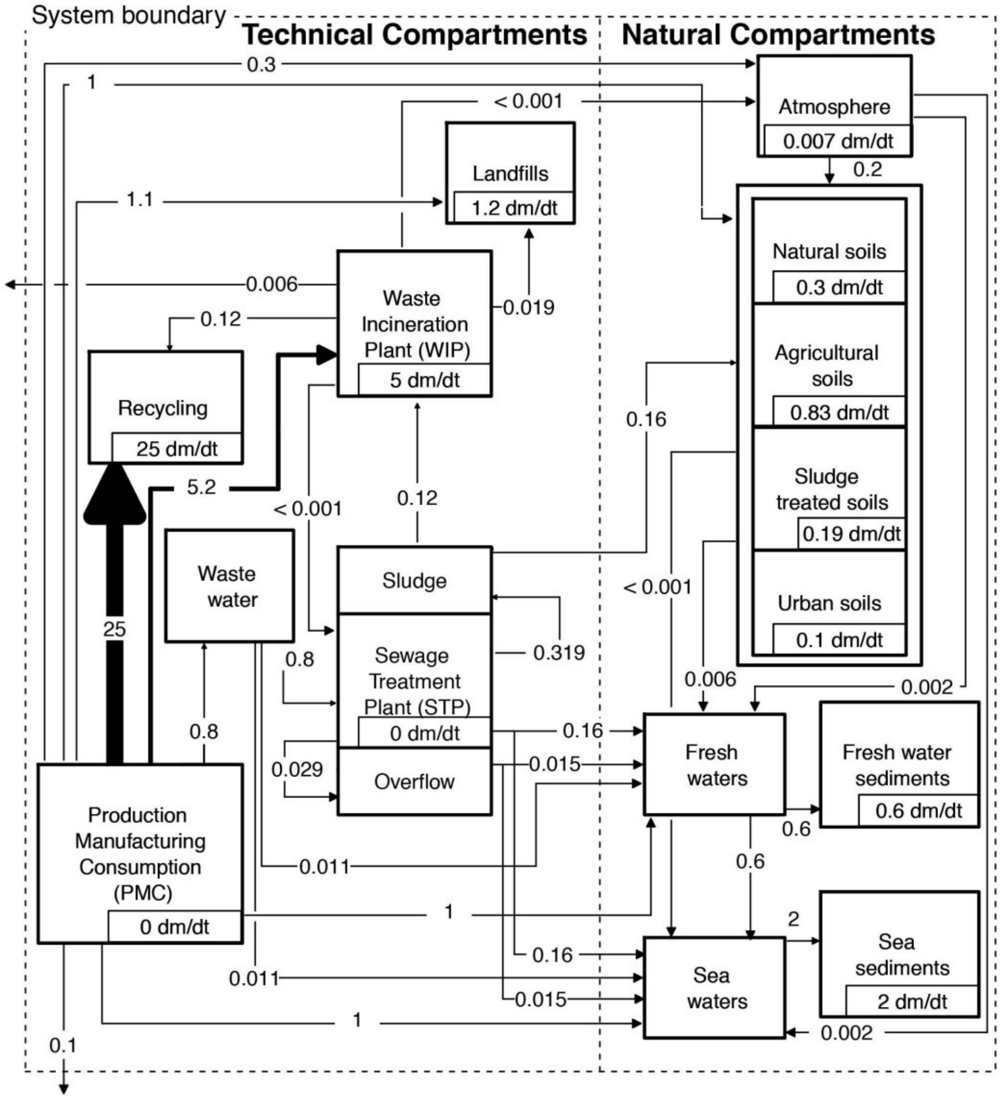

FIGURE 5.21.
MASS FLOW SYSTEM OF CARBON CLACK (CB) WITH ROUNDED MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) IN KT/A. BOXES SHOW ACCUMULATION OR TRANSFORMATION MASS. THESE MODES, EXTRACTED FROM THE MONTE CARLO SIMULATIONS, REPRESENT HIGH PROBABILITY RESULTS AT DIFFERENT STAGES OF THE MODEL WITHOUT PRECISELY ILLUSTRATING HOLISTIC MASS-BALANCE IN THE FIGURE.

ENM sources of environmental release and its recipients

Figure 5.22 confirms the just-mentioned environmental release of carbon black that mostly occurs directly from the use of products containing this carbon nanomaterial. Approx. 87% (modal values) of the nanomaterial sources is covered by such use, followed by approx. 13% of release via sewage treatment plants. Due to nearly complete combustion in waste incineration plants, the WIP pathway is of almost no importance. On the right-hand side of Figure 5.22, we see the primary natural recipients (natural compartments) for such carbon black. Roughly speaking, one-third ends up in soils and the rest in surface waters. The total Danish carbon-based air pollution already there does thus not to receive any significant increase contribution of such black carbon emissions.

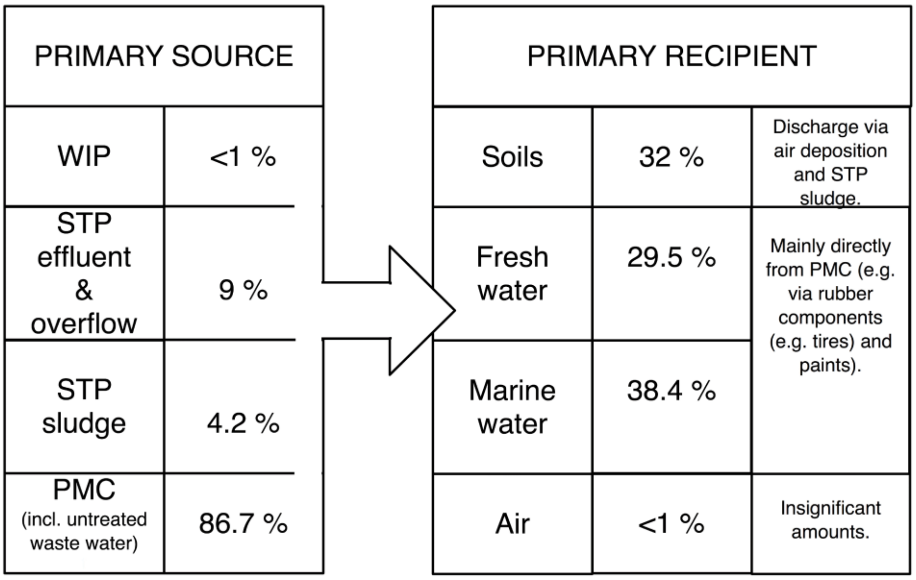

FIGURE 5.22.
OVERVIEW OF THE MOST IMPORTANT CARBON BLACK (CB) SOURCES AND RECEIVERS. THE PERCENTAGES REFLECT MODAL RESULTS (THE MOST FREQUENTLY MODELLED VALUES).

5.10.2 Exposure concentrations in technical compartments

All the PECs predicted for the technical (and natural) compartments are by far higher than all the ones for the other nanomaterials studied in this report. This results directly from much higher use amounts that partially play in kt/a levels, and is thus thousands of times higher than the ones of other nanomaterials, revealing t per year amounts at most. The modal PECs for the STP effluents are (modal value) around 1 mg/l, which is approx. 100 times higher than the ones for photostable nano-TiO_2. These high STP effluent load and the direct release via carbon black products use will contribute to relatively high values in surface water (see next chapter). The sewage treatment sludge results arrive at values ranging from some hundred mg/kg to a few g/kg for some extreme exposure scenarios. These values are in similar ranges, but approximately double as high than the ones for photostable and other nano-TiO_2. The waste mass and waste incineration ashes PECs mostly reveal values ranging from mg/kg (bottom ashes and fly ashes) to 1.4 g/kg levels (waste mass), which are by far the highest ones among all materials in this report, and again, roughly speaking, 50 times higher than the ones of photostable nano-TiO_2.

TABLE 5.17.
PREDICTED ENVIRONMENTAL CONCENTRATIONS (PEC) FOR CARBON BLACK (CB) IN DIFFERENT TECHNICAL AND NATURAL COMPARTMENTS, AS MODELLED FROM COMPUTER-BASED STOCHASTIC SIMULATIONS ON CARBON CLACK RELEASE TO, AND SCENARIOS FOR, FATE/RESIDENCE TIME IN THOSE COMPARTMENTS. THE RESULTS ARE SHOWN AS MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) AND AS LOWER AND UPPER LIMITS CONSIDERED BY 95% RANGES THAT ALSO ILLUSTRATE A 95% PROBABILITY OF THE PECS PRODUCED FALLING WITHIN THEM. FOR SOILS AND SEDIMENTS, AN ANNUAL INCREASE OF PECS IS GIVEN.

Compartments (sources)	**Concentrations**				
	Unit	Mode *median	95% range		
Technical compartments					
Sewage treatment effluent	µg/l	1241	291.8	-	3896
Sewage treatment sludge	mg/kg	2455	582.0	-	7684
Waste mass incinerated	mg/kg	1418	659	-	2523
Bottom ash of waste incineration	mg/kg	140	44	-	1314
Fly ash of waste incineration	mg/kg	539	146	-	8630
Natural compartments					
Surface water (fresh water)	µg/l	0.5	0.1	-	6.0
Sea water	µg/l	0.034	0.015	-	0.080
Sediments (fresh water)*	mg/kg	112.2	5.5	-	335.8
Sediments (sea water)	mg/kg	6.3	2.8	-	14.9
Agricultural soils	mg/kg	0.1	0.047	-	0.2
Natural soils	mg/kg	0.2	0.1	-	0.6
Urban soils	mg/kg	0.4	0.2	-	0.8
Sludge treated soils	mg/kg	0.8	0.2	-	2.6
Air	µg/m3	0.2	0.1	-	0.3

*inconclusive, bipolar (or pluripolar) results or insignifact difference between mode and median

5.10.3 Exposure concentrations in natural compartments

For carbon black, our model reveals by far the highest (compared to all other nanomaterials studied in this report) water exposure concentrations. In fresh water, values around 0.5 µg/l are predicted (fresh water modal value); for some high exposure scenarios, they range up to 6 µg/l. The marine water loads show approx. values ranging from 15 to 80 ng/l. Consequently, the sediment loads are, according to high water exposure, also higher than that of all other substances studied. In 2020, the Monte Carlo-based computations predict modal values of approx. 100-1000 mg/kg and 85 mg/kg for fresh and marine water sediments. The fresh water results do not show a clear modal value since their values almost shaped as uniform probability distributions (see Annex II).

Similar findings may be reported for the carbon fraction in soils where the carbon black load has an expected modal value of 10 mg/kg (STP sludge-treated areas) in 2020, around 100 times higher than that for the copper carbonate. The non-fertilized soil areas (agricultural, natural and urban soils) show approx. modal values between 1 and 5 mg/kg in 2020.

In line with the results presented above, the air concentrations in the model reveal the highest values for carbon black among the nanosubstances studied in this report. Concentrations ranging from 100 to 300 ng/m3 are predicted when considering a 95% value confidence range for all of the Monte Carlo-based computer simulations.

TABLE 5.18.

PREDICTED ENVIRONMENTAL CONCENTRATIONS (PEC) FOR CARBON BLACK (CB) IN SEDIMENTS AND SOILS MODELLED FROM COMPUTER-BASED STOCHASTIC SIMULATIONS ON CARBON CLACK RELEASE TO THOSE COMPARTMENTS. THE PREDICTIONS ARE SHOWN AS MODAL VALUES (MOST FREQUENTLY MODELLED VALUES) AND AS LOWER AND UPPER LIMITS CONSIDERED BY 95% RANGES THAT ILLUSTRATE A 95% PROBABILITY OF THE MODELLED PECS FALLING WITHIN THIS RANGE. THE PEC VALUES REFLECT NANO-TIO_2 CONCENTRATIONS AFTER BEING DEPOSITED IN SEDIMENTS AND SOILS UNTIL THE BEGINNING OF THE YEARS 2014 AND 2020. ALL THE CURVES ARE SHOWN IN ANNEX II OF THIS REPORT.

Compartments	**Concentrations**				
	Unit	Mode *median	95% range		
Prediction for 2014					
Sediments (fresh water)*	mg/kg	729.5	35.9	-	2183
Sediments (sea water)	mg/kg	40.8	18.1	-	97.1
Agricultural soils	mg/kg	0.7	0.3	-	1.3
Natural soils	mg/kg	1.5	0.7	-	3.9
Urban soils	mg/kg	2.6	1.2	-	5.2
Sludge treated soils	mg/kg	5.0	1.6	-	16.6
Prediction for 2020					
Sediments (fresh water)*	mg/kg	1523	75.1	-	4557
Sediments (sea water)	mg/kg	85.2	37.8	-	202.7
Agricultural soils	mg/kg	1.4	0.6	-	2.8
Natural soils	mg/kg	3.2	1.4	-	8.1
Urban soils	mg/kg	5.4	2.5	-	10.9
Sludge treated soils	mg/kg	10.5	3.4	-	34.7

*inconclusive, bipolar (or pluripolar) results or insignifact difference between mode and median

5.10.4 Discussion and conclusions

For all natural compartments, the carbon black study shows the highest exposure results of all nanomaterials studied in this report. This finding also means that some attention should be paid to a general contribution of carbon black to an augmentation of carbon material in the environment. Furthermore, we conclude that the high exposure concentration values are a consequence of the much higher use amounts (kt per year levels instead of t per year) as well as its main use in rubber component mixtures. Such components build an ideal basis for significant material release of all kinds into natural environments because they are exposed to significant and permanent material degradation processes (wear and tear).

However, the high values must be qualified in the sense that they represent for all Monte Carlo scenarios a kind of worst case scenario. Our model assumes the whole released fraction of carbon black to be nanosized material. This certainly represents the needed results for a conservative risk assessment; however, it neglects the fact that such nanomaterial may also be released as parts of non-nanoparticulated material components that still belong to the initial mixture material. Hence, in reality, the pure carbon black nanoparticulated exposure could be lower.

Summary

- The modelled carbon black annual use volumes display kilotonnes values. Such amounts stand for large-scale commercialization of such material.
- The model for carbon black shows for waters and soils an annual load into the environment that exceeds 1,000 tonnes-per-year levels. Most of the target carbon material (approx. 90%) is, however, caught by recycling and other waste mass treatment (landfilling and waste incineration).
- Modal fresh water concentrations are around 0.5 µg/l. The ones in marine waters are roughly ten times lower.
- For terrestrial exposure, we predict some significant contributions to the total carbon load. Concentrations for 2020 of about 10 mg/kg (STP sludge-treated areas) and 1 to 5 mg/kg (non-STP sludge-fertilized areas) are not excluded.
- Among the nanosubstances studied, modal air concentrations are the highest seen in this report, ranging from 100 to 300 ng/m^3.
- This report certainly presents carbon black results for a conservative exposure assessment. We have to emphasize that it neglects that such carbon may also be released as parts of non-nanoparticulated product components of the initial product mixture. Hence, in reality, the pure carbon black nanoparticulate exposure may be lower.
- For general summary points on the assessment of Danish ENM use quantities, please see the summary box on photostable and other nano-TiO_2.

6. Conclusions

Taking an overall view, our results show that currently none of the studied nanomaterials are discharged in high quantities into the natural environment. We did not observe a particularly high Danish nanomaterial production or use (including environmental release). Some noteworthy environmental discharges and exposure were modelled for photostable and other nano-TiO_2 and carbon black (CB) (in the aquatic and terrestrial environment). The same applies to nano-copper carbonate in soils. For those substances particular attention will be paid to possible environmental effects and risks in the subsequent two NanoDEN reports on environmental effects and risk assessment, respectively.

In summary, we are able to state that most of the modelled case studies revealed only a small annual discharge into the natural environment. By “small” we mean that just a few tonnes of ENM are discharged annually into the total environment. In some cases (e.g. nano-Ag, CNT, nano-CeO_2) the discharge load does not reach (even in the high release scenarios) a tonne per year dimension. These conclusions on environmental discharge are in line with earlier Swiss and European results.

In addition to possible exposure concentrations, our model also provides clear concentration limits that exclude non-realistic (not to be expected) exposure levels. In this context, however, we have to explicitly emphasize the limits of interpretation of the reported exposure concentrations. The exposure may in the future be considerably higher with increasing production and use of the target nanomaterials. Companies are currently reluctant to provide current (or anticipated) use quantities of engineered nanomaterials but higher transparency regarding nanomaterial production and use volumes on the part of the industry would make the assessment of exposure considerably more precise. Hence, empirical data on the Danish use of nanomaterials and import quantities would be, by far, the most important factor for improving the environmental exposure model.

Since, it was very difficult to collect specific Danish data on nanomaterial production, imports, applications and amounts, our model is in part (in relation to nano-TiO_2, nano-ZnO, nano-Ag and CNT) based on knowledge of nanomaterial use gathered in the general European (or Swiss) context. However, in investigating these materials we did collect, as far as possible, knowledge that was specific to Denmark and we created a new modelling approach that cannot be considered just a re-work of the earlier studies mentioned above. Annex I lists in detail the new parameters collected, and also for which types of ENM. The clear distinction between our work and the earlier work is also seen in the discrimination (to our knowledge for the first time) between the modelling of photostable nano-TiO_2 and photocatalytic nano-TiO_2. Finally, to the best of our knowledge, we have for the first time presented comprehensive data collection and subsequent modelling for the nanosized substances $CUCO_3$, ZVI, CeO_2, CB, QDs. First results were presented for all target engineered nanomaterial in all studied marine environments (water and sediments).

The novelty of the work presented in this report is also reflected in additional factors: This Danish environmental exposure work benefits from new knowledge presented in the NanoDEN project report 1 (Environmental fate and behaviour of nanomaterials). Report 1 collected and evaluated the latest scientific data on the most important environmental fate and behaviour parameters, which included photochemical degradation, oxidation, reduction, dissolution, precipitation, speciation / complexation, agglomeration, aggregation, sedimentation, adsorption, desorption and biotransformation. It showed, inter alia, that the current database is too thin for incorporating e.g.

photochemical degradation, oxidation, reduction, adsorption, desorption and biotransformation in detail into our mass transfer model. However, new data on the engineered nanomaterial dissolution and aggregation/agglomeration (leading to sedimentation) could be used in our model. Dissolution is observed for metals (e.g. Ag, CeO2 or ZnO) upon contact with water that may occur during the nanoproduct consumption process (e.g. of cosmetics, textiles, paints) or during nanomaterial treatment in sewage treatment plants after being released into waste water from a variety of nanoproducts (cosmetics, textiles, paints, coatings, food, cleaning agents etc.). Another updated parameter is sedimentation, which is crucial for the residence time of the nanomaterial in surface water, including sewage treatment waters (and air) as well as its subsequent discharge into sediments and sewage treatment sludges (and from air into soils and water). Regarding agglomeration/aggregation and subsequent sedimentation, report 1 confirmed all the above across a wide range of possible scenarios. Thus, in our work a large spectrum involving immediate or almost no sedimentation (water-sediment transport) has been used. However, in the context of nano-TiO_2 and nano-ZnO in sewage treatment processes, the Danish computer simulations based, for example, on improved data that shows much higher removal from the water phase compared to the reference studies based on Swiss or European conditions.

For air residence time we used the available knowledge of ultrafine particles. Due to consistently low air release, such a roughness in the model should not have a significant influence on the results. Furthermore, the novelty of the work is also based on its use of the newest and first specific Danish parameters for the quantities of engineered nanomaterials in use. This applies also to the information about the full life cycle of the targeted nanoproducts, which, together with the usage amounts of ENM, have the greatest influence on the environmental release of the nanomaterials studied.

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Nanomaterials in the Danish environment

Rapporten ved hjælp af modelberegninger at forudsiges hvor man kan finde nogle af de mest udbredte nanomaterialer i miljøet i Danmark. Rapportens resultater skal anvendes i en samlet vurdering af nanomaterialers betydning for miljøet i Danmark.

Using modeling techniques the report predicts where to find some of the most widespread nanomaterials in the environment in Denmark. The report's findings are to be used in an overall assessment of the impact of nanomaterials on the environment in Denmark.

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