

Low risk posed by engineered and incidental nanoparticles in drinking water

Paul Westerhoff^{1*}, Ariel Atkinson¹, John Fortner², Michael S. Wong³, Julie Zimmerman⁴, Jorge Gardea-Torresdey⁵, James Ranville⁶ and Pierre Herckes⁷

Natural nanoparticles (NNPs) in rivers, lakes, oceans and ground water predate humans, but engineered nanoparticles (ENPs) are emerging as potential pollutants due to increasing regulatory and public perception concerns. This Review contrasts the sources, composition and potential occurrence of NNPs (for example, two-dimensional clays, multifunctional viruses and metal oxides) and ENPs in surface water, after centralized drinking water treatment, and in tap water. While analytical detection challenges exist, ENPs are currently orders of magnitude less common than NNPs in waters that flow into drinking water treatment plants. Because such plants are designed to remove small-sized NNPs, they are also very good at removing ENPs. Consequently, ENP concentrations in tap water are extremely low and pose low risk during ingestion. However, after leaving drinking water treatment plants, corrosion by-products released from distribution pipes or in-home premise plumbing can release incidental nanoparticles into tap water. The occurrence and toxicity of incidental nanoparticles, rather than ENPs, should therefore be the focus of future research.

With limited occurrence or toxicity data for nanoparticles (NPs) in tap water, uncertainty exists regarding potential human risks from engineered nanoparticles (ENPs) in drinking water. In the drinking water community, some consider ENP risks as an important issue based on their potential toxicity^{1–3}. Others believe the expected low exposure concentrations in tap water^{4–6} make the risks negligible, especially when viewed relative to the persistent inability of many water systems to achieve current drinking water standards for pollutants with known acute or chronic human health risks⁷, or the significant infrastructure funding needed to keep public water systems operational⁸. Beyond a limited number of research-scale field occurrence studies^{4,6}, there are no large-scale occurrence datasets or regulatory mandates to monitor the presence of NPs in drinking water. In this Review, we apply the operational definition of NPs as having at least one dimension below 100 nm in size. Analytical tools are available to quantify NP size, chemistry and morphology in relatively simple ultrapure water matrices. However, due to their expected low concentrations in complex drinking water matrices containing differing types and levels of inorganic ions and organic matter concentrations, analytical methods to differentiate ENPs from naturally derived colloidal materials remain relatively nascent.

Drinking water systems in developed countries take a multi-barrier approach, from source to tap, to provide safe drinking water^{9–11}. Surface waters (rivers, lakes) generally provide over 80% of the water supply in developed countries, usually with smaller communities or private residences relying on ground water. This Review therefore focuses on the potential for ENPs to occur and be detected in untreated water surface sources, after centralized water treatment, and at consumer taps. We can say little about ENP occurrence in private wells or municipal ground water systems because of the paucity of data relative to information on surface water supplies for drinking water treatment plants (DWTPs). We relate ENP

occurrence predictions from materials-flow models and limited field measurements to occurrence predictions and measurements of natural nanoparticles (NNPs) or incidental nanoparticles (INPs) in drinking water. We conclude with views regarding the relative significance of NPs and their low risk to human health from drinking water NP exposure.

Nanoparticle occurrence in lakes and rivers

Watersheds have numerous sources of natural, incidental and engineered NPs^{12,13} that can enter DWTPs. Mineral weathering, sea spray, volcanoes and forest fires contribute natural particles (organic and inorganic) over a broad range of sizes, including at the nanoscale, to the atmosphere and surface waters¹³. Combustion, wear and corrosion processes release particles and molecular precursors to the air and water, which can produce INPs. ENPs in outdoor facades, vehicle components, foods, cosmetics, personal care products, textiles, industrial polishing processes, agriculture and urban infrastructure can be released over the product's lifespan and enter watersheds^{14–16}. For example, rainfall conveys stormwater containing ENPs (for example, TiO₂, Ag and ZnO ENPs weathered from building facades^{17–19}) into rivers and lakes that may serve as water supplies downstream. ENPs with industrial, commercial or in-home uses (for example, Ag, SiO₂, TiO₂ or CeO₂) enter sewage systems^{16,20–22}. Though wastewater treatment plants (WWTPs) can remove over 90% of ENPs from sewage through chemical, biological and physical processes, any remaining ENPs are discharged into rivers^{22–25}. Treated wastewater effluent also contains non-engineered colloidal-sized materials; 30% of the natural organic matter is below 100 nm in at least one dimension, including nanoscale fibrils, vesicles, inactivated viruses and other cellular debris²⁶. Because approximately half of the DWTPs in the United States are located downstream of at least one WWTP discharge²⁷, NPs in treated wastewater are potentially an important source of ENPs entering

¹Nanosystems Engineering Research Center for Nanotechnology-Enabled Water Treatment, School of Sustainable Engineering and the Built Environment, Arizona State University, Tempe, AZ, USA. ²Department of Energy, Environmental and Chemical Engineering, Washington University in St. Louis, St. Louis, MO, USA. ³Nanosystems Engineering Research Center for Nanotechnology-Enabled Water Treatment, Department of Chemical Engineering, Rice University, Houston, TX, USA. ⁴Nanosystems Engineering Research Center for Nanotechnology-Enabled Water Treatment, Department of Chemical and Environmental Engineering, Yale University, New Haven, CT, USA. ⁵Nanosystems Engineering Research Center for Nanotechnology-Enabled Water Treatment, Department of Chemistry, University of Texas – El Paso, El Paso, TX, USA. ⁶Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO, USA. ⁷School of Molecular Sciences, Arizona State University, Tempe, AZ, USA. *e-mail: p.westerhoff@asu.edu

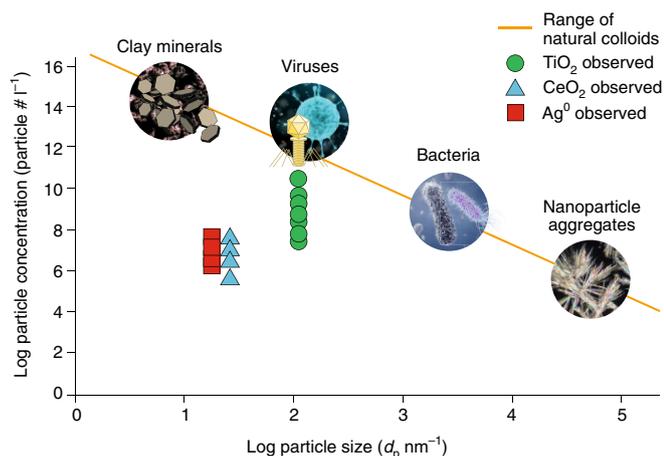


Fig. 1 | Distribution of particle sizes and number concentrations reported in surface, ocean and ground waters. The orange line represents a regression ($N \approx 3 \times 10^6 \times (d_p)^{-2.5}$) through multiple datasets^{32,33,42,150} of particle number (N) concentrations (number of particles per litre, $\# \text{ l}^{-1}$) as a function of particle diameter (d_p , nm^{-1}). Symbols represent reported ENP ranges of N from mass flux models, and field observations and were assigned to an average diameter^{4,5,15,16,52,78}.

drinking water sources¹⁵. For example, a modelling study of 126 products containing ENPs in the United Kingdom, most of which would enter surface waters via wastewater discharges, concluded that sufficient data existed to qualitatively rank ENPs from 62 products as potential drinking water contaminants⁵. The likelihood of higher ENP occurrence in surface waters parallels global production levels^{16,20}. Consequently, TiO_2 , ZnO , SiO_2 and Ag NPs were the most likely nanomaterials to be found at DWTPs⁵.

Our understanding of the exact composition, morphology and potential toxicity of natural or engineered colloids below 500 nm in our drinking water sources remains incomplete²⁸. Furthermore, such insight is complicated by the difficulty of analytical measurements, namely when discriminating ENPs from NNPs and INPs in water^{29–31}. NNPs are present in essentially all environments at mass concentrations ranging from 1–1,000 mg l^{-1} in surface waters³². Colloids in the 1–1,000 nm size range account for 40–60% of the organic carbon, 50–100% of the iron, and 30–70% of the aluminium in rivers, with the largest portion associated with smaller (1–100 nm) colloids^{33,34}. NNPs, INPs and ENPs have similar elemental compositions (for example, Si, Ti and Fe) or geometries (for example, spherical, two-dimensional and elongated rod^{3,35}), which means that shape or composition is not useful when discriminating ENPs from NNPs and INPs^{36,37}. Two promising techniques to size, quantify and potentially differentiate ENPs from other NPs are to modify existing instrumentation such as single particle (SP) inductively coupled plasma mass spectroscopy (SPICP-MS) or use a new time of flight (SP-TOF-ICP-MS) instrument. These techniques fingerprint NPs by simultaneously detecting multiple elements^{38,39}.

The distinction between NP mass concentration, number concentration and size distribution is important when interpreting NP occurrence, detection, fate modelling, regulation and exposure data. NNPs in water exhibit a very broad size distribution^{32,40,41}. Figure 1 was prepared from numerous reports on combined NNP/INP number-based size distributions, which can be fit by Pareto's Law ($N \approx 3 \times 10^6 \times (d_p)^{-2.5}$, where N is the number of NNPs), and shows that particle number concentrations (number of NNPs per litre) increase logarithmically per order of magnitude decrease in particle diameter (d_p , nm^{-1}), with mass and number concentrations for NPs being inversely related⁴⁰. The distributions illustrated in Fig. 1 are analytically time consuming to collect in field samples and often

involve combining data from discontinuous sizing analytical tools⁴². For example, the NP tracking analysis method is not effective in the range of 1–20 nm, leading to a drop-off in measured particle number^{43,44} at the smallest sizes. However, field flow fractionation with in-line ICP-MS detection has shown a bi-modal distribution of macromolecular- to colloidal-sized dissolved organic matter complexed with metals (for example, copper and lead) at approximately 1–10 nm, along with larger (>50 nm) inorganic NPs and colloids^{45–47}. These ligated dissolved metals likely behave very differently in water than colloids with crystalline or other physical structure⁴⁸. The ability to differentiate NPs from ligated metals at low concentration may depend on whether the measurement technique is sensitive to mass concentration or number concentration.

It is also important to consider analytical units, in part because the European Union definition of nanomaterials (that is, NPs) relies on a number concentration (that is, >50% of the particles in products being less than 100 nm in size^{49,50}), while most toxicity testing and drinking water regulations use mass concentration units. ENPs also often become associated (that is, hetero-aggregated) in natural waters⁵¹, which further complicates the analytical challenges in differentiating ENPs from NNPs. Thus, because NNPs and ENPs can (and will) co-occur in drinking water sources, there must be greater public and regulatory awareness regarding operational definitions of NPs⁵⁰ and potentially a need to differentiate between NNPs from ENPs analytically.

As illustrated in Fig. 1, ENPs are predicted, and in very limited cases field-validated, to occur at several orders of magnitude below the NNP number concentration in surface waters^{16,20,52,53}. Insights into ENP occurrence in source waters largely rely on empirical or mechanistic modelling of ENP sources, fate and transport in the environment^{51,44,43}. Such studies are useful in prioritizing the types of element (Ag, Ti, Si and Zn) and mass concentrations (ng l^{-1} to $\mu\text{g l}^{-1}$) of ENPs that could be monitored in rivers and lakes that serve as source waters. NP detection in rivers and other complex water matrices can be conducted directly on the whole water matrix or after extraction^{37,44,54,55}. Using spICP-MS^{56–60}, one study was consistent with modelled ENP concentration and was able to detect Ag NPs (average size 15 nm) at 0.3–2.5 ng l^{-1} , CeO_2 NPs (average size 19 nm) at 0.4–5.2 ng l^{-1} , and larger-sized TiO_2 particles (300 nm) at higher concentrations (0.2–8.1 $\mu\text{g l}^{-1}$) in all samples from two Dutch rivers⁶¹. Another study used spICP-MS to detect titania concentrations and particle sizes similar to that in the Dutch study, but found only a few TiO_2 particles upon extraction from river water and examination using transmission electron microscopy^{60,62}. Titanium mostly seemed to be part of other minerals in this study^{60,62}, which is consistent with other findings that titanium primarily associates to humics and other particles in surface waters⁶³. Limited field measurements for ENP occurrence in rivers that serve as drinking water supplies provide some validation for regional or national mass flow models⁶⁴, and these models predict ENP concentrations to be lower than any total metal concentrations enforced as part of drinking water regulations⁴. However, site-specific mechanistic models show the potential for elevated ENP hot spots in river systems when flow rates decrease^{65–67} or below point sources of ENPs (for example, WWTP discharges⁶⁸). These hot spots may be problematic if they co-occur with DWTP intakes. Field monitoring focused on ENP hot spots may provide useful data for applying and validating analytical methods that differentiate ENPs from NNPs and for developing ENP fate and transport models.

Nanoparticle removal during water treatment

DWTPs are designed to remove particles of varying sizes efficiently, from nanoscale viruses to micrometre-sized bacteria, oocysts and debris⁶⁹. Numerous review articles describe specific mechanism(s) for removing NPs at DWTPs^{4–6,70,71}. One lab study using ENPs spiked into surface waters and bench-scale drinking water treatment

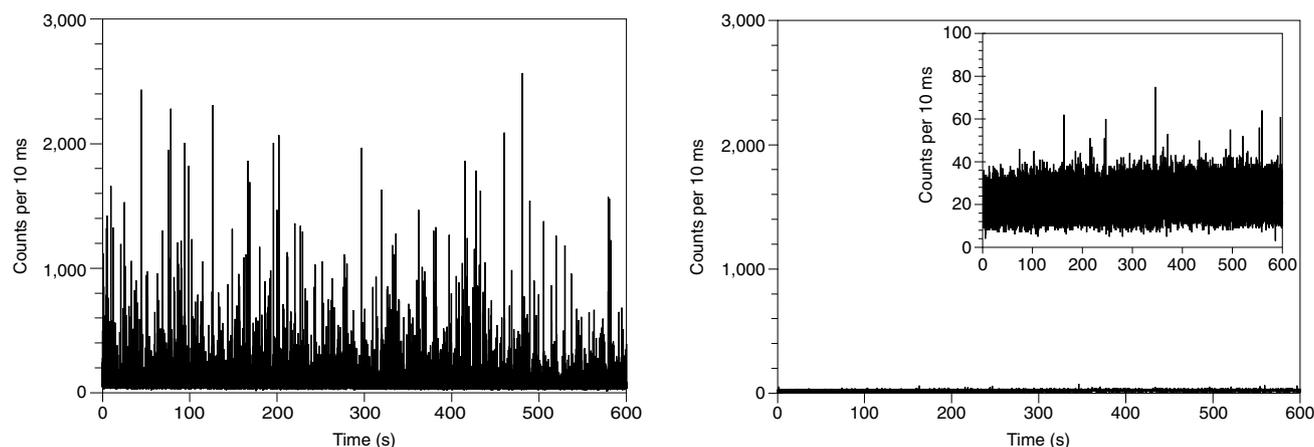


Fig. 2 | Time-resolved ^{49}Ti data for Verde River (left), and tap water from a DWTP treating Verde River water (right). Figure adapted from ref. ⁷⁸, Springer.

unit processes concluded that conventional DWTPs remove >80% of nano Ag, TiO_2 , ZnO, quantum dots and C_{60} (ref. ⁴). Elsewhere, authors identified a worst-case scenario, after applying estimated removal rates of 97%, 99% and 99.99% of NPs, depending on unit processes used at DWTPs (direct filtration, conventional processes or membrane treatment, respectively), where the highest-predicted ENP mass concentrations in drinking waters were in the low- to sub- $\mu\text{g l}^{-1}$ range⁵. More realistic scenario estimates were tens of ng l^{-1} or less⁵, which is significantly lower than most regulatory requirements for metals (see below). Laboratory and limited pilot testing that spiked ENPs into real or simulated drinking waters have shown that ENPs are removed after coagulation plus flocculation, which together form larger particles that will settle out of water or be removed during granular media filtration^{72–77}.

Very few studies report NP concentrations in tap water. Figure 2 illustrates one study's spICP-MS data for Ti in river water serving as an untreated supply for a DWTP, and the associated Ti in tap water after conventional treatment⁷⁸. Each spICP-MS 'pulse' represents non-ionic metal response by the spICP-MS. The river water (Fig. 2a) contains numerous pulses, equating to Ti-bearing minerals (such as clays) or possibly ENPs⁶⁰. The sensitive nature of this technique allows for the differentiation of particulate Ti (895 ng l^{-1}) from dissolved Ti (4,812 ng l^{-1}) in the river water. The observation that part-per-billion levels of soluble Ti occurs is surprising — the common perception is that titania is insoluble — yet consistent with other reports using ultra-filtration separation and other techniques to validate its presence⁷⁹. The pulses yield a distribution of Ti particle sizes⁷⁸, and faster data acquisition systems continue to improve the sensitivity in distinguishing particulate from ionic signals⁶⁰. The tap water (Fig. 2b) has almost no pulses and contains only 3.1 ng l^{-1} particulate Ti with a median equivalent spherical diameter of 124 nm, indicating >99% removal of Ti-containing NP by the DWTP. On a particle number basis, the river water contained $3.5 \times 10^4 \text{ ml}^{-1}$, compared with $7.5 \times 10^2 \text{ ml}^{-1}$ in tap water. The same study indicated >99% removal across the DWTP of Ce-based particles, which had mean equivalent spherical diameters of 10–40 nm (influent concentrations of 18 ng l^{-1} and 45 ng l^{-1} for particulate and dissolved Ce, respectively). The smaller diameter of the Ce-containing particulates equates to the tap water number concentration of $1.8 \times 10^4 \text{ ml}^{-1}$. This example illustrates the current analytical technology capabilities and efficiency of DWTPs to remove NPs, plus the application of spICP-MS for monitoring the mass or number and size distributions of NPs.

With decreasing access to freshwater supplies, many communities are increasingly relying on the treatment and reclamation of wastewater or stormwater to augment their potable water supplies. These alternative water supplies are hot spots that have elevated

ENP concentrations. Natural and engineered systems seem to be effective at removing ENPs from these impaired sources. Estimated ENP concentrations after membrane treatment of wastewater were 0.04 $\mu\text{g l}^{-1}$, 147 $\mu\text{g l}^{-1}$ and 0.28 $\mu\text{g l}^{-1}$ for Ag, TiO_2 and ZnO, respectively⁸⁰. Some drinking water utilities rely on bank filtration treatment, where wells located beneath or closely adjacent to rivers pull water through 10 to >100 m of sediment; predicted concentrations for bank filtration of the same ENPs were 3.3 $\mu\text{g l}^{-1}$, 13 $\mu\text{g l}^{-1}$ and 0.25 $\mu\text{g l}^{-1}$ (ref. ⁸⁰), respectively. Thus, while these ENP mass concentrations are very low, the work does illustrate how untreated sewage or treated wastewater can result in location-specific hot spots with ENP concentrations higher than those predicted by regional mass flux models. Additional hot spots may be associated with stormwater from urban areas or ENP spills⁸¹ into source waters (such as bridges or overturned trucks during rain events), including in developing countries, where industrial accidents or un-monitored discharges are more common than in developed countries.

Though DWTPs are not required to monitor for ENPs or NNPs, they do periodically measure nanoscale materials, either directly or indirectly. Historically, DWTPs have not differentiated nanoscale particles from ions. Drinking water regulations (United States Environmental Protection Agency (USEPA) or ASTM International specifications) and practitioners use an operational definition of 0.45 μm to differentiate dissolved from particulate^{82–84}, despite their long-standing recognition that colloidal materials and ligated-ions can at least partially pass these filters⁸⁵. This operational definition differentiates dissolved from particulate organic carbon, and size-differentiated fractions have been measured within dissolved organic carbon. DWTPs periodically directly measure colloidal organic material (that is, >10,000 Daltons, which equates to roughly >3 nm spherical NP⁸⁶), which some attribute to rod-shaped or transparent exopolymer particles⁸⁷ or vesicles, because these materials cause operational challenges (for example, membrane fouling)^{88,89}. The operational definition originated before 1970, when 0.2–0.45 μm filters were recognized to slow or prevent the biological transformation (that is, filter sterilization) of reactive chemicals (such as ammonium ion). To ensure consistent filtration process performance, DWTPs rely on surrogate optical measurements (that is, turbidity) rather than the direct measurement of biological particles, some of which are NNPs (for example, viruses are 40–400 nm). In some cases, particle counters that detect particles larger than 1 μm are used as surrogates for oocyst-sized particles (5–20 μm)⁹⁰. Particle-counting equipment for submicrometre particles in water is applied in ultrapure industrial processing applications where particle counts are low, but they are difficult to apply to tap water owing to the larger number of submicrometre particles^{91–93}.

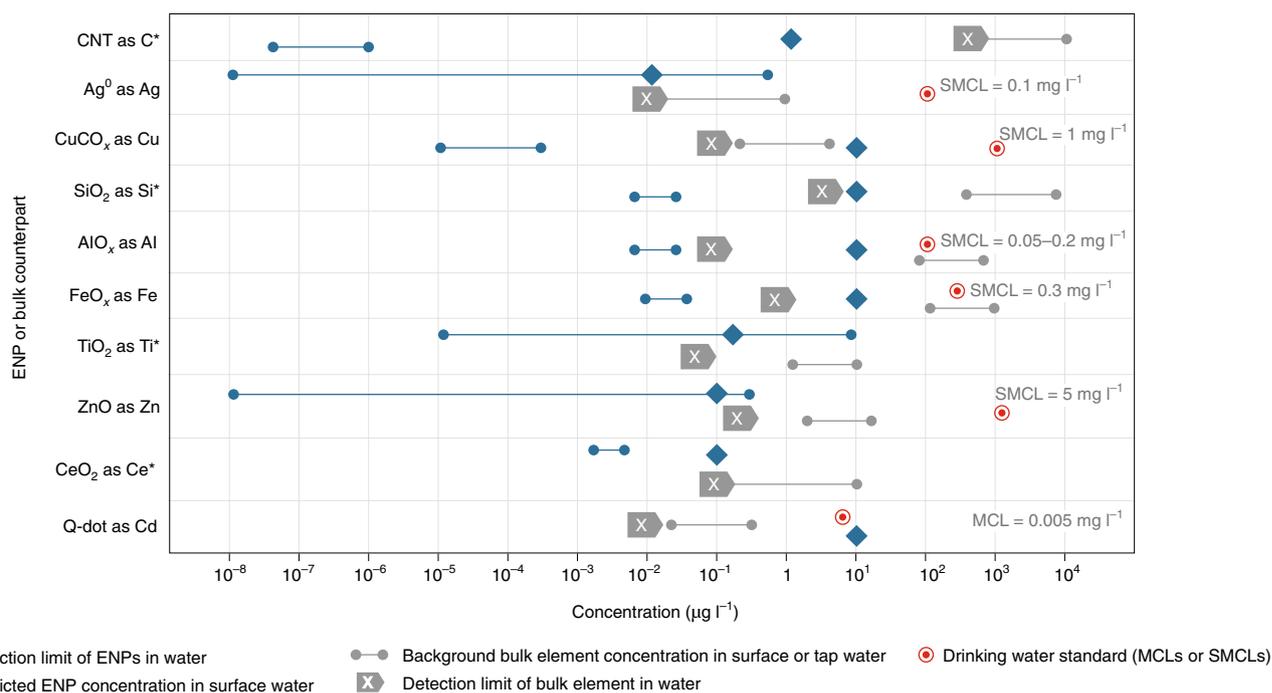


Fig. 3 | ENP predicted surface water concentrations, background bulk concentrations, detection limits and drinking water standards. Mass concentrations associated with MCLs or SMCLs are noted for metals with USEPA regulatory limits. *Element is not currently regulated by the USEPA in drinking waters. CNT, carbon nanotube; Q-dot, quantum dot. Figure adapted from ref. ⁴, Wiley.

As part of a recent six-year review process for the Fourth Unregulated Contaminant Monitoring Rule (UCMR4) conducted by the USEPA, nanomaterials were nominated for inclusion in DWTP monitoring. However, due to the general lack of evidence from modelling and research measurements that indicate their toxicity and presence in drinking water, nanomaterials were excluded from the 2018 UCMR4. Figure 3 illustrates drinking water regulatory limits for elements (Ag, Cu, Al, Fe, Zn and Cd) that compose some ENPs. In nearly all cases, regulatory limits are orders of magnitude higher than the predicted ENP surface water concentrations⁴. Figure 3 also illustrates that for many ENPs, current analytical techniques are probably unable to detect ENPs in water because ENP concentrations are predicted to occur at orders of magnitude lower than current instrument detection limits. No regulations exist for gold, palladium, platinum, ceria or titania, which are commonly used in ENPs, but these metals tend to occur at <50 ppt in tap waters, based on a limited number of field measurements. Thus, even without relying on 80% to >99% removal of NPs within DWTPs, the expected NP concentrations are well below current regulatory concerns.

Nanoparticles sources after the water treatment plant

After purification at centralized DWTPs, tap water travels under pressure for between several hours and more than 10 days through miles of pipe before reaching domestic taps. Extended travel times are a major cause of drinking water violations, being causative in disinfection by-product formation (for example, trihalomethanes), bacterial growth or contamination, and corrosion by-product release (such as Fe, Pb and Cu)⁷. ENPs and INPs can enter tap water during this travel time, the former releasing from pipe material coatings or leaching from in-home point of use (POU) devices (for example, ion exchange, membrane, activated carbon and disinfection technologies) and the latter from pipe corrosion by-products. Pipe materials and linings can contain NPs, including elongated rod-shaped particles like asbestos (for example, <1 to >10 billion fibres per litre have been detected in drinking waters due to use of

asbestos in pipe materials)^{94,95}, to more modern coatings that can include nanosilver or other ENPs⁹⁶. Polyvinyl chloride piping materials contains 1–2 wt% TiO₂, which is added for colour, strength and UV protection⁹⁷, and is used in potable water systems and premise plumbing. However, data is lacking on TiO₂ NP release from pipes under variable operating conditions (for example, temperature and water quality) or extended operation periods (decades). More significant is the formation of lead, copper or iron corrosion scales in city and household pipe networks, which can slough off during hydraulic surges or changes in water chemistry^{98–101}. Beyond separating dissolved from particulate forms using 0.2–0.45 µm filters^{99,101–103}, little is known about the presence or reactivity of <100-nm-sized corrosion products. However, our recent unpublished work, which requires only modifications to conventional spICP-MS, demonstrates the ability to differentiate and quantify dissolved and nano-sized elements in tap waters. In this study, tap waters ($n = 44$, where n is the number of samples analysed from different tap waters) were collected from three buildings, and particles containing Pb, Sn, Fe and Cu were detected at average concentrations (ng l⁻¹) of 1.2 ± 1.3 , 1.8 ± 3.0 , 88 ± 144 and 69 ± 45 , respectively, representing a minimum of 0.4%, 18%, 16% and 0.2% of the corresponding total dissolved concentrations. Figure 4 shows the particle size distribution frequency. The minimum detectable size¹⁰⁴ for the elements was 26, 13, 55 and 140 nm, respectively. While nanoscale forms of these metals were detected, the mass concentrations (ng l⁻¹) are 1,000 times less than levels of regulatory concern (Fig. 3).

POU treatment devices installed under sinks and in locations such as refrigerators, garages and restaurants represent a >US\$20 billion yr⁻¹ market for treating private well-water or tap water provided by municipalities, and some of these devices can contain NPs (nanosilver, copper or carbon nanotubes)^{105–112}. POU devices seek, and all water treatment plant contact-materials require, certification from National Sanitation Foundation International^{113,114}, a private-public partnership, but nano-specific guidelines do not currently exist that allow companies to claim “nanoparticles are removed by the device” or “nanoparticles are not released from the device.” Some POU

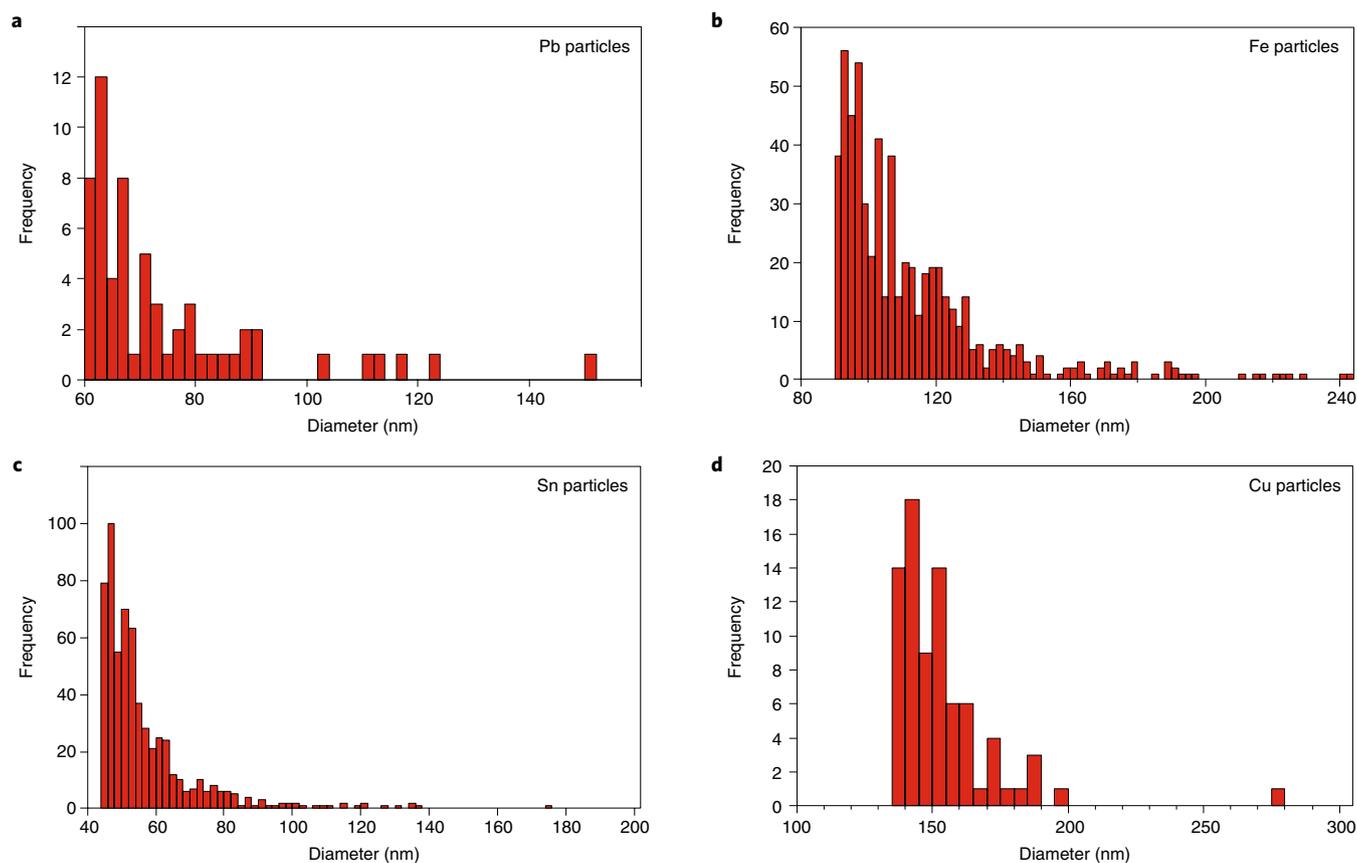


Fig. 4 | Typical size distribution of metal-containing particles detected in tap waters collected from Phoenix, AZ.

devices use nanosilver, and in the United States, silver has a non-enforceable secondary maximum contaminant level (SMCL) of 0.1 mg l^{-1} due to its potential to discolour human skin (that is, argyria, which is a cosmetic effect) or turn grey the white part of the eye. The USEPA acknowledges “A [SMCL] standard has been set; however, because silver is used as an antibacterial agent in many home water treatment devices, it presents a potential problem that deserves attention”¹¹⁵. An example POU system that benefits from ENPs is an intentional release or dissolution of NPs from membranes embedded with silver NPs to inhibit biofouling permeate¹¹⁶. Silver loading of the order of $1\text{--}10 \mu\text{g cm}^{-2}$ inhibits biological growth on membranes, most likely due to the slow dissolution of silver NPs, thus releasing Ag^+ ions that inhibit bacterial growth^{117,118}. Static leaching tests or small-volume permeation tests suggest an initial short-term silver occurrence in membrane permeates at $0.001\text{--}0.010 \text{ mg l}^{-1}$ (refs ^{119–121}). A POU spiral wound reverse-osmosis membrane — impregnated using in situ methods that achieve similar silver loadings and operated for 60 days using tap water — found $0.01\text{--}0.03 \text{ mg l}^{-1}$ of silver released during the first few hours and then $<0.002 \text{ mg l}^{-1}$ of silver released thereafter. Only ionic silver was detected in the membrane permeate¹¹⁶. Thus, silver concentrations in drinking water (reverse-osmosis permeate) from membranes impregnated with silver NPs designed to control microbial growth seem to be well below the silver SMCL of 0.1 mg l^{-1} . POU devices are often considered a luxury, but as urban water systems evolve, expanded reliance on whole-building or tap POU-like devices may play more significant roles in cities¹²². While ENP leaching from POU devices is expected to be low, little data exists on ENP release from nano-enabled POU devices, and guidelines for such devices and technologies (for example, from the American National Standards Institute or the European Committee for Standardization) may be warranted.

Nanoparticles pose low risk in tap water

NNPs have always been ubiquitous components in surface and ground waters, and hence have been present at some level in our tap water for nearly a century since the installation of centralized potable water treatment systems. However, the low occurrence of ENPs in tap water does not necessarily equate to an elevated human health risk. The limited measurements of ENPs in source water, treated water leaving DWTPs, and even tap water, generally agree with occurrence models, which have found that elemental concentrations (Ag, Cu, Al, Fe, Zn and Cd) that compromise some ENPs are more than 1,000 times below the primary health maximum contaminant levels (MCLs) or non-enforceable SMCLs (Fig. 3). Therefore, the hazard (that is, toxicity) of ENPs would have to be more than 1,000 times higher than the ionic metal form, which was the basis for establishing the MCLs. Studies suggest the opposite is the case for most ENPs, relative to their equivalent ionic form¹²³. For example, many studies show nanosilver to serve primarily as a silver ion delivery mechanism¹²⁴ and, when dosed into solution, nanosilver is often less toxic than the equivalent mass concentration of silver ions^{125–127}. Similar observations have been made for copper and zinc¹²⁸. Reported LC_{50} ranges for mammalian cells are of the order of $10\text{--}50 \text{ mg l}^{-1}$ for silver, copper and zinc ENPs¹²⁸, which would exceed existing MCLs and SMCLs. Additional knowledge on elimination versus uptake of ingested metal-based ENPs would be helpful. For example, if NPs were less (more) able to be cleared by the gut, greater (lesser) exposure would occur. Nearly all existing MCLs for metals are based on mass concentration, though a number-based MCLs do exist for asbestos in drinking water (7×10^6 fibres per litre) and bacteria (heterotrophic plate count <500 bacterial colonies per millilitre). There are currently no MCLs that are specific to NPs.

At the time of writing, there are no published reports that show toxicity or human disease associated with ENP ingestion in drinking water at relevant exposure levels. Most available toxicology data related to NP ingestion is associated with either consuming nanomaterials in food or investigating ENP concentrations significantly higher than those present in drinking water¹²⁹. For non-regulated metals that are reported to occur as ENPs with high global usage potential (for example, Ti, Ce, Au and Si)^{16,20}, limited occurrence data exists for drinking water systems. These ENPs tend to be fairly insoluble in typical drinking water matrices and have high threshold concentrations before inducing toxicity in humans. In fact, Ti and Si are widely used in foods and are consumed by people already at mg day⁻¹ levels^{54,129–133}, though debate continues regarding their potential health effects^{134–136}. The bio-availability of ENPs in the intestinal track is thought to be low but remains debatable¹³⁵, with some studies showing that TiO₂ NPs could translocate through the epithelium and Peyer's patches¹³⁷, and that silver ions could dissolve from Ag-NP to become bio-available¹³⁸. This high intake of food-grade Ti and Si ENPs subsequently leads to their occurrence in wastewaters and, hence, occurrence at very low levels in DWTP source waters. While research has shown food-grade TiO₂ and SiO₂ is well-removed during wastewater treatment and resides in sludge, the TiO₂ in WWTP effluent seems to be smaller (20–30 nm) than food-grade (30–300 nm) TiO₂, and may have differing origins^{23,24,130,131,139,140} or potentially differing hazards during ingestion.

The ability to differentiate ENPs from NNPs and INPs could have several benefits for the water industry. The relative abundance of each class provides insights into their sources. Hence, the differentiation of ENPs could aid in mitigation measures as part of a multi-barrier strategy to improve tap water quality. This may be increasingly important over the coming decades as ENP use in society is expected to increase⁵ and corresponding projections of ENP occurrence in untreated drinking waters may become greater, thus necessitating monitoring, regulation and control strategies. With increased use of ENPs to improve the treatment of drinking water¹⁴¹, differentiation could validate that no ENP release occurs from POU or other DWTP treatment technologies and materials. Aging water distribution system infrastructure and premise plumbing may lead to INP increases, and techniques to detect INPs may aid in identifying mitigation measures. The interactions of some pollutants with INPs (for example, lead or arsenic associate with iron pipe corrosion-based INPs) may alter their residence times in the gastrointestinal tract compared with ionic forms. As such, the ability to differentiate ionic from NP-associated elements could be helpful. Finally, differentiating ENPs from NNPs and INPs in tap water may reduce the uncertainty in perceived ENP risks in drinking waters by regulators or the public, especially if ENPs are shown to be a tiny fraction of the number or mass concentrations of an elemental species.

Adverse acute health risks from ingesting drinking water are generally associated with microbial pollution and are well-managed in developed countries. Chronic health risks associated with drinking water consumption are generally driven by pollutants (for example, arsenic) with carcinogenic endpoints. Compared with chronic exposures to chemical pollutants, considerably less is known regarding NP toxicity during tap water ingestion. Current drinking water regulations do not, in most-cases, differentiate natural from industrial sources of chemical pollutants (for example, arsenic and nitrate). But when it is possible to differentiate (for example, radionuclides), more stringent regulations exist for anthropogenic chemical pollutants. The assumption that NNPs or ENPs of similar composition exhibit similar toxicity may not be appropriate. For example, while silica dioxide is abundant, and isomorphically substituted silica dioxide is a common structure in most clays in natural waters, there is evidence

of size-dependent toxicity of engineered SiO₂ if ingested; smaller sized (15 nm) SiO₂ exerts more toxic effects than 55 nm SiO₂ on Caco-2 cells, but only at concentrations above 10 mg l⁻¹ (ref. ¹⁴²). Dissolved and colloidal silica both occur in drinking waters at 1–50 mg l⁻¹ (ref. ¹⁴³), but nearly all the silica would have to be present as 15-nm-sized SiO₂ to begin observing effects similar to those reported for Caco-2 cells. Likewise, not all titanium oxides exhibit comparable toxicity¹⁴⁴. While there is a low risk due to low NP exposure, systematic studies could be used to better understand transformations within the gut^{129,145} and hypothesize toxicity mechanisms during low-level chronic ingestion exposure to INPs and ENPs of different sizes.

The water industry tends to be cautious and conservative in regulating, designing and operating DWTPs because of the potential health impact on large populations. It will be prudent for the drinking water community to conduct occurrence studies in tap water for the most common metallic ENPs in industry (SiO₂, TiO₂, Fe, Al₂O₃, ZnO, CeO₂, CNT, nanoclays, Cu and Ag). Data collection should focus on occurrence and total metal concentrations for ENP elements not currently regulated in drinking water (for example, Ce, Si and Ti) because nanosized materials are a subset, and are thus more difficult to quantify, of the total elemental concentration. Risk assessment could be advanced using the more conservative total metal concentrations. Occurrence data already exists for elements associated with primary or secondary MCLs (Ag, Al, Cu, Fe and Zn), and there is clear evidence that the nanoscale forms of these metals are not many thousands of times more toxic than the ionic forms. Nanoclays contain silicon, so understanding total Si concentrations in drinking water would provide a worst case, maximum estimate of nanoclay occurrence (assuming all the silicon was present solely in nanoclays). Carbon nanomaterials are currently predicted to occur at very low levels in source waters, so unless global production rates increase by more than 1,000 times, the focus for carbon NPs should be on preventing and quantifying their release from materials used in water infrastructure (for example, pipe coatings) or POU devices. A focus for monitoring should be hot spots where ENP releases could impact DWTP intakes (for example, DWTPs located downstream of dense urban communities that produce stormwater runoff and wastewater discharges).

Compared with traditional pollutants, considerably less is known about NP toxicity during tap water ingestion, and this uncertainty underpins public concern. Even for chemical pollutants (for example, pharmaceuticals) with known health risks and low (ng l⁻¹) occurrence in drinking water, public perception regarding the safety of water cannot be overstated or avoided by water utilities. While such perception is often influenced by aesthetics (taste, odour and colour)¹⁴⁶, the perception of drinking water safety extends to other classes of chemicals (for example, pharmaceuticals and personal care products)^{147–149}. Nearly two decades of intensive data collection on low-level pharmaceutical occurrence at DWTPs has allowed water professionals to better communicate with the public, pre-empt regulations due to the lack of data, bring together aquatic ecosystem and human health communities, and provide tools for individual DWTPs to install technologies as needed to address concerns regarding this class of chemical pollutants. The drinking water community can learn from experience with these other classes of non-regulated pollutants, and should continue developing more selective ENP analytical detection methods and monitoring for ENPs in numerous drinking water systems. Gaining the ability to differentiate the tiny fraction of ENPs in tap water from the higher occurrence of NNPs and INPs in tap water may alleviate public, DWTP operator and regulator concerns.

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Competing interests

The authors declare no competing interests.

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