NanoRem NEWSLETTER

N° 2 Autumn 2014

Nanotechnology for Contaminated Land Remediation

Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment

NanoRem Consortium at the 1st Annual Meeting April 2014

HIGHLIGHTS

Summer 2013 Workshop (© Land Quality Management)

Interview with Dr. Hans-Peter Koschitzky

Project coordinator

Hans-Peter is the coordinator of the European Project NanoRem and thanks to this interview he gives us an overview about the project .

For him "NanoRem really is an adventure but also a great challenge. At the beginning with such a large number of partners of which some you do not know, and with such a large project you are unsure how well everything is going to run to achieve the ambitious goals. "

Please go to page 5 to read the complete interview !

UPCOMING EVENTS

- **Annual Meeting (Internal) - April 14th - 17th 2015, Barcelona and Manresa, Spain.**
- **Third International Symposium on Bioremediation & Sustainable Environmental Technologies - May 18th - 21st 2015, Miami, USA.**
- **Aqua Consoil - June 9th - 12th 2015, Copenhagen, Denmark.**

This project has received funding from the European Union's Seventh Programme for research, technological development and demonstration under grant agreement No. 309517.

The 1st Annual Meeting

The first year research within NanoRem has been very active. The 1st Annual Meeting took place on 7th to 9th April 2014 in Vienna and Neusiedl am See, Austria, where the consortium presented the developments and the results achieved since the start of NanoRem on 1st February 2013. In the course of the year NanoRem welcomed a new partner: Scientific Instruments Dresden GmbH, SciDre, who will contribute to the large-scale production of Carbo-Iron.

Nearly eighty participants including the external experts (stakeholders) of the Project Advisory Group (PAG) and the Project Technical Advisor (PTA) for the EU took part in the presentations, work package meetings and plenary discussions. The meeting was opened on Monday by the coordinator, who presented the news from a management point of view, followed by the responsible person for the finances. Work package leaders then presented the work packages' achievements of the first year followed by short discussion.

Most of the second day was dedicated to Work Package (WP) meetings. Work plans for the second year were identified along with the exchange needed between different WPs were specified in detail. Furthermore, the NanoRem website was presented, followed by a training session.

The agreed results of the WP meetings were presented to the consortium on the third day. Moreover a special plenum session of WP 10: "Pilot site Application and Demonstration" impressively gave the whole project team the idea of the overall goal of NanoRem and how it is to be achieved.

During the three day meeting two further meetings of the Project Management Group (PMG), the Project Advisory Group (PAG) and a joint meeting of PMG / PAG took place. In the latter, at the end of the second day, the external experts gave their first impressions of what had been presented and discussed and provided their advice and recommendations for the upcoming work to the work package leaders. After the meeting the PAG summarised their recommendations for the NanoRem consortium.

During the whole meeting, even more linkages than before were established between the different work packages. Project partners enjoyed the multi-cultural exchange and the wine tasting on a boat on Lake Neusiedl.

The consortium especially would like to thank the project technical advisor for his presence and the PAG for their very valuable feedback to the work performed and the plans for the further project.

The results of the first NanoRem Annual Meeting has been documented in detailed minutes, agreed by the PMG and provided to the consortium. The next Annual Meeting will take place 14 to 17 April 2015 in Barcelona and Manresa, Spain.

NanoRem so far

NanoRem is now 18 months old and has made some great progress to date. The project is looking at many different aspects relating to the use of nanoparticles in remediation and is split into the following work packages:

- Investigating zero valent iron nanoparticles (NPs)
- Non ZVI and composite nanoparticles
- Mobility and fate of nanoparticles
- Environmental impact of reactive nanoparticles
- Analytical methods
- Modelling tools
- Up-scaling (large tank trials), risk and sustainability
- Field tests at case study sites
- Dissemination, dialogue and exploitation

For more detailed information about the different work package activities, visit the project website www.nanorem.eu

The goal of the NanoRem project is to show that the application of NPs is a practical and reliable method for the treatment of contaminated soil and groundwater. NanoRem will provide a direct link between the production side and application of groundwater remediation using NPs. NanoRem is exploring the use of two broad classes of NPs, nano zero valent iron (nZVI) and others including iron oxides and composite NPs.

Investigating zero valent iron nanoparticles

As part of the NanoRem project, nZVI is being produced by either solid-state thermal reduction or by low temperature milling of larger particles (cryomilling). The final product of the thermal process is being tested in unmodified and modified forms. Materials are being made available as a slurry or dry powder.

Table 1. Summary of Nanoparticles being used in NanoRem

	NanoFer 25S	NanoFer Star	Milled Iron	Bio-magnetite	Carbo-Iron	Fe-Zeolites	Fe-oxides	Al and Mg
Type of particle	Nano scale zero valent iron (nZVI)	Air-stable powder nZVI	Mechanically ground nZVI particles	Produced from nano-Fe(III) minerals	Composite of Fe (0) and activated carbon	Nanoporous alumosilicate loaded with iron	Pristine iron oxides stabilized with HA	Zero valent metals
Process of contaminant removal	reduction	reduction	reduction	reduction	Adsorption + reduction	Adsorption + oxidation	oxidation (catalytic effect on bioremediation)	reduction
Lab-scale	X	X	X	X	X	X	X	X
Large scale tests	X				X		X	
Field scale tests	X		X		X		X	
Field sites: Site name (country */ main contaminant)	**Spolchemie 1** (CZ / PCE)		**Zurzach** (CH / PCE)		**Balassagyarmat** (HU / PCE) **Neot Hovav** (IL / n/a)		**Spolchemie 2** (CZ / Toluene) **Barreiro** (PT / heavy metals) **Nitrastur** (ES / arsenic)	

***Country Key**
CZ – Czech Republic; CH – Switzerland; HU – Hungary; IL – Israel; PL – Poland
ES - Spain; PT—Portugal

Non ZVI and composite nanoparticles

NanoRem is developing non ZVI and composite NPs, progressing with particle design, optimisation of self-manufactured and/or purchased particles. A new procedure for up-scaled production of the NP composite Carbo-Iron and an up-scaled coating process for nano-Goethite have been developed ensuring supply of both particle types in larger amounts for field tests, with other particles being provided for laboratory tests, see Table 1 for details. Referral for use and material safety data sheets are being provided for all nZVI, non ZVI and composite NP.

For the first time, NanoRem brings all these particles together in the context of groundwater remediation and test them uniformly to better understand their characteristics and to optimize their performance. All particles are either pre-manufactured (e.g. Carbo-Iron and Biomagnetite) or bought and further processed in some way e.g. for the nano-Goethite a special coating procedure is applied which provides the particles with better mobility which helps target microbial contaminant degradation. For Fe-Zeolites, further processing occurred to optimize the particle-size and Fe-content . Milled Aluminium (Al) and Magnesium (Mg) particles were studied by VEGAS and were used in small-scale experiments only.

Mobility and fate of nanoparticles

Characterisation and mobility tests have been carried out for the range of NPs listed in Table 1, applying experimental protocols that have been developed as part of the project. Based on these results and volumes of material available, NanoFer 25S, Iron Oxide, Milled Iron and Carbo-Iron has been selected for further optimization of mobility and reactivity, upscaling and field scale tests at case study sites. Optimised particles developed by NanoRem have revealed a significant improvement in terms of mobilisation and reactivity.

Environmental impact of reactive nanoparticles

A protocol has been developed for assessment of the ecotoxicity of NanoRem's NPs. Tests have been based on exposure of terrestrial and aquatic organisms to several types of NP. NanoFer STAR, nano-magnetite, nano-goethite, Fe-zeolite, Carbo-Iron, biogenic nano-magnetite, and Fe milled particles generally showed no negative effects at environmentally relevant concentrations, but occasionally weak effects at high concentrations. The highest toxicity was seen in the presence of Fe milled particles, whereas positive effects on some organisms were observed in the presence of Carbon-Iron.

Field based analytical methods

Work has been carried out on the development and testing of various analytical methods available for NP characterisation of Fe-based and other remediation NPs. A magnetic susceptibility array has been developed for field site monitoring of nZVI, and test arrays have been installed into a large scale tank experiment and two field sites. A variety of *in situ* and at site methods are now ready for field application testing, including new methods for tracing Carbo-iron and Fe-zeolites.

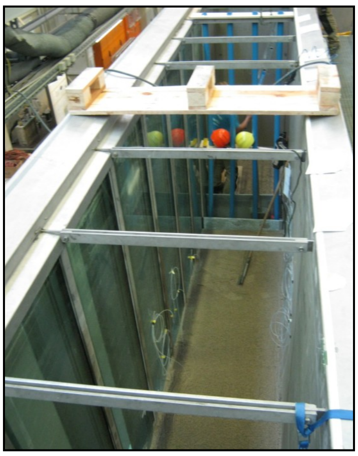
Modelling tools

NanoRem uses computer models that simulate the movement of NPs in the subsurface, to help in the design and interpretation of laboratory and field tests. A pore-network model - with enhanced pH and ionic strength dependency for colloid transport - is being used as a digital experimental environment at the pore scale. New pre- and post-processing tools generate the input and analyse the output of the many pore-network experiments. The necessary pore scale model parameters (pore size distribution, pore distance, and average pore connectivity) for average sand were identified from the literature and a sensitivity analysis was performed for these parameters against common upscaled parameters and rules for water flow, like porosity and Darcy's law.

A numerical tool for macro-scale simulation of solute and nanoparticles transport in porous media, called MNMs 2014 (http://areeweb.polito.it/ricerca/groundwater/software/MNMs.php) was developed and released for laboratory transport test design and interpretation. MNMs provides a user-friendly graphical interface for DLVO calculation, solute and colloid transport in 1D (including linear and non linear deposition kinetics under both constant and transients in ionic strength, clogging, non Newtonian flow), and nanoparticle radial injection for the preliminary design of pilot- and field-scale injections. The ionic strength-dependent nanoparticle transport equations were also implemented in a RT3D-based plug-in, providing an extended tool for pilot- and field scale applications in complex 3D geometries. Numerical models have been created for the simulation of the two large-scale laboratory experiments.

Up-scaling (large tank trials), risk and sustainability

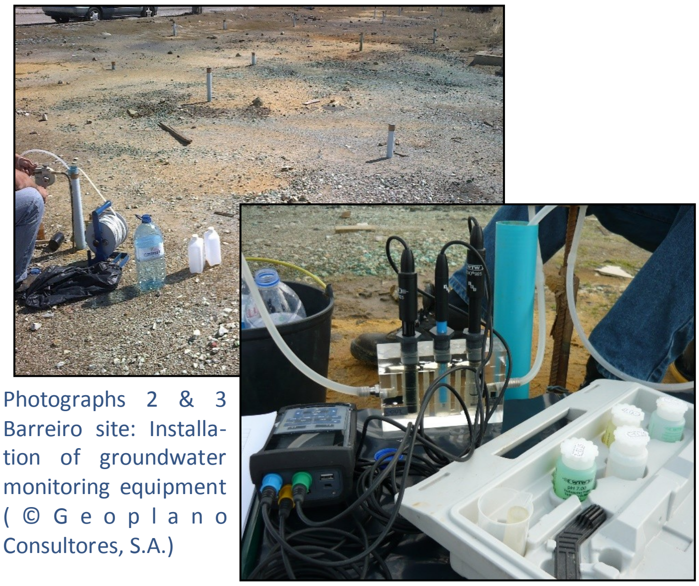
Three large scale experiments using large contained tank systems (see photograph 1) were carried out to better understand up-scaling effects to assist planning for field scale deployments (including emplacement of contaminant sources/plumes). These experiments were set up, monitoring equipment has been installed and the contaminant is emplaced. Injection equipment, particle suspensions and procedures have been set up; injections will be performed after steady state contaminant conditions are reached. Sustainability appraisal and preliminary life cycle assessment approaches are in preparation.



Photograph 1 Large scale tank experiments (© VEGAS/University of Stuttgart, Germany)

Field tests at case study sites

An essential part of the NanoRem project is the proof of concept of NP based remediation at a range of field sites. Case study sites have now been confirmed, with any necessary additional investigations and installations underway (see photograph 2 & 3). Remediation goals have been defined and evaluated and communication with regulating agencies has yielded injection permits for most of the sites. Conceptual site models have been designed to enhance discussion and dissemination with key stakeholders.



Photographs 2 & 3 Barreiro site: Installation of groundwater monitoring equipment (© Geoplano Consultores, S.A.)

Dissemination, dialogue and exploitation

The NanoRem web site and intranet systems have been developed and are in use, including information for decision-makers; (http://www.nanorem.eu/Informationfordecisionmakers.aspx). Reports have been published on deployment risks of nZVI use (based on an expert elicitation workshop) and risk-benefit appraisal of the use of nZVI (http://www.nanorem.eu/Displaynews.aspx?ID=525). Engagement with stakeholder networks, market appraisal and sustainability assessment tasks are underway.

Future

The next 12 months will prove to be very important to the success of the NanoRem project. The pilot trials will be up and running, results will be being collated and the profile of the project will be rising. Engagement with stakeholder networks, presentations at key conferences will be an important measure of the project's success showing that the application of NPs is a practical and reliable method for the treatment of contaminated soil and groundwater.

Dr. Hans-Peter Koschitzky

Coordinator of NanoRem Project

Hans-Peter is the coordinator of the European Project NanoRem and today we have the pleasure in interviewing him. First of all, thank you for giving us this interview, because your experiences are invaluable for all of us to understand about the project. Opening the interview with an easy question.

Q. How did you embark on this adventure?

A. Yes NanoRem really is an adventure but also a great challenge. At the beginning with such a large number of partners of which some you do not know, and with such a large project you are unsure how well everything is going to run to achieve the ambitious goals. However, on the other hand, there are partners in the project I personally have known and worked with for many years from other projects. Many I know through my long standing international activities - especially from the NICOLE network and from a number of EU projects in the 5th and 6th Framework Programme. I know their fields of activity, their competence and I can rely on them. This is very important because even in the case of potential problems that may arise in such a large project, I can talk to them without hesitation and resolve issues. These partners and a strong VEGAS team, ensure the project will deliver on its objectives. These are the reasons I finally was convinced to take over the coordination of the adventure NanoRem.

Q. What is the aim of the project?

A. NanoRem's aim is to develop and improve different types of nanoparticles to remove contamination from groundwater bodies. The focus is on highly contaminated areas, to treat the source of the contamination. With this in mind, an important issue will be to develop lower cost production possibilities for already lab scale developed and usable particles and to increase the operating windows of particles to treat a wider spectrum of contaminants. All nanoparticles are characterised with regard to their physical and chemical properties, their mobility and migration potential in the subsurface and their potential to cause harm (ecotoxicology). Subsequently, the nanoparticles are tested in large container experiments (artificial aquifers with dimensions of many metres). After which the application of different particles will be demonstrated on several pilot sites in different European countries on different contaminants. For the design of the remedies, a numerical model tool for investigating the remediation performance a "monitoring toolbox" has been developed. Finally, dissemination and dialogue with key stakeholder interests will be provided to ensure that research, development and demonstration meets end-user and regulatory requirements.

Q. It is striking that the consortium is 28 partners from 12 countries, how was the network created?

A. In July 2011, the EU published in the 7th Framework a very large call NANO SCIENCES, NANOTECHNOLOGIES, MATERIALS AND NEW PRODUCTION TECHNOLOGIES. One of the themes (with the number NMP.2012.1.2-1) was Nanotechnology solutions for in-situ soil and groundwater remediation. This call explicitly required a large consortium to be formed, which should treat the subject comprehensively with a clear focus on developing "ready for use" technologies and to demonstrate their applicability and be "ready for market" in several countries in Europe.

Since we in VEGAS at the University of Stuttgart have been involved in national and EU funded R&D projects for several years working in this topic area, our idea was to participate in a project in this call. We asked some of our previous partners whether they were interested in participating, but were also asked independently by various other interested parties to join their consortia. Rapidly a small "core" group of about 6 to 8 partners was formed and met for a first exchange of ideas in Stuttgart and a proposed outline structure of a project was formed. The core group did not cover all aspects required by the EU call, so each partner was asked to suggest additional partners to fill the skills gaps. These people were approached and asked to complete a questionnaire asking them for their specific expertise in certain topic areas and asked if they were interested in being involved. Initially we had more than 30 interested parties. In a second meeting in Stuttgart in mid September 2011 with nearly 30 partners, the proposal was already very well structured into different work packages (WP), the WP leaders selected and tasks and partners assigned. At the unanimous request of the partners, VEGAS was asked to undertake the coordination role, which actually was not our intention, but at last we agreed.

Q. Nanoremediation, nanoparticles are technical words that for the general public are difficult to understand. In understandable language what does it mean? How does it translate to our daily lives?

A. Nanoparticles, as used in the NanoRem project, are intended to have at least one dimension at the nanoscale (<100 nm). One nm is a billionth of a metre – so this is incredibly small. For example looking at a human hair under a microscope you can see only a part of the surface (the bending), a nano particle on this hair would look like a small sand grain. However, it is still bigger than an iron atom which has a diameter of about 0.3 nm.

Some of the nanoparticles applied in NanoRem are not spherical but can have forms like flakes or can clump together to form bigger irregular shapes. Nanoremediation means to inject these nano particles into a contaminated subsurface to bring these particles in contact with the contamination to remediate *in situ* contaminated groundwater bodies (aquifers).

Q. Nano zero-valent iron (nZVI), exactly what is it? what's its function in nanoremediation?

A. Nano zero-valent iron (nZVI) is elementary iron at the nanoscale. It is used as a reducing agent (electron donor) for the decomposition of contaminants like polychlorinated hydrocarbons, highly toxic substances such as As(III), As(V), Cu(II), Co(II), Cr(VI), nitrite, amoxicillin and ampicillin, TNT, chemical warfare agents and cyanobacteria. The nZVI particles are designed in a way that interaction with the soil is minimised, avoiding large iron agglomerates forming. This is mainly achieved by the production method of the nZVI particles being coated with different layers.

In NanoRem, not only nZVI particles are being developed and optimised but also other particles like a new iron-based colloidal composite "Carbo-Iron". This is an air-stable, sorption-active reducing material where nano-iron clusters are placed within the pore structure of colloidal activated carbon particles. Moreover NanoRem is also testing iron oxides such as goethite and biomagnetite, particles based on aluminium and magnesium, Fe-zeolites and ferrates to increase the range of contaminants which could be treated.

Dominique Darmendrail
Chair member of the Project Advisory Group representing COMMON FORUM

Dominique you are the chair member of our Project Advisory Group representing COMMON FORUM, the network of European regulators, thank you for giving this interview.

Q. Can you tell us a little bit about the COMMON FORUM?

A. The COMMON FORUM on Contaminated Land in the European Union, initiated in 1994, is a network of contaminated land policy makers and advisors from national ministries and Environment Agencies in European Union Member States. 18 European countries are currently active within Common Forum. The general objectives of COMMON FORUM are to develop strategies for the management and treatment of contaminated sites and for land recycling with respect to "sustainable resource protection" for contaminated land and groundwater.

Q. What does the project advisory group do and how would you describe your role?

A. The Project Advisory Group (PAG) has been created for:

- Providing the viewpoint of end-users by commenting on and contributing to the review of project objectives / products / deliverables;
- Ongoing monitoring of progress / performance of the research, including compliance with environmental regulations;
- Making recommendations on the scientific & technological orientations of work from the perspective of an end user.

As PAG chair, I'm in continuous contact with the project coordinator and the work package leaders for ensuring the best contributions of the PAG members who represent the different stakeholder communities involved in site remediation. It's our privilege to support the team for achieving the scientific and technical objectives of this ambitious project.

Q. How do you hope NanoRem will advance knowledge in nanoremediation in Europe?

A. NanoRem is looking to address key issues for the implementation of nanoremediation technologies, such as:

- The risk of dissemination of NP in groundwater;
- Potential ecosystem risks related to these particles;
- The possibility of discovering transformation / degradation products (metabolites) associated with the NP due to mediated reactions;
- The exposure models to address in any residual risk assessment;
- How to design a sustainable remediation using nanoparticles;
- How to monitor sites using these innovative remediation technologies;

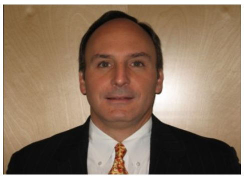
All these issues will be crucial for identifying nanoremediation options and its promotion.

Q. What will help regulators embrace this new technology?

A. Regulators' main concerns about any new innovative technology are related to:

- The sustainability of proposed remediation solution(s), with a clear idea of the possible secondary products;
- The effectiveness of nanoremediation compared to other types of remediation, with potential restrictions to future land use;
- The way to verify this effectiveness, by defining what the remediation end point will be and how it will be proven.

Communicating on case studies where these technologies have been successfully used and controlled will also support regulators' acceptance.



Dan Elliott

Member of the Project Advisory Group of NanoRem

Dan Elliott, you were one the inventors of nanoremediation in the early 2000s so we are delighted that you are a member of the Project Advisory Group of NanoRem, thank you for giving this interview.

Q. Could you give us a very brief history of your career and interests in nanoremediation?

A. It is an honour to be part of NanoRem. I am a PhD environmental engineer with a deep interest in the technical aspects of environmental investigation and remediation as well as in corporate environmental affairs (environmental management, due diligence, compliance, permitting, and sustainability). I really straddle the fence regarding my technical and non-technical interests. Perhaps not surprisingly, my career thus far has been similarly quite varied featuring roles in industry (Merck & Co., Inc. and American Standard Inc.), academia (University of North Carolina-Chapel Hill, USA), and consulting (Whitman and Geosyntec). I left industry in 1999 to get into the then embryonic environmental nanotechnology field with research on nanoscale zero valent iron (nZVI) at Lehigh University, USA because I felt that someday, it might revolutionize the remediation industry and represent a tremendous benefit for underutilized brownfield sites in Europe and around the world.

Q. What motivated you to join the NanoRem advisory group?

A. The major motivation was the opportunity to work with some of the leading researchers, environmental practitioners, and venerable institutions throughout Europe. After 15 years of very mixed progress with the nanoscale iron (nZVI) technology in the field, despite burgeoning growth of articles in the peer-reviewed literature, I am hopeful that NanoRem will represent a new beginning for the nZVI and allied nanotechnologies.

Clearly, the European Union is investing considerable resources (€14M) and through the leadership of the University of Stuttgart and the other NanoRem partners, we have the opportunity to delve into and hopefully answer some of the vexing key questions surrounding the use of nanotechnologies in environmental remediation.

Finally, I am very interested in contributing not only my nZVI experience but also the "owner's perspective" borne from many years as an environmental affairs professional in industry.

Q. What do you see as the strengths of the project and what might be the points we need to watch out for?

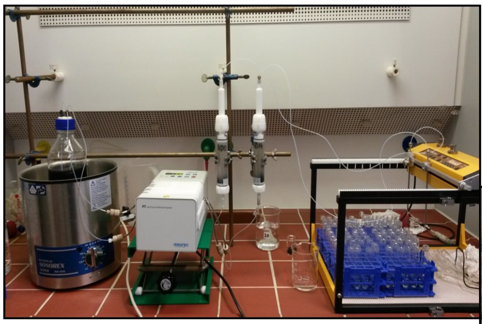
A. The over-arching strength of NanoRem is the excellent calibre of the participants, the high quality of the research, and the vision contributed by its partnering universities, national research laboratories, consultants, and problem owners. There is considerable research and development strength for novel nanomaterials, excellent talent focusing on the all important implications of using environmental nanotechnologies, and a willingness to actively engage a Project Advisory Group to assist the NanoRem leadership in maximizing the scientific utility of the results. I believe our most significant challenges are essentially two-fold: (1) to ensure that the large-scale field studies are well-designed and adequately funded to facilitate the development of new knowledge and experience that advances the state of the art and (2) to vigorously maintain lines of open, direct, and clear communications between the many project teams so as to maximize the alignment of goals and outcomes. Regarding the former, the field sites need to be a good match for the nanotechnology(ies) selected (from a hydrogeological, geochemical, suite of contaminants, and land use perspective), feature adequate post-injection monitoring, and include sufficient costing data.

Q. How much have you enjoyed your time with NanoRem?

A. It would be difficult to overstate how valuable and fun the NanoRem experience has been for me thus far. My involvement with the excellent cadre of scientists and engineers on the Project Advisory Group, and the opportunity to collaborate with and get to know many of the outstanding researchers and environmental managers in the work groups has been one of the truly seminal experiences of my career. Despite our differing nationalities, cultures, and languages, we share a common interest and objective in advancing the responsible utilization of nanotechnology to help address decades-long challenges associated with environmental impairment from brownfield sites. I am very proud to be part of NanoRem and am very excited about the potential scientific advancements it will contribute to the tool box of remediation technologies.

Q. How do you think NanoRem will advance knowledge in nanoremediation?

A. I will answer this in two ways. In general, I expect NanoRem to significantly contribute to the advancement of the state of the art of environmental technologies used in investigations and remediation through publications in the peer-reviewed literature on such topics as novel nanoparticles, robust fate and transport studies, innovative delivery and monitoring systems, and well-designed field studies. More specifically, I believe that NanoRem will: (1) produce significant materials characterization and applications data for novel nanomaterials; (2) elevate awareness of the use of nanotechnology in environmental remediation, which could result in the change of use restrictions or possibly bring about regulatory paradigms concerning such use; (3) result in a deeper understanding of the fate and transport of engineered nanomaterials in subsurface environments; (4) contribute to the growing realization that comprehensive and efficacious remediation strategies require synergistic technology combinations, such as that which exists between nZVI-mediated abiotic transformation of chlorinated aliphatic hydrocarbons and in-situ anaerobic biodegradation; and (5) result in the development of new understanding and expertise regarding the safe and effective production, handling, storage, and deployment of novel nanomaterials.



(Above) Column setup for nanoparticle transport experiment (Source: University of Vienna). (Right) Heads of monitoring arrays for *in-situ* susceptibility measurement (© VEGAS/University of Stuttgart, Germany)

(Right) Monitoring arrays for *in situ* susceptibility measurement ready for installation on pilot site (© VEGAS/University of Stuttgart, Germany)

Risks from Renegade Nanoparticles during field deployments within NanoRem

Paul Nathanail, Andy Gillett, Caroline McCaffrey & Judith Nathanail

Land Quality Management Ltd (www.lqm.co.uk)

The aim of NanoRem is to support and develop the appropriate use of nanotechnology for contaminated soil and groundwater remediation. NanoRem focuses on facilitating practical, economic and exploitable nanotechnology for in-situ remediation. This can only be achieved in parallel with a comprehensive understanding of the environmental risk-benefit balance for the use of nanoparticles (NPs).

One of NanoRem's objectives is to provide field evidence of the safe and effective deployment of NPs to remediate polluted groundwater. The health and safety aspects of injecting nanoparticles do not pose a particularly novel challenge. However it is necessary to consider the potential risks of injecting NPs into groundwater. Risk assessment specialists from Nottingham-based SME Land Quality Management (LQM) developed a protocol to allow the NanoRem field trials to evaluate the risks posed by NPs that do not get consumed in the remediation process. The fate, transport and toxicity of these so called renegade NPs was considered during an expert elicitation workshop organised by LQM at its University of Nottingham Innovation Park offices. The workshop outcomes supported with evidence from the literature formed the basis for a simple protocol for field trial sites to use to evaluate the risk posed by their NP deployment and demonstrate to regulators the trials would be safe.

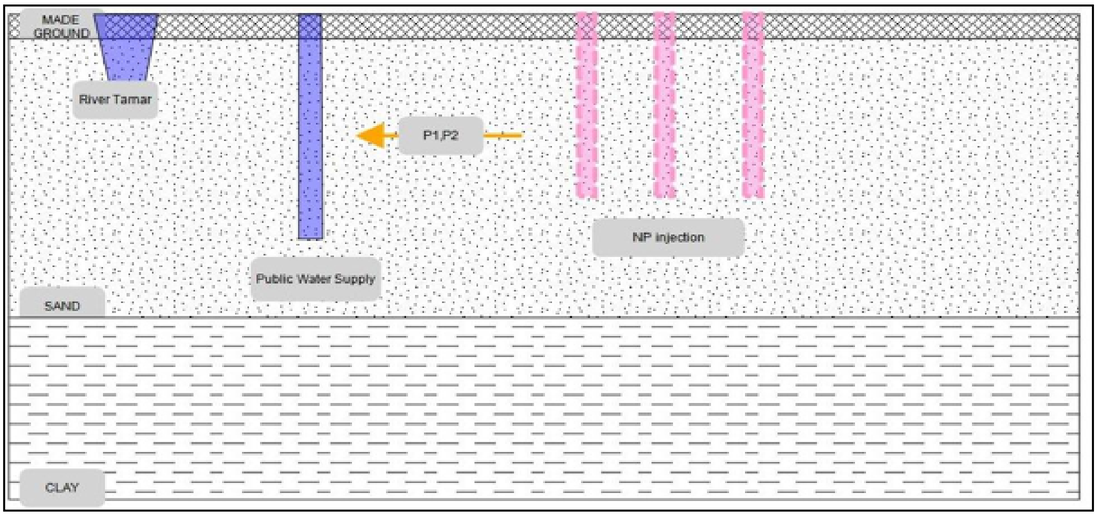


Figure 1 Cross section from CSM (This site is an example only and does not represent any of the pilot sites) (© Land Quality Management 2014)

LQM's work focused on the NanoRem NPs. While these NPs could have a significant toxicity, they are less potent than nano Silver (nano Ag). They are likely to interact with the aquifer matrix, each other and groundwater to rapidly cease to be mobile NPs. They are therefore likely to be difficult to penetrate into the aquifer more than a few metres from the point of injection.

For an environmental risk to exist all of the following must be present: a source of contamination (S), a receptor (R) and a pathway(s) (P) linking the two - i.e. a contaminant linkage (S-P-R) and such linkages are shown on the Conceptual Site Model (CSM) see Figure 1.

A CSM addressing the possible risk from renegade nanoparticles needs to be created separately from, and is in addition to the CSM which should already have been developed for the contamination problem at the site. For the pre-deployment risk assessment for NP injection, the NP themselves are considered as the source, with the CSM used as a tool to consider whether there are potential pathways for NPs to relevant receptors.

Receptors that could be affected by NPs include: human health, surface and ground water, or ecosystems, although for some of these the potential exposure scenarios are unlikely. Despite the uncertainties, LQM identified a range of circumstances that indicate NP can be safely deployed. These include an absence of receptors, where a site has pathway interruption though (e.g. a down gradient Permeable Reactive Barrier) or the limited NP transport means the receptor would not be reached by fugitive NP.

Overall while there are considerable uncertainties particularly with regards to the transport of NanoRem NPs the ability of NP to penetrate far into the formation is likely to be very limited. At this stage such a protective situation is welcome. Once the results of the field trials are available, LQM will update the risk assessment protocol for eventual publication and consideration for wider take up.

Case Study Site: Spolchemie site remediation and NanoRem field site application

Petr Kvapil

AQUATEST (www.aquatest.cz)

Site Remediation

The Spolchemie site was chosen as one of the NanoRem case study sites, to test two types of nanoparticles (NPs) (zerovalent iron - nZVI and iron oxide NPs) for *in situ* remediation of BTEX (Benzene, Toluene, Ethylbenzene, and Xylenes) contamination. Nanoremediation was seen as an opportunity to enhance the *in situ* biodegradation of the BTEX contaminants and to reduce the current remediation method of skimming free product from the groundwater surface waters and contining the use of a pump and treatment system that have been ongoing since 2005. Spolchemie is one of the leading synthetic resin manufacturers in Europe. Besides synthetic resins it also produces other chemicals (e.g. potassium and sodium hydroxide, epichlorohydrin, allylchloride, sodium hypochlorite, perchloroethylene, hydrochloric acid, liquid chlorine). This production site is located in an area of approx. 52 hectares at Usti nad Labem (Czech Republic) in the heart of Europe. The main Spolchemie complex comprises industrial buildings, roads and railway sidings, with a few vegetated areas. The site is in a rural setting. The plant was established in 1856, and began the production of inorganic chemicals followed by the manufacture of organic dyes at the turn of the 20th century, and from the middle of the last century Spolchemie started to produce resins and freons based on tetrachlormethane and tetrachlorethene.

The production, treatment, storage and distribution of these various products has led to extensive contamination of the subsurface by chlorinated ethenes and methanes and organic solvents including BTEX compounds, which in many cases have dispersed widely from the original source areas. Some parts of the subsurface are also contaminated by high concentrations of iron and other inorganics (mainly chlorides and sulphates) which have increased the salinity of the groundwater.

A number of groundwater monitoring campaigns has been undertaken followed by a preliminary site investigation. Based on this work a Conceptual Site Model (CSM) has been developed detailing the subsurface conditions followed by a preliminary risk analysis. This initial CSM was refined by further targeted investigation and subsequent updating of the risk analysis. This work indicated that remediation requirements would be complex. With further funding being secured, the CSM was expanded following delineation of the contamination, geological and hydrogeological surveys, well logging, development of a hydrogeological model of the site and a remediation feasibility study. Exploration of the site is still ongoing to further improve the conceptual site model and review further the most appropriate overall remedial strategy.

Six contamination plumes have been identified at Spolchemie, based on the type of contamination, geology and hydrogeology [see Box 1] of the subsurface areas identified in the conceptual site model.

BOX 1 – Geology and Hydrogeology at the site

The geological formations underlying the site are complex with the lower geological formations consisting of Mesozoic Cretaceous siltstones and claystones (thickness of several tens of metres) overlain by Tertiary Miocene tuffitic clays. From north to south of the site the thickness of the tuffite clays decreases, and is infilled by overburden of Cretaceous sediments. Overlying the Mesozoic and Tertiary sediments is a Quaternary terrace formed mainly by fluvial sediments and deluvio fluvial sediments of the Bilina River, the Elbe River and Klissky Stream. The Quaternary terrace consists of gravel, sand and gravel with large boulders with an average thickness of 6m. The Quaternary terrace is overlain by aolian loess loams, which are located at a depth of 1.5 to 3.5 m below ground level (max. thickness 2.5 m) with made ground overlying that. This consists of backfill of various thicknesses of clay, loam, sand, tarmacadam, pieces of brick and concrete.

The groundwater levels mirror the interface of the loess overburden in the overlying Quaternary terrace deposits. The groundwater level is from 3.0 to 4.0 m below ground level. The general horizontal groundwater flow direction is South East to South East East to the Bilina and Elbe

The general remedial concept is based on a combination of pump and treat technology, a passive reactive barrier and enhancing physical, chemical and biological *in situ* methods. The different methods being applied depending on the character of the contamination. For example permanganate infiltration or *in situ* oxidation accompanied by heating and sparging by a modified Fenton process, supported by venting, are being applied in the source zones, with pump and treat being combined with biological processes such as dehalogenation in a treatment station. This is being monitored in detail by molecular biology analysis in collaboration with the Technical University of Liberec.

The main principle underpinning the remediation design being considered is to pump the contaminated groundwater, treat it above ground and then allow the treated groundwater to infiltrate back into the ground. The costs associated with this type of pump and treat approach tend to be very high, and its operating lifetime tends to be rather long. Nanoremediation may offer a way of dealing with the source terms *in situ* so reducing the requirement for pathway management, and therefore lowering pump and treat costs and treatment time. NanoRem will explore this concept at this site.

The NanoRem case study at Spolchemie

The NanoRem case study at Spolchemie includes two large scale field tests.

Test Site 1: Two contamination plumes in the western part of the Spolchemie area, with Chlorinated Hydrocarbon Contamination (CHCs), are being treated by a 500 m long impermeable underground wall with 10 reactive gates filled with zerovalent iron chips. A pump and treat remedial system was also installed to decrease the concentration of CHCs on the inlet side of the wall. However, routine monitoring showed an overflow of contamination behind the wall from a secondary contamination source (storage tank) was occurring see Figure 1.

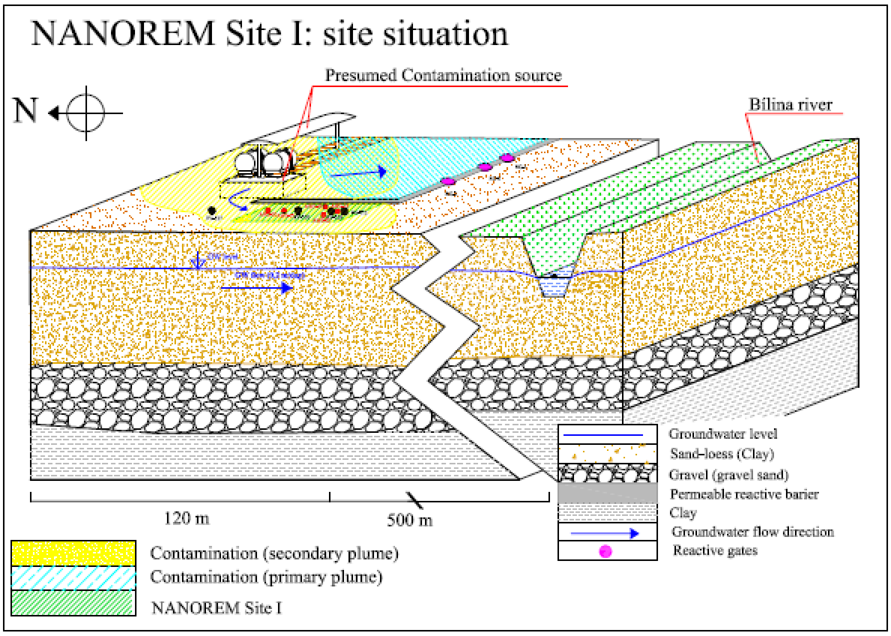


Figure 1 Site Situation (© Aquatest 2014)

The application of nZVI is being evaluated as an *in situ* technology for the clean-up of this secondary source area. A field test will be used to validate its suitability as a full scale remediation option. This field test is being conducted by AQUATEST with participation of several NanoRem partners (TUL, Nanoiron, Palacky University in Olomouc and VEGAS Stuttgart). Detailed monitoring including installation of new wells for vertical contaminant distribution is being carried out in collaboration with VEGAS including the use of micro pumps installed in the original ZVI system for nanoparticle monitoring in the field test. A preliminary tracer test has already been undertaken. nZVI (NanoFer 25S) supplied by Nanoiron will be injected in the autumn of 2014.

Test Site 2: The middle part of the Spolchemie site was also extensively contaminated by BTEXs. A general approach in this area has been to excavate the contaminated soils from the unsaturated zone in the source zone area and then remediate the underlying aquifer by pump and treat. The pumping of free phase from several wells is also ongoing. Treated water is discharged back into the ground. Enhanced *in situ* bioremediation has been identified as a suitable remediation technology to treat residual free phase product and BTEX compounds in this area based on laboratory and pilot tests. Tests confirmed the ability of natural microflora to degrade the present contamination under anoxic conditions with nitrate being used as an electron acceptor. This has created an opportunity for NanoRem to look at nanoremediation and *in situ* bioremediation processes working in tandem, using of oxidic NPs (based on Goethite) as another possible electron acceptor. The NanoRem partners involved in this trial are the Helmholtz Institute in Muenchen, UNIVI and VEGAS Stuttgart.

This area of the site has been investigated in detail. Additional wells have also been drilled and tracer tests undertaken before application to precisely delineate the plume. Undisturbed soil samples were taken for laboratory test verification (reactivity and migration tests) to assist with the NanoRem field test design.

Permitting: Permission for NPs application (for both sites) required negotiation with multiple agencies: the Municipality of Usti nad Labem, the Regional Authority, Czech Inspection of Environment, Ministry of Environment and Ministry of Finance. The permitting process was facilitated by an open process of discussion over many years, which provides information in detail about the whole remediation process, including the preliminary studies of proposed technologies, which are first applied as a small pilot test in the areas covered by the hydraulic barrier.

The importance of risk based conceptual site models

Judith Nathanail

Land Quality Management Ltd (www.lqm.co.uk)

This article highlights the importance of Conceptual Site Models (CSMs) to NanoRem. CSMs summarise the source-pathway-receptor linkages (SPRL) and significant uncertainties at a site in easily understood diagrams. They are updated as more information becomes available. Used in the relevant legal context, they inform risk assessment and risk management decision making.

The NanoRem pilot sites need CSMs to ensure shared understanding site conditions and to design an appropriate remediation strategy. To assist them, in July 2014 LQM delivered an online seminar on creating a CSM.

CSMs provide a simplified vision of the site

The CSM highlights the relevant features of the site and adjacent area. It comprises plans and cross section(s) together with a matrix or network diagram to identify source-pathway-receptor linkages (SPRL) accompanied by summary text (Table 1).

CSMs aid understanding and communication among stakeholders.

Creating the CSM deepens its creator's understanding of the site thereby improving risk assessment and remediation outcomes.

The CSM is a communication tool that focuses attention on the key risk driving features of the site. This allows all stakeholders to rapidly understand the nature of problem. It also facilitates dialogue, allowing stakeholder questions to be addressed, which in turn further improves the understanding of the site.

Table 1. Information for inclusion in CSM based on (Nathanail, Bardos, and Nathanail 2007)

Information	Mark on plan	Mark on cross section	Mark on Network Diagram	Summary text
Site summary				Y
History of site and surrounding area	Y	Y		Y
Topography of site and surrounding area	Y	Y		
Geology including possible variations across site	Y	Y		Y
Hydrogeology including possible variations across site	Y	Y		Y
Source characteristics (including findings of any investigation carried out, materials present and contamination found)	Y	Y	Y	
Potential pathways	Y	Y	Y	
Potential receptors	Y	Y	Y	
Possible/significant pollutant linkages	Y	Y	Y	
Uncertainties and assumptions	Y	Y	Y	Y

CSMs highlight the relevant legal context

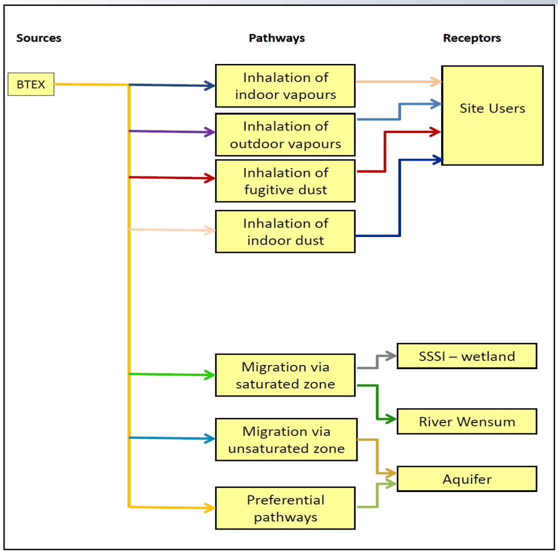
Legal drivers affect what actions may be required to manage the presence of contaminants at a site or dictate the nature or location of relevant receptors. The CSM is developed in the light of these drivers and the legal context is clearly stated within the CSM.

Plans and cross sections usefully summarise the site conditions while relevant source pathway receptor linkages (SPRLs) can be depicted on a network diagram (Figure 1). Candidate remediation strategies can then be tested against the CSM to see whether they break the SPRLs.

CSMs identify uncertainties and drive the risk assessment

As the CSM is created, unknowns become apparent. The CSM captures such uncertainties and assumptions, so the level of understanding of the problem is apparent. Examples of uncertainties and assumptions are in Box 1.

Uncertainties identified during one phase of investigation can comprise the objectives of subsequent phases; thereby refining the risk assessment.



Box 1. Example uncertainties and assumptions

Example uncertainties

- Thickness of sand layer
- Depth to water table

Example assumptions

- There are no preferential pathways to the river
- The plume is not migrating off site

Figure 1 Extract from a conceptual site model: The Network Diagram

CSMs explain the problem at hand.

Several CSMs may be created to consider different aspects of the project. For NanoRem there will be CSMs for:

- "the problem" driving the need for remediation e.g. contaminant reaching river;
- The "remediation solution" e.g. nanoparticles destroying the contaminant;
- The predeployment risk assessment (PDRA) for renegade nanoparticles.

The latter considers the NPs as the "Source" in order to consider possible risks of injecting nano particles into groundwater.

Figure 2 shows a plan view for the remediation solution showing where injection wells are to be located; Figure 3 is the associated network diagram showing how the linkage would be broken by removing the source.

Concluding thoughts: CSMs in NanoRem

NanoRem will produce CSMs for each pilot site showing the problem to be solved and demonstrating the extent to which nanoremediation has solved the problem. A separate CSM will be produced to consider possible risks of injecting NPs into groundwater. CSMs will form part of the evidence NanoRem will require to provide field evidence of the safe and effective deployment of nanoparticles (NPs) to remediate polluted groundwater.

Reference

Nathanail, J.F, P Bardos, and C.P. Nathanail. 2007. Contaminated Land Management: Ready Reference. Vol. Release 2. Nottingham, UK: Land Quality Press.

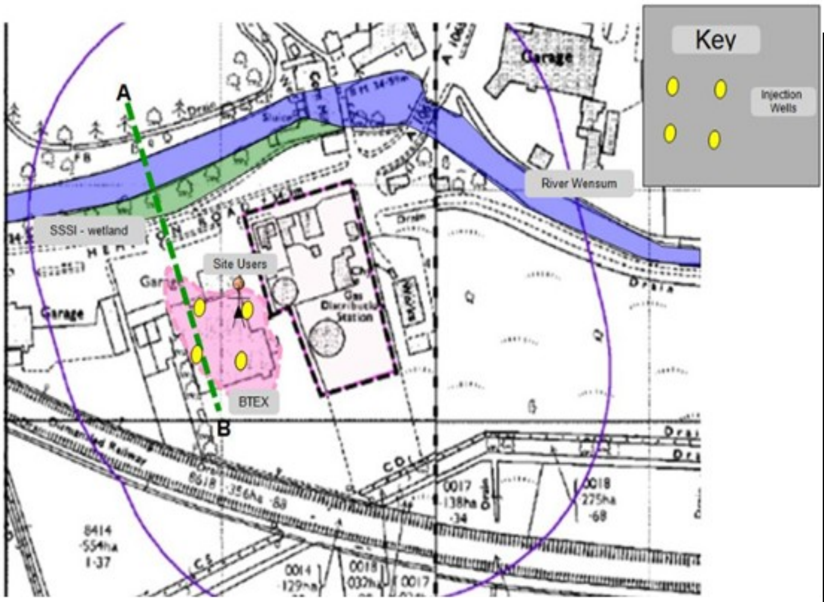


Figure 2 Plan View for CSM of Proposed Remediation Solution

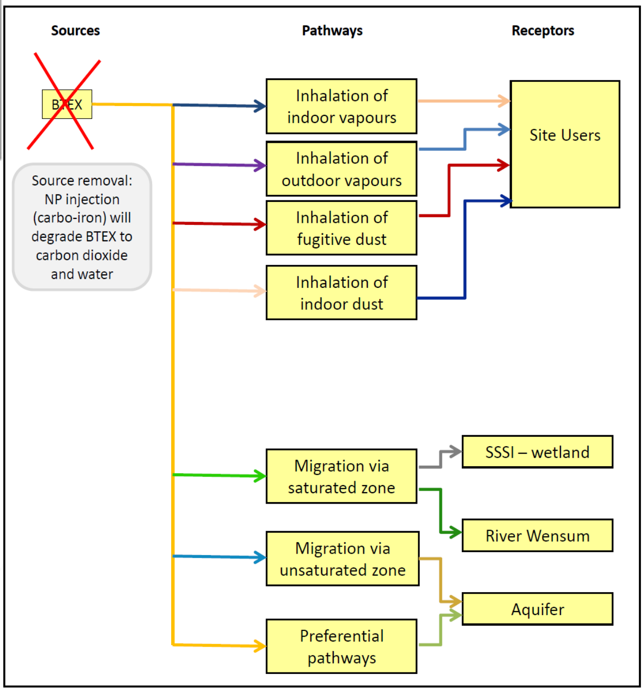


Figure 3 Network Diagram for CSM of proposed remediation

Nanomaterials: Challenges facing industry and policy makers

Dr. Roger Pullin

Chemical Industries Association

Expectations are that nanomaterials will be critical to the UK and Europe's long-term growth and sustainability. Many expect they will underpin major technological advances in automotive, aerospace, communications, energy products, medicines food and consumer goods. Remediation of land is a further example where nanomaterials have the potential to provide a highly effective solution to addressing the issue of soil contamination. The safety of such materials to humans and the environment is therefore of paramount importance. ***Dr. Roger Pullin, Head of Health at the Chemical Industries Association in the UK provides a brief insight into some of the regulatory challenges currently facing industry and policy makers.***

Background

For the past decade, the debate on nanomaterials with regards to their safe use and whether they need to be managed differently to standard sized chemicals has been steadily growing. Some deem this to be a new emerging technology whilst others see this as a simple renaming of what was previously known as 'ultrafines'. What is definite though, is that the word nanomaterial is here to stay.

Industry contributes to this debate and is working with national and European authorities. It also works with international bodies including the Organization for Economic Co-operation and Development (OECD) and many other stakeholders to demonstrate the safety of chemical substances defined as nanomaterials. Industry is building up evidence to show that nanomaterials can be produced and used responsibly under current existing EU legislation.

EU policy makers are giving careful consideration to the following challenges:

- Around the difficulties of identifying whether a substance is a nanomaterial;
- Ensuring testing requirements in the REACH (Registration, Evaluation and Authorisation of Chemicals) Annexes covering nanomaterials; and
- Whether consumer transparency needs to go further than that needed for other chemical substances.

Definition

First of all what qualifies as a nanomaterial? This is not as straightforward to define as we might think. Due to diverging scientific opinions, international bodies such as International Standards Organisation (ISO), the European Commission and EU Member States have different views on how this should be defined. An easier place to start is what is meant by the term nanoscale i.e. this being 10^{-9} or 1 nanometre (nm) is one billionth of a metre. In terms of nanomaterials, it is generally agreed that they are substances with a size in the range of 1-100 nm; in comparison, a human hair has a typical diameter of between 80,000-100,000 nm. In October 2011, the European Commission adopted a recommendation for a definition of a nanomaterial and agreed that this would be reviewed during the course of 2014 to evaluate whether it remains fit for purpose. The Review of the recommended definition is now in progress; the 2011 definition can be found on the Commission website at: http://ec.europa.eu/environment/chemicals/nanotech/faq/definition_en.htm. Prior to this the ISO published its own definition, yet this differs to the one from the European Commission. There are also differences between the definitions used within EU Member State reporting schemes, these being those in France, Belgium and Denmark.

Carbon - Iron is air stable (©K. Mackenzie, UFZ)

Industry has reservations over the definition due to its impracticality in the absence of standard and certified measurement techniques for determining the metric number size distribution of particles. A practical universal definition that is related to the normal mode of use would be welcomed, as in its view the EU definition is currently too broad. In 2015, it will be interesting to see what the Review concludes and as a consequence if any changes will be made.

REACH Annexes

As nanomaterials are chemical substances, the European Commission is pressing ahead to integrate their management under the existing horizontal REACH Regulation; the purpose of which is to ensure the safety of producers and users, as well as the environment, of chemical substances on the European market.

Stakeholders recognise and accept that some adjustments will be needed, yet how does the Commission do this. In line with the conclusion of the REACH Review, amendments to the REACH Annexes are currently under discussion. Industry believes the implementation of a concern-driven integrated approach would be the most effective whereby a substance is first checked to see it meets the nanomaterial definition and if so, whether the physicochemical properties together with information on use and exposure give any cause for potential concern. Identified nanomaterials with a potential concern would then be required to undergo further tiered and targeted testing. A legislative proposal for amending the REACH Annexes is expected later in 2014.

Transparency measures

Some stakeholders call for more transparency on the use of nanomaterials through the development of national registers/ inventories and more recently the idea of an EU inventory is being explored. Industry fully supports openness and transparency, believing that an 'Observatory' approach to be the most beneficial way forward to bringing reassurance to all stakeholders. This would be achieved by expanding the existing European Commission's Joint Research Centre web platform on nanomaterials to include information in the public domain for notifications of nanomaterials to all current regulatory schemes. It would include information on nanomaterials used in food, cosmetics, medical devices, biocidal products as well as substances submitted under REACH and CLP (Classification, Labelling and Packaging). Industry believes that with this in place, there would be no need for establishing a separate EU register, or national inventories, on top of existing regulatory requirements. It is likely that the debate on how to manage the information on nanomaterials will continue for some time.

Carbon - Iron (© A. Künzelmann, UFZ)

Conclusion

Whatever the outcome of the discussions, future regulatory decisions need to be pragmatic and not only protect human health and the environment, but also allow competitiveness and innovation in the UK and Europe to not be hampered. This can be achieved and achieving it will enable society to enjoy current and future benefits from these novel materials called nanomaterials; these may very well underpin the next generation of things we take today for granted such as cars, aeroplanes, communication devices, water treatment, energy production, medical provision and food preservation.

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NEWSFLASH

COMMON FORUM DISCUSS NANOREM PROJECT

At the recent COMMON FORUM (European Regulators) meeting on Contaminated Land in the European Union held in Berlin Germany in May 2014, Hans-Peter Koschitzky of University of Stuttgart (NanoRem Project Co-ordinator) was invited to give a presentation on the NanoRem project. He provided an introduction, its main goals, how the project is structured and details of the different nanoparticles that the project is looking to use in the seven different pilot sites. Hans-Peter Koschitzky finished by presenting the key outcomes after the project's first year. Dominique Darmendrail (Secretariat of the Common Forum) then welcomed an open discussion amongst its members to share their experiences/acceptance/ issues/concerns that different European countries have with respect to the use of nanoparticles being used for remediation of soil and groundwater.

Questions / issues of concern for regulators and policy-makers will be compiled by the COMMON FORUM secretariat for further discussion with the NanoRem project team.

NEW “INFORMATION PAGE” FOR DECISION MAKERS ON WEBSITE

A Risk/Benefit Appraisal for the Application of Nano-Scale Zero Valent Iron (nZVI) for the Remediation of Contaminated Sites


NanoRem

Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment

Project Nr.: 309517
EU, 7th FP, NMP.2012.1.2

WP9: Dissemination, Dialogue with Stakeholders and Exploitation

A Risk/Benefit Appraisal for the Application of Nano-Scale Zero Valent Iron (nZVI) for the Remediation of Contaminated Sites

Supporting MS3 - NanoRem information for decision makers – initial version

Paul Bardos (r3), Brian Bone (r3), Padraig Daly (r3), Dan Elliott (Geosyntec), Sarah Jones (r3), Gregory Lowry (CEINT), Corinne Merly (BRGM)

October 1, 2014

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 309517

NANOREM NZVI risk benefit issues paper FINAL.PDF

This NanoRem report paper assesses the relative risks and benefits of nZVI usage for *in situ* remediation, and identify the areas where further investigation might be required. An overview of nZVI use in field, pilot and laboratory trials to date is provided. This paper supports Milestone 3 of the NanoRem project, and is intended to help stakeholders by providing a basis for evidence-based decisions.

http://www.nanorem.eu/Displaynews.aspx?ID=525

Frequently Asked Questions

You can find our full list of partners on our project website (www.nanorem.eu). If you would like any further information please contact Hans-Peter Koschitzky at koschitzky@iws.uni-stuttgart.de.

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