Nanoparticles in Natural Aquatic Environments: A physical, chemical and eco-toxicological study of cerium dioxide and silver

Paula Cole

School of Geography, Earth & Environmental Sciences, University of Birmingham, Birmingham UK

Background to Research

Over the past decade the ability to engineer and produce materials at the nano-scale has triggered rapid product development (Brunner *et al*., 2006). It is estimated that 50,000 kg/year of nano-sized materials are being produced (Borm *et al.,* 2006), yet the knowledge about possible adverse effects of nanomaterials and nanoparticles (NPs) is essentially nonexistent.

Over the past four decades, a large number of studies have been performed to assess the availability and toxicological impact of numerous NPs on specific organisms. These particles have included metal oxides, organic fullerenes and carbon nanotubes. Of particular interest in this research, is that of cerium dioxide (ceria) and silver NPs.

Ceria is currently used as catalysts (Toshiyuki *et al.,* 2003), in metallurgy (Oxonica, 2005) and used as additives in polymers and dental materials (Brunner *et al.,* 2006). Ceria is also used in polishing glass (Masui *et al.,* 2002), as a luminescent material (Gu and Soucek, 2007) and is currently used in diesel fuels (Zhang *et al.,* 2005), to reduce the temperature at which carbon combusts (Park *et al.,* 2007). Silver NPs have been known to destroy bacteria (Tillman, 2004) and have recently been found to be useful as photosensitive components (Liu *et al.,* 2007).

Through their accelerated use, ceria and silver NPs may unintentionally be released into natural environments, inevitably entering aquatic systems. Many studies have been performed on the uptake and accumulation of silver and ceria NPs with algae, *Daphnia magna*, fish and more recently, plants. To date, however, very little is known about the interaction of silver or ceria NPs *within* natural aqueous environments. Ecotoxicology of particles is known to be altered by abiotic factors (Handy *et al.,* 2008). Therefore, understanding the effect of different environments including varying pH, temperature and salt concentrations on these particles, will help our understanding of the accumulation and bio-uptake of such particles and their associated toxicological effects, within these systems. Understanding the impact of particular NPs within such systems is imperative to ensure the reduction of risk and increase our knowledge of associated remediation. This area of research will also allow a greater understanding for manufacturing, transporting and disposal pathways to be met.

Recent research has found that the toxicity of naturally occurring materials results from their physical size (Colvin, 2003). Considerably more experimental evidence shows that NPs are markedly more toxic than the same material at a larger scale (Seaton, 2006). These differences associated with NPs may produce negative responses in organisms (Robichaud, *et al.,* 2005) potentially causing a greater impact on aquatic organisms. Understanding the implications of size dependency of such materials is also an important factor. This has given rise to a comparative investigation into ceria and silver microparticles (MPs) within this study.

Aims

This project involves the development, execution and evaluation of effective methodologies and approaches to determine the characteristics of ceria and silver NPs and MPs, when found in natural conditions favourable for fish, algae, aquatic plants, *Daphnia magna* and in the growth of human and trout Hepatocyte cells. An additional investigation will involve comparing these characteristics of silver and ceria NPs and MPs in environments actually exposed to specific organisms. This is to be performed in collaboration with three organizations including the Commonwealth Science Industrial Research Organisation (CSIRO), Exeter University and Napier University.

Techniques

With support from the collaborators, it is proposed to investigate the physicochemical characteristics of silver and ceria NPs and MPs, with exposure to algae, exposure to cold water fish (carp), *Daphnia magna*, human and trout Hepatocyte cell cultures and exposure to tropical fish (zebra fish) respectively. These characteristics include aggregation, surface chemistry, surface area, charge, size, morphology, structure, and solubility. Techniques to characterise these will include transmission electron microscopy, BET, dynamic light scattering, ultraviolet-visible spectroscopy, NanoSight, inductively coupled plasma mass spectrometry with associated filtering techniques, fluorescence spectroscopy, X-ray diffraction and electrophoresis.

Work to date

Exposure investigations of silver NPs and MPs to a cold water environment with carp have been carried out by Napier University. The environment was at an average temperature of $10.2^{O}C$, an average pH 7.45, with salt concentrations of NaCl at 8.27 mg L^{-1}, $CaCl_2$ at 24.5 mg L^{-1}, $MgCl_2$ at 4.38 mg L^{-1} and KCl at 2.07 mg L^{-1}. Five tanks of 60 L were prepared, one with 0.1 mg L^{-1} Ag NPs and one with 0.1 mg L^{-1} Ag MPs and repeated for 0.01 mg L^{-1} Ag NPs and 0.01 mg L^{-1} MPs, with one tank kept as a control. A sample was taken and termed Day 0. Carp were added to the tanks and a sample taken one hour later and termed Day 1. Subsequent samples were taken on Day 7, Day 14 and Day 21 for characterisation of size, charge and solution.

Results

Both Ag NPs and MPs reduced in size on the addition of carp. The charge on the particles was also seen to change, on the addition of carp. Ag MPs were found to increase in charge, suggesting a decrease in reactivity, and increase in aggregation. Ag NPs were found to decrease in charge, suggesting an increase in availability amongst single particles. The solubility of Ag ions from NPs was also found to be greater than that from Ag MPs for the first 14 days.

Discussion and conclusive remarks

The reduction in size and associated decrease in charge of Ag NPs, after exposure, is possibly due to individual particles repelling others and becoming more stable and less aggregated. An increase in charge observed from the MPs with the associated reduction in size of particles, is possibly due to them becoming more reactive and attractive to themselves, aggregating, settling and therefore not taken within the sample. Solution data suggests any uptake, accumulation and associated toxicity found within the fish, would potentially be due to silver ions and not because of the specific particle sizes.

References

Borm, P. J. A., Robbins, D., Haubold, S., Kuhlbusch, T., Fissan, H., Donaldson, K., Schins, R., Stone, V., Kreyling, W., Lademann, J., Krutmann, J., Warheit, D., and Oberdorster, E. 2006. The potential risks of nanomaterials: a review carried out for ECETOC. Particle and Fibre Toxicology BioMed Central **3**:11

Brunner, T. J.; Wick, P.; Manser, P.; Spohn, P.; Grass, R. N.; Limbach, L. K.; Bruinink, A.; Stark, W. J., 2006. In vitro cytotoxicity of oxide nanoparticles: comparison to Asbestos, Silica and the effect of particle solubility. Journal of Environmental Science and Technology. **40:**(14) 4374-4381

Colvin, V. L. The potential environmental impact of engineered nanomaterials, 2003. National Biotechnology **21**:(10) 1166-1170

Gu, H and Soucek, M. D., 2007. Preparation and Characterization of Monodisperse Cerium Oxide Nanoparticles in Hydrocarbon Solvents. Chemistry of Materials, **19**: (5)1103-1110.

Handy, R. D., von der Kammer, F., Lead, J. R., Hassellöv. M., Owen, R., and Crane, M., 2008. The ecotoxicology and chemistry of manufactured nanoparticles. Ecotoxicology. **17**:(4)287-314

Liu, R., Lead, J. R., Baker, A., 2007. Fluorescence characterisation of cross flow ultrafiltration derived freshwater colloidal and dissolved organic matter. Chemosphere **68**: (7)1304-1311.

Masui, T., Hirai, H, Imanaka, N., Adachi, G., Sakata, T., and Mori, H. 2002. Synthesis of cerium oxide nanoparticles by hydrothermal crystallisation with citric acid. Journal of Materials Science Letters **21**: (6)489-491.

Oxonica. 2005. Catalysis: Catalytic function of cerium oxide. Commercial solutions from nanotechnology,

Park, B., Martin, P., Harris, C., Guest, R., Whittingham, A., Jenkinson, P., Handley, J., 2007. Initial in vitro screening approach to investigate the potential health and environmental hazards of Envirox^{TM} – a nanoparticlulate cerium oxide diesel fuel additive. Particle and Fibre Toxicology **4**:12

Robichaud, C. O.., Tanzil, D., Weilenmann,U., Wiesner, M.R., 2005. Relative Risk analysis of several manufactured nanomaterials: An insurance industry context. Environmental Science and Technology, **39**:8985-8994.

Seaton, A. 2006. Nanotechnology and the occupational physician. Occupational Medicine, **56**:312-316

Tillmann, P., 2004. Stability of Silver Nanoparticles in Aqueous and Organic Media. NNIN REU Research Accomplishments 140-141.

Toshiyuki, M., Hirai, H., Hamada, R., Imanaka, N., Adachi, G-y., Sakatac, T., and Moric, H. 2003. Synthesis and characterization of cerium oxide nanoparticles coated with turbostratic boron nitride. Journal of Materials Science. **13**:622–627

Zhang, J., Z.Y. Wu, L. X. Rong and B. Z. Dong., 2005. Temperature Dependence of the Growth of Cerium Oxide Nanoparticles investigated by SAXS and XANES Physica Scripta. **115**:661–663.