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Foreword

Foreword to the Research Front on Detection of nanoparticles in the environment

Engineered nanoparticles (ENPs) such as carbon nanotubes, silver nanoparticles, quantum dots and metal oxides can now be found in thousands of commercial products (Project on emerging nanotechnologies http://www.nanotechproject.org, accessed 26 September 2013) including non-stick cookware, tennis racquets and fuel cells. Owing to changes in the chemical properties that occur as one approaches the nanoscale, ENPs show significantly different reactivity from either the bulk materials or dissolved ions. In spite of the growing and wide-spread use of ENPs, their impacts on the environment and human health are largely unknown. As with any new product, environmental regulators are currently asking questions about the fate and effects of the ENP.

- Q1. What concentrations of ENPs will end up in the environment?
- Q2. Will the ENPs survive in the receiving media?
- Q3. Will traditional toxicity tests be sufficient to detect the effects of ENPs?

Indeed, ecological risk assessments require data on both environmental exposure and hazard. Despite a recent flurry of research activity into the hazards of ENPs (Q3), the answers to questions 1 and 2 are not obvious, in large measure because we don't yet know how to quantify ENPs in the environment or track their fate.^[1,2] Virtually no data are available on the concentrations of ENPs in the environment.^[3] Estimates have been produced from the modelling of Nowack^[4,5] and others, who base their predictions on estimation of worldwide production volumes, the allocation of these volumes to different product categories, estimations of particle release from products, and flow coefficients within environmental compartments. For example, for Ag nanoparticles (nAg), concentrations of 0.03–0.08 μ g L⁻¹ in water and 0.02–0.1 μ g kg⁻¹ in soil were predicted.^[4] However, the authors noted a very large uncertainty because of the poor quality of input data and remarked that they could not extrapolate to the future where inputs are expected to greatly increase. Therefore, the main thrust of the current research front is to focus on analytical methods that will enable the detection of ENPs in complex environmental matrices.

The detection and quantification of ENPs are becoming routine under well-defined *laboratory conditions*. For example, ENPs have been fluorescently labelled for use in biomedical applications.^[6, 7] Isotope-labelling techniques also exist^[8] as do specialised analytical techniques such as particle-counting techniques that function well in the absence of matrix effects. In contrast, few analytical methods have been rigorously tested for use for the detection of ENPs in environmental or complex biological samples, although inspiration has been taken from previous work on natural colloids^[9]: microscopic techniques (e.g. scanning or transmission electron microscopy; atomic force microscopy), size fractionation techniques (e.g. ultrafiltration; ultracentrifugation) and chromatographic techniques (e.g. size-exclusion chromatography). Additional work is also clearly required to quantify the artefacts being produced during sample preparation, storage and analysis.^[1]

In the toxicological literature, electron microscopy and dynamic light scattering are most often used to identify and characterise the ENPs and their aggregates.^[10,11] Unfortunately, dynamic light scattering does not function well in heterogeneous samples, especially at the low concentrations that we expect to find ENPs in the environment. Furthermore, it is often extremely difficult to obtain representative samples for microscopy since only very small fractions of the sample can be observed at any given time and sample preparation techniques can result in modifications to the structure of the ENP.^[11] To that end, the paper of Tuoriniemi et al.^[12] evaluates some of the limits of electron microscopy and provides guidelines for making the technique more quantitative for determining both particle numbers and particle size distributions. Johnston et al. use high resolution transmission electron microscopy to identify iron oxide and green rust nanoparticles in metal polluted mine drainage.^[13] Wohlleben et al.^[14] employ multiple techniques including electron microscopy, thermogravimetric analysis and Fourier transform infrared spectroscopy to characterise nanosilica release due to weathering from polymer composites.

Single particle inductively coupled plasma mass spectrometry (SP-ICPMS) has also received significant recent attention for the identification and quantification of ENPs in environmental samples^[15–17]; however, it is presently limited when measuring very small particles, those with significant dissolution or those outside a fairly restrictive concentration range.^[16,17] The paper by Furtado et al.^[18] has succeeded in analysing silver nanoparticles under the near natural conditions of a lake mesocosm using SP-ICPMS (along with other confirmatory techniques). Another solution examined by several researchers has been the coupling of field flow fractionation^[18–20] or hydrodynamic chromatography^[21] with ICPMS in order to reduce some of the problems associated with matrix effects. The paper by Proulx and Wilkinson couples HDC with SP-ICPMS in order to detect nAg in a spiked natural river water sample.^[22]

Overall, significant advances have been made recently to detect ENPs in environmental samples and in toxicological media. Although measurements are still not routine, as the papers in this issue show, promising developments have been made that will soon allow us to have greater confidence in our measurements of ENP concentrations and size distributions, thus enabling environmental regulators to evaluate the presently missing, yet key component of environmental risk, i.e. exposure.

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