Review

Current status and future direction for examining engineered nanoparticles in natural systems

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Environmental context. The detection and characterisation of engineered nanomaterials in the environment is essential for exposure and risk assessment for this emerging class of materials. However, the ubiquitous presence of naturally occurring nanomaterials presents a unique challenge for the accurate determination of engineered nanomaterials in environmental matrices. New techniques and methodologies are being developed to overcome some of these issues by taking advantage of subtle differences in the elemental and isotopic ratios within these nanomaterials.

Abstract. The increasing manufacture and implementation of engineered nanomaterials (ENMs) will continue to lead to the release of these materials into the environment. Reliably assessing the environmental exposure risk of ENMs will depend highly on the ability to quantify and characterise these materials in environmental samples. However, performing these measurements is obstructed by the complexity of environmental sample matrices, physiochemical processes altering the state of the ENM and the high background of naturally occurring nanoparticles (NNPs), which may be similar in size, shape and composition to their engineered analogues. Current analytical techniques can be implemented to overcome some of these obstacles, but the ubiquity of NNPs presents a unique challenge requiring the exploitation of properties that discriminate engineered and natural nanomaterials. To this end, new techniques are being developed that take advantage of the nature of ENMs to discern them from naturally occurring analogues. This paper reviews the current techniques utilised in the detection and characterisation of ENMs in environmental samples as well as discusses promising new approaches to overcome the high backgrounds of NNPs. Despite their occurrence in the atmosphere and soil, this review will be limited to a discussion of aqueous-based samples containing ENMs, as this environment will serve as a principal medium for the environmental dispersion of ENMs.

Introduction

Nanotechnology is a rapidly burgeoning industry. New capabilities to control matter at scales of 1 to 100 nm are producing an enormous range of novel nanomaterials, often having properties that are unique compared to matter of a similar chemical composition but larger in size. Many of these nanomaterials are already incorporated into industrial and consumer products.[1] A search of recent patent literature indicates that the trend towards incorporation of nanomaterials into products such as computers, solid state lighting, solar cells, etc. will likely continue for decades to come.[2] Governments throughout the world, and public interests groups have called for regulation to encourage the safe deployment of these new materials. This includes an assessment of potential risks that nanomaterials may pose to human health and to the environment.

Risk assessment will require an understanding of the inherent toxicity of the nanomaterials, the properties of those materials that lead to toxicity and the potential for exposure to those materials.[3] The nanotoxicology research community is currently working to modify established toxicity testing protocols to work for nanomaterials, or in some cases establishing new testing paradigms.[4] However, toxicity and ecological effects will ultimately be dose dependent and therefore accurate risk assessment also requires an ability to predict and measure environmental concentrations of engineered nanomaterials (ENMs) so that exposures can be determined. Accurately assessing exposure potential to nanomaterials has significant challenges that have not yet been adequately addressed by the nano Environmental Health and Safety (EHS) research community. In particular, the fundamental processes affecting the fate

of ENMs and their distribution in the environment have not yet been determined.[5] This stems in part from the inherent kinetic instability of nanomaterials and in part from the vast number of potential 'environmental' conditions that an ENM may encounter.[6] Each of these environmental conditions may transform the nanomaterial, thereby changing its toxicity potential.[7,8] As noted in several recent reports by the National Research Council, significantly more work is needed to determine the 'critical elements of interaction' influencing ENM fate and distribution in the environment, and to develop a reliable testing strategy and suite of tools for assessing the exposure potential through the lifecycle of the nanomaterial.[9]

Releases of ENMs into the environment may occur sporadically by accidental spills, but a significant portion of ENMs' long-term release may come from consumer product manufacture, use and disposal and from intentional nanotechnology applications such as groundwater remediation and agricultural uses.[10–12] Determining environmental concentrations will rely on rigorous detection, characterisation and quantification of these materials in environmental samples.[13–15] Accurately detecting and characterising these materials in the environment is beset by several obstacles. Their small size (1–100 nm), low expected concentrations (ng L^{-1}), and the high background of naturally occurring nanoparticulate matter (NNPs), particularly NNPs having compositions similar to ENMs, make detection of ENMs in environmental samples very difficult. In addition, a variety of environmental processes may alter the pristine, manufactured state of the engineered nanoparticles (ENPs), requiring an understanding of how these processes will affect their quantification and characterisation.[14]

In this special collection of papers, the chemical factors that influence the fate and distribution of ENMs in the environment are explored. The ultimate goal of these types of studies is to better assess the distribution of ENMs in the environment, exposure potential and ultimately biouptake into a highly complex ecosystem. Achieving this goal will require new nanometrology instrumentation or adaptation of existing instruments to make them specific towards ENMs, and to work at the very low concentration of ENMs expected in environmental and biological media. Given the central role of metrology in exposure assessment, this first paper provides a review of the challenges for the detection and characterisation of ENMs in environmental samples. A short review of instrumentation used for ENP characterisation is included. A selection of recent work

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performed to differentiate between naturally occurring and ENMs will be discussed. In addition, new approaches that are currently being developed to differentiate ENMs from their naturally occurring analogues will be discussed. The research reviewed herein will focus on ENMs found in aqueous environments, as life cycle assessments (LCAs) consider aqueous and soil and sediment environments to be especially important reservoirs for released ENMs.[16,17] For brevity, atmospheric and incidental nanoparticles (those created unintentionally) have been excluded from this discussion despite being a significant source of nanomaterials in the environment. Methods for the characterisation and detection of these nanomaterials have been reviewed elsewhere.[18]

Properties of ENMs

Nanomaterials are commonly defined as materials with at least one size dimension between 1 and 100 nm.[14] In addition to nanoparticles (three nano dimensions), fibres, rods, films and plates are all common nanomaterials that are manufactured and produced for their novel properties. The upper size limit of 100 nm is arbitrary and it may be more appropriate to utilise the size at which chemical and physical properties differ from their bulk counterparts as the proper nano upper size cut-off.[19] In addition to their high specific surface area and higher proportion of surface atoms, some nanomaterials can exhibit quantum confinement and novel optical-electrical properties at the nanoscale, particularly at sizes below 20 nm. For instance, the catalytic activity of gold is found to be highly dependent on the size of the nanoparticle.[20] Quantum dots specifically can have significantly different emissions depending on nanocrystal size, and thus have a very low tolerance for changes in diameter.[21]

Although any material with a size dimension between 1 and 100 nm may be classified as a nanomaterial, only certain materials at the nanoscale will exhibit properties desirable for engineering and subsequent commercial applications. These nanomaterials can possess a varying degree of composition and complexity. Some nanomaterials are composed of a single element (i.e. carbon nanotubes (CNTs), nano-Ag), whereas others can be very complex (i.e. quantum dots (QDs) with CdSe–ZnS–polymer core shell organisation). Metallic nanomaterials have many potential uses such as heterogeneous catalysis with nano-gold, and antimicrobial applications of nanosilver in such products as textiles and plastics.[22–24] Metal oxide nanoparticles such as titanium dioxide and zinc oxide are commonly found in coatings and sunscreens for their photocatalytic properties.[25–28] Cerium dioxide nanoparticles can be found in fuel additives for their ability to produce cleaner diesel exhausts.[29,30] Semiconductor nanoparticles such as QDs have found applications in both the energy sector and in biomedical imaging and drug delivery.[31–35] Lastly, carbonaceous materials such as fullerenes and CNTs have broad application in energy products, solar cells and the strength improvement of materials.[36–38]

In addition, ENMs may possess highly engineered surface coatings, aiding in the control and utilisation of properties such as dispersability, solubility, reactivity and surface binding selectivity of the nanomaterial. Commonly used surface coatings can provide electrostatic (i.e. citrate, tannic acid) or steric (i.e. poly(vinylpyrrolidine)) stabilisation to prevent aggregation and maintain a monodisperse particle population. In addition to stabilisation, some surface coatings are applied to nanomaterials to enhance their biocompatibility and transport through biological systems. Chitosan, polypeptides, fatty acids and polyethylene glycol (PEG) are common choices.[39,40]

The multitude of properties and inherent complexities of these materials require robust and comprehensive analytical techniques to study them. This necessitates a multi-faceted approach for accurate characterisation. In addition, there are several environmental factors that may impede the ability to detect and characterise ENMs in the environment. The vastly greater quantity of naturally occurring nanomaterials, coupled with the multitude of environmental processes that alter the pristine nature of the ENM, will further complicate the quantification and characterisation needed for assessment of ENM risk. This is illustrated in Fig. 1, where the different inputs from environmental and anthropogenic sources will lead to a complex mixture of nanomaterials in the aqueous environment. These materials can potentially share similar or identical morphologies, compositions and properties that render most current analytical techniques inadequate for detection and characterisation. The current aim of developing methodologies and techniques is to exploit slight differences in the discriminating properties of ENMs and natural particles, which will be discussed later in this review.
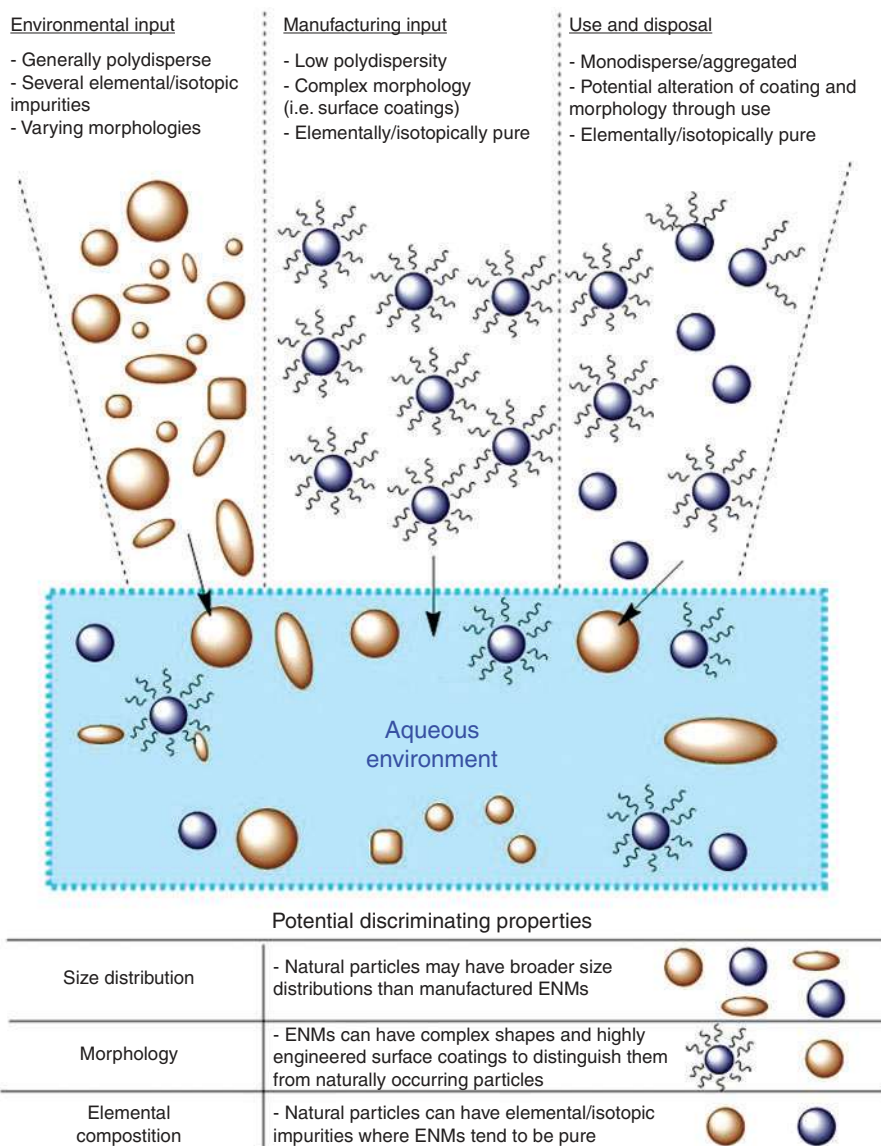
Nanomaterials in the environment

Arguably the largest obstacle to the detection and characterisation of ENMs in environmental samples is the large proportion of naturally occurring nanomaterials and colloids. Their presence makes analyses of ENMs difficult for a variety of reasons. Because all particles scatter light to some degree, light scattering methods will be rendered useless because of their non-specific nature. Similarity in chemical composition with NNPs can obscure the concentration of ENMs obtained by elemental analysis (inductively coupled plasma mass spectrometry (ICP-MS) and optical emission spectroscopy (ICP-OES)). Particle morphologies and sizes may also be similar, making non-specific sizing methods utilising imaging (electron microscopy, particle tracking) and spectroscopy ineffective. In addition to the high background of naturally occurring nanomaterials, the environmental processes to which ENMs are subjected and subsequent transformations also make their detection and characterisation challenging.

Occurrence of natural nanomaterials

Naturally occurring nanomaterials are present in essentially all environmental samples at mass concentrations ranging from 1 to 1000 mg L^{-1} in surface waters and 0.01 to 80 mg L^{-1} in marine environments.[41] Comparatively, ENMs are expected to enter into the environment at much lower mass concentrations (ng L^{-1}), several orders of magnitude below the concentration of natural materials.[42–44] Natural colloids have been found to follow Pareto's power law, implying a very broad size distribution and a high degree of polydispersity.[45] Specifically, particle number concentrations increase logarithmically per decade of particle size decrease. This presumably will also be the case for natural nanoparticles over the three orders of magnitude (1–100 nm) in the defined nanoparticle size range. This is in contrast to ENPs, which are often produced to have a specific mean size with a defined upper and lower boundary. NNPs vary in size, compositions and morphology (Table 1) and can serve as interferences for detection of most engineered materials.

These NNPs can be formed from different pathways either through mechanical erosion and weathering (top-down synthesis) or through precipitation and biogenic pathways (bottom-up

Environmental input

- Generally polydisperse
- Several elemental/isotopic impurities
- Varying morphologies

Manufacturing input

- Low polydispersity
- Complex morphology (i.e. surface coatings)
- Elementally/isotopically pure

Use and disposal

- Monodisperse/aggregated
- Potential alteration of coating and morphology through use
- Elementally/isotopically pure

Aqueous environment

Potential discriminating properties

Size distribution	- Natural particles may have broader size distributions than manufactured ENMs
Morphology	- ENMs can have complex shapes and highly engineered surface coatings to distinguish them from naturally occurring particles
Elemental compostition	- Natural particles can have elemental/isotopic impurities where ENMs tend to be pure

Fig. 1. Different nanomaterials inputs will lead to a complex mixture of naturally occurring and engineered nanomaterials (ENMs) in the aqueous environment. Though these materials may share similar properties, morphologies, and composition, slight differences in these properties may be exploited for detection and characterisation in the environment.

Table 1.   Potential naturally occurring nanomaterial (NNPs) interferences for engineered nanomaterials (ENMs) in the environment

NNP	Chemical composition	Analogous ENM
Clay (phyllosilicates)	Variable Al, Si, O (other potential metal cations)	Al_2O_3, TiO_2, SiO_2, CeO_2
Iron and aluminium oxides	Fe_2O_3 (hematite)	Fe_3O_4 (Magnetite), Al_2O_3, zero-valent iron
	FeOOH (–OCl) (Akaganéite)	
	$Fe_5O_3(OH)_9 \cdot 4H_2O$ (Ferrihydrite)	
	$AlOH_3$ (Gibbsite)	
Metal sulfides	Ag_2S, ZnS, CdS	Nano-Ag, ZnO, quantum dots (i.e. CdSe, CdTe)
Humics, biological materials (cells and detritus)	Variable C, H, O, N, abundance of carboxylic acid and phenolic groups	Carbon nanotubes, fullerenes

synthesis).[16,17,46,47] These materials play an important role in a multitude of environmental processes ranging from nutrient and contaminant transport to soil stability.[46,48] NNPs can further complicate the potential ENP fate and exposure by affecting the transport of these materials either by stabilising them in solutions (i.e. humic acid surface coatings) or accelerating the aggregation of these materials (i.e. NNP–ENP heteroaggregation).[49–55] NNPs interfere with the bulk chemical analysis of

ENMs in environmental samples because of their similar elemental compositions. Heteroaggregation between NNPs and ENMs will also alter the effectiveness of separation-based methods such as field flow fractionation (FFF) and hydrodynamic chromatography (HDC) for characterising NNPs. Similarities in size and morphology of NNPs and ENMs greatly complicate the application of imaging techniques such as electron microscopy. Clearly the abundance of these natural materials presents a considerable, and possibly the greatest challenge to the detection and characterisation of ENMs in the environment. New methods of ENP analysis must address this challenge, as well as be sensitive to the consequences of various environmental processes acting upon and altering the pristine nature of the ENMs.

Transformation of ENMs

In their initial pristine state, ENMs are generally chemically well defined. When used for highly engineered applications (e.g. nanomedicine, photonics) there are typically monodisperse to maximise their desired function. Furthermore pristine ENMs often have specific, sometimes complex surface functionalities; in the simplest cases meant to prevent aggregation or facilitate incorporation into products. Conceivably these surface functionalities could be utilised in their detection and quantification. However, when exposed to the environment, several different chemical processes act upon these materials leaving them in an altered state that may be very different from their initial engineered or commercial form.[7] This alteration makes the detection and characterisation of these materials more difficult, and requires some knowledge of how these processes may have changed the nanomaterial, in order to identify the ENM of interest. The properties unique to ENMs as opposed to NNPs (i.e. monodispersity, well defined chemical composition, highly engineered surface coatings) are all subject to change upon entry into the environment.

Dissolution and oxidation–reduction reactions can alter the original chemical structure of the ENM. Metal and metal oxide nanomaterials, made with soft metal cations (e.g. Ag, Zn, Cu), are particularly susceptible to these reactions and may undergo dissolution or complexation with strong ligands in the environment. Silver nanoparticles for instance may oxidise rapidly to Ag^+ and in reducing environments form Ag_2S, or in fully oxic environments reform into halogenated insoluble precipitates (i.e. AgCl(s)).[56–58] Other nanomaterials may form an oxide shell, altering the surface composition of the material and subsequently changing its physical and chemical properties.[59–64] In addition to chemical oxidation–reduction reactions, some materials may be susceptible to photooxidation and photoreduction, which can act to change the structure and properties of the ENM. Carbonaceous nanomaterials such as CNTs and fullerenes are prone to producing carboxy and hydroxyl groups on its surface as well as generating reactive oxygen species (ROS) in the presence of sunlight.[65] The chemical alteration of the ENP, possibly accompanied by size changes, require characterisation techniques that can capture these changes and detection methods that remain sensitive to the ENPs.

Changes to the engineered surface coatings of ENMs (Fig. 2) are expected to be commonplace in the environment. Coatings that are weakly bound to the surface to provide stabilisation are expected to be removed with relative ease in environmental samples; whereas those covalently linked to the surface of the particle may be irreversibly bound and difficult to remove.[66,67]
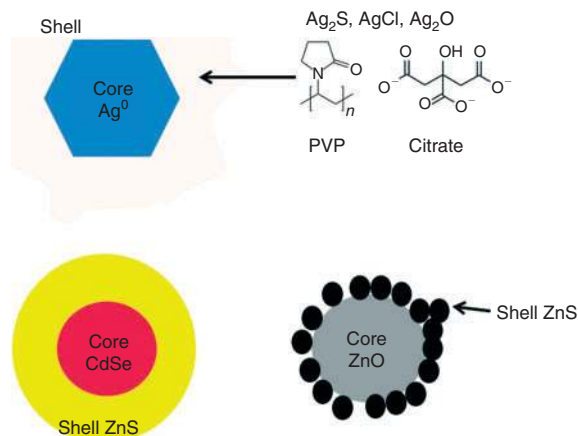
Fig. 2. Common nanomaterial coatings and surface groups. (PVP, polyvinylpyrollidone.)

A major pathway that may cause the loss of coatings is sunlight exposure, as sunlight-catalysed redox reactions can degrade some polymeric coatings present on ENMs.[68] The loss of engineered polymeric coatings may induce instability and facilitate (hetero-)aggregation. Conversely, polymeric-like molecules may be present in the environment and upon sorption, are capable of imparting strong electrostatic charges or steric stability to the surface of the nanomaterial preventing aggregation. Humic substances in particular have been shown to overcoat or replace the surface groups of ENMs, and impart a strong negative electrostatic charge through the numerous carboxylic acid and phenolic groups intrinsic in their molecular structure.[49,50] Other small proteins and organic molecules have been known to interact with nanomaterial surfaces resulting in changes to the dissolution, reactivity and aggregation of the ENMs.[69–71] The presence of chemically unique surface coatings could conceivably be exploited for detection through techniques such as mass spectrometry. The alteration of ENP surfaces has the effect of removing this property as a means of ENP detection and characterisation.

Lastly, the monodisperse nature of ENMs is not expected to persist in environmental matrices. As the surface coatings of ENMs are expected to be altered, over-coated or replaced in the environment, chemical constituents present in the environment can play a significant role in the transport and subsequently the detection and characterisation of these materials. Aggregation is generally the result of the loss of repulsive behaviour between particles, resulting in an attraction generated from van der Waals forces between particles. This can be brought on either by constriction of the electrical double layer in high ionic strength solutions, or bridging between particles by oppositely charged counter ions in solution.[72–74] Many unique 'nano' effects are a function of the size and surface area of the ENMs (i.e. fluorescence, surface plasmon resonance), these properties, and thus their use for ENP detection, may be lost upon aggregation. Heteroaggregation (aggregation between particles of dissimilar composition) is also expected to be a prevalent mechanism in the environment, which can further complicate the analysis of ENMs in environmental samples.[51,52,75,76] In particular, the presence of heteroaggregated ENMs leads to the need for further development of sample pretreatment methods such as chemical and mechanical dispersion and sample prefractionation by coarse filtration or centrifugation, e.g. the use of specific

molecular weight cut-offs, or analytical centrifugation methods used for protein separation and characterisation.[77]

The current means of analysing ENMs in environmental samples requires a multi-faceted approach as individual analytical methods are ill-equipped to address the various obstructions that arise in the analysis of these materials. Although a great deal of work has been performed to accurately assess ENM fate and behaviour in the environment, there are still several obstacles to the application of existing nanometrology for environmental ENP quantification and characterisation, and are currently a point of emphasis in environmental research.

Current state of ENM analysis for environmental media

Owing to the intricate nature of ENMs and their subsequent alteration in environmental samples, a multifaceted approach is required for the accurate determination of these materials, as ENP detection, quantification and characterisation are all highly interrelated. An important characteristic to be determined is the size and polydispersity of the ENP. This analysis can be carried out for pristine ENMs in simple matrices, utilising a variety of techniques, yet each have their inherent drawbacks when applied to environment samples. Dynamic light scattering (DLS) is the most commonly employed high-throughput method to measure nanoparticle size in aqueous dispersions, but is less useful for the analysis of polydisperse samples because of difficulty interpreting the scattering signal. Being an ensemble technique, that is the instrument response arises from many particles, DLS is rendered essentially useless when interfering particles are present, as would generally be the case for ENMs extracted from environmental media.[49,50,78] Direct coupling to FFF and HDC at least partially overcomes the problem of polydispersity and interfering particles by providing separation of different particle sizes and presenting narrow size fractions to the DLS detector.[79,80]

An emerging light scattering technique is nanoparticle tracking analysis (NTA), tracking the Brownian motion of particles to determine diffusion coefficients and subsequently the size of the nanoparticle. The particle is first detected by light scattering, and then the distance the particle travels from its initial position within a given time interval as determined by the frame rate speed of a charge-coupled device (CCD) camera. A modified Stokes–Einstein relationship is then used to calculate the hydrodynamic diameter according to the distance travelled by the particle. Additionally, particle composition might be determined by comparing scattered light intensity from particles of the same size. The major obstacle of NTA is choosing the appropriate track length to size a statistically relevant number of particles and attain an ample particle size distribution.[81–83]

Electron microscopy (EM) techniques such as scanning (SEM) and transmission electron microscopy (TEM) are other very common analytical techniques, used in the sizing of nanomaterials. Unfortunately sample preparation for EM, as well as the imaging of the sample, requires that the sample be under vacuum, which may introduce artefacts that can alter the true environmental state of the ENM.[83,84] Some improvements have been made to preserve environmental sample integrity for EM imaging (i.e. WetSEM).[85] However, EM methods are single particle methods, and as such a size distribution is built up one particle at a time. Although this approach makes EM a low-throughput method even with automated image processing, it does offer the potential to size ENMs in the presence of interfering particles, something that DLS is incapable of.

Obtaining size information by EM methods when background particles are present requires that morphological or chemical features of the ENP can still be used for identification of the ENP fraction of particles. As previously noted, environmental alteration of the ENMs may make this difficult.

An emerging sizing technique is differential centripetal sedimentation (DCS), which can provide high-resolution size information if the density of the material is known. In a common DCS analysis (disc centrifugation), the sample is injected into a spinning disc filled with liquid, in which a density gradient is generated. The sample migrates towards the outside of the disc and passes through a beam of visible light, allowing for the absorbance with time to be converted into a diameter by Stokes law (assuming a spherical geometry). Although the analysis times are dependent on the polydisperisty and density of the sample, most analyses take place on the order of only a few minutes. This rapid analysis makes it an attractive technique for the sizing of nanomaterials. However, only a few samples may be run before the fluid in the spinning disc must be drained and replaced.[86,87]

Fractionation techniques such as field flow fractionation (FFF) (e.g. flow-field flow fractionation, Fl-FFF; sedimentation-field flow fractionation, Sed-FFF) and hydrodynamic chromatography (HDC) can size nanomaterials in aqueous matrices, and for ENMs separated from soil or any solid matrix, and have the added benefit of providing size fractions for further characterisation. However they should be considered ensemble techniques as many particles are eluting from the FFF or HDC at any given time. These methods can only distinguish between natural and engineered particles if differences in chemical composition can be utilised. The most commonly used approached for this chemical identification is FFF coupled to an element-specific detector (e.g. ICP-MS). FFF and HDC are limited by extensive method development, high detection limits (dependent on detector), and non-ideal sample behaviour during separation, which may require additional sample preparation and pre-fractionation steps.[88–91] Analysis times range from tens of minutes up to an hour, making it generally faster than EM analysis but still far from being a high-throughput approach. Single particle (sp) ICP-MS, a very recently introduced technique, has the ability to size and characterise a range of metal and metal oxide nanomaterials in environmental matrices at low concentrations (ng L^{-1}).[92–96] However, the size detection limit for this technique is dependent on the signal generated by the ablation of the nanoparticle, which may require a significant amount of ions to generate a recognisable intensity pulse. In addition, although its elemental specificity is a desirable attribute, it may be unable to differentiate between an engineered and naturally occurring nanomaterial of the same elemental composition.[81,92–95,97] Despite the limitations of FFF-ICP-MS and sp-ICP-MS, the use of these methods for ENP detection may be a significant step forward and will be elaborated upon in a subsequent discussion.

ENP surface groups and surface charge are also properties that may be important to characterise for ENMs, as they will directly influence the fate and transport of these materials in the environment. Both NMR and IR spectroscopy have been used in this respect to characterise the surface functionality of ENMs, specifically FTIR has been used to study humic acid adsorption onto silica and magnetite nanoparticles.[98–100] Yet, as previously discussed, the surface functionality of the ENM is subject to change upon exposure to the environment and may conform to the surface coatings of other naturally occurring materials in the

system (i.e. humic acid coatings, biofilms). Surface charge is primarily determined through electrokinetic measurements and commonly reported as zeta potential for nanomaterials, but as an ensemble technique, the determination of surface charge for a specific nanomaterial is not possible without a prior prefractionation step that could alter the representativeness of the environmental sample.[49,50,78]

Other parameters such as particle number concentration and morphology are also very difficult to obtain in environmental samples. Particle counting techniques are obstructed by the higher number of naturally occurring particles. Aggregation of the pristine ENM may result in significant underestimates of particle number concentrations. Particle composition is subject to the many chemical reactions and processes that may severely affect the pristine or crystalline nature of the ENM, making it difficult to discern between natural and engineered analogues.

Assessing the fate of ENMs requires an ability to assess chemical composition, oxidation state, and structure. X-Ray absorption spectroscopy (XAS) is presently the only established method that allows for in situ determination of these ENM properties in environmental samples, primarily for metal and metal oxides. The advantage of XAS over other techniques is that it is non-destructive, absorption spectra can be collected directly from wet samples, including soil, sediment and tissue, and it is element specific, i.e. you collect information only on a specific element in the sample such as cerium, silver or titanium. Disadvantages are that metal concentrations of 10 to 100 mg kg^{-1} are required in the sample to get adequate signal. However, with fairly simple sample concentration techniques, e.g. collection of fines from specific samples, the lower end of the detection limit may be extended. XAS provides an 'average' speciation of the specific element in the samples and therefore does not provide ENM specific information. ENMs made from very common environmental elements such as iron or aluminium could be difficult to characterise using XAS because of the presence of high background concentrations of that element. Some recent examples of the use of XAS to assess NP fate include the ZnO and Ag NP fate in wastewater treatment plants (Ma et al.,[101] Lombi et al.[26,102]), the transformations of Ag NPs in a freshwater wetland mesocosm[26,101–103] and speciation of ZnO, CuO and TiO$_2$ NPs in wheat and cucumber plants exposed to these nanomaterials.[104,105]

An accurate determination of environmental ENP concentration is a necessary measurement for exposure assessment. Although size is arguably the most important physical characteristic of ENMs, chemical composition is not only an important ENP characteristic, but may also serve as the best means for determining environmental concentrations. Through differences in chemical composition, ENMs might be quantified in the presence of background particles. Particle counting techniques that are non-chemical specific, such as NTA, are compromised by the higher number of naturally occurring particles. Furthermore, aggregation of the pristine ENM may result in significant underestimates of particle number concentrations.

Table 2 reviews current analytical approaches for characterising ENMs in environmental samples as a framework for determining potential future directions, namely element specific methods (i.e. sp-ICP-MS, FFF-ICPMS and XAS), for the detection, quantification and characterisation of ENMs in the environment.

New approaches

Perhaps the most direct and robust means of characterising and counting ENMs remains to be through visualisation methods,

most commonly by electron microscopy. Although this is generally straightforward for simple systems, it is also obvious that visual identification is problematic for environmental samples as many naturally occurring nanomaterials share similar morphologies to commonly used ENMs. Fig. 1a, b illustrates this issue using Fe$_2$O$_3$ as an example. Perhaps in some unique cases highly crystalline ENMs having complex shapes might be discernable from more irregular natural materials, but as previously discussed, transformation of the ENPs may quickly alter this property.

As a result, a better discriminating property may be elemental and isotopic composition, which might be used to differentiate naturally occurring and ENMs. Although the elemental composition approach might be obvious for nanoparticulate elements that are rare (i.e. Au, Ag) it may not be possible for more commonly occurring nanoparticulate elements. The hematite example (Fig. 3a) would seem to fit this case, as both materials contain primarily iron by weight. However, natural hematite is known to contain significant amounts of impurity elements including V, Ti, Mg and Ca, among others. In contrast, hematite prepared by precipitation in the laboratory (Fig. 3b) is low in impurity elements. The following sections provide hypothetical methodologies, and discuss challenges to using elemental composition data as a means to differentiate engineered and naturally occurring nanomaterials for the purpose of quantifying and characterising ENMs in environmental samples.

Bulk elemental ratio approaches

One possible method of detecting the presence of inorganic ENMs in a specific environment is to examine the elemental ratios of the nanoparticulate matter present in the system (von der Kammer et al.[106]). NNPs in aquatic systems, as well as in soils and sediments, contain several elements, in ratios that may be specific to a given geographic location, which should be a fingerprint of the natural particle population and reflect the source materials (i.e. watershed soils or aquifer materials). This can be the result of the geology of the underlying rock from which most of the particles are formed, the sources of river sediments and sediment diagenesis, dissolution, precipitation, the heteroaggregation of several different minerals or the formation of surface precipitates or coatings on the particles. Furthermore, as previously discussed, even individual mineral phases may contain minor and trace element impurities that may display ratios characteristic of a geographic region or specific field site of interest. This can directly contrast with elementally and isotopically uniform anthropogenic ENMs. Nanoparticles prepared from bottom-up syntheses are likely to be either elementally pure (e.g. metal oxides, metals) or have fixed elemental ratios (e.g. CdSe/ZnS quantum dots (QDs), Al/Ti sunscreens). In the conceptual example illustrated below (Fig. 4), a natural system will contain an assortment of natural mineral particles that contain a certain ratio of two elements, in this example cerium and lanthanum. As particle concentrations vary, either temporally or geographically, the elemental concentrations may closely co-vary. If engineered cerium dioxide (CeO$_2$) were introduced into the system in sufficient mass, the ratio will shift towards more cerium, as lanthanum is nearly absent in these ENPs. Application of the element ratio approach requires that the elemental ratios are determined specifically for the nanoparticulate fraction of the soil or sediment, or that the ratios established on bulk samples are identical to those in the nano-range. Also, isolating the particulate fraction of the sample by filtration or centrifugation, followed by elemental

Table 2. Need for improved analytical approaches

TEM, transmission electron microscopy; SEM, scanning electron microscopy; sp-ICP-MS, single particle inductively coupled plasma–mass spectrometry; DLS, dynamic light scattering; Fl-FFF, flow-field-flow fractionation; Sed-FFF, sedimentation field-flow fractionation; ENMs, engineered nanomaterials; NNPs, naturally occurring nanoparticulate matter; FFF, field flow fractionation; NTA, nanoparticle tracking analysis; EDX, elemental X-ray analysis; OES, optical emission spectroscopy; XAS, X-ray absorption spectroscopy

| Measured property	Current analytical approaches	Obstacles to accurate detection and characterisation	Potential need
Particle size	TEM, SEM, sP-ICP-MS, UV-vis, DLS, Fl-FFF, Sed-FFF	Introduction of artefacts from sample drying (TEM/SEM)	Analysis of samples in situ with minimal sample preparation
		No elemental specificity (DLS)	Elemental specificity to differentiate between dissimilar nanomaterials
		Inability to differentiate between ENMs and NNPs of similar elemental composition (sP-ICP-MS, TEM, SEM)	Requires another measured property to differentiate between particles of similar elemental composition
		Obstructed by high background of natural particles (sP-ICP-MS, TEM, SEM, DLS, FFF)	
Surface groups	NMR spectroscopy, FTIR spectroscopy, zeta potential	Original coating may have been replaced or overcoated in the environment (all current approaches)	Ability to differentiate between different particle populations in situ
		Ensemble techniques unable to characterise individual particle populations without prior fractionation steps (all current approaches)	Knowledge of how surface groups are attached may help determine if original coating
Particle number concentration	sp-ICP-MS, NTA	Unable to distinguish aggregates from single particle without parallel imaging or sizing technique	Require knowledge pertaining to aggregation state of ENMs
Elemental composition	EDX, sp-ICP-MS, ICP-MS, ICP-OES, XAS	Unable to discern particles of natural or engineered origins	Determination of elemental composition in situ with additional sample preparation (i.e. acidification)
		May require acidification, eliminating particle integrity (ICP-MS, ICP-OES)	
		Sample preparation may alter sample representativeness	Improve detection levels for X-ray based spectroscopy
		Concentration of ENM in sample may be too low (XAS)	
General considerations			
Mass detection limit		ENMs are expected to enter into the environment at very low concentrations (nanograms per litre)	
Size detection limit		Most nanomaterials are between 1 and 100 nm (many smaller than 20 nm)	
Aggregation state		Most nanomaterials are not expected to preserve monodisperse state in the environment	
		Need ability to discern aggregated from single particle material.	
NNPs		Concentration of NNPs in the environment are several orders of magnitude above that of ENMs (milligrams per litre *v.* nanograms per litre)	
		Some NNPs have similar elemental composition and morphologies to ENMs.	
		NNPs tend to be very polydisperse and can interact with ENMs in the environment.	

analysis, will be required to improve sensitivity of the method. Whereas several techniques can provide elemental or phase data on solids (e.g. neutron activation, X-ray methods) the sensitivity and precision of ICP-MS will be needed for the concentrations of ENMs expected.

The ability to detect ENMs through perturbations in the natural ratio depends both on the amount of ENMs introduced, the magnitude of the elemental ratio in the ENP and the NNP, the variation of the ratio in the NNPs at the sampling location, the concentration of the natural nanoparticulate element and the ability of the MS to quantify the ratios with high precision. The analytical precision of the measurement on each element in the ratio will depend on several instrumental factors, including the sample processing procedures and the choice of ICP-MS (e.g. quadrupole, magnetic sector, multi-collector). The analytical methods likely contribute least to the uncertainties that limit the application. In general, high-resolution ICP-MS instruments can measure element ratios to 0.1 % (one part per thousand) accuracy. For a bulk sample analysis of element ratios, in order for an engineered CeO_2 particle to be detected, it must contribute on the order of 1/1000 of the total Ce mass in a sample. If background particulate matter is in the milligrams per litre range, with Ce present as a few tenths of a percent of the particle mass, then Ce from ENMs must be present in the range of a few tens of micrograms per litre. The practical application of a bulk

isotope measurement for ENP detection at realistic environmental concentrations will likely depend mostly on the natural variability of elemental ratios in the system under investigation and the concentration of background particles. Fig. 4 shows data for the correlation between La and Ce for natural waters across a wide geographic range of Europe. In principle engineered CeO_2 would be detectable if it is introduced into European surface water in a quantity sufficient to shift the La/Ce ratio out of the 95 % confidence interval of the regression line. Based on the data presented in Fig. 4 concentrations on the order of $0.1–5\,\mu g\,L^{-1}$ are needed, depending on the total particulate Ce concentration. Focussing on a specific geographic site, or reducing the time-scale of investigation, might reduce this value, as localised Ce/La ratios are likely to be more constant than across a widespread region. This can be illustrated even by data retrieved from sites separated by large distances, but with similar characteristics. Fig. 5 compares the Ce/La ratios for filtered surface waters ($<0.45\,\mu m$) retrieved from Saliminen[107] with those locally established for small catchments draining peat bogs and wetlands in Germany, Sweden and Austria. Further data on variability of elemental ratios are needed to further evaluate the potential for success of the bulk elemental ratio approach.

Although bulk elemental ratios may provide a method by which to monitor the presence of ENMs, it provides minimal
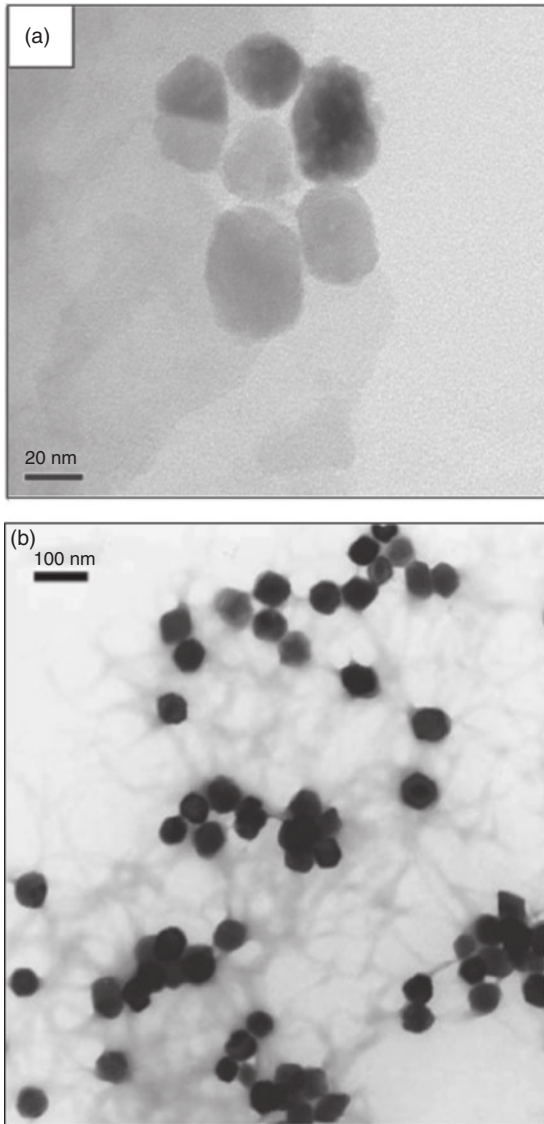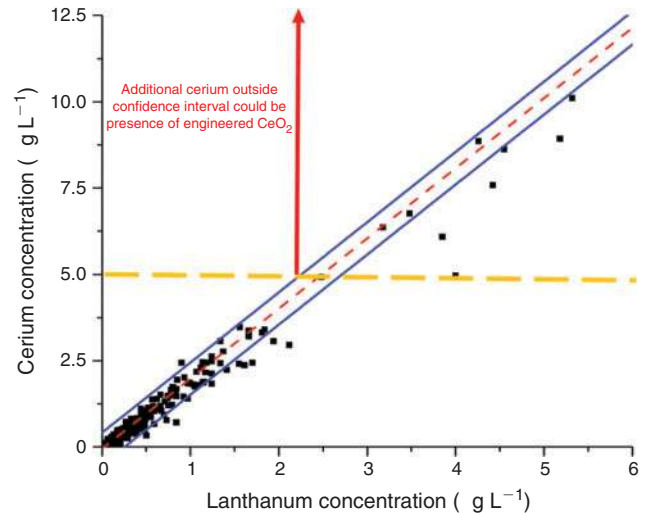
Fig. 3. (a) Hematite (Fe$_2$O$_3$) nanoparticles found in free drifting ice-bergs.[110] (b) Aggregated alginate-coated engineered hematite nanoparticles.[111]

**Fig. 4.** Hypothetical scenario investigating bulk elemental ratios in a natural system and one affected by engineered CeO$_2$ nanoparticles. Natural data points (■, $n = 805$) come from the Geochemical Atlas of Europe showing a relationship between cerium and lanthanum.[107] The red arrow represents a hypothetical situation where engineered cerium nanoparticles are introduced into the system at increasing mass concentrations, altering the Ce/La ratio.
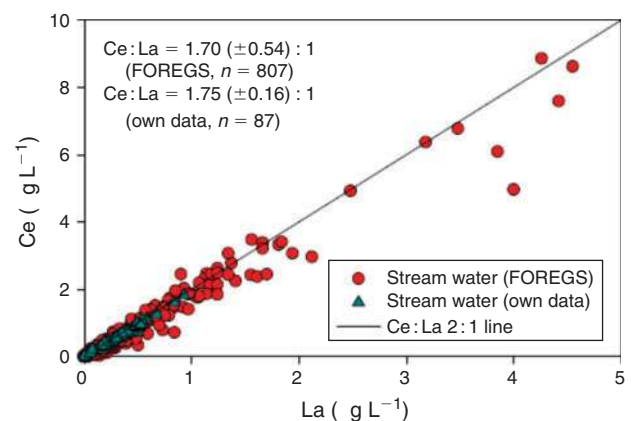
Fig. 5. Comparison of Ce and La concentrations derived from the Geochemical Atlas of Europe and own data collected from creek catchments in Sweden, Germany and Austria.[112–114] The much lower variation in the locally established ratios is clearly visible. (FOREGS, Forum of the European Geological Survey.)

information on the ENM properties, and is subject to a variety of environmental factors (e.g. redox, pH) that may alter the composition of the naturally occurring mineral population in the system, particularly if particle composition is influenced by heteroaggregation. Further characterisation of the system may yield pertinent information such as size and size distribution, which combined with the elemental ratios may facilitate ENP detection.

Separation methods with elemental detection: FFF-ICP-MS

In addition to taking advantage of differences in the elemental ratios between naturally occurring and anthropogenic nanoma-terials, possible differences in the size distributions of nano-materials might be utilised to improve the element ratio approach for differentiating ENMs from NNPs. For highly engineered ENMs, in the absence of heteroaggregation with natural nanoparticles, the expected size distribution is expected to be much narrower than background nanoparticulate and colloidal matter. If an approach to isolate and measure element ratios on only the size fraction of total particulate matter that overlaps with the ENP is applied, ENP detection may be facil-itated. Although serial filtration or centrifugation are possible approaches, the superior size resolution of FFF is likely to prove more successful. Additionally the direct coupling of FFF to ICP-MS provides simultaneous separation and elemental analysis, unlike sequential batch fractionation approaches. This is particularly useful as environmental processes, particularly heteroaggregation, may alter the monodisperse nature of the engineered particles, preventing the identification of a mono-disperse population of ENMs. This is potentially overcome by also employing chemical or mechanical dispersion in order to examine the primary particles present in the sample.

The advantages of a front-end size fractionation coupled to element ratio measurements become apparent in the following
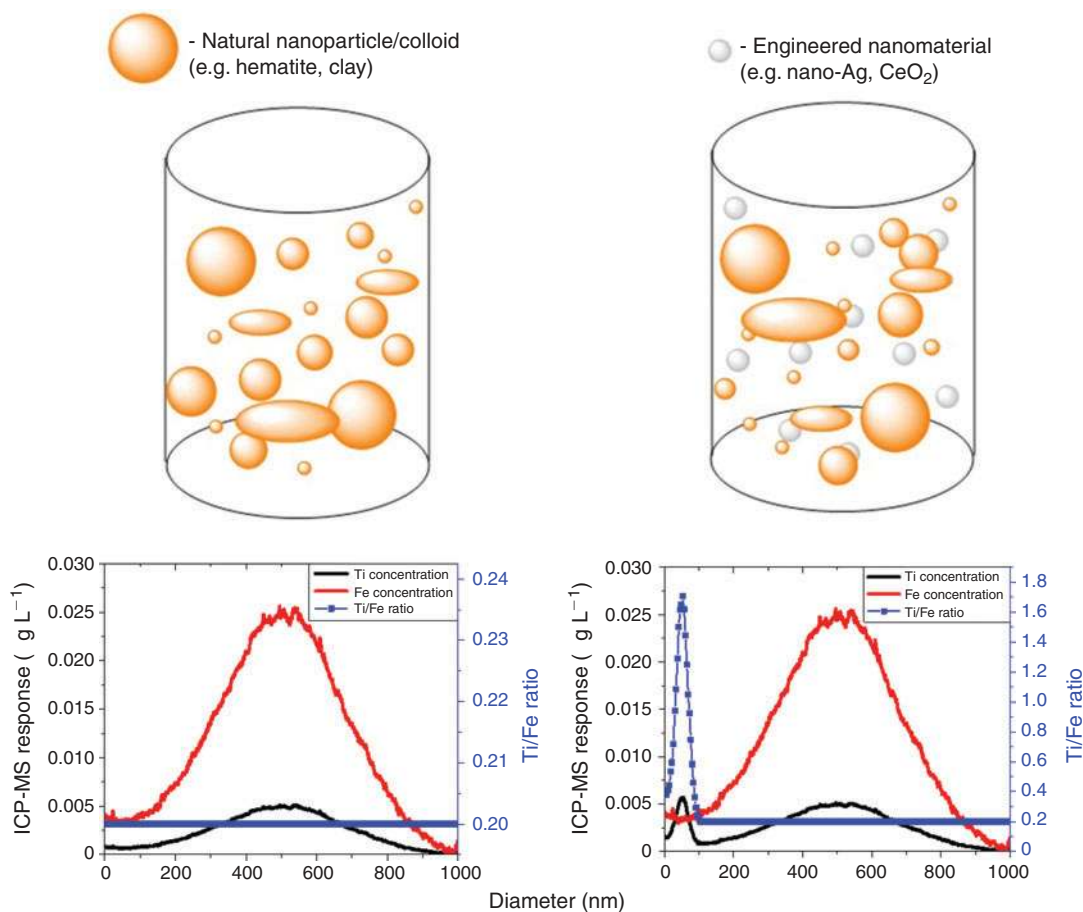
Fig. 6. Hypothetical field flow fractionation–inductively coupled plasma–mass spectrometry (FFF-ICP-MS) fractogram comparisons of a natural systems containing both naturally occurring Ti- and Fe-containing minerals, and a system (right) that has been spiked with engineered TiO$_2$. Naturally occurring colloids will generally be polydisperse resulting in a broad ICP-MS signal, whereas engineered nanoparticle (ENP) populations tend to be monodisperse, resulting in a sharp increase in ICP-MS signal in narrow size ranges.

example. Fig. 6 demonstrates a possible scenario comparing a natural system where Ti- and Fe-containing minerals are present. The fractogram shows a hypothetical clay mineral with a broad distribution from ~200 to 800 nm. When engineered titanium dioxide nanoparticles are introduced, a narrow population of additional titanium containing particles is detected in the fractogram, with no change in the iron concentrations.

In this particular scenario we assume the background iron concentration is 30 µg L^{-1}, and titanium background concentration is ~6 µg L^{-1}, giving a Ti/Fe ratio of 0.2 as follows (Eqn 1).

$$\frac{\text{Ti concentration } (\mu g\,L^{-1})}{\text{Fe concentration } (\mu g\,L^{-1})} = \frac{6\,\mu g\,Ti\,L^{-1}}{30\,\mu g\,Fe\,L^{-1}} = 0.2 \quad (1)$$

An introduction of 50 nm (25–75 nm) of titanium dioxide nanoparticles at a concentration of 60 ng Ti L^{-1} will change the bulk ratio of titanium to iron in the system. Averaging the concentration across the entire size range, in this example 0–1000 nm, the difference between natural and perturbed environmental ratios is minimal (Eqn 2):

$$\frac{6\,\mu g\,Ti\,L^{-1} + 60\,\mu g\,TiO_2\,L^{-1}\,NPs}{30\,\mu g\,Fe\,L^{-1}} = 0.219 \quad (2)$$

However, if we use FFF we can determine the Ti/Fe ratio at specific size ranges, allowing for the potential identification of ENMs outside the natural elemental ratio. If in fact the conditions of this example are actually met, which are: the ENMs' elemental size distribution is narrower than the natural distribution (questionable) and elemental ratios do not display much variation across the size distribution of the natural particle size range (likely), the FFF-ICP-MS approach will be more successful than a bulk elemental ratio approach. A database of bulk elemental ratios exists,[107] which allows examination of future samples in order to observe perturbations indicative of the introduction of detectable levels of ENMs. However no such database exists for the size distribution of elemental ratios. If the size interval that is likely to be affected by ENMs displays significant variation from the bulk ratio the method will be significantly affected. Successful application might be limited to site specific studies where a suitable 'background' sample can be characterised for its elemental ratio size distribution and compared to a potentially affected downstream site.

The absence of heteroaggregation between ENMs and natural nanoparticles and the ability of FFF-ICP-MS to differentiate these particles could be shown on a mixture of stabilised soil nanoparticles and colloids and a 30-nm gold nanoparticle dispersion (citrate-coated gold NPs of BBI, UK). Fig. 7
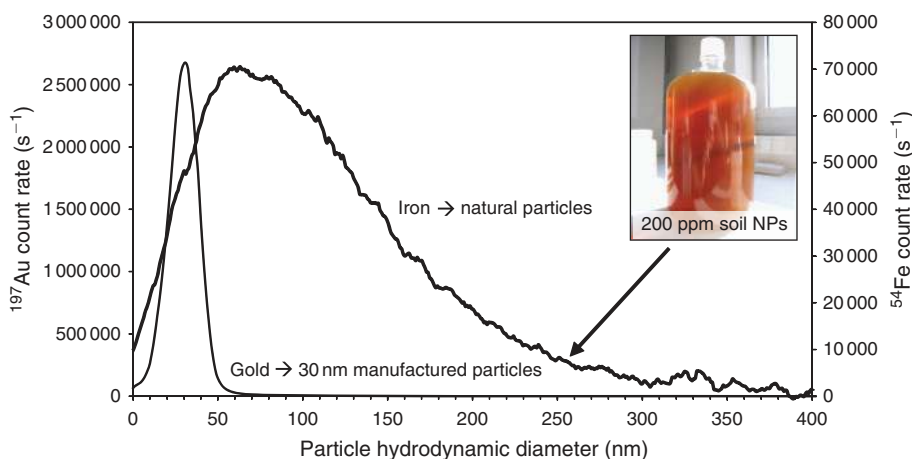
Fig. 7. Field flow fractionation–inductively coupled plasma–mass spectrometry (FFF-ICP-MS) elemental distributions of soil derived natural nanoparticles and colloids mixed with gold nanoparticles of 30-nm diameter (B. Meisterjahn, E. Neubauer, F. von der Kammer, D. Hennecke, T. Hofmann, unpubl. data). The Fe trace is used to show the size distribution of the natural particles, the Au trace is specific for the engineered nanomaterials (ENMs), because the background of Au in the natural sample is very low.

shows the specific detection of the gold nanoparticles in the presence of the natural particles and also the absence of hetero-aggregation because the gold ENMs are only found in their specified size region.

Time-resolved elemental analysis: microsecond-sp-ICP-MS

In recent years, sp-ICP-MS, has been used to detect and characterise engineered nanoparticles on a particle-by-particle basis in aqueous samples.[81,92,93,95,97] Utilising millisecond to microsecond dwell times, the count intensity arising from a single particle ablation event can be detected. This count intensity can then be converted into a mass using a calibration curve of dissolved standards that relate elemental mass to count intensity. From the particle mass, a diameter can also be determined assuming the appropriate geometry.

In addition to size information, determining the particle number concentration is a simple matter of counting the number of pulses and having knowledge of the sample flow rate and efficiency of the instrument's nebuliser. Several advantages of this technique include the inherent specificity and selectivity of ICP-MS, which allows for detection and characterisation down to environmentally relevant concentrations of nanograms per litre. This technique however can be hindered by two major obstacles: a high particle number concentration and low size detection limit. High particle number concentrations may result in 'coincidence', where two particles are ablated and detected within the same dwell time window. This results in the apparent detection of a particle with twice the mass, as opposed to two individual particles. Additionally, smaller particles may not possess enough mass to generate a detectable signal. Single particle ICP-MS so far has been used to characterise several metallic and metal oxide nanoparticles, but is limited in its ability to only monitor for one mass at a time. Recent advances may allow for differentiating between NNPs and ENPs.

At conventional millisecond dwell times only one element can be selected by the quadrupole. Dwell times in the microsecond range allow for temporal detection of the nanoparticle as a distribution of pulse intensities, as nanoparticle events occur over the span of several hundred microseconds.[108] These pulse intensities are then summed to equate to the overall pulse intensity

for a single particle. This intensity is then converted into a mass and subsequently a diameter assuming a spherical geometry. In addition to size information, the number of pulses correlates to the particle number concentration present in the sample.

At these sufficiently low settling times, where the width of the nanoparticle pulse spans several hundred milliseconds, the quadrupole can switch from one mass to the other with a short settling time. As a result, two elements can be detected within the same particle. As a result, elemental ratios can be determined on a particle-by-particle basis.[109] Naturally occurring nanomaterials may contain elemental impurities that can be detected by microsecond-sp-ICP-MS and be used to differentiate from ENMs that may have fewer elemental impurities than their natural analogues. Fig. 8 shows the analysis of river water where the minerals detected contain an elemental ratio of cerium and lanthanum. Cerium oxide particles that have been spiked into the sample will not contain a lanthanum peak, allowing for differentiation from the naturally occurring clays and minerals.

In addition to differentiating between particles containing different elemental ratios, ICP-MS allows for the detection of isotopic ratios. As a result, the detection and characterisation of isotopically labelled ENMs or those carrying an isotopic shift compared to natural particles is possible on a single particle basis. Some ENMs may have complex core–shell structures, with multiple elements comprising the inner and outer fractions of the particle.

Although many clay minerals in the environment will contain a mixture of elements, it is also likely that single metal oxides (e.g. CeO_2, TiO_2, Fe_2O_3) will be ubiquitously present. As with other techniques, this may require a thorough analysis of background concentrations of these particles to accurately determine the presence of ENMs. In this respect, significant deviations in the particle number concentration of these metal oxides may be a metric by which to identify the presence of anthropogenic nanomaterials.

However, to make a multi-element, high speed sp-ICP-MS analysis possible we need to reduce settling times (the time the spectrometer needs to switch to another isotope) to those much shorter than the currently encountered ones in the range on several tens of microseconds. The problem is pointed out in
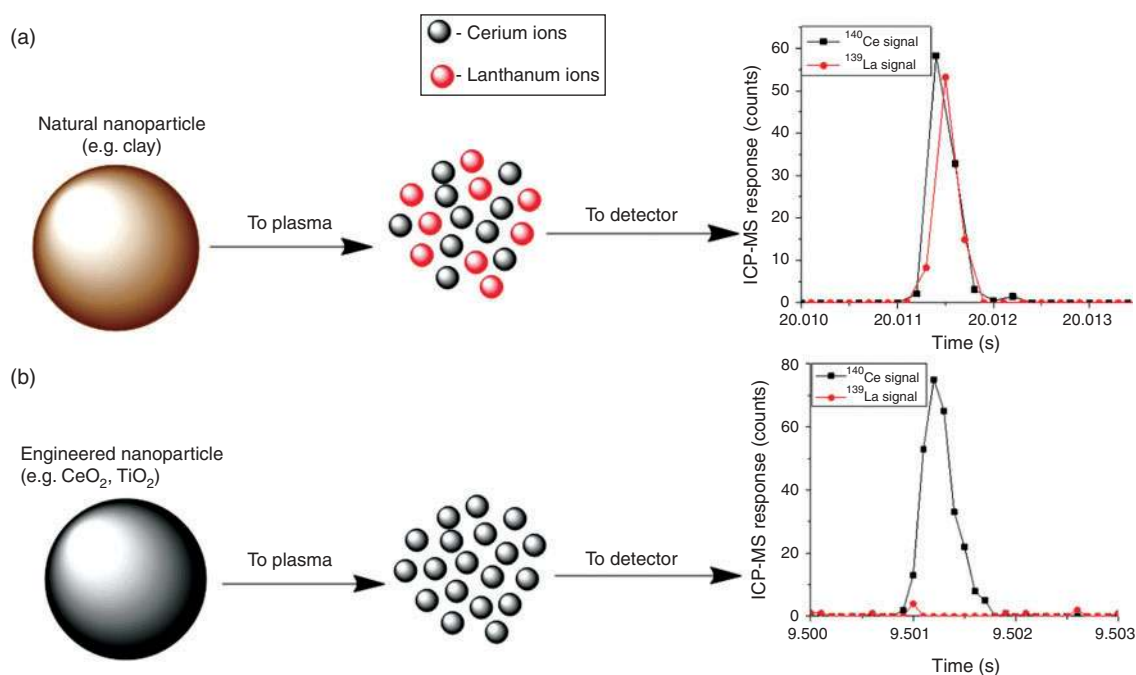
Fig. 8. (a) Analysis of a single naturally occurring clay particle that contains both cerium and lanthanum. (b) Analysis of an engineered cerium oxide particle showing only the ^{140}Ce signal.
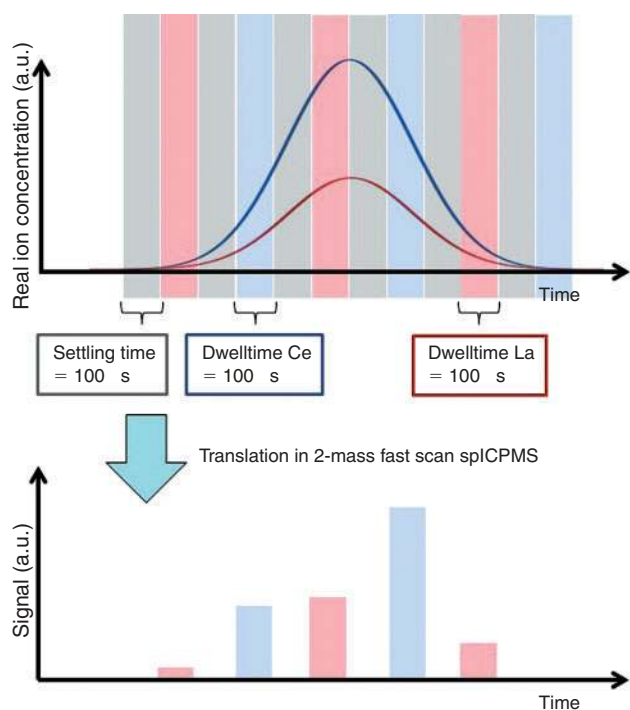
Fig. 9. The resulting peak information (bars for Ce and La in the lower graph) when switching between masses of Ce and La. Dwell and settling times are all 100 μs, what can be considered as short for current instrumentation. (sp-ICP-MS, single particle inductively coupled plasma–mass spectrometry.)

Fig. 9. The more often the spectrometer switches between masses, the more peak information is lost in these settling times in which no data are retrieved. This might end up in nearly total loss of the analytical information. Solutions are the decrease of settling times and the reconstruction of peaks by a convolution routine.

Conclusion

The development of accurate risk assessment models for ENMs will require the accurate determination of their fate and behaviour in environmental samples. Currently this is limited by underdeveloped methodologies that can accurately characterise these materials with sufficient specificity and sensitivity. The magnitude of naturally occurring nanomaterials, and the environmental transformations of ENMs will lead to a complex aqueous mixture of these particles requiring a multi-faceted approach necessary to accurately identify and characterise ENMs in the environment.

New highly sensitive approaches utilising differences in the elemental ratios of natural nanomaterials and likely elementally enriched ENMs may be a viable option for differentiating between these two kinds of nanomaterials. Accurate determination of elemental ratios in the background sample compared to affected sites may provide a means to identify the presence of ENMs, if the elemental ratio difference is statistically significant. This method can be improved by utilising a front-end fractionation step (i.e. field flow fractionation) to monitor changes in the elemental ratio on a size-specific basis. Lastly, improvements in single particle mass based techniques (sp-ICP-MS), may allow for the detection of elements on a particle-by-particle basis, providing a means to differentiate between complex naturally occurring nanomaterials and the more pristine ENMs. These proposed methodologies add to an ever-growing field of nanometrology. In order to develop useful life cycle assessments of ENMs for risk analysis, the accurate detection of ENMs in environmental matrices is of paramount importance.

Acknowledgements

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