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ORIGINAL ARTICLE

How important is drinking water exposure for the risks of engineered nanoparticles to consumers?

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Abstract

This study explored the potential for engineered nanoparticles (ENPs) to contaminate the UK drinking water supplies and established the significance of the drinking water exposure route compared to other routes of human exposure. A review of the occurrence and quantities of ENPs in different product types on the UK market as well as release scenarios, their possible fate and behaviour in raw water and during drinking water treatment was performed. Based on the available data, all the ENPs which are likely to reach water sources were identified and categorized. Worst case concentrations of ENPs in raw water and treated drinking water, using a simple exposure model, were estimated and then qualitatively compared to available estimates for human exposure through other routes. A range of metal, metal oxide and organic-based ENPs were identified that have the potential to contaminate drinking waters. Worst case predicted concentrations in drinking waters were in the low- to sub-μg/l range and more realistic estimates were tens of ng/l or less. For the majority of product types, human exposure *via* drinking water was predicted to be less important than exposure *via* other routes. The exceptions were some clothing materials, paints and coatings and cleaning products containing Ag, Al, TiO_2, Fe_2O_3 ENPs and carbon-based materials.

Keywords

Concentration, estimation, human health, market penetration, nanomaterials, release, surface water, waste water

History

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Introduction

Humans may be exposed to engineered nanoparticles (ENPs) *via* inhalation (e.g. from cleaning aids, spray cosmetics and coatings), dermal penetration (e.g. from cosmetics), ingestion (e.g. from food and drinks containing nano-based ingredients) or intravenous routes (e.g. some medicines and diagnostic aids). The rapid proliferation of nanotechnology in the consumer product sector has therefore raised a number of technological, health and safety, environmental, ethical, policy and regulatory issues (Boxall et al., 2007b; Maynard et al., 2006; Royal Society and Royal Academy of Engineering, 2004).

However, it is also possible that ENPs will be released to the natural environment and will enter drinking waters or the food chain. Such environmental exposure may arise from emissions during manufacture, use and/or disposal of ENP-containing products. Some applications may involve a deliberate release of ENPs into the environment, e.g. for water treatment or broader environmental remediation. Assessment of the extent of exposure arising from these indirect routes is a major challenge and exposure data of humans to ENPs in the environment is lacking. In addition, the many applications of ENPs are very new or yet to be realized so current releases of some ENPs may be very low or non-existent but could increase rapidly in the future.

The lack of exposure data is partly due to the fact that robust and sensitive analytical methods are not yet available for detecting and characterizing ENPs in complex environmental matrices such as soils and natural waters (Rauscher & Roebben, 2014; Tiede et al., 2009). One approach to establish the current and future risks to humans of ENPs arising from indirect exposure is to use information on the amounts of particles in use or expected to be in use, product usage patterns and environmental characteristics alongside environmental exposure models to estimate levels in different matrices. Such exposure model predictions can aid the design of toxicological and environmental fate research and provide data for use during nanoparticle risk assessment and subsequent regulatory decision-making. A range of modelling exercises have been done to assess environmental exposure to a range of ENPs, including carbon nanotubes, metal nanoparticles and metal oxide nanoparticles (Blaser et al., 2008; Boxall et al., 2007a; Gottschalk et al., 2010; Mueller & Nowack, 2008). However, these exercises have generally not considered drinking water exposure and are mainly based on engineered nanomaterial production estimates rather than estimates of ENMs contained in consumer products.

The aim of this study was therefore to investigate the potential contamination of drinking water supplies in UK by ENPs occurring in consumer products. As a first step, those ENP-containing products on the UK market that are likely to result in

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ENP release to source waters were identified based on the nature in which the ENPs are incorporated into different product types. ENP concentrations in raw and treated drinking waters were then estimated using simple exposure models. The exposure estimates were compared with assessments of human exposure *via* other routes to determine whether drinking water is a significant exposure route for different ENPs or not. The results of the study should benefit numerous stakeholders such as national and international regulatory bodies allowing them to better understand the potential for ENPs to reach drinking water and the relative risks from drinking water exposure compared to other exposure routes.

Material and methods

Types of products containing ENPs currently used in UK

An extensive literature search was performed to identify products containing nanomaterials that are available on the UK market. This included databases of the scientific literature, the use of internet search engines and internet databases such as www.nanoprotect.co.uk, www.nanotechproject.org, www.corporate-watch.org.uk. For products that were identified that claim to potentially contain nanomaterials, these claims were further investigated by directly accessing the manufacturers' internet pages, respective patents and lists of ingredients. Products only available from abroad and *via* the internet were not considered for two reasons: (1) it was anticipated that the market penetration in UK of those products will be relatively small and in any case unverifiable and (2) due to language barriers and the large number of products, this could not be achieved within the remit of the study.

Available information on trends in use of the different ENP-containing products was obtained from the scientific literature where available or based on assumptions in order to determine market penetration. Information on the general usage rates of different product types [in grams per capita per day (g/pc/d)] were also obtained from guidance documents such as TGD (European Chemicals Bureau, 2003) and the scientific literature. Information on how this data were obtained for each product or product category including references is provided in the Supplementary Material.

Usage and concentration data are necessary to estimate likely concentrations of ENPs in raw and treated drinking waters. If no information could be obtained for a specific product, then data were extrapolated from available information on usage and concentration levels from similar products (e.g. sunscreens) or usages assuming, e.g. that a product type will contain ENPs in a similar concentration independent of the type of ENP (e.g. 10% nano-TiO_2 in paint $\approx$10% nano-Fe_2O_3 in paint). In instances where the nanoparticle concentration was not specified, data on the typical level of the same material in bulk form used in the same product were used; if available (e.g. 10% bulk TiO_2 in paint $\approx$ 10% nano TiO_2 in paint). Also, information from the scientific literature (e.g. best functionality of SiO_2 in clothing at 4%; Wu et al., 2009) and regulatory bodies (e.g. 25% maximum concentration of ZnO in sunscreen in EU) was used. For products for which no data were available on usage and NP concentrations, assumptions and extrapolations were made based on expert judgment. We anticipate that the approach adopted will provide a worst case estimate of potential emissions of an ENP and can therefore be regarded as precautionary.

Product usage likely to result in ENPs reaching water sources

To provide insight into which kinds of ENP are most likely to reach water sources, the identified products were categorized according to the way in which the ENP is incorporated into the product using the categorization framework developed by Hansen et al. (2007, 2008a,b). Hansen et al. (2007) distinguished between four different categories: (1) ENPs bound to the surface of another solid structure; (2) ENPs suspended in a liquid; (3) ENPs suspended in solids; and (4) airborne ENPs. According to the incorporation of the ENP, products can be further grouped into three different exposure categories: (i) expected to reach water sources, (ii) may reach water sources and (iii) not expected to reach water sources. Products that would typically fall under the first category are products with ''nanoparticles suspended in liquids'' or ''airborne nanoparticles'', whereas products with ''surface-bound nanoparticles'' and ''nanoparticles suspended in solids'' would fall into the second and third exposure categories, respectively. Products that fell under the category (iii) not expected to reach water sources (e.g. their ultimate fate would be to landfill or incineration) as well as unclassifiable products were excluded from further assessment.

Expected release of ENPs to raw and treated drinking water

Qualitative ranking of consumer products containing ENPs

As the collated data on market penetration, usage and ENP concentration is heavily reliant on assumptions, a scoring system was developed for a qualitative ranking of consumer products available in the UK that contain ENPs to evaluate their likelihood to reach drinking water sources (Table 1). Based on this approach, the lower the total score of a specific particle and product type, the higher the likely level of contamination of drinking water sources.

Estimation of ENP concentrations in raw water and treated drinking water

For the estimation of the potential environmental exposure to different ENPs from use and disposal of materials and products of nanotechnologies, models previously developed and applied to predict environmental exposure to ENPs were used as described below.

Many of the identified ENP-containing products will be released to the aquatic environment *via* the sewage system. Release patterns of ENPs to the aquatic environment have been identified as: (1) run-off from surfaces or (2) ''down the drain''. For this modelling approach, it has been assumed that both routes of entry will lead to ENPs being released to wastewater and that all the wastewater is collected prior to entering the aquatic environment (rivers). ENP emissions from wastewater treatment plants (WWTP) will then be diluted in the aquatic environment before being treated in drinking water treatment plants (WTP). Conservative estimates of ENP concentrations in WWTP effluent and river waters were obtained using an adaptation of the surface water exposure modelling approach developed by the Committee for Medicinal Products for Human Use (CHMP, 2006). Using the approach, estimates of concentrations in surface water were estimated based on the concentration of ENP in a product, the amount of product used per capita per day and the market penetration of a product. The approach assumed that the usage of a product is even over the year and that the sewage system is the main route of entry. A default value of 150 l/capita/d waste water production was adopted based on the OFWAT (The Water Services Regulation Authority for England and Wales) report (2007) on International comparison of water and sewerage service. Where information was available on removal on a specific type of ENP during waste water treatment, lowest available specific removal efficiencies were incorporated into the calculations: 79% for C60 (Wang et al., 2010), 95% for CeO

Table 1. Scoring system for consumer products available in the UK-containing ENPs based on their likelihood to reach drinking water sources.

	Release	Ranking
Exposure route/release pattern		
''Down the drain'' (WWTP)	Likely	Included
Hard surface/''run-off''	Likely	Included
Landfill	Unlikely	Excluded
Unknown	Unclassifiable	Excluded
	Release	Score
Likelihood of nanomaterials to be released to drinking water		
Suspended in liquids (expected to reach water sources)	Highly likely	1
Surface bound (may reach water sources)	Likely	2
Suspended in solid (not expected to reach water sources)	Unlikely	3
Unknown	Unclassifiable	4
Emission or usage data (in g/pc/d)		
<0.1	Very low	4
0.1–1	Low	3
1–10	Medium	2
10–100	High	1
Concentration in product (in %)		
0.01–0.1	Very low	4
0.1–1	Low	3
1–10	Medium	2
>10	High	1
Unknown	High	1
Market share (in %)		
<1	Very low	4
1–10	Low	3
10–50	Medium	2
>50	High	1
Unknown (=100%)	High	1

(Limbach et al., 2008), 39% for Ag ENPs and 23% for TiO_2 (Westerhoff et al., 2011). In cases where no data were available on removal, two scenarios were considered: (1) a conservative scenario where the removal efficiency was assumed to be 0% and (2) a more realistic scenario, where a removal efficiency of 97% for particles $< 0.1\,\mu m$ in packed-bed filters was applied (after O'Melia, 1980). This assumption has also been used in environmental ENP concentration predictions by Mueller & Nowack (2008). A dilution factor in the receiving water bodies was set at the default EU value of 10 (EMEA, 2006). Due to the lack of data, potential losses of ENPs in aquatic systems (rivers) were not considered.

Estimated river water concentrations were then used as a basis for estimating concentrations in treated drinking water. Drinking water treatment plants (WTP) are designed to physically remove particles ranging in size from viruses (10–100 nm) to *Cryptosporium* oocysts (3–7 μm), *Giardia* oocysts (8–15 μm) and larger organic and inorganic detritus. Removal efficiencies depend on the treatment processes applied. We incorporated three different WTP treatments in our modelling approach:

(1) Conventional treatment (combination of coagulation, flocculation, sedimentation and filtration) representing the majority of water treatment facilities across developed countries, including the UK. The USEPA Safe Drinking Water Act states that conventional treatment plants are capable of physically removing 99.6% of *Giardia* and 99% of viruses. These values represent conservative estimates of physical removal of particles, which when in river or lake water are stable and of similar sizes to single ENPs (e.g. virus size) or aggregates of ENPs. Therefore, for conventional treatment plants, we applied the minimum ENP removal (most conservative estimate) of 99%;
(2) Direct filtration treatment which according to the USEPA Safe Drinking Water Act is capable of physically removing 99% of *Giardia* and 96.8% of viruses. Therefore a removal efficiency of 97% was adopted.
(3) Membrane filtration, increasingly common throughout the UK, EU and USA with particle neutralization (i.e. coagulation and flocculation), routinely exceeding 99.9% removal of virus-sized challenge particles (bacteriaphage) (Laine et al., 2000; Nishijima & Okada, 1998; Schafer et al., 2000; Yuasa, 1998). Therefore, for an integrated membrane treatment plant, we applied the minimum ENP removal of 99.9%.

Where general market penetration data were available for a product category, this information was used. In cases where market penetration data were estimated per product, all the products with their individual market share estimations have been included in the estimates. Predicted concentrations are given as mass concentrations in μg/l and where possible, particle number concentrations (PNC) have also been estimated (#/l), based on mean particle diameter, if available, and density for each particle type (based on the chemical composition of the ENP). If a size range was given, then the smallest value was chosen for PNC estimation, so as to provide a worst case scenario (smallest particle size equals highest PNC). If more than two possible particle sizes for a product were found, then PNC calculations are provided for a maximum of the two different particle sizes. Firstly, the two most commonly reported particle sizes were chosen. If more than two possible particle sizes for a product were found, but each was only reported once, then the smallest and the biggest reported size were chosen. All the applied equations are given in Table 2.

Comparison of exposure from drinking water with human exposure through other routes (qualitative assessment)

The available information on human exposure to nanoparticles from the identified products *via* routes other than drinking water was also reviewed. The principal route(s) of exposure and the results of a focussed survey of the toxicology literature were used to inform on the likely exposures and the consequences for each product. The exposure characteristics chosen are consistent with previous studies. Wijnhoven et al. (2009) identified three main categories for the exposure assessment of nanomaterials from consumer products (nanomaterial properties, application/frequency and exposure route). A fourth category (release potential) has been included in the present work.

It was aimed to produce ranked estimates of exposure taking account of the likely variation and uncertainty in the estimates. Where there were no suitable data specific for ENPs from the products, proxy measures from available data on release of other chemical components from the products were used.

The rating system sums the assigned scores from the concentration, consumer contact, market penetration and release potential, using a value of 1 for a high score (see Supplementary Material S1).

Estimated nanomaterial concentrations were based on information disseminated by the manufacturer, or assumptions/estimations based on literature searches. Release potential of the nanomaterials was categorized, where possible, from review of existing published data. Where data could not be found then expert judgement was used to assign scores. Assessment of the likely exposure routes was based predominately on the physical

Table 2. Equations for estimation of ENP concentrations in WWTP effluent, surface waters and WTP effluent.

	Equation	Where
Effluent concentration from WWTP	$PEffC_{WWTP} = \frac{CENP.Uprod.(1-Rstp).Fpen}{WWinhab}$	$PEffC_{WWTP}$ = predicted effluent concentration from WWTP (μg l^{-1}) C_{ENP} = concentration of ENPs in product (gNP g^{-1}) U_{prod} = daily usage of product (g $capita^{-1}$ d^{-1}) R_{stp} = fraction of ENP removed during sewage treatment (conservative estimate = 0%; Realistic estimate after O'Melia (1980) = 97%; Available data of particle removal for specific ENP types) F_{pen} = market penetration of nano-containing product WW_{inhab} = amount of wastewater produced (l $capita^{-1}$ d^{-1}) (default = 150)
Concentration in biosolids/ sewage sludge	$PBsC_{WWTP} = \frac{CENP.Uprod.Fpen}{WWinhab} - \frac{CENP.Uprod.(1-Rstp).Fpen}{WWinhab}$	$PBsC_{WWTP}$ = predicted concentration in biosolids/sewage sludge (μg l^{-1})
Concentration in surface water or raw drinking water (WTP influent)	$PEC_{sw} = \frac{CENP.Uprod.(1-Rstp).(1-M).Fpen}{WWinhab.D}$	PEC_{sw} = predicted concentration in surface water/influent NP concentration into WTP (μg l^{-1}) D = dilution factor in the receiving water (default = 10) M = NP losses in river (removal/transformation) (default = 0%; unknown)
Effluent concentration from WTP (tap water)	$PEffC_{WTP} = \frac{CENP.Uprod.(1-Rstp).(1-M).Fpen}{WWinhab.D} \times (1 - R_{WTP})$	$PEffC_{WTP}$ = predicted concentration in tap water (μg l^{-1}) R_{WTP} = fraction of ENP removed during drinking water treatment (conventional treatment = 99%; Membrane treatment = 99.99%; Direct filtration = 97%)
Particle number concentrations	$PNC = \frac{C_{particle}}{M_{particle}}$ With: $V_{particle} = \frac{\pi \times D^3_{particle}}{6 \times 10^{-21}}$ And: $M_{particle} = V_{particle} \times \rho_{particle} \times 1000000$	PNC = particle number concentration (#/l) $C_{particle}$ = NP mass concentration (μg/l) $M_{particle}$ = mass per particle (μg/#) $V_{particle}$ = volume per particle (cm^3) $D_{particle}$ = mean NP diameter (nm) $M_{particle}$ = mass per particle (μg/#) $V_{particle}$ = volume per particle (cm^3) $\rho_{particle}$ = density (g/cm^3)

nature of the product (solid, liquid), its application by the consumer and the location of the nanomaterial within the product (surface bound, suspended in liquid, suspended in solid). The categories for potential exposure are given as: inhalation, dermal, ingestion and a combination of exposure routes. Where no specific information could be found in the literature, analogous information was sought.

For comparison of relative exposure *via* drinking water (designated ''Rating *F*'') and non-drinking water sources (designated ''Rating *I*''), a qualitative scoring system was developed. The difference between ratings provides information on whether drinking water will be the main route of exposure to ENPs and hence how important drinking water will be in terms of possible risks (i.e. when Rating F − Rating I is less than zero). The scoring system involved the following categories: (1) Exposure risk to nanoparticle is higher from particles in drinking water: <0; (2) Exposure risk to nanoparticle is equivalent from particles in drinking water: $=0$; (3) Exposure risk to nanoparticle is lower from particles in drinking water: >0 and (4) No comparison possible due to unavailability of data.

Results

Types of existing products containing ENPs currently used in UK

Results of the literature search on products containing ENPs and currently available on the UK market are listed in the Supplementary Material (S2) including type of ENP, source and estimated global production (initial product search started in 2010). It was assumed that nanoparticles were used in the product when this was claimed on the product's or manufacturer's website, even if the type of nanomaterial itself or the size/size range was not provided. In total, 126 products matched these criteria (Table S2) and 62 of these had data allowing for a qualitative assessment.

Of the 126 products, 15 contain more than one type of nanomaterial [e.g. TiO_2 and C (=carbon)]. In total, 23 different kinds of nanomaterials were used, the most predominate was silver (16%), followed by silica (11%) and zinc oxide (11%), carbon nanotubes (10%) and titanium dioxide (10%). For some products, it was not possible to identify the type of ENP used. It should be noted that ''carbon-based nanomaterials'' were often not further defined by the manufacturer, therefore ''C'' or ''carbon'' nanoparticles could relate to, e.g. carbon black, CNTs or C60, although when specified products containing CNT or C60 were assessed separately.

Product usage likely to result in ENPs reaching water sources

Most of the 126 products fell into the following categories: clothing, cosmetics, sporting goods, sunscreens and personal care products. One product fell within the categories ''automotive'' as well as ''cleaning'', raising the number of products by categories to 127. A figure demonstrating the categorization is presented in Supplementary Material (S3).

In 43% of the products, the nanoparticles used were suspended in liquids. Surface bound nanoparticles and nanoparticles suspended in solids were found in 21% and 17% of the products, respectively. It was not possible to determine the location of the nanostructure in 19% of the products. It was also found that nanosilver is predominately used in the form of surface bound nanoparticles (in 14 out of 20 nanosilver products), whereas zinc

oxide is predominately suspended in liquids and titanium dioxide is often used in the form of surface bound particles and particles suspended in liquids in commercially available products. Five products were found to contain C60 used in some form of liquid suspension, whereas carbon nanotubes were only used in a solid suspension. No product was identified that used nanoparticles in the form of airborne particles.

For the 32 products, where it could not be determined what kind of nanomaterial was being used, 28% used the nanomaterial as suspended in liquid, 9% as surface bound nanoparticles and 6% were applied as nanoparticles suspended in solid. For 56% of the products that fell into this category, the location of the nanostructure could not be determined.

Sorting the 126 products into exposure categories shows that the majority of the current uses of nanoparticles fall into categories for which environmental exposure is possible or expected. The exception being carbon nanotubes, for which no exposure is to be expected. For the majority of products for which the type of ENP used could not be determined, the potential for exposure, if known, is possible or expected due to the nature of the product. For instance, if a liquid sunscreen is claimed to be using nanoparticles, skin exposure is to be expected independent of whether the producer reports the identity of the ENP.

Comparing the product category with the location of the nanoparticle shows that most cosmetics and sunscreens used nanoparticles suspended in liquids whereas most sporting goods used nanoparticles suspended in solids. If we assume that products that contain nanoparticles ''suspended in liquids'' and ''airborne nanoparticles'' are to be expected to reach water sources, this indicates that nanoparticles used in cosmetics and sunscreens as well as in automotive applications are candidates for nanoparticles that might reach water sources.

If we study what kind of material is used in various product categories, then one can see that a number of different nanomaterials are being used in the product category of cosmetics. These nanomaterials include Ag-, ZnO-, C60-, SiO_2-, Al_2O_3-, Si- and Ti-based ENPs. However, we know very little about what kind of material is actually being used in about half of all the cosmetics since we could only classify the nanomaterial being used in 11 out of 22 cosmetic products. For sunscreens, TiO_2 and ZnO are the predominant materials used.

Expected release of ENPs to raw and treated drinking water

Qualitative ranking of consumer products containing ENPs based on their likelihood to reach drinking water sources

Of the identified 126 products on the UK market that contain ENPs, 62 could be ranked qualitatively in terms of their potential to contaminate drinking water (Table 3; background information on the calculations as well as additional information on ENP concentration and size (range) is given in the SI parts 4–6). The remaining products could not be assessed due to a lack of information. ENPs contained in sunscreen and personal care products (release pattern ''down the drain'') showed the highest likelihood of relative exposure, followed by home and garden products such as paint and car polish (release pattern ''run off'') and cosmetics (release pattern ''down the drain''). Lower exposure products include some home and garden and personal care products as well as clothing products. It has to be noted that the assumed market share plays a major role within this ranking approach. Among the ENP types with the highest likelihood of relative exposure which are also showing high production levels are titanium dioxide, zinc oxide, silica and silver nanoparticles.

Estimation of ENP concentrations in raw water and treated drinking water

Estimated exposure concentrations in drinking water are summarized in Table 4 and more detailed information is provided in the Supplementary Material (S8.1 and S8.2). Titanium oxide-based nanoparticles are likely to be found in the highest concentrations in treated waste and drinking waters, followed by zinc- and silicon-based ENPs. Of the more commonly known and discussed ENPs, carbon-based (C), iron oxide and silver nanoparticles rank in positions 6, 7 and 8, whereas cerium oxide nanoparticles are estimated to be found in the lowest concentrations. Based on particle number concentration (PNC) estimates, however, silica-based ENPs are predicted to be found in the highest particle number concentrations, followed by titanium oxide, iron oxide and zinc oxide-based ENPs – for smallest reported particle sizes.

Comparison of exposure from treated drinking water with human exposure through other routes (qualitative assessment)

Comparison of the significance of indirect exposure to ENPs in the environment to other routes of exposure (Table 5) shows that for most of the products either dermal or inhalation exposure during the use of a product by a consumer is greater than exposure to contaminated drinking water. There are however some exceptions such as silver in clothing and some paint products where human exposure *via* drinking water appears to be greater than the other exposure pathways.

Discussion

Our data for predicted environmental concentrations (PEC_{SW}) in receiving water bodies (here: WTP influent concentrations) can be compared to estimates from the scientific literature (e.g. Boxall et al., 2007a; Gottschalk et al., 2009; Mueller & Nowack, 2008; Musee 2012; O'Brien & Cummins, 2010; Praetorius et al., 2012). In most cases, the predicted concentrations are within the same order of magnitude despite the different approaches used. For example, our estimates are in line with the prediction of nano-TiO_2 concentrations in the Thames region, UK (8.8 µg/l), based on sunscreen usage and experimental estimations of TiO_2 removal in an activated sludge plant (Johnson et al., 2011) as well as predictions for CeO_2 concentrations in surface waters based on fuel additive usage in the UK considering direct aerial deposition and indirect contamination *via* runoff in the water and entrained soil sediment, with the highest level of 0.02 ng/l predicted (Johnson & Park, 2011). An exposure scenario for Swiss rivers at high spatial and temporal resolution however suggests highly variable local PECs and a location- and time-dependent risk evaluation for nano-TiO_2, nano-ZnO and nano-Ag (Gottschalk et al., 2011).

To our knowledge, only one study has been published in the literature estimating ENP concentrations in treated drinking water, predicting concentrations in Irish drinking waters for TiO_2 ENPs from exterior paints at 44.1–1448.2 µg/m^3 (=0.0441–1.4482 µg/l), for Ag ENPs from food packaging at 0.9–29.5 µg/m^3 (=0.0009–0.0295 µg/l) and CeO_2 from fuel at 0.74–24.3 µg/m^3 (=0.00074–0.0243 µg/l) (O'Brien & Cummins, 2010). These estimates are somewhat higher compared to our estimates of 4.91E−4 to 1.55E−1 µg/l (TiO_2), 3.21E−5 to 1.02E−2 µg/l (Ag) and 1.40E−10 to 4.43E−8 µg/l (CeO_2) depending on WTP treatment. This is most likely due to the differences in the removal efficiencies assumed (59.8% and 70.2% removal for Irish WWTPs and 96.95% and 0% for Irish WTPs compared to 97% removal in UK WWTP and 97–99.9% for UK WTPs in this study). When comparing to our results assuming 0% removal in UK WWTPs,

Table 3. Nanomaterials from ENP-containing products most likely to reach drinking water sources (qualitative ranking).

ENP type	Product type	Release pattern	Concentration (qual)	Emission (qual)	Release (qual)	Market share (%)	Score
TiO_2	Sunscreen	Down the drain	High	Low	Highly likely	High	6
ZnO	Sunscreen	Down the drain	High	Low	Highly likely	Medium	7
Ca peroxide	Toothpaste	Down the drain	High	Medium	Highly likely	Low	7
SiO_2	Toothpaste	Down the drain	High	Medium	Highly likely	Low	7
ZnO	Cosmetics	Down the drain	Medium	High	Highly likely	Low	7
Keratin fibres	Hair loss treatment	Down the drain	Medium	Low	Highly likely	High	7
TiO_2 (Mn doped)	Sunscreen	Down the drain	Medium	Low	Highly likely	High	7
C	Paint	Run off	Medium	High	Highly likely	Very low	8
Fe_2O_3	Paint	Run off	Medium	High	Highly likely	Very low	8
SiO_2	Car polish	Run off	Medium	Low	Highly likely	Medium	8
ZnO	Car polish	Run off	Medium	Low	Highly likely	Medium	8
ZnO	Sunscreen	Down the drain	Medium	Low	Highly likely	Medium	8
SiO_2	Cosmetics	Down the drain	High	Low	Highly likely	Very low	9
Ag	Washing machine	Down the drain	High	Medium	Likely	Very low	9
Ceramic	Coating	Run off	Medium	High	Likely	Very low	9
TiO_2	Coating	Run off	Medium	High	Likely	Very low	9
TiO_2	Paint	Down the drain	Medium	High	Likely	Very low	9
Lipid encaps.	Cosmetics	Down the drain	Medium	Low	Highly likely	Low	9
Proteins	Cosmetics	Down the drain	Unknown (=high)	Low	Highly likely	Very low	9
Ceramid nanocaps.	Cosmetics	Down the drain	Unknown (=high)	Low	Highly likely	Very low	9
Vit. E nanocaps.	Cosmetics	Down the drain	Unknown (=high)	Low	Highly likely	Very low	9
Micelles	Supplement	Down the drain	High	Very low	Highly likely	Very low	10
SiO_2	Coating	Down the drain	High	Very low	Highly likely	Very low	10
Ag	Clothing	Down the drain	Low	High	Likely	Very low	10
SiO_2	Clothing	Down the drain	Medium	High	Unlikely	Very low	10
Lipid encaps.	Cosmetics	Down the drain	Medium	Low	Highly likely	Very low	10
Silazane	Car polish	Run off	Medium	Low	Highly likely	Very low	10
SiO_2	Car polish	Run off	Medium	Low	Highly likely	Very low	10
ZnO	Car polish	Run off	Medium	Low	Highly likely	Very low	10
Al_2O_3	Cosmetics	Down the drain	Medium	Low	Highly likely	Very low	10
Lipid encaps.	Cosmetics	Down the drain	Medium	Low	Highly likely	Very low	10
CeO	Fuel additive	Run off	Very low	Very low	Highly likely	Unknown	10
C60	Cosmetics	Down the drain	Low	Low	Highly likely	Very low	11
C60	Sunscreen	Down the drain	Low	Low	Highly likely	Very low	11
Al_2O_3	Cosmetics	Down the drain	Medium	Very low	Highly likely	Very low	11
Lipid encaps.	Cosmetics	Down the drain	Medium	Very low	Highly likely	Very low	11
Ag	Clothing	Down the drain	Very low	High	Likely	Very low	11
Ag	Coating	Run off	Very low	High	Likely	Very low	11
Al	Clothing	Down the drain	Very low	High	Likely	Very low	11

the estimates are in better agreement for TiO_2 (0.0164–5.18 μg/l) and Ag (0.00107–0.339 μg/l), especially when noting that the data by O'Brien & Cummins (2010) considers less products. Our estimates for CeO_2 concentrations are however still much lower (4.67E−9 to 1.48E−6 μg/l), despite the same application considered (fuel additive).

It should be noted that the suggested models currently provide ''worst case'' estimates of exposure and do not consider stabilization, dissolution and aggregation in the environment. These simulations assume that there are no other sources of the ENP, so it is important that they are updated when new information becomes available.

Future research and regulatory efforts should focus on those products and ENPs contained within these products for which human exposure *via* drinking water appears to be greater than other exposure pathways. It is however important to recognize that the pattern of exposure to ENPs in drinking water will be different than the other routes of exposure so even though exposures are generally lower, they may still be significant in terms of health impacts. For example, this exposure will occur throughout the lifetime of consumers, so long-term effects from these low levels of exposure might be important. There may also be some potential for bioaccumulation, and it is possible that regulatory authorities may need to aggregate (e.g. add) drinking water exposure to other routes of exposure to come up with more accurate risk estimates. This is also a topic of great interest for other environmental contaminants such as pharmaceuticals (Boxall et al., 2012).

As the collated data on market penetration, usage and nanomaterial concentration is heavily reliant on assumptions, a qualitative approach was additionally used to the quantitative assessment of the drinking water exposure to establish exposure relative to other pathways. While this approach is not ideal, we believe that these results are valuable and could assist in prioritizing substances for further scrutiny. The approach may also be useful in other geographies with a lack of data. In the future, we would advocate that efforts are made to get a much better understanding of the use and make-up of the materials in use in different regions.

Conclusions and recommendations

In this article, we have presented a framework for identifying the potential for humans to be exposed to ENPs in drinking water and the significance of this exposure route compared to other routes of exposure. We believe that the findings and framework should be invaluable to researchers and decision makers in focusing future research. It is however clear from this study that there are significant gaps in our current knowledge regarding the use, environmental fate and exposure of ENPs in the environment.

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Table 4. ENP mass and PNC estimates for WWTP and WTP effluents for different removal efficiencies and particle sizes in alphabetical order.

				WWTP effluent			WTP conventional			WTP membrane			WTP filtration		
Particle type	Application	Removal WWT	Particle sizes (nm)	µg/l	#/l (small)	#/l (large)	µg/l	#/l (small)	#/l (large)	µg/l	#/l (small)	#/l (large)	µg/l	#/l (small)	#/l (large)
Aluminium and Al oxide	All products	0%	50, 5000	1.29E+00	7.30E+09	7.30E+03	1.29E−03	7.30E+06	7.30E+00	1.29E−05	7.30E+04	7.30E−02	4.08E−03	2.31E+07	2.31E+01
		97%	50, 5000	3.87E−02	2.19E+08	2.19E+02	3.87E−05	2.19E+05	2.19E−01	3.87E−07	2.19E+03	2.19E−03	1.22E−04	6.92E+05	6.92E−01
Ca peroxide	Toothpaste	0%		7.17E+01			7.17E−02			7.17E−04			2.27E−01		
		97%		2.15E+00			2.15E−03			2.15E−05			6.80E−03		
Carbon and C60	All products	0%		2.21E+02			2.21E−01			2.21E−03			6.98E−01		
		97%		6.62E+00			6.62E−03			6.62E−05			2.09E−02		
Carbon	All products	0%		2.20E+02			2.20E−01			2.20E−03			6.96E−01		
		97%		6.60E+00			6.60E−03			6.60E−05			2.09E−02		
C60	All products	0%	20, 80	5.77E−01	8.00E+10	1.25E+09	5.77E−04	8.00E+07	1.25E+06	5.77E−06	8.00E+05	1.25E+04	1.82E−03	2.53E+08	3.95E+06
		79%	20, 80	1.21E−01	1.68E+10	2.63E+08	1.21E−04	1.68E+07	2.63E+05	1.21E−06	1.68E+05	2.63E+03	3.83E−04	5.32E+07	8.31E+05
		97%	20, 80	1.73E−02	2.40E+09	3.75E+07	1.73E−05	2.40E+06	3.75E+04	1.73E−07	2.40E+04	3.75E+02	5.47E−05	7.59E+06	1.19E+05
Cerium oxide	All products	0%	8	4.67E−04	2.44E+08		4.67E−07	2.44E+05		4.67E−09	2.44E+03		1.48E−06	7.72E+05	
		95%	8	2.33E−05	1.22E+07		2.33E−08	1.22E+04		2.33E−10	1.22E+02		7.38E−08	3.86E+04	
		97%	8	1.40E−05	7.32E+06		1.40E−08	7.32E+03		1.40E−10	7.32E+01		4.43E−08	2.32E+04	
Ceramic	Coating	0%		3.67E+02			3.67E−01			3.67E−03			1.16E+00		
		97%		1.10E+01			1.10E−02			1.10E−04			3.48E−02		
Encapsulates	All products	0%		1.41E+01			1.41E−02			1.41E−04			4.45E−02		
		97%		5.92E−01			5.92E−04			5.92E−06			1.87E−03		
Iron oxide	Paint	0%	10	2.20E+02	8.13E+13		2.20E−01	8.13E+10		2.20E−03	8.13E+08		6.96E−01	2.57E+11	
		97%	10	6.60E+00	2.44E+12		6.60E−03	2.44E+09		6.60E−05	2.44E+07		2.09E−02	7.71E+09	
Keratin	All products	0%		8.27E+01			8.27E−02			8.27E−04			2.61E−01		
		97%		2.48E+00			2.48E−03			2.48E−05			7.84E−03		
Silazane	Car polish	0%		1.00E+00			1.00E−03			1.00E−05			3.16E−03		
		97%		3.00E−02			3.00E−05			3.00E−07			9.49E−05		
Silica	All products	0%	10, 1000	4.00E+02	2.90E+14	2.90E+08	4.00E−01	2.90E+11	2.90E+05	4.00E−03	2.90E+09	2.90E+03	1.26E+00	9.16E+11	9.16E+05
		97%	10, 1000	1.20E+01	8.69E+12	8.69E+06	1.20E−02	8.69E+09	8.69E+03	1.20E−04	8.69E+07	8.69E+01	3.79E−02	2.75E+10	2.75E+04
Silver	All products	0%	25, 150	1.07E+02	1.25E+12	5.78E+09	1.07E−01	1.25E+09	5.78E+06	1.07E−03	1.25E+07	5.78E+04	3.39E−01	3.95E+09	1.83E+07
		39%	25, 150	6.54E+01	7.62E+11	3.53E+09	6.54E−02	7.62E+08	3.53E+06	6.54E−04	7.62E+06	3.53E+04	2.07E−01	2.41E+09	1.12E+07
		97%	25, 150	3.21E+00	3.75E+10	1.73E+08	3.21E−03	3.75E+07	1.73E+05	3.21E−05	3.75E+05	1.73E+03	1.02E−02	1.18E+08	5.48E+05
Titanium oxide	All products	0%		1.64E+03			1.64E+00			1.64E−02			5.18E+00		
		23%		1.26E+03			1.26E+00			1.26E−02			3.99E+00		
		97%		4.91E+01			4.91E−02			4.91E−04			1.55E−01		
Titanium oxide	Sunscreens	0%	20, 70	1.05E+03	5.93E+13	1.38E+12	1.05E+00	5.93E+10	1.38E+09	1.05E−02	5.93E+08	1.38E+07	3.32E+00	1.87E+11	4.37E+09
		23%	20, 70	8.09E+02	4.56E+13	1.06E+12	8.09E−01	4.56E+10	1.06E+09	8.08E−03	4.56E+08	1.06E+07	2.56E+00	1.44E+11	3.37E+09
		97%	20, 70	3.15E+01	1.78E+12	4.15E+10	3.15E−02	1.78E+09	4.15E+07	3.15E−04	1.78E+07	4.15E+05	9.96E−02	5.62E+09	1.31E+08
Zinc oxide	All products	0%	n/a	6.36E+02	n/a	n/a	6.36E−01	n/a	n/a	6.35E−03	n/a	n/a	2.01E+00	n/a	n/a
		97%	n/a	1.91E+01	n/a	n/a	1.91E−02	n/a	n/a	1.91E−04	n/a	n/a	6.03E−02	n/a	n/a
Zinc oxide	Sunscreens	0%	20, 200	4.50E+02	1.92E+13	1.92E+10	4.50E−01	1.92E+10	1.92E+07	4.50E−03	1.92E+08	1.92E+05	1.42E+00	6.06E+10	6.06E+07
		97%	20, 200	1.35E+01	5.75E+11	5.75E+08	1.35E−02	5.75E+08	5.75E+05	1.35E−04	5.75E+06	5.75E+03	4.27E−02	1.82E+09	1.82E+06

Table 5. Products expected to have higher and the same exposure risk from drinking water.

Products	NP	Sector	Nanomaterial location	Rating F	Rating I	ΔRating $F - I$
Business and sports socks	Ag	Clothing	Suspended in solids	10	11	−1
Socks	Ag	Clothing	Suspended in solids	6	7	−1
Socks	Ag	Clothing	Suspended in solids	6	7	−1
Socks	Ag	Clothing	Suspended in solids	10	11	−1
Cotton clean-sheet	Ag	Clothing	Suspended in solids	11	12	−1
Various clothing lines	Al	Clothing	Suspended in solid	11	12	−1
A range of surface coatings and paints	Carbon	Paints and coatings	Suspended in liquid	8	9	−1
Self cleaning glass	TiO_2	Paints and coatings	Suspended in liquid	9	12	−3
Water-based paints	Fe_2O_3	Paints and coatings	Suspended in liquid	8	9	−1
Tiles	TiO_2	Paints and coatings	Suspended in liquid	9	11	−2
Wipe	Ag	Cleaning	Surface bound	11	12	−1
Fuel-borne catalyst	CeO	Auto	Suspended in liquid	10	10	0
Various clothing lines	SiO_2	Clothing	Surface bound	10	10	0
Various clothing lines	SiO_2	Clothing	Surface bound	10	10	0
Various clothing lines	SiO_2	Clothing	Surface bound	10	10	0
Finish on paint	Ceramic	Paints and coatings	Suspended in liquid	9	9	0
Various cosmetics	ZnO	Cosmetics	Suspended in liquid	7	7	0

This makes it very difficult to assess the actual risks of ENPs to drinking water supplies. We would therefore advocate that work in the future focuses in better understanding the nature and use of ENP-containing products in different regions and in understanding the behaviour of ENPs as they move through the environment into drinking water systems. This will allow a much better characterization of exposure to ENPs in the future.

Declaration of interest

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Supplementary material available online.
Supplementary Materials S1–S9