



## Review

## Vulnerability of drinking water supplies to engineered nanoparticles

Martin Troester<sup>a, b, \*</sup>, Heinz-Juergen Brauch<sup>a</sup>, Thilo Hofmann<sup>b, \*\*</sup><sup>a</sup> DVGW-Technologiezentrum Wasser, Karlsruhe Str. 84, 76139 Karlsruhe, Germany<sup>b</sup> Department of Environmental Geosciences, University of Vienna, Althanstr. 14 UZA II, 1090 Vienna, Austria

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## ABSTRACT

The production and use of engineered nanoparticles (ENPs) inevitably leads to their release into aquatic environments, with the quantities involved expected to increase significantly in the future. Concerns therefore arise over the possibility that ENPs might pose a threat to drinking water supplies. Investigations into the vulnerability of drinking water supplies to ENPs are hampered by the absence of suitable analytical methods that are capable of detecting and quantifying ENPs in complex aqueous matrices. Analytical data concerning the presence of ENPs in drinking water supplies is therefore scarce. The eventual fate of ENPs in the natural environment and in processes that are important for drinking water production are currently being investigated through laboratory based-experiments and modelling.

Although the information obtained from these studies may not, as yet, be sufficient to allow comprehensive assessment of the complete life-cycle of ENPs, it does provide a valuable starting point for predicting the significance of ENPs to drinking water supplies.

This review therefore addresses the vulnerability of drinking water supplies to ENPs. The risk of ENPs entering drinking water is discussed and predicted for drinking water produced from groundwater and from surface water. Our evaluation is based on reviewing published data concerning ENP production amounts and release patterns, the occurrence and behavior of ENPs in aquatic systems relevant for drinking water supply and ENP removability in drinking water purification processes. Quantitative predictions are made based on realistic high-input case scenarios. The results of our synthesis of current knowledge suggest that the risk probability of ENPs being present in surface water resources is generally limited, but that particular local conditions may increase the probability of raw water contamination by ENPs. Drinking water extracted from porous media aquifers are not generally considered to be prone to ENP contamination. In karstic aquifers, however, there is an increased probability that if any ENPs enter the groundwater system they will reach the extraction point of a drinking water treatment plant (DWTP).

The ability to remove ENPs during water treatment depends on the specific design of the treatment process. In conventional DWTPs with no flocculation step a proportion of ENPs, if present in the raw water, may reach the final drinking water. The use of ultrafiltration techniques improves drinking water safety with respect to ENP contamination.

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\* Corresponding author. DVGW-Technologiezentrum Wasser, Karlsruhe Str. 84, 76139 Karlsruhe, Germany.

\*\* Corresponding author.

E-mail addresses: [martin.troester@tzw.de](mailto:martin.troester@tzw.de) (M. Troester), [thilo.hofmann@univie.ac.at](mailto:thilo.hofmann@univie.ac.at) (T. Hofmann).

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### Abbreviations

|       |                                    |
|-------|------------------------------------|
| CCC   | Critical coagulation concentration |
| CFT   | Colloid filtration theory          |
| CNT   | Carbon nanotube                    |
| DWTP  | Drinking water treatment plant     |
| ENP   | Engineered nanoparticle            |
| GAC   | Granular activated carbon          |
| HA    | Humic acid                         |
| IEP   | Isoelectric point                  |
| IS    | Ionic strength                     |
| MF    | Microfiltration                    |
| MWCNT | Multi-walled carbon nanotube       |
| NOM   | Natural organic matter             |
| NP    | Nanoparticle                       |
| PAC   | Powdered activated carbon          |
| SWCNT | Single-walled carbon nanotube      |
| TOC   | Total organic carbon               |
| UF    | Ultrafiltration                    |
| WWTP  | Wastewater treatment plant         |

## 1. Introduction

The use of engineered nanoparticles (ENPs) has now become widespread in a variety of consumer products and also in industrial applications. Examples include the use of TiO<sub>2</sub> nanoparticles (NPs) in sunscreens (Popov et al., 2005; Samontha et al., 2011) or in photovoltaics (Chen and Mao, 2007), Ag NPs in a range of consumer products including, for example, socks (Geranio et al., 2009; Lorenz et al., 2012) due to their antimicrobial properties, CeO<sub>2</sub> NPs as fuel additives (Casseo et al., 2011; US EPA, 2009), and C<sub>60</sub>-fullerenes in cosmetics (Benn et al., 2011).

With increasing production volumes and applications (Khan and Asmatulu, 2013), together with anticipated further development in the stabilization and functionalization of ENPs (Khan and Asmatulu, 2013), it is clear that ENPs will enter into natural environments, including aquatic environments.

A number of investigations have shown that ENPs can be toxic to organisms and pose ecotoxicological risks in aquatic environments, as summarized by Bhatt and Tripathi (2011) and Baun et al. (2008).

Consequently, possible risks posed to humans and the risk of

ENPs being present in drinking water have come into focus, attracting the attention not only of the scientific community and regulatory authorities, but also of the general public.

Once released, the occurrence, distribution and persistence of ENPs in aquatic systems depend on their colloidal stabilities. ENPs can, for example, dissolve, or they can aggregate/agglomerate and sediment, or they can remain stable within an aqueous phase (Fig. 1).

The results of laboratory investigations proved that the stability of ENPs is controlled by both their physico-chemical properties (or those of the particle populations) and the hydrochemical conditions, as has already been established for natural particles (Buffle and Leppard, 1995). However, little data is available regarding their actual occurrence in aquatic environments. This absence of data is mainly due to the lack of sensitive and selective analytical methods suitable for detecting and characterizing ENPs in complex natural matrices (von der Kammer et al., 2012). Only first approaches exist to selectively detect and characterize ENPs in complex matrices with a high background of natural NPs (Gondikas et al., 2014).

The possible presence of ENPs in raw waters raises the question of the extent to which they can be removed in drinking water treatment plants (DWTPs), in order to ensure the safety of drinking water supplies in the case of ENPs being present in the raw waters.

Particle removal is one of the main objectives of drinking water treatment. Processes such as coagulation, flocculation and sedimentation, and granular media filtration or membrane filtration are specifically designed to remove particulate matter. The mechanisms, influencing parameters, and removal efficiencies of the technologies have been well investigated and are generally well understood for particles in the micrometer size range or larger (Lawler, 1986; Crittenden et al., 2012).

However, much less is known about the ability of different treatment processes to remove particles smaller than 1 µm, and the mechanisms and influencing parameters affecting the behavior and eventual fate of such particles within water treatment systems are much less well understood. This is particularly true for ENPs.

ENP production amounts, release patterns and the fate in the aquatic environment and in water treatment processes have been addressed in a variety of experimental and theoretical investigations. Even though the potential risks to aquatic environments associated with the increasing proliferation of ENPs in many aspects of society is widely acknowledged, the significance of ENP contamination in drinking water supplies has not yet been sufficiently addressed through any comprehensive evaluation of relevant scientific publications and the current state of knowledge.

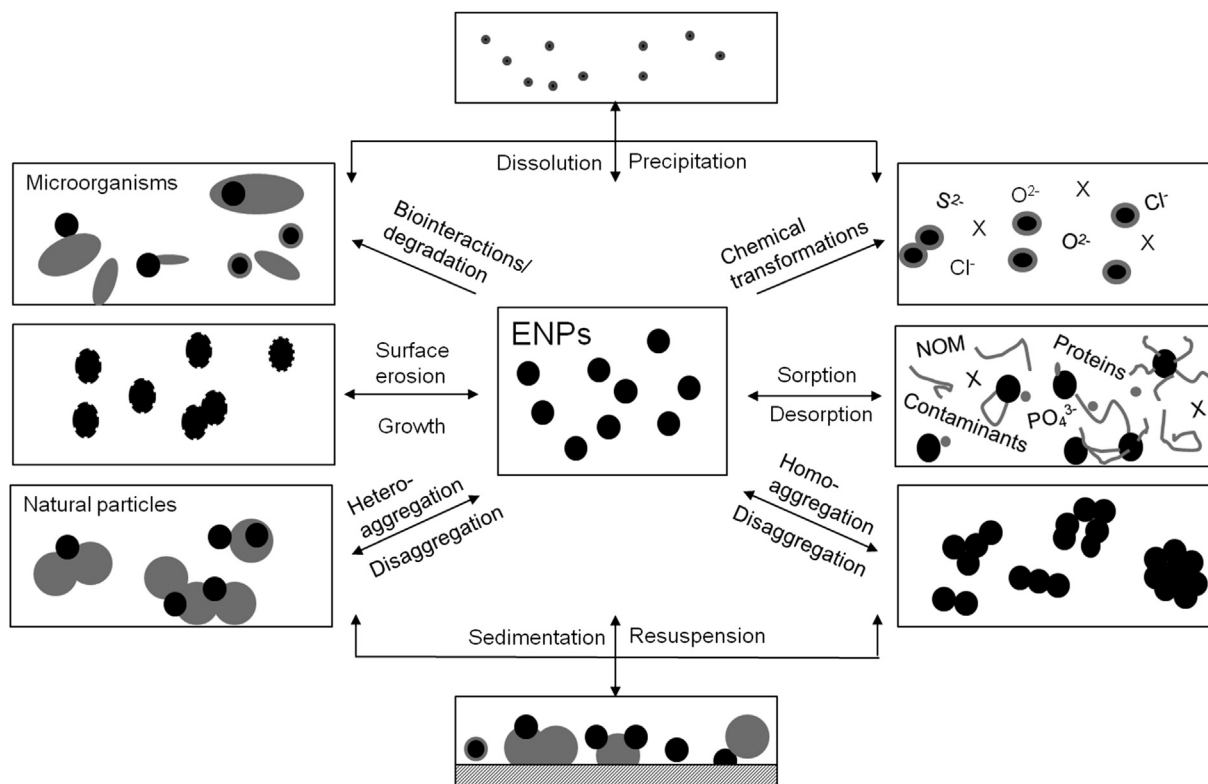


Fig. 1. Schematic representation of possible reactions of ENPs within an aquatic environment.

This article therefore evaluates the significance of ENPs as emerging contaminants for the drinking water sector. The vulnerability of different drinking water production chains to ENPs is identified, including drinking water produced from groundwater and drinking water produced from surface water. The risk of ENPs entering drinking water is predicted by reviewing and summarizing existing published data that focuses on ENP production amounts and release patterns, the behavior of ENPs in aquatic systems relevant for drinking water production and the capabilities of technical water purification processes to remove ENPs and integrating relevant aspects of colloid/particle science. Rather than focusing on any particular type of ENP, the authors have followed a broader approach in an attempt to present those aspects of ENPs in general that are relevant to drinking water supplies. High input scenarios are also developed for TiO<sub>2</sub> NPs based on a merger of available data, in order to identify the possible vulnerability of drinking water systems to TiO<sub>2</sub> NPs. Quantitative estimates of TiO<sub>2</sub> NP concentrations are made at the sequential stages of the high input scenarios.

## 2. Sources of ENPs and their release into the natural environment

Although comprehensive risk assessments require information on ENP release patterns and the quantities involved, the amount of data available on ENP release into aquatic environments remains extremely limited. This scarcity of data applies to both calculated data and experimental data and is due largely to uncertainties surrounding input parameters such as production quantities, to the secrecy of companies with regard to developments in the new field of nanotechnology, to the multitude of different pathways to enter the environment, to the variety of transformation processes that affect ENPs, and to the analytical challenges posed in the

identification and characterization of ENPs in complex matrices (Tiede et al., 2008).

The likelihood of anthropogenic substances (including ENPs) ending up in aquatic environments is strongly dependent on the volume of industrial production and on how they are used. Various estimates of the quantities of different ENPs currently being produced have been published (e.g. Schmid et al., 2010; Hendren et al., 2011; Piccinno et al., 2012; Sun et al., 2014). However, such estimates of the annual production volumes for different ENPs are associated with high levels of uncertainty and exhibit considerable variance (commonly up to two or three orders of magnitude), not only between different studies but also between different scenarios within the same study. Hendren et al. (2011), for example, estimated the annual U.S. production of TiO<sub>2</sub> NPs to be between 7800 t and 38,000 t, and the worldwide production was estimated to be lower (Piccinno et al., 2012). Despite the wide range of these estimates certain ENPs are clearly produced in the tons-per-year range and have therefore the potential to be released in significant amounts into the environment. Examples are given in Table 1.

TiO<sub>2</sub> NPs and SiO<sub>2</sub> NPs belong to the group with the highest production volumes. These are materials that have long been in use in (nano-)particulate form, even before the upcoming of nanotechnology (Piccinno et al., 2012). Fullerenes, Ag NPs and carbon nanotubes are produced in much smaller amounts, but estimated production volumes are still in the tons-per-year range. As for SiO<sub>2</sub> NPs and TiO<sub>2</sub> NPs, production volumes of newly developed ENPs are likely to increase strongly once established for certain applications.

ENPs can be introduced intentionally into the environment for different purposes. Examples are TiO<sub>2</sub> NPs for water treatment (Q. Li et al., 2008; Savage and Diallo, 2005) or nano zero valent iron for groundwater remediation (Grieger et al., 2010; Zhang, 2003). Nanopesticides are considered to be promising new plant-

**Table 1**  
Estimated ENP production volumes and predicted ENP concentrations in technical compartments.

| ENP                       | Production volumes/(t/a) |                        |                        | Fields of application                             | Predicted concentrations                     |  |  |
|---------------------------|--------------------------|------------------------|------------------------|---|--|--|--|
|                           | Worldwide <sup>a</sup>   | Within US <sup>b</sup> | Within EU <sup>c</sup> |   | Within EU <sup>c</sup>                       |  |  |
|                           |                          |                        |                        |   | WWTP effluent                                | WWTP sludge                                  | Solid waste                                  |
|                           |                          |                        |                        |   | Mode (Q <sub>0.15</sub> ;Q <sub>0.85</sub> ) | Mode (Q <sub>0.15</sub> ;Q <sub>0.85</sub> ) | Mode (Q <sub>0.15</sub> ;Q <sub>0.85</sub> ) |
| Median (25/75 percentile) | Range                    | Mode                   |                        |   |  |  |  |
| Ag                        | 55 (5.5–550)             | 2.8–20                 | 30                     | Antimicrobials, cleaning agents, textiles, paints | 0.17 (0.06; 16) ng/L                         | 0.02 (0.01; 0.08) µg/g                       | 0.06 (0.05; 0.08) µg/g                       |
| CeO <sub>x</sub>          | 55 (5.5–550)             | 35–700                 |                        | Fuel additives                                    |  |  |  |
| FeO <sub>x</sub>          | 55 (5.5–550)             |                        |                        | Biomedical applications                           |  |  |  |
| SiO <sub>2</sub>          | 5500 (55–55,000)         |                        |                        | Paints, coatings, food additives                  |  |  |  |
| TiO <sub>2</sub>          | 3000 (550–5500)          | 7800–38,000            | 10,000                 | Paints, coatings, cosmetics, water treatment      | 16 (13; 110) µg/L                            | 170 (150; 540) µg/g                          | 12 (8.3; 20) µg/g                            |
| ZnO                       | 550 (55–550)             |                        | 1600                   | Cosmetics, coatings, cleaning agents              | 2.3 (1.7; 21) µg/L                           | 24 (17; 110) µg/g                            | 0.89 (0.47; 2.4) µg/g                        |
| Fullerenes                | 0.6 (0.6–5.5)            | 2–80                   | 20                     | Cosmetics, lubricants                             | 1.7 (1.3; 7) ng/L                            | 0.09 (0.05; 0.22) µg/g                       | 0.07 (0.04; 0.13) µg/g                       |
| Carbon nanotubes          | 300 (55–550)             | 55–1101                | 380                    | Composite materials, batteries                    | 4.0 (3.6; 12) ng/L                           | 0.15 (0.12; 0.23) µg/g                       | 1.7 (1.3; 2.6) µg/g                          |

<sup>a</sup> Piccinno et al., 2012.

<sup>b</sup> Hendren et al., 2011.

<sup>c</sup> Sun et al., 2014.

protection products (Kah et al., 2013; Kah and Hofmann, 2014). The intentional use of ENPs in the natural environment is still an ongoing field of research and not yet widespread due to technical obstacles (Laumann et al., 2013) and not yet able to compete with existing technologies in terms of cost (Bhattacharya et al., 2013). Potentially, application of nanopesticides in agriculture will result in the largest intentional diffuse input of ENPs into the environment. Information on amounts and characteristics of used ENPs will be available when introduced intentionally into the environment. ENP-specific regulations can then be developed in order to reduce the risk of water resource contamination (Kookana et al., 2014).

Release can also occur unintentionally during any stage in the lifecycle of the ENPs. This includes the release during production of ENP or ENP containing products (Aitken et al., 2004; Gottschalk et al., 2009; Gottschalk and Nowack, 2011). Unintentional release of ENPs during the use of a product has been experimentally verified (Göhler et al., 2010; Kaegi et al., 2010, 2008a; Benn and Westerhoff, 2008; Geranio et al., 2009; Lorenz et al., 2012). At this stage ENPs might have been already modified to suit the particular product or application, be embedded in the product matrix (Kaegi et al., 2010) or be chemically transformed due to chemical interactions with other substances present (Lorenz et al., 2012). In fact, ENPs are rather released in a modified form than in their pristine state (Mitrano et al., 2015). At the end of their use materials and products containing ENPs are likely to be disposed of either as solid waste or in wastewaters. Consequently, the main pathways into aquatic environments are expected to be through solid and liquid waste streams, and through diffuse entry resulting from the use and/or abrasion of products containing ENPs (Duester et al., 2014; Sun et al., 2014; Nowack et al., 2012; Keller et al., 2013).

When ENP containing products are disposed on landfill, they may become mobilized and stabilized when in contact with a liquid phase moving through the landfill and thus enter aquatic environments via landfill leachate (Reinhart et al., 2010; Bolyard et al., 2013). The possibility of such a pathway is supported by the detection of TiO<sub>2</sub> NPs, possibly of anthropogenic origin, in Swiss landfills (Kaegi et al., 2014). However, an adequate sealing and leachate treatment can hinder the entry of ENPs in surface waters or groundwaters.

Both treated and untreated wastewater streams can be

important routes for ENP proliferation. With removal efficiencies generally greater than 90% (Kaegi et al., 2011; Westerhoff et al., 2011; Kiser et al., 2009; Limbach et al., 2008), WWTPs clearly serve as sinks for the investigated classes of ENP although a small proportion of certain types of ENPs may not be retained. In a WWTP effluent, for example, an Ag NP concentration of 100 ng/L was measured (Mitrano et al., 2012) which is in good agreement with modelled effluent concentrations between 19 ng/L and 89 ng/L (Hendren et al., 2013), but higher than predicted Ag NP effluent concentrations by Sun et al. (2014) (Table 1). Fullerenes (C<sub>60</sub>, C<sub>70</sub> and N-methylfullerolpyrrolidine-C<sub>60</sub>) have been detected in Spanish WWTP effluents (Farre et al., 2010), with concentrations ranging from 0.5 ng/L to 67 µg/L. TiO<sub>2</sub> NPs with diameters in the range from 4 to 30 nm were detected within the effluent of WWTPs in the USA (Westerhoff et al., 2011). Experimental partitioning studies have indicated that ENPs are largely removed (generally > 90%) from a wastewater matrix during secondary treatment by sorption to sewage sludge. Such partitioning has, for instance, been reported for CeO<sub>2</sub> NPs (Limbach et al., 2008), Ag NPs (Musee et al., 2014; Kaegi et al., 2011; Yi. Wang et al., 2012), ZnO NPs (Lombi et al., 2012), TiO<sub>2</sub> NPs (Kiser et al., 2009; Yi. Wang et al., 2012), SiO<sub>2</sub> NPs (Park et al., 2013) and C<sub>60</sub>-fullerenes (Yi. Wang et al., 2012). ENPs sorbed to sludge can still reach the natural environment if sludge that contains ENPs (Table 1) is used as a fertilizer in agricultural areas. ENPs can also undergo transformation during wastewater treatment. Ag NPs, for example, are mainly present in the effluent and in the sludge as Ag<sub>2</sub>S (Kaegi et al., 2011). ZnO NPs are also converted to other species (mainly sulfides) during wastewater treatment and anaerobic digestion of the excess sludge (Lombi et al., 2012). Other ENPs, such as CeO<sub>2</sub> NPs (Limbach et al., 2008) or TiO<sub>2</sub> NPs (Yi. Wang et al., 2012) may, in contrast, not experience any chemical transformation during wastewater treatment and be present in sewage sludge of WWTPs, as shown for TiO<sub>2</sub> NPs (Kiser et al., 2009; Johnson et al., 2011; Kim et al., 2012).

For a particular ENP type, the stability and removability may strongly be influenced by its surface characteristics and coatings (Lombi et al., 2012). Currently, there is only a limited understanding of the transformations that ENPs are likely to undergo in a WWTP, and the forms in which they are released. It also remains unclear how ENPs behave under particular conditions such as, for example, hydraulic shocks.

Existing waste treatment facilities are effective first measures to reduce ENP input into compartments relevant for drinking water supply. Nevertheless, these facilities might still emit ENPs and therefore drinking water production sites that are recipients from landfill or WWTP effluents are prone to ENP contamination.

Deducing quantitative ENP release data from experimental investigations that is generally valid is limited by the complex interplay of ENPs and matrix constituents, the multitude of release patterns and spatial and temporal variations. This applies for both, point-sources and especially for non-point sources, which are highly challenging to monitor. Furthermore, release studies are often conducted under simplified conditions in order to ensure analytical feasibility. Hence, additional matrix-interactions are likely to occur in real-world release scenarios. Consequently, release coefficients and transfer coefficients during production, usage, and disposal are largely unknown.

Therefore, estimating release levels has currently to rely on material flow analyses which are assumption- or probability-based modeling studies (e.g. Sun et al., 2014; Keller et al., 2013). While such models are crucial for gaining holistic views of ENP release, their validation is hampered by the lack of analytical data. In addition, knowledge on the forms in which ENPs are released is required for assessing the risk they pose to drinking water supply. Currently, this is hardly incorporated in these models since only few studies have tried to establish what changes ENPs undergo during their life cycle (Mitrano et al., 2015).

To summarize, ENPs are released into the aquatic environment. Pathways and sources exist that will lead to ENP proliferation to both, surface water and groundwater resources. However, quantitative estimations of ENPs released are associated to high uncertainties and the forms of ENPs released are largely unknown. As the need for more information on the form of ENPs released is acknowledged, latest research has increasingly focused on this topic (Mitrano et al., 2015; Al-Kattan et al., 2014; Kaegi et al., 2014). When this information becomes available to a greater extent, it can be integrated into more detailed mass flow models, also on regional scales. This will significantly contribute to assessing the risk that ENP pose on drinking water production sites.

### 3. ENPs in raw water resources

Once released into an aquatic environment, the significance of ENPs to drinking water supplies depends upon their stability and mobility, and ultimately on their presence and morphology in water resources used for drinking water production. A number of factors affect the stability, mobility and eventual fate of ENPs in water and is dependent on both, the properties of the ENPs and of the aqueous systems (see Fig. 1). The mobility and eventual fate of ENPs in surface waters and in groundwater systems is reviewed in the next section and the likelihood of ENPs, if released, occurring in water resources is discussed.

#### 3.1. ENPs in surface water resources

Raw water resources used for drinking water production include surface waters such as rivers, lakes or reservoirs. Since surface waters are direct recipients of waste streams and in direct contact with the atmosphere they are exposed to human and industrial activities and discharges. In view of the multitude of possible release patterns for ENPs, surface waters are prone to be recipients of ENPs.

##### 3.1.1. ENP stability in surface waters

The behavior and mobility of ENPs in aquatic environments is largely determined by their colloidal stability. Because of their high

surface-to-volume ratios ENPs have high surface energies and tend to aggregate, as do natural particles in the sub-micron size range (Buffle and Leppard, 1995; Christian et al., 2008). A stronger aggregation is expected for relatively small particles (including ENPs) than for larger particles, as has been verified experimentally (He et al., 2008; C. Wang et al., 2012).

Although suspensions are thermodynamically unstable, barriers can exist that hinder the aggregation of colliding particles and promote colloidal stability, typically through electrostatic or steric stabilization (Christian et al., 2008). Engineered coatings are often used to impose electrostatic (e.g. citrate) or steric (e.g. PVP) stabilization on ENPs.

Laboratory studies show that where repulsive electrostatic forces are dominant an increase in ionic strength (IS) leads to reduced ENP stability and an increase in aggregation (Delay et al., 2011; Zhang et al., 2009; Smith et al., 2009; Chen and Elimelech, 2007; Van Hoecke et al., 2011; Liu et al., 2012), as explainable by DLVO theory (Verwey and Overbeek, 1948; Derjaguin and Landau, 1941).

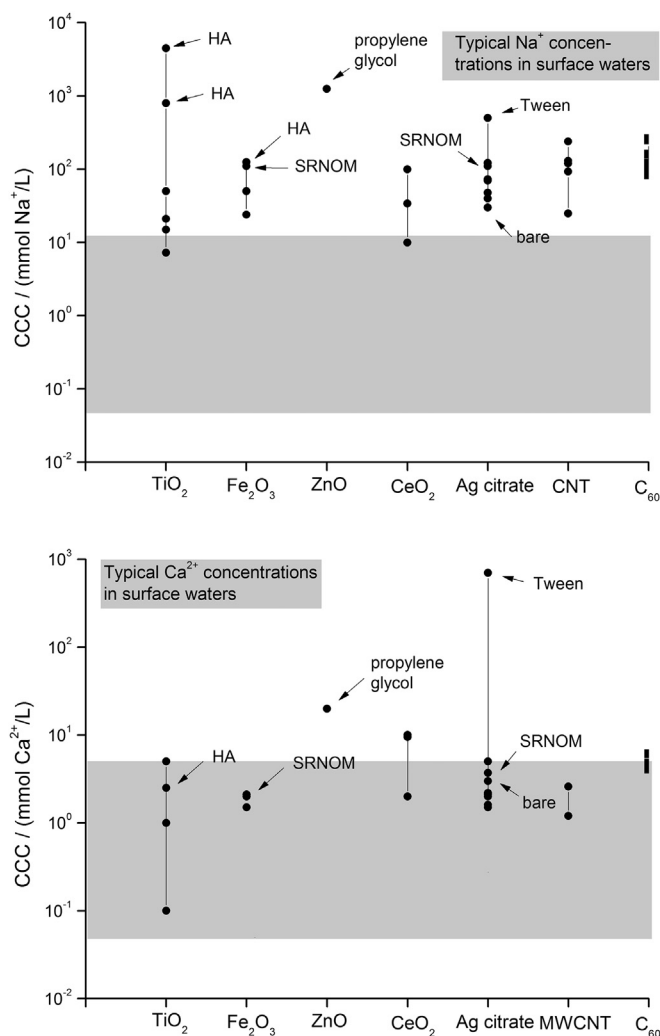


Fig. 2. Published CCC values for selected ENPs.

References: TiO<sub>2</sub>: Chekli et al., 2015; Thio et al., 2011; Hsu and Chang, 2000; Zhu et al., 2014. Fe<sub>2</sub>O<sub>3</sub>: Chekli et al., 2015; Kretzschmar and Sticher, 1997; Hu et al., 2010. ZnO: Liu et al., 2012. MWCNT: Ju et al., 2012; Smith et al., 2009; Saleh et al., 2008. CeO<sub>2</sub>: Li and Chen, 2012; Chen et al., 2012. Ag: Chekli et al., 2015; Li and Lenhart, 2012; Huynh and Chen, 2011; Akaighe et al., 2013; Baalousha et al., 2013; El Badawy et al., 2012. C<sub>60</sub>: Chen and Elimelech, 2006; Chen and Elimelech, 2007; Bouchard et al., 2009; Zhang et al., 2013; Qu et al., 2010; Mchedlov-Petrosyan et al., 1997.

At a particular electrolyte concentration known as the critical coagulation concentration (CCC), the aggregation rate no longer increases with increasing IS because each collision leads to attachment and aggregation becomes diffusion-limited. The CCCs (for  $\text{Na}^+$  and  $\text{Ca}^{2+}$ ) are shown for different ENPs in Fig. 2, and the ranges for concentrations of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  that are typically encountered in surface waters are also presented. The figure indicates that  $\text{Na}^+$  concentrations in surface waters are often too low to fully destabilize ENPs.  $\text{Ca}^{2+}$  concentrations that are encountered in moderately hard waters are in the range of the  $\text{Ca}^{2+}$  CCCs determined for most of the ENPs presented in Fig. 2. This suggests that in such waters ENPs are only of limited stability. However, engineered coatings and/or the presence of NOM in surface waters are able to stabilize ENPs in such conditions, resulting in higher CCCs. If the coatings provide high levels of stabilization and are persistent in an aquatic environment, electrolyte concentrations exceeding the CCC might rarely prevail in surface waters. For example, Ag NPs coated with Tween (polyoxyethylen(20)-sorbitan-monolaurat) have a CCC as high as 700 mM  $\text{Ca}^{2+}$  ( $\Delta$  28 g/L) (Li and Lenhart, 2012), a concentration not found in surface waters. Note that the stated CCCs shown in Fig. 2 are only valid for homoaggregation and not for heteroaggregation.

If the pH is equal to the isoelectric point (IEP) of an ENP no electrostatic stabilization will occur to hinder aggregation (Van Hoecke et al., 2011; Romanello and Fidalgo de Cortalezzi, 2013; Baalousha et al., 2008; Bian et al., 2011; Jiang et al., 2009). The pH of surface waters is typically between 6.5 and 8.5; the  $\text{pH}_{\text{IEP}}$  values for bare  $\text{CeO}_2$  and bare iron oxide NPs are reported to also lie within this range and only limited electrostatic stabilization can therefore be expected for these particles in surface waters (Fig. 3). In contrast, if the  $\text{pH}_{\text{IEP}}$  value is below the typical pH values of surface waters, a negative surface charge would, for example, be expected for bare  $\text{C}_{60}$ -fullerenes, citrate-coated Ag NPs, and MWCNTs (Fig. 3). The negative surface charge results in electrostatic stabilization of these types of ENPs against aggregation with other negatively charged

particles.

The constituents of naturally occurring surface waters (e.g. proteins or phosphates) can interact with ENPs and influence suspension stability (Klaine et al., 2008). NOM originating from the aqueous matrix can act as a coating for ENPs. For  $\text{TiO}_2$  NPs, for example, it has been shown that spontaneous association processes with alginate (Loosli et al., 2015a) and Suwanee River humic acid (HA) (Loosli et al., 2015b) are favorable from an enthalpic and entropic point of view with exothermic binding reactions. NOM coatings can increase ENP stability when present in sufficiently high concentrations (Wagner et al., 2014; Zhang et al., 2009; Delay et al., 2011; Chen and Elimelech, 2007; Chen and Elimelech, 2008; Y. Chen et al., 2012). The extent of stabilization also depends on the exact NOM properties (Phenrat et al., 2010; Hyung and Kim, 2008; Ghosh et al., 2011; Zhang et al., 2013). At elevated concentrations of  $\text{Ca}^{2+}$  and NOM bridging flocculation can occur which enhances aggregation of ENPs (Baalousha et al., 2013; Huynh and Chen, 2011; Philippe and Schaumann, 2014; Chen and Elimelech, 2007).

Disaggregation is as important as aggregation in determining the behavior and eventual fate of ENPs. Investigations into ENP disaggregation are, however, far less common than those focusing on aggregation processes. Partial disaggregation can occur due to adsorption of HA, a decrease in IS or an increase in NOM concentration (Loosli et al., 2013; Mohd Omar et al., 2014; Baalousha, 2009; Huynh and Chen 2014; Metreveli et al., 2015), or by temperature changes and sunlight (Zhou et al., 2012). These results show that partial disaggregation can be encouraged by natural events such as seasonal variations in hydrochemistry, by mixing of two aqueous streams of different water quality (e.g. of wastewater with a surface water stream), by precipitation events, or by local variations in shear stress within a fluid stream. The formation of smaller aggregates due to disaggregation could lead to resuspension and enhanced mobility of ENPs within the water column.

ENPs and ENP surfaces can undergo modifications or transformations within natural aquatic systems. Engineered coatings can be either persistent or may, for example, desorb or become biodegraded (Auffan et al., 2010; Kirschling et al., 2011; Wagner et al., 2014). When ENPs lose their stabilizing coatings, their mobility in surface waters is greatly reduced and the risk of these ENPs reaching water resources used for drinking water production decreases. Consequently, tailoring ENP coatings that suit a particular application but lose their stabilizing function in surface waters would be a precautionary measure to avoid ENP contamination of drinking water.

Dissolution and chemical transformation are of importance especially when redox-sensitive elements are present in ENPs (Liu and Hurt, 2010; Misra et al., 2012). As well as being affected by intrinsic particle properties, solubility and dissolution kinetics are also strongly influenced by interactions with other water constituents that can either increase (Xia et al., 2008; Borm et al., 2006; Chappell et al., 2011) or reduce (Borm et al., 2006; Chappell et al., 2011; Ahlberg et al., 2014) dissolution. The pH has been shown to be a governing factor in ENP dissolution. Under pH values encountered in surface waters (6.5–8.5) dissolution of metal or metal oxide ENPs is of less significance than under highly acidic or basic conditions (Studer et al., 2010; Liu et al., 2011; Bian et al., 2011; Wagner et al., 2014).

Oxidative dissolution correlates directly to the concentration of dissolved reaction partners (Liu et al., 2011; Levard et al., 2013; Dwivedi et al., 2015) and can also lead to changes in metal speciation. In the presence of sulfide, ZnO NPs (Ma et al., 2013), CuO NPs (Ma et al., 2014) and Ag NPs (Kaegi et al., 2013; Liu et al., 2011; Thalmann et al., 2014) have been reported to undergo partial or complete sulfidation. Thalmann et al. (2014) concluded that Ag NPs in surface waters can be transformed into  $\text{Ag}_2\text{S}$  within a few hours

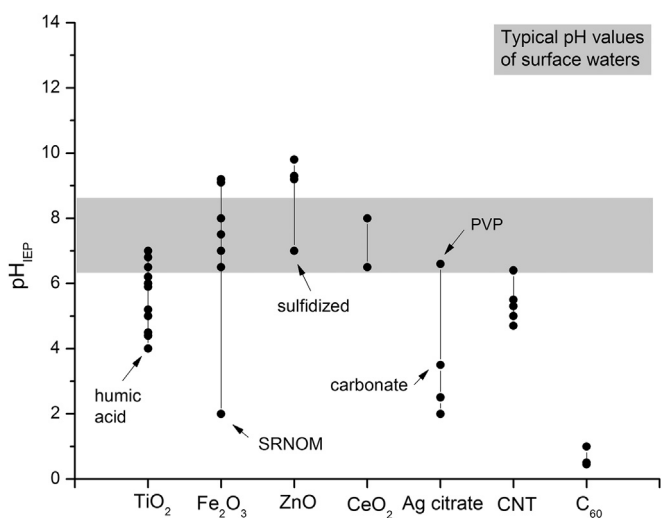
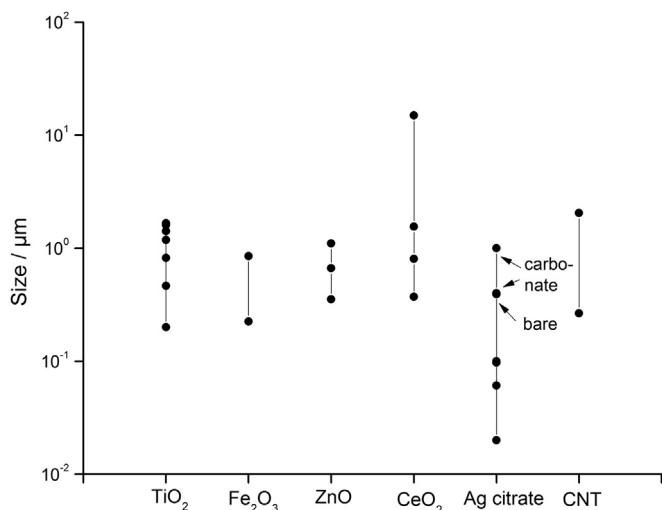


Fig. 3. Published  $\text{pH}_{\text{IEP}}$  values for selected ENPs.

References:  $\text{TiO}_2$ : Jiang et al., 2009; Zhang et al., 2008; Fang et al., 2009; Kiser et al., 2009; Yang and Xing, 2009; French et al., 2009; Chekli et al., 2015; Loosli et al., 2013; G. Chen et al., 2012; Ottofuelling et al., 2011; Zhu et al., 2014; Shih et al., 2012.  $\text{Fe}_2\text{O}_3$ : Baalousha et al., 2008; Illés and Tombácz, 2006; Zhang et al., 2008; Chekli et al., 2015; Yu and Chow, 2004; Kretzschmar and Sticher, 1997.  $\text{ZnO}$ : Zhang et al., 2008; Mohd Omar et al., 2014; Ma et al., 2013; Petosa et al., 2012.  $\text{MWCNT}$ : Lin and Xing, 2008; Sheng et al., 2010; Wang et al., 2005; Li et al., 2003.  $\text{CeO}_2$ : Quik et al., 2010; Quik et al., 2014.  $\text{Ag}$ : Chekli et al., 2015; Lawler et al., 2013; Piccapietra et al., 2012; Quik et al., 2014.  $\text{C}_{60}$ : Bouchard et al., 2009; Ma and Bouchard, 2009; Zhang et al., 2013; Yang et al., 2013.



**Fig. 4.** Aggregate sizes in surface waters for selected ENPs. (Note that the aggregation times varied in the different investigations).

References: TiO<sub>2</sub>: Abbott Chalew et al., 2013; Ottofuelling et al., 2011; Chekli et al., 2015; Sillanpää et al., 2011; Tong et al., 2014. Fe<sub>2</sub>O<sub>3</sub>: Chekli et al., 2015. ZnO: Abbott Chalew et al., 2013; Tong et al., 2014. CeO<sub>2</sub>: Quik et al., 2012; Van Hoecke et al., 2011. Ag: Abbott Chalew et al., 2013; Chekli et al., 2015; Chinnapongse et al., 2011; Gao et al., 2009; Piccapietra et al., 2012. CNT: Bennett et al., 2013.

to a few days as a result of reactions with metal sulfides, even in the absence of free sulfide. Ag NPs also react with chloride in an oxidative dissolution and precipitation process to form AgCl (Levard et al., 2013). Thus ZnO NPs, CuO NPs and Ag NPs are not expected to be present in surface waters without any chemical transformation. However, the formation of surface layers such as AgCl on Ag NPs can reduce or inhibit dissolution processes (Dwivedi et al., 2015).

The current understanding of the influence that different parameters have on ENP behavior in aquatic environments has been largely acquired from fate studies that were conducted under well-defined, simplified, experimental conditions. Data sets obtained from such tests are a valuable starting point for estimating ENP stability in natural waters (Liu et al., 2013). However, the multitude and complex interplay of influence parameters makes both quantitative and qualitative predictions of ENP stability very challenging. Extrapolation of results from laboratory fate studies may not be straightforward, and there remains no general understanding of how concentrations of ENPs can be predicted from basic chemistry (Peijnenburg et al., 2015).

Stability investigations conducted in natural surface waters are not very common, mainly due to the difficulties involved in analyzing ENP behaviour within a complex matrix. Furthermore, elucidation of acting mechanism and transformation might become very difficult. An overview of investigations into the stability and fate of ENPs that were conducted in natural surface waters is provided in the supplementary information (SI) (Table S–1). ENP aggregate sizes reported from investigations in natural surface waters are presented in Fig. 4. Aggregate sizes of smaller than 100 nm have only been reported for citrate stabilized Ag NPs. For TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, ZnO, CeO<sub>2</sub> and CNT NPs observed aggregate sizes ranged from a few hundred nm to a few μm.

From Fig. 4 and the investigations presented in Table S–1 (in the SI) it can be concluded that conditions commonly found in surface waters lead to the aggregation of ENPs. Trends identified from mechanistic investigations (such as increasing colloidal stability with increasing concentration of NOM, or with decreasing ionic strength) have been confirmed by investigations with natural

waters. The Ca<sup>2+</sup> concentration and NOM concentration are clearly key factors affecting ENP stability in surface waters, but the size of the resulting aggregates depends on a variety of different factors. In filtered river water of comparable key parameters (pH ≈ 8; TOC ≈ 6 mg/L; IS = 10 mM), Quik et al. (2012) determined CeO<sub>2</sub> NP aggregate sizes of one order of magnitude lower than Van Hoecke et al. (2011). These results highlight the fact that even when the type of ENP and the values of key parameters are all similar, additional factors such as, for example, the type of NOM, the ENP concentration, or the origin of the ENPs (supplier, production process, etc.) also affect the aggregation behavior of particles. Due to aggregation, large proportions of the aggregated ENPs will be removed from the water column by sedimentation, as indicated by the majority of the studies summarized in Table S–1 (in the SI). However, these studies are conducted with ENP concentrations exceeding the ones expected to occur in surface waters and mainly with filtered surface waters. Thus the role of homoaggregation of ENPs might be overestimated compared to heteroaggregation. As heteroaggregation with natural particles is a dominant fate mechanism (Quik et al., 2012) this should be consequently included in stability studies. The dissolution of Ag NPs has been shown to occur under natural conditions, although the rate of dissolution was low (Li and Lenhart, 2012; Quik et al., 2014; Teo and Pumera, 2014), but chemical transformation was not in the focus of these studies. ZnO NPs have a tendency to dissolve in natural surface waters (Tong et al., 2014) and to undergo sulfidation (Ma et al., 2013), which strongly reduces the risk of pristine ZnO NPs being present in surface water resources. However, under certain conditions, different types of ENPs can also remain stable in the water column over prolonged times. This mainly applies for surface waters which are characterized by low IS and high NOM concentrations (Sillanpää et al., 2011; Quik et al., 2014; Bennett et al., 2013; O'Driscoll et al., 2010; Lin et al., 2010a). A stabilizing coating, either synthetically engineered or due to natural water constituents, is a necessary requirement for colloidal stability, except for ENPs with strongly hydrophilic surfaces such as graphene oxide NPs or fullerenes, which might remain stable within a water column without any stabilizing agents. If ENPs remain suspended in the water column the necessity for any further ENP-specific risk assessment will largely depend on the persistence of their nanoeffects and properties (including those of their engineered coatings). It has, for example, been reported that the properties of nZVI, including those of their engineered coatings, can persist in water over a number of months (Kim et al., 2009), which exceeds the water residence time in some reservoirs (Rueda et al., 2006). In such cases, ENPs could reach extraction points for drinking water inlets while still in possession of their imposed functionalities. In contrast, it seems unlikely that Ag NPs (for example) would reach water extraction points with their intrinsic properties still intact because of the sulfidation of Ag NPs that can occur within a few hours to a few days (Thalmann et al., 2014), unless there is direct short-cut between the contamination source and the water extraction point.

### 3.1.2. Modelled and measured ENP concentrations in surface waters

Analytical data concerning the actual occurrence of ENPs in surface waters is very scarce. This is mainly due to the analytical challenges faced in detecting and characterizing low concentrations of ENPs in natural waters, with high background levels of natural particles (von der Kammer et al., 2012). Data on the distribution of ENPs is therefore mainly derived from modelling (Gottschalk et al., 2013). Published data (both modelled and experimental) on the distribution of ENPs in surface waters has been comprehensively reviewed by Gottschalk et al. (2013). Only one study (Neal et al., 2011) had been published until 2013 that included experimental NP concentrations, and modelled or

**Table 2**  
Overview of ENP concentrations in surface waters (modelling studies and measured data).

| Modelling study        | Materials   | Model scale                   | Approach and main assumptions   | Results  |
|------------------------|---|-------------------------------|---|--|
| Sun et al., 2014       | TiO <sub>2</sub> ; Ag; ZnO; C <sub>60</sub> ; CNT | European surface waters       | Probabilistic modeling. Spatial and temporal variations not taken into account.   | Predicted concentrations (Mode (Q <sub>0.15</sub> ; Q <sub>0.85</sub> )): TiO <sub>2</sub> : 0.53 (0.40; 1.4) µg/L, Ag: 0.66 (0.51; 0.94) ng/L, ZnO: 0.09 (0.05; 0.29) µg/L, C <sub>60</sub> : 0.11 (0.07; 0.28) ng/L, CNT: 0.23 (0.17; 0.35) ng/L                   |
| Tiede et al., 2015     | 14 different ENPs                                 | Rivers in UK                  | Extensive review of ENP market share. All ENPs are released via WWTPs. Removal efficiencies in WWTPs either 0% or 97% or data from literature. ENP concentration attenuation in rivers only by dilution (10%)   | Predicted concentrations for most of the ENPs in the ng/L to µg/L-range. Highest concentration predicted for TiO <sub>2</sub> NPs (4.91 µg/L (97% removal in the WWTP) and 164 µg/L (0% removal in the WWTP))  |
| Dumont et al., 2015    | Ag; ZnO   | European rivers               | ENP released via WWTPs. Effluent concentrations based on Sun et al. (2014). Spatial WWTP distributions and temporal weather variations are considered. Variations in water chemistry not taken into account   | Predicted concentrations: In 50% of river stretches: Ag NP: > 0.002 ng/L; ZnO > 1.5 ng/L In 10% of river stretches: Ag NP: > 18 ng/L; ZnO > 150 ng/L   |
| Sani-Kast et al., 2015 | TiO <sub>2</sub>                                  | River Rhone (France)          | One WWTP as single emission source. TiO <sub>2</sub> effluent concentrations based on Sun et al. (2014). Spatial variations in homo- and heteroaggregation rates taken into account.  | Predicted concentrations: 0 km after emission source: 30 ng/L, 151 km after emission source: 10 ng/L, 303 km after emission source: ~0 ng/L Major removal by heteroaggregation and sedimentation   |
| Quik et al., 2015      | Ag, CeO <sub>2</sub>                              | River Dommel (Netherlands)    | One WWTP as single emission source. Assumed ENP emission concentration 10 ng/L. ENP specific process descriptions linked to a 1D spatially explicit hydrological model. Homo- and heteroaggregation, dissolution, sedimentation and resuspension spatially explicit considered. | Rapid transformation to heteroaggregates within the first few km. ~50% of initial ENP mass removed at model's end (Model length: 40 km). Main removal by sedimentation of heteroaggregates in the µm-range.  |
| Experimental study     | Material  | Location                      | Analysis methods  | Results  |
| Neal et al., 2011      | TiO <sub>2</sub>                                  | Various rivers in England     | Sequential filtration and Ti-quantification   | Ti-concentrations ranged from 0.94 to 1.81 µg/L. Highest concentrations in urban and industrialized areas, indicating that Ti-containing NPs were of anthropogenic origin  |
| Gondikas et al., 2014  | TiO <sub>2</sub>                                  | Lake Old Danube (Austria)     | Discrimination between natural and engineered TiO <sub>2</sub> NPs by purity (electron microscopy) and Ti/Al ratio  | Suspended TiO <sub>2</sub> NPs detected that are similar to TiO <sub>2</sub> NPs used in sunscreens. TiO <sub>2</sub> NP concentration: 1.38 µg/L (with the assumption that the observed Ti/Al-increase was solely due to TiO <sub>2</sub> NP input from sunscreens) |
| Sanchis et al., 2015   | C <sub>60</sub> -/C <sub>70</sub> -fullerenes     | Various rivers in Spain       | Filtration and liquid chromatography – mass spectrometry  | C <sub>60</sub> -fullerenes detected in all samples (31 pg/L – 4.5 ng/L), but more likely derived from combustion processes than from emission of intentionally engineered ENPs  |
| van Wezel et al., 2014 | C <sub>60</sub> -/C <sub>70</sub> -fullerenes     | Surface waters in Netherlands | Filtration and liquid chromatography – mass spectrometry  | No C <sub>60</sub> -fullerenes detected in any sample (<5 ng/L)  |

predicted concentrations in surface waters were approximately 1 µg/L to 10 µg/L for TiO<sub>2</sub> NPs, 10 ng/L to 100 ng/L for Ag NPs, 1 µg/L for ZnO NPs, 0.01 ng/L for CeO<sub>2</sub> NPs, 10 ng/L to 100 ng/L for C<sub>60</sub>-fullerenes, and 1 µg/L for CNTs (Gottschalk et al., 2013). Table 2 summarizes latest modeling studies that predict ENP concentrations in surface waters and published analytical data of ENP occurrence in surface waters. The summarized modelling studies mainly agree on ENP concentrations from < ng/L-to low µg/L-range.

Highest concentrations are predicted for TiO<sub>2</sub> NPs, SiO<sub>2</sub> NPs and ZnO NPs (Sun et al., 2014; Tiede et al., 2015; Dumont et al., 2015), which correlates with estimated production volumes (see section 2). However, incorporating all possible ENP sources in an ENP distribution model is one major challenge, and in most of the studies it is assumed that ENPs are released solely with WWTP effluents. Furthermore, it is generally assumed that ENPs are released in their pristine state (or as homoaggregates) which might not represent the actual release form. Heteroaggregation with natural suspended solids and sedimentation are governing mechanisms that determine ENP concentrations and should consequently be considered when predicting ENP concentrations in raw water resources. Modelling studies with high spatial resolution (Quik et al., 2015; Sani-Kast et al., 2015) have shown that ENP concentrations are highly dependent on space and time. Therefore, a high spatial and temporal resolution of a model is vital for predicting ENPs at a specific drinking water production site. Development of such models is in the focus of ongoing research (Quik et al., 2015) and will become increasingly available, but such models need a variety of site-specific input parameters.

In summary, the data currently available suggests that ENPs may be present in certain surface waters but modelling does not indicate any elevated concentrations. Although there are high levels of uncertainty and significant assumptions associated with these models, the available analytical data (Neal et al., 2011; Gondikas et al., 2014; Sanchis et al., 2015) indicates concentrations of the same order of magnitude as those predicted by the most recent modelling (Table 2). The amount of analytical data available, however, remains too small for it to be taken as validation of the modelling results. The low concentrations predicted for surface waters are mainly a result of the limited discharge of ENPs into surface waters, together with the removal mechanisms operating within these waters. Since ENP removal can occur under a wide range of water conditions (see section 3.1.1), ENPs are not generally expected to be persistent in surface waters, particularly in waters with moderate or high ionic strengths, elevated concentrations of higher valent ions, and low NOM concentrations. ENPs do therefore not currently pose any threat to the majority of surface waters that are used for drinking water production. However, the aforementioned expected increase of production amounts and use of ENPs might increase the risk of contamination for raw water resources in future. Furthermore, localized high-input scenarios are very likely to exist. With regard to the removal of ENPs from surface waters, conditions can exist in which a proportion of certain ENPs remain stable over a period of time, as suggested by stability studies with natural surface waters (see section 3.1.1). If such stabilizing water conditions encounter high levels of ENP input, localized high ENP concentrations can occur. Unless waters facing such a scenario



become highly diluted or there are prolonged periods between ENP input and the use of the water, there will be a chance of increased ENP concentrations in the surface waters used for drinking water production. It is to be expected that the major fraction of the ENPs released will settle and accumulate in sediments. Strong perturbation following ENP deposition (due, for example, to storm water flow) can lead to temporarily elevated ENP concentrations in surface waters resulting in possible disaggregation and remobilization. Should such events occur in proximity to a drinking water extraction point there is an increased possibility of ENPs reaching the DWTP. There is, however, no data available that could be used to either corroborate or contradict such a possible scenario. Thus further investigations into possible disaggregation and remobilization, especially under turbulent flow conditions, would significantly contribute to assessing the vulnerability of drinking water supplies to ENPs.

### 3.1.3. Scenario for $\text{TiO}_2$ NPs

Fig. 5 shows a possible high input scenario that is based on realistic conditions. The model comprises a lake reservoir that is located within a densely populated area and receives water from four surface streams, as well as discharge water from two WWTPs. The reservoir is also used for recreational activities. Despite the high potential for contaminants input the reservoir is used as a raw water source for a DWTP. The  $\text{TiO}_2$  NP concentrations in the reservoir were estimated by combining data on the water chemistries and volumes of the various inflows, with potential  $\text{TiO}_2$  NP input concentrations and behavior derived from published literature. Two different cases were considered for the  $\text{TiO}_2$  NPs: i) the settling rate of  $\text{TiO}_2$  NPs that would occur under the water conditions in the reservoir (von der Kammer et al., 2010), and ii) highly stabilizing water conditions with no settling (Sillanpää et al., 2011). Stationary residual concentrations of  $\text{TiO}_2$  NPs were calculated for both settling rates, and for both treated and untreated wastewater input, respectively.

The hydrochemistry of the reservoir water was used with

experimentally-derived sizes for  $\text{TiO}_2$  NP aggregates depending on multiple parameters (von der Kammer et al., 2010), which indicated that a  $\text{TiO}_2$  NP aggregate size of 750 nm could be expected in the reservoir, with a stable fraction of 60%. For this case (with settling rates based on the water chemistry in the reservoir),  $\text{TiO}_2$  NP concentrations of 0.97  $\mu\text{g/L}$  (if the wastewater has been treated) and 30  $\mu\text{g/L}$  (if the wastewater has not been treated) were estimated to occur in the reservoir water. Assuming water conditions that were highly stabilizing for  $\text{TiO}_2$  NPs the residual stationary concentration of  $\text{TiO}_2$  NPs were estimated to be 1.6  $\mu\text{g/L}$  and 50  $\mu\text{g/L}$  for treated and untreated wastewater inflow, respectively. Since the main  $\text{TiO}_2$  NP input mass originates from the WWTPs, an efficient wastewater treatment step is an important factor in protecting water resources from ENP contamination. Assuming that the wastewater reaches the reservoir untreated (or that  $\text{TiO}_2$  NPs are not efficiently removed during wastewater treatment) results in  $\text{TiO}_2$  NP concentrations in the reservoir of up to 50  $\mu\text{g/L}$ . This shows that surface waters can be prone to ENP pollution under high input conditions.

### 3.2. ENPs in groundwater resources

Topsoil and the unsaturated zone can act as natural barriers against groundwater pollution. As a consequence of natural attenuation processes in the subsurface, groundwaters are generally less prone to pollution than surface waters and the water quality is less subject to seasonal variation. However, once contaminated, pollution in groundwater can survive for long periods of time and groundwater remediation can be very complicated.

The following discussion applies mainly to upper level aquifers since deeper aquifers receive additional protection from an aquiclude layer (often clay or other fine grained material that is quasi-impermeable to ENPs) with a low hydraulic conductivity and excellent filter properties.

Aquifers can consist of porous media, fractured rocks, or karst

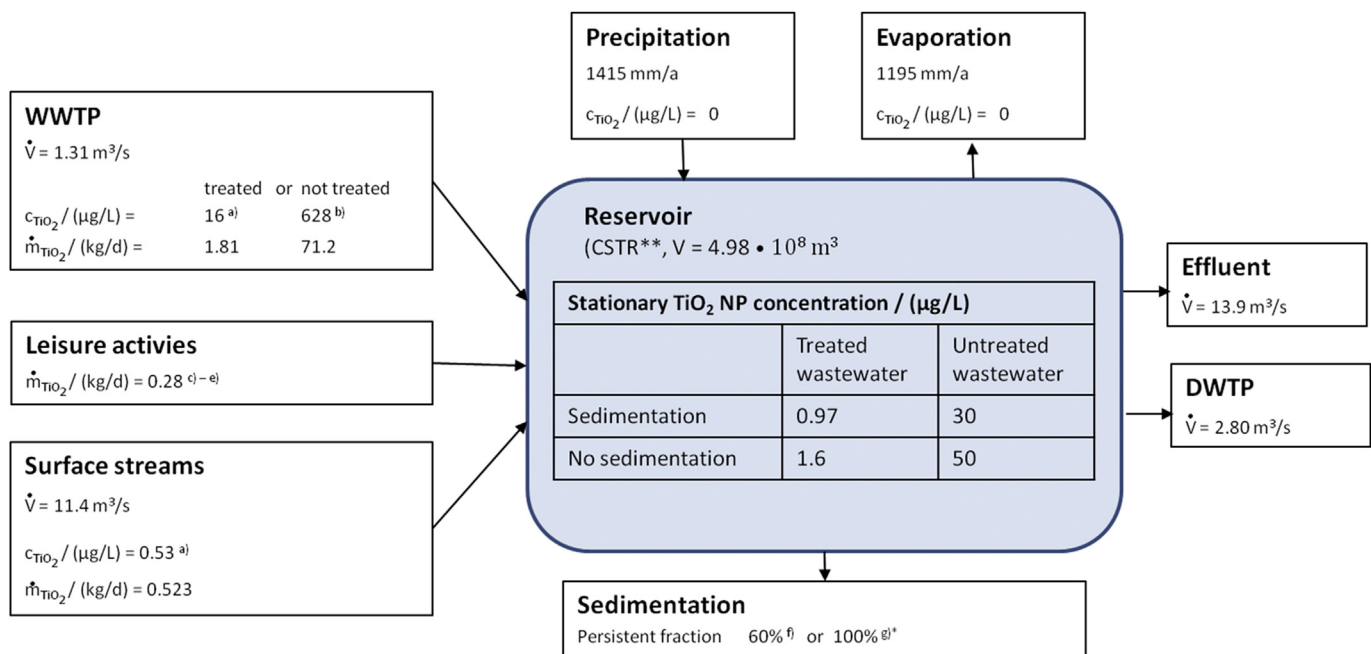


Fig. 5. Scenario for surface water with high  $\text{TiO}_2$  NP input.

References: a) Sun et al., 2014 b) Westerhoff et al., 2011; c) Duquia et al., 2007 d) Johnson et al., 2011 e) US EPA, 2010 f) von der Kammer et al., 2010 g) Sillanpää et al., 2011. \* not expected under prevailing water conditions; \*\* continuously stirred tank reactor. All concentrations shown are for stationary conditions.

(Hiscock and Bense, 2014), with each type of aquifer having its own distinct vulnerabilities. Karstic and fractured rock aquifers are, in theory, likely to be the most susceptible to particle relocation and in some cases their particle retention potential must be considered to be negligible. For porous media aquifers, the size, shape, size distribution, and mineralogy of an aquifer's solid matrix can vary significantly and these parameters have a strong influence on particle removal from the aqueous matrix. In general, except for special situations in very coarse grained aquifers with extremely high apparent flow velocities, particle removal in porous aquifers is likely to be high or very high in porous aquifers.

To the authors' best knowledge there is at present no analytical data available on the occurrence of ENPs in groundwaters, which is probably a result of the analytical challenges involved. Modelling has also to date tended to focus on surface waters (Dumont et al., 2015; Sun et al., 2014; Gottschalk et al., 2013).

Major sources of ENPs entering the soil or groundwaters are considered to be landfill leachates and sewage sludge that is applied to soils as a fertilizer and contain ENPs (Sun et al., 2014; Gottschalk et al., 2013; Duyster et al., 2014). In fact, Titanium-containing particles with diameters in the range from 50 nm to 250 nm and micron-sized TiO<sub>2</sub> particles have been detected in sludge-amended soil by Yang et al. (2014). The potential of ENPs to partition from sludge-amended soils into pore waters has been demonstrated in laboratory experiments, with the remobilized fraction of ENPs depending on type of ENPs and on the chemistry of the extraction solution (Whitley et al., 2013; Navarro et al., 2013, 2014). Nanopesticides are also likely to become a significant source of ENP input into soils, and possibly into groundwaters, (Kah et al., 2013; Kah and Hofmann, 2014).

No investigations have been published regarding the transfer of ENPs to groundwater as a result of surface water infiltration, but this could be a potential source of ENP contamination for groundwaters, although the estimated concentrations of ENPs in surface waters are currently very low (Sun, T.Y. et al., 2014; Dumont et al., 2015) (see Section 3.1).

### 3.2.1. ENP stability in groundwaters

Once relocated to subsurface aquatic environments ENPs can interact with gas phases, with soil/aquifer matrices, and with suspended colloids (including humic matter). Within the aqueous phase ENPs can in theory undergo aggregation, dissolution, or transformation (Cornelis et al., 2014; Lin et al., 2010b; Pan and Xing, 2012), as previously discussed for surface waters (see Section 3.1). ENPs can interact with soil-borne water constituents, leading to either enhanced or reduced stability (Cornelis et al., 2012; Lin et al., 2010b; Pan and Xing, 2012; Navarro et al., 2014; Li et al., 2010; Fang et al., 2009; Klitzke et al., 2015). Because of the counteracting processes affecting the stability of ENPs in soil pore water, their stability is largely dependent on the properties of the specific types of soil and ENP involved (Fang et al., 2009). The stability of ENPs in soil pore water generally increases with increasing NOM concentration and with decreasing ionic strength. The pH of the soil pore waters is of considerable importance since electrostatic repulsion or attraction can occur between the solid surfaces, depending on the pH (as well as on the IEPs of the soil grains and ENPs).

Groundwaters are often characterized by relatively low concentrations of organic matter (0.2–2 mg/L) (Crittenden et al., 2012). In aquifers containing carbonates Ca<sup>2+</sup> and Mg<sup>2+</sup> are often present in elevated concentrations. Since these conditions favor aggregation (see Section 3.1) the stability of ENPs can be expected to be low in any such systems. Few investigations have focused on the stability of ENPs in natural groundwaters (Table S–2 in the SI). Rapid aggregation in groundwater has been reported for all ENPs investigated (Keller et al., 2010; Ottofuelling et al., 2011; Tugulea et al.,

2014; Abbott Chalew et al., 2013; Bennett et al., 2013), which was mainly attributed to the high ionic strengths of the investigated groundwaters. Investigations into the removal of ENPs by sedimentation (Keller et al., 2010; Tugulea et al., 2014; Ottofuelling et al., 2011) have consistently reported the removal of a large proportion of aggregated ENPs from water columns as a result of sedimentation, even where PVP was used as a stabilizing agent for Ag NPs (Tugulea et al., 2014).

### 3.2.2. ENP mobility in granular porous media

Topsoil and certain types of aquifers consist of granular porous media. Suspended particles can be removed either by size exclusion or by transport to the filter grains and subsequent attachment (depth filtration), with the latter being the main mechanism for particles in the nm-to low μm-range (Crittenden et al., 2012). Depth filtration has been described as a first order kinetic process (Iwasaki, 1937) and colloid transport during depth filtration can be described according to colloid filtration theory (CFT) (Yao et al., 1971; Tufenkji and Elimelech, 2004; Crittenden et al., 2012).

Based on CFT, the transport of particles is dependent on their characteristics (size, density, Hamaker constant, diffusion coefficient), the size of the collector grains, and the system parameters (temperature, fluid velocity, viscosity, and gravitational acceleration). Attachment is dependent on electrostatic interactions between particle and collector surfaces. In addition attachment efficiency is also influenced by a number of forces such as those due to hydrophobic interactions, steric interactions (Crittenden et al., 2012), or by attachment of NPs to the air–water interface.

CFT has often been used to quantitatively describe the transport behavior of ENPs in porous media (e.g. Fang et al., 2009; Lecoanet et al., 2004). However, differences between experimental observations and CFT predictions have been frequently reported (e.g. Liang et al., 2013; Kasel et al., 2013; Sun, P. et al., 2015; Wang et al., 2014). These differences have been attributed to a variety of factors that are not taken into account by CFT, including the influences of surface charge heterogeneities, roughness, pore straining, and hydrodynamic drag. Various transport models that have been developed to take into account these additional influences have been summarized and reviewed by Goldberg et al. (2014).

Under conditions favorable for attachment ENPs are strongly retained, while under unfavorable attachment conditions ENPs can be highly mobile in model porous media (e.g. glass beads, cleaned quartz sand), as shown by experimental investigations (Zhao et al., 2012; Solovitch et al., 2010; Espinasse et al., 2007; Jaisi et al., 2008). It has been shown that the mobility depends on ENP type, surface functionalization and size (Lecoanet et al., 2004; Zhuang et al., 2005; Petosa et al., 2012), but also strongly on water chemistry. A variety of ENPs including TiO<sub>2</sub> NPs (Kiser et al., 2009), CNTs (Kasel et al., 2013), quantum dots (Torkzaban et al., 2013), C<sub>60</sub>-fullerenes (Wang et al., 2014), Ag NPs (Liang et al., 2013) and Au NPs (Albarran et al., 2013), are negatively charged at pH values close to neutral, with the charge also depending on their surface coatings. Unfavorable attachment conditions are therefore expected for these ENPs in natural porous media, since soil grains and grains of porous media aquifers also typically possess negative surface charges (Ryan and Elimelech, 1996; Kretzschmar et al., 1999). However, ENPs can also be retained under unfavorable conditions due to deposition in an energy minimum, as explainable by DLVO theory. ENPs in the nm-range are more likely to be irreversibly deposited in a primary energy minimum than larger particles. At ionic strengths typically encountered in groundwaters, ENPs with diameters larger than approximately 0.5–1 μm can be reversibly retained in a secondary energy minimum (Elimelech et al., 1995; Petosa et al., 2010; Pelley and Tufenkji, 2008). Therefore ENP aggregates formed in groundwater (Table S–2 in the SI) can also be retained even in the

presence of an energy barrier acting against attachment. Under unfavorable attachment conditions, ENP retention increases with increasing porewater or groundwater IS (Ren and Smith, 2012; Petosa et al., 2012; Espinasse et al., 2007; Wang et al., 2008). Furthermore ENPs can be retained by pore straining, which does not depend on electrostatic interactions. It becomes significant when the ratio of ENP diameter to filter grain diameter ( $d_{\text{ENP}}/d_{\text{filter}}$ ) exceeds 0.003 (Bradford et al., 2003, 2007). For highly bundled single-walled CNTs (SWCNTs), a ratio as low as 0.0008 has been reported at which pore straining becomes significant (Jaisi et al., 2008). Interactions with water constituents present in pore water or groundwater can either enhance or reduce ENP mobility. Although the majority of studies have reported enhanced mobility of ENPs in the presence of NOM (Cornelis et al., 2014; Wang et al., 2010), some investigations have reported that NOM has little or no influence on their transport (L. Zhang et al., 2012) or that whether or not NOM enhances mobility depends on the water chemistry (Lawler et al., 2013; Espinasse et al., 2007). Decreasing ENP retention with increasing flow velocity has been observed experimentally for ENPs in a number of different investigations (Espinasse et al., 2007; Liang et al., 2013; Godinez and Darnault, 2011), which is consistent with CFT (Yao et al., 1971; Ryan and Elimelech, 1996). Since the flow velocities in unconsolidated granular aquifers are relatively low, typically ranging from a few mm/d in silts and fine sands to 5–10 m/d in clean, coarse gravels (Gupta, 2011), the hydraulic conditions in these aquifers encourage ENP retention. Additional retention mechanisms can occur in the unsaturated zone due to the presence of the air–water interface (Bradford et al., 2007). The vadose zone can therefore act as a barrier against the migration of ENPs into groundwater, especially at low water saturations (which has been reported to be between 0.1 (Tian et al., 2011) and 0.4 (Chen et al., 2010)) due to film straining. The physicochemical characteristics of the granular media also influence ENP filtration. This includes porosity, the pore size distribution, and the geometry and interconnectivity of pores (Bradford et al., 2007). The presence of macropores, fractures, or other open structures can result in preferential flow and enhanced ENP transport (Jaisi and Elimelech, 2009). Experimental investigations show that a reduction in collector grain size leads to increased ENP retention (Y. Li et al., 2008; Liang et al., 2013; Ren and Smith, 2012; Ko and Elimelech, 2000) which is consistent with the CFT prediction (Yao et al., 1971; Elimelech et al., 1995). Surface roughness (Elimelech et al., 1995; Ko and Elimelech, 2000; L. Zhang et al., 2012) and surface charge heterogeneities (Y. Li et al., 2008; W. Zhang et al., 2012a; Wang and Keller, 2009) can provide localized areas that are favorable for ENP attachment. Due to their small size, such heterogeneities are of greater importance for ENPs and other nano-sized particles than for micron-sized particles, since ENPs encounter such localized charged heterogeneities while micron-sized particles mainly face the average surface charge (Petosa et al., 2010).

The majority of transport investigations have been conducted in well-defined model porous media such as glass beads or homogeneous quartz sand (Cornelis et al., 2014; Petosa et al., 2010). These investigations have been extremely helpful for understanding the basic mechanisms governing the transport of ENPs in porous media. However, the extent to which the results of these investigations into the overall mobility of ENPs are applicable to natural porous media remains uncertain due to the complex interplay of numerous different parameters and the heterogeneities encountered under natural conditions.

Investigations using model porous media do not take into account heteroaggregation with dispersed particles originating from within the porous media (e.g. clay particles). Since heteroaggregation rates appear to be higher than homoaggregation rates over a wide range of pH values and IS, and since natural particles

will outnumber ENPs in natural environments, heteroaggregation may be quantitatively more important than homoaggregation (Cornelis et al., 2014). The effect of heteroaggregation on the transport of ENPs has, however, hardly been investigated to date. Heteroaggregates can be transported more rapidly than smaller pristine ENPs (or ENP homoaggregates) due to size exclusion under macroporous conditions (Cornelis et al., 2013; Zhao et al., 2012), but on the other hand size increase due to heteroaggregation can lead to enhanced removal by pore straining (Sun et al., 2015; Fang et al., 2009; Cornelis et al., 2013).

Published investigations into the retention of ENPs under similar conditions in both defined (or model) porous media and natural porous media have consistently reported that the retention of ENPs under unfavorable attachment conditions is lower in model porous media than in natural porous media (Sun et al., 2015; Wang et al., 2014; W. Zhang et al., 2012a; Quevedo and Tufenkji, 2012; Qi et al., 2014). These studies have attributed the increased retention to physical and chemical surface heterogeneities that provide favorable localized attachment sites, to less uniform grain size distributions, to larger total surface areas of grains within the porous media, to interactions with clay particles, and to enhanced occurring of pore straining.

In view of these differences in ENP retention between model porous media and natural porous media it appears to be important to use natural porous media in column experiments in order to predict the behavior of ENPs within the vadose zone or in porous media aquifers (Heidmann, 2013) (even though this might make it difficult to interpret the exact retention mechanisms involved). An overview of column transport investigations using natural porous media is provided in Table S–3 in the SI.

Various processes such as the formation of large aggregates, attachment to (localized) favorable attachment sites, pore straining, or film straining, have been reported to occur in natural porous media that retain ENPs (Table S–3 in the SI). Consequently, natural porous media serve as effective filters for ENPs. None of the studies presented in Table S–3 (in the SI) showed that any ENPs could travel through natural porous media without attenuation. Therefore, ENP travel distances greater than a few meters are not expected to occur. Leaching of ENPs through the topsoil and vadose zone is highly unlikely, and groundwater contamination is only likely to occur in very shallow aquifers. If ENPs do leach into porous media aquifers then further retention can be expected, especially as groundwaters are often characterized by high levels of salinity which can enhance aggregation and deposition. With the predicted low mobility of ENPs in porous media aquifers, their occurrence at the extraction point for a DWTP can be considered to be very unlikely unless there is a contamination source (e.g. nanopesticides) in very close proximity to the extraction point. The ENPs whose concentrations are likely to be the least attenuated in natural porous media are those with negatively charged, hydrophilic, surface functional groups, such as fullerenes or graphene oxide NPs (Qi et al., 2014).

Despite the indications of high levels of retention for ENPs in natural porous media, some uncertainties remain. Further investigations are clearly warranted into whether NOM is able to stabilize ENPs in such a way that they can be transported over large distances, even in the presence of divalent cations. Preferential flow could lead to enhanced particle transport compared to that measured in packed columns with well-arranged porous medium (Duester et al., 2011). However, in most cases the raw water intake of a DWTP would not be expected to be in the immediate proximity of a source of ENP contamination. Although preferential flow paths in porous media could enhance particle mobility, it is very unlikely that structures forming a “direct shortcut” between a contamination source and the extraction point will exist

Once deposited, particles such as clay particles (Ryan and Gschwend, 1992) or micron-sized latex particles (Bergendahl and Grasso, 1999) can be remobilized if the system is perturbed (e.g. transient flow conditions, changes in ionic strength of the aqueous matrix). Nevertheless, consistently irreversible attachment in the presence of  $\text{Ca}^{2+}$  ions has been reported for  $\text{C}_{60}$ -fullerenes (L. Chen et al., 2012), CNTs (Jaisi et al., 2008) and CdTe quantum dots (Torkzaban et al., 2013), which was attributed to deposition in the primary energy minimum and cation bridging. It has been shown that ENP deposition in the primary energy minimum can be reversible in monovalent ion solutions due to reduced energy detachment barriers as a result of the exchange of monovalent for divalent ions (Torkzaban et al., 2013; Jaisi et al., 2008; Shen et al., 2012).

Following deposition in monovalent solutions, the release of Ag NPs (Liang et al., 2013),  $\text{TiO}_2$  NPs (Godinez and Darnault, 2011), CNTs (Jaisi et al., 2008), CdTe quantum dots (Torkzaban et al., 2013), latex NPs (Shen et al., 2007) and  $\text{C}_{60}$ -fullerenes (Cheng et al., 2005) have been reported to occur when the IS of the solution decreased. The proportions of deposited NPs that were remobilized varied from relatively small (e.g. less than 7% for Ag NPs; Liang et al., 2013) to almost complete remobilization (e.g. 99% for CdTe quantum dots; Torkzaban et al., 2013), depending on the particle type, solution chemistry, flow conditions, and conditions of initial attachment. These authors attributed remobilization to diminishing secondary energy minima, in which the originally deposited ENPs were trapped.

In contrast, no remobilization of  $\text{TiO}_2$  NPs that had been deposited on grains of porous media (glass beads) in a monovalent solution could be observed by Chen et al. (2010). Mechanisms that led to irreversible attachment (such as film straining and the formation of  $\text{TiO}_2$  NP aggregates in low velocity regions) were suggested to be a result of unsaturated conditions during the drainage experiments (Chen et al., 2010).

In most cases hydraulic and hydrochemical conditions are expected to be relatively constant in groundwaters (which include the presence of higher valent ions such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ), hence the remobilization of ENPs that have been deposited in saturated porous media aquifers will not be a dominant mechanism. Remobilization is more likely for ENPs deposited in topsoil when strong system perturbations occur, such as heavy rainfall events, or in groundwater systems with strong temporal hydraulic and hydrochemical changing conditions. Further research is, however, necessary to obtain a clearer understanding of the remobilization potential of ENPs, especially in natural porous media. Since surface heterogeneities, surface roughness, grain size distributions, and non-ideal pore structures have been shown to be important factors affecting particle deposition, such physical properties are also likely to be of major importance to detachment processes in natural porous media.

### 3.2.3. ENP mobility in fractured rock aquifers

Rapid flows can occur through macropores and conduits in fractured rock aquifers (McCarthy and McKay, 2004), which are also used as raw water resources for drinking water production (Sharp, 2014).

A number of researchers have observed that rapid transport of nano-sized or micron-sized particles (such as clay particles, latex spheres, or viruses) can occur within rock fractures, with these particles travelling faster than conservative solute tracers (Albarran et al., 2013; Zvikelsky and Weisbrod, 2006; Zvikelsky et al., 2008; Toran and Palumbo, 1992; Hinsby et al., 1996). A combination of size exclusions and segregation into fast-flowing sections of the channel by charge exclusion and Taylor dispersion have generally been considered to be the reasons for the enhanced transport velocities of particles compared to those of solute tracers (W. Zhang et

al., 2012b). However, retention of nano-sized or micron-sized particles in fractured rock aquifers can still occur, despite their rapid transport (Albarran et al., 2013).

Particle retention can occur within conduits in fractured rock due to diffusion to fracture surfaces and attachment, interception, physical straining, matrix diffusion, sedimentation, and also, under unsaturated conditions, to film straining and air–water interface capture (W. Zhang et al., 2012b; Elimelech et al., 1995). However, the underlying mechanisms are not as well understood as those for retention in porous media (W. Zhang et al., 2012b). Interception and physical straining may be of minor significance for particles smaller than  $1\ \mu\text{m}$  in cracks that are  $100\ \mu\text{m}$  or more wide (Zvikelsky and Weisbrod, 2006). Under saturated conditions diffusion and attachment to fracture surfaces and/or sedimentation therefore appear to be the main retention mechanisms in fractures for particles in the nm-range, but the degree of retention can vary considerably, depending on the characteristics of the fractured rock (Zvikelsky and Weisbrod, 2006; Albarran et al., 2013). Under unfavorable attachment conditions retention of nano- or micron-sized particles range has been shown to increase with ionic strength (McCarthy et al., 2002; Mondal and Sleep, 2012). Attachment can also occur under unfavorable attachment conditions as a result of surface heterogeneities (Albarran et al., 2013). A reduction in flow velocity has consistently been observed to result in an increase in particle deposition, which has been explained as being a result of the longer time available for interactions between matrix and particles as well as for sedimentation (Vilks and Bachinski, 1996; Albarran et al., 2013; Vilks and Miller, 1999). The fluid shear acting on deposited particles also decreases with decreasing velocity, which leads to reduced detachment of deposited particles (W. Zhang et al., 2012b).

Particle retention is dependent on the particle size. It has been observed by Zvikelsky and Weisbrod (2006) that latex particles with diameters of  $200\ \text{nm}$  were found to be more mobile than  $20$  and  $1000\ \text{nm}$  latex particles. In another investigation with latex particles with diameters of  $30$ – $500\ \text{nm}$ , mobility was found to increase with decreasing particle size in fractured rock (Albarran et al., 2013). In contrast, Mondal and Sleep (2012) found a decreasing mobility with decreasing latex particle size. Vilks and Bachinski (1996) did not observe any size dependence in the mobility of particles with diameters of between  $20\ \text{nm}$  and  $90\ \text{nm}$  within fractured granite. Variations in reported size-dependency of particle transportation may be due to differences characteristics of the fractures and rock porosity and in the extent, size, and occurrence of heterogeneities in the solid stationary matrix. (Note that sedimentation is no significant retention mechanism for latex particles  $< 1\ \mu\text{m}$  due to their low density (Zvikelsky and Weisbrod, 2006)). A number of system parameters clearly influence the size-dependency of mobility behavior. Despite the number of investigations into the most mobile size fractions, it remains very difficult to draw any general conclusions (Albarran et al., 2013), as clearly illustrated by the variety of results obtained from the investigations outlined above.

When sedimentation dominates Brownian motion sedimentation becomes an important process in removal of particles from the aqueous phase within fractures that have a strong horizontal component (Becker et al., 1999). Whether or not sedimentation becomes dominant can be estimated from the ratio of sedimentation length ( $L_S$ ) to diffusion length ( $L_D$ ) (Becker et al., 1999):

$$\frac{L_S}{L_D} = \frac{(\rho_p - \rho_f)gd^{\frac{5}{2}}\sqrt{\tau}}{18\sqrt{\frac{2}{3\pi}}kT\mu} \quad (1)$$

where  $\mu$  is the dynamic viscosity,  $\rho_f$  is the fluid density,  $\rho_p$  is the particle density,  $g$  is the acceleration due to gravity,  $d$  is the particle diameter,  $k$  is the Boltzmann constant and  $T$  is the absolute temperature and  $\tau$  is the time interval.

Equation (1) shows that sedimentation becomes an important process for large, high-density particles and is dependent on the time that the particle spends in the system. Furthermore, for sedimentation to become significant for retention, Equation (2) needs to be fulfilled:

$$L_s > B \quad (2)$$

where  $B$  is the fracture half-aperture (Becker et al., 1999). Both homoaggregation and heteroaggregation can enhance settling by forming larger aggregates (Becker et al., 1999). Removal by sedimentation correlates directly with particle density (Zvikelsky et al., 2008). Inorganic ENPs often consist of materials such as Ag, Au, ZnO, which have higher densities than naturally occurring particles (Cornelis et al., 2014). Therefore, settling may become significant for inorganic ENPs at smaller sizes as compared to natural particles or buoyant artificial particles (e.g. latex particles).

Published research on the fate of ENPs in fractured rock aquifers is very scarce. The fate of Au NPs (40 nm and 100 nm) in cores of fractured granite was investigated by Albarran et al. (2013). The results of these investigations by Albarran et al. (2013) suggest that the concentrations of Au NPs smaller than 100 nm can become attenuated in aquifers of fractured granite and that particle mobility is limited, especially at low groundwater velocities, even under unfavorable attachment conditions. Retention was assumed to be due to depositional processes triggered by the presence of charge heterogeneities and roughness at a micron-scale (Albarran et al., 2013). Gravity settling may have contributed to the retention of the 100 nm Au NPs, as indicated by calculations based on Equations (1) and (2).

The transport of stabilized Ag NPs (diameter in suspension: 22–27 nm) in fractured porous sandstones under unfavorable attachment conditions was investigated by Neukum et al. (2014a). Three different types of sandstone were used. The mobility of the tested Ag NPs was found to be highly dependent on physics and chemistry of the rock material and on the water conditions.

The results obtained by Neukum et al. (2014a) indicate that Ag NP concentrations become attenuated in fractured sandstones in many cases. Ag NPs can, however, be mobile in groundwater with a low ionic strength if it is contained within an aquifer that has a solid matrix with relatively large fissures and a low level of mineralogical heterogeneity. Time-dependent blocking of favorable attachment sites and colloid-facilitated transport can also enhance mobility (Neukum et al., 2014a).

The mobility of Ag NPs in fractured sandstones was found by Neukum et al. (2014b) to be enhanced compared to their mobility in similar undisturbed sandstones, which was assumed to be due to the larger voids and greater hydraulic conductivity. Tellam et al. (2015) did not observe any breakthrough for metal and metal oxide NPs during their transport in artificial groundwater solutions through undisturbed sandstones, suggesting that ENPs might have only limited mobility in undisturbed sandstones.

### 3.2.4. ENP mobility in karst aquifers

Karst aquifers are formed by the dissolution of soluble rock formations (e.g. limestone or dolomite) and are usually characterized by solution-enlarged fractures. As a result of ongoing dissolution, conduits exist that allow high permeability. Karstic systems are important sources of fresh water for drinking water supplies but can be highly vulnerable to contamination from pollutants that enter the aquifer through thin soils or holes (Göppert and

Goldscheider, 2008). Attenuation of contaminants in karst aquifers is expected to be much less than in porous media or fractured rock with small fissures due to the general absence of a natural filtration system (Kacaroglu, 1999). Karst aquifers can experience rapid flows of about a kilometer per day, especially during or after heavy rainfall (Shevenell and McCarthy, 2002). As a result solutes and suspended matter can be rapidly transported over large distances (McCarthy and McKay, 2004). Transported suspended matter can comprise a variety of particle types ranging in diameter from a few nanometers up to several micrometers (Atteia and Kozel, 1997). Increased turbidity at high flow rates indicates that strong remobilization or particle generation can occur under such conditions due to hydraulic changes (Shevenell and McCarthy, 2002). From what is known about particle behavior karst aquifers are vulnerable to ENP contamination, but to the best of the authors' knowledge no investigations have been carried out into the fate of ENPs in karstic aquifers. This lack of relevant research is probably due to the highly complex experimental setup (large-scale experiments or field studies) that would be required, together with the analytical challenges faced when attempting to detect ENPs in natural environments (von der Kammer et al., 2012).

The ratio of the surface area of the solid matrix to the fluid volume decreases as the void space increases. The transport of ENPs to attachment sites on the solid aquifer surfaces therefore becomes less likely and the tendency of ENPs to sediment presumably becomes the main determining factor in ENP transport (Mahler et al., 1998).

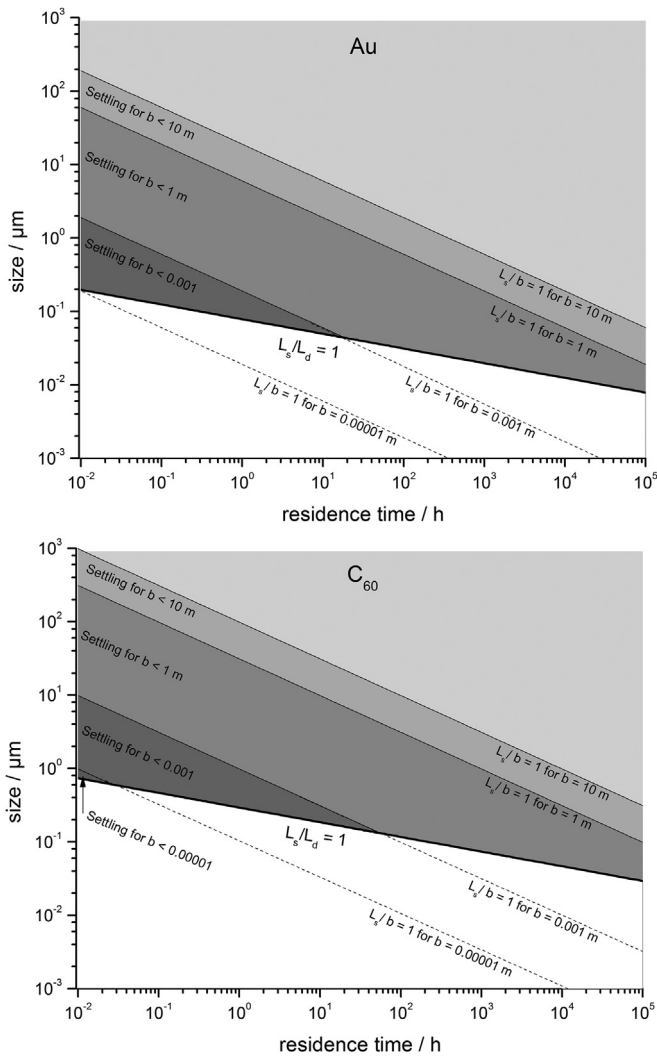
Fig. 6 plots the theoretically predicted sedimentation behavior based on Equations (1) and (2) of Au NPs (high density, 19.3 g/mL) and of C<sub>60</sub>-fullerenes (low density, 1.7 g/mL) for different aperture dimensions ( $b = 10 \mu\text{m}$  to 10 m). These theoretical predictions ignore specific electrostatic interactions and heteroaggregation and should therefore only be considered to be rough estimates. For settling to be predicted the  $L_s/L_d$  ratio and the particle size both need to be greater than 1.

For example, a residence time (i.e. time for settling) of 3.5 h is required to remove 100 nm Au NPs from the water column in a fracture with a half-aperture of 0.001 m. This value increases to 3600 h (0.41 years) if the half-aperture is 1 m. Particle sizes in the upper  $\mu\text{m}$  range would be required for settling to occur within a few hours in conduits with larger apertures. Lower density ENPs require larger aggregate sizes and/or longer settling times to settle out of the water column, as predicted for C<sub>60</sub>-fullerenes.

Fig. 7 shows a plot of the residence times which are theoretically necessary for removing ENPs with sizes reported to occur in natural groundwaters (Abbott Chalew et al., 2013; Ottofuelling et al., 2011) from the aqueous matrix by settling, depending on the aperture size. Note that Abbott Chalew et al. (2013) reported sizes for Ag NPs, ZnO NPs and TiO<sub>2</sub> NPs in a groundwater with relatively low IS and Ca<sup>2+</sup> concentrations.

For apertures that are a few mm wide the theoretical settling time can range from a few minutes to a few hours. If fractures have widths larger than 1 m, the settling times for ZnO NPs, Ag NPs and TiO<sub>2</sub> NPs with diameters of 292 nm, 223 nm, and 276 nm, respectively, as reported by Abbott Chalew et al. (2013), would amount to > 1000 h (42 days), increasing to more than one year for 10 m apertures. For TiO<sub>2</sub> NPs with diameters of 1160 nm the time required for settling is an order of magnitude less than that required for TiO<sub>2</sub> NPs with diameters of 276 nm.

The above considerations show that ENPs can settle out of an aqueous groundwater matrix if the groundwater remains beneath the surface for a prolonged period of time. Groundwater in karstic aquifers can diffuse into the solid stationary matrix and remain there for several years, while the residence time in fractures with high groundwater flow can be as low as a few hours (Worthington,



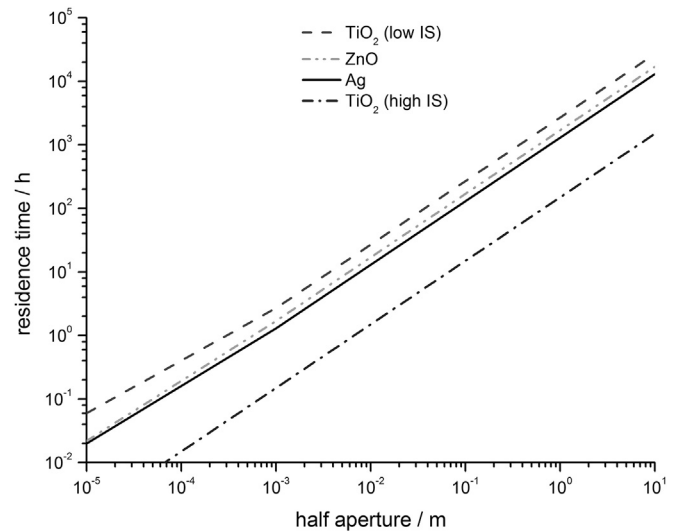
**Fig. 6.** Theoretical expectation of settling for high-density ENPs (Au, 19.3 g/mL) and low density ENPs ( $C_{60}$ , 1.7 g/mL).

2007). Unless raw water is used from subsurface locations that are not affected by high-velocity flows, ENP concentrations in karstic aquifers will experience only limited attenuation. The levels of risk increase for small ENPs with low states of aggregation and low densities.

If groundwaters are artificially recharged or if bank filtrate is used for drinking water production, the subsurface travel time to the water extraction point may, in some cases, not exceed a few days (Kühn and Müller, 2005). If large fractures or conduits are present within an aquifer and ENPs are able to reach the groundwater then there is an increased chance of ENPs being present in groundwater that is used for drinking water production.

### 3.2.5. Scenario for $TiO_2$ NPs

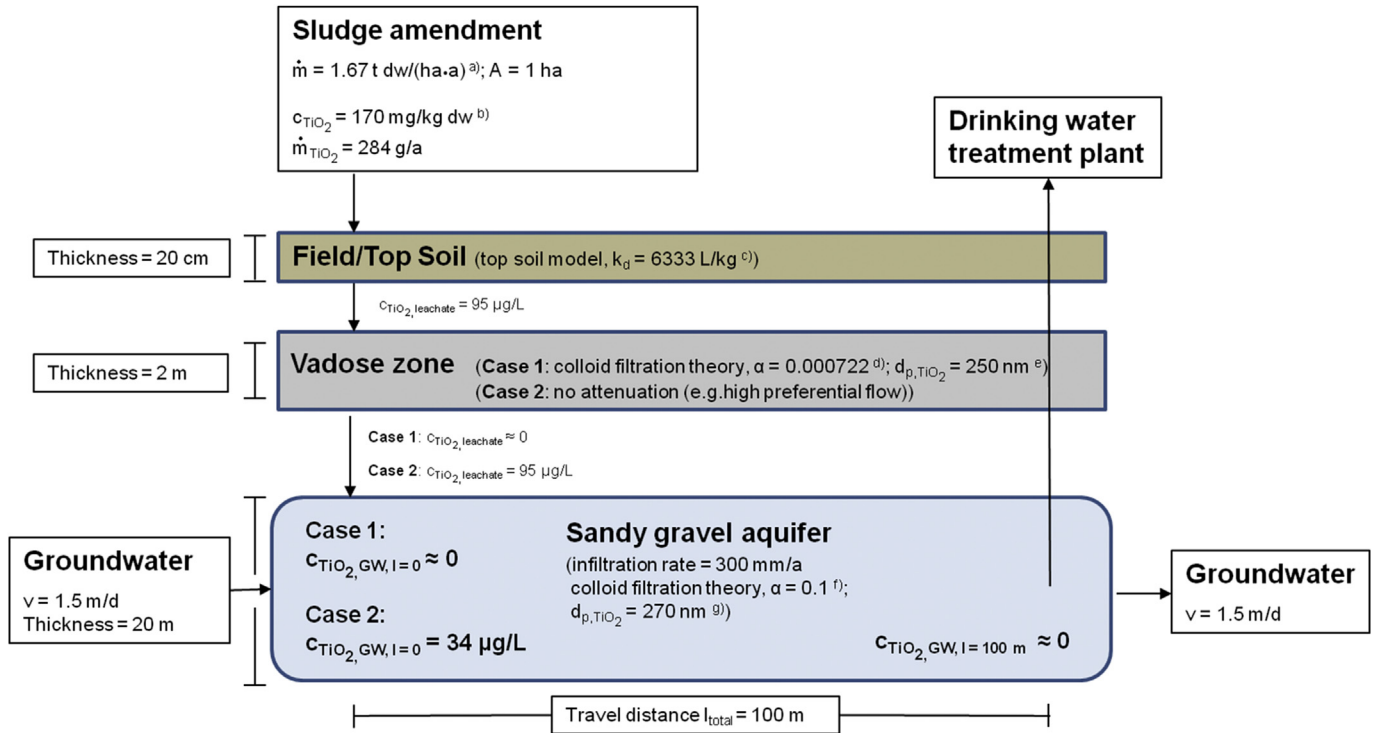
In order to make a quantitative estimate of the vulnerability of a particular groundwater resource to ENPs, a scenario was developed based on data from a natural groundwater system. A hypothetical high-input ENP source was assumed to exist. ENP fate descriptors were obtained from published literature. For the ENP contamination source a theoretical field whose soil had been fertilized with sludge containing  $TiO_2$  NPs was assumed to overlie a shallow porous aquifer. The soil and aquifer characteristics and the groundwater conditions were based on an actual groundwater



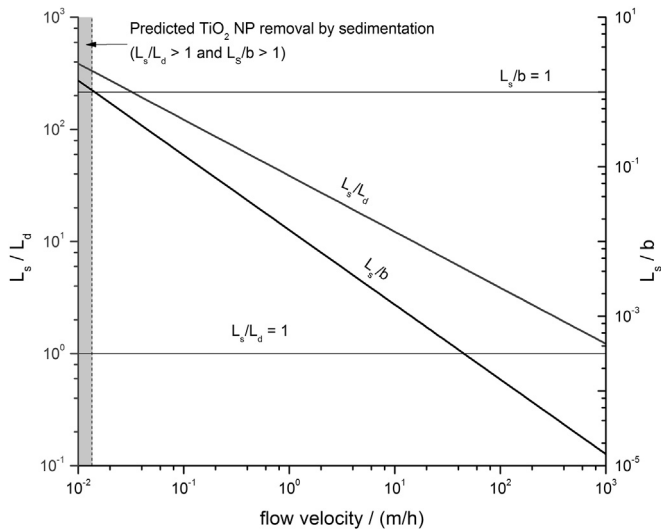
**Fig. 7.** Predicted residence times necessary for ENP removal by sedimentation depending on the aperture size for ZnO NPs (292 nm), Ag NPs (223 nm), and  $TiO_2$  NPs (276 nm) with sizes occurring in groundwater with low  $Ca^{2+}$  concentration (Abbott Chalew et al., 2013), and for  $TiO_2$  NPs (1160 nm) in groundwater with a relatively high  $Ca^{2+}$  concentration (Ottofuelling et al., 2011).

system in Germany from which raw water is extracted for drinking water production. Two possible cases were considered: in the first case the  $TiO_2$  NPs were retained in the vadose zone, while in the second case the  $TiO_2$  NPs were assumed to pass through the vadose zone without any attenuation due, for example, to high rates of preferential flow. A schematic representation of these scenarios and the resulting modelled  $TiO_2$  NP concentrations are shown in Fig. 8.

Assuming that the field was fertilized once a year with the maximum legal sludge load in Germany (Bundesministerium der Justiz und Verbraucherschutz, 1992),  $TiO_2$  NP concentrations in the leachate at stationary conditions would amount to 95  $\mu\text{g/L}$ . The vadose zone, (which is 2 m thick) has a relatively low attachment efficiency of 0.0007222 (Fang et al., 2009). However, in Case 1 the  $TiO_2$  NP concentrations would become almost completely attenuated by granular media filtration due to a low leachate velocity. Assuming no attenuation in the vadose zone due to, for example, high preferential flow (Case 2), the  $TiO_2$  NP concentration in the leachate when it reached the groundwater would remain at 95  $\mu\text{g/L}$ . On dilution with the groundwater (calculated using the dilution-attenuation-factor: US EPA, 1996) the  $TiO_2$  NP concentration in the groundwater affected by the leachate would be 34  $\mu\text{g/L}$ . In this case the  $TiO_2$  NP concentrations would become further reduced as the groundwater passes through the sandy aquifer, with 99.9% of the initial concentration in the groundwater after infiltration being lost after a travel distance of 1.3 m. With an assumed horizontal distance of 100 m between the position of sludge amendment and the drinking water extraction point, virtually no  $TiO_2$  NPs are predicted to be present in the raw water entering the DWTP. These results demonstrate that even under elevated-risk scenarios (high input source, preferential flow, shallow aquifer, and relatively low attachment efficiencies) the subsurface is an effective filter of ENPs and the risk of ENPs being present in groundwater from a porous aquifer can be considered to be low. Assuming the same boundary conditions as used in the scenario for a porous aquifer (see Fig. 8), attenuation of  $TiO_2$  NP concentrations in a 5 m thick karstic aquifer as a result of sedimentation is only predicted at low flow velocities of 0.015 m/h or less (Fig. 9). When sedimentation dominates Brownian motion ( $L_s/L_d > 1$ ) residence times are too short to allow



**Fig. 8.** Groundwater scenario for high input of TiO<sub>2</sub> NPs. References: a) Bundesministerium der Justiz und Verbraucherschutz (1992), b) Sun et al., 2014, c) Kiser et al., 2010, d) Fang et al., 2009, e) Park et al., 2013, f) Solovitch et al., 2010, g) Abbott Chalew et al., 2013. All concentrations stated for stationary conditions.



**Fig. 9.** Sedimentation behavior of TiO<sub>2</sub> NPs in a karstic aquifer with TiO<sub>2</sub> NP input conditions as shown in Fig. 6.

TiO<sub>2</sub> NPs to settle from the water column ( $L_s/b < 1$  for flow velocities  $> 0.015 \text{ m/h}$ ).

**4. ENP removability in drinking water treatment plants**

A major aim of drinking water treatment is the removal of particles and turbidity. Despite the removal of some particles by natural processes, particles and turbidity-causing substances are always present to a greater or lesser extent in raw water used for drinking water production. Water treatment for drinking water

production therefore involves processes such as sedimentation and filtration processes, which are especially designed to remove these particles and substances. Other processes, such as ozonation are not primarily designed for particle removal but can also affect particulate matter in the aqueous matrix. The mechanisms, influencing parameters, and removal efficiencies of different water treatment processes for micron-sized or larger particles are well understood (Lawler, 1986; Crittenden et al., 2012). Despite the fact that current water treatment systems include processes specially designed to remove turbidity and particles, NPs can still be present in treated drinking water (Kaegi et al., 2008b; Bundschuh et al., 2001). This raises the question of whether or not ENPs can be removed by the various treatment processes that are used in DWTPs.

**4.1. Coagulation, flocculation and sedimentation**

The combined processes of coagulation and flocculation are commonly used in water treatment for drinking water production to enhance the removability of particles in a subsequent solid–liquid separation step (involving, for example, sedimentation or filtration).

In laboratory-scale experiments metal and metal oxide ENPs could not be completely removed by coagulation – flocculation – sedimentation (Zhang et al., 2008; Abbott Chalew et al., 2013; Surawanvijit et al., 2010). Removal efficiencies ranged from 20% to  $>90\%$ . For C<sub>60</sub>-fullerenes, a removal efficiency of 60–97% was reported (Hyung and Kim, 2009). The removal efficiencies were dependent on the type of ENP, type of flocculation agent and dosage and on the water matrix (Zhang et al., 2008; Abbott Chalew et al., 2013; Surawanvijit et al., 2010; Hyung and Kim, 2009). These experimental studies show that a large proportion of different ENPs can be removed by coagulation–flocculation–sedimentation

processes. However, under the typical operating conditions of a DWTP a proportion of the ENPs can remain stable within the water, as formed ENP aggregates are not fully destabilized by the coagulation and flocculation process (Zhang, Y., et al., 2010) and do not settle in the time frame typical available. The presence of high concentrations of NOM significantly reduces the removability of ENPs (Zhang, Y., et al., 2010; Hyung and Kim, 2009).

#### 4.2. Granular media filtration

In DWTPs, granular media can be used as filters in either slow or rapid sand filtration processes. Rapid sand filtration uses a processed granular material with a more uniform grain size than slow sand filtration, allowing higher flow velocities and less loss of head than slow sand filtration. The same mechanisms and influencing parameters apply to sand filtration in water treatment as to granular media filtration processes in natural environments (see Section 3.2). The more uniform and homogenous grains of the sand filters used in drinking water treatment and the higher water velocities compared to groundwater flow suggest that a lower level of retention can be expected in sand filters than in the porous media of groundwater aquifers.

In a study by Li et al. (2013) simulating the sand filtration processes of a DWTP, low levels of retention were observed for coated metal and metal oxide ENPs in natural surface water, whereas the same ENPs without a stabilizing coating were removed to a great extent. Aged sand was more efficient in retaining ENPs than new sand. However, the type of sand had a minor effect compared to the particle coatings (Li et al., 2013).

In DWTPs coagulation and flocculation are usually induced prior to rapid sand filtration. To the authors' best knowledge there is little experimental data available to date on ENP removal efficiencies for this combination of processes. In a combined process that simulated granular filtration by using an 8  $\mu\text{m}$  filter, a further 20% of  $\text{C}_{60}$ -fullerenes were removed by filtration when the previous coagulation and sedimentation step had removed less than 20%, but if removal by the coagulation and sedimentation step was already high (>60%) then no additional removal was recorded (Hyung and Kim, 2009).

A number of different parameters are likely to affect the removability of ENPs by sand filtration in DWTPs. A key factor affecting the mobility of ENPs is the coating or capping that is used for their stabilization. Results from a number of different studies (see section 3.2) indicate that sterically stabilized and negatively charged ENPs can be mobile in uniform sands and in processed sands of low heterogeneity, such as are likely to be used in DWTPs. ENPs that occur in the raw water of a DWTP are likely to be stabilized, either by intentionally imposed functional groups or by natural coatings such as NOM. Sand filtration systems in DWTPs that do not include any pre-treatment therefore appear to have only limited capabilities of removing ENPs from the aqueous matrices. Further experimental investigation is required to establish the effectiveness of pre-treatment (such as ozonation or coagulation) on ENP retention by sand filtration.

#### 4.3. Ozonation

Ozonation enhances coagulation and consequently assists in the reduction of turbidity and removal of suspended particles during subsequent solid–liquid separation steps (Crittenden et al., 2012; Jekel, 1983; Petrusevski et al., 1995). By reacting with ozone the adsorbed organic compounds can become more polar and desorb from the particle, leading to a reduction in electrostatic and steric stabilization (Crittenden et al., 2012). Polymerization of NOM under the influence of ozone can lead to particle aggregation through

bridging reactions (Reckhow and Singer, 1984). However, destabilization by ozonation is strongly dependent on the hydrochemical conditions. As reported by Chandrakanth and Amy (1996), in the absence of  $\text{Ca}^{2+}$  ozonated NOM constituents will sorb to the surfaces of alumina particles and hence increase their stability.

Metal oxide NPs such as  $\text{ZnO}$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  or  $\text{CeO}_2$  are not expected to undergo chemical reactions with ozone as their metallic ions are in the highest oxidative state. Their stability in ozonation processes can, however, be altered due to the interaction of ozone with organic coatings or stabilizing agents, as demonstrated for  $\text{Al}_2\text{O}_3$  NP by Chandrakanth and Amy (1996).

Ag NPs can react with ozone and form water insoluble  $\text{Ag}_2\text{O}_2$  particles (Cataldo et al., 2013). The oxidized  $\text{Ag}_2\text{O}_2$  particles remained suspended unless mechanical stress was introduced by shaking, in which case the particles aggregated strongly and then precipitated (Cataldo et al., 2013). A loss of aggregation stability and aggregate enlargement was also observed for Ag NPs stabilized with polyphosphate (Morozov et al., 2011), when interacting with ozone. This loss of aggregation stability was suggested to be caused by oxidation of the metallic Ag NP surface and a decrease in the stabilizing effect of polyphosphate. In contrast to Ag NPs, as observed by Puckett et al. (2005), there was no change in diameter for Au NPs (25 nm–30 nm) stabilized with citrate in double distilled water, when exposed to ozone.

Oxidation of CNTs by ozone has been reported by Simmons et al. (2006). The formation of different functional groups such as epoxides, ethers, or hydroxyls on the surface of  $\text{C}_{60}$ -fullerenes has been experimentally determined (Weisman et al., 2001; Heymann et al., 2000). Fortner et al. (2007) observed that  $\text{C}_{60}$ -fullerenes suspended in water are highly reactive with ozone over a wide range of pH values, resulting in highly derivatized (C:O  $\approx$  2:1), water soluble, fullerene oxides.  $\text{C}_{60}$  molecules therefore lose their agglomeration state and hence their particle character, but water soluble species are formed (with unknown health and environmental consequences) which are more difficult to remove from the liquid matrix than their aggregated, underivatized parent compounds (Hyung and Kim, 2009).

#### 4.4. Membrane filtration

Microfiltration (MF) (with pore sizes typically larger than 0.1  $\mu\text{m}$ ) and ultrafiltration (UF) (with pore sizes typically between 0.001 and 0.1  $\mu\text{m}$ ) are processes especially designed to remove particles, with the latter becoming increasingly in use to treat drinking water (Lipp and Baldauf, 2008). Kaegi et al. (2008b) reported that the use of UF (cut-off 100 kDa) in a full scale DWTP improved the removal of suspended (natural nano)particles compared to conventional treatment. Laboratory-scale experiments with artificial waters demonstrated that metal and metal oxide ENPs are efficiently retained by UF (Ladner et al., 2012; Springer et al., 2013; Kim et al., 1993). However, hydrophilic ENPs with sizes in the low nm-range might not be retained completely, as shown for fullerols (Jassby et al., 2010). The presence of Mg and Ca ions increased the removal of fullerols, but complete removal was not achieved using an UF membrane with a nominal pore size of 20 nm (Jassby et al., 2010). With increasing pore size, the retention diminishes. Consequently, MF is less efficient in retaining ENPs than UF (Ladner et al., 2012; Abbott Chalew et al., 2013). A coagulation and flocculation step can further enhance the removability of ENPs by UF (Abbott Chalew et al., 2013; Surawanvijit et al., 2010). The results of the above investigations suggest that almost complete removal of most ENP classes can be achieved through the use of UF membranes as a result of size exclusion, since their pore sizes are typically smaller than those of the ENP aggregates. This also applies for aggregate sizes formed in natural waters



(Tables S–1 and S–2 in the SI). However, the application of UF membranes is still hampered by fouling and associated flux reduction. Fine suspended and nanoparticulate matter, including ENPs, has been shown to contribute strongly to membrane fouling (Lipp et al., 2009). However, as the expected concentration of ENPs in natural waters of ENPs is several orders of magnitude lower than that of natural NPs, ENPs presumably make a less significant contribution to membrane fouling in drinking water treatment processes than natural particles.

#### 4.5. Sorption

The most commonly used sorbent material in drinking water treatment is activated carbon, either as powdered activated carbon (PAC) or as granulated activated carbon (GAC), due to its effectiveness and low cost. Other materials such as zeolites, synthetic polymer resins, or activated alumina are also used as adsorbents. Since ENPs have a large surface-to-volume ratio they are expected to have a high sorption tendency. The efficiency of activated carbon as an adsorbent for dispersed Ag NPs was investigated by Gicheva and Yordanov (2013). Activated carbon was found to be an efficient adsorbent with the exact efficiency depending on the type of carbon used and on ionic strength. As reported by Salih et al. (2010)  $\text{TiO}_2$  NPs were attracted to GAC, which was attributed to electrostatic interactions since the GAC surface was positively charged under the experimental conditions, in contrast to the negative charge of the  $\text{TiO}_2$  NPs. Sorption processes might therefore be an effective means of hindering ENPs from reaching the product water. Since ENPs with a high net negative charge are the most likely to pass through liquid–solid separation steps such as sedimentation or granular filtration, the use of an adsorbent with a positive surface charge might be a useful addition to water treatment processes, as it would tend to adsorb these ENPs electrostatically and thus improve the safety of the product water (with respect to ENP pollution). Activated alumina, for example, has an IEP of between 8 and 10 (Yang, 2003) and hence a positive surface charge at pH values between 7 and 8. It could therefore have a high sorption

capacity for negatively charged particles. Further investigations are however required to elucidate the influences, mechanisms, and capacities of different sorption processes for removing ENPs from aqueous matrices.

So far investigations on ENP removability in DWTP have been carried out in laboratory-scale experiments for single treatment steps, but DWTPs consist of a series of treatment steps. Investigations into how ENPs behave during their whole passage through water works (i.e. several consecutive treatment steps) would be highly beneficial for further elucidating the likelihood of ENPs to pass DWTPs. Determining the influence of coagulation and flocculation on the ENP removability in a subsequent sand filtration step would be of high interest since this process combination is applied in many DWTPs. The major knowledge gap, however, is that the form of which ENPs are present in raw water resources is unknown, which has a high impact on their removability. It can be expected that ENPs reaching raw water resources are highly stabilized, and might be more mobile drinking water treatment steps than their pristine counterparts, which have been often used for determination of removal efficiencies in laboratory scale-experiments.

#### 4.6. Scenario for $\text{TiO}_2$ NPs

Modelled residual concentrations following treatment for drinking water, based on the raw water  $\text{TiO}_2$  NP concentrations modelled from the high input scenarios for surface water (Fig. 5) and groundwater (Fig. 8), are presented in Fig. 10 (surface water) and Fig. 11 (groundwater). The modelled designs of the treatment processes and other relevant data were based on the real DWTPs which produce drinking water at the locations of which the respective scenarios are based on. Two cases are distinguished for the surface water scenario: (i) treated wastewater reaches the reservoir and sedimentation occurs ( $c_{\text{TiO}_2, \text{rawwater}} = 0.97 \mu\text{g/L}$ ), and (ii) untreated wastewater reaches the reservoir and stabilizing conditions prevail ( $c_{\text{TiO}_2, \text{rawwater}} = 50 \mu\text{g/L}$ ; see Fig. 5). Residual concentrations in the drinking water following UF were estimated

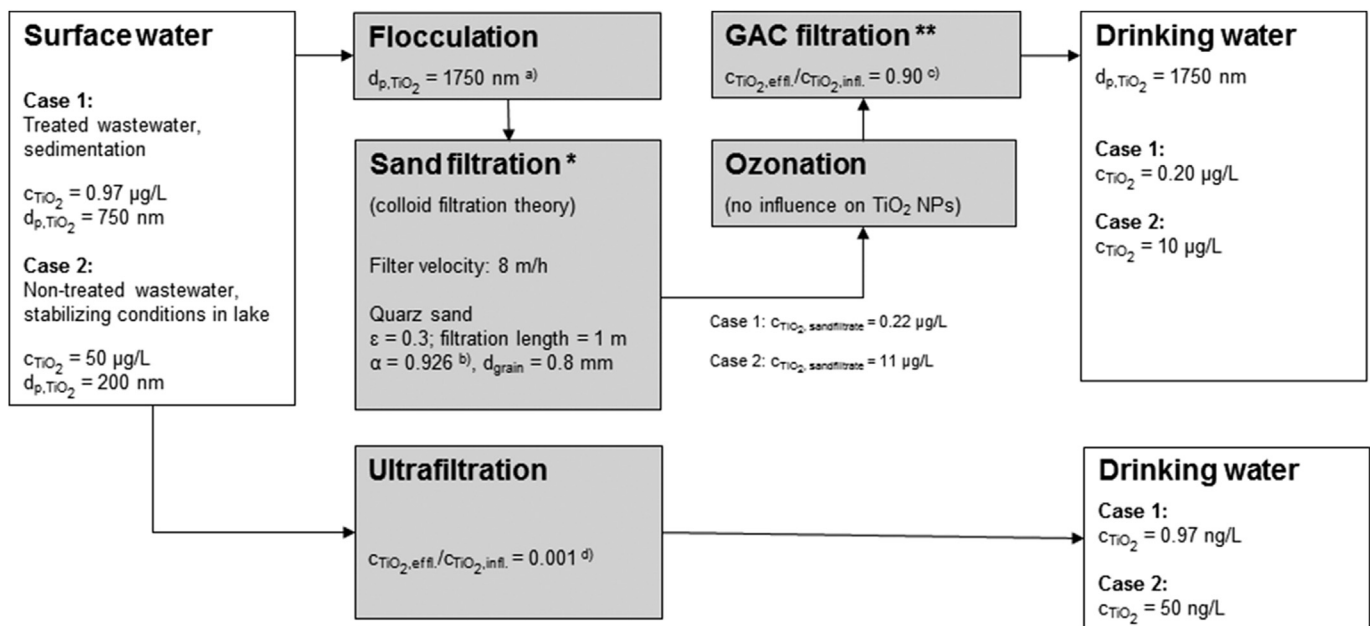
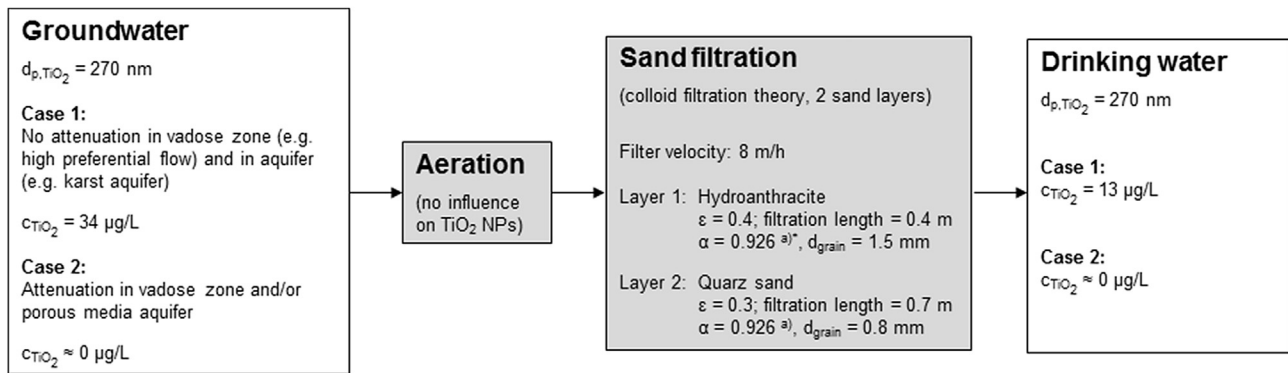


Fig. 10. Drinking water treatment of raw water based on a high  $\text{TiO}_2$  NP input scenario for surface water (Fig. 5).

References: a) Zhang et al. (2008) b) Liu et al. (2013) c) Rottman et al. (2013) d) Tröster et al. (2013). \* no process data available, assumption of a 1 m monolayer quartz sand filter with a flow velocity of 8 m/h; \*\* GAC = granular activated carbon.



**Fig. 11.** Drinking water treatment of raw water based on a high  $\text{TiO}_2$  NP input scenario for groundwater (Fig. 8). References: a) Li et al. (2013). \* no data for hydroanthracite available, assumption of same attachment efficiency as for quartz sand filters.

in addition to those following conventional treatment.

The surface water treatment involves flocculation, sand filtration, ozonation, and granular activated carbon filtration. The aggregate sizes increase following the addition of flocculant. A final aggregate size of 1750 nm is estimated on the basis of laboratory investigations by Zhang et al. (2008). Transport through the subsequent sand filtration process is calculated by applying CFT with an attachment efficiency close to unity, as determined by Li et al. (2013). This high attachment efficiency is also justified by the low absolute values for the zeta potential (<10 mV) of  $\text{TiO}_2$  NP aggregates following flocculation (Zhang et al., 2008). After passing through the sand filter the  $\text{TiO}_2$  concentrations are 0.22  $\mu\text{g/L}$  and 11  $\mu\text{g/L}$  for the two cases. Flocculation and sand filtration therefore remove 77% of the particles. Ozonation is assumed to have no influence on  $\text{TiO}_2$  NPs. A 10% reduction in  $\text{TiO}_2$  NP concentration is assumed for the final filtration process using GAC (Rottman et al., 2013).  $\text{TiO}_2$  NP concentrations in the drinking water of 0.20  $\mu\text{g/L}$  and of 10  $\mu\text{g/L}$  are calculated for the two cases. Although the conventional processes of flocculation and sand filtration are to be able to remove a large proportion of  $\text{TiO}_2$  NPs, the estimated concentrations show that they do not achieve complete removal. The case scenarios (Figs. 5 and 10) indicate that if there is a high input source of  $\text{TiO}_2$  NPs close to the DWTPs and little reduction in  $\text{TiO}_2$  NP concentration occurs prior to the extraction point, concentrations of  $\text{TiO}_2$  NP in the  $\mu\text{g/L}$  range can be present in the drinking water produced. With a removal efficiency greater than 3 log units (Tröster et al., 2013), UF is expected to be an optimal process for  $\text{TiO}_2$  NP retention. Assuming that 99.9% of the  $\text{TiO}_2$  NPs are removed, the  $\text{TiO}_2$  NP concentration in the drinking water produced amounts to 0.97 ng/L for case 1 and 50 ng/L for case 2. This suggests that if UF processes are used in drinking water production only trace amounts of  $\text{TiO}_2$  NPs are expected to be present in the treated drinking water, even under high input scenarios.

Tiede et al. (2015) estimated  $\text{TiO}_2$  NP concentrations in treated drinking water in the UK, based on their DEFRA-report (Tiede et al., 2010). Based on their predictions of  $\text{TiO}_2$  NP concentrations in UK rivers (see section 3.1.2)  $\text{TiO}_2$  concentrations in the treated drinking water were calculated using removal efficiencies of 99% (conventional treatment), 97% (direct filtration) and 99.9% (membrane filtration). The predicted  $\text{TiO}_2$  NP concentrations were between 0.491 ng/L and 5.18  $\mu\text{g/L}$ . These values are in good agreement with our predicted  $\text{TiO}_2$  NP concentrations (between 0.97 ng/L and 10  $\mu\text{g/L}$ ), despite the different modelling approaches (e.g. Tiede et al. (2015) used generalized fate descriptors for various classes of ENPs for predicting  $\text{TiO}_2$  NP concentrations on a regional scale (UK), while for our estimates  $\text{TiO}_2$  NP specific fate descriptors were used and the predictions were made for a specific location). Our

predicted values are approximately two times higher as the concentrations predicted by Tiede et al. (2015). Apart from different input data, these differences are due to that our values are predicted for a localized scenario with high  $\text{TiO}_2$  NP input while the predicted values by Tiede et al. (2015) are generalized for a larger region (UK).

In the groundwater high input scenario  $\text{TiO}_2$  NPs are estimated to be completely removed during their passage through the porous medium aquifer, resulting in a raw water concentration of zero (Fig. 8) and consequently no  $\text{TiO}_2$  NP contamination of the drinking water. Furthermore, a  $\text{TiO}_2$  NP concentration of 34  $\mu\text{g/L}$  was assumed in the raw water as found after infiltration of the  $\text{TiO}_2$  NP containing leachate from the sludge amended field if no attenuation in the vadose zone occurs. This ignores the strong attenuation estimated to occur within the porous aquifer and could therefore be relevant for karst groundwaters, or if the pollution source is located very close to the raw water extraction point. The groundwater is treated by aeration and sand filtration. Due to the lack of data aeration is assumed to have no influence on  $\text{TiO}_2$  NPs. CFT is used to calculate  $\text{TiO}_2$  NP transport in the subsequent 2-layer sand filtration step, using an attachment efficiency ( $\alpha$ ) of 0.926. While this attachment efficiency was determined for quartz sand filters in DWTPs (Li et al., 2013), it is assumed to also be valid for the hydroanthracite layer. The sand filter reduces the  $\text{TiO}_2$  NP concentration from 34  $\mu\text{g/L}$  to 13  $\mu\text{g/L}$ , a reduction of 62%. Sand filtration therefore reduces the  $\text{TiO}_2$  NP load but sand filtration alone may not be sufficient to achieve complete ENP removal.

Strong attenuation of  $\text{TiO}_2$  NP concentrations can be expected in the vadose zone and in porous media aquifers and hence, with additional removal in a DWTP, the likelihood of  $\text{TiO}_2$  NPs reaching drinking water supplies derived from porous media aquifers can be considered to be very low. Where there is no significant attenuation in the natural environment (for example in shallow karst aquifers with short residence times) there may be an elevated risk of  $\text{TiO}_2$  NPs reaching the final drinking water (assuming that an ENP source is present), as indicated by the estimated concentration of 13  $\mu\text{g/L}$  in the scenario discussed above.

## 5. Conclusions

This review elucidates the vulnerability of drinking water systems to ENPs by predicting the likelihood of ENPs being present in drinking water. It shows that certain types of ENP (e.g.  $\text{TiO}_2$  NPs,  $\text{SiO}_2$  NPs,  $\text{ZnO}$  NPs) are produced in large quantities (tons per year) and are readily released to the aquatic environment. With increasing production and application, the quantity of ENPs released will also increase in the future. Thus potential risk exists

that ENPs enter surface water or groundwater resources used for drinking water production and could be regarded as potential emerging contaminants.

This review shows that the likelihood of ENPs being present in drinking water is small to date. Apart from the limited quantities of most ENPs produced today, many natural attenuation mechanisms exist that reduce ENP concentrations in the aquatic environment. Consequently, we show that ENPs are unlikely to reach water extraction points of DWTPs in most cases. If membrane filtration or conventional treatment including a flocculation step is applied for drinking water production, further ENP retention can be expected in the water treatment train. An elevated risk for ENPs being present in the drinking water exists only if the following conditions are fulfilled concurrently:

- A source is releasing elevated quantities of ENPs in close proximity to a DWTP plant inlet. Such a source might, for example, be wastewater that is released into surface waters. Sewage sludge containing ENPs that is applied for field fertilization, or future nanopesticide use are two possible sources of groundwater pollution.
- Water chemistry supports colloidal stability and retains the effects related to their nano-size over a prolonged period of time.
- For water works using groundwater: ENPs are migrating by preferential flow, or by fast bank filtration, or the retention potential of the unsaturated zone is very low (e.g. if very shallow) and the ENPs are mobile within the aquifer system. A high mobility of ENPs is very likely to be the case in karst systems.
- Conventional treatment (with no flocculation-filtration step) is used for drinking water production, or water is consumed without treatment.

Although each one of these situations can occur, not all of them exist together at most drinking water production sites and barriers therefore remain to reduce the chances of ENPs reaching the final drinking water. However, at certain specific locations, all of these situations might be encountered concurrently.

The high-input case scenarios discussed in sections 3 and 4, for example, represent such “hot spots” vulnerable to ENP contamination. For these cases, TiO<sub>2</sub> NP concentrations of up to 10 µg/L are predicted to be present in drinking water produced from surface water. For drinking water produced with conventional treatment from groundwater in a karstic aquifer, with no attenuation in the vadose zone, the predicted TiO<sub>2</sub> NP concentration is 13 µg/L.

A decision tree is proposed in Fig. 12 that summarizes the conditions under which there is a risk of ENP contamination of drinking water.

It should be emphasized that predictions and estimations made on the basis of available data and published literature include many uncertainties. The following topics will need to be addressed in future research in order to reduce these uncertainties:

- Suitable analytical methods need to be developed for characterizing and quantifying ENPs in complex matrices.
- More accurate information is required on the quantities of ENPs produced and released, especially for modelling approaches aiming to predict ENP concentrations in the natural environment.
- Information is required on the form of ENPs released into the natural environment (e.g. whether they are pristine, weathered, matrix-bound, etc.) as this is of considerable importance for their behavior and fate.
- Models might require a high spatial and temporal resolution for predicting ENP concentrations at specific drinking water production sites.

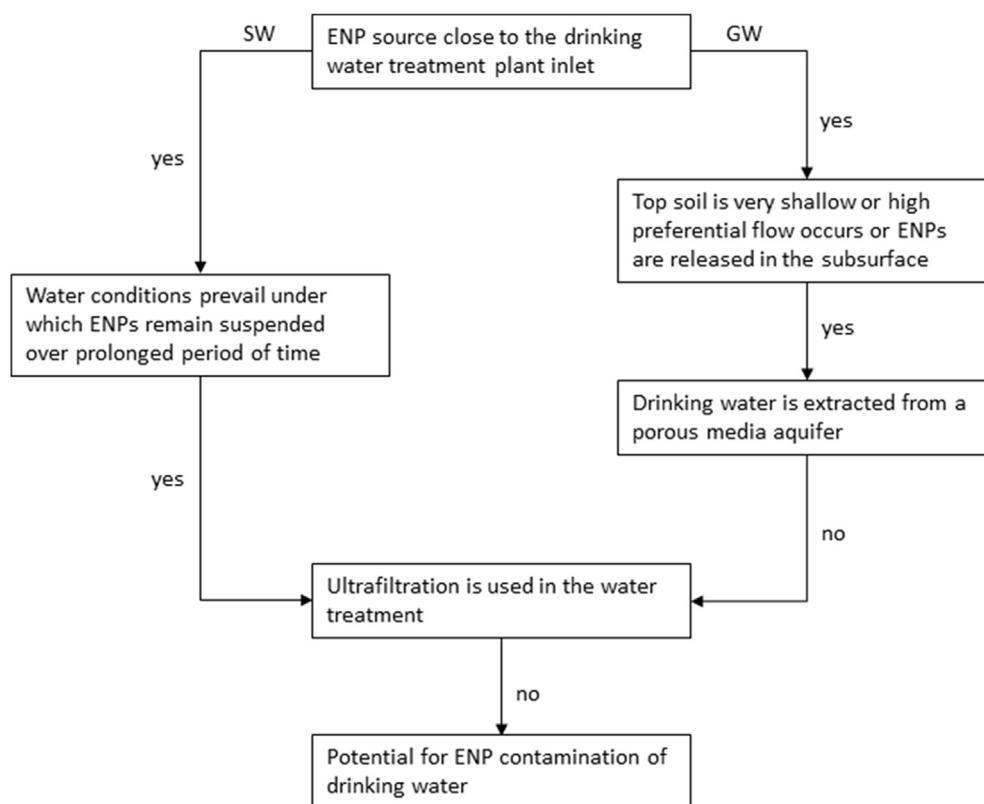


Fig. 12. Schematic representation of a decision tree model for assessing the risk potential for ENP contamination of drinking water from a production site. SW: Surface water; GW: Groundwater.

- The role of heteroaggregation (i.e. the aggregation of ENPs with natural particles) needs to be further addressed when investigating the parameters that influence the fate of ENPs in the natural environment.
- The potential remobilization of ENPs warrants further investigation, including the resuspension of settled ENPs and the disaggregation of aggregates containing ENPs. In order to estimate the vulnerability of groundwaters to ENP contamination it would be very useful to ascertain the conditions under which ENPs retained in porous media can be remobilized.
- With regard to the removal of ENPs during water treatment processes, additional information is required on the effectiveness of the combined processes of flocculation and sand filtration at removing ENPs.
- The fate of ENPs during their passage through an entire DWTP (i.e. through the different sequential treatment steps) requires further investigation.
- There is need to constantly update existing assessments and predictions for new particles showing up on the market, which might have a differing environmental behavior.

## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2016.03.038>.

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