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ORIGINAL ARTICLE

Probabilistic environmental risk assessment of five nanomaterials (nano-TiO₂, nano-Ag, nano-ZnO, CNT, and fullerenes)

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Abstract

The environmental risks of five engineered nanomaterials (nano-TiO₂, nano-Ag, nano-ZnO, CNT, and fullerenes) were quantified in water, soils, and sediments using probabilistic Species Sensitivity Distributions (pSSDs) and probabilistic predicted environmental concentrations (PECs). For water and soil, enough ecotoxicological endpoints were found for a full risk characterization (between 17 and 73 data points per nanomaterial for water and between 4 and 20 for soil) whereas for sediments, the data availability was not sufficient. Predicted No Effect Concentrations (PNECs) were obtained from the pSSD and used to calculate risk characterization ratios (PEC/PNEC). For most materials and environmental compartments, exposure and effect concentrations were separated by several orders of magnitude. Nano-ZnO in freshwaters and nano-TiO₂ in soils were the combinations where the risk characterization ratio was closest to one, meaning that these are compartment/ENM combinations to be studied in more depth with the highest priority. The probabilistic risk quantification allows us to consider the large variability of observed effects in different ecotoxicological studies and the uncertainty in modeled exposure concentrations. The risk characterization results presented in this work allows for a more focused investigation of environmental risks of nanomaterials by consideration of material/compartments combinations where the highest probability for effects with predicted environmental concentrations is likely.

Keywords

Environmental risk assessment; probabilistic modeling; species sensitivity distributions

History

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Introduction

A vast body of literature exists which examines the potential effects of engineered nanomaterials (ENM) on organisms living in freshwater, soils and sediments. Reviews are available that discuss the approaches used and problems encountered of testing the effects of ENMs on organisms (Handy et al., 2012a,b; Petersen et al., 2014). From these reviews, patterns begin to emerge, for example, about the importance of dissolution that may explain the specific effects and the underlying mechanisms of toxicity of ENM observed in these tests (Bondarenko et al., 2013; Johnston et al., 2013; Kahru & Ivask, 2013; Notter et al., 2014).

Whereas a lot is already known about effects of ENM, much less information is available about environmental exposure of ENMs (Holden et al., 2014). From the analytical point of view, there are still many challenges to master before trace analysis of engineered ENM in natural samples is possible, especially with respect to the distinction between natural and engineered nanoparticles (von der Kammer et al., 2012). Reports on the analysis of ENM in environmental samples are, therefore, very rare and most of the time restricted to the identification of particles by TEM as being engineered materials (Gondikas et al., 2014; Kaegi et al., 2008; Kim et al., 2010). Even with single

particle ICP-MS, specific identification of engineered NMs among the natural nanoparticles is not yet possible (Mitrano et al., 2012). Also the specific detection of fullerenes in water and air samples was attributed mainly to natural sources of these materials (Farré et al., 2010; Sanchis et al., 2012).

In the current situation, with very little data existing on measured environmental concentrations of ENMs, material flow modeling and environmental fate models are useful tools to obtain estimates of environmental exposure. Such models have been used to predict concentrations in water, soils and sediments (Dale et al., 2015; Gottschalk et al., 2013b) and although there are still major knowledge gaps (e.g. on ENM production, application and release) that affect the modeled values, the same order of magnitude of the environmental concentrations has been predicted in different studies and across various modeling approaches (Gottschalk et al., 2013b). Over the years, these models have been improved and refined, including the growing understanding on their use in technical systems (e.g. wastewater treatment plants or waste incineration) as well as release to and fate in the environment (Arvidsson et al., 2012; Gottschalk et al., 2009; Keller et al., 2013; Mueller & Nowack, 2008; Sun et al., 2014). Whereas several studies have also provided estimates for concentrations in environmental systems (Arvidsson et al., 2012; Keller et al., 2013; Liu & Cohen, 2014; O'Brien & Cummins, 2010), only the studies by Gottschalk et al. (2009) and Sun et al. (2014) present complete probability distributions that fully incorporate the uncertainties with respect to many model parameters.

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In environmental risk assessment, the predicted environmental concentrations (PECs) are compared with predicted no effect concentrations (PNECs), which are derived from ecotoxicological studies (ECHA, 2008a). This simple approach was applied to ENMs where the first risk characterization ratios were obtained and discussed by Mueller and Nowack (2008) and subsequently by Gottschalk et al. (2009). Also, Species Sensitivity Distributions (SSDs) for nanomaterials have been produced and used for a first look at probabilistic risk assessment of ENM (Gottschalk et al., 2013a). Garner et al. (2015) have constructed ten ENM-specific SSDs, analyzing the range of toxic concentrations, comparing them to the bulk or ionic form, and identifying the important parameters that influence variability in toxicity. In an SSD, all available toxicological data for one material are considered instead of just the most sensitive one. The results from that work indicate that there is based on currently predicted concentrations only a marginal risk from metal-based nanomaterials for the surface water compartment and some potential risk for aquatic organisms in undiluted sewage treatment plant effluents. In sludge-treated soils, virtually no risk from the ENMs evaluated is currently predicted. These risk assessments were carried out with the PEC values published in 2009 (Gottschalk et al., 2009). In the meantime, updated PEC values have been published, incorporating the newest available information on production, use and behavior of ENMs (Sun et al., 2014) and also the ecotoxicological literature is rapidly expanding, which gives us an improved understanding of PNEC values.

This work aims to perform an environmental risk assessment of five ENMs (nano-TiO₂, nano-Ag, nano-ZnO, CNT, and fullerenes) using the latest ecotoxicological literature and the newest probability distributions of PEC values provided by Sun et al. (2014). In order to fully take into consideration the uncertainty in both modeled exposure concentrations and ecotoxicological evaluations, we have used a probabilistic risk assessment method, applying for the first time both probability distributions for PEC values and for PNEC values (Gottschalk & Nowack, 2013).

Materials and methods

Data collection

This current work contains an updated evaluation of the hazard literature compared to the work of Gottschalk et al. (2013a), on which our database is based. The peer-reviewed literature search was performed for ecotoxicological endpoints for nano-TiO₂, nano-Ag, nano-ZnO, CNT, and fullerenes. Only papers before March 2014 were considered for this update. Of the many endpoints published in the literature, we included only those which met our selection criteria that were based on the REACH guidance (ECHA, 2008b) and upon the previous study by Gottschalk et al. (2013a). These criteria are discussed in the following section.

Only effects on survival, growth, reproduction, and changes in significant metabolic processes (such as photosynthesis) were considered. Minor effects like change in behavior, coloring, mild biochemical adjustments, or enzyme regulations were excluded. Lastly, only studies on living organisms exposed to the selected three compartments (freshwater, soil, and sediment) were used; endpoints from tissue experiments, *in vitro*, marine water, biosolids, or hydroponic conditions (instead of soil) were not used. Chronic endpoints were preferred over acute if both were available in the same study. In studies where even the highest exposure concentration showed no adverse effect to the test organism, this value was used as the Highest Observed No Effect Concentration (HONEC) for our calculations. A HONEC was not used when it was the lowest endpoint. When different particle

types, particle sizes, or media were tested in the same study, all the different endpoints were used. Therefore, the evaluation presented here is not related to a specific nanomaterial form or particle property, e.g. specific surface coating or surface charge, but rather encompasses a suite of possible ENM characteristics making the model more applicable to the wide range of ENMs currently used across multiple studies.

Very few studies were found for freshwater sediments, only enough to assess the hazard of CNTs in this medium. Estuarine or marine sediment studies were not considered because only PEC values for freshwater are available. Several studies for soils measured toxic effects on bacteria or microbial communities in general and were analyzed as a whole consortium instead at the individual species level. For fullerenes, special care was taken to discard experiments that used tetrahydrofuran in preparing the suspensions, as breakdown products from this substance were found to be toxic to the organisms which lead to an overestimation of fullerene toxicity (Spohn et al., 2009).

Data evaluation

In accordance with REACH guidance (ECHA, 2008b), each of the endpoint concentrations was transformed by two different assessment factors (AFs) to derive the PNEC because in most cases, chronic NOEC values were not available. Acute studies received higher assessment factors than the ones that documented chronic effects. The first AF is used to extrapolate the observed effect into no effect concentrations. An AF of 10 was used for LC/EC₂₅₋₅₀, an AF of 2 for LC/EC₁₀₋₂₀ LOEC, LED and MIC and an AF of 1 for LOEC, LED, MIC, HONEC, and NOEC values. From each experiment, only one endpoint was used, preferably a NOEC if available or an EC_{10/20}. LOEC or HONEC values were only used if no other endpoint was provided, a HONEC only when it was not the lowest endpoint. Some available data from studies providing both EC₅₀ and NOEC values indicate that the use of a factor of 10 is well supported also for ENM (Das et al., 2013; Ji et al., 2011; Kim et al., 2011; Schwab et al., 2011).

The second assessment factor accounts for the extrapolation from short- to long-term effects. Long-term studies are assigned an AF of 1, short-term studies an AF of 10. The exposure time needed to categorize as long-term varies according to the species/taxonomic group, as shown in Tables S1–S3 (Supporting information).

More than 600 data points were found from our literature search, but only 431 data points met our criteria (as specified above); the summarized results are shown in Table 1. By far, most of the toxicological studies of the selected ENM focus on freshwater systems, followed by soil and lastly freshwater sediment. A few studies based on other media as sewage sludge, marine water, and estuarine water or sediment were also found but not taken into account for this sum.

All studies are listed in Tables S1–S3 in the Supporting information. Marine and estuarine water or sediment studies were excluded from this count.

Species sensitivity distribution modeling

The ecotoxicity values obtained after the transformation with the AFs were fed into the Monte Carlo based model described in Gottschalk and Nowack (2013). This method helps to overcome challenges associated with the variability and uncertainty of endpoint concentrations found in the studies, which are mostly due to the diverse or unspecified experimental conditions and ENM characteristics. With this model, a probabilistic Species Sensitivity Distribution (pSSD) was first calculated for every single species, using all the endpoints available for it. Three different procedures were used to create these single species

Table 1. Summary of ecotoxicological dose endpoints used for the selected ENM.

ENM	Compartment	Number of Endpoints	Number of Species	Number of taxonomic groups
Nano-TiO ₂	Water	73	31	5
	Soil	4	2	2
	Sediment ^a	1	1	1
Nano-Ag	Water	194	33	5
	Soil	6	4	2
	Sediment ^a	0	0	0
Nano-ZnO	Water	69	21	5
	Soil	20	7	3
	Sediment ^a	0	0	0
CNT	Water	25	12	4
	Soil	8	9	3
	Sediment	4	2	1
Fullerenes	Water	17	10	4
	Soil	9	9	3
	Sediment ^a	1	1	1

^aStudies were not sufficient to produce a probabilistic species sensitivity distribution.

distributions depending on the number of existing ecotoxicity values as described in Gottschalk and Nowack (2013). Using a Monte Carlo approach with 10 000 samplings, the final probabilistic single species sensitivity curve was obtained. For the next step, all the single SSDs corresponding to one compartment were combined based on Monte Carlo routines (assigning 10 000 sample values for each distribution).

From the SSD-curves, the HC5 (5th percentile of the distribution) was extracted and is used according to (ECHA, 2008b) as PNEC value. The probability distribution of the HC5 was obtained by random variation considering up to a 50% deviation on each side of the product of the two AFs. The same deviation was applied for the confidence ranges added to the model input values that determine the upper and lower extremes of a particular single species sensitivity distribution. By varying those two types of model parameters, 10 000 different pSSD computer simulations were performed in order to extract from each of those pSSDs the HC5. These HC5s, taken together, formed the PNEC distribution for each compartment.

Risk calculation

In the previous work by Gottschalk and Nowack (2013), the risk was assessed as a percentage of overlap between the PEC and the pSSD. However, in the present study the Risk Characterization Ratio (RCR) distribution (also referred as Risk Quotient – RQ) was calculated following the established formula that follows REACH guidance:

$$RCR = \frac{PEC}{PNEC}$$

Therefore, a $RCR < 1$ would indicate that no risk is expected for the particular environmental compartment and conditions. A $RCR > 1$ would mean the predicted environmental concentrations are high enough to cause adverse effects on the organisms and could show the need to implement additional risk management measures.

In our RCR model, the PECs and PNECs are provided as probability density curves. The actual RCR value distributions were then computed by dividing each single PEC value of a particular environmental compartment by all the PNEC values that could be assigned to the same compartment and subsequently

performed this for all PEC values. Thus, generally speaking, each Monte Carlo PEC scenario was divided by 10 000 possible PNEC scenarios. The PECs were taken from Sun et al. (2014) as probability distributions in freshwater and yearly increments in sediments, soils, and sludge-treated soils for the year 2012 in the European Union. The PNEC distributions correspond to the ones of HC5 values computed in this work as described in the previous section.

Results

The pSSD for the five ENMs in water and soil are shown in Figures 1 and 2 for Ag, CNT, TiO₂, and ZnO in freshwater and soils. Results corresponding to Fullerenes and CNTs in sediments can be found in the Supporting information (Figures S1 and S2, respectively). The individual species NOEC data calculated from the endpoints are shown as points grouped by species or taxa, blue for the raw points and red for the geometric mean. The individual points illustrate the range in which the data vary for one ENM and one species between different studies. The range of individual NOEC values can span many orders of magnitudes for many species. For example, the response of *Daphnia magna* with TiO₂, the range is six orders of magnitude between the highest and lowest NOEC values and for *Daphnia magna* and *Danio rerio* with nano-Ag, five orders of magnitude is found. A range of 3–4 orders of magnitude is the typical range for many other species investigated across the study conditions. Fewer reports providing endpoints that could be used for an SSD were found for soil organisms (Figure 2). For freshwater sediments, this is even more pronounced with only a few studies which provided adequate data for our analysis (Figure S2, Supporting information). No studies were found for TiO₂ and nano-Ag, and only one was available for ZnO and fullerenes, respectively.

PNEC distributions were derived from the 5th percentiles of the pSSD models with the median values of the distributions shown in Table 2. The full probability distributions of the PNECs are shown in Figure S4. Table 2 presents both the mode and the 95% confidence interval of the distributions. For the freshwater dataset, the PNEC increases from ENMs which are likely to be most sensitive to least sensitive in the order of $Ag \ll ZnO < fullerenes < TiO_2 \ll CNT$, while for soil the order is $ZnO < fullerenes < Ag < CNT < TiO_2$ indicating that ZnO has the lowest probability of no effect concentrations in this media at the current time.

The comparison of the PNEC derived in this work and the probabilistic PEC results from Sun et al. (2014) are shown in Figures 3 and 4 for freshwater and soils and in Figure S2 for sediments. These figures allow a very simple evaluation of possible environmental risks, designated as an overlap between the PEC and the PNEC curves. If curves are shown to overlap, it indicates a greater potential for concentrations of ENMs to reach the PNEC and hence a higher risk level in the given environment. For the freshwater compartment (Figure 3), the curves for TiO₂ and Ag are not overlapping but are close to each other whereas the CNT curves are separated by concentration differences of many orders of magnitude. For ZnO, there is a slight overlap of the two curves. In the soil compartment (Figure 4), the curves for Ag, ZnO, and CNT do not overlap at all and are clearly separated, indicating that no risk is expected. However, the PEC and PNEC for nano-TiO₂ show some overlap.

In order to make a quantitative evaluation, the PEC and PNEC distributions have been used to derive the probabilistic RCR curves. These resulting curves are shown in Figure 5 on a logarithmic scale (in Figures S5 and S7, they are shown for each single material on a linear scale). The mode values and the 95% interval from these curves are given in Table 3. All the RCR mode

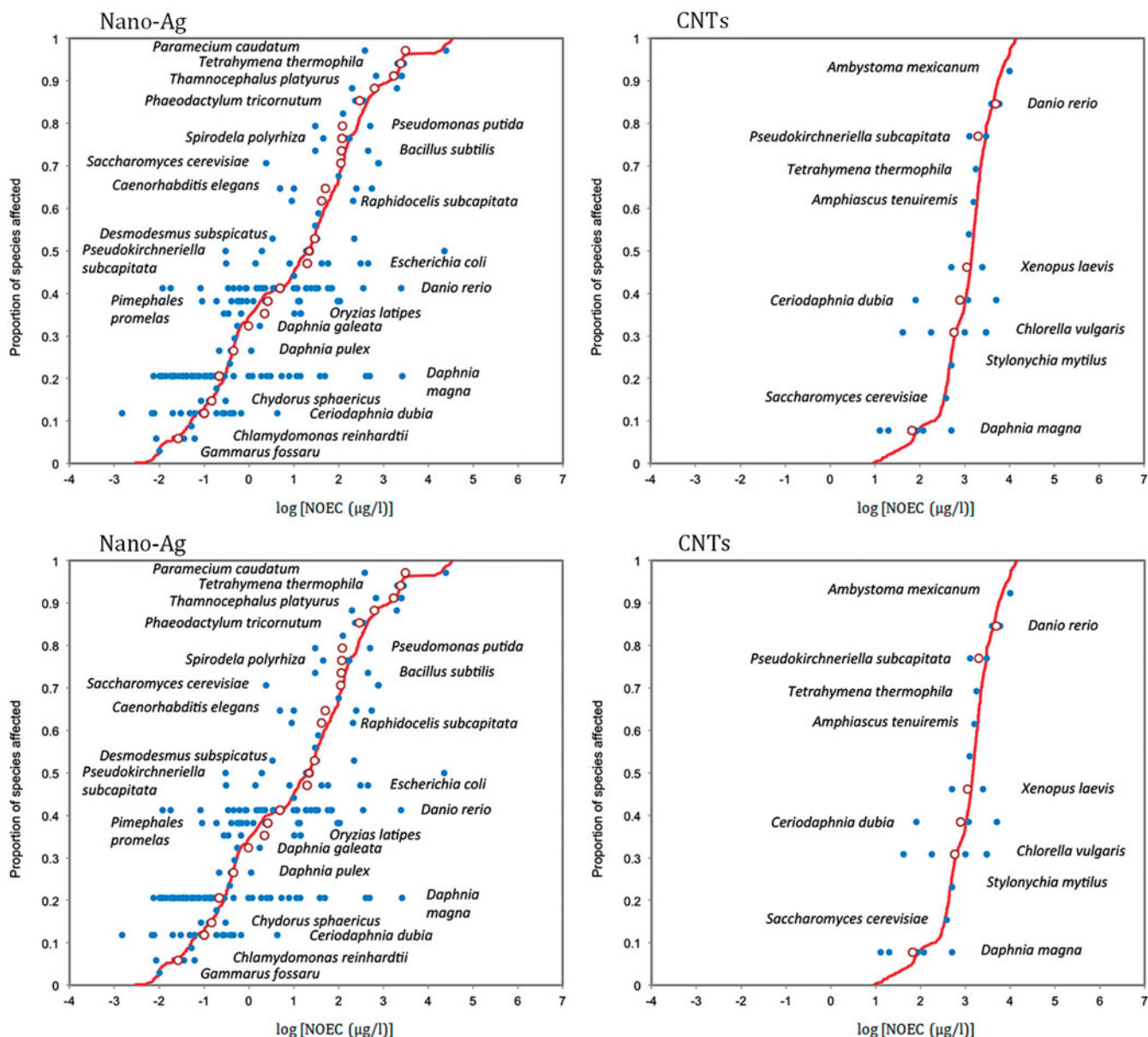


Figure 1. Probabilistic species sensitivity distributions (pSSD) for nano-Ag, CNTs, nano-TiO₂, and nano-ZnO for the freshwater compartment. The blue circles represent all data points considered for the modeling, the red outlined circles are the geometric means per species (for illustration only), the red line represents the probabilistic pSSD. Selected species names are added.

values (and the corresponding 95% confidence intervals) calculated for freshwater and soil are lower than 1. This indicates that most of the toxicity values found are greater than any of the predicted environmental concentrations in a given compartment. Nevertheless, in one case, we can find RCR values higher than 1. For nano-ZnO in freshwater, the maximum value of RCR in the distribution is 1.52, followed by nano-TiO₂ in soil with a maximum value of 0.17. However, in both cases, the probability of these values to be recognized in the environment is very small as they are far outside the 97.5% quantile of 0.55 and 0.07 for ZnO and TiO₂, respectively. The order of the RCR is for freshwater is CNT = fullerenes < TiO₂ < Ag < ZnO, and for soils, the order is fullerenes = CNT = ZnO = Ag < TiO₂. The risk ratios for the carbon-based ENMs (i.e. fullerenes and CNT's) are, therefore, the lowest for freshwater and soil compartments, which are very close to zero. The metallic nanomaterials have a slightly higher risk values. In freshwater, nano-Ag, nano-ZnO, and nano-TiO₂, the distribution reaches above 0.01; in soils, only the distribution for

nano-TiO₂ reaches slightly higher values. In sediments (Figure S5), only CNTs could be evaluated and their RCR is 0.03.

Discussion

The validity of the risks of ENMs to the environment predicted in this work hinges on two main aspects: the choice of the model for exposure assessment providing the predicted environmental concentration and the evaluation of the hazard literature. A similar risk assessment approach was used in Gottschalk et al. (2013a) and the current study, but several adjustments have been made for the exposure and effects models, which reduce the uncertainty of the outcome and enabled us to better deal with the variability of the inputs. In general, the predicted environmental concentrations provided by Sun et al. (2014) are larger than by Gottschalk et al. (2009), mainly due to a higher estimated production volume. However, for nano-Ag and nano-ZnO in soil and water, much lower concentrations are predicted. The reasons

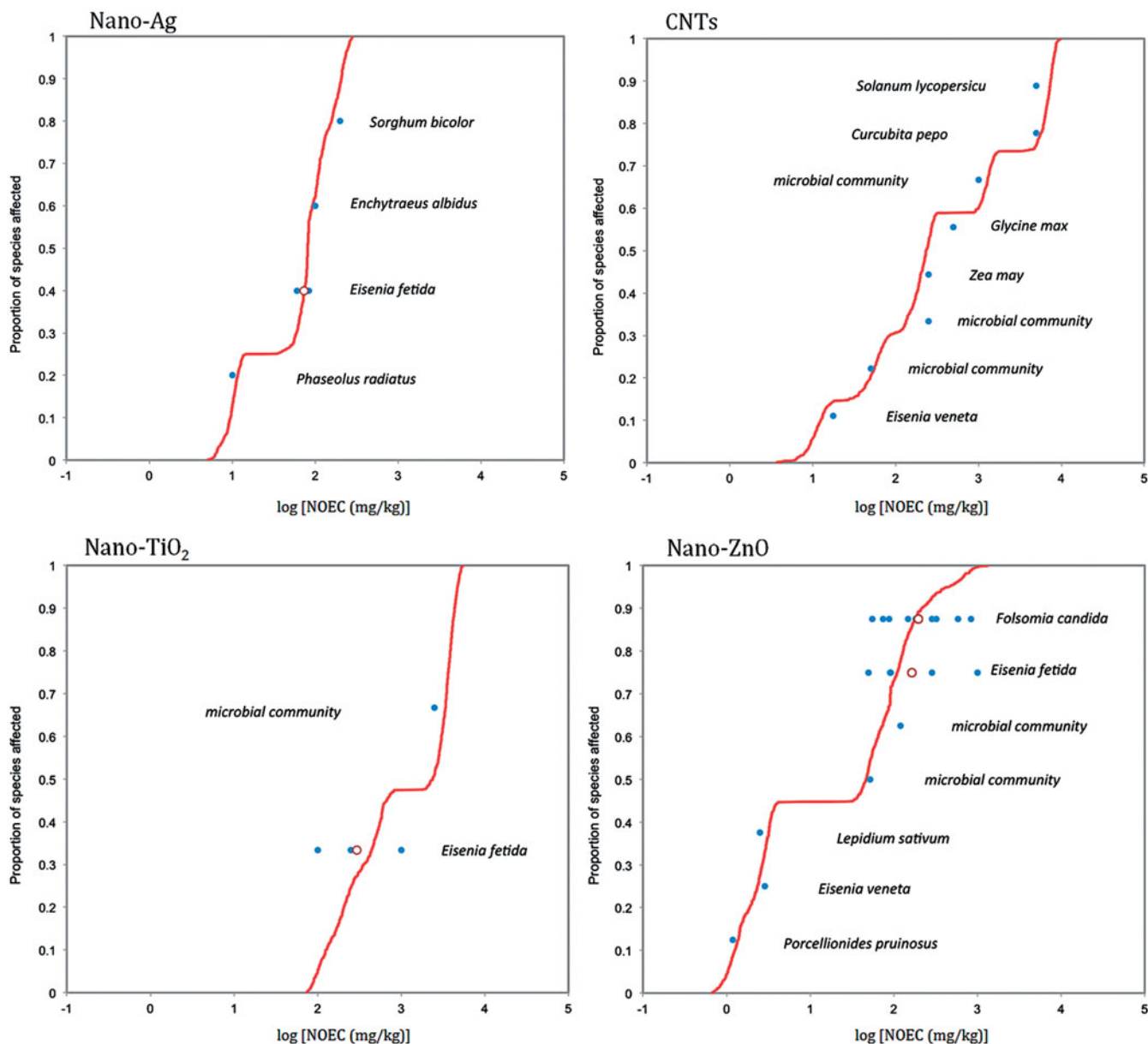


Figure 2. Probabilistic species sensitivity distributions (pSSD) for nano-Ag, CNTs, nano-TiO₂, and nano-ZnO for the soil compartment. The blue circles represent all data points considered for the modeling, the red outlined circles are the geometric means per species (for illustration only), and the red line represents the probabilistic pSSD.

Table 2. Predicted no effect concentrations (PNEC) derived from the 5th percentile median values in all three environmental compartments.

ENM	Freshwater (µg/l)	Soil (mg/kg)	Sediment (mg/kg)
Nano-TiO ₂	15.7 (10.6–20.7)	91.1 (47.6–134.9)	n.a.
Nano-Ag	0.017 (0.014–0.021)	8.2 (4.3–12.5)	n.a.
Nano-ZnO	1.0 (0.60–1.38)	1.1 (0.6–1.6)	n.a.
CNT	55.6 (39.9–78.0)	16.2 (8.5–23.8)	26.8 (14.0–39.9)
Fullerenes	3.84 (2.7–5.3)	2.4 (1.3–3.5)	n.a.

The 95% confidence interval is shown in brackets. The full PNEC distributions are shown in the supporting Figures S4, S6, and S8. n.a., not available.

being the lower production estimates for nano-Ag and consideration of sulfidation during water treatment for nano-ZnO and nano-Ag (Sun et al., 2014). The PEC values used in this work represent probability distributions of environmental concentrations that consider the uncertainty of production volumes,

application and fate in technical systems. Thus these PEC values provide the probable range of concentrations. At the moment, they constitute the most comprehensive set of predictions for environmental exposure to nanomaterials.

The ENMs are assessed in the effect and exposure models as single entities but are in fact a collation of a wide range of very different nanoparticles with corresponding different properties. Nano-TiO₂, for example, can be found in rutile, photocatalytic anatase, and brookite forms. In addition, the particles may be coated with silica or aluminum oxides to inhibit photocatalytic reactions. The pure anatase form displays a high photocatalytic activity when exposed to UV radiation (Kim et al., 2014; Ma et al., 2012). Because only PEC data for a “generic nano-TiO₂” are available to date, it was not possible to separately evaluate the ecotoxicological data for the different forms of TiO₂. However, there are several clues which point to a trend that the risks associated with each varying forms of ENMs exist and may need to be treated differently when more data is available and modeling efforts continue in the future. For example, in the case of TiO₂,

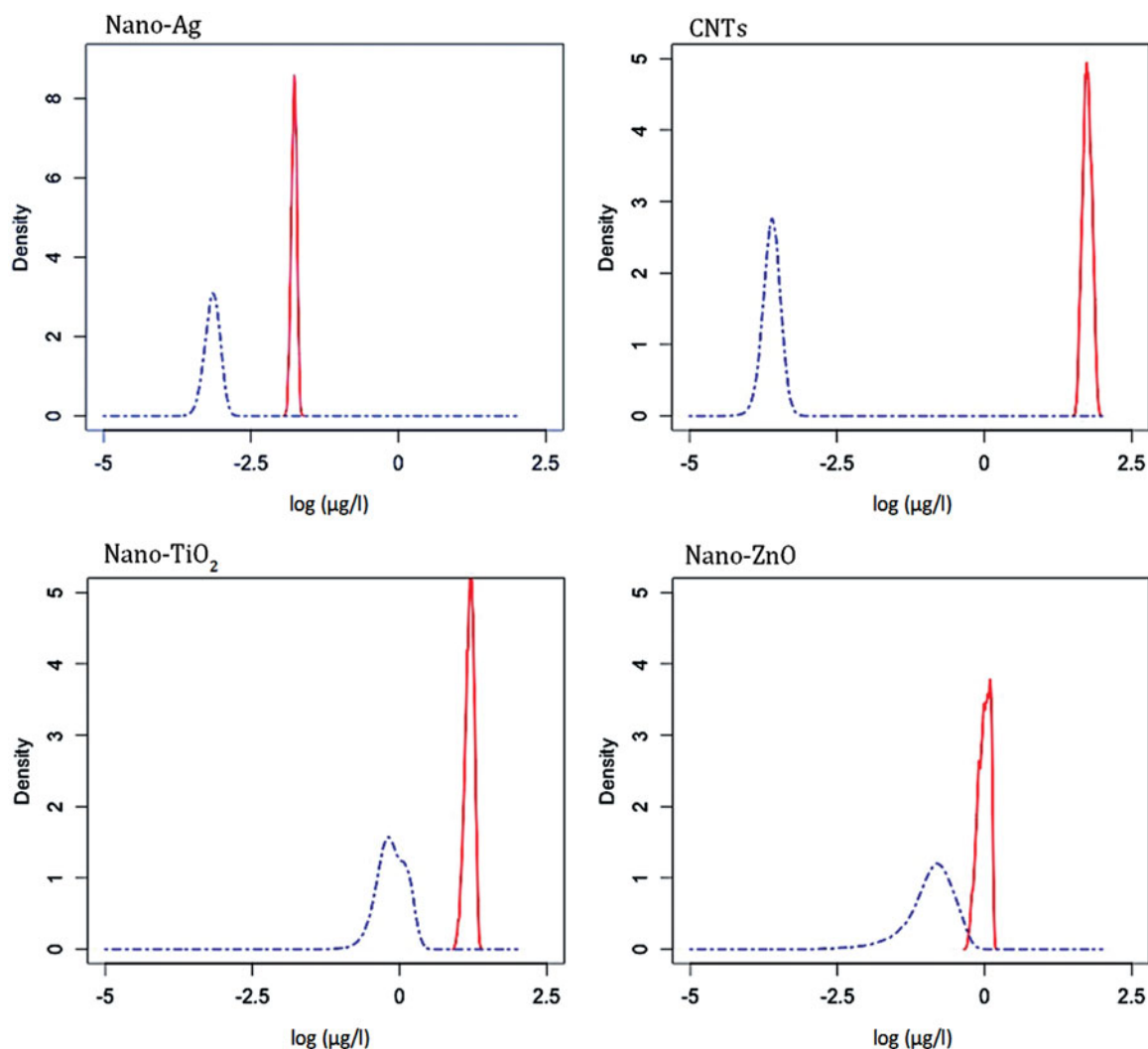


Figure 3. Comparison of predicted environmental concentration (PEC) in blue and predicted no-effect concentration (PNEC) distribution obtained from the HC5 in the probabilistic species sensitivity distribution (pSSD) in red for the freshwater compartment for nano-Ag, CNTs, nano-TiO₂, and nano-ZnO. The PEC values were taken from Sun et al. (2014), the PNEC curve corresponds to the curves shown in Figure S3 (Supporting Information).

studies corresponding to the lowest concentrations (i.e. lowest NOEC) seem to be associated with the photocatalytic activity of the anatase type of TiO₂. The data point corresponding to the most sensitive species, the amphipod *Gammarus fossaru* was extracted from a study under UV light (Bundschuh et al., 2011). In simulated solar irradiance conditions, TiO₂ showed enhanced toxicity to *Daphnia magna* and the Japanese rice fish- *Oryzias latipes* (Ma et al., 2012). Similarly, for *Escherichia coli*, the most sensitive value was also associated to photoinduced toxicity (Dasari et al., 2013). Other low data points, such as Dabrunz et al. (2011), Clement et al. (2013), and Zhu et al. (2010), used TiO₂ in the anatase form for their experiments. Once separate PEC values for photocatalytic and photo-stable TiO₂ become available, different SSDs for the two forms should be produced which would allow a better evaluation of the risks emanating from these two forms of TiO₂.

Another example is the group of fullerenes, which can easily be functionalized with surface modifications and are available in slightly different forms with different numbers of carbon atoms (C₇₀, C₈₀, and C₉₄). All forms seemingly display different dose responses from the same organisms under the same study conditions (Aschberger et al., 2010; Oberdörster et al., 2006; Seda et al., 2012; Zhu et al., 2008) but here are simply treated as one entity due to the absence of specific PEC data currently available.

The same is true for every ENM: each comes in many forms, sizes, and behaves differently according to these characteristics. The different media and conditions during experimentations only make variability more pronounced. Physical (stirred or sonicated) or chemical means to disperse nanoparticles, pH, temperature, light (e.g. with or without UV) are added to the variables that can influence the organisms' response. With the advancement of the environmental fate modeling of ENMs (Praetorius et al., 2012, 2013), it may be possible in the future to also include the speciation and precise form of the ENM in the PEC-modeling. In the current state, not only are generic ENMs modeled but also all physical forms (single, agglomerated, surface attached, etc.) are included together in the risk assessment framework and are not distinguished.

The PEC values from Sun et al. (2014) also do not consider any sedimentation or other removal processes in natural waters or assume complete ENM removal from the sediment compartment and, therefore, constitute worst-case assumptions in both instances. Only with advanced environmental fate models can an accurate prediction of true freshwater concentrations be achieved. The work spearheaded by the models presented by Praetorius et al. (2012) and Meesters et al. (2014) suggest that the inclusion of agglomeration and sedimentation of ENMs in these systems should be possible in the near future. However, for both compartments, these improvements will likely only lead to

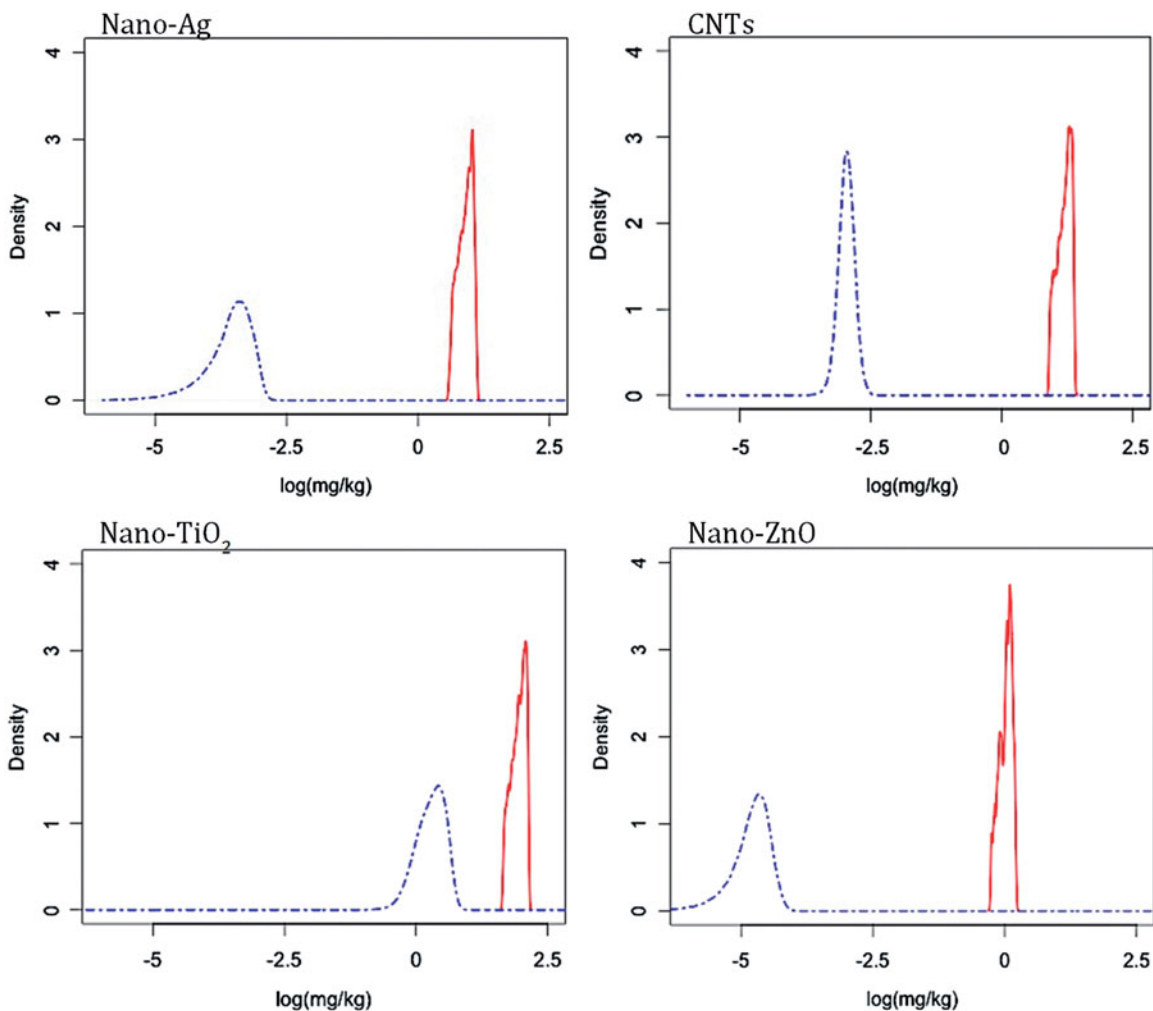


Figure 4. Comparison of predicted environmental concentration (PEC) in blue and predicted no-effect concentration (PNEC) distribution obtained from the HC5 in the probabilistic species sensitivity distribution (pSSD) in red for sludge treated soils for nano-Ag, CNTs, nano-TiO₂, and nano-ZnO. The PEC values were taken from Sun et al. (2014), the PNEC curve corresponds to the curves shown in Figure S4 (Supporting Information).

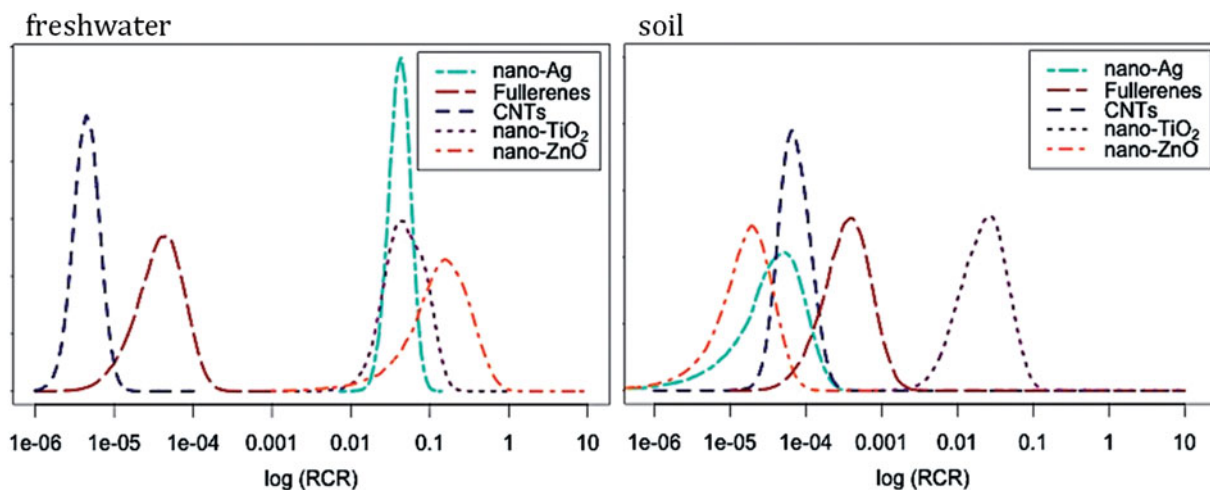


Figure 5. Risk characterization ratio (RCR) distributions for freshwater and soil for nano-TiO₂, nano-Ag, nano-ZnO, and CNT shown in a logarithmic scale.

smaller PEC values, as consideration of sedimentation would lead to lower concentrations in water and non-complete sedimentation would lead to lower PEC values in the sediment. Thus, the results provided in this work constitute a worst-case scenario with respect to both compartments.

It is also important to highlight that the predicted concentrations for soils and sediments from Sun et al. (2014) reflect only the material flows of ENM in 2012 and not the accumulated environmental concentrations over several years. For soils and sediments, yearly increases in concentrations are given. In order

Table 3. Probabilistic risk characterization ratios obtained from the risk characterization distributions (mode values).

ENM	Freshwater	Sludge treated Soil	Sediment
Nano-TiO ₂	0.03 (0.01–0.14)	0.013 (0.005–0.07)	n.a.
Nano-Ag	0.038 (0.02–0.07)	<0.01	n.a.
Nano-ZnO	0.09 (0.01–0.54)	<0.01	n.a.
CNT	<0.01	<0.01	0.03 (0.01–0.08)
Fullerenes	<0.01	<0.01	n.a.

The 95% confidence interval is shown in brackets. The full distributions are shown in supporting Figures S5, S7, and S8. n.a., not available.

to obtain true environmental concentrations, a dynamic modeling considering the increase in ENM production and accumulation processes in soil and sediments over time would be needed (Bornhöft et al., 2013). The present evaluation for soil and sediments reflects a lower limit of PEC values, and thus results in an underestimation of RCR-values for these environmental compartments. Therefore, they need to be adjusted once results from dynamic models become available.

The rise in the number of ecotoxicity studies has allowed us to increase the number of data points for the water and soil pSSDs compared with Gottschalk et al. (2013a) and to produce the first pSSDs and risk quantifications for the sediment compartment. Undoubtedly, freshwater organisms are the main focus of ecotoxicological experiments that report endpoints for our evaluation; more toxicity studies are definitely needed for marine, terrestrial, and benthic organisms (vertebrate or invertebrate) and for terrestrial plants. This overrepresentation of the freshwater compartment is problematic because exposure models clearly show that ENMs mainly accumulate in soil and sediments. The most vulnerable species in these compartments should, therefore, be tested and given priority rather than additional freshwater species. Organisms in ecotoxicity tests should also be exposed to nanoparticles in a way that is environmentally relevant and produces results that can be used by risk assessors. Many studies in our evaluation were discarded for soil and sediment compartments because benthic/terrestrial species were studied in aqueous suspensions, and these inappropriate testing conditions were deemed not to be useful for risk assessment purposes.

Particularly, very few studies are available for organism responses in sediments. Overall, only 20 studies (3% of the total ecotoxicity studies found) were based on toxicity in marine and freshwater sediments. Furthermore, acute toxicity, opposed to the more useful chronic endpoints, was used for the majority of these studies. Therefore, the risk for this compartment is still largely unknown, because there is only a small number of endpoints available. At the same time, let us not forget that journals often discard studies that show no effect on the studied organism (Krug, 2014). Whether this causes a significant bias or overestimation of the environmental effects is still unknown, but at least for hazard assessment, no effect concentrations would still be very useful.

The two carbon-based ENMs considered (fullerenes and CNTs) do not represent a significant risk for the environment, and should be of lower concern in comparison with the other materials studied. Aschberger et al. (2011) also concluded that the exposure potential is low due to limited production of fullerenes and low releases of CNT's. Based on the present results, continuous future emissions would not lead to critical exposure concentration in the environment, as the lowest toxicity values are still 100 or more times higher than the highest environmental concentrations in most compartments considered here.

The low risk for nano-Ag can be explained mainly by the low environmental concentrations modeled by Sun et al. (2014) that included transformation of nano-Ag to silver sulfide, which is

greatly reducing the release of metallic nano-Ag to the environment. Despite being the most toxic of the ENM in water according to the HC5 and its wide use as bactericide, release of nano-Ag could be increased significantly before the probabilistic curves overlap enough to result in any risk.

According to our results, ZnO is the ENM of highest concern. ZnO exhibited very high toxicity in all the compartments in accordance with Stone et al. (2009) and Aschberger et al. (2011). Additionally, the predicted exposure concentrations for the environment were also high in the µg/L (water), µg/kg (soil), and mg/kg (sediment) range (Sun et al., 2014). The risk characterization results presented in this work thus allow now a more focused investigation of environmental risks of nanomaterials by considering material/compartment combinations where the highest probability for effects under environmental concentrations is likely.

Declaration of interest

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