

Industrial production quantities and uses of ten engineered nanomaterials in Europe and the world

Fabiano Piccinno · Fadri Gottschalk ·
Stefan Seeger · Bernd Nowack

Received: 22 May 2012 / Accepted: 31 July 2012 / Published online: 19 August 2012
© Springer Science+Business Media B.V. 2012

Abstract Not much is known so far about the amounts of engineered nanomaterials (ENM) that are produced but this information is crucial for environmental exposure assessment. This paper provides worldwide and Europe-wide estimates for the production and use of ten different ENM (TiO₂, ZnO, FeO_x, AlO_x, SiO₂, CeO₂, Ag, quantum dots, CNT, and fullerenes) based on a survey sent to companies producing and using ENM. The companies were asked about their estimate of the worldwide or regional market and not about their company-specific production, information that they would be less likely to communicate. The study focused on the actual production quantities and not the production capacities. The survey also addressed information on distribution of the produced ENM to different product categories. The results reveal that some ENM are produced in Europe in small amounts (less than 10 t/

year for Ag, QDs and fullerenes). The most produced ENM is TiO₂ with up to 10,000 t of worldwide production. CeO₂, FeO_x, AlO_x, ZnO, and CNT are produced between 100 and 1000 t/year. The data for SiO₂ cover the whole range from less than 10 to more than 10,000 t/year, which is indicative of problems related to the definition of this material (is pyrogenic silica considered an ENM or not?). For seven ENM we have obtained the first estimates for their distribution to different product categories, information that also forms the base for life-cycle based exposure analysis.

Keywords Production quantities ·
Nanomaterials · Europe

Introduction

Nanotechnology is one of the fastest growing and most promising technologies in our society (Forster et al. 2011). Possible fields for the use of engineered nanomaterials (ENM) comprise advanced materials, display technologies, electronics, nutrition, cosmetics, medical drug designing, and numerous other applications. On the other hand, this exciting technological progress may also be associated with risks. The small size of ENM, for example, can have major toxicological consequences since ENM could possibly enter human cells (Krug and Wick 2011; Oberdörster et al. 2005). Even though the literature contains many

Electronic supplementary material The online version of this article (doi:10.1007/s11051-012-1109-9) contains supplementary material, which is available to authorized users.

F. Piccinno · F. Gottschalk · B. Nowack (✉)
Empa–Swiss Federal Laboratories for Materials Science
and Technology, Technology and Society Laboratory,
Lerchenfeldstrasse 5, 9014 St. Gallen, Switzerland
e-mail: nowack@empa.ch

F. Piccinno · S. Seeger
Institute of Physical Chemistry, University of Zurich,
Winterthurerstrasse 190, 8057 Zurich, Switzerland

studies about toxicological and environmental characteristics of ENM (Klaine et al. 2008; Nowack and Bucheli 2007; Wiesner et al. 2009), it is striking that there is a lack of information about effective quantities of engineered ENM in circulation (Hendren et al. 2011). For material-flow modeling of ENM from products to the environment and the prediction of environmental exposure, an important input variable is the production amount (Gottschalk and Nowack 2011).

For most of the ENM only few and sometimes conflicting data about production amounts are available, and this lack of information presents one of the major obstacles in assessing possible risks to the environment (Hendren et al. 2011). Additionally, this data often refers to the production capacities rather than the actual production amounts, which can differ significantly. Only three refereed publications with such data are available that also describe the method by which the data were obtained (Hendren et al. 2011; Robichaud et al. 2009; Schmid and Riediker 2008). Schmid and Riediker (2008) report results from a targeted survey of Swiss companies for usage of seven ENM in Swiss industry, thus only for a small region. ENM of which more than 10 t are used each year in Switzerland were Fe-oxides, SiO₂, TiO₂, and ZnO. Robichaud et al. (2009) calculated the US production of nano-TiO₂ assuming that a certain proportion of the total TiO₂ production is in nanof orm. They came to the conclusion that at the time of their evaluation about 2.5 % of the total TiO₂ production of 2.5 million tons was nanoparticulate. Hendren et al. (2011) estimated upper and lower bound production quantities for five ENM in the US. A variety of sources (web sites, patents, direct communications) were used to identify companies producing ENM and to determine the production volumes. Ranges of production quantities were estimated using assumptions to attribute production amounts from companies with more reliable data to companies with little to no data.

Other production numbers are found in reports, leaflets, or as data snippets in publications that do not deal with the issue in detail. Mueller and Nowack (2008) have extracted from this literature a realistic and a high-production scenario for TiO₂, Ag, and CNT, while Gottschalk et al. (2009, 2010a, b) have used probabilistic modeling to account to the high variability of data from different sources and provided estimates for worldwide production of five different ENM (TiO₂, ZnO, Ag, CNT, fullerenes). Given the

uncertain source of the production data, the extrapolation method that was used to scale regional to worldwide amounts and the wide range of values from one ENM (up to a factor of 100 variation between the lowest and highest estimates), these estimates have to be used very cautiously.

Even less is known about the distribution of ENM over different product categories. The knowledge on the life-cycle of products is crucial for predicting the environmental fate and effects of ENM (Gottschalk and Nowack 2011; Som et al. 2010). Many papers and reports list possible application areas of ENM (Aitken et al. 2006; Lo et al. 2007; Wijnhoven et al. 2010) and the Woodrow Wilson Database is well-known for its list of products (Berube et al. 2010). A first evaluation of product distribution was attempted as a basis for exposure modeling, based on information of commercially available products (Gottschalk et al. 2009, 2010b; Mueller and Nowack 2008).

One critical point to be considered when dealing with ENM is the definition of the terminology given that there is no official definition existing. The International Organization for Standardization (ISO) provides a proposal for a definition that is commonly used. ISO defines a nano-object as a material with at least one external dimension in the nanoscale. That comprises the size range from 1 nm to 100 nm. If all three external dimensions are in the nanoscale, the conditions for a nanoparticle are given (ISO 2008). In October 2011, the European Commission published a recommendation on the definition of nanomaterials which defines nanomaterial as 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” (EU 2011). While the theoretical definition on a scientific basis of nanomaterials itself is a challenge, the use of standardized measurement methods is an additional problem linked to that issue (Bleeker et al. 2012).

The aim of this paper is to provide new information on production amounts and product distribution of ten different ENM: TiO₂, ZnO, FeO_x, AlO_x, SiO₂, CeO₂, Ag, quantum dots (QDs), CNT, and fullerenes. We focused our investigation on Europe but also aimed to obtain data on worldwide production and use. The method we chose was to send a survey to industrial representatives from companies producing or using

ENM. These representatives were asked for their appraisal of the worldwide or Europe-wide production of ENM whereas it was clearly specified that the production capacities were out of scope. The main hypothesis of our work was that companies possess knowledge not only on their own production amount but also have an idea about the size of the market and that they are more likely to communicate this estimate than their own production amount. In addition we aimed to obtain from these companies also information on the use of ENM, again with the hypothesis that companies producing ENM possess knowledge of the amounts used by their customers.

Materials and methods

This work is based on a survey carried out among experts in various companies and institutions within the nanomaterial industry sector. The survey comprised an inquiry about the estimates of global, national, and regional production and utilization quantities of ENM as well as the allocation of this production to different product categories. Since the production amounts of ENM are a delicate matter for companies to reveal, the formulation of the survey made it clear that there was no need to know the quantities produced by single companies, but that we were only interested in expert estimates of the worldwide/continent-wide or national production or use, and that all the answers would be treated anonymously and confidentially. It was also clearly mentioned that no production capacities but only actual quantities produced were the scope of the survey. Hereby, the terms “production” and “utilization” were intentionally used together. Since the recommendation of the European Commission about the definition of a nanomaterial (EU 2011) had not been published when this survey was sent out, no precise definition of ENM was given to the experts which left them some room for interpretation. The first part was further subdivided into global, regional, and national production and utilization quantities with Europe, North America, and Asia/Pacific being the three possible regions. The experts were given two choices: either they could provide a production number or they could select a category in predefined ranges (<1, 1–10, 10–100, 100–1000, 1000–10,000,

10,000–100,000, >100,000 t/year). In this manner, experts with an exact estimate were able to provide it, while all others having a less accurate estimate could indicate the most likely range.

The second section of the survey was dedicated to the product distribution of these ENM. The intention was to get information as to what proportions of the total production quantities of these NPs end up in what commercially available products. In other words, the aim was to identify, for example, what percentage of the total nano-TiO₂ is used as UV-protection in sunscreens. No answer framework regarding products or percentages was given, but the answer type was deliberately chosen to be open text boxes, not multiple choice. This assured that the respondents would not be influenced or misled by our inputs.

This survey required expertise and insider knowledge to reply, and it was a fundamental step to select experts working in companies and institutions that were producers or manufacturers (users) of ENM. First we conducted an internet search for companies producing ENM to find the email addresses on the company's website, publications, or presentations. If no personal contacts could be found, the firms standard email address was taken. Secondly, NanoPerspective (NanoCentral 2010), a British professional journal for the nanotechnology sector, served as a very helpful source for contact information.

The survey was sent via SurveyMonkey (www.surveymonkey.com) to 360 different email addresses of which 51 could not be delivered. If the survey was sent to more than one contact within the same company and region, they were counted together as one. Using this procedure, 70 duplicates were detected leaving 239 (Europe 196, US 26, other 17) countable recipients and of which 82 (34 %) gave a feedback. An evaluation of online surveys concluded that the average response rates to such surveys was 32.5 % (Hamilton 2009), indicating that our response rate was good. Of all feedbacks received, 36 (15 %) replied by email informing that they would either not be qualified enough or not allowed to fill out the survey. Nevertheless, 46 (19 %) answered the survey completely or at least partly and 36 (15 %) of these replied to the first part of the inquiry. The return was 45 from Europe, 1 from the US and 0 from the other regions. However, those regions do not reflect the company's origin or headquarters but the local office of the contact person. In other words, several US

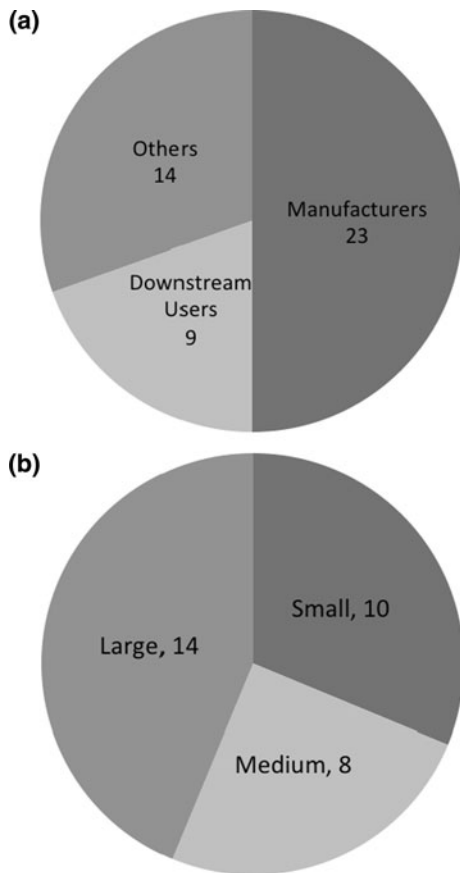


Fig. 1 **a** Survey respondents categorized into manufacturers, downstream users and other companies; **b** company size of the survey respondents (manufacturers and downstream users) divided into small (<100 employees), medium (100–4,999) and large (>5,000) companies

companies were counted as Europe if the contact person was situated in Europe.

Furthermore, the respondents were categorized according to their position in the supply chain of ENM (Fig. 1a), which shows that most of the replies came from manufacturers (23). Additional answers came from downstream users (9) and other companies (14) involved in the nanotechnology sector. The latter category comprises research facilities, consultancies, authorities, instrumentation suppliers, and related firms. The assessment of the company sizes for all the manufacturers and downstream users together shows an equal distribution of small (10), medium (8), and large (14) companies. The number of employees was used as a size criterion (small: <100 employees, medium: 100–4,999, and large: >5,000).

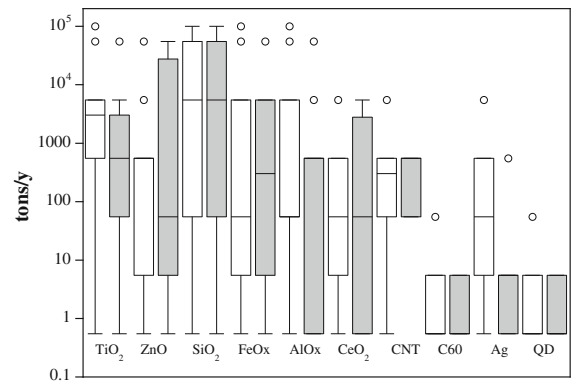


Fig. 2 Boxplots of the ENM production (in tons/year) showing the median and the 25/75 % quantiles. *White* worldwide, *grey* Europe

Results

Production and utilization quantities

The answers for the different ENM were grouped together and the results are shown in Fig. 2 using boxplots for all ENM, both for the world and for Europe. In Table 1 the most likely range of production amounts is shown for the world and for Europe, given by the median and the 25 and 75 % percentiles. Figure S1 in the Supporting Information shows all answers that were received. In the following each ENM is discussed separately:

Nano-TiO₂

With 18 answers from the survey for the global quantities, nano-TiO₂ shows a clear peak within the range of 101–1,000 and 1,000–10,000 t/year. Ten out of 18 (56 %) estimated the annual production or utilization for 2010 to be in this area. Furthermore, there is only one answer for each of the two extreme values and hence the experts agree on this point. For nano-TiO₂ in Europe, the answer diagram looks similar with the main difference that the peak has shifted towards a lower order of magnitude. Hence, most of the responses received lie between 11–100 and 101–1,000 t. However, some experts estimate the annual European nano-TiO₂ production or utilization at a higher amount than 10,000 t.

Nano-ZnO

According to the survey results, nano-ZnO was most likely produced in global quantities between 101 and

Table 1 Production/utilization quantities of ten nanomaterials in the world and in Europe (in t/year)

ENM	Worldwide (t/year) Median and 25/75 percentile	Europe (t/year) Median and 25/75 percentile	US (t/year) (Hendren et al. 2011) Range	Switzerland (t/year) (Schmid and Riediker 2008) In brackets values extrapolated to Europe
TiO ₂	3,000 (550–5,500)	550 (55–3,000)	7,800–38,000	435 (38,000) ^a
ZnO	550 (55–550)	55 (5.5–28,000)		70 (6,100)
SiO ₂	5,500 (55–55,000)	5,500 (55–55,000)		75 (6,500)
FeO _x	55 (5.5–5,500)	550 (30–5,500)		365 (32,000)
AlO _x	55 (55–5,500)	550 (0.55–500)		0.005 (0.4)
CeO _x	55 (5.5–550)	55 (0.55–2,800)	35–700	
CNT	300 (55–550)	550 (180–550)	55–1,101	1 (87)
Fullerenes	0.6 (0.6–5.5)	0.6 (0.6–5.5)	2–80	
Ag	55 (5.5–550)	5.5 (0.6–55)	2.8–20	3.1 (270)
Quantum dots (QDs)	0.6 (0.6–5.5)	0.6 (0.6–5.5)		

The median and the 25/75 percentile are given, rounded to two significant numbers. The values in the fourth and fifth columns are from the literature for the US (Hendren et al. 2011) and Switzerland (Schmid and Riediker 2008)

^a The values in brackets for Switzerland have been extrapolated using the population of Switzerland (6.9 Million) to Europe (593 million)

1,000 t/year in 2010 with seven answers in this range, which is equal to 44 %. The same diagram also implies that smaller amounts (<100 t/a) are more realistic than higher outputs (>1,000 t/a). In contrast, the responses for nano-ZnO in Europe have two outliers which estimate the production level at 10,001–100,000 t/year while all the other answers indicate yearly amounts of 100 t/year and lower.

Nano-SiO₂

The answers imply that not much is known about the production and utilization of nano-SiO₂ since there is a wide variation of the answers ranging from the very low end (< 1 t/year) to the high end with over 100,000 t/year. The most responses are found for 10,001–100,000 t/year. Furthermore, opinions on the European amounts seem to be divided. Almost half of the experts estimated an output of 100 t/year or less, while the remaining five respondents assumed higher quantities of over 1,000 t/year.

Nano-FeO_x

Nano-iron oxide shows, similarly to nano-SiO₂, a broad statistical spread of the answers for the global production and utilization quantities. Most answers

were given for 11–100 t/year. The situation looks similar for Europe. There is a wide range of responses with no clear peak.

Nano-AlO_x

The responses for nano-aluminum oxide also span the whole range, however, with a peak at 11–100 t/year. The answers for Europe look similar. Nano-aluminum oxide is either produced by less than ten or more than 100 t yearly.

Nano-CeO₂

Nano-CeO₂ reaches the maximal number of answers for the global quantities at 101–1,000 t/year. For Europe, the responses appear to be more confusing. They are almost equally distributed over different quantities.

Carbon nanotubes

Carbon nanotubes are estimated to be globally produced in quantities between 11 and 1,000 t/year according to 75 % of the responding experts. The estimates for Europe are positioned in the same range, but here it is surprising that seven out of ten respondents rated the annual CNT production at

Table 2 Survey results for the product distribution

Nanomaterial	Product group	% of total use
Nano-TiO ₂	Cosmetics (incl. sunscreens)	70–80
	Coatings & cleaning agents	<20
	Plastics	<20
	Paints	10–30
	Cement	1
	Others	<10
Nano-ZnO	Cosmetics (incl. sunscreens)	70
	Paints	30
CeO _x	Chemical mechanical planarization	45–80
	Fuel catalyst	1–50
	UV-coatings, paints	5–10
CNTs	Composites & polymer additives	20
	Materials	80
	Composites	50
	Batteries	50
Fullerenes	R&D	80
Nano-Ag	Paints, coatings & cleaning agents	10–30
	Textiles	30–50
	Consumer electronics & conductivity	10–20
	Cosmetics	20
	Medtech	20
	Anti-microbial coatings	80–100
Quantum dots	Light conversion for LED/OLED	90
	Lab use for imaging	10

Each line represents different answers and therefore the percentages do not sum up to 100 %

101–1,000 t/year. One producer of CNTs gave a more accurate answer by estimating the worldwide capacity at 2,000 t/year and the Europe-wide at 1,000 t/year. Furthermore, this expert mentioned that the actual production quantities were less than 1,000 or 500 t/year for these geographical areas, respectively.

Fullerenes

A clear tendency for the worldwide Fullerene output is visible. This nanoparticle is evidently produced on a small scale. The response density is concentrated on the very low end of the diagram. With the exception of one responding expert, all answers estimated the fullerene quantity at 10 t/year or lower. The circumstances for Europe are comparable. No response exceeds 10 t/year in that case.

Nano-Ag

The survey shows that nano-Ag is produced only in moderate quantities. The number of responses decreases towards higher production amounts with no expert estimating the worldwide nano-Ag output to be more than 10,000 t/year. According to almost 90 % of the answers, Europe produces and uses maximally 10 t/year of nano-silver.

Quantum dots

Not even one single expert estimates that the global output of QDs exceeded 100 t/year in 2010. Furthermore, 11 out of 12 respondents believe the worldwide quantity to be below 11 t/year. Given that the diagram shows decreasing number of answers from left to right,

there is an analogy to the nano-silver results. The difference lies in the fact that the responses for QDs are clearly more concentrated on the low end. That is to say that QDs are, as per the experts' opinions, produced on almost negligible quantities on the global level. Hence, it is plausible that the answers for the European amount of QDs are all settled on the position equal to 10 t/year or lower.

Product distribution

The survey results for the allocation of production amounts to product categories are shown in Table 2. The total number of respondents for all ENM was 18, but not for all of the examined ENM were answers obtained (e.g., no answers for nano-silicon dioxide, nano- AlO_x , and nano- FeO_x).

Nano-TiO₂

Four answers were obtained for this material. It is apparently used in considerable quantities for UV-protection, especially in sunscreens and coatings, ranging from 50 % to more than 80 %. Another product containing nano- TiO_2 , which was mentioned by all respondents is paint, which is estimated at 10–30 % of all applications. Additionally, plastics and cement are other answers that resulted from the survey.

Nano-ZnO

Only two answers were given for nano- ZnO . As in the case of nano- TiO_2 , ZnO seems to be mainly used for UV-protection in sunscreens with one answer estimating that to be 70 %. The second only informed us that all the nano- ZnO is incorporated in UV and antimicrobial coatings without giving any further distribution.

Nano-CeO_x

Both respondents named the chemical mechanical planarization (CMP) as an important application for nano- CeO_2 . The responses clearly differed in the assumed proportions of nano- CeO_x used as a fuel catalyst in diesel. While one of the experts estimated this application to be around 50 %, the other one rated it at a ratio of only 1 %. Further product groups

containing nano- CeO_x are UV coating, paints and others.

CNT

Three responses were received about the use of CNT in composites with 20, 50, and 80 %. An additional answer was given that 50 % of the production is used in batteries.

Fullerene

The only answer clearly shows that fullerenes are mainly (80 %) used for research purposes and have not found suitable applications in commercially available products yet.

Nano-Ag

Nano-silver received the highest number of answers (5). Anti-microbial properties are the main reason why nano- Ag is commercially used. Also the ENM incorporated in textiles and medical technology are used for this purpose. Another useful property turned out to be the conductivity of nano- Ag .

Quantum Dots

QDs are according to the only survey respondent mainly used for the light conversion in LEDs and OLEDs. This application is rated at 90 % with the remaining 10 % of QDs being used in laboratories for imaging purposes.

Discussion

Companies are reluctant to provide production amounts of chemicals, yet this information is pivotal for environmental risk assessment as it forms the basis for all exposure models. The main hypothesis of our work was that companies possess knowledge not only of their own production amount but also have a good idea of the size of the market and that they are more likely to communicate this estimate than their own production amount. Companies, especially the larger ones, surely perform market analyses and have knowledge about their competitors. Since none of

the surveys conducted before ours used a similar approach, our results constitute a completely new source of information about production amounts. Our survey also provides first estimates for the European production of ENM. The fact that several companies took the time to answer that they would not be able to estimate those quantities shows on the one side how few is known about this topic but on the other hand enhances the quality of our results by excluding vague estimates. Having only few but accurate responses is more advantageous than numerous responses with higher uncertainty.

With 12–18 answers for every ENM, we base our evaluation on a data basis similar to the previous three studies on ENM production (Hendren et al. 2011; Robichaud et al. 2009; Schmid and Riediker 2008). Normally the estimates of the responding industrial experts should not be completely out of range or far from reality, yet we received a very broad range of answers for several ENM. There are several causes of uncertainty in the data and these are discussed in the following.

It is evident that especially nano-SiO₂ as well as nano-TiO₂ show a high variance of the reported production amounts. This means that responses were given from the low to the very high end. It is not a coincidence that these two materials have already been produced for decades now, a long time before the word “nanoparticle” was even invented. Both materials, produced mainly by flame-processes or precipitation methods, consist of primary particles in the nano-range that are aggregated and agglomerated to form larger structures (Barthel et al. 1999; Schaefer and Justice 2007; Stark and Pratsinis 2002). Once the word “nano” became fashionable and gained attention in the public, a discussion emerged as to whether these materials represented ENM or not (Bosch et al. 2012). Since these ENM can easily agglomerate to build larger particles, not all the companies named them “nano”. This is also the case for other metal oxides and is the most likely explanation for the broad shape of the reported production amounts for these ENM. One well-known company producing ENM wrote back as a feedback that they are not producing ENM but only nanostructured materials and are therefore not answering the survey. The survey answers for nano-SiO₂ global quantities are distributed over the whole range from less than 1 to more than 100,000 t per year with the most responses at the higher end (<1,001 t/a).

The fact that no precise definition and measurement were available might therefore be a cause for this wide distribution. Therefore, depending on the definition of nano-SiO₂, the two source types are in line and state that this ENM is most likely used in elevated quantities. This result shows again the importance of a binding definition of ENM so that every industry representative reports the same material either as nanomaterial or as conventional material (Lövestam et al. 2010; Stone et al. 2010). It is especially important to agree on how to deal with materials that clearly have a nanostructure and a primary particles size in the nano-range but that are heavily aggregated or agglomerated as it is the case for SiO₂.

If we compare our values with those available for the US (TiO₂, CeO₂, CNT, Ag, fullerenes) (Hendren et al. 2011), we see that the ranges for the US and Europe are roughly comparable and overlap with the exception of the fullerenes, where Hendren et al. (2011) have reported values with an upper boundary that is about 40 times higher. If the values reported by Schmid and Riediker (2008) are extrapolated from Switzerland to Europe, we see that for TiO₂, ZnO, and SiO₂ the values are roughly comparable with the US or European values of our study, whereas the FeO_x and Ag are much higher and CNT and AlO_x are much lower. One factor that could result in discrepancies between different values reported for one ENM is the temporal development of the use of ENM. However, an analysis of the published data (Gottschalk et al. 2009, 2010a, b; Hendren et al. 2011) with respect to the temporal development reveals no trend for any ENM except for CNT. Figure 3 shows the data for TiO₂ and CNT. There is a large scatter of the reported data for TiO₂ with no obvious trend. However, CNT production shows a clear increase based on various literature sources (Borm et al. 2006; Cientifica 2004; Eklund et al. 2007; Healy et al. 2008; Kuzma 2005; Ray et al. 2009) and our new value for 2010. The difference between CNT and TiO₂ might be as discussed above that CNT are a new substance, whereas TiO₂ has been produced for many decades and therefore the issue of definition whether a produced material is counted as conventional or nanomaterials results in a large variability between different sources. Again, the distinction between particles in unbound state, aggregated and agglomerated particles is crucial for the definition. The lower number reported by Schmid and Riediker (2008)

therefore fits into the general trend of increasing CNT production. For FeO_x and AlO_x the problems discussed above with respect to the definition of the materials may also explain the lower of higher values compared the later studies. The newer numbers for the production amounts of nano-Ag seem to be lower than older values. Blaser et al. (2008) reported for example in 2008 an amount of 110–230 t of biocidal silver use in Europe, a number that has been used as equivalent to nano-Ag. However, only about 10 % of this silver is actually in the form of nano-Ag (Scheringer et al. 2010). Again, the issue of the correct definition of the materials and also the history of nomenclature (Nowack et al. 2011) is hampering the evaluation of data from different sources.

It is also important to bear in mind that the survey targeted the actual production amounts and not the production capacities. Our experience demonstrates that capacity and actual production can considerably differ from each other and that the degree of capacity utilization for some companies does not exceed 10 %. The companies are obviously expecting a huge increase in sales in the near future but this has not yet happened. Therefore, information about capacities may give answers about the expected future development of production quantities. This is also in line with answers from single companies that provided more information than only completing the survey. Therefore, it is always important to distinguish between capacity and actual production amounts.

For a realistic exposure assessment it is not only important to have information on the production amounts of ENM but also on the distribution of these amounts over different product categories. This is especially important for ENM, as they can be used in a very wide variety of different products with widely varying release potential. Our survey provides—at least for some ENM—first data on product distribution based on responses from industry. The different responses are rough estimates, but given the complete absence of data so far, they represent a very important first estimate based on expert knowledge. They show, for example, that major uses for nano-TiO₂ and nano-ZnO are in cosmetics. Because during this use a very high proportion of the ENM ends up in water or wastewater, this information is of utmost importance to exposure assessment. For nano-Ag there are many uses mentioned, but most of them involve some

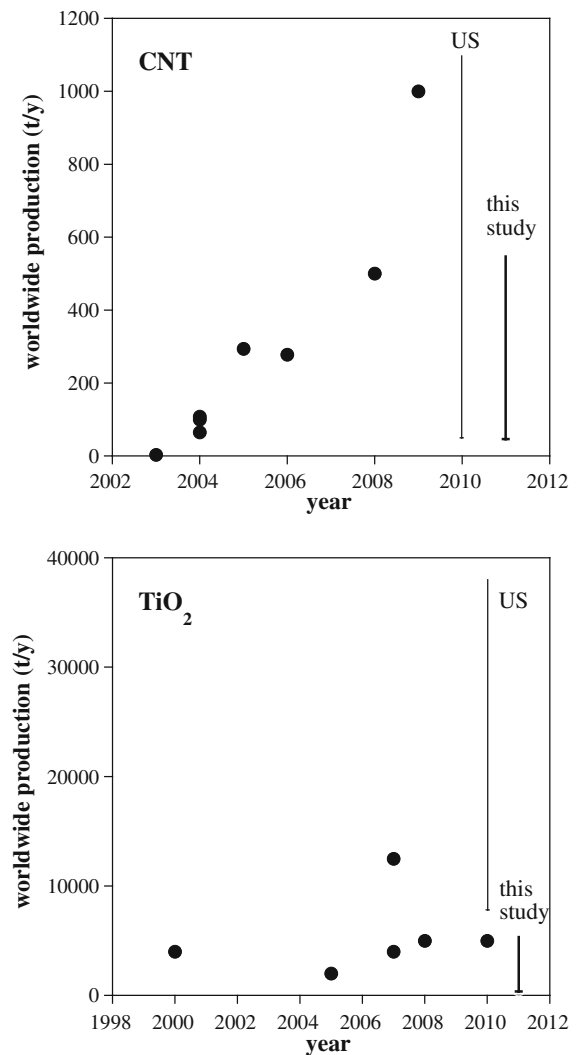


Fig. 3 Temporal development of reported worldwide CNT and TiO₂ production/production capacity. *Black dots* show literature data [CNT (Borm et al. 2006; Cientifica 2004; Eklund et al. 2007; Healy et al. 2008; Kuzma 2005; Ray et al. 2009), TiO₂ (Nightingale et al. 2008; Park 2007; Thayer 2000; UNEP 2007; US EPA 2010a, b)], the *thin black line* is the range for the US (Hendren et al. 2011), and the *thick black line* the range from this work

contact with water (e.g., paints, textiles, cosmetics). Nano-CeO₂ on the other hand has an important industrial use for CMP and has therefore much more likely a few point sources compared to the wide dispersive use of TiO₂, ZnO, and nano-Ag. The CeO₂ use in fuels received a wide range of answers from 1 to 50 %—it is therefore still uncertain whether this use is important or not, or whether the ambiguity in the

answers is caused by a rapidly changing market. Two other ENM with uses in product categories where they are tightly bound are CNT and QD, and therefore release during use is much less likely. However, for these ENM the fate during end of life treatment becomes much more relevant.

The product distributions obtained by the survey agree quite well with the modeled distributions that Mueller and Nowack (2008) and Gottschalk et al. (2009, 2010b) used as basis for first environmental exposure assessments. The data provided with the current survey therefore supports the environmental exposure modeling that is strongly determined by the product categories that have a high likelihood of release to water (e.g., cosmetics, textiles) (Gottschalk and Nowack 2011). Gottschalk et al. (2010b), for example, used a mean percentage of nano-Ag use in textiles of 25 % (with a range from 12 to 49 %), the survey results are 30–50 %. For nano-TiO₂ in cosmetics, for example, Gottschalk et al. (2010b) used an average of 42 % (with range from 0.3 to 81 %) whereas the survey yielded 70–80 %.

Production amounts and product distribution form the basis for any material flow modeling and are thus crucial for predicting environmental concentrations of nanomaterials. Even though the number of experts in this field is currently small, the data about production and product distribution provided in this study will enable modelers to provide improved estimates for ENM flows to the environment and also allow them to model ENM that have so far not been considered due to lack of production and use data, e.g., QD or CeO₂.

Acknowledgments We thank all the respondents of the company survey who made this study possible. We also thank Martin Birtel from Empa for help with the SurveyMonkey online tool and Thomas Ruddy for correcting the English.

References

- Aitken RJ, Chaudhry MQ, Boxall ABA, Hull M (2006) Manufacture and use of nanomaterials: current status in the UK and global trends. *Occup Med* 56:300–306
- Barthel H, Heinemann M, Stintz M, Wessely B (1999) Particle sizes of fumed silica. *Part Part Syst Charact* 16:169–176
- Berube DM, Searson EM, Morton TS, Cummings CL (2010) Project on emerging nanotechnologies—consumer product inventory evaluated. *Nanotechnol Law Bus* 7:152–163
- Blaser SA, Scheringer M, MacLeod M, Hungerbühler K (2008) Estimation of cumulative aquatic exposure and risk due to silver: contribution of nano-functionalized plastics and textiles. *Sci Total Environ* 390:396–409
- Bleeker EAJ, Cassee FR, Geertsma RE, de Jong WH, Heugens EHW, Koers-Jacquemijns M, van de Meent D, Oomen AG, Popma J, Rietveld AG, Wijnhoven SWP (2012) Interpretation and implications of the European Commission Recommendation on the definition of nanomaterial, RIVM Letter report 601358001/2012. National Institute for Public Health and the Environment, Bilthove, The Netherlands
- Bosch A, Maier M, Morfeld P (2012) Nanosilica? Clarifications are necessary! *Nanotoxicology* 6:611–613
- Borm PJA, Robbins D, Haubold S, Kuhlbusch T, Fissan H, Donaldson K, Schins R, Stone V, Kreyling W, Lademann J, Krutmann J, Warheit D, Oberdorster E (2006) The potential risks of nanomaterials: a review carried out for ECE-TOC. *Part Fiber Toxicol* 3:11
- Cientifica (2004) Nanotubes, executive summary. http://www.cientifica.com/www/summaries/Nanotubes_2004_ExSum.pdf
- Eklund PC, Ajayan P, Blackmon R, Hart AJ, Kong J, Pradhan B, Rao A, Rinzler A (2007) Assessment of international research and development on carbon nanotube manufacturing and applications. WTEC Panel Report. World Technology Evaluation Center, Inc. Available at http://www.wtec.org/cnm/CNM_final_report.pdf
- EU (2011) Commission Recommendation of 18 October 2011 on the definition of nanomaterial (2011/696/EU). *O. J. L* 275:38–40
- Forster SP, Oliveira S, Seeger S (2011) Nanotechnology in the market: promises and realities. *Int J Nanotechnol* 8:592–613
- Gottschalk F, Nowack B (2011) Release of engineered nanomaterials to the environment. *J Environ Monit* 13: 1145–1155
- Gottschalk F, Sonderer T, Scholz RW, Nowack B (2009) Modeled environmental concentrations of engineered nanomaterials (TiO₂, ZnO, Ag, CNT, fullerenes) for different regions. *Environ Sci Technol* 43:9216–9222
- Gottschalk F, Scholz RW, Nowack B (2010a) Probabilistic material flow modeling for assessing the environmental exposure to compounds: methodology and an application to engineered nano-TiO₂ particles. *Environ Model Softw* 25:320–332
- Gottschalk F, Sonderer T, Scholz RW, Nowack B (2010b) Possibilities and limitations of modeling environmental exposure to engineered nanomaterials by probabilistic material flow analysis. *Environ Toxicol Chem* 29:1036–1048
- Hamilton MB (2009) Online survey response rates and times background and guidance for industry. Ipathia, Inc./SuperSurvey. http://www.supersurvey.com/papers/supersurvey_white_paper_response_rates.htm
- Healy ML, Dahlben LJ, Isaacs JA (2008) Environmental assessment of single-walled carbon nanotube processes. *J Ind Ecol* 12:376–393
- Hendren CO, Mesnard X, Dröge J, Wiesner MR (2011) Estimating production data for five engineered nanomaterials as a basis for exposure assessment. *Environ Sci Technol* 45:2562–2569
- International Organization for Standardization ISO (2008) Technical specification ISO/TS 27687:2008(E):

- Nanotechnologies—terminology and definitions for nano-objects—nanoparticle, nanofibre and nanoplate
- Klaine SJ, Alvarez PJJ, Batley GE, Fernandes TF, Handy RD, Lyon DY, Mahendra S, McLaughlin MJ, Lead JR (2008) Nanomaterials in the environment: behavior, fate, bioavailability, and effects. *Environ Toxicol Chem* 27:1825–1851
- Krug HF, Wick P (2011) Nanotoxicology: an interdisciplinary challenge. *Angew Chem Int Ed* 50:1260–1278
- Kuzma J (2005) The nanotechnology–biology interface: exploring models for oversight. Workshop Report. Available at http://www.hhh.umn.edu/img/assets/9685/nanotech_jan06.pdf
- Lo LY, Li Y, Yeung KW, Yuen CWM (2007) Indicating the development stage of nanotechnology in the textile and clothing industry. *Int J Nanotechnol* 4:667–679
- Lövestam G, Rauscher H, Roebben G, Sokull Klüttgen B, Gibson N, Putaud JP, Stamm H (2010) Considerations on a definition of nanomaterial for regulatory purposes. Publications Office of the European Union, Luxembourg. ISBN 978-92-79-16014-1. doi:10.2788/98686
- Mueller NC, Nowack B (2008) Exposure modeling of engineered nanoparticles in the environment. *Environ Sci Technol* 42:4447–4453
- NanoCentral (2010) NanoPerspective—the nanotechnology resource library. NanoCentral, Sedgfield, Durham, UK. <http://www.nanocentral.eu/nanoperspective>
- Nightingale P, Morgan M, Rafols I, van Zwanenberg P (2008) Nanomaterials innovation systems: their structure, dynamics and regulation. A Report for the Royal Commission on Environmental Pollution, UK
- Nowack B, Bucheli TD (2007) Occurrence, behavior and effects of nanoparticles in the environment. *Environ Pollut* 150:5–22
- Nowack B, Krug HF, Height M (2011) 120 years of nanosilver history: implications for policy makers. *Environ Sci Technol* 45:1177–1183
- Oberdörster G, Oberdörster E, Oberdörster J (2005) Nanotoxicology: an emerging discipline evolving from studies of ultrafine particles. *Environ Health Perspect* 113:823–839
- Park B (2007) Current and future applications of nanotechnology. *Environ Sci Technol* 24:1–18
- Ray PC, Yu HT, Fu PP (2009) Toxicity and environmental risks of nanomaterials: challenges and future needs. *J Environ Sci Health Part C* 27:1–35
- Robichaud CO, Uyar AE, Darby MR, Zucker LG, Wiesner MR (2009) Estimates of upper bounds and trends in nano-TiO₂ production as a basis for exposure assessment. *Environ Sci Technol* 43:4227–4233
- Schaefer DW, Justice RS (2007) How nano are nanocomposites? *Macromolecules* 40:8501–8517
- Scheringer M, MacLeod M, Behra R, Sigg L, Hungerbühler H (2010) Environmental risks associated with nanoparticulate silver used as biocide. *Household Pers Care Today* 1:34–37
- Schmid K, Riediker M (2008) Use of nanoparticles in Swiss industry: a targeted survey. *Environ Sci Technol* 42:2253–2260
- Som C, Berges M, Chaudhry Q, Dusinska M, Fernandes TF, Olsen SI, Nowack B (2010) The importance of life cycle concepts for the development of safe nanoproducts. *Toxicology* 269:160–169
- Stark WJ, Pratsinis SE (2002) Aerosol flame reactors for manufacture of nanoparticles. *Powder Technol* 126:103–108
- Stone V, Nowack B, Baun A, van den Brink N, von der Kammer F, Dusinska M, Handy R, Hankin S, Hassellöv M, Joner E, Fernandes TF (2010) Nanomaterials for environmental studies: classification, reference material issues, and strategies for physico-chemical characterisation. *Sci Total Environ* 408:1745–1754
- Thayer AM (2000) Firms find a new field of dreams. *Chem Eng News* 78:36–38
- United Nations Environment Programme UNEP (2007) Chapter 7: emerging challenges—nanotechnology and the environment, *Geo Year Book 2007*
- US EPA (2010a) Nanomaterial case studies: nanoscale titanium dioxide in water treatment and in topical sunscreen. US Environmental Protection Agency, Report EPA/600/R-09/057F
- US EPA (2010b) State of the science literature review: nano titanium dioxide environmental matters. U.S. Environmental Protection Agency, Washington, DC
- Wiesner MR, Lowry GV, Jones KL, Hochella MF, Di Giulio RT, Casman E, Bernhardt ES (2009) Decreasing uncertainties in assessing environmental exposure, risk, and ecological implications of nanomaterials. *Environ Sci Technol* 43:6458–6462
- Wijnhoven SWP, Dekkers S, Kool M, Jongeneel WP, De Jong WH (2010) Nanomaterials in consumer products. Update of products on the European market in 2010. RIVM Report 340370003/2010. <http://www.rivm.nl/bibliotheek/rapporten/340370003.pdf>