Danish Ministry of the Environment
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Annex I: Parameters for estimation of releases of nano-materials to the environment in Denmark

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Title:

Annex I - Parameters for estimation of releases of nano-materials to the environment in Denmark

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Contents

Foreword

This document is Annex I to the report "Nanomaterials in the Danish environment. Modelling exposure of the Danish environment to selected nanomaterials". The main report is report 2 of a series of reports from the project “Nanomaterials – Occurrence and effects in the Danish Environment” (“NanoDEN”). The data presented in this annex is the result of a separate sub-project in NanoDEN, which has been running from January 2013 to December 2013 with some revisions in November-December 2014. COWI is the lead institution for the work on this annex.

The data presented in this Annex I has been used to feed into the modelling of total releases and the dispersion and fate of the substances in the environment in Denmark (Report 2). Such engineered nanomaterial data encompasses total releases of these substances from solid waste and waste water treatment, from relevant industrial processes and from a comprehsively estimated diffusive release via wide dispersive uses of nanoproducts and their disposal.

The types of information to be found in this annex report cover two categories:
i) general geography, geometry (and infrastructure) data of the Danish environmental and technical compartments studied, and
ii) engineered nanomaterial (ENM) specific environmental release and fate in those natural and technical environments.

The first category refers to sewage treatment plants (STP) and waste incineration plants (WIP), landfills and recycling processes, as well as to the natural compartments fresh and marine water and sediments, air and soils. The information given in this category ranges from geographical and physical (aquatic) data to waste handling and generic environmental fate data that covers among other the area and population of Denmark, the relevant volume, height and depth of the target compartments, water consumption and waste water production, sewage treatment connection rate, residence time of water in rivers, waste mass fraction incinerated or e.g. generic parameters for material sedimentation from air and waters.

The second category focuses on substance specific environmental release that may occur during production and formulation processes as well as during nanoproduct use and disposal (life cycle based analysis). In addition, the ENM fate (dissolution, sedimentation, residence time etc.) in the target compartments is described for the following engineered nanomaterials: silver (Ag), titanium dioxide (TiO_2)[1] (rutile and anatase), zinc oxide (ZnO), carbon nanotubes (CNTs) , copper carbonate ($CUCO_3$), zero valent iron (ZVI)[2], cerium oxide (CeO_2), carbon black (CB), quantum dots (QDs).

In the chapters on "substance specific model parameters" used to feed the model the reader may also find useful information of a more general character about the ENMs studied such as e.g. data on nanomaterial use quantities and use volume tendencies, discussion on potential manufacturing (formulation) and nanoproduct application fields and their data gaps. Such nanomaterial usage information is complemented by nanomaterial appearance and size distribution data.

[1] In this case we present two modelling studies, one focused on photostable and other nano-TiO_2 and a second one for photo-catalytic nano-TiO_2.
[2] For this nanomaterial this Annex I only provides general information, all the parameters used for the mdoeling – that mostly focus on local scenarios – are shown in detail in the main report (Report 2).

1. General model parameters

The model parameters used for the national, regional and local scenarios are shown in the table below.

Parameters used for the specific local scenario for nano-ZVI are provided in section 2.7.

Name of parameter	Unit	Value	Remark, data source
1.1.1 Geographical data			
Population of Denmark	mill. inhabitants	5.60	Population 2012 (Statistics Denmark, 2013).
Population of the EU	mill. inhabitants	504.4	Wikipedia, List of European Union member states by population
Total area of Denmark	km²	43,000	Southern Denmark including islands (not including Faroe Islands or Greenland). (Statistics Denmark, 2013)
Height of the air compartement	km	1	Height of air considered affected. ECB, 2003. Technical Guidance Document on Risk Assessment. European Chemicals Bureau. Institute for Health and Consumer Protection, European Commission, Dublin.
Area of natural soil	%	21	12% forest + 9% grasslands, heather and moors etc. (Gyldendal, 2013)
Area of agricultural soil	%	66	Agriculture and horticulture (Gyldendal, 2013)
Area of urban soil	%	11	Urban areas and infrastructure (roads, railways, airports) (Gyldendal, 2013)
Area of sludge treated soil	km²	800	Estimate based on max. 7 tons dw/ha/year according to the Danish regulations on use of sludge on soils (Statutory Order No. 1650/2006). (DEPA, 2009 and DANVA, 2009a)
Mean depth of natural soil	m	0.05-0.1	Depth of agricultural soil compartment considered. Low average value: ECB, 2003. Technical Guidance Document on Risk Assessment. European Chemicals Bureau. Institute for Health and Consumer Protection, European Commission, Dublin. Hi average value: Vanwalleghem, T., Poesen, J., McBratney, A., Deckers, J., 2010. Spatial variability of soil horizon depth in natural loess-derived soils. Geoderma 157, 37-45.

Name of parameter	Unit	Value	Remark, data source
Mean depth of agricultural soil	m	0.2	Depth of agricultural soil compartment considered. ECB, 2003. Technical Guidance Document on Risk Assessment. European Chemicals Bureau. Institute for Health and Consumer Protection, European Commission, Dublin.
Mean depth of urban soil	m	0.05	Depth of agricultural soil compartment considered. ECB, 2003. Technical Guidance Document on Risk Assessment. European Chemicals Bureau. Institute for Health and Consumer Protection, European Commission, Dublin.
Soil density	kg m-3	1500	The dry soil density 1500 kg m-3 was computed by neglecting the water content from the standardized 1700 kg. ECB, 2003. Technical Guidance Document on Risk Assessment. European Chemicals Bureau. Institute for Health and Consumer Protection, European Commission, Dublin.
Water-covered surface (fresh water)	km^2 and %	700 (2 %)	Lakes and rivers (Statistics Denmark, 2013)
Water-covered surface (sea waters)	km^2	31,500	Estimate of area within limit of territorial waters (12 nautical miles = 22 km) based on visual assessment of a map of Denmark
Mean depth of fresh water	m	3	Depth of water compartment considered. ECB, 2003. Technical Guidance Document on Risk Assessment. European Chemicals Bureau. Institute for Health and Consumer Protection, European Commission, Dublin.
Mean depth of the sea	m	10	Rough estimate of mean depth within limit of territorial waters (12 nautical miles = 22 km) based on visual assessment of a map of Denmark showing sea depth isocurves.
Sediment density	kg m^{-3}	260	The dry sediemnt density was computed by neglecting the water content from the standardized 1300 kg m^{-3} resulting in 260 kg m^{-3}. ECB, 2003. Technical Guidance Document on Risk Assessment. European Chemicals Bureau. Institute for Health and Consumer Protection, European Commission, Dublin.
Coast line (sea water)	km	7,300	Official figure (Gyldendal, 2013). Use of it for calculation of the sea volume will lead to a serious overestimate.
Coast line (fresh water)	km	128,000	Official figure (Gyldendal, 2013). The length of the Danish shoreline (7300 km) is the length of the shoreline to the sea. The total length of Danish river and streams (mainly the latter) is 64,000 km of which 48.00 km are streams with a width of <2.5 metres, while 14.500 km are between 2.5-8.0 metres wide and only 1.500 km are >8 metres wide. And this has to be multiplied by 2 as each stream/river has two banks/shores.
Sea volume relevant (for discharge of ENM: coastal length, distance from the coast and water depth	km^3	350	Estimate using the width of the Danish territorial waters (12 nautical miles = 22 km) and the estimated mean sea depth within this limit (10 m).

Name of parameter	Unit	Value	Remark, data source
Locations of the sewage treatment plants (STP), distance from the river source	km		All the largest STPs in Denmark are located at the coast. A list is provided separately, which gives the names/locations and effluent volumes (2011) of the 12 largest STPs (data from Danish Nature Agency, 2012).
1.1.2 Aquatic parameters			
Daily water consumption per inhabitant	l/d	130	In 2011 the total effluent volume from Danish STPs was 769 mill. m^3 corresponding to 137 l/d/person. The figure includes the volume of urban runoff in combined sewers, therefore some litres have been subtracted (Danish Nature Agency, 2012)
Residence time of water in rivers (from the source to the stream mouth into the sea)	days	2-2.5	The mean velocity is 0.33 m/s, but in the largest rivers the velocity is typically a little higher i.e. 0.4-0.5 m/s. This gives a residence in the longest river of approx. 3.5-4 days. The average is estimated at some 2-2.5 days.
Fraction of the wastewater treatment plants connected to a) freshwater and b) sea water	%	50 and 50	Danish Nature Agency (2014). Danish Nature Agency (2012).
1.1.3 Waste handling			
Annual sewage treatment sludge production	t dw/year	130,000	Dry weight (2005).(DEPA, 2009)
Sludge disposed of to agricultural soils	%	55	3 % of the agricultural area in DK receives sludge. Dosage is regulated through criteria for N and P per year and a 5 year period. The figures differ from year to year, and from source to source. Estimated average figures. (DANVA, 2009a; Kirkeby *et al.*, 2005; DEPA, 2009)
Sludge incinerated	%	45	
Connection rate of waste water from households and industry to sewage treatment plants	%	97	Based on estimate of the number of homes not connected to sewers (2006) divided by the total number of homes (Statistics Denmark). (Organisation of the Municipalities & Ministry of the Environment, 2010: Report from a working group regarding the performance related to sewage treatment as part of the consultations in connection with the planning in the water sector (in Danish)
Sewage treatment plant overflows (due to heavy rain and flood, overflows escaping STP treatment processes)	% of total water flow to the treatment plants	4	DANVA (2009b): Water in figures (in Danish)
Fraction of the industrial and household waste ending up in waste incineration plants (WIP)?	%	24 and 54	From Danish waste statistis (DEPA, 2013).

Name of parameter	Unit	Value	Remark, data source
Fraction of the industrial and household waste ending up in recycling processes	%	appr. 67 and 38	From Danish waste statistis DEPA, 2013
Fraction of the industrial and household waste ending up in landfills	%	appr. 4 and 4	From Danish waste statistis DEPA, 2013
MSWI: burning, filtration, and acid washing			Detailed modelling according to (Walser and Gottschalk, 2014). See also the following information.
Use of bottom ash in construction works	%	100	Bottom ash is recycled almost 100 % in road construction, soil consolidation and anti-frost layers under buildings. A few percent are landfilled. Virksomhedernes Miljøguide (Environmental guide for entreprises), 2013: Slagger fra affaldsforbrændingsanlæg (Bottom ash from waste incinerators) .
Fly ash ending up in recycling (cement production), export and landfill	%	39 22 39	According to Sun *et al.* (2014) that base their values on (Walser *et al.*, 2012).
Landfills: leachate escape to soils waters?	% of total leachate	0	At one Danish landfill, leachate from inert waste and other less contaminated waste (7%) is leached through the soil to the sea after recirculation. (DEPA, 2010; RenoDjurs I/S, 2013) However, due to the uncertainties that are too large when considered the whole area of Denmark and totally missing data for ENM fate analysis the modellimg was stopped at the landfill compartment by considering it as an ENM sink. This occurred in accordance to a zero leaching out of landfills as suggested by others (Sun *et al.*, 2014).
Recycling processes: escape to soils waters etc.?		0	See line above second paragraph.
Annual volume of slag from WIPs	t/y	Approx. 850.000	Hansen and Olsen, 2004
Annual volume of fly ash from WIPs	t/y	Approx. 53.000	Hansen and Olsen, 2004
Annual volume of municipal solid waste	t/y	3.8	Computed based on the bottom ash volume: After burning, 1 tonne of MSW there will be e.g. a production of 221 kg of bottom ash (slag) (Salzmann, C. Modelling and Quantification of Emissions from Municipal Solid Waste Incineration in Europe. Swiss Federal Institute of Technology Zürich Zurich, 2008).

Waste incineration processes were organized as illustrated i Figure 1 and modelled (see Table 1) as suggested by others (Walser and Gottschalk, 2014).

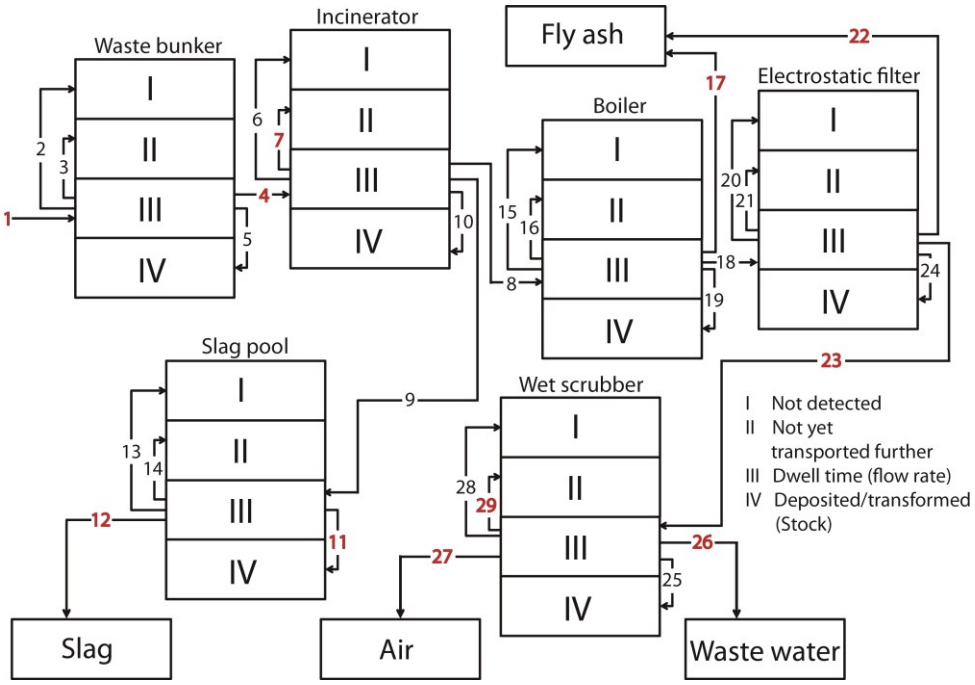


FIGURE 1
MODEL STRUCTURE FOR THE ENGINEERED NANOMATERIAL (ENM) TRANSPORT AND FATE IN WASTE INCINERATION PLANTS SHOWN IN (WALSER AND GOTTSCHALK, 2014). RED: MEASUREMENT POINTS. THE ENM TRANSPORT AND TRANSFER WERE 11ODELLED BASED ON THE MEASUREMENT DATA AND TRANSFER COEFFICIENTS BETWEEN THE COMPARTMENTS (AND SUBCOMPARTMENTS) OF THE PROTOTYPICAL WASTE INCINERATION PLANT.

TABLE 1
MASS TRANSFER AND FATE FRACTIONS FOR ALL RELEVANT PATHS OF THE METALLIC ENM STUDIED IN A WASTE INCINERATION PLANT SYSTEM DERIVED FROM (WALSER AND GOTTSCHALK, 2014)

Transfer path	Transfer factors 5% quantiles	Medians	95 % quantiles
1.	1.000E+00	1.000E+00	1.000E+00
2.	*Considered either in path 4 or path 5*		
3.	*Considered either in path 4 or path 5*		
4.	9.524E-01	9.762E-01	1.000E+00
5.	1.228E-13	2.379E-02	4.757E-02
6.	*Considered either in path 8, 9 or path 10*		
7.	*Considered either in path 8, 9 or path 10*		
8.	1.179E-01	1.817E-01	2.455E-01
9.	3.625E-01	5.585E-01	7.545E-01
10.	1.232E-13	2.598E-01	5.195E-01
11.	2.679E-28	5.189E-02	1.038E-01

Transfer path	Transfer factors 5% quantiles	Medians	95 % quantiles
12.	8.962E-01	9.481E-01	1.000E+00
13.	*Considered either in path 11 or path 12*		
14.	*Considered either in path 11 or path 12*		
15.	*Considered either in path 17, 18 or path 19*		
16.	*Considered either in path 17, 18 or path 19*		
17.	3.165E-01	3.328E-01	3.490E-01
18.	6.498E-01	6.504E-01	6.510E-01
19.	8.224E-13	1.683E-02	3.367E-02
20.	*Considered either in path 22, 23 or path 24*		
21.	*Considered either in path 22, 23 or path 24*		
22.	9.039E-01	9.517E-01	9.995E-01
23.	2.023E-04	3.680E-04	5.337E-04
24.	1.265E-12	4.794E-02	9.587E-02
25.	3.352E-09	3.501E-01	7.001E-01
26.	2.999E-01	6.499E-01	1.000E+00
27.	3.352E-09	7.264E-09	1.118E-08
28.	*Considered either in path 25, 26 or path 27*		
29.	*Considered either in path 25, 26 or path 27*		

*The same marked transfer categories do not necessarily exactly add up to one in a particular column of quantiles, for mass balance computations one value has to be derived in dependence of the others.

Name of parameter	Unit	Value	Remark, data source
1.1.4 Environmental fate			
Sedimentation from air	d/year	10 retention time in air	No quantitative values on ENM deposition from the atmosphere are available. Sedimentation factors were derived as suggested earlier (Sun *et al.*, 2014) from information on life-time of ultrafine particles (Anastasio and Martin, 2001)
Sedimentation from fresh water	%	0-100	The sedimentation processes in natural waters could not be considered mechanistically due to an inconclusive data situation (Praetorius *et al.*, 2012; Praetorius *et al.*, to be submitted). Due to a highly complex Danish river and lake scenery the mass transfer from the fresh water phase into sediments (not reaching sea water) was accounted for by considering all events between and including two extreme scenarios of complete sedimentation and absolutely no sedimentation.
Sedimentation from sea water	%	100	Sea water sediments represent the final sink for ENM that ends up in sea water. The modeled ENM sea water concentrations reflect the worst case situation before the ENM sedimentation process started.
Terrestric compartments	na	na	Material fate processes were not conisdered in any kind of soils. All solis are therefore modeled as final sinks.
Soil-water transfer	%	Approx. 0.6	ENM in soil may be trasnported to surface waters due to ersoion or during storm events etc. According to others (Sun *et al.*, 2014) 0.549% was used as a transfer factor from soils to surface water, a mean value that has been derived from data of diffuse transfer of linear alkylbenzene sulphonate (LAS) (Kannan *et al.*, 2007).
Dissolution upon contact with water	%	See data below for each specific material.	The elimination of ENM in the product use phase was modeled as dissolution upon contact with water for different products as indicated below in each specifi case. For carbon based ENM or e.g. for nano-TiO2 such dissolution was not considered.
1.1.5 Volumes of the technical and environmental compartments			
Agricultural soils	kg	8.3e+12	43,000*10^6*(0.2*0.66*0.97)*0.6*2500 43,000 km² total area of Denmark 10^6 is the transformation factor from km2 to m2 0.2 m is the depth considered for agricultural soil 0.66 is the share of agricultural land area 0.97 is the proportion of agricultural land not treated with sewage treatment plant (STP) sludge 0.6*2500=1500 kg/m³ used density of dry soil
Natural soils	kg	1.1e+12	43,000*10^6*((0.05-0.1)*0.21) *0.6*2500 43000 km² total area of Denmark 10,^6 is the transformation factor from km2 to m2 0.05 -0.1 m depth used for natural soil (mean value) 0.21 is the share of natural land area 0.6*2500=1500 kg/m³ used density of dry soil

Name of parameter	Unit	Value	Remark, data source
Urban soils	kg	3.5e+11	43,000*10^6*(0.05*0.11)*0.6*2500 43,000 km² total area of Denmark 10^6 is the transformation factor from km2 to m2 0.05 m depth used for natural soil 0.11 is the share of urban land area 0.6*2500=1500 kg/m³ used density of dry soil
Sludge (biosolid) treated soils	kg	2.4e+11	800*10^6*0.2*0.6*2500 800 km² sludge treated area 10^6 is the transformation factor from km2 to m2 0.2 m is the depth considered for agricultural soil 0.6*2500=1500 kg/m³ used density of dry soil
Surface water (fresh water)	l	2.1e+12	700*10^6*3*1000 700 km² water covered surface (fresh water) 10^6 is the transformation factor from km2 to m2 3 m is the depth of water compartment considered 1000 is the transformation factor from m³ to litre
Surface water (sea water)	l	3.5e+14	350*10^9*1000 350*10^9 m³ relevant water volume 1000 is the transformation factor from m³ to litre
Sewage treatment plant (STP) effluents	l	2.57288135 e+11	130*365*5,590,000*0.97 130 l/head is the daily water consumption 5590000 Danish population 0.97 is the connection rate to central sewage facilities
Sediments (fresh water)	kg	5.46e+09	700*10^6*0.03*0.2*1300 700 km2 water covered surface (fresh water) 10^6 is the transformation factor from km2 to m2 0.03 m sediment depth 0.2*1300=260 kg/m³ density of sediments soil
Sediments (sea water)	kg	2.73e+11	3.5*10^10*0.03*0.2*1,300 3.5*10^10 m² relevant surface (sea water sediment) 0.03 m sediment depth 0.2*1300=260 kg/m³ density of sediments soil
Atmosphere	m³	4.3e+13	43,000*1*10^9 43000 km² total area of Denmark 1 km assumed depth of air affected by ENM transformation factor from km³ to m³
Sewage treatment plant (STP) sludge	kg	1.3e+08	130,000*1,000 130,000 t annual sewage treatment sludge volume in Denmark 1,000 is the transformation factor from t to kg

Name of parameter	Unit	Value	Remark, data source
Municipal waste for incineration	kg	1.86e +9	2,590,000*1000/7997000*5590000 2.59 million tons Swiss waste volume scaled to Danish conditions based on the population numbers 1000 is the transformation factor from t to kg
Waste incineration plant (WIP) bottom ash	kg	8.5e+08	850,000*1000 Annual volume of slag from Danish waste incineration plants (WIP) 1000 is the transformation factor from t to kg
Waste incineration plant (WIP) fly ash	kg	5.3e+07	53,000*1000 Annual volume of fly ash from Danish waste incineration plants (WIP) 1000 is the transformation factor from t to kg

2. Substance-specific model parameters

2.1 Photostable nano titanium dioxide (TiO_2)

Photostable nano-TiO2 and other applications of nano-TiO2		
2.1.1 General description		
Name	Nanosized titanium dioxide, photo-stable	 Source: Wikipedia
CAS number	13463-47-7	
Chemical composition	TiO2	
Appearance	White powder	

Nanomaterial description

Titanium dioxide is the naturally occurring oxide of titanium. Often a distinction is made by TiO2 manufacturers between pigmentary grade and ultrafine grade. The primary crystal size typically ranges from 150 to 300 nm for TiO2 of a pigmentary grade. The ultrafine grade typically has a primary crystal size from 10 to 150 nm. The pigmentary TiO2 has a white colour and is therefore widely used in paints etc. The ultrafine TiO2 including nano-sized TiO2 is transparent.

The rutile and anatase crystal forms of TiO2 are the most important in relation to the use of TiO2 in consumer products. In contrast to the bulk TiO2 (>100 nm) that is considered chemically inert, nano-scale TiO2 and in particular the anatase form can act as a photo-catalyst that can generate reactive oxygen species upon illumination. Both UV-light and visible light can induce the catalytic activity of TiO2 and the anatase crystal form is a more efficient photocatalyst than the rutile form. Although normally considered to be insoluble material it can be made water dispersible by applying certain surface treatments. (Mikkelsen *et al.*, 2011)
In dry form, TiO2 nanomaterials will tend to agglomerate due to interaction of the particle surfaces, but the degree of agglomeration is depended on the specific surface treatment, relative humidity, sample aging, etc. Both fine and ultrafine TiO2 may be surface treated to increase their applicability in products, e.g. to ensure a uniform distribution in sunscreens or to optimize UV absorption properties. (Mikkelsen *et al.*, 2011).

The total global production of pigmentary TiO2 is about 4.4 million tonnes and account for about 99% of the total consumption of TiO2 (DuPont, 2010). Even the typical crystal size of the pigmentary grade is above 100 nm, crystals in the nano-size may take up a significant part of the pigmentary grade TiO2 and the pigmentary grade may thus be a source of nano-TiO2 to the environment. Electron microscopy and stability testing of food-grade TiO2 suggests that approximately 36% of the particles are less than 100 nm in at least one dimension and that it readily disperses in water as fairly stable colloids (Weir *et al.*, 2012). However, filtration of water solubilized consumer products and personal care products indicated that less than 5% of the titanium was able to pass through 0.45 or 0.7 µm pores. Data on the content of nano-TiO2 in in quantitative terms of different grades of pigmentary TiO2 have not been available. Sun *et al.* (2014) provide mass balances for the EU of the pigmentary TiO2, but do not estimates the potential releases of nano-TiO2 as a consequence of the use of the pigmentary TiO2.

Photostable nano-TiO2 and other applications of nano-TiO2

General applications

A wide range of applications exist for TiO_2 nanomaterials exploiting the various properties of TiO_2 nanomaterials. Pigmentary TiO_2 is widely used as a pigment in paints, whereas nano-scale TiO_2 is widely used in sunscreens and cosmetics due to the UV-absorption of the material. In paints and for water treatment nano-scale TiO_2 is used as a photo-catalyst producing reactive oxygen that may degrade organic contaminants. Finally, a number of other and very diverse set of applications exists such as ointments, toothpaste, catalysts, catalyst supports, adsorbents, delustrants, semiconductors, etc. In some consumer products, e.g. sunscreens, the percentage of nano-TiO_2 may constitute several percent of the product. TiO_2 rank as one of the most used chemicals world-wide (mainly as a pigment), but the tonnages of nano-TiO_2 used nationally, in the EU or worldwide can at present not be estimated. Given the range of possible applications of nano-TiO_2, the use is anticipated to increase significantly in the near future. (Mikkelsen *et al.*, 2011)

In order to discriminate varying life cycle and release (environmental exposure) pathways the report distribute the use categories of TiO2 nanomaterials reported in Sun *et al.* (2014) into two groups:

- Photostable nano-TiO2 and other nano-TiO2 applications: cleaning agent, spray, cosmetics, paper, plastics, batteries & capacitors, light bulbs, glass & ceramics, consumer electronics, textiles, food, ink, sport goods (covered by the next chapter)
- Photocatalytic nano-TiO2: Paints, metals, cement, filters. (covered by this chapter).

Photostable and other nano-TiO2 applications - It is difficult to define that other applications only use photostable TiO2, it may be a mixture of those properties. Therefore, the second category comprises both application where the photostability of nano TiO2 is applied and other applications. In such applications the chemical stability is crucial, hence, the photocatalytic properties – when exposed to ultraviolet (UV) radiation – have to be avoided/suppressed by coating the TiO2 nanomaterial e.g. with silica and alumina and other (US EPA, 2010a).

Photocatalytic TiO2 - Photocatalytic TiO2 is a material category defined as application where the photolytic effects represent the main target material property. The photocatalytic properties of TiO2 are used in experimental and some commercial fields e.g. for the following purposes: degradation of organic compounds, and destruction of microbiological organisms as well as for transforming e.g. metals to less soluble material forms in waters and air environments (waste and drinking water, indoor air (US EPA, 2010). Photostable nano-TiO2 applications include : e.g. cosmetics, coatings and paints etc.

2.1.2 Manufacturing and import/export of the substance on its own

Manufacturing processes	A large number of manufacturing processes exist for ultrafine grade of TiO_2 many of which use either titanium tetrachloride or titanyl sulfate as starting material. These include precipitation, thermal hydrolysis and flame hydrolysis. For the ultrafine grade, the crystal may be further processed involving milling, then coating and milling again. Depending on the medium relevant to the application for marketing, a possible last dispersion step (with water / cosmetic oils) can be applied for example for UV attenuation dispersion grades. If no further dispersion is done, the products obtained are UV attenuation powder grades. Both fine and ultrafine TiO2 may be surface treated to increase their applicability in products, e.g. to ensure a uniform distribution in sunscreens or to optimize UV-absorption properties. (Mikkelsen *et al.*, 2011)		
Manufacturing in Denmark	Nanosized TiO_2 is not manufactured in Denmark		
Name of parameter	**Unit**	**Value**	**Remark, data source**
Import of the substance on its own or in mixtures to Denmark	t/year	2.5-30	Estimated as the total of the uses for formulation processes in Denmark mentioned below.
Re-export	% of import	no data	No export of the substance on its own has been identified

2.1.3 Formulation in Denmark

Photostable nano-TiO_2 and other applications of nano-TiO_2			
Identified formulation processes in Denmark	Titanium dioxide is widely used as a pigment i various mixtures and materials and used for many different formulation processes in Denmark such as manufacture of pigments, paint and varnishes, adhesives, plastics, cosmetics, and food items. Intentional use of photostable TiO_2 in nanoform for the manufacture of pigments, paint and varnishes, and cosmetics has been confirmed. In all the mixtures the TiO_2 is used for UV protection. TiO_2 in nanoform may potentially be used to some extent for the manufacture of UV protective plastics and textiles, but an actual use for manufacturing processes in Denmark has not been confirmed. A survey of nanomaterials in products on the Danish market indicates the use of titanium dioxide as pigment in ostomy and incontinent devices and plasters (Tønning *et al.*, 2014). According to information obtained from industry, the used titanium dioxide is pigment grade and thus not here considered as nano-material.		
Name of parameter	**Unit**	**Value**	**Remark, data source**
Formulation 1: Production of pigments, paint and lacquers and adhesives			
Number of companies	companies	2-10	The use of TiO_2 in nanoform for these formulation processes have been grouped for confidentiality reasons as less than three companies are involved in the production of some of the product types.
Quantities used	t/year	2-20	
Ending up in final products	%	97%	

Photostable nano-TiO2 and other applications of nano-TiO2			
Release* to municipal waste water system * without any other indications the release values were reduced/ enlarged on each side by 50% for the modeling of symmetrical triangular distributions around the specified quantities. The symmetry may possibly be by the absolute border values (highest or lowest possible release value, 1 and 0). In cases were more values are given, the mean is taken as modeal value for such distributions.	%	<0,25	The emission scenario document (ESD) for the paint industry from the OECD (2009) assume for manufacture of aqueous dispersion coatings that the total fraction of raw materials lost to waste from the manufacturing process is 1.5%. This includes 1% lost due to residues in the mixing vessels and 0.5% due to residues in bags, spills and product returns. It is in the ESD assumed that half of the residue material in the mixing vessels will be re-used in the manufacturing process (recycling. For aqueous dispersion coatings the remaining equipment residue is assumed to be removed in water washings and hence to waste water. According to information from Danish manufactures waste water originates from cleaning of tanks and other production equipment. Approximately 1-2% of the total used may be released to the waste water for pre-treatment/treatment at the manufacturing sites. The first step at all sites is a precipitation/flocculation where the majority of the TiO2 is precipitated and ends up in a sludge/filter cake which is disposed of for external incineration or gasification. The pre-treated waste water is either directed to municipal waste water plants or further treated at the manufacturing sites. In the latter case, the waste water is further treated. The waste water is first treated by pre-precipitation tank, then by biological treatment (do not remove TiO2) and ultimately by a final polishing. As a worst case estimate, the releases to municipal waste water treatment plants or surface water is estimated to be <0,5%. The actual release is probably significantly below this value. As the pre-treated waste water is either directed to municipal waste water treatment plants or to surface water, the emission to each of the pathways is estimated to be <0.25 %
Direct release to surface water (after internal WW treatment)	%	<0,25	Worst case estimate – the total release is probably significantly below the <0.25%.
Direct release to air	%		The TiO2 is imported as pastes in which the TiO2 is dispersed in water. The generation of dust by handling of the pastes is considered insignificant.
Disposed of as solid waste for incineration	%	2	Filtercake/sludge and TiO2 remaining in packaging are disposed of for incineration or gasification.
Transformation during use into other forms	%		Considered insignificant

Photostable nano-TiO2 and other applications of nano-TiO2			
Percentage of produced products exported	% of quantity in final product	Majority	
Formulation 2: Production of cosmetics			
Number of companies	companies	<4	
Quantities used	t/year	0,5-10	According to a new survey, sunscreens manufactured in Denmark for the Danish market in general do not contain TiO2 in nano-form (Tønning *et al.*, 2014). Most Danish cosmetic producers offer a range of products in compliance with the ecolabel 'Svanemærket' which does not allow the use of nanomaterials with a few exceptions. This has led to a substitution of the former widespread use of titanium dioxide for the benefit of chemical UV filters in sunscreen (Tønning *et al.*, 2014). According to information from Danish manufacturers of cosmetics, nano-TiO2 is still used for UV protection in mascara, eyeliner, face powder and foundation. The use of TiO2 for these applications has been introduced within the last year. A few years ago one of the major manufacturers was reported to use 1-10 tonnes nano TiO2 for sunscreens (Tønning and Poulsen, 2007). It has not been possible to obtain updated information on the use of TiO2 in the Danish cosmetics industry.
Ending up in final products	%	95%	
Release to municipal waste water system	%	2	Water used to wash containers is handled as common waste water (Tønning and Poulsen, 2007). The percentage is roughly estimated from the experience from other formulation processes.
Direct release to surface water (after internal WW treatment)	%		No direct discharges to surface water
Direct release to soil	%		No direct releases to soil

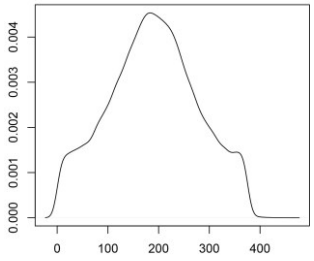
Photostable nano-TiO2 and other applications of nano-TiO2			
Direct release to air	%	<0.01	According to Tønning and Poulsen (2007), TiO2 nanoparticles are purchased as a powder. The powders are handled in 25 kg bags which are cut open, hereafter the content is dispersed in the mixture that constitutes the base of the products. The OECD has not developed an Emission Scenario Document (ESD) for the cosmetics industry but some of the mixing processes may be comparable with the paint industry. According to the ESD (OECD, 2009) for the paint industry when using pigments and fillers in powder form the emissions are estimated at 0.5-1.0% by weight of the raw materials in powder form. It is supposed, that 95% of this will be removed by the ventilation system. The remaining is assumed to settle on the surfaces inside the workshop. The percentage captured by air extraction systems is assumed to be 95% - and the percentage of solid raw materials released to the atmosphere is estimated at 0.0095% of the raw materials used. The remaining part of the generated dust is assumed to be disposed of as solid waste.
Disposed of as solid waste for incineration	%	1	Empty bags containing small amounts of material are disposed as regular waste. (Tønning and Poulsen, 2007). 0.5-1% in the form of generated dust is estimated to be disposed of as regular waste. The percentage is roughly estimated from the experience from other formulation processes.
Disposed of for other waste management	%	2	Whole bags and miss productions are disposed as hazardous waste (Tønning and Poulsen, 2007) The percentage is roughly estimated from the experience from other formulation processes.
Transformation during use into other forms	%		Considered insignificant
Percentage of produced products exported	% of quantity in final product	no data	

Photostable nano-TiO2 and other applications of nano-TiO2

2.1.4 Import/export and end-use in articles and mixtures

	End use	Percentage of total *1 Lower, mean, higher value (l,m,h)
1	Plastics	0, 3.6, 12
2	Cosmetics	0.33, 59.4, 94
3	Cleaning agents	0, 6.2, 16
4	Consumer electronics	0,6.9, 18
5	Battery	0, 0.4, 2
6	Light bulb	0, 0.2, 1
7	Glass & ceramics	0, 1.7, 10
8	Textiles	0,0.3, 1
9	Food	0, 0.4, 2
10	Paper	0, 0.003, 0.02
11	Ink	<0.0003
12	Sporting goods	0, 1.5 , 6
13	Spray	0, 0.2, 1
14	Metals	0, 0.1, 1

1 Note that these values due not sum up to 100% since they refer to the total of both applications (photostable and photocatalytic) nano-TiO2

Photostable nano-TiO2 and other applications of nano-TiO2	
Identified uses in articles and mixtures	In the model, the total use in Denmark will be computed by scaling raw data from other regions into Danish dimensions based on the comparison of the population figures. Sun *et al.* (2014) summarize current available quantitative estimations: The US EPA (US EPA, 2010) reports for the global use/production of nano-TiO2 12'500 t/y; while a study by Nightingale *et al.* (2008) suggests such amounts being around 5'000 t/y. A market analysis from 2011 (FutureMarkets, 2011a) indicates that the global production of nanoparticle TiO2 in 2010 was 50,400 t/y and project the production to reach 201,500 tons by 2013. Dupont (2010) indicates the global market to be less than 26,000 t/y in 2010. Considering the different estimates, most likely the total global consumption of nano TiO2 will be in the range of 10,000-50,000 t/y. Piccinno *et al.* (2012) provided an industry survey indicating European use ranging from 55 to 3'000 tons. The figures are reached by adding up the estimates for each application area. Others (Hendren *et al.*, 2011) reported for US production volumes a range between 7'800 and 44'400 tons. Schmid *et al.* (2008) came up with survey based production/use volumes per year of nano-TiO2 for Switzerland of 436 tons. On the basis of the survey of use of nano-TiO2 in Europe (Piccinno *et al.*, (2012)), the total consumption of nano-TiO2 (both photostable and photocatalytic) in Denmark with finished products (import and domestic production) is roughly estimated at 0.6-465 t/y. This range is used to complement the annual use volume modelled in a reference study by others (Sun *et al.*, 2014) and scaled down for Danish conditions. The latter work uses raw values (for Switzerland and appr. by a factor 1.43 higher than equivalent Danish figures) that range from 1.8t/a (Piccinno *et al.*, 2012) to 1'606 t/a (Schmid and Riediker, 2008). This approach seems to be rather conservative and result in a very high uncertainty, but is used in order to the approach is used in order to ensure that the model estimates span the full range of possible outcomes. Based on the ENM use categorization in Sun *et al.* (2014) we could attribute in average 19.2 % of TiO_2 nanomaterial to the photocatalytic titanium and the rest to the material categorization photostable and other nano-TiO_2. Lower, upper boundary and mean mass fraction of nano-TiO2 modelled for the allocation to different product applications represent the basis for computing nano-TiO2 release from those applications.  Figure 2 Annual and total nano-TiO2 use in Denmark (t/a).

Such a release model tracks nano-TiO2 emissions throughout the complete life cycle of these categories.

The distribution on end uses and parameter values are taken from the 2014 study (Sun *et al.*, 2014) and reflect the fraction of the total nano-TiO production that is used in a specific product category. The mean, the lower and upper limit values describe the average quantities of triangular shaped probability distributions produced via the used MC model procedure (Gottschalk *et al.*, 2010).
numbers containing such ENM.

In order to count the relevant (only commercially available) nanoproducts and allocate them to these product categories, data from several sources was used for this allocation (Sun *et al.*, 2014):

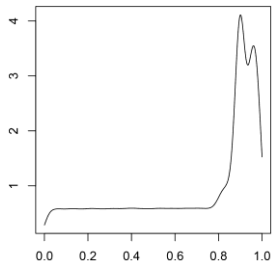
- Company survey with direct distributional data (Piccinno *et al.*, 2012)
- Inventories of nano-products: Woodrow Wilson Centre for Scholars' Project on Emerging Nanotechnologies (Woodrow Wilson Institute, 2012) ANEC/BEUC Inventory (ANEC/BEUC, 2010); the BUND inventory (BUND, 2011); nanotechnology patents (Lem *et al.*, 2012)
- A market report (Future Markets, 2011).
- Internet search on Google, Yahoo and EC21 in order to count the numbers of products on the market.

The knowledge available from these data were either the fraction of ENM in a particular application category or the product numbers containing such ENM.
Lower, upper boundary and mean mass fraction of ENM modelled for the allocation to different product applications. Details on such computation from different sources are explained in detail below and exemplary for the nano-TiO2 and based on a recent study (Sun *et al.*, 2014).
The distribution on end-uses of nano-TiO2 presented by Sun *et al.*, 2014 is here divided into two groups: photostable and other applications of TiO2 (this section) and photoactive TiO2 (next section).

Photostable nano-TiO2 and other applications of nano-TiO2			
Name of parameter	**Unit**	**Value**	**Remark, data source**
End-use 1: Plastics			
Total consumption	% of total consumption of TiO_2	3.6	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%		
Disposed of to MSWI	%	100	
End-use 2: Cosmetics			
Total consumption	% of total consumption of TiO_2	59.4	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%	85	
Direct release to surface water	%	10	
Disposed of to MSWI	%	5	
End-use 3: Cleaning agent			
Total consumption	% of total consumption of TiO_2	6.2	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%	95	
Disposed of to MSWI	%	5	
End-use 4: Consumer electronics			
Total consumption	% of total consumption of TiO_2	6.9	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Disposed of to MSWI	%	5	
Disposed of for recycling (excl. energy recovery)	%	75	
Export	%	20	
End-use 5: Batteries and Capacitors			
Total consumption	% of total consumption of TiO_2	0.4	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Disposed of to MSWI	%	13	
Disposed of for recycling (excl. energy recovery)	%	33	

Photostable nano-TiO2 and other applications of nano-TiO2			
Export		54	
End-use 6: Light bulbs			
Total consumption	% of total consumption of TiO_2	0.2	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Disposed of to MSWI	%	80	
Disposed of for recycling (excl. energy recovery)	%	20	
End-use 7: Glass and ceramics			
Total consumption	% of total consumption of TiO_2	1.7	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%	1	
Disposed of to MSWI	%	20	
Disposed of for recycling (excl. energy recovery)	%	79	
End-use 8: Textiles			
Total consumption	% of total consumption of TiO_2	0.3	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%	1	
Direct release to air	%	1	
Disposed of to MSWI	%	50	
Export	%	48	
End-use 9: Food			
Total consumption	% of total consumption of TiO_2	0.4	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%	90	
Disposed of to MSWI	%	10	
End-use 10: Ink			
Total consumption	% of total consumption of TiO_2	<0.003	Not quantified in the model due to extremely low assumed amounts.
Release to municipal waste water system	%	80	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).

Photostable nano-TiO2 and other applications of nano-TiO2			
Disposed of to MSWI	%	20	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
End-use 11: Paper			
Total consumption	% of total consump-tion of TiO_2	0.003	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%	10	
Disposed of for recycling (excl. energy recovery)	%	80	
Export	%	10	
End-use 12: Sporting goods			
Total consumption	% of total consump-tion of TiO_2	1.5	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%	2	
Direct release to air	%	2	
Disposed of to MSWI	%	96	
End-use 13: Spray			
Total consumption	% of total consump-tion of TiO_2	0.2	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%	85	
Direct release to air	%	10	
Disposed of to MSWI	%	5	
End-use 14: Metals			
Total consumption	% of total consump-tion of TiO_2	0.1	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%	5	Release specific data for all end uses were used as presented in the newest study for Swiss conditions (Sun *et al.*, 2014). This seems reasonable since the crucial release parameters e.g. in landfilling, waste and wastewater treatment are e.g. very similar in these countries. Single data points are given. However, according to Sun *et al.* (2014) these single values are deviated on each side by 50% and a triangular distribution computed.
Disposed of to MSWI	%	5	
Disposed of for recycling (excl. energy recovery)	%	90	

Photostable nano-TiO2 and other applications of nano-TiO2			
2.1.5 Waste water treatment			
Name of parameter	**Unit**	**Value**	**Remark, data source**
Transformation during STP treatment into other forms	%	0	See next line.
Percentage ending up in sludge	% (l, m, u)	20, 60, 98	We modelled empirical distributions with mean, an the lower and upper limit values as indicated in the column adjacent that follow the newest evidence that in turn is based on the following sources: real plant experiments conducted by others (Westerhoff *et al.*, 2011) showed removal efficiency for Ti between 96.1% to 99.4% with a mean value of 98.3%. Gomez-Rivera *et al.* (Gomez-Rivera *et al.*, 2012) (2012) showed in a laboratory-scale activated sludge system the removal of CeO2 that probably can also be used for a TiO2 case. These authors came up with a total CeO2 removal of 96.6%, for the CeO2 smaller than 200 nm removal efficiency of 98.5% was seen. Other CeO2 removal experiments in a model wastewater treatment plant and showed an efficiency between 95% and 98% (Limbach *et al.*, 2008). Our values reflect also other sources that cover and confirm the spectrum as describedabove .(Zhang *et al.*, 2008; Hwang *et al.*, 2011; Johnson *et al.*, 2011; Wang *et al.*, 2012)  Figure 3. Modelled probability distribution of STP removal efficiency for generic nano-TiO2. In the model procedure the data from these sources were computed by using weighting factors: the highest factors were given to data taken from full scale STP experiments/measurements, lower ones to evidence taken from pilot STP experiments, and the lowest weighting factor for quantitative values from batch laboratory experiments. The weighting factor assignment is given in detail in the annex of the report of subprojects 2 and 4 and corresponds to (Sun *et al.*, 2014).
Percentage discharges	% (l, u)	2-80	See line above.
2.1.6 Solid waste treatment (incineration and landfill)			
Name of parameter	**Unit**	**Value**	**Remark, data source**

Photostable nano-TiO2 and other applications of nano-TiO2			
Transformation or deposition during incineration into other forms (average Danish MSWIs)	%	approx. 0.1-52 (deposition, transformation)	According to Mueller *et al.* (2013) three main processes of waste incineration processes are relevant: i) burning, ii) filtration, and iii) acid washing (wet-flue gas cleaning). We considered the nanoparticle fate during such processes based on measurement evidence for CeO2 (Walser *et al.*, 2012). In line with the above mentioned CeO2 study the partition of all target metallic nanomaterials between waste bunker, incinerator, boiler, electrostatic filter, wet scrubber, slag and fly ash was modelled as done in Walser and Gottschalk (2014). Mass transfer and fate parameters (see please Figure 1) are modelled as shown below in Table 1 that reflects the values derived from computer based simulations combined with real analytic/experimental results. These results show the steady state mass transport/transformation for all relevant WIP paths reached after steady state mode of such plants (infinite time scale). This means that analytically not detected and not further transported material mass has been assigned to the subsequent further transport and/or to the subsequent deposition/transformation by covering at each stage in the WIP process the entire range of transport and fate possibilities. A distinction between material deposition and transformation was not possible due to analytical limitations. However, in contrast to others we quantified also such not further studied mass volumes that were ignored by others (Gottschalk *et al.*, 2009; Sun *et al.*, 2014) assuming zero deposition and transformation for nano-TiO2.
Percentage emitted to the air (average Danish MSWIs)	%	~0	See line above. The efficiency of filter processes depends on the particle-size rather than on material composition (Sun *et al.*, 2014). Others (Walser *et al.*, 2012) report removal efficiency of filter up to to 99.9%. This is totally in line with earlier evidence (Burtscher *et al.*, 2001) (> 99.5% efficiency) used in other occasions (Gottschalk *et al.*, 2009; Sun *et al.*, 2014). Regarding the removal of acid washing processes the mentioned studies agree on values higher than 99.9%.
Percentage ending up in residues (average Danish MSWIs)	%	approx. 36-75 (slag) approx. 3-9 (fly ash)	See line above on nanoparticle deposition transformation for sources and data. Reijnders (2005) reports for Denmark over 72% of the ash of waste incineration processes being reused for the construction of cycling tracks, parking lots, roads etc.
Release from landfills to municipal waste water treatment	kg/year	0	For landfill, no leachate out is assumed (Sun *et al.*, 2014).
Direct release from landfills to surface water	kg/year	0	See line above.

Photostable nano-TiO2 and other applications of nano-TiO2			
Transformation during landfilling into other forms	%	No data	At this point we stopped our modelling. Nanomaterial fate and behaviour during landfilling was not considered. See also general comments on landfilling.
2.1.7 Recycling			
Type of recycling activities	Recycling of the bottom ash of waste incineration processes		
Name of parameter	**Unit**	**Value**	**Remark, data source**
Transformation during recycling into other forms	**%**	No data	Currently quantitative information that could be used to model fate and behaviour of ENM during and after recycling is not available. Hence according to others (Sun *et al.*, 2014), we did not track the material fate and mass flows of the studied nanoparticles during and after the recycling process.
Ending up in recycled products	**%**	72 (of the bottom ash of waste incineration processes)	See comments above for percentages ending up in residues (average Danish MSWIs).
Release from recycling process	**% of recycled**	0	See first line on transformation during recycling into other forms.

2.2 Photocatalytic titanium dioxide (TiO2)

Photocatalytic titanium dioxide (TiO_2)		
2.2.1 General description		
Name	Nanosized titanium dioxide, photocatalytic	 Source: Wikipedia
CAS number	13463-47-7	
Chemical composition	TiO2	
Appearance	White powder	

Photocatalytic titanium dioxide (TiO_2)

Nanomaterial description

The overall description TiO2 is included in section 2.1.1.

In contrast to the bulk TiO2 (>100 nm) that is considered chemically inert, nano-scale TiO2 and in particular the anatase form can act as a photo-catalyst that can generate reactive oxygen species upon illumination. Both UV-light and visible light can induce the catalytic activity of TiO2 and the anatase crystal form is a more efficient photocatalyst than the rutile form. Although normally considered to be insoluble material it can be made water dispersible by applying certain surface treatments. (Mikkelsen *et al.*, 2011)

Both the anatase and rutile crystal structures act as photocatalysts; however, it is widely accepted that the anatase polymorph generally shows higher photocatalytic or photoreactive effect than the rutile polymorph (Carp, Huisman *et al.* 2004; Chen and Mao 2007 as cited by Sørensen *et al.*, 2014). As a consequence, most photocatalytic consumer products contain nano-sized anatase titanium dioxide. (Sørensen *et al.*, 2014)

Doping of photocatalytic titanium dioxide - Contrary to titanium dioxide used as pigments, photocatalytic titanium dioxide grades are generally not coated since this would inhibit the desired photoreactivity. Instead, various dopants have been widely studied to improve the photocatalytic performance of titanium dioxide on the degradation of various organic substances. It has been found that the presence of a metal ion in the titanium dioxide matrix significantly influences the photoreactivity of titanium dioxide. Doping with small amounts of Fe3+, Mo5+, Ru3+, Os3+, Re5+, V4+ or Rh3+ (0.1-0.5 w%) may significantly increase the photoreactivity, while Co3+ and Al3+ doping may decrease the photoreactivity (Chen and Mao 2007 as cited by Sørensen *et al.*, 2014).

Applications

A new survey for the Danish EPA lists the following applications of photoactive TiO2 (Sørensen *et al.*, 2014). The survey is not limited to uses in Denmark and for most of the applications limited evidence of use in Denmark has been obtained.

General applications

Paints – One use of nano-TiO2 in paint in the intentional use of nano-sized anatase titanium dioxide in paint, which has been developed to exploit the photo-reactive properties of nano-sized anatase titanium dioxide for decomposing organic substances and bacteria on the surface to achieve self-cleaning/antibacterial effects. In the preliminary product screening, a total of 16 paint undertaken by Sørensen *et al.* (2014) products that apply photo-reactive TiO2 particles were identified. Among the paints applied in Denmark is roof paint with photo-reactive TiO2.

Coatings - The use of coatings for surfaces has the explicit purpose of protecting the surfaces from bacteria and other pollutants; the so-called Clean Catalytic Surfaces. Herein, the specific use of nano-sized anatase titanium dioxide is very much desired due to its photocatalytic properties. Many of the commercially available coatings are aimed at the DIY market, where surfaces on buildings and metal, stone and glass can be coated to gain the self-cleaning property. The application techniques of the coatings include spray coating at room temperature or elevated temperatures (400-600 ºC) and application by brush. In the preliminary product screening by Sørensen *et al.* (2014), a total of 43 coating products that contain photocatalytic titanium dioxide particles were identified.

Construction materials - The major applications of titanium dioxide-based photocatalytic construction and building materials are air pollution remediation, self-cleaning and self-disinfection. For all products the driving force is solar light (and the presence of water). Construction and building materials are optimal media for applying the photocatalytic nano materials because large areas are exposed to light. Several pilot projects have been carried out to verify the effectiveness of photocatalytic construction and building materials. Successful commercialization of self-cleaning surfaces includes concrete, mortar, glass, titles and ceramic products. These products enable buildings to maintain their aesthetic appearance over time. Similar, a number of self-disinfecting building materials have been commercialized to achieve a microorganism free environment. Lastly, a number of building materials enable of decomposing air pollutant (including volatile organic compounds and oxides such as NO, NO2 and SO2) have been commercialized; including roofing felt and pavement blocks.

Water treatment systems - Photocatalytic water treatment systems are applied for the removal of trace contaminants and pathogens (Savage and Diallo 2005; Qu, Alvarez *et al.* 2013 as cited by Tønning *et al.* (2014)). Two configurations are commonly used:

slurry reactors and immobilized. Photocatalytic water-treatment applications have almost become a mature market as systems based on artificial UV light have been on the market for several years and systems for treating municipal, industrial, swimming facility, drinking and ballast water are also available (Saari, Iler *et al.* 2010 as cited by Sørensen *et al.* (2014)).

Photocatalytic UV irradiation using titanium dioxide nanoparticles as a catalyst is applied for removal of bacteria and other pollutants in water treatment systems, air cleaners and construction materials. Contrary to the product groups mentioned above, the nano-sized titanium dioxide has been deposited as a thin film to the surface of most of these product groups at the time of purchase. Most thin films are synthesized using a gas phase method, i.e. chemical/chemical vapour deposition, spray pyrolysis deposition (Carp, Huisman *et al.* 2004). In the preliminary product screening by Sørensen *et al.* (2014), a total of 35 products that apply photo-reactive titanium dioxide particles were identified.

Air cleaners - A limited number of air cleaners using artificial UV light and titanium dioxide as a catalyst for the removal of pathogens, viruses and volatile organic compounds are marketed. Most of the air cleaners have one or more pre-filtration steps before the air is passed over the titanium dioxide-coated surface.

2.2.2 Manufacturing and import/export of the substance on its own

Manufacturing processes	The overall description the manufacturing of tiO2 is included in section 2.1.2.		
Manufacturing in Denmark	Nanosized TiO_2 is not manufactured in Denmark		
Name of parameter	**Unit**	**Value**	**Remark, data source**
Import of the substance on its own uses to Denmark	t/year	1-10	
Re-export	% of import		No export of the substance on its own has been identified

2.2.3 Formulation in Denmark

Identified formulation processes in Denmark	The use of photoactive TiO2 for the manufacture of paint in Denmark has been confirmed by Sørensen *et al.* (2014). The photoactive TiO2 is among others used for protection against microbial growth on roof paints.		
Name of parameter	**Unit**	**Value**	**Remark, data source**
Formulation 1: Production of paint and lacquers			
Number of companies	companies	<4	
Quantities used	t/year	1-10	Exact figures not available. The quantities are roughly estimated.
Ending up in final products	%	97.5%	

Photocatalytic titanium dioxide (TiO_2)			
Release to municipal waste water system * Unless otherwise noted the release values were reduced/ enlarged on each side by 50% for the modeling of symmetrical triangular distributions around the specified quantities. The symmetry may possibly be by the absolute border values (highest or lowest possible release value, 1 and 0). In cases were more values are given, the mean is taken as modeal value for such distributions.	%	<0,5	The emission scenario document (ESD) for the paint industry from the OECD (2009) assume for manufacture of aqueous dispersion coatings that the total fraction of raw materials lost to waste from the manufactring process is 1.5%. This includes 1% lost due to residues in the mixing vessels and 0.5% due to residues in bags, spills and product returns. It is in the ESD assumed that half of the residue material in the mixing vessels will be re-used in the manufacturing process (recycling. For aqueous dispersion coatings the remaining equipment residue is assumed to be removed in water washings and hence to waste water. According to information from Danish manufactures waste water originates from cleaning of tanks and other production equipment. Approximately 1-2% of the total used may be released to the waste water for pre-treatment at the manufacturing sites. The first step at all sites is a precipitation/flocculation where the majority of the TiO2 is precipitated and ends up in a sludge/filter cake which is disposed of for external incineration or gasification. The pretreated waste water is directed to municipal waste water plants. As a worst case estimate, the releases to municipal waste water treatment plants are estimated to be <0,5%. The actual release is probably significantly below this value.
Direct release to surface water (after internal WW treatment)	%	0	No direct discharge to surface water
Direct release to soil	%	0	
Direct release to air	%	0	The TiO2 is imported as pastes in which the TiO2 is dispersed in water. The generation of dust by handling of the pastes is considered insignificant.
Disposed of as solid waste for incineration	%	2	Filtercake/sludge and TiO2 remaining in packaging are disposed of for incineration or gasification.
Transformation during formulation into other forms	%		Considered insignificant
Percentage of produced products exported	% of quantity in final product	No data	

Photocatalytic titanium dioxide (TiO_2)

2.2.4 Import/export and end-use in articles and mixtures

Identified uses in articles and mixtures

The distribution on end-uses of nano-TiO2 presented by Sun *et al.* (2014) is here divided into two groups: photostable and other applications of TiO2 (previous section) and photoactive TiO2 (this section).

Please note that the indicated percentages of the use of photoactive TiO2 shown below are percentage of the total consumption of nano-TiO2. The terms in the brackets indicated the terms used for the application areas in Sun *et al.* (2014)

	End use	Percentage of total TiO_2 consumption Lower, modal , higher value (l,m,h)
1	Paints	0, 8.9, 26
2	Coatings	0, 3.7, 19
3	Construction materials (Cement)	0, 0.1, 1
4	Waste water treatment	0, 0.7, 4
5	Cleaning of water and air (Filters)	0, 5.8, 26

Name of parameter	Unit	Value	Remark, data source
End-use 1: Paints			
Total consumption	% of total consumption of TiO_2	8.9	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014). A part of the nano TiO2 used for paint may in fact be photostable TiO2 applied for UV protection. The transfer coefficients used in the Swiss study has been reconsidered for the Danish situation as shown below
Release to municipal waste water system	%	1	Dust and flakes from maintenance of painted surfaces and from abrasion of painted surfaces
Direct release to surface water	%	1	Dust and flakes from maintenance of painted surfaces and from abrasion of painted surfaces
Direct release to soil	%	1	Dust and flakes from maintenance of painted surfaces and from abrasion of painted surfaces
Direct release to air	%	1	Dust and flakes from maintenance of painted surfaces and from abrasion of painted surfaces
Disposed of to MSWI	%		Paint remaining in packaging and paint on wood and other combustible materials
Disposed of to landfill	%	50	Paint on concrete and other non-combustible building materials
Disposed of for recycling (excl. energy recovery)	%	46	Paint on metals
End-use 2: Coatings			

Photocatalytic titanium dioxide (TiO_2)			
Total consumption	% of total consum-ption of TiO_2	3.7	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Direct release to surface water	%		[In the Danish situation probably a part will be discharged directly to the environment from areas with municipal separate storm water sewer systems]
Release to municipal waste water system	%	90	
Direct release to air	%	5	
Disposed of to MSWI	%	5	
End-use 3: Construction material (Cement)			
Total consumption	% of total consump-tion of TiO_2	0.1	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%	1	
Disposed of to landfill	%	19	
Disposed of for recycling (excl. energy recovery)	%	80	
End-use 4: Waste water treatment			
Total consumption	% of total consump-tion of TiO_2	0.7	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%	95	[The information on the use of nano TiO2 for waste water treatment in the Danish survey indicates that the nano TiO2 has been deposited as a thin film and is not released to the waste water - Should be reconsidered]
Disposed of to MSWI	%	5	
End-use 5: Cleaning of water and air (Filters)			
Total consumption	% of total consump-tion of TiO_2	5.8	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%	25	(Sun *et al.*, 2014)
Direct release to air	%	5	(Sun *et al.*, 2014)
Disposed of to MSWI	%	70	(Sun *et al.*, 2014)

2.2.5 Waste water treatment

Name of parameter	Unit	Value	Remark, data source
Transformation during STP treatment into other forms	%	-	See indications for Photo-stable and other nanomaterial titani-um dioxide (TiO2)

Photocatalytic titanium dioxide (TiO_2)			
Percentage ending up in sludge	% (l, m, u)	-	See line above.
Percentage discharges	% (l, u)	-	See line above.
2.2.6 Solid waste treatment (incineration and landfill)			
Name of parameter	**Unit**	**Value**	**Remark, data source**
Transformation or deposition during incineration into other forms (average Danish MSWIs)	%	approx. 0.1-52 (deposition, transformation)	See remarks on data and sources for phostostable nano-TiO2.
Percentage emitted to the air (average Danish MSWIs)	%	~0	See line above.
Percentage ending up in residues (average Danish MSWIs)	%	approx. 36-75 (slag) approx. 3-9 (fly ash)	See line above.
Release from landfills to municipal waste water treatment	kg/year	0	For landfill, no leachate out is assumed (Sun *et al.*, 2014).
Direct release from landfills to surface water	kg/year	0	See line above
Transformation during landfilling into other forms	%	No data	At this point we stopped our modelling. Nanomaterial fate and behaviour during landfilling was not considered. See also general comments on landfilling.
2.2.7 Recycling			
Type of recycling activities	No recycling activities identified		

2.3 Zinc oxide (ZnO)

Zinc oxide (ZnO)		
2.3.1 General description		
Name	Zinc oxide (ZnO)	 Source: (Wikimedia, 2013)
CAS number	1314-13-2	
Chemical composition	Zinc: 80.34%, Oxygen: 19.6%	
Appearance		

Zinc oxide (ZnO)

Nanomaterial description

Crystalline ZnO may show a wurtzite (B4) crystal structure with hexagonal dimensions (space group C6mc) (Wang, 2004). Zinc oxide (ZnO) nanomaterial is available in the form of dispersions and powders that show in general antibacterial, anti-corrosive, antifungal and/or UV filtering effects (AZoNano, 2013). These authors underline that such nanomaterial is addressed in the literature also by various synonyms such as permanent white, zinci oxicum, oxydatum, ketozinc and oxozinc. Wang (2004) showed that ZnO displays one of the richest variety on nanostructures and material properties among all nanomaterials: strong piezoelectric and pyroelectric properties and the use as semiconductor (that can be made highly conductive by doping) suitable for short wavelength applications are e.g. emphasized among other properties such as that ZnO crystals that ensure efficient excitonic emission, or ultraviolet (UV) luminescence shown in disordered ZnO nanoparticles and thin films, as well as that ZnO is transparent to visible light.

General applications

Piccinno *et al.* (2012) report for nano-ZnO very similar (compared to nano-TiO_2) applications by listing all above paints, cosmetics and sunscreens. The cosmetic use is confirmed also by others (AZoNano, 2013) by mentioning popularly known calamine lotions containing zinc oxide powder and the use in ointments for treating skin diseases. Filter application in rubber and cigarettes and the application as an additive in the manufacture of concrete and zinc oxide powders for the Ceramic industry and as additive material for the food industry are also mentioned. Others (Steinfeldt *et al.*, 2013) focused on nano-ZnO application in glass coatings by stressing that this type of ENM would improve the optical material characteristics by reducing (as seen above) UV permeability while simultaneously increasing the visible transmittance. These authors also refer to others (Lowry *et al.*, 2008) that for their part emphasize the use in coatings due to material properties, such as being stable and nonmigratory within coating matrices, ending up in a longer service life for the target coated products. Coating agent use is also mentioned for paints (AZoNano, 2013). A promising future field of applications has been demonstrated for optoelectronics, sensors, transducers and biomedical sciences due to the fact that such ZnO is as seen above a multi-functional material and due to its high variety of growth morphologies, such as nanocombs, nanorings, nanohelixes/nanosprings,nanobelts, nanowires and nanocages (Wang, 2004). Wang (2004) pays particular attention to nanobelts as nanosensors, nanocantilevers, field effect transistors and Nanoresonators.

Nano-ZnO is according to the Cosmetics Regulation (Regulation (EC) No 1223/2009) not included in the list of UV filter allowed in cosmetic products in the EU and Denmark.

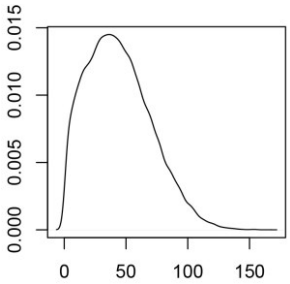
2.3.2 Manufacturing and import/export of the substance on its own

Manufacturing processes			
Manufacturing in Denmark	Nanosized zinc oxide is not produced in Denmark.		
Name of parameter	**Unit**	**Value**	**Remark, data source**
Import of the substance on its own uses to Denmark	kg/year		
Re-export	% of import		

2.3.3 Formulation in Denmark

Identified formulation processes in Denmark	No formulation processes involving nanosized zinc oxide in Denmark have been identified.

2.3.4 Import/export and end-use in articles and mixtures

Zinc oxide (ZnO)	
Identified uses in articles and mixtures	 Figure 4. Annual nano-ZnO use in Denmark (t/a). Total use of the substance in articles and mixtures in Denmark is estimated at 0.6-165 t/year (minimal and maximal value used in our MC based mass flow model. The figure is adapted from Swiss values declared to show different levels of reliability expressed as degree of belief (DoB) of 80% and 20% (Sun *et al.*, 2014) and based on a comparison of the population numbers Denmark-Switzerland. According to Sun *et al.* (2014) the DoB was considered as a combination of Bayes inference and Monte Carlo calculations in a Markov Chain Monte Carlo (MCMC) approach by computing more or fewer values (in relation to their DoB) based on each corresponding rough input production value. 80% reliability was attributed to 70 t/y (Schmid and Riediker, 2008) and to the range between 0.2 and 911 t/y (Piccinno *et al.*, 2012), 20% reliability used as prior knowledge to 0.15 (Nightingale *et al.*, 2008), 4.4 (Zhang and Saebfar, 2010) and 84 t/y (Aschberger *et al.*, 2011). In our model these raw values for total use valid for Switzerland were scaled down data from other regions (Switzerland; Europe and global dimensions) into Danish levels based on the comparison of the population numbers. Sun *et al.* (2014) summarize current available quantitative estimations: Nightingale *et al.* (2008) suggest global 18 t/y nano-ZnO production, Zhang and Saebfar (2010) reported 528 t/y; others (Aschberger *et al.*, 2011) suggest 10,000 t/y. Another group (Schmid and Riediker, 2008) suggests 70 t/y for the Swiss nano-ZnO production/use; European results of 5.5 to 28,000 t/y were reported as well (Piccinno *et al.*, 2012). In a further step the total annual use volume was allocated to end use categories. Such categories integrate ENM containing products with similar material life-cycles characteristics where we could assume identical environmental release kinetics

Zinc oxide (ZnO)			
	The computed ENM fraction in each category reflects as described in detail in Gottschalk *et al.* (2009) the counted number of products per category multiplied by the assumed share of the overall distributed ENM mass in each product. Lower, upper boundary and mean mass fraction of ENM modelled for the allocation to different product applications. Details on such computation from different sources are explained in detail below and exemplary for the nano-TiO2 and based on a recent study (Sun *et al.*, 2014). Such comprehensive data collection and preparation bases on information from the ANEC/BEUC Inventory (ANEC/BEUC, 2010), the nanomaterial market report (Future Markets, 2011), the Woodrow Wilson Centre inventory of the for Scholars' Project on Emerging Nanotechnologies (WWI, 2012), the BUND inventory (BUND, 2011) as well as a summary of nanotechnology patents (Lem *et al.*, 2012) and an own internet search using Google, Yahoo and EC21.		

	End use	Percentage of total Lower, modal, higher value (l,m,h)
1	Cosmetics	27, 83, 100
2	Paints	0, 14, 57
3	Filters	0, 0.1, 1
4	Consumer electronics	0, 0.2, 1
5	Plastics	0, 2, 11
6	Textiles	0, 0.01, 0.02
7	Paper	0, 0.02,0.14
8	Woods	0, 0.01, 0.04
9	Foods	0, 0, 0.01
10	Cleaning agents	0, 0.15, 1
11	Metals	0, 0, 0.02
12	Glass & ceramics	0, 0.7, 4

Name of parameter	Unit	Value	Remark, data source Unless otherwise noted mean values used for triangular distributions with 50% deviation on each side that refer to Sun *et al.* (2014).
End-use 1: Cosmetics			
Total consumption	% of total consumption	83	Percentage (mean value) of the total nano-ZnO. As mentioned elsewhere, nano-ZnO is not included in the list of UV filter allowed in cosmetic products in the EU and Denmark. Even some products may not be in compliance with the Regulation it seems unlikely that cosmetics should account for a majority of the use nano-ZnO. The figures are kept here for the first round of computing as a worst case estimate.

Zinc oxide (ZnO)			
Release* to municipal waste water system * Unless otherwise noted the release values were reduced/ enlarged on each side by 50% for the modeling of symmetrical triangular distributions around the specified quantities. The symmetry may possibly be by the absolute border values (highest or lowest possible release value, 1 and 0). In cases were more values are given, the mean is taken as modal value for such distributions.	%	75	
Direct release to surface water	%	10	
Disposed of to MSWI	%	5	
Transformation during use into other forms	%	10	Transformation in the form of dissolution during the use phase was considered as material elimination due to contact with water (Sun *et al.*, 2014).
End-use 2: Paints			
Total consumption	% of total consump-tion	14	Percentage (mean value) of the total nano-ZnO use (Sun *et al.*, 2014).
Release to municipal waste water system	%	1	
Direct release to surface water	%	1	
Direct release to soil	%	1	
Direct release to air	%	1	
Disposed of to MSWI	%		
Disposed of to landfill	%	50	Disposed off with non-combusible building materials
Disposed of for recycling (excl. energy recovery)	%	41	
Transformation during use into other forms	%	5	Transformation in the form of dissolution during the use phase was considered as material elimination due to contact with water (Sun *et al.*, 2014).
End-use 3: Filters			

Zinc oxide (ZnO)			
Total consumption	% of total consump-tion	0.1	Percentage (mean value) of the total nano-ZnO use (Sun *et al.*, 2014).
Release to municipal waste water system	%	20	
Direct release to air	%	5	
Disposed of to MSWI	%	70	
Transformation during use into other forms	%	5	
End-use 4: Consumer Electronics			
Total consumption	% of total consump-tion	0.2	Percentage (mean value) of the total nano-ZnO use (Sun *et al.*, 2014).
Disposed of to MSWI	%	5	
Disposed of for recycling (excl. energy recovery)	%	75	
Transformation during use into other forms	%	20	
End-use 5: Plastics			
Total consumption	% of total consump-tion	2	Percentage (mean value) of the total nano-ZnO use (Sun *et al.*, 2014).
Disposed of to MSWI	%	100	
End-use 6: Textiles			
Total consumption	% of total consump-tion	0.01	Percentage (mean value) of the total nano-ZnO use (Sun *et al.*, 2014).
Release to municipal waste water system	%	1	
Direct release to air	%	1	
Disposed of to MSWI	%	58	
Transformation during use into other forms	%	30	
Export		30	
End-use 7: Paper			
Total consumption	% of total consump-tion	0.02	Percentage (mean value) of the total nano-ZnO use (Sun *et al.*, 2014).
Disposed of to MSWI	%	25	

Zinc oxide (ZnO)			
Disposed of for recycling (excl. energy recovery)	%	70	
Export	%	10	
End-use 8: Woods			
Total consumption	% of total consump-tion	0.01	Percentage (mean value) of the total nano-ZnO use (Sun *et al.*, 2014).
Release to municipal waste water system	%	1	
Disposed of to MSWI	%	94	
Transformation during use into other forms and re-lease to air	%	5	Transformation in the form of dissolution during the use phase was considered as material elimination due to contact with water (Sun *et al.*, 2014).
End-use 9: Foods			
Total consumption	% of total consump-tion	<0.01	Percentage (mean value) of the total nano-ZnO use (Sun *et al.*, 2014).
Transformation during use into other forms	%	100	Complete dissolution is considered due to contact with gastric acid in stomach (Sun *et al.*, 2014).
End-use 10: Cleaning agent			
Total consumption	% of total consump-tion	0.15	Percentage (mean value) of the total nano-ZnO use (Sun *et al.*, 2014).
Release to municipal waste water system	%	90	
Direct release to air	%	5	
Disposed of to MSWI	%	5	
End-use 11: Metals			
Total consumption	% of total consump-tion	<0.02	Percentage (mean value) of the total nano-ZnO use (Sun *et al.*, 2014).
Release to municipal waste water system	%	5	
Disposed of to MSWI	%	5	
Disposed of for recycling (excl. energy recovery)	%	90	
Transformation during use into other forms	%		
End-use 12: Glass & ceramics			

Zinc oxide (ZnO)			
Total consumption	% of total consump-tion	0.7	
Release to municipal waste water system	%	1	
Direct release to air	%		
Disposed of to MSWI	%	20	
Disposed of to landfill	%		
Disposed of for recycling (excl. energy recovery)	%	74	
Transformation during use into other forms	%	5	
Export	%		

2.3.5 Waste water treatment

Name of parameter	Unit	Value	Remark, data source
Transformation during STP treatment into other forms	%	100	(Lombi *et al.*, 2012) reported on the fate and behaviour of zinc oxide nanosized particles during anaerobic digestion in wastewater and post-treatment processes of sewage sludge. These authors concluded that after such treatments the target particles were transformed into non-nanomaterial forms.
Percentage ending up in sludge	%	-	See comments above.
Percentage discharges	%	-	See comments above.

2.3.6 Solid waste treatment (incineration and landfill)

Name of parameter	Unit	Value	Remark, data source
Transformation or deposi-tion during incineration into other forms (average Danish MSWIs)	%	approx. 0.1-52 (deposition, transfor-mation)	Mass transfer and fate parameters (see please Figure 1) for all metallic ENMs in a waste incineration system are modelled as shown below in Table 1 that reflects the values derived from computer based simulations that were combined with real analytic/experimental results of a detailed nano-CeO_2 case study (Walser and Gottschalk, 2014). These results show the steady state mass transport/transformation for all relevant WIP paths reached after steady state mode of such plants (infinite time scale). This means that analytically not detected and not further transported material mass has been assigned to the subsequent further transport and/or to the subsequent deposition/transformation by covering at each stage in the WIP process the entire range of transport and fate possibilities. See also comments on the nano-TiO_2 cases.
Percentage emitted to the air (average Danish MSWIs)	%	~0	See line above.

Zinc oxide (ZnO)			
Percentage ending up in residues (average Danish MSWIs)	%	approx. 36-75 (slag) approx. 3-9 (fly ash)	See line above.
Release from landfills to municipal waste water treatment	kg/year	0	For landfill, no leachate out is assumed (Sun *et al.*, 2014).
Direct release from landfills to surface water	kg/year	0	See line above.
Transformation during landfilling into other forms	%	No data	At this point we stopped our modelling. Nanomaterial fate and behaviour during landfilling was not considered. See also general comments on landfilling.
2.3.7 Recycling			
Type of recycling activities	**description**		
Name of parameter	**Unit**	**Value**	**Remark, data source**
Transformation during recycling into other forms	**%**	No data	Currently quantitative information that could be used to model fate and behaviour of ENM during and after recycling is not available. We did not track the material fate and mass flows of the studied nanoparticles during and after the recycling process. See also comments on the previus cases.
Ending up in recycled products	**%**	~20	Most part directly after product use. Bottom ash is e.g. recycled up to 100 % in road construction, soil consolidation and anti-frost layers under buildings. A few percent are landfilled. Virksomhedernes Miljøguide (Environmental guide for entreprises), 2013: Slagger fra affaldsforbrændingsanlæg (Bottom ash from waste incinerators) .
Release from recycling process	**% of recycled**	0	See lines above.

2.4 Silver (AgNP)

Silver (Ag)		
2.4.1 General description		
Name	Silver; Nano-AG; AgNP	
CAS number	7740-22-4 (elemental Ag)	
Chemical composition	Ag	

Silver (Ag)		
Appearance	White lustrous powder	 Source: http://www.tradevv.com/

Nanomaterial description

Nanosilver particles (AgNP) is the nanoform of silver characterized by being spherical particles of sizes ranging from 1-250 nm. AgNP is commercialized as powder, flakes, grains, ingots, etc., and is sold in suspension (in water, alcohol or surfactant) and as a dry powder. AgNP also available in preparations (e.g. as a coating agent, in alloys, etc.) and in articles (electrodomestic appliances, in textiles, in food packages, etc.). In its pure form AgNP will aggregate and hence nanosilver is often surface modified with for instance dextran, citrate, or PVP. Sometimes AgNP is also found to be deposited on or used as a coating of a substrate such as plastic, silica or polymers, to give a desired adhesion, electrical conductivity, etc. In aqueous solutions AgNP forms dissolved free silver ions in aqueous by dissolution and subsequent oxidation. (Mikkelsen *et al.*, 2011)

General applications

The use of AgNP is very diverse and include therapeutic applications (diet supplement), personal care products, powdered colours, varnish, textile, paper, interior and exterior paints, printing colours, water and air-purification, polymer-based products and foils for antibacterial protection such as washing machines, kitchenware and food storage. The AgNP concentrations used are unknown for most applications. The scale of use of AgNP is unknown at this point in time, but expected to increase rapidly as more and more consumer products with AgNP are entering the market. (Mikkelsen *et al.*, 2011)
In some types of applications, the AgNP is dispersed in mixture (e.g. paint or printing colours) whereas in others it may be adhered to a surface (e.g. in textiles), or it may be embedded in a polymer matrix as in hygienic surfaces of kitchenware and equipment for food storage.

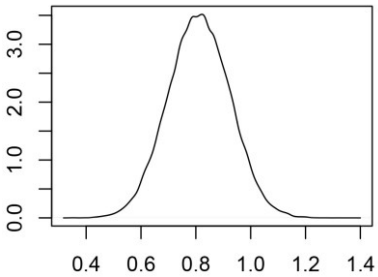
2.4.2 Manufacturing and import/export of the substance on its own

Manufacturing processes	Ultra-sonic precipitation, chemical vapour deposition, exploding wire synthesis. The size, shape, surface area, etc. can be modified by adding various surface active agents and coatings to syntheses involving silver salts.		
Manufacturing in Denmark	AgNP is not manufactured in Denmark		
Name of parameter	**Unit**	**Value**	**Remark, data source**
Import of the substance on its own uses to Denmark	kg/year	No data indentified	
Re-export	% of import	No data indentified	

2.4.3 Formulation in Denmark

Identified formulation processes in Denmark	No formulation processes with the use of AgNP in Denmark have been identified.

2.4.4 Import/export and end-use in articles and mixtures

Silver (Ag)	
Identified uses in articles and mixtures	 Figure 5. Annual nano-Ag use in Denmark (t/a). Total Danish use of nanao-Ag in articles and mixtures is modelled between x-x t/year (minimal and maximal value used in the MC model). The figure 5 reflects data of different levels of reliability modeled as degree of belief (DoB) of 80% and 20% (Sun *et al.*, 2014) considered as a combination of Bayes inference and Monte Carlo calculations by computing more or fewer values (in relation to their DoB) and by comparing the population numbers Denmark-Switzerland. For nano-Ag annual global productions/use volumes were presented from different groups (Sahasrabudhe, 2010; Scheringer *et al.*, 2010; Aschberger *et al.*, 2011; Piccinno *et al.*, 2012; Windler *et al.*, 2013). The raw data of use volume for Switzerland (that have been scaled down for Denmark approx. with a factor of 0.7)) with Degree of Belief as reported in detail in Sun *et al.* (2014): 80% reliability was attributed to values ranging from 0.02 t annual use (Piccinno *et al.*, 2012) to 3 t annual use (Schmid and Riediker, 2008). 20% reliability was attributed to values ranging from 0.36 t/a (Blaser *et al.*, 2008) to 4.2 t/a (Aschberger *et al.*, 2011) As shown in figure 5 the modelled final use of the substance in Denmark is assumed to range approx. from 0.3-1.4 t/a with modal values around 0.8 t/a. In an additional step the total annual use volume was linked to end use categories. Such categories integrate ENM containing products with similar material life-cycles properties leading to (assumed) identical environmental release characteristics. Lower, upper boundary and mean mass fraction of ENM modelled for the allocation to different product applications. Details on such computation from different sources are explained in detail below and exemplary for the AnNP and based on a recent study (Sun *et al.*, 2014).

Silver (Ag)			

	End use	Percentage of total Lower, mean, higher value (l,m,h)
1	Textiles	15, 25, 35
2	Cleaning agents	2, 6, 15
3	Paints	0, 3, 15
4	Consumer electronics	11, 38, 60
5	Cosmetics	4, 10, 31
6	Medtech	0, 4, 15
7	Plastics	0, 3, 7
8	Food	0, 7, 24
9	Glass & ceramics	0, 1, 4
10	Metals	0, 2, 12
11	Soil remediation	0, 1, 4
12	Filtration	0, 0.3, 0.6
13	Sanitary	0, 0.16, 0.5
14	Paper	0, 0.1, 1

Name of parameter	Unit	Value	Remark, data source
End-use 1: Textiles			
Total consumption	%	25	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system * Unless otherwise noted the release values were reduced/ enlarged on each side by 50% for the modeling of symmetrical triangular distributions around the specified quantities. The symmetry may possibly be by the absolute border values (highest or lowest possible release value, 1 and 0). In cases were more values are given, the mean is taken as modal value for such distributions.	%	32	Derived from empirical data as suggested by others (Sun *et al.*, 2014)
Direct release to air	%	5	
Disposed of to MSWI	%	32	
Disposed of for recycling (excl. energy recovery)	%	6.4	
Transformation during use into other forms	%	5	

Silver (Ag)			
Export	%	25.6	
End-use 2: Cleaning agent			
Total consumption	%	6	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%	85	
Direct release to air	%	5	
Disposed of to MSWI	%	5	
Transformation during use into other forms	%	5	Transformation in the form of dissolution during the use phase was considered as material elimination due to contact with water (Sun *et al.*, 2014).
End-use 3: Paints			
Total consumption	%	3	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%	1	
Direct release to surface water	%	1	
Direct release to soil	%	1	
Direct release to air	%	1	
Disposed of to landfill	%	50	
Disposed of for recycling (excl. energy recovery)	%	41	
Transformation during use into other forms	%	5	Transformation in the form of dissolution during the use phase was considered as material elimination due to contact with water (Sun *et al.*, 2014).
End-use 4: Consumer electronics			
Total consumption	%	38	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%		
Disposed of to MSWI	%	5	
Disposed of for recycling (excl. energy recovery)	%	75	
Export	%	20	

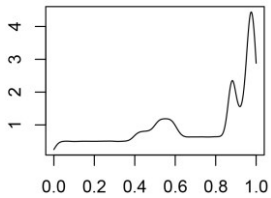
Silver (Ag)			
End-use 5: Cosmetics			
Total consumption	%	10	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%	80	
Direct release to surface water	%	10	
Disposed of to MSWI	%	5	
Transformation during use into other forms	%	5	
End-use 6: Medtech			
Total consumption	%	4	Percentage (mean value) of the total nano-Ag use (Sun *et al.*, 2014).
Release to municipal waste water system	%	5	
Disposed of to MSWI	%	5	
Disposed of for recycling (excl. energy recovery)	%	90	
Transformation during use into other forms	%	0	
End-use 7: Plastics			
Total consumption	%	3	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Disposed of to MSWI	%	95	
Transformation during use into other forms	%	5	Transformation in the form of dissolution during the use phase was considered as material elimination due to contact with water (Sun *et al.*, 2014). Such dissolution was modelled based on data presented in Blaser *et al.* (2008) when studying the release of Ag from biocidal plastics. Sun *et al.* (2014) did not assume complete dissolution of Ag for natural waters, although suggesting that a continuous dissolution was in principle possible, and that the particle form could persist sufficiently long for allowing new pathways of silver partitioning and mass transfer.
End-use 8: Food			
Total consumption	%	7	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%	90	

Silver (Ag)			
Disposed of to MSWI	%	10	
End-use 9: Glass & ceramics			
Total consumption	%	1	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%	1	
Disposed of to MSWI	%	20	
Disposed of for recycling (excl. energy recovery)	%	74	
Transformation during use into other forms	%	5	Transformation in the form of dissolution during the use phase was considered as material elimination due to contact with water (Sun *et al.*, 2014).
End-use 10: Metals			
Total consumption	%	2	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%	5	
Disposed of to MSWI	%	5	
Disposed of for recycling (excl. energy recovery)	%	90	
End-use 11: Filtration			
Total consumption	%	0.3	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014)
Release to municipal waste water system	%	25	
Direct release to air	%	5	
Disposed of to MSWI	%	60	
Transformation during use into other forms	%	10	Transformation in the form of dissolution during the use phase was considered as material elimination due to contact with water (Sun *et al.*, 2014).
End-use 12: Sanitary			
Total consumption	%	0.16	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%	5	
Direct release to surface water	%		
Direct release to soil	%		

Silver (Ag)			
Direct release to air	%		
Disposed of to MSWI	%	95	
Disposed of to landfill	%		
Disposed of for recycling (excl. energy recovery)	%		
Transformation during use into other forms	%		
Export	%		
End-use 13: Paper			
Total consumption	%	0.1	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%		
Direct release to surface water	%		
Direct release to soil	%		
Direct release to air	%		
Disposed of to MSWI	%	10	
Disposed of to landfill	%	16	
Disposed of for recycling (excl. energy recovery)	%	63	
Transformation during use into other forms	%		
Export	%	10	

2.4.5 Waste water treatment

Name of parameter	Unit	Value	Remark, data source
Transformation during STP treatment into other forms	%	85-100	85%-100% of the metallic nano-Ag was reported to be transformed into Ag_2S (Kaegi *et al.*, 2011), which means only less than 15% of initial nano-Ag entering into STP with wastewater can survive STP process.

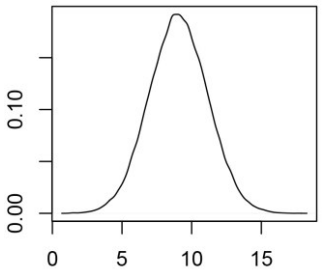
Silver (Ag)			
Percentage ending up in sludge	%	Approx. 0-100	As seen above empirical distributions with mean, an the lower and upper limit values as indicated in the column on the left that follow the newest evidence (Sun *et al.*, 2014) were modeled. These values reflect data taken from different sources (Kiser *et al.*, 2010; Tiede *et al.*, 2010; Kaegi *et al.*, 2011; Hou *et al.*, 2012; Wang *et al.*, 2012).  Figure 6. Modelled probability distribution of STP removal efficiency for nano-Ag (Sun *et al.*, 2014) See please for detailed model procedure explanations the equivalent information on the nano-TiO2 case.
Percentage discharges	%	0-15	See line above.
2.4.6 Solid waste treatment (incineration and landfill)			
Name of parameter	**Unit**	**Value**	**Remark, data source**
Transformation during incineration into other forms (average Danish MSWIs)	%	approx. 0.1-52 (deposition, transformation)	Sources of data and all technical details on the processes of waste incineration and landfilling correspond to the ones reported for other metallic nanoparticles (Walser and Gottschalk, 2014). See also comments on the previous nano-ZnO case.
Percentage emitted to the air (average Danish MSWIs)	%	~0	See line above.
Percentage ending up in residues (average Danish MSWIs)	%	approx. 36-75 (slag) approx. 3-9 (fly ash)	See line above.
Release from landfills to municipal waste water treatment	kg/year	0	For landfill, no leachate out is assumed, see also comments on previus cases.
Direct release from landfills to surface water	kg/year	0	See line above.
Transformation during landfilling into other forms	%	No data	At this point we stopped our modelling. Nanomaterial fate and behaviour during landfilling was not considered. See also general comments on landfilling.
2.4.7 Recycling			
Type of recycling activities	Recycling of bottom ash from waste incineration		
Name of parameter	**Unit**	**Value**	**Remark, data source**

Silver (Ag)			
Transformation during recycling into other forms	%	Not considered in the model.	See general comments on recycling processes.
Ending up in recycled products	%	Not considered in the model.	Most part directly after product use. Bottom ash is e.g. recycled up to 100 % in road construction, soil consolidation and anti-frost layers under buildings. A few percent are landfilled. Virksomhedernes Miljøguide (Environmental guide for entreprises), 2013: Slagger fra affaldsforbrændingsanlæg (Bottom ash from waste incinerators).
Release from recycling process	**% of recycled**	0	See lines above.

2.5 Carbon nanotubes (CNT)

Carbon nanotubes (CNT)		
2.5.1 General description		
Name	Carbon nanotubes (CNT)	 Source: (Wikipedia, 2013)
CAS number	308068-56-6 for carbon nanotubes (SIGMA, 2013) 1333-86-4 (Guidechem, 2013) Varying CAS numbers for different material modifications.	
Chemical composition		
Appearance		
Nanomaterial description		
Carbon nanotubes (CNT) have draw a lot of scientific attention that bases on a broad field of particular physicochemical characteristics (Koehler *et al.*, 2008). The term carbon nanotube may include multi walled carbon nanotube (MWNT), single walled carbon nanotube(SWCNT), double walled carbon nanotube, (DWNT), thin walled carbon nanotube (TWNT), short carbon nanotubes (short CNT), industrial grade carbon nanotubes (IGMWNT), carbon nanotube dispersions, graphitized nanotubes (GMWNT); possibly also carbon fullerenes, buckytubes, nanotubes, C-60, buckminster fullerenes (READE, 2013). The most mentioned material properties may be summarized as follows (READE, 2013): i)Electrical conductivity, one of the best conductor of electricity on nanoscale dimensions, ii) mechanical properties leading to one of the strongest (stiffest and toughest) nanofibers , thermal conductivity similar to diamond along its tube axis, self-assembly possibilities due to strong van der Waals attraction and material advantages due to molecular perfection (free of defects).		

Carbon nanotubes (CNT)			
General applications			
Steinfeldt *et al.* (2013) emphasized a widespread usage due to properties such as being persistent against degradation, or CNT as composite material (Ma *et al.*, 2010) due to outstanding mechanical properties made perfect by multi-functional properties based e.g. on thermal and electrical conductivity (Bokobza, 2007; Gibson *et al.*, 2007; Hu *et al.*, 2006; Tsu-Wei *et al.*, 2010). Survey results of (Piccinno *et al.*, 2012) show that currently most material is probably used in Composites & polymer additives and Batteries. This includes probably flat panel displays, super composite fibres, and conductive plastics, field storage batteries, micro-electronics based on semiconductors and other conductive material (READE, 2013). Future applications are expected in a very broad (probably the widest one of all studied materials in this report) spectrum, READE (2013) list among other: ‚nano-lithography/-tweezers/-balance/-doping, data storage, magnetic nanotube, nano gear, nanotube actuator, molecular quantum wires, hydrogen storage, noble radioactive gas storage, solar storage, waste recycling, electromagnetic shielding, dialysis filters, thermal protection, reinforcement of armour and other materials, avionics, collision-protection materials, fly wheels, body armour and other.			
2.5.2 Manufacturing and import/export of the substance on its own			
Manufacturing processes			
Manufacturing in Denmark			
Name of parameter	**Unit**	**Value**	**Remark, data source**
Import of the substance on its own uses to Denmark	kg/year		
Re-export	% of import		
2.5.3 Down stream use of CNT for production proceses in Denmark			
Identified formulation processes in Denmark	No information on actual use of carbon nanotubes in production processes in Denmark has been identified. In the Nanoplast project "Nano-technological materials and products in the plastics industry: Exposure assessment and toxicological properties" published in 2012, the exposure to CNTs in the production of fibre-reinforced polymer nano composites was studied (Clausen *et al.*, 2012). The study mentions the large potential of the use of CNTs in the composite industry but no actual large scale uses.		
Name of parameter	**Unit**	**Value**	**Remark, data source**
2.5.4 Import/export and end-use in articles and mixtures			

Carbon nanotubes (CNT)	
Identified uses in articles and mixtures	Total annual use of the substance in Denmark is modelled from approx. 1-18 t/y. The figures are adapted from Swiss (European) values declared to show varying reliability expressed as degree of belief of 80%and 20% (Sun *et al.*, 2014) on a comparison of the population numbers Denmark-Switzerland. Sun *et al.* (2014) report current available quantitative estimations for CNT: global production/use: 55 - 3'300 t/y (Healy *et al.*, 2008; Aschberger *et al.*, 2011; Future Markets, 2011; Piccinno *et al.*, 2012). Our values leading to anormal use volume distribution reflect different estimations (80% reliability) (Schmid and Riediker, 2008; Future Markets, 2011; Hendren *et al.*, 2011; Piccinno *et al.*, 2012) and (20% reliability) (Healy *et al.*, 2008; Ray *et al.*, 2009; Aschberger *et al.*, 2011).  Figure 7. Annual use volumes computed for Denmark. Please note that Research and Development (R&D) could be significant, but this is not considered an end use, and would be included under the use of the carbon nanotubes for formulation/production processes. Some R&D on the use of CNT has been undertaken in Denmark, among these the Nanoplast project "Nano-technological materials and products in the plastics industry: Exposure assessment and toxicological properties" (Clausen *et al.*, 2012). The environmental releases from the R&D activities are assumed to be insignificant and no attempt has been done to estimate the potential releases of CNT from R&D in Denmark. Lower, upper boundary and mean mass fraction of ENM modelled for the allocation to different product applications. Details on such computation from different sources are explained in detail below and exemplary for the CNT and based on a recent study (Sun *et al.*, 2014)

	End use	Percentage of total Lower, modal, higher value (l,m,h)
1	Polymer composites	25 ,84, 100
2	Paints	0, 1, 10
3	Textiles	0, 0.02, 0.07
4	Automotive	0, 1, 10
5	Consumer electronics	0, 3, 24
6	Energy	0, 9, 50
7	Sensor	0, 0.4, 3
8	Aerospace	0, 0.6, 5

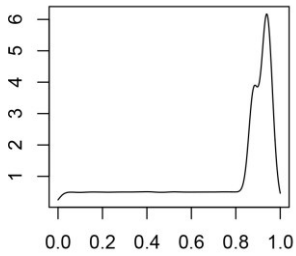
Name of parameter	Unit	Value	Remark, data source
End-use 1: Polymer composites			

Carbon nanotubes (CNT)			
Total consumption	%	84	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Direct release* to air	%	1	* Unless otherwise noted the release values were reduced/ enlarged on each side by 50% for the modeling of symmetrical triangular distributions around the specified quantities. The symmetry may possibly be by the absolute border values (highest or lowest possible release value, 1 and 0). In cases were more values are given, the mean is taken as modal value for such distributions.
Disposed of to MSWI	%	99	
Transformation during use into other forms	%		For all uses (and the uses listed below) no dissolution or transformation/elimination during use and production was considered (Gottschalk *et al.*, 2009; Sun *et al.*, 2014).
End-use 2: Paints			
Total consumption	%	1	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%	1	
Direct release to surface water	%	1	
Direct release to soil	%	1	
Direct release to air	%	1	
Disposed of to landfill	%	50	
Disposed of for recycling (excl. energy recovery)	%	46	
End-use 3: Textiles			
Total consumption	%	0.02	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Release to municipal waste water system	%	2	
Direct release to air	%	2	
Disposed of to MSWI	%	96	
End-use 4: Automotive			
Total consumption	%	1	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Direct release to air	%	1	
Disposed of to MSWI	%	39	
Disposed of for recycling (excl. energy recovery)	%	40	
Export	%	20	

Carbon nanotubes (CNT)			
End-use 5: Consumer electronics			
Total consumption	%	3	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Disposed of to MSWI	%	5	
Disposed of for recycling (excl. energy recovery)	%	75	
Export	%	20	
End-use 6: Energy			
Total consumption	%	9	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Disposed of to MSWI	%	5	
Disposed of for recycling (excl. energy recovery)	%	75	
Export	%	20	
End-use 7: Sensor			
Total consumption	%	0.4	Percentage (mean value) of the total nano-TiO2 use (Sun *et al.*, 2014).
Disposed of to MSWI	%	5	
Disposed of for recycling (excl. energy recovery)	%	75	
Export	%	20	
End-use 8: Aerospace			
Total consumption	%	0.6	
Disposed of to MSWI	%	39	
Disposed of for recycling (excl. energy recovery)	%	60	
Direct release to air	%	1	
Export	%		

2.5.5 Waste water treatment

Name of parameter	Unit	Value	Remark, data source
Transformation during STP treatment into other forms	%	0	

Carbon nanotubes (CNT)			
Percentage ending up in sludge	% (l,m,u)	0, 88 , 100	According to some evidence for Fullerenes used in Sun *et al.* (2014) we also base the computations on different Fullerene studies (Kiser *et al.*, 2010; Kiser *et al.*, 2012; Wang *et al.*, 2012).  Figure 8. Removal of Fullerene into sewage treatment sludge.
Percentage discharges	% (l,m,u)	0,12,100	See line above.

2.5.6 Solid waste treatment (incineration and landfill)			
Name of parameter	**Unit**	**Value**	**Remark, data source**
Transformation during incineration into other forms (average Danish MSWIs)	% (l,m,u)	75, 98, 100	As suggested by others (Sun *et al.*, 2014) and in accordance to (Mueller *et al.*, 2013).
Percentage emitted to the air (average Danish MSWIs)	%	0.05, 0.1, 0.15	See line above.
Percentage ending up in residues (average Danish MSWIs)	%	40, 81, 100 (bootom ash) 0,19,60 (fly ash)	See line above.
Release from landfills to municipal waste water treatment	kg/year	0	For landfill, no leachate out is assumed, see also comments on previus cases.
Direct release from landfills to surface water	kg/year	0	See line above.
Transformation during landfilling into other forms	%	No data	At this point we stopped our modelling. Nanomaterial fate and behaviour during landfilling was not considered. See also general comments on landfilling.

2.5.7 Recycling	
Type of recycling activities	No relevant recycling activities identified

2.6 Copper (Cu)

Copper (Cu)		
2.6.1 General description		
Name	Nanosized copper carbonate Nanosized copper oxide Nanosized copper (elemental)	 Nano CuO. Source: http://www.nanoparticles-micro-spheres.com/Products/Nano-CuO.html
CAS number	12069-69-1 (copper carbonate) 1317-39-1 (copper(I)oxide) 1317-38-0 (copper(II)oxide) 7440-50-8 (elemental copper)	
Chemical composition	Copper carbonate: $CoCO_3$ Copper(II)oxide: more than 99% CuO Metallic copper of a purity of about 99.8%	
Appearance	Copper carbonate is a blue-green powder Copper(II) oxide is a black powder Elemental nanocopper is a red powder	 Nano copper. Source: http://www.made-in-china.com

Nanomaterial description

Several types of nanosized copper particles are described in the literature.

Copper carbonate - Micronized particles of copper carbonate used for wood preservatives range from 1 to 25,000 nm. The particulate character may affect penetration of wood cell walls and reaction with wood's molecular constituents. (Freeman and MacIntyre, 2008). According to Preston *et al.* (2008) a mean particle size of 190 nm is described as being optimal. Smaller size would increase leachability and potentially bring health issues related to nano-particles, while larger particle sizes would be detrimental to the treatment of even the highly permeable pine species which are currently practicable to treat (Preston *et al.*, 2008). It has been confirmed by industry contacts that it is not intended that the particles are in the nanosize (Osmose, 2013) and companies try to optimise the grinding process in order to have less particles below 100 nm.

It may be questioned if the micronized copper meets the general definition of nanomaterials: "A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm" However " In specific cases and where warranted by concerns for the environment, health, safety or competitiveness the number size distribution threshold of 50 % may be replaced by a threshold between 1 and 50 %.". (European Commission,2011). With the optimization of the grinding process, in the nearest future the situation may be that the micronised copper carbonate will not meet the nanomaterial definition.

Copper oxide – Nano-CuO with an average particle size of 29 nm and a purity of more than 99% CuO is manufactured by Nanophase Technologies Corporation (Azonanano, 2006). The nanocrystalline CuO typically have a mean particle size less than 100 nm, are non-porous single crystals, have defined surface chemistry, and are chemically pure (Azonanano, 2006).

Copper – Nano-Cu with an average particle size of 70 nm, a purity of 99.9% and a specific surface area of 6.8 m2/g is manufactured (U.S. Research Nanomaterials, Inc., 2013)

Copper (Cu)

General applications

Copper carbonate - Micronized particles of cobber carbonate are used as wood preservative as alternative to other copper-based wood preservatives.

Copper oxide - Kiaune and Singhasemanon (2011) report that copper oxide nanoparticles are used as additives in inks, plastics, lubricants; as coatings for integrated circuits and batteries; and as bactericides for air and liquid filtration.

According to Azonano (2006) NanoArc® copper oxide nanomaterials may be used for wood preservation, antimicrobial agents for textile fibres, marine antifouling, antimicrobial agent in permanent coatings for healthcare, industrial and institutional cleaning, food processing, food service, and general paints and coatings, and as dispersed antimicrobial agent in plastics.

The manufacturer of nanomaterials EPRUI (2013) indicates that copper oxide nanoparticles have been applied to catalysts, superconducting materials, thermoelectric materials, sensing materials, glass, ceramics and other fields. In addition, the nano-copper oxide can be used as rocket propellant combustion catalyst.

Ren *et al.*, (2009) mention that CuO nanoparticles have attracted particular attention because it is the simplest member of the family of copper compounds and exhibits a range of potentially useful physical properties such as high temperature superconductivity, electron correlation effects and spin dynamics. As an important p-type semiconductor, CuO has found many diverse applications such as in gas sensors, catalysis, batteries, high-temperature superconductors, solar energy conversion and field emission emitters. In the energy-saving area, energy transferring fluids filled with nano CuO particles can improve fluid viscosity and enhance thermal conductivity. They further mention that in theory, metal nanoparticles could be combined with polymers or coated onto surfaces, which may then have a variety of potential antimicrobial applications. The antimicrobial properties of both silver and copper nanoparticles have been reported, and both of these have been coated onto or incorporated into various materials. CuO is cheaper than silver, easily mixed with polymers and relatively stable in terms of both chemical and physical properties. Highly ionic nanoparticulate metal oxides, such as CuO, may be particularly valuable antimicrobial agents as they can be prepared with extremely high surface areas and unusual crystal morphologies. (Ren *et al.*, 2009.

Copper

The manufacturer Hefei Quantum Quelle Nano Science and Technology Co. Hefei (2013) indicates the following applications of nano-Cu powder:

- Efficient catalysts: The large and highly active surface area, nano copper has a greatly enhancement catalytic efficiency. Instead of conventional micro copper can be used for methanol industry.
- Conductive paste: Electronic paste is widely used in microelectronics industry packaging, connectivity, miniaturization of microelectronic devices. Nano copper electronic paste has superior performance as micro copper. It is widely used in MLCC.
- Sintering additives: Nano-powder has large volume ratio of surface atoms, which have so high energy state. In the powder metallurgical industry, it can be used as sintering additive to reduce sintering temperature in ceramic and diamond tools production.
- Medicine and anti-bacterial: Nano copper can be used widely in medical industry and to anti-bacterial applications.
- Lubricant addictive: Nano copper powder can be dispersed into lubricant to decrease the surface friction and repair micro defect of the friction surface.

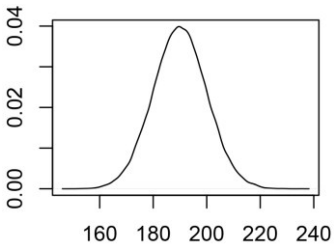
The Nanodatabase of the Danish Consumer Council (Tænk/Forbrugerrådet) include two products with nano copper, where links still exist:

- MesoCopper® - Nanoparticle Colloidal Copper: a mineral supplement in the form of a copper colloid consisting of nanometer particles of 0.9999 pure copper suspended in pure deionized water.

- DS Laboratories Revita.COR Hair-Growth Conditioner with nano-copper peptides.

Very limited information on the quantites of nanosized copper oxide and elemental copper has been available, and the modelling will consequently focus on the use of copper carbonate for wood treatment because 1) quantitative data are available for estimating the potential consumption in Denmark and 2) the quatities potentially used and releases to the environment will be significant.

Copper (Cu)			
2.6.2 Manufacturing and import/export of the substance on its own			
Manufacturing processes	**Cobber carbonate** - Micronized particles of cobber carbonate are produced by mechanical grinding of water or oil-insoluble copper compounds with aid of dispersing/wetting agents in a carrier using a commercial grinding mill or by chemical means resulting in 90% or more of the particles being less than 1000 nm size. The commonly used carrier is water, and commonly used dispersing agents are polymeric dispersants, which attach to the surface of particles and keep the particles away from each other. Also, the presence of dispersing/wetting agents improves particle size reduction during milling and stabilizes the particles during storage and treating.		
Manufacturing in Denmark	Micronized particles of cobber carbonate are not manufactured in Denmark. Nanosized copper oxides are not manufactured in Denmark		
Name of parameter	**Unit**	**Value**	**Remark, data source**
Import of the substance on its own uses to Denmark	kg/year	no data – expected to be zero	According to industry contact it is expected that micronized copper carbonated will be imported as a concentrate
Re-export	% of import	no data	
2.6.3 Formulation and industrial uses in Denmark			
Identified formulation processes in Denmark	**Copper carbonate** -According to the Danish Pesticide Statistics, 91 tonnes of copper carbonate was used as active substances in wood preservatives in Denmark in 2011 whereas the consumption was 63.5 tonnes in 2009 and 84.5 tonnes in 2010 (DEPA, 2012). According to industry contacts (Osmose, 2013) none of the copper carbonate in 2012 was of the micronized type, but potentially in the future all the used copper carbonate could be of this type – resulting in a consumption of the same magnitude as the present use. In the USA, the market penetration of the new technology is about 75-80% (Osmose 2013). It is expected that the formulation of concentrates used by the impregnation companies will take place abroad. By the formulation the micronized copper carbonate is mixed with a solvent. This concentrate is by the impregnation companies mixed with water. The concentrate is typically used in a 2% solution. In Denmark the impregnation of wood currently takes places in automatic closed processes according to BAT. It would be the same if the new technology is introduced. **Copper oxide** - Antifouling products have previously been formulated in Denmark but today all production of antifouling paints takes place abroad. The use of copper(II)oxide and copper(I)oxide for "Non-agricultural pesticides and preservatives" was according to the SPIN database in 2011 in total 98 tonnes. It is expected that "Non-agricultural pesticides and preservatives" covers antifouling paint. According to industry contacts there are no incentives for using the more expensive nanosized copper oxides for antifouling paints. The copper oxide particles are typically in the 1-5 µm range with 95% of particles finer than 5 µm and 20% finer than 2 µm. The copper is released as the paint is polished (hydrolysing of the polymer matrix). The copper is encapsulated in a polymer matrix and the paint was some years ago marketed as based on "nano capsules", but the capsules are not in nanosize as defined by the Commission (the copper particles are inside the capsules). According to industry contacts nanosized copper oxides are most probably not used in antifouling paints sold on the Danish market.		

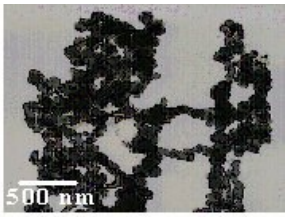
Copper (Cu)			
	 Figure 9. Annual use (in average 91 t for own formulation in Denmark and 100 t imported as part of impregnante material) in Denmark of copper carbonate for wood treatment. Modelled normal distribution around a relative precise mean of 191 t/a (according to the Danish Pesticide Statistics) and a default standard deviation of 10.		
Name of parameter	**Unit**	**Value**	**Remark, data source**
Formulation 1: Production of preserved wood (model estimates assuming all copper carbonate is of the micronized type)			
Number of companies	companies	4	Number of companies for pressure impregnation members of Dansk Træbeskyttelse (Danish Wood impregnation)
Quantities used	tonnes/year	91	Assuming the consumption is on the 2011 level.
Ending up in final products	%	~99	Hansen *et al.*, 1997
Release* to municipal waste water system * Unless otherwise noted the release values were reduced/ enlarged on each side by 50% for the modeling of symmetrical triangular distributions around the specified quantities. The symmetry may possibly be by the absolute border values (highest or lowest possible release value, 1 and 0). In cases were more values are given, the mean is taken as modal value for such distributions.	%	~0	According to Hansen *et al.* (1997) in the late 1990'es pressure impregnation took place in closed systems without any losses to waste water. Small releases could be due to leakages in the collection systems or by cleaning of working clothes and cleaning of filters.
Direct release to surface water (after internal WW treatment)	%	~0	
Direct release to soil	%	~0	
Direct release to air	%	~0	
Disposed of as solid waste for incineration	%	~0	
Disposed of for other waste management	%	~1	Small amounts of sludge disposed of as hazardous waste – not quantified in Hansen *et al.* (1997). Rough estimate.
Transformation during use into other forms	%	Data not available	

Copper (Cu)			
Percentage of produced products exported	% of quantity in final product	Data not available	
2.6.4 Import/export and end-use in articles and mixtures			
Identified uses in articles and mixtures	The micronised copper carbonate is present in pressure impregnated wood. The majority of the wood is various timber used for out-door applications		
Name of parameter	**Unit**	**Value**	**Remark, data source**
End-use 1: Pressure impregnated wood			
Net-import with articles and mixtures	Tons/year	100	(Osmose, 2013) assuming a potential market penetration of the new technology by 100%
Total consumption	Tons/year	190	The amount of impregnated wood in Denmark is about 250.000 m^3, about 50% imported and about 50% produced in Denmark (Osmose, 2013 based on data from the Danish Impregnation branch)
Trend in consumption	Unit-less	Stagnating	In the model it is anticipated that the micronized copper carbonate has a market penetration of 100%
Average service life time	year	30	Hansen *et al.*, 1997. The authors mentions that actual data are not available, but an average of 30 years is expected.
Release to municipal waste water system	%	1	Hansen *et al.*, 1997 estimate that 25% of copper from CCA (copper/chromium/arsenic) treated wood and 30-40% of the copper from CC (copper/chromium) treated wood during the life time. The releases from wood treated with micronized copper may be lower. The releases from wood below ground is higher than from wood above ground. It is roughly assumed that the total is 30% - a minor part of this is released to surfaces with run off to urban sewage treatment plants and rain water run off directly to surface water [Most probably the micronized copper is released as dissolved copper ions]
Direct release to surface water	%	1 (via urban rainwater run off)	
Direct release to soil	%	28	
Direct release to air	%	0	
Disposed of to MSWI	%	7%	According to current regulation pressure impregnated wood should be disposed of for landfill. A small part may be disposed of with non-impregnated wood for recycling (manufacture of wood-chip boards) and a part may be disposed of for incineration. For the current model estimates it is assumed that 80% (of the 70% remaining in the wood) is disposed of in accordance with the legislation and 10% to MSWI and recycling.
Disposed of to landfill	%	56%	
Disposed of for recycling (excl. energy recovery)	%	7%	

Copper (Cu)			
Transformation during use into other forms	%	0	Low levels of copper were detected at every stage of a leaching test of wood treated with micronized copper quat suggesting micronized copper may be capable of redistributing into cell walls. Copper-containing particles were detected in the lumens of micronized copper quat- and but were not present in un-treated samples (Stirling *et al.*, 2008). While confirming the presence of copper in the cell wall was difficult, X-ray analysis indicated that there was a small amount of Cu in the cell walls in both Micronized copper quat- and ACQ-treated samples, and not in the untreated samples. [most probably a major part of the micronized copper is trans-formed before release]
2.6.5 Waste water treatment			
Name of parameter	**Unit**	**Value**	**Remark, data source**
Transformation during STP treatment into other forms	%		No data
Percentage ending up in sludge	%	82	General values for copper in 1995 (Lassen *et al.*, 1996)
Percentage discharges	%	18	
2.6.6 Solid waste treatment (incineration and landfill)			
Name of parameter	**Unit**	**Value**	**Remark, data source**
Transformation or deposi-tion during incineration into other forms (average Danish MSWIs)	%	approx. 0.1-52 (deposition, transformation)	Sources of data and all technical details on the processes of waste incineration and landfilling correspond to the ones reported for other metallic nanoparticles (Walser and Gottschalk, 2014). See also comments on the previous nano-Ag case.
Percentage emitted to the air (average Danish MSWIs)	%	~0	General values for copper in 1995 (Lassen *et al.*, 1996) were around 0.1 % and have been confirmed in the CeO2 study for metallic nanoparticles (Walser and Gottschalk, 2014). We used the model input values for waste incineration processes as done for other metals in our report (see please the correspond-ing chapters).
Percentage ending up in residues (average Danish MSWIs)	%	approx. 36-75 (slag) approx. 3-9 (fly ash)	General values around 99% for copper in 1995 (Lassen *et al.*, 1996) and see line above.
Release from landfills to municipal waste water treatment	kg/year	0	Lassen *et al.*, 1996 provides general data for releases of copper from landfills. Specific data on releases from pressure impreg-nated wood are not available. It is assumed that pressure impregnated wood is disposed of to landfill with discharge of percolate to municipal waste water treatment plants. In our model landfills represent final sinks, a further material fate model for such plants is not considered.
Direct release from landfills to surface water	kg/year	0	
2.6.7 Recycling			

Copper (Cu)	
Type of recycling activities	Recycling of pressure impregnated wood is not expected to take place. Small amount of pressure impregnated wood may end up in wood recycled for manufacturing of shipboard.
2.6.8 Further parameters for a soil exposure scenario	
Model considerations	The releases of copper carbonate from the treated wood is considered a diffuse source and treated as such in a regional model. It should be noted that in the context of the Biocidal Products Regulation (Regulation (EU) 528/2012) preserved wood is considered a point source in contrast to the terminology used in this project where such use is considered a diffuse source. Point sources in the present model are sources which on a regional scale can be attributed to a specific geographic location (e.g. an outlet from a specific sewage treatment plant).

2.7 Zero valent iron, nano-ZVI

Zero valent iron, nano-ZVI		
2.7.1 General description		
Name	Nano-scale zero-valent iron (nano-ZVI)	 Source: US EPA, 2002
CAS number	8053-60-9	
Chemical composition	Fe	
Appearance	Dark powder	
Nanomaterial description		
nano-ZVI is the nanoform of zero-valent iron. In its most basic form it consists of spherical iron (Fe0) nanoparticles with individual particle dimensions less than 100 nm. Substantial variations exist in the properties of nano-ZVI in regard to average particle size, particle size distribution, specific surface area, surface charge and the presence of trace metals. nano-ZVI may furthermore often be coated in order to prevent agglomeration and better control their reactivity and mobility. Polymers, polyelectrolytes, and surfactants are among the main types of coatings used for nano-ZVI. (Mikkelsen *et al.*, 2011)		
General applications		
nano-ZVI has been used as an in-situ remediation technology for contaminated sites (e.g. for degradation of PCBs, chlorinated organic solvents, and organochlorine pesticides). A few medical applications have also been reported, but it is the use in soil and groundwater remediation that is anticipated to be the major use of nano-ZVI in the future. (Mikkelsen *et al.*, 2011) Zero valent iron (ZVI) is known to be very reactive and its reducing power has (in its non-nanoform) been used for a while to remediate contaminated groundwater (see e.g. US EPA, 2009). Due to the smaller size and larger surface, nano-ZVI is even more reactive and gaining increasing attention as a soil/groundwater remediation agent. nano-ZVI is claimed to be able to reduce chlorinated organics and other organic substances/pesticides such as DDT, lindan and PCB to less toxic materials. nano-ZVI also has the potential to remove from dissolution heavy metals like arsenic, uranium and chromium and thus immobilize/precipitate these making them less bioavailable. Finally, the reducing power of nano-ZVI can also be used to reduce inorganic anions, such as e.g. NO_3^- and $PO4^{3-}$ (see e.g. US EPA, 2009, Müller and Nowack, 2010 and NanoIron, 2013). These nano-ZVI reducing properties are being exploited in ground water/soil remediation applications. According to a main European supplier, although in its infancy, the nano-ZVI reducing properties are also being exploited in relation to treatment of waste water and even drinking water (NanoIron, 2013). Beside the reduction capacity, nano-ZVI may also "…exhibit excellent catalytic, magnetic (strong ferromagnetic material) and me-		

Zero valent iron, nano-ZVI			
chanical properties due to which they are, for example, used as a catalyst in Fischer-Tropsch synthesis of hydrocarbons, in the production of carbon nanotubes, in petrochemistry, in the production of magnetic fluids or as an admixture in powder metallurgy." (NanoIron, 2013)			
2.7.2 Manufacturing and import/export of the substance on its own			
Manufacturing processes	A number of different synthesis methods exist including the sol-gel methods and the sodium boron hydride method. (Mikkelsen *et al.*, 2011)		
Manufacturing in Denmark	No manufacture of nano-ZVI in Denmark has been identified.		
2.7.3 Import/export and end-use in articles and mixtures			
Name of parameter	**Unit**	**Value**	**Remark, data source**
End-use 1: Use of nano-ZVI for soil remediation			
Net import of (non-nano) ZVI for soil remediation	Tons/year	0	Only one pilot study case so far (see below).
Potential net-import of nano-ZVI for soil remediation	Tons/year	100	So far, mainly iron filing or iron sponge, which are not in the nano size and not regarded nano-ZVI have been used for soil remediation in Denmark. To the knowledge of the authors, iron filing or iron sponge have been used for in-situ groundwater remediation at four sites in Denmark. In three of the sites 110 270, 330 tonnes were used, respectively. At the fourth site, in total 1300 m^3 soil was remediated, but the quantities of iron used is not reported. It is estimated that the potential net-import of nano-ZVI could be around 100 t/y if nano-ZVI substituted for iron filing or iron sponge for all in situ groundwater remediation.
Potential total consumption of nano-ZVI for soil remediation	Tons/year	100	
The following describes the relevant parameters for a local scenario of the use of nano-ZVI for soil remediation			
Scenario description	The applications of nano-ZVI for soil remediation are by nature "local" and due to the reactivity of nano-ZVI, the scenario considered in this project will thus be a "local scenario". By courtesy, data from a Danish case study applying nano-ZVI in a Danish location have been made available to the project by Geosyntec Consultants, Inc. In addition, we have attempted to give an overview of the total volume of nano-ZVI currently used in Denmark as well as an estimate of the trend. Geosyntec Consultants, Inc., and FRx Inc., conducted – in 2012 and on behalf of the Capital Region of Denmark – Jet Injection tests of micro- and nano-sized ZVI into clay. This pilot test has been conducted at a clean test site in Taastrup located about 21 km west of Copenhagen and comprehensively described in a final report (Geosyntec Consultants, Inc., and FRx Inc. 2012). The goal of this pilot study was to evaluate the "feasibility and performance of Jet Injection for delivering remediation amendments into low permeability glacial clay moraine deposits that are prevalent in the shallow subsurface in Denmark". Such Jet Injection had been applied before and successfully in e.g. in sand aquifer environments, for dense and highly naturally fractured clay this study presents the first known and successful tests of Jet Injection.		

Zero valent iron, nano-ZVI			
	In the nanomaterial case and at the first well, a nanosized ZVI suspension containing nano-ZVI particles (Nanofer 25S (Nano Iron, Czech Republic) with approximately 50 nm size was applied. A non-specified surfactant was used to avoid/limit agglomeration of the nanoparticles. Additionally, a fluorescent dye tracer – RWT (CAS No. 37299-86-8) – was added to the slurry (in total approx. 91% water, 5% nanoparticles, 4% RWT solution) in order to monitor the distribution and identify the location of the injected iron when excavating the target soil. All the tests took place on 2 November 2011 and were performed at five different injection intervals and at multiple depths by injecting in total 24 kg mass of nano-ZVI. All tests followed a precise injection schedule combining hydraulic fracturing and inertia forces of high-pressure water jets. In order to perforate the well casing as well as the grout the pilot injection test has been started by a waterblaster working at the beginning at 69 MPa (10,000 psi) and 40 L/min flow (for 20 sec). After 20 seconds a roller pump then injected at the same time the target slurry at appr. 20 L/min. Approximately 5 minutes later the waterblaster was turned down to 23 MPa (3300 psi) and 22 L/min flow while the actual injection went on until the target slurry mass for the particular interval was used. Having completed these injections excavations were conducted around the well by a Danish contractor Frisesdahl under the guide of Geosyntec and COWI A/S and Danish excavation regulations (Arbejdstilsynets bekendtgørelse nr. 1516 af 16. december 2010 om Bygge og Anlægs arbejde). This allowed to identify the location (postinjection) of the nano-ZVI and to reconstruct the distribution kinetics. Hence, such localization was the basis for describing the total distribution volume of the target nanoparticles in the test site. Excavations of 1 m wide for every 1.8 m profundity were necessary to fully capture the iron at each depth interval. The findings on the nano-ZVI distribution for each interval were documented by visual identification, photographs, dimensional delineates, magnetic susceptibility (MS) analysis and soil sampling (for total iron analysis). The advantage of this study is that it provides unusually accurate material release and fate data (for nanomaterial and environmental assessment contexts) that may be applied for modelling purposes that focus on quantifying direct release of nano-ZVI into (and fate in) soil environments (see please also the following subsection). All above, the new evidence on the nano-ZVI horizontal and vertical distribution as well as on agglomeration and reactivity of such iron helps to estimate the fate of such nanoparticles in soil environments. The model focuses on the uncertainties and variability on the distribution and aggregation behaviour of nano-ZVI in such soils and the scenario may be applied for any particular sites in Denmark or elsewhere with varying soil characteristics and nano-ZVI use amounts.		
Concentration of nano-ZVI in the slurry	kg/L	0.014	
Volume of slurry injected	L	1.694	Divided up between 5 injections.
Quantity of nano-ZVI injected	kg	24	See comment above.
Total distribution volume	m^3	Will be computed during modelling procedure 8see main report for the modelling)	The total distribution of nano-ZVI is visualized in 3-D pictures illustarting the total nano-ZVI distribution space. However ,for the model we assume a generic homogeneous nanoparticle spread in Danish soils. The computations on the target volumes are given in the main report.
Soil mass density	kg/dm^3	1.7	Assuming a specific density of the soil of 1.7 kg/dm^3

Zero valent iron, nano-ZVI			
Concentration (Avg. Iron Conc. (85% of Total Iron) of nano-ZVI in distribution volume of the observed primary fracture	g/L	84	The average estimates of iron concentrations in the fracture reflected the semiquantitative estimates of iron concentrations in the primary fracture from the calibrated magnetic susceptibility (MS) readings (Geosyntec, 2012). However, as reported (Geosyntec, 2012) the real fraction of total iron finally emplaced in the primary fractures was at the most up to 85% due to iron ending up in secondary fractures and losses due to surface venting.
Rate of aggregation in soil		Not estimated	Aggregation is probably not important due to the fast reactivity and formation of iron oxide.
nano-ZVI transport in the soil		Not estimated	The maximum injection radius was 7.2 m, significantly larger than the injection distances earlier and other fracturing technologies tested in a Danish basal clay till. The depth of the primary fracture was approx. 2.5 m. However, for the model we assumed a generic homogeneous nanoparticle spread in Danish soils. See please the coments on soil volumes and the main report that contains all the data.
Concentration of iron in the soil	%	[Estimated in the modelling context in the main report]	Concentration of iron not reported. Fe2O3 in Danish clays range from 3.7 to 7.0 % across the country (GEUS, 2007)
2.7.4 Formulation in Denmark			
Identified formulation processes in Denmark	No formulation processes involving nano-ZVI in Denmark have been identified.		
2.7.5 Import/export and end-use in articles and mixtures			
Identified uses in articles and mixtures	No information on the use of nano-ZVI in articles and mixtures has been identified.		

2.8 Cerium dioxide (CeO_2)

Cerium dioxide (CeO_2)		
2.8.1 General description		
Name	Cerium dioxide. cerium oxide	 Source: Wikipedia
CAS number	1306-38-3	
Chemical composition	CeO_2	
Appearance	Pale yellow-white powder	
Nanomaterial description		
Cerium(IV)oxide (CeO2) is an oxide of the element cerium. The crystal form of CeO2 is cerianite. CeO2 is an oxide of the metal cerium, a rare earth metal compound. CeO2 is commercially available in a number of different size ranges below 100 nm (Mikkelsen *et al.*, 2011) and 15-105 nm in textiles (Rezic. 2011)		

Cerium dioxide (CeO_2)			
General applications			
CeO2 has several applications and due the catalytic ability of CeO2 to adsorb and release oxygen it is used e.g. to coat the inside of self-cleaning ovens and for hydrogen production in fuel cells. The most widespread use of CeO2 is as an additive to diesel. This use may be particularly important from an environmental point of view, since it may lead to direct emissions during the use phase. For this application CeO2-NP is mixed completely with the diesel (concentration: 5-8 ppm; average particle size: 8-10 nm). The advantage of using CeO2-NP as a fuel catalyst is the improved engine combustion efficiency that results in reduced emissions of soot. CO and NOx. Furthermore, the fuel efficiency has been reported to increase by 8-9 %. The production and use of CeO2 nanoparticles (CeO2-NP) is rapidly growing and CeO2 is used as a fuel additive in countries like the Philippines, New Zealand and the UK. However, the amounts produced and used are at present unknown (Mikkelsen *et al.*, 2011). Other applications involve its ultraviolet (UV) protective properties and its anti-microbial effects.			
2.8.2 **Manufacturing and import/export of the substance on its own**			
Manufacturing processes	Industrial bulk cerium is extracted from mined minerals. primarily monazite and bastnasite and CeO2 is formed by thermal treatment processes		
Manufacturing in Denmark			
Name of parameter	**Unit**	**Value**	**Remark. data source**
Import of the substance on its own uses to Denmark	kg/year		None identified
Re-export	% of import		
2.8.3 **Formulation in Denmark**			
Identified formulation processes in Denmark	**Application of CeO2 as UV filter in paint and lacquers**		
Formulation 1: Application of CeO2 as UV filter in paint and lacquers			
Number of companies	companies	<4	
Quantities used	kg/year	200	The estimated use of cerium oxide for manufacturing of wood oil in DK is in the range of 100-500 kg/y
Ending up in final products	%	97.5%	It is assumed that the dispersion of CeO2 is mixed with no major losses into the final product

Cerium dioxide (CeO_2)			
Release* to municipal waste water system * Unless otherwise noted the release values were reduced/ enlarged on each side by 50% for the modeling of symmetrical triangular distributions around the specified quantities. The symmetry may possibly be by the absolute border values (highest or lowest possible release value, 1 and 0). In cases were more values are given, the mean is taken as modal value for such distributions.	%	<0,5	The emission scenario document (ESD) for the paint industry from the OECD (2009) assume for manufacture of aqueous dispersion coatings that the total fraction of raw materials lost to waste from the manufactring process is 1.5%. This includes 1% lost due to residues in the mixing vessels and 0.5% due to residues in bags, spills and product returns. It is in the ESD assumed that half of the residue material in the mixing vessels will be re-used in the manufacturing process (recycling. For aqueous dispersion coatings the remaining equipment residue is assumed to be removed in water washings and hence to waste water. According to information from Danish manufactures waste water originates from cleaning of tanks and other production equipment. A small part (not quantified) of the total used may be released to the waste water for pre-treatment at the manufacturing sites. The first step at all sites is a flocculation where the majority of the CeO2 is precipitated and ends up in a filter cake which is disposed of for external incineration or gasification. The pretreated waste water is directed to municipal waste water plants. As a worst case estimate, the releases to municipal waste water treatment plants are estimated to be <0,5%. The actual release is probably significantly below this value.
Direct release to surface water (after internal WW treatment)	%	0	No direct discharge to surface water
Direct release to soil	%	0	No direct releases to soil
Direct release to air	%	0	The TiO2 is imported as pastes in which the CeO2 is dispersed in water. The generation of dust by handling of the pastes is considered insignificant.
Disposed of as solid waste for incineration	%	2	Filtercake/sludge and CeO2 remaining in packaging are disposed of for incineration
Transformation during use into other forms	%	0	Not likely
Percentage of produced products exported	% of quantity in final product	No data	It is assumed that all of the product is sold in Denmark

Cerium dioxide (CeO_2)

2.8.4 Import/export and end-use in articles and mixtures

Identified uses in articles and mixtures

Global estimations of the content (in percent) of CeO2 in consumer products and articles. As no Danish specific information has been possible to obtain, global information have been used for estimations are included in the table. For a range of the possible uses it has not been possible to estimate the percentage.

Piccinno *et al.* (2011) estimate the total global production of nano CeOx (all cerium oxides) at 55 t/y (25-75 percentile: 5.5-550 t/y). Hendren *et al.* (2011) indicate as summerized elsewhere (Piccinno *et al.*, 2012) for US values for such a volume a range between 35 and 700 t/y.
We computed normally distributed values for the Danish use volume by reffering our computations on the global and US data. A minimal value of 0.03 t/y was fixed based on the ranges indicated above and the global estimation had to be scaled down to European and Swiss conditions based on the proportion of the Gross Domestic Product as suggested by (Sun *et al.*, 2014). The sacling EU-US and Switzerland-Denmark reflects population numbers, due to similar consumption capability of these countries.

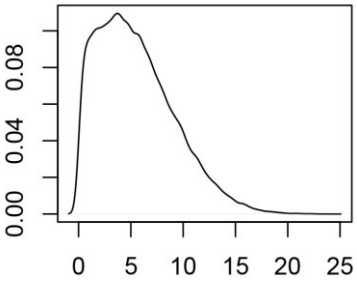


Figure 10. Annual use volumes covering nanomaterial mass of import and own formulation processes Denmark.

	End use	Percentage of total Lower, modal, higher value (l*** ,m, h***)
1	Automotive catalysts converter	16,2**
2	Fuel borne catalyst/fuel additive	1-50*
3	Glass polishing	44,1**
4	Paint and coatings	5-10*
5	NiMH batteries	9,6**
	Medicinal	No data available
	Solar panels and fuel cells (SOFC)	No data available
	Sunscreen and make-up	No data available
	Self-cleaning oven	No data available
	Fluid cracking catalyst	No data available

* Based on a survey covering 239 companies (82% of which were European) (Piccinno, Gottschalk, Seeger, & Nowack, Industrial production quantities and uses of ten engineered nanomaterials in Europe and the world , 2012)

** (Goonan, 2011)

***50% reduction and augmentation

Cerium dioxide (CeO_2)			
Name of parameter	**Unit**	**Value**	**Remark. data source**
End-use 1: Automotive catalyst converter			
Net-import with articles and mixtures	kg/year	-	No data available
Total consumption	kg/year	780-1,830	The total mass of catalysts in catalyst-containing vehicles registered in Denmark in 2012 is estimated at 342-802 t/y. The total consumption of CeO2 is based on the total mass (1st interval) and the percentage of CeO2 mass in the catalysts. (Belcastro, 2012); (Aliexpress, 2013); (Statistics Denmark, 2013)
Trend in consumption	Unit-less	Decreasing	Article I. (Wijnhoven, Dekkers, Hagens, & de Jong, 2009)
Average service life time	year	12	The average service life of cars in Denmark is 16.3 years (Danmarks Statistik 2010-2011). The service life of car catalysts is expected to be around 75% of the service life of the car. car longevity cannot be used for catalysts longevity
Release to municipal waste water system	%	0	The CeO2 is embedded in a solid matrix and a potential release to water can only happen during use (i.e. driving the car or exchange of the catalyst). It is expected to be very unlikely that this will involve a release to the municipal waste water system.
Direct release to surface water	%	<1	The CeO2 is embedded in a solid matrix and a potential release to water can only happen during use (i.e. driving the car or exchange of the catalyst). It is expected to be very unlikely that this will involve a direct release to the surface water soil in any significant amounts.
Direct release to soil	%	<1	The CeO2 is embedded in a solid matrix and a potential release to water can only happen during use (i.e. driving the car or exchange of the catalyst). It is expected to be very unlikely that this will involve a direct release to soil in any significant amounts.
Direct release to air	%	<51 %	(Angelidis & Sklavounos, 1995)
Disposed of to MSWI	%	<1	The CeO2 is embedded in a solid matrix and will not be disposed of in the municipal solid waste fraction
Disposed of to landfill	%	<1	The CeO2 is embedded in a solid matrix and will not be disposed of in the municipal solid waste fraction
Disposed of for recycling (excl. energy recovery)	%	>49%	According to the Danish EPA. all catalyst are recycled; see 60803 Used Catalysts (Miljøstyrelsen, 2009) The reuse process for catalyst materials are not known, but if up to 51% is released to air during use, the remaining 49%will be found in the catalysts for recycling.

Cerium dioxide (CeO_2)			
Transformation during use into other forms	%	-	A transformation of CeAlO3 in the car catalyst has been reported but neither the percentage nor the transformation product were not given (Chen *et al.*, 2011) Ce2(SO4)3 (Zhao *et al.*, 2005)
End-use 2: Fuel borne catalyst/fuel additive			
Total consumption	kg/year	488	No figures are available to indicate that CeO2 is used as a fuel additive in Denmark. The number listed refers to the calculated amount of CeO2 scaled if it were to be used in Denmark at a level similar to the international use (Mayer, 2008)
Trend in consumption	Unit-less	stagnant	
Average service life time	year	<0.1	Depending on the refuelling which is expected to be more than once per month.
Release to municipal waste water system	%	0	During use, the loss to the municipal wastewater system is not likely. Spills during refuelling are anticipated to be collected in the collection system at gas stations.
Direct release to surface water	%	1	1% release was found by (Johnson & Park, 2012)
Direct release to soil	%	<1%	0.06-0.3% release to soil was found by (Johnson & Park, 2012) Futhermore, (Park, et al., 2008) noted that: "No major contamination of the soil would be expected and that soil levels of cerium oxide would be similar of those found naturally."
Direct release to air	%	1-5	(Johnson & Park, 2012)
Disposed of to MSWI	%	0	Since CeO2 is added to the diesel it is not likely to end up in MSWI
Disposed of to landfill	%	0	Since CeO2 is added to the diesel it is not likely to end up in landfills
Disposed of for recycling (excl. energy recovery)	%	95-99	In the scrap metal fraction from cars assuming that untransformed CeO2 will be deposited during use in parts of the motor and exhaust system (particle filter as the most likely part).
Transformation during use into other forms	%	0	There are no exact figures or estimates for transformation. but some indications are identified in the literature. "Some agglomeration and partial reduction of Ce(IV)." (Jung, Kittelson, & Zachariah, 2005) "n-ceria could impact transformations of other atmospheric species." (Majestic BJ, 2010) "Nanoparticulate cerium dioxide (nano-CeO2). when combusted as an additive to diesel fuel. was transformed from 6 nm to 14 nm sizes into particles near 43 nm. with no obvious change in the unit cell dimensions or crystalline form." (Batley, et al., 2013)
End-use 3: Glass polishing			

Cerium dioxide (CeO_2)			
Total consumption	kg/year		It has not been possible to find any specific information in this area about the use in Denmark or how CeO2 is used for this purpose. Therefore, no estimated released has been given below. Release values were taken from glass & ceramics product category of the ZnO case study.
Release to municipal waste water system	%	1	
Direct release to air	%		
Disposed of to MSWI	%	20	
Disposed of to landfill	%		
Disposed of for recycling (excl. energy recovery)	%	74	
Transformation during use into other forms	%	5	
Export	%		
End-use 4: Use of wood oil			
Total consumption	kg/year	100-500	Dispersions for preparation of oil containing 0.8 %(w/w) of CeO2 in the formulated product Corresponding to 25,000 liters of formulated product containing 0.8 %(w/w) of CeO2.
Trend in consumption	Unit-less	stagnant	
Average service life time	year	1	One yearly application can be assumed
Release to municipal waste water system	%	<5	The final wood oil is water-based. By application a small part will be discharged to the municipal sewage system by cleaning brushes and other equipment (from less than 1% to a few %).
Direct release to surface water	%	<1	Not likely unless a spill occurs.
Direct release to soil	%	<5	Related to spill during outdoor application
Direct release to air	%	0	After curing of the wood oil the cerium oxide is bound in the polymer matrix. Over time release of larger dust particles and flakes is possible, but the contribution to the overall mass balance is considered to be marginal.
Disposed of to MSWI	%	>88	Some 2-10 percent may be disposed of to MSWI with oil left in the container. This kind of wood oil is typically applied by brush and not by air brush. Dust from maintaining the wood is expected to be disposed of the MSWI By the end of its service life the treated wood (not pressure impregnated) is ultimately expected to be disposed of to MSWI
Disposed of to landfill	%	0	Not likely for Denmark
Disposed of for recycling (excl. energy recovery)	%	0	Not likely for Denmark

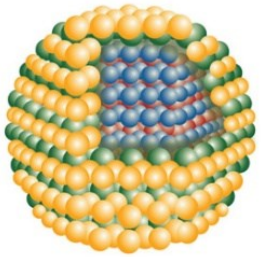
Cerium dioxide (CeO_2)			
Transformation during use into other forms	%	0	Not likely under normal use scenarios. Weathering of painted surfaces may cause some release, but transformations are not expected.
End-use 5: NiMH-batteries			
Total consumption	kg/year	290*	The total mass of NiMH batteries is estimated at 12-98 t/y- The 290 kg/y is an estimate of the amount of CeO 2 in NiMH batteries per / year based on (Miljøstyrelsen, Indsamlingssystemer for batterier, 2003)
Trend in consumption	Unit-less	Increasing Decreasing	Article II. (Binnemans, et al., 2013) Article III. Article IV. (Miljøstyrelsen, Status for batteriområdet i Danmark, 2005)
Average service life time	year	10 1-1.5	(Binnemans, et al., 2013) (forbrug.dk, 2012)
Release to municipal waste water system	%	0	CeO2 is incorporated in a solid matrix and release to municipal waste water is not likely during use or disposal.
Direct release to surface water	%	0	CeO2 is incorporated in a solid matrix and direct release to surface water is not likely during use or disposal.
Direct release to soil	%	5	(Mudgal, et al., 2011)
Direct release to air	%	0	CeO2 is incorporated in a solid matrix and direct release to air is not likely during use or disposal.
Disposed of to MSWI	%	22	(Mudgal, et al., 2011)
Disposed of to landfill	%	68 89.3*	Article V. (Mudgal, et al., 2011) Article VI. *Of collected batteries according to (Miljøstyrelsen, Indsamlingssystemer for batterier, 2003)
Disposed of for recycling (excl. energy recovery)	%	10 50 10.7*	(Mudgal, et al., 2011) (Miljøstyrelsen, Status for batteriområdet i Danmark, 2005) In the EPA report it is stated that the current system is the collection rate estimated to be around 50%., which the Environmental Protection Agency deems are not sufficient. From the collected batteries are separated manually, by both private and municipal waste companies; Pb batteries; NiCd batteries; NiMH batteries; and cell batteries for recycling. " The 10.7% is an estimate calculated from the 2003 report. i.e. of the collected batteries. (Miljøstyrelsen, Indsamlingssystemer for batterier, 2003)
Transformation during use into other forms	%	0	No data available, but transformation during use is not likely

Cerium dioxide (CeO_2)			
2.8.5 **Waste water treatment**			
Name of parameter	**Unit**	**Value**	**Remark. data source**
Transformation during STP treatment into other forms	%	-	Unknown percentage, though Westerhof *et al.* (2013) found that interaction with wastewater constituents altered the sorption properties of CeO2. (Westerhoff, Kiser, & Hristovsk, 2013) Limbach *et al.* (2008) reported that CeO2 agglomerated strongly in STP
Percentage ending up in sludge	% (l. u) uniform distribution	96.6 94	(Gómez-Rivera, *et al.*, 2012) (Limbach, *et al.*, 2008)
Percentage discharges	% (l. u) uniform distribution	3.4 6	(Gómez-Rivera, *et al.*, 2012) (Limbach, *et al.*, 2008)
Processes in surface waters after discharge	%	98 (out of the emitted)	"CeO2 nanoparticle hetero-aggregate with or deposition onto natural colloids. followed by sedimentation" (Quik. *et al.*. 2012) Modeled based on zwo extreme scenarios on sedimentation 0 and 100%, see comments e.g. for nano-TiO2.
2.8.6 **Solid waste treatment (incineration and landfill)**			
Name of parameter	**Unit**	**Value**	**Remark. data source**
Transformation or deposition during incineration into other forms (average Danish MSWIs)	%	approx. 0.1-52 (deposition, transformation)	The CeO2 partition between waste bunker, incinerator, boiler, electrostatic filter, wet scrubber, slag and fly ash was modelled as suggested in (Walser and Gottschalk, 2014). Mass transfer and fate parameters (see please Figure 1) are modelled as shown below in Table 1 that reflects the values derived from computer based simulations combined with real analytic/experimental results. These results show the steady state mass transport/transformation for all relevant WIP paths reached after steady state mode of such plants (infinite time scale). Analytically not detected and not further transported nano-CeO2 has been assigned to the subsequent further transport and/or to the subsequent deposition/transformation by covering at each stage in the WIP process the entire range of transport and fate possibilities. A distinction between material deposition and transformation was not possible due to analytical limitations
Percentage emitted to the air (average Danish MSWIs)	%	~0	See line above.

Cerium dioxide (CeO_2)			
Percentage ending up in residues (average Danish MSWIs)	%	approx. 36-75 (slag) approx. 3-9 (fly ash)	See line above.
Transformation during landfilling into other forms	%	No data	At this point we stopped our modelling. Nanomaterial fate and behaviour during landfilling was not considered. See also general comments on landfilling.
Release from landfills to municipal waste water treatment	kg/year	0	For landfill, no leachate out is assumed, see comments on previous cases.
Direct release from landfills to surface water	kg/year	0	See line above. Expected to be low due to sorption and straining of CeO2 in the waste matrix. For soils Cornelis *et al.* (2011) found aggregation and sorption to negatively charged soil constituents such as clay (Cornelis, et al., 2011)

2.8.7 **Recycling**			
Type of recycling activities	Recycling CeO2 in the batteries		
Name of parameter	**Unit**	**Value**	**Remark. data source**
Transformation during recycling into other forms	**%**	No data	Not likely during recycling, however recycling of batteries in Denmark (End-use 3) has not shown how the CeO2 in the batteries are recycled. At this point we stopped our modelling. Nanomaterial fate and behaviour during recycling was not considered.
Ending up in recycled products	**%**	-	No data available
Release from recycling process	**% of recycled**	0	See lines above. No data avaiable

2.9 Quantum dots

Quantum dots		
2.9.1 **General description**		
Name	Quantum dots; cadmium-free quantum dots	 Source: photonics.com
CAS number	1306-24-7 (CdSeS/ZnS) 22398-80-7 (InP). 1314-98-3 (ZnS) and more	
Chemical composition	Cadmium selenide/zinc selenide/zinc sulphide (CdSeS/ZnS); Cadmium selenide/cadmium sulphide (CdSe; CdS); Indium phosphide/zinc sulphide (InP/ZnS); Cadmium Mercury Telluride (CdHgTe). Cadmium Cadmium Telluride (CdTe). Cadmium Telluride/Cadmium Sulfide (CdTe/CdS); Lead Selenide (PbSe). Lead Sulfide (PbS). Other rare earth metal oxide phosphide.	
Appearance	Solid dry powder often dispersed in liquid media (water. organic solvents e.g. toluene) as described in the MSDSs.	

Nanomaterial description

Quantum dots are semiconductor materials; traditionally chalcogenides (selenides or sulphides) of metals such as Cd and Zn, which range from 2 to 10 nanometres in diameter (Nanoco). Due to the RoHS directive (2002/95/EC) implemented in 2006 and limiting the use of Cd, Cr(IV), Hg, Pb as well as brominated flame retardants (also WEEE-directive (2012/19/EU)) new quantum dots formulations are supposedly cadmium-free, and include rare earth metals such as indium and tellurium.

Quantum dots display unique optical and electrical properties visible to the human eye and the wavelength depends not on the material, but the size and shape of the quantum dot. Smaller dots are closer to the blue end of the spectrum; the larger closer to the red end, but dots tuned beyond visible light (infra-red or ultra-violet) are available (Nanoco, 2012; McDaniel, 2012).

General applications

Applications of quantum dots in products and commodities include semiconductors transistors, solar cells, light emitting devices (e.g. LEDs), and diode lasers, medical imaging (and diagnostics/detection) and as possible qubits in quantum computing.

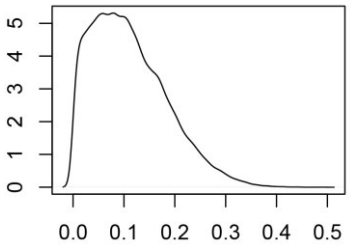
2.9.2 **Manufacturing and import/export of the substance on its own**

Manufacturing processes	None known, but manufacturing in Denmark cannot be excluded		
Manufacturing in Denmark			
Name of parameter	**Unit**	**Value**	**Remark. data source**
Import of the substance on its own uses to Denmark	kg/year	-	No data available for Denmark. The worldwide production is 600 kg/year (Piccinno, *et al.*, 2012)
Re-export	% of import	-	No data available

2.9.3 **Formulation in Denmark**

Identified formulation processes in Denmark	None known. But formulation in Denmark cannot be excluded

2.9.4 **Import/export and end-use in articles and mixtures**

Quantum dots	
Identified uses in articles and mixtures	The worldwide production is 600 kg/year Piccinno *et al.* (2011) estimates the total global production of quantum dots (QDs) at 0.6 t/y (25-75 percentile: 0.6-5.5 t/y) and the consumption in Europe at the same level. A normal distribution around the European values was modelled with standard deviation 0.1 and by eliminating negative values. As no Danish specific information has been possible to obtain the possible consumption of quantum dots in final articles is estimated on the basis of European/worldwide consumption figures. When no data is given there is no global estimate available; or the end-use known but not quantified; or in marginal percentages; or placed on a future/merging market where there is not data yet.  Figure 11. Annual quantum dots use volumes for Denmark. |	End use	Percentage of total Lower. modal. upper value (l**,m,u**) | |---|---|---| | 1 | Light conversion for LED/OLED (electronics etc.) | 90* | | 2 | Lab use for imaging | 10* | | | Solar cells | No data | | | Biomedical | No data | | | Product security and anti-counterfeiting | No data | | | Sensors | No data | | | Solid-state lighting | No data | * (Piccinno, *et al.*, 2012) **50% reduction and augmentation up to the absolute limits

Name of parameter	Unit	Value	Remark. data source
End-use 1: Light conversion for LED/OLED			
Total consumption	% of total consumption	90	Percentage (mean value) of the total QD use (Piccinno, *et al.*, 2012)
Trend in consumption	Unit-less	Increasing	Article VII. (Wijnhoven, Dekkers, Hagens, & de Jong, 2009)
Average service life time	year	-	Highly dependent on the type of electronics

Quantum dots			
Release* to municipal waste water system	%	0	QDs are incorporated in a solid matrix in the electronics and are not likely to be released under normal use conditions * Unless otherwise noted the release values were reduced/ enlarged on each side by 50% for the modeling of symmetrical triangular distributions around the specified quantities. The symmetry may possibly be by the absolute border values (highest or lowest possible release value, 1 and 0). In cases were more values are given, the mean is taken as modal value for such distributions.
Direct release to surface water	%	0	QDs are incorporated in a solid matrix in the electronics and are not likely to be released under normal use conditions
Direct release to soil	%	0	QDs are incorporated in a solid matrix in the electronics and are not likely to be released under normal use conditions
Direct release to air	%	0	QDs are incorporated in a solid matrix in the electronics and are not likely to be released under normal use conditions
Disposed of to MSWI	%	10	For electronic products nearly 100% will be disposed of for recycling (Miljøstyrelsen, ISAG Udtræksmodul, 2009), however if QDs are used for LED lamps and for these the majority is expected to be disposed of for MSWI (even LED lamps contain electronic components) will be higher since light sources usually end up in MSWI of which most is incinerated in Denmark. The spilt in QD use between separate light sources (lamps) and LEDs in electronic equipment is not known.
Disposed of to landfill	%	0	Electronic will not be landfilled in Denmark
Disposed of for recycling (excl. energy recovery)	%	90	The part of the LEDs in electronic equipment is expected nearly 100% to be disposed of for recycling of electronics (Miljøstyrelsen, ISAG Udtræksmodul, 2009)
Transformation during use into other forms	%	0	Not likely under normal use scenarios.
End-use 2: Lab use for imaging			
Total consumption	% of total consumption	10	Percentage (mean value) of the total QD use (Piccinno, *et al.*, 2012)
Trend in consumption	Unit-less	-	
Average service life time	year	-	Highly dependent on the type of electronics
Release to municipal waste water system	%	0	QDs are incorporated in a solid matrix in the electronics and are not likely to be released under normal use conditions
Direct release to surface water	%	0	QDs are incorporated in a solid matrix in the electronics and are not likely to be released under normal use conditions
Direct release to soil	%	0	QDs are incorporated in a solid matrix in the electronics and are not likely to be released under normal use conditions
Direct release to air	%	0	QDs are incorporated in a solid matrix in the electronics and are not likely to be released under normal use conditions

Quantum dots			
Disposed of to MSWI	%	0	For electronic products nearly 100% will be disposed of for recycling (Miljøstyrelsen, ISAG Udtræksmodul, 2009)
Disposed of to landfill	%	0	Electronic will not be landfilled in Denmark
Disposed of for recycling (excl. energy recovery)	%	100	The part of the LEDs in electronic equipment is expected nearly 100% to be disposed of for recycling of electronics (Miljøstyrelsen, ISAG Udtræksmodul, 2009)
Transformation during use into other forms	%	0	Not likely under normal use scenarios.

2.9.5 Waste water treatment

Name of parameter	Unit	Value	Remark. data source
Transformation during STP treatment into other forms		Possible, but not quantified. We used a zero value for trans-formation as done also for the nano-TiO2 studies.	Changes to the core/shell structure may occur due to e.g. changes in redox conditions. pH, and light conditions may occur as shown by the following quotes: Showed degradation and reduced mobility in soil. (Navarro, Banerjee, Watson, & Aga, 2011) "At pH 4.0. the number and the fluorescence of the individual particles decrease significantly. indicating changes in the electronic environment of the ZnS shell and/or dissolution of the QDs." (Slaveykova & Startchev, 2009) "quantum dots cause toxicity to bacterial cells by releasing harmful components…" (Jafar & Hamzeh, 2013) "slight changes in pH degraded quantum dot coatings. releas-ing the core metals and killing bacteria." (Mahendra, 2009) "most environmental conditions seem to favour QD degrada-tion" (Blickley, 2010) "QDs will become hydrophilic when dispersed in bodies of water" The Toxicological Effects of Engineered Nanoparticles. Quan-tum Dots. in Estuarine Fish.pdf (Blickley, 2010) "QDs are also photo - oxidized by visible light." (Blickley, 2010)
Percentage ending up in sludge	%	70-80	(Zhang, Chen, Westerhoff, & Crittenden, 2007) reports that the phase distribution of CdTe QD favour the solid phase, hence the majority sediment.
Percentage discharges	%	20-30	(Zhang, Chen, Westerhoff, & Crittenden, 2007)

Quantum dots			
2.9.6 **Solid waste treatment (incineration and landfill)**			
Name of parameter	**Unit**	**Value**	**Remark. data source**
Transformation or deposition during incineration into other forms (average Danish MSWIs)		approx. 0.1-52 (deposition, transformation)	The incineration model values for metal nanomaterials has been used also for metallic cadmium and zink based quantum dots. See please the details given in the previous CeO_2 case study that is based on Wasler and Gottschalk (2014).
Percentage emitted to the air (average Danish MSWIs)		~0	See line above. If Cd-QDs in LED lights are incinerated cadmium can be be volatilized, and condense on small particles. (Institute, 1993) The release will depend on the efficiency of the electrostatic filter for cleaning of the flue gas.
Percentage ending up in residues (average Danish MSWIs)	%	approx. 36-75 (slag) approx. 3-9 (fly ash)	See line above
Release from landfills to municipal waste water treatment	kg/year	0	Electronics are not expected to be landfilled
Direct release from landfills to surface water	kg/year	0	Electronics are not expected to be landfilled
2.9.7 **Recycling**			
Type of recycling activities	Not known – but expected to follow the normal procedures for EEE waste. Is it not likely that further environmental release occurs than the QD by the recycling may be melted or dissolved and not further present as a QD as modelled in this study.		
Name of parameter	**Unit**	**Value**	**Remark. data source**
Transformation during recycling into other forms	**%**	-	No data available
Ending up in recycled products	**%**	-	No data available
Release from recycling process	**% of recycled**	-	No data available

2.10 Carbon black

Carbon black		
2.10.1 **General description**		
Name	Carbon black	
CAS number	1333-86-4	
Chemical composition	Mono constituent substance (REACH registration)	

Carbon black		
Appearance	Carbon black is virtually pure elemental carbon in the form of colloidal particles. Its physical appearance is that of a black, finely divided pellets or powder. It is odourless. (REACH registration)	Source: Wikipedia

Nanomaterial description

Carbon black is elemental carbon in the form of an extremely fine black powder consisting of near-spherical colloidal particles and particle aggregates. Depending on the manufacturing process, carbon blacks are categorized as furnace black, lampblack, acetylene black, channel black, gas black or thermal black. These types of carbon black are characterized by the size distribution of the primary particles, the degree of their aggregation and agglomeration and the various chemicals adsorbed onto the surfaces. (OECD 2006

The primary carbon black particle, also known as the nodule, is approximately 10 to 500 nm in diameter (OECD 2006). The molecular structure of carbon black consists of a condensed aromatic ring system of carbon atoms arranged in large sheets of variable size and alignment (Environment Canada, 2013). During the production process, the carbon black nodules coalesce to form aggregates, the primary dispersible unit, which are about 80–810 nm in size and consist of a few up to hundreds of particles (Environment Canada, 2013). Further along the production process, electrical forces (e.g., van der Waals forces) promote the formation of agglomerates 1–100 mm in diameter that consist of hundreds to thousands of adhering aggregates. This is the form of carbon black often encountered in commerce.

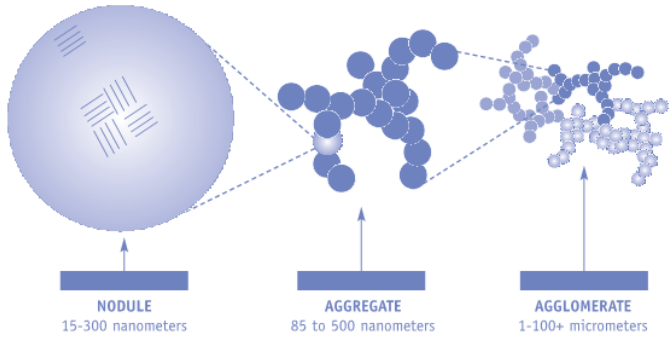


Figure 12. Carbon black forms. Source: ICBA (2004)

Carbon black should not be confused with black carbon, which is an entirely different substance (Environment Canada, 2013). Black carbon is formed through the incomplete combustion of fossil fuels, biofuel, and biomass (e.g. diesel exhaust) and is often referred to as soot, whereas carbon black is produced by the controlled vapour phase pyrolysis of gaseous or liquid hydrocarbons (Environment Canada, 2013).

Hence, while agglomerates may dissociate into aggregates under certain circumstances, aggregation that spontaneously occurs in manufacturing processes produces aggregates of average size, generally over 100 nm, that are effectively unbreakable (ICBA 2004 as cited by Environment Canada, 2013). For example, in a series of experiments where intense mechanical energy was applied to carbon black products via uniaxial compression, elastomer mixing, or ultrasonication, there was little or no release of nodules and only limited fracture of the largest agglomerates (Gray and Muranko 2006, as cited Environment Canada, 2013).

Although the aggregation that spontaneously occurs in manufacturing processes produces unbreakable aggregates of an average size that is generally over 100 nm (IBCA 2004), carbon black can include a limited fraction of materials that are smaller than this i.e., nano-scale materials (Environment Canada, 2013).

Two major processes are presently used to manufacture carbon black, the oil furnace black process and the thermal black process; the first accounting for about 90% of production, and the latter for about 10% (Environment Canada, 2013).

The four major types of carbon black can be characterized by size distribution of the primary particles, the degree of particle aggre-

Carbon black

gation and agglomeration, the various chemicals adsorbed on the particle surface, and the functional groups located at sheet extremities (OECD 2006).

Property	Acetylene black	Furnace black	Lampblack	Thermal black	Gas black
Average aggregate diameter	Not reported	80–500 nm	Not reported	300–810 nm	Not reported
Average primary particle diameter	35–50 nm	17–70 nm	50–100 nm	150–500 nm	13–29 nm
Surface area (m2/g)	60–70	20–200	20–95	6–15	90–320
Density (g/mL)	Not reported	1.80	1.77	Not reported	1.20–1.80

General applications

Worldwide carbon black consumption in 2010 was 9 million t/y and were expected to reach 13 million t/y 2015.

In the EU the registered production and import of carbon black is in the 1,000,000-10,000,000 t/y tonnage band.

Tires and other rubber products - Globally, approximately 90% of carbon black produced is used in the rubber industry as a reinforcing filler in a variety of products. The 70% is used as a reinforcement in tyres for automobiles and other vehicles, and 20% is used for other rubber products such as hoses, gaskets, mechanical and moulded goods, and footwear (OECD, 2005; Environment Canada, 2013). The production of tires of all sorts consumed over 7.8 million tonnes in 2011 (Ceresana, 2013). In tires and other rubber articles the carbon black is used for reinforcement. Carbon black constitutes approximately 22% of the mass of a tyre (OECD, 2005).

Other industrial sectors - About 9% of the global consumption is used as black pigment in other industrial sectors like plastics, paints, varnishes and printing inks. The remaining 1% is used in hundreds of diverse products, including batteries, high temperature insulating material, and thickeners for certain high temperature petroleum and synthetic greases. In addition, carbon black is used to impart electrical conductivity in rubber and plastics (Environment Canada, 2013)

According to the U.S. Household Products Database (HPD, 2009 as cited by Environment Canada, 2013), carbon black is used in a variety of household products including paints (liquid and aerosol), primers, stains, paint protectors (i.e., undercoating), rubber gaskets, caulking, concrete repair and sealants, cement colour pigments, fibreglass insulation, pipe seals, shoe polish, laserjet printer toners, inkjet printer cartridges, electronic sealants, and diaper ointment.

The International Carbon Black Association (ICBA, 2013) indicates the following applications in addition to the applications in rubber mentioned above:

Plastics - Carbon blacks are now widely used for conductive packaging, films, fibres, mouldings, pipes and semi-conductive cable compounds in products such as refuse sacks, industrial bags, photographic containers, agriculture mulch film, stretch wrap, and thermoplastic molding applications for automotive, electrical/electronics, household appliances and blow-moulded containers.

Electrostatic Discharge (ESD) Compounds - Carbon blacks are carefully designed to transform electrical characteristics from insulating to conductive in products such as electronics packaging, safety applications, and automotive parts.

High Performance Coatings - Carbon blacks provide pigmentation, conductivity, and UV protection for a number of coating applications including automotive (primer basecoats and clearcoats), marine, aerospace, decorative, wood, and industrial coatings.

Toners and Printing Inks - Carbon blacks enhance formulations and deliver broad flexibility in meeting specific colour requirements.

Carbon black			
2.10.2 Manufacturing and import/export of the substance on its own			
Manufacturing processes	The following description is extracted from OECD (2005). The oil furnace black process uses heavy aromatic oils as feedstock. The production furnace is a tightly enclosed reactor used to react the feedstock under carefully controlled conditions and at extremely high temperatures. The feedstock is atomized in a hot gas stream where it vaporizes and then pyrolyzed in the vapour phase to form microscopic carbon particles. In most furnace reactors, the reaction is controlled by steam or water sprays. The carbon black produced is conveyed through the reactor, cooled, and collected in bag filters in a continuous process. Furnace black is available in several grades. They are mainly used in rubber products, inks, paints and plastics. The thermal black process uses natural gas, mainly consisting of methane, as the starting material in a cyclic operation in which the gas is thermally decomposed (cracked). The process uses a pair of furnaces that alternate approximately every five minutes between preheating and carbon production. The methane is injected into a hot refractory-lined furnace. In the absence of air, the heat from the refractory material decomposes the methane into carbon black and hydrogen. The aerosol material stream is quenched with water sprays and filtered. The exiting carbon black may be further processed to remove impurities, pelletized, screened, and then packaged for shipment. The process yields relatively coarse particles. Two other processes (the lamp process for production of lampblack and the cracking of acetylene to produce acetylene black) are use for small-volume specialty carbon blacks that constitute less than 1% of the total production. Lampblack is produced by burning liquid hydrocarbons, e.g. kerosene. Lampblack is often oily. It is used for contact brushes in electrical apparatus.		
Manufacturing in Denmark	Carbon black is not produced in Denmark		
Name of parameter	**Unit**	**Value**	**Remark, data source**
Import of the substance on its own uses to Denmark	kg/year	no information	In the trade statistics carbon black is registered together with other forms of carbon not elsewhere specified and specific data on carbon black cannot be extracted
Re-export	% of import	no information	
2.10.3 Formulation in Denmark			
Identified formulation processes in Denmark	According to the SPIN database (SPIN 2013), based on registrations in the Danish Product Registry, the total content of carbon black in mixtures placed on the Danish market for professional purposed in 2010 was as shown in the table below. It is not indicated whether the mixtures placed on the Danish market are produced in Denmark or imported. The Danish Product Register includes substances and mixtures used occupationally and which contain at least one substance classified as dangerous in a concentration of at least 0.1% to 1% (depending on the classification of the substance). Carbon black is not classified and the registration will only occur if the substance is constituent of mixtures which contain other substances classified as dangerous above the indicated limits. The application area "colouring agents" are probably imported agents used in the formulation of lacquers and varnishes, reprographic agents (printing inks), pigments, textiles, cosmetics and adhesives, whereas the other application areas are the final mixtures – either produced in Denmark or imported. Raw materials for manufacture of plastics such as compounds or masterbatches are likely not register in the Product registry. A previous survey on the use of nanomaterials in the Danish industry reports that more than 1		

Carbon black

t/y carbon black was used for the manufacture of paints and printing inks, more than 10 t/y was used for textiles. Tønning *et al.* (2014) reports that carbon black is used in the manufacture of cosmetics (mascara, eyeliner and nail polish).

For the current survey a use of more than 100 t/y for manufactures of paint and varnishes has been confirmed.

Based on the available data it is estimated that around (100-400 t/y) carbon black is used for manufacture of various mixtures while 10-50 t/y is used for manufacture of textiles.

Application area	Content in mixtures placed on the Danish market , tonnes/year *
Colouring agents	201
Reprographic agents (printing inks)	156
Paints, lacquers and varnishes	119
Fillers	30
Construction materials	14
Impregnating materials	6
Adhesives and binding agents	4
Non-agricultural pesticides and preservatives**	4
Surface treatment	3
Others	5

* Production + import – export

**Assumed to be antifouling paints

For comparison with Danish figures, for the year 2006, the Canadian Chemical Producers' Association (now called Chemistry Industry Association of Canada) emissions inventory reported total carbon black emissions from member companies of 1.1 t/y (CCPA 2006). None of the companies that reported releases were producers of carbon black.

Name of parameter	Unit	Value	Remark, data source
Formulation 1: Production of paint, lacquers, pigments, reprographic agents, adhesives, cosmetics			
Number of companies	companies	10-50	
Quantities used	t/year	100-400	Based on the registration of 201 t/y carbon black in colouring agents. The majority is expected to be used for the manufacture of paint and varnishes.
Ending up in final products	%	97%	
Release* to municipal waste water system * Unless otherwise noted the release values were reduced/ enlarged on each side by 50% for the modeling of symmetrical triangular distributions around the specified quantities. The symmetry may possibly be by the absolute border values	%	<0,5	The emission scenario document (ESD) for the paint industry from the OECD (2009) assume for manufacture of aqueous dispersion coatings that the total fraction of raw materials lost to waste from the manufacturing process is 1.5%. This includes 1% lost due to residues in the mixing vessels and 0.5% due to residues in bags, spills and product returns. It is in the ESD assumed that half of the residue material in the mixing vessels will be re-used in the manufacturing process (recycling. For aqueous dispersion coatings the remaining equipment residue is assumed to be removed in water washings and hence to waste water.

Carbon black			
(highest or lowest possible release value, 1 and 0). In cases were more values are given, the mean is taken as modal value for such distributions.			According to information from Danish manufactures waste water originates from cleaning of tanks and other production equipment. Approximately 1-2% of the total used may be released to the waste water for pre-treatment/treatment at the manufacturing sites. The first step at all sites is a precipitation/flocculation where the majority of the carbon black is precipitated and ends up in a sludge/filter cake which is disposed of for external incineration or gasification. The pre-treated waste water is either directed to municipal waste water plants or further treated at the manufacturing sites. In the latter case, the waste water is further treated. The waste water is first treated by pre-precipitation tank, then by biological treatment and ultimately by a final polishing. As a worst case estimate, the releases to municipal waste water treatment plants or surface water is estimated to be <0,5%. The actual release is probably significantly below this value. The pre-treated waste water is mainly directed to municipal waste water treatment plants but a small fraction may be discharged to surface water
Direct release to surface water (after internal WW treatment)	%	<0,1	Worst case estimate – the total release is probably significantly below the <0.1%.
Direct release to soil	%		The carbon black is imported as pastes in which the TiO2 is dispersed in water. The generation of dust by handling of the pastes is considered insignificant.
Direct release to air	%		The carbon black is imported as pastes in which the TiO2 is dispersed in water. The generation of dust by handling of the pastes is considered insignificant
Disposed of as solid waste for incineration	%	2	Filtercake/sludge and carbon black remaining in packaging are disposed of for incineration or gasification.
Disposed of for other waste management	%		Considered insignificant
Percentage of produced products exported	% of quantity in final product	No data	
2.10.4 Import/export and end-use in articles and mixtures			
Identified uses in articles and mixtures	The total global carbon black market is approximately 10 million t/y (Ceresana. 2013). No exact data on the consumption in the EU is available (registration toannge band 1-10 million t/y), but most likely it is in the range of 1-4 million t/y. Assuming the same per capita consumption in Denmark as the EU average, the annual con-		

sumption in mixtures and articles would be some 10,000-40,000 t/y (own expert estimate). If 90% is +imported with tyres and other rubber products, the remaining 10% would correspond to approximately 1,000-4,000 t/y. The data from the Product Registry indicates a total consumption of 340 t/y in various mixtures (excluding colouring agents which are expected to be used in production processes). As the carbon black is not assigned a harmonised classification in accordance with the CLP Regulation, the substances would only be registered in the Product Registry if the mixture other classified constituents. For water-based paints, adhesives, XX, etc. the registered tonnage may be significantly underestimated. Furthermore, compounds and masterbatches for plastic manufacture may not be covered by the registration in the Product Registry.

We computed normally distributed values for the Danish use volume by basing our computations on values indiacted above (globally 10 million t/y, 10,000 and 40,000 t/y for Denmark). However, a minimal value of 5'000 t/y was fixed and the global estimation had to be scaled down to European and Swiss conditions based on the proportion of the Gross Domestic Product as suggested elsewhere (Sun *et al.*, 2014). The sacling Denmark Switzerland occurred by using the population volume, since the consumption capability of these two countries is similar.

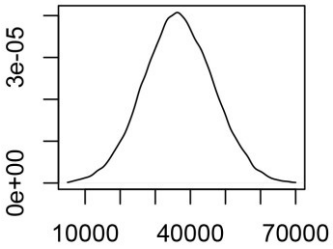


Figure 13. Annual use volumes covering nanomaterial mass of import and own formulation processes Denmark.

	End use	Percentage of total Lower, modal, upper value (l*,m,u*)
1	Tires	35 ,70, 100
2	Other rubber components (various articles)	10, 20, 30
3	Paint and varnishes	1.5, 3, 4.5
4	Antifouling paints	0.05, 0.1, 0.15
5	Inks	1.5, 3, 4.5
6	Plastic components (various articles)	1.5, 3, 4.5
7	Filters	0.1, 0.2, 0.3
8	Other	0.4, 0.7, 1.1
*50% reduction and augmentation		

Name of parameter	Unit	Value	Remark, data source
End-use 1: Tires			
Total consumption	% of total consumption	70	Mean values, based on information on global consumption figures
Release to municipal waste water system	%	3	Approximately 22% of a tire is composed of carbon black, and on average a tire loses from 10 to 20% of its weight during use over its service life (OECD, 2006). As it is bound

Carbon black			
			within the elastomer complex, carbon black is unlikely to be released from tires as an unbound particle through wear or abrasion (US EPA 1976; OECD 2006; ChemRisk, Inc. and DIK, Inc. 2008 as cited by Environment Canada, 2013). According the Naturstyrelsen (2012) the paved area in areal appoximately 77.000 hectares, of this 35.500 hectares has common sewerage system and the remaining 41.500 hectares has separate storm water sewerage system. The significant part of dust from the tires will be generated outside areas with sewer systems and here the dust will either be released to soil or to surface water. The 15% lost from the tires are roughly estimated to distributed as follows: 4% to soil 8% to surface water 3% to municipal waste water
Direct release to surface water	%	8	Release via separate storm water sewerage system from paved areas and direct loss to surface water from areas without sewer systems
Direct release to soil	%	4	Losses to soil around roads in the countryside
Direct release to air	%	1	Some of the dust may be considered a release to air but is expected to . Value according to the one for CTNs.
Disposed of to MSWI	%	5	Even the majority of tires are disposed of for recycling a small part may end up on MSWI. According to Dækbranchens Miljøfond (2012), 97% of the tires collected in 2011 were recycled. It is not indicated what happened to the remaining 3%. In addition as small percentage may be disposed of directly the MSWI without collection
Disposed of to landfill	%		Tires are not disposed of to landfills in Denmark
Disposed of for recycling (excl. energy recovery)	%	80	[we have not yet identified data showing the collection efficiency of tires in Denmatk] 97% of the tires collected in 2011 were recycled (Dækbranchens Miljøfond, 2012)
Transformation during use into other forms	%	-	
End-use 2: Other rubber components (various articles)			
Total consumption	% of total consumption	20	Mean values, based on information on global consumption figures
Direct release to surface water	%	<0.1	The releases to the environment and waste water of particles of other rubber products to the environment is considered insignificant but small releases cannot be excluded
Direct release to soil	%	<0.1	See above
Direct release to air	%	<0.1	See above
Disposed of to MSWI	%	95	

Carbon black			
Disposed of to landfill	%	5	Roughly estimated. Rubber parts of in vehicles (gaskets, hoses, etc.) may be disposed of to landfills in waste from shredder plants
Disposed of for recycling (excl. energy recovery)	%	0	The recycling of other rubber products is considered insignificant
Transformation during use into other forms	%	-	No data
End-use 3: Paint and varnishes			
Total consumption	% of total consumption	3	Mean values, based on information on global consumption figures
Release to municipal waste water system	%	1	Dust and flakes from maintenance of painted surfaces and from abrasion of painted surfaces
Direct release to surface water	%	1	Dust and flakes from maintenance of painted surfaces and from abrasion of painted surfaces
Direct release to soil	%	2	Dust and flakes from maintenance of painted surfaces and from abrasion of painted surfaces
Direct release to air	%	1	Dust and flakes from maintenance of painted surfaces and from abrasion of painted surfaces
Disposed of to MSWI	%	50	Paint remaining in packaging and paint on wood and other combustible materials
Disposed of to landfill	%	10	Paint on concrete and other non-combustible building materials
Disposed of for recycling (excl. energy recovery)	%	35	Paint on metals
Transformation during use into other forms	%		No data
End-use 4: Antifouling paints			
Total consumption	% of total consumption	0.1	Estimates on the basis of information on carbon black in antifouling paint marketed in Denmark (data from the Product Registry) Antifouling paint is a complicated category as paint applied in Denmark may not necessarily be applied on vessels sailing i Danish waters, and thus not release to Danish waters. At the same time a significant part of the releases to Danish waters is from vessels passing the waters og foreign vessels visiting Danish harbours. A study on the use of organotin compounds for antifouling estimated that the total releases to the Danish waters was less than half of the releases due to organotin applied in Denmark (released in Denmark and elsewhere). In the following for simplicity the releases from antifouling paint used (applied) in Denmark is assumed to be released to Danish waters.

Carbon black			
Release to municipal waste water system	%		
Direct release to surface water	%	67	A study on the use of organotin compounds in antifouling paints in Denmark estimates that 60-70% of the paint is released to the water during use (Lassen *et al.*, 1999). In addition small quantities will be lost by maintenance of boats and vessels. The main part is released to the sea while a very small part is releases to streams and lakes.
Direct release to soil	%	0.1	A small percentage may be lost to soil by maintenance of boats
Disposed of to MSWI	%	1	Disposed of with dust from maintenance
Disposed of to landfill	%		
Disposed of for recycling (excl. energy recovery)	%	32	Remaining on the metal ultimately disposed of for recycling
Transformation during use into other forms	%		
End-use 5: Inks			
Total consumption	% of total consumption	3	Mean values, based on information on global consumption figures
Release to municipal waste water system	%		
Direct release to surface water	%		
Direct release to soil	%		
Direct release to air	%		
Disposed of to MSWI	%	10	In analogy with nanomaterial in paper (nano-TiO2) as estimated elswhere (Sun *et al.*, 2014).
Disposed of to landfill	%		
Disposed of for recycling (excl. energy recovery)	%	80	See lines above.
Export	%	10	See lines above.
End-use 6: Plastic components (various articles)			
Total consumption	% of total consumption	3	Mean values, based on information on global consumption figures
Release to municipal waste water system	%	<0.1	The releases to the environment and waste water of particles of other rubber products to the environment is considered insignificant but small releases cannot be excluded
Direct release to surface water	%	<0.1	See above
Direct release to soil	%	<0.1	See above

Carbon black			
Disposed of to MSWI	%	96	The recycling of those plastic parts that contain carbon black (see description in the section on general applications) is considered very small, and the majority is thus disposed of for incineration
Disposed of to landfill	%	2	Roughly estimated. Plastic parts in vehicles may be disposed of to landfills in waste from shredder plants
Disposed of for recycling (excl. energy recovery)	%	2	The recycling of those plastic parts that contain carbon black (see description in the section on general applications) is considered very small
Transformation during use into other forms	%		No data
End-use 7: Fillers			
Total consumption	% of total consumption	0,2	Mean values, based on information on global consumption figures
Release to municipal waste water system	%	25	In analogy to application in filters of nano-TiO2 (Sun *et al.*, 2014)
Direct release to surface water	%		
Direct release to soil	%		
Direct release to air	%	5	See lines above.
Disposed of to MSWI	%	70	See lines above.
Disposed of to landfill	%		
Disposed of for recycling (excl. energy recovery)	%		
Transformation during use into other forms	%		
End-use 8: Other uses – not further considered			

2.10.5 Waste water treatment

Name of parameter	Unit	Value	Remark, data source
Transformation during STP treatment into other forms	%		no data – not expected to be significant
Percentage ending up in sludge	% (l, m, u)	0, 50, 100	Environment Canada (2013) conservatively estimate the carbon black removal efficiency from influent resulting from the wastewater treatment process at 50% where lagoons or primary treatments exist.
Percentage discharges	% (l, m, u)	0, 50, 100	See above.

2.10.6 Solid waste treatment (incineration and landfill)

Name of parameter	Unit	Value	Remark, data source
Transformation during incineration into other forms (average Danish	%	75, 98, 100	The degradation temperature of carbon black is in principle 3652–3697°C and it is not expected that carbon black will be degraded during incineration under non-oxidative conditions

Carbon black			
MSWIs)			(Environment Canada, 2013). In this report carbon-based materials /CNT and CB) are assumed to almost completely burn under standard oxidative conditions in the furnace (Mueller *et al.*, 2013). Complete combustion is expected for carbon black with low air release and almost no residual ash (ICBA, 2014).
Percentage emitted to the air (average Danish MSWIs)	%	<1	Despite the presence of pollution control devices, some dust containing carbon black may escape into air. (Environment Canada, 2013). With the filters used in Danish waste incinerators it is expected that less than one percent of the carbon black will be released to the air.
Percentage ending up in residues (average Danish MSWIs)	%	~99	It is expected that the majority of the carbon black ends up in the ashes from the flue gas cleaning which as disposed of for landfilling. A minor part is expected to end up in the bottom ashes which to some extent are used for construction works. Mass allocation to diferent ashes according to others and as done for CNT: 18 % reaching fly ashes and 81% ending up in bottom ashes (Sun *et al.*, 2014)
Release from landfills to municipal waste water treatment	kg/year	0	For landfill, no leachate out is assumed.
Direct release from landfills to surface water	kg/year	0	See line above.
Transformation during landfilling into other forms	%	No data	At this point we stopped our modelling. Nanomaterial fate and behaviour during landfilling was not considered. See also general comments on landfilling.
2.10.7 Recycling			
Type of recycling activities	Recycling processes include recycling of tires and recycling of printed paper. [to be elaborated]		
Name of parameter	**Unit**	**Value**	**Remark, data source**
Transformation during recycling into other forms	**%**	No data	No data available. We did not track the material fate and mass flows of the studied nanoparticles during and after the recycling process.
Ending up in recycled products	**%**	No data	See lines above.
Release from recycling process	**% of recycled**	0	See lines above.

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Nanomaterials in the Danish environment

The report is Annex 1 to the report ""Nanomaterials in the Danish environment. Modelling exposure of the Danish environment to selected nanomaterials".

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