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Journal:	*Journal of Analytical Atomic Spectrometry*
Manuscript ID	JA-PER-05-2019-000168.R2
Article Type:	Perspective
Date Submitted by the Author:	07-Aug-2019
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PERSPECTIVE

Opportunities for Examining the Natural Nanogeochemical Environment Using Recent Advances in Nanoparticle Analysis

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

The characterization of engineered nanoparticles (ENPs) has been a main pillar in the advancement of nanotechnology in recent decades. Because the properties of ENPs are closely linked to their size, shape, morphology, and surface coatings, development of nanoanalysis methods capable of assessing these parameters was necessary. Many advanced instruments and data analysis tools have now been established for analysis of ENPs in complex matrices, providing a comprehensive assessment of not only their intended virtues, but also the unintended consequences of their manufacture, use, and disposal. Current generation electron microscopy enables atom-scale imaging. Hyphenated (FFF-ICP-MS), and single particle (spICP-MS) techniques now possess the requisite sensitivity and elemental selectivity to quantify and characterize inorganic ENPs. These tools also provide a means to examine processes involving naturally-occurring nanoparticles (NNPs) to a degree not previously attainable. Though colloids and nanominerals have been investigated for decades, modern nanoanalysis offers a wealth of opportunities to improve our understanding of the natural nanogeochemical environment. Applying nanoanalysis on a single particle basis may lead to a more mechanistic understanding of particle formation and reactivity, global biogeochemical cycling, quantifing nanoparticle transport and impacts as they relate to hydrochemical and geochemical factors, and possibly differentiating ENPs from NNPs.

Introduction

The importance of nano-geochemical analysis

Understanding environmental chemical processes relies above all else on knowing the composition and concentration of the species of interest. In the case of particulates, early studies relied on filtration, or less frequently centrifugation, to separate the colloidal phase from the 'dissolved' fraction (0.2-0.5 µm). However, as analytical chemistry grew more sophisticated, this binary separation has been found to be too simplistic (Figure 1). Particulate constituents within the dissolved fraction have been demonstrated to play an important role in environmental processes. Though the importance of colloids (< 1000 nm) has long been established, they garnered increased attention given their ability to transport contaminants and nutrients in surface and subsurface environments. Moreover, the cycling of elements in the environment is intrinsically tied to nanoscale processes on mineral and biological surfaces. Vast quantities (teragrams) of nanomaterials are cycled at the global scale, and these materials govern diverse processes such as soil development, transport of nutrients to the ocean, and atmospheric chemistry, among many others.[1] Given the inverse power-law distribution of particle number concentration with size, relegating nanoscale materials (< 100 nm) to the dissolved fraction may limit our understanding of their distinct roles in transport and chemical processes.

Fully understanding colloidal and nanoparticulate (NP) behavior requires sensitive tools and techniques to measure these substances at low concentrations and at small length scales. While serial filtration and/or centrifugation offer an operationally simple window into this world, they are time-consuming, highly prone to analytical artifacts, and have low size resolution. Moreover, analyzing these particulates in broad groupings conflates the information that is most important to particle behavior at this scale, such as size, shape, and surface chemistry.

As engineered nanotechnology entered into technological maturity, the intrinsic nature of engineered nanoparticles (ENPs) necessitated the development of sensitive and sophisticated analytical tools to measure their size-dependent properties (Figure 1).[2] The ability to measure the properties of many individual particles has been a recent highly significant advancement. Many of the challenges brought on by measuring ENP in more complex samples (environmental, biological) are tied to their small sizes (< 100 nm), low expected concentrations (ng L^{-1}), and potential instability caused by high reactivity. These difficulties are further compounded by the abundance of naturally-occurring colloids and nanominerals, which may be present at concentrations that are orders of magnitude above anticipated ENP levels. Moreover, these varying nanoparticle

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

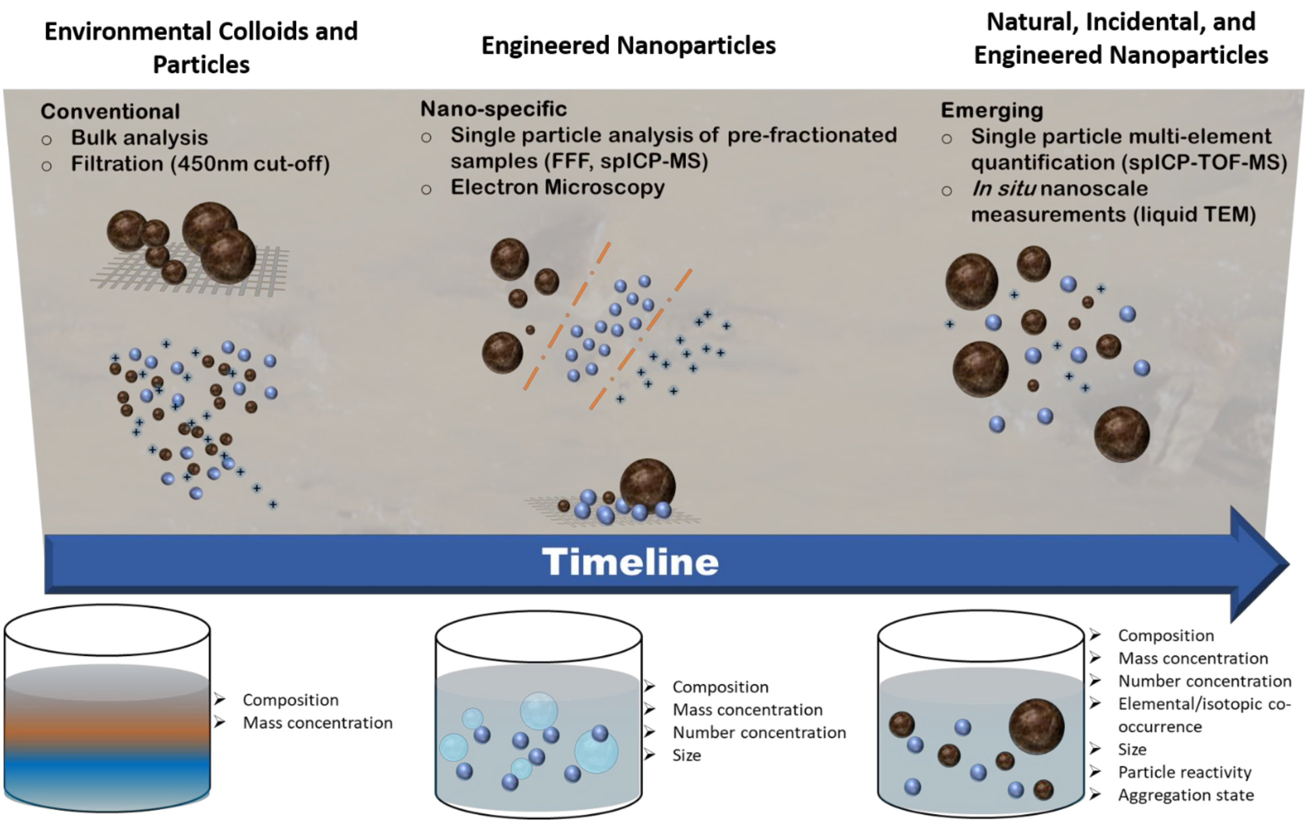

Figure 1. Developments in nanoanalysis leading toward the study of the nanogeochemical environment.

populations may associate with each other (agglomeration) when weak attractive interparticle forces exceed repulsive electrostatic/steric forces. Covalent bonding leads to aggregation, which by definition is irreversible under environmental conditions. It must be noted; however, that it is common to describe unstable NPs as aggregates, without adhering to this mechanistic definition.

To fully understand the nanogeochemical environment, techniques are needed that are capable of measuring these particles with more selectivity, and the requisite sensitivity in environmental matrices.. A range of analytical instrumentation and techniques have slowly developed the capability to discern nanoparticles with different elemental composition, size, and behavior. These developments have opened the door to advanced nanogeochemistry research.

Advances in Environmental Nanoparticle Analysis

It was recognized early in the development of nanotechnology that existing instrumentation and tools were insufficient to characterize or quantify NPs. The United States National Nanotechnology Strategic Initiative highlighted, as a key program component, “research and development pertaining to the tools needed to advance nanotechnology research and commercialization”.[3] In the decade since, major developments in spectroscopy, microscopy, and mass spectrometry have enabled more detailed study of nanomaterials with the goal of studying processes and behavior at nanometer resolution in fully representative media (biological, geological, environmental, etc.). In the case of inorganic NPs, ICP-MS has been adapted and configured to detect and characterize NPs with the requisite specificity and sensitivity. Driven by the need to assess the environmental health and safety of nanotechnology, the techniques presented herein have provided substantial utility for examining ENPs in the environment. However, earth scientists are only beginning to utilize these methods for the detailed study of natural nanogeochemical and biological systems. While highly-developed, further advancement in this field is needed to provide a more integrated picture of nano-biogeochemical processes.

Current Approaches

Single-element single particle ICP-MS

One of the most promising techniques to develop in recent years has been single particle ICP-MS (spICP-MS). By utilizing the excellent speed, sensitivity, and selectivity of quadrupole and sector-field ICP-MS, spICP-MS has found widespread use as a potentially routine tool for nanoanalysis, particularly in the environmental sciences. The ability to count and measure the size of NPs by spICP-MS has been notably useful for assessing inorganic NPs as potential contaminants, since their toxicological behavior is driven primarily by composition, size, shape, and aggregation state. In spICP-MS, intact NPs are introduced into the plasma by conventional nebulization, and their conversion into ion clouds produces transient pulses in counts above a background signal. Samples must often be diluted to avoid the simultaneous entrance of multiple NPs into the plasma, such that environmental samples often require dilution.[4]

Early work on spICP-MS provided a strong foundation upon which the analytical principles were developed.[4] Specifically, this work provided the methods and calculations necessary to determine number concentration and convert transient elemental signals into NP mass, which can then be converted into a dimension (diameter, thickness) assuming a density and shape. In subsequent years, spICP-MS has been applied to detect and characterize ENPs in biological fluids, food products, wastewater streams, and nano-enabled household products.

The overwhelming abundance of geochemically derived and biogenic NNPs with compositions and morphologies similar to those of the released ENPs is a key challenge for identifying ENPs in natural waterways. Although ENPs comprised of rare and precious elements may be detected above the relatively low dissolved and particulate environmental backgrounds (e.g. Au, Ag, Pt), this is not the case for ENPs that contain more abundant crustal elements such as Si, Fe, Al and Ti. Similarly, elucidating natural biogeochemical processes will require examining NPs which contain multiple elements. Furthermore, the complexity and variety of nanomineral populations complicate the assignment of particle density and shape needed for computing particle size.

Field-Flow Fractionation-ICP-MS

The online coupling of FFF with an element-specific detector was a major advance for studying environmental colloids, first performed by coupling ICP-MS to sedimentation FFF (SdFFF, aka centrifugal FFF).[5] Coupling flow (FlFFF) to ICP-MS has since become far more common, due to its versatility and the broader range of particle sizes that can be separated (1–5,000 nm). The particles that are separated by FFF can also be collected and analyzed offline using other techniques such as TEM, to complement the information provided by ICP-MS.

An open channel and relatively mild flow rates minimize shear forces, and hence, agglomerates may be minimally disrupted under the proper flow conditions. However, FFF analysis is most reliable when carrier compositions are optimized to prevent both interaction of sample with the channel and agglomeration during the analysis. It is prudent to consider that optimized FFF size data best represents the non-agglomerated "primary particle" size. For some nanogeochemical systems, for example dissolved organic matter in freshwaters, the pH and ionic strength of the carrier solution can be tuned to provide an analysis of properties based on *in-situ* conditions. Great care must be taken if non-optimized conditions are chosen however. If any of the pH, ionic strength or field strength are not within the range of acceptable conditions, experimental artifacts are possible. Additional information about NP characteristics may also be provided by analyzing size properties under a range of separation conditions if the impacts of changing these variables are incorporated into the interpretation. Further information to aid such interpretations can be provided by coupling any of several available detectors in line between the FFF and ICP-MS (e.g. absorbance, fluorescence, light scattering, refractive index, and viscometry).

Flow FFF separation conditions can be tuned to provide required resolution over the size range of interest. Metal-free conditions combined with thorough membrane cleaning and conditioning procedures facilitate the reproducible and routine analysis of nanogeochemical systems at ultra-trace concentrations.[6] The large number of tunable parameters (carrier composition, flow rate, membrane composition) provides excellent versatility to optimize separations in FlFFF, but this has largely limited the use of FlFFF-ICPMS to experts. Throughput can be limited by the long analysis times needed to achieve adequate resolution over broad size ranges; however, a decaying field strength can be used to reduce elution time. Largely, the challenges associated with optimizing FFF separations for nanogeochemical systems can be overcome by relying on the wide range of published methods.

Emerging Approaches

The wealth of data and opportunity provided by recent advances in spICP-MS and FFF-ICPMS have set the stage for their increased application in nanogeoscience. Yet, their limitations still inhibit a more integrated picture of the nanogeochemical environment. By only examining a few facets of nanomaterial properties (size, composition, etc.), the picture of nanogeochemical behaviour remains limited. Consequently, emerging techniques (Figure 1) are aimed at: augmenting elemental specificity to discern nanomaterial populations; increasing routinization and throughput (especially for FFF) to generate large data sets (needed to spatially and temporally resolve nanomaterial behaviour), and pushing the boundaries of resolution to investigate dynamic processes at the atomic and nanoscale regimes.

Emerging techniques such as single particle ICP-time-of-flight-mass spectrometry (spICP-TOF-MS) have shown considerable promise for quantifying and characterizing NPs on an individual particle basis. The use of field-flow fractionation to separate polydisperse particles in systems that mimic *in-situ* conditions has aided single-particle analysis, and direct coupling to element-specific detectors can add new layers of system-level information. The development of TEM techniques capable of examining NPs at atom-scale resolution and the emerging technique of time-resolved NP imaging in fully liquid conditions have provided new insight into nanomaterial synthesis and behaviour.

Multi-element spICP-MS

Despite the power of current spICP-MS methods and their successful application to environmental studies, the technique is limited by an inability to monitor more than one element at a time. As the length of a nanomaterial ionization event is approximately between 200–1000 μsec,[4] the time required for ions to clear a quadrupole or single collector sector-field MS severely limits the information that is provided about multi-element particles. These particles comprise the majority of those found in the natural environment. The development of spICP-MS with microsecond dwell times permits the switching of a quadrupole from one element to another within the period of a nanomaterial event. While this inevitably leads to lost signal when the quadrupole switches from one mass to another and requires time for ion clearance, it is possible to partially-capture at least two elemental signals per particle. From its first preliminary application to stream water,[7] this dual-element or fast-switching method has been also been applied to the analysis of more complex nanostructures.[8]

The recent introduction, and continued development of, a commercial ICP-time-of-flight-mass spectrometer has provided the potential for single particle analysis to take considerable steps forward in nanogeochemical analysis. Though still in its infancy, this technique has demonstrated the capacity to fully realize bimetallic and multi-element nanoparticle compositions,[9] isotopic ratios,[10] and discern between naturally occurring and engineered nanomaterial populations.[11] The ion beam is sampled to produce nearly the entire atomic mass spectrum (7–250 m/z^+) every 33–46 μs.[10] As a consequence, the elemental and isotopic ratios of each particle event can be quantified, permitting a deeper investigation into nanomaterial geochemical behaviour.

FFF Coupling to spICP-MS and routinization

The size distribution of trace elements measured by FlFFF-ICP-MS indicates their "environmental size", which is relevant to reactivity, uptake, fate and transport due to the organic matter layer which coats the mineral core. This contrasts with single-particle ICP-MS, and most EM methods. On the other hand, the co-elution of multiple elements in FFF-ICP-MS indicates only that the associated particles are the same hydrodynamic size and does not guarantee their co-habitation in a single particle. Using spICP-MS to analyze size fractions from FFF is thus an obvious advance.

The challenges related to method optimization, analysis times and membrane interactions in FlFFF-ICP-MS have largely limited the analysis of particle systems to exploratory and proof-of-concept studies. Achieving the precise, routine separation of these systems will facilitate high throughput analysis, providing temporally-, spatially- and size-resolved information at the nanoscale, both at the level of individual particles and integrated particle systems. Developing standard analytical methods with an integrated FFF-ICP-MS system and associated data analysis software will help to overcome these limitations. This will allow the application of FFF-ICP-MS to new research areas of nanogeoscience.

Atom-Scale and Liquid Electron Microscopy

Despite all the advances made in other branches of nanoanalytics, electron microscopy remains the premiere technique for direct visualization of nanoparticles. Artifacts introduced by sample preparation and the requirement of vacuum conditions for imaging, have long plagued conventional transmission electron microscopy. However, nanotechnology also provides a potential solution. By encapsulating liquid droplets between graphene sheets (termed graphene liquid cells or GLCs), the NP in solution can be monitored under the conditions necessary for TEM imaging. This technique has been used to monitor crystalline growth of platinum nanoparticles and the attachment between iron oxyhydroxide nanoparticles at nanoscale resolutions.[12] Though still in its infancy, being able to image at the atomic scale may provide new insights into mineral weathering, aggregation and agglomeration processes, and mineral precipitation.

Opportunities and Challenges

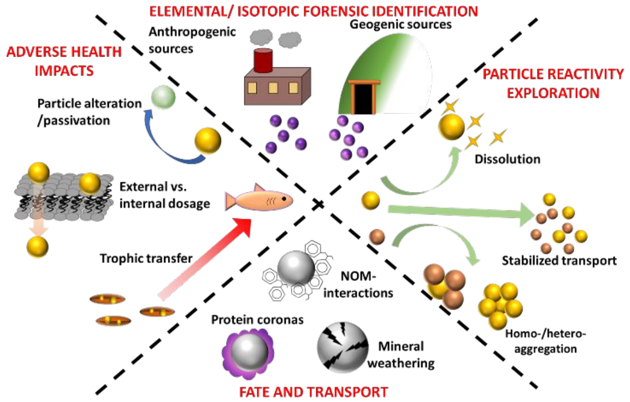

Figure 2. Opportunities in nanogeochemical analysis

Development of the aforementioned techniques presents a wealth of opportunities to better study the geochemical environmental with nanoscale resolution. Among the many potential possibilities of these techniques, there are four readily identifiable applications summarized in figure 2:

1) Mechanistic Understanding of Adverse Health Impacts

The study of NP hazard, regardless of anthropogenic or natural source, has suffered from a poor understanding of the relevant dose parameters. The advances in nanocharacterization tools give us the ability to further identify the controlling factors. Continuous quantification and characterization of NPs in both the exposure media and the organism (tissues) will more clearly define the time-dependent dose metrics (external and internal). Normalizing organism response to number, mass, or surface area concentrations can lead to better understanding of toxicity mechanisms arising from nanoparticle reactivity such as dissolution of NPs to release toxic metals, generation of reactive oxygen species, or the passivation of NP toxicity by surface modification (for example sulfidization of Ag^0).

2) Exploration of Particle Reactivity

The transport and reactivity of particulates differs considerably from that of truly dissolved solutes. Dissolution, agglomeration, and stabilization processes are a dominant factor in their ability to remain suspended in surface and groundwater. Yet, many techniques are unable to delineate between homo- and hetero-aggregated materials from multi-element colloids in environmental samples. These techniques may promote a better understanding of these processes and the factors that play a role in determining particle transport as it relates to their potential ecotoxicological risk.

3) Biogeochemical Cycling and Transport

Nanoparticles and nanominerals have long been known to be important drivers for a number of biogeochemical and physical processes. As these particles serve as vector for contaminant and nutrient transport, establishing their fate and transport behaviour provides key insight into how these other species are distributed in the environment. Particularly with the advent of global climate change and the introduction of incidental nanoparticles, there is potential for the composition, number, and morphology of these materials to differ considerably from established nanomineral populations. As such, these emerging techniques may offer an avenue to 'prospect' and study these materials in relevant environments.

4) Forensic Identification of Nanomaterial Sources

Current techniques available for source-tracking contaminants rely on bulk isotopic signatures, which obscure the morphological data that may be important in assessing their transport. By being able to quantify the isotopic ratios on a per-particle basis, it may be possible to discern anthropogenic from geogenic sources.

Sample collection and preparation considerations

Nanoparticles are not solutes nor are they fine-grained sediments, and thus their distribution in environmental media may be unique. Non-integrated grab samples, which may be effective for dissolved solutes may miss nano-specific effects such as the accumulation of NPs at surface layers. Similarly, the exhaustive methods used to account for spatial and temporal variability in coarser-grained suspended sediments may not be required for NPs. While acidification, refrigeration, or freezing are common storage methods prior to elemental analysis, their effects on NPs is largely unstudied. Particle number concentrations can be especially susceptible to post-sampling agglomeration and loss to container walls. The high degree of characterization and quantification provided by the nanometrology described here can be applied to develop sampling and storage methods that could not be achieved by traditional methods.

Data analysis and integration

Large amounts of data from different analytical techniques must be compared and interpreted correctly, with deep understanding of analytical limitations and associated artifacts. Standard methods for data processing and analysis will be needed to facilitate the integration and comparison of data from multiple analytical techniques and different research groups. Reliable and high-throughput analysis of the natural nanogeochemical environment at multiple scales will facilitate the prediction of ecologically and geochemically relevant impacts at the system level. However, the large number and apparent diversity of natural nanoparticles, the large number of potential interactions there between, and the dependence of many properties on physicochemical conditions may require new mathematical and conceptual approaches.

Conclusions

The continuing maturation of these techniques provides new opportunities to reexamine the natural nanogeochemical environment with a degree of precision and sophistication not previously possible, further expanding our understanding of the biogeochemical, chemical and geochemical processes that occur in the size range between ionic species and suspended particulates.

Conflicts of interest

The authors have no conflicts of interest to declare.

Acknowledgements

The authors would like acknowledge funding from the National Science Foundation (NSF-CBET 1512695).

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