FACILITY FOR NANOSCIENCE ANALYSIS AND CHARACTERISATION (FENAC)
ANNUAL REPORT - FY April 2011 to March 2012

TYPE OF SERVICE PROVIDED:

The Facility for Environmental Nanoscience Analysis and Characterisation (FENAC) provides a unique service meeting the needs of the 'environmental nanoscience' community. Originally envisaged as a service supporting the (eco)toxicological community investigating the biological impact of manufactured nanomaterials*, FENAC also underpins the wider environmental community looking at manufactured nanoparticle chemistry and transport, along with nanoparticle investigations of other types of material sources including incidental (combustion, industry etc) and natural (microbial, weathering etc) nanomaterials. FENAC provides access and sample analysis for relevant samples, acting in a fully collaborative manner with FENAC users, helping users through the whole process from experimental design to data analysis. FENAC also provides training for doctoral and postdoctoral researchers during the sample and data analysis period and, more formally through 2 day summer schools, also leveraging NERC KE programmes and University of Birmingham support.

The FENAC Director is Professor Jamie Lead, with Dr Bjorn Stolpe the current Manager, supported by Dr Gillian Kingston (5%), with access through competition, with submissions due every 6 months. The facility offers a unique combination of experimental, analytical and metrological methodologies and the expertise to deploy such methods appropriately. Using a multi-method approach, FENAC incorporates a number of methods grouped as:

- microscopy (TEM, SEM, STEM, ESEM, AFM, CLSM),
- spectroscopy (EELS, X-EDS, XPS, FCS, ICP-MS)
- separation (FlFFF, SdFFF, CFUF, AUC, CE and disc ultracentrifugation) and
- other (DLS, XRD etc).

FENAC offers a unique, proven ability to characterise and interpret the physico-chemical properties of nanoparticles from all sources (below), including size, aggregation properties, surface behaviour, dissolution and morphology.

*Nanomaterials are defined as having at least one dimension between 1 and 100 nm; NMs are of three types: manufactured (deliberately produced), incidental (accidentally produced) and natural (produced by natural sources).

ANNUAL TARGETS AND PROGRESS TOWARDS THEM

FENAC has made significant progress on all approved projects. Of the 6 approved projects during the 2011-2012 year, 3 are completed, 2 on-going and 1 not yet started. Given the high demand, significant method development has not been possible, requiring further staff or demand management, which has been discussed. Given the cuts required by NERC, no more staff will be employed and more rigorous demand management will need to be introduced. Method development has been undertaken by other research projects led by the FENAC Director, ensuring FENAC remains internationally leading. FENAC has been widely marketed and availability disseminated at conferences, workshops and other venues. Demand is healthy, with increased numbers of new applicants. A number of research papers have been published and a review paper detailing the minimum characterisation required for nanotoxicology studies, especially in relation to regulation, has been submitted to ACS Nano.

OVERVIEW & ACTIVITIES IN FINANCIAL YEAR (2011/12):

General Given the scale of the nanotechnology industry and the importance that NERC, other research councils, the EU and end users attach to the environmental and human health hazards and risks of nanomaterial, the start up of FENAC's operation has proved to be of great interest to the relevant NERC research community and to a range of governmental and industrial, both globally and nationally. There is also considerable interest in FENAC from researchers investigating incidental and natural nanoparticles and this interest has grown steadily over the three years of operation. FENAC has raised the profile of UK nanoscience research globally, for instance contributing to at least one of the US-UK consortium awards based on the NERC ENI round and to a successful EU FP7 Infrastructure bid. Two current NERC standard grant applications are currently being considered. FENAC has also had discussions with organisations such as OECD and standards organisations (ISO, BSI) and the Director is technical author on a BSI PAS document to be published in 2012. Details of the completed or current projects are given below. FENAC has also negotiated potential collaborations and links with the synchrotron facilities ISIS and DLS with current applications submitted to Diamond related to FENAC projects.

Methods, Training and Staff Development. The facilities available to FENAC at the programme start (April 2009) were substantial and are listed above in brief and the FENAC website in full. Further University of Birmingham funding has been leveraged to provide DLS, CE, BET, disc ultracentrifugation and FCS analysis (the latter with NERC support), with a value of ca £400 000. All instrumentation has now been installed and is routinely available. More recently, a cryo TEM capability has been added and this is now operational, although as yet unused by FENAC.

Major method development work has not been possible due to the limited manpower and large demand, although routine method development and training, along with method development by others in Lead's research group, has continued and informed FENAC practices, maintaining FENAC as an internationally leading centre. The increased (technical) support requested and approved by the SRG has not been forthcoming and is unlikely to be made available due to budget cuts and changes within NERC. More rigorous demand management is therefore required and need discussion. A number of planned method development areas have been developed within 2011-2012, including developments in FlFFF, TEM and reference materials, although these have utilised much of the rest of Lead's research group to support FENAC.

Of the 6 projects approved, 3 have involved PhD students; 2 of these PhD students and an additional 2 postdoctoral researchers have been based at FENAC for training purposes for 1-3 weeks each, 9 weeks in total. In addition, we have run a second summer school attended by ca 15 doctoral and postdoctoral researchers (September 2010), with a third one planned for September 2011, at the Royal Society, London. The FENAC manager has been given specific instrument training and been involved in training others. User surveys are routinely distributed and indicate high satisfaction with the FENAC facility but will be used critically to ensure this level is maintained.

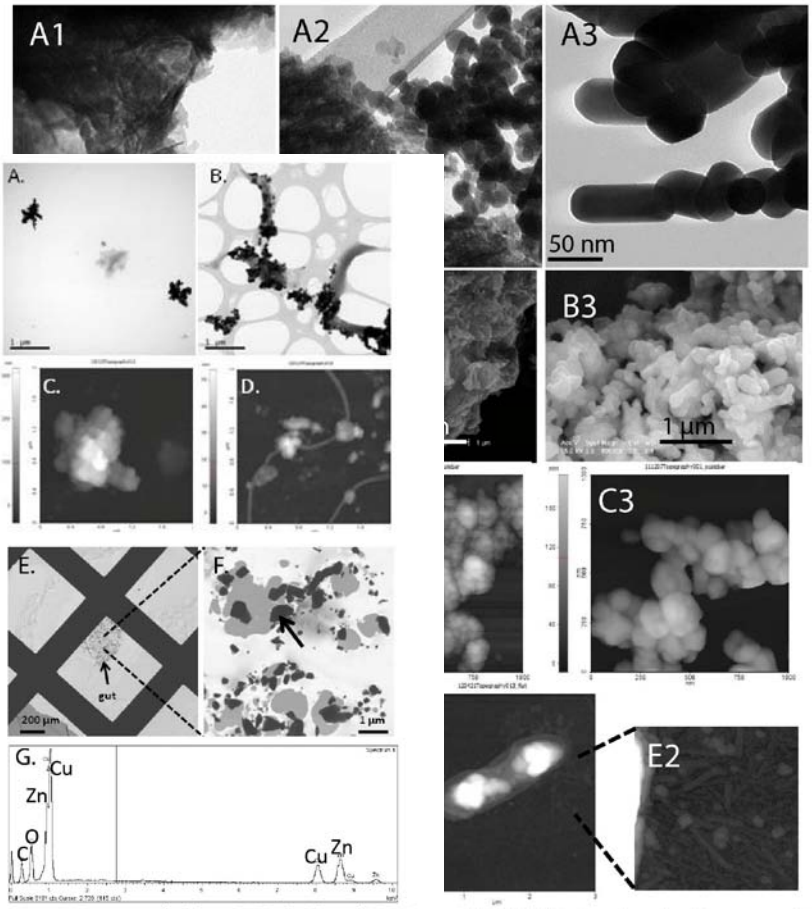

Fig. 2: Micrographs from TEM (A,B) and AFM (C,D) showing aggregates of ZnO-nanoparticles before (A,C) and after (B,D) 10 day exposure to Lumbriculus variegatus. STEM images with different magnifications (E,F) showing particles in the gut of Lumbriculus variegatus, with high concentrations of Zn verified by EDX (G).

nd AFM (C) showing hydroxyapatite
l to 450˚C (2) and 700˚C (3).
ınd XRD crystallite diameter
g temperature (D). AFM-micrographs
nt exudate-like objects (E2).

SCIENCE HIGHLIGHTS

Collaboration with other Schools within the University of Birmingham has continued to investigate the potential use of hydroxyapatite for radionuclide decontamination in the nuclear industry. Previous work demonstrated a much higher metal sorption capacity of bacterial compared with synthetic hydroxyapatite, which could be related to its smaller crystallite size and larger BET surface area. The new project aimed to deepen our understanding of the variations in metal uptake by particle morphology and crystallinity, investigated by heating the bacterial hydroxyapatite to different temperatures. The samples were characterized using TEM, SEM, AFM, BET and XRD (images to left), showing a dramatic change in particle morphology, specific surface area crystallite size with increasing temperature, accompanied by change in metal sorption capacity. The work was performed in a

collaborative manner, with the postdoctoral researcher on the application spending considerable time with FENAC for training. Previous work in the project has resulted in a publication in Environmental Science and Technology, and a presentation at the 2011 Goldschmidt conference in Prague, and the new work will shortly be submitted in a manuscript to Nature Materials.

Collaboration with the Herriot Watt University has resulted in new insights in nanoparticle bio-uptake and toxicity. Exposure to ZnO-nanoparticles has resulted in dose dependent behavioural response on the sediment dweller *Lumbriculus variegate*. FENAC has performed the physico-chemical characterisation on the particles, both as prepared, in relevant ecotoxicological media, and in filtered exposure medium after 4 day exposure to the sediment dwellers, using a wide range of techniques including TEM, AFM, DLS, XRD and BET (images to left). In addition, exposure of the ZnO-particles to *Lumbriculus variegate* was performed in the FENAC laboratory, and the presence of ZnO-particles in the gut of the sediment dweller was verified using STEM-EDX on tissue samples prepared through FENAC (images left). The PhD student affiliated to the project visited FENAC during a two week period, to learn both characterisation techniques and the preparation of biological samples for STEM-EDX. In order to further increase our understanding of ZnO-nanoparticle biouptake, an application has been submitted to the Diamond Light Source, aiming to determine the distribution and speciation of Zn in the tissue of *Lumbriculus variegate* using synchrotron µ-XRF and XANES.

A third project in collaboration with the PML has investigated the presence of iron-rich nanoparticles in seawater around fumaroles off the Vulcano Island near Sicily. Knowledge about the source and character of iron from marine fumaroles is crucial for our understanding of the marine iron budget and its control of the climate. Shipboard preparation of samples for AFM and TEM were prepared immediately after sampling, both of seawater and of gas from the fumaroles, sampled using a TSI Nanometre aerosol sampler. TEM-EDX revealed the high abundance of iron-rich colloids composed of nanoparticles (images below) and AFM showed a small but significant increase in nanoparticle diameter with increasing pH and distance from the fumaroles. The project has resulted in a manuscript, submitted to Marine Chemistry.

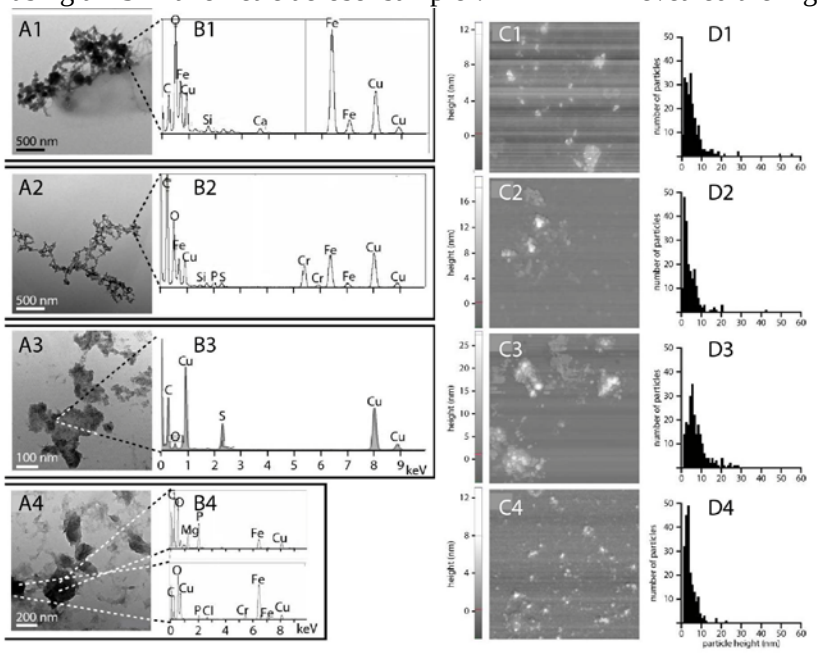

Fig. 3: TEM-micrographs (A) with associated EDX-spectra (B), AFM-micrographs (C) with associated particle height distributions (D) of particles in seawater samples with pH 7.4 (1), 7.8 (2), 8.0 (3) and 5.9 (4) taken near the fumaroles of the hydrothermal vents around Vulcano island, Sicily.

Selected FENAC Publications 2011-12

1) M.A. Baalousha, B. Stolpe, J. R. Lead (2011). Flow field-flow fractionation for the analysis and characterization of natural colloids and manufactured nanoparticles: critical review. Journal of Chromatography, 27, 4078-4103

2) S. Handley-Sidhu, J.C. Renshaw, S. Moriyama, B. Stolpe, P. Yong, C. Mennan, S. Bagheriasl, A. Stamboulis, M. Paterson-Beedle, K. Sasaki, R.A.D. Pattrick, J.R. Lead, L. E. Macaskie (2011). Uptake of Sr^{2+} and Co^{2+} into biogenic hydroxyapatite: implications for biomineral ion exchange synthesis. Environmental Science and Technology, 45, 6985-6990.

3) M.A. Baalousha. Y. Ju-Nam, P. A. Cole, C. R. Tyler, V. Stone, T. Fernandes, M. A. Jepson, J. R. Lead (2012). Characterization of cerium oxide NPs. Part 1: size measurement by AFM, TEM, XRD, DLS and BET. Environmental Toxicology and Chemistry, 31, 983-993

4) M.A. Baalousha, Y. Ju-Nam, P. A. Cole, C. R. Tyler, V. Stone, T. Fernandes, M. A. Jepson, J. R. Lead (2012). Characterization of cerium oxide NPs. Part 2: non-size measurement. Environmental Toxicology and Chemistry, 994-1003.

5) J. Fabrega, R, Tantra, A. Armer, B. Stolpe, J. Tompkins, J.R. Lead, C. R. Tyler, T. S. Galloway (2012). Sequestration of zinc from zinc oxide nanoparticles and life cycle effects in the sediment dweller and amphipod Corophium volutator. Environmental Science and Technology, 46, 1128-1135.

6) N. A. Sherain, M. A. Volker, P. E. Frickers, J.W. Readman, B. Stolpe, J. R. Lead, A. J. Moody, A. N. Jha (2012). Interactive toxic and genotoxic effects of C_{60} fullerenes and fluoranthene in marine mussels, *Mytilus* sp. Mutation Research, 745, 92-103

FUTURE DEVELOPMENTS/STRATEGIC FORWARD LOOK

FENAC will continue with the progress made to date in supporting the 'nano' community, in broadening its reach and access of the potential user community. Demand is high and increasing and some demand management is likely to be necessary. FENAC will continue to meet these needs in particular in the NERC themes of Environment, Pollution and Human Health and of Technologies. Applications to FENAC are increasing as are collaborations on NERC responsive mode and thematic programme applications. FENAC will continue to perform, improve and widen access to essential training via one-to-one laboratory training and summer schools, which also act as valuable outreach mechanisms.