CL:AIRE

NanoRem 1
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NanoRem Bulletin

CL:AIRE's NanoRem bulletins describe practical aspects of research which have direct application to the characterisation, monitoring or remediation of contaminated soil or groundwater using nanoparticles. This bulletin provides an overview of the NanoRem project.

Nanotechnology for Contaminated Land Remediation – Possibilities and Future Trends Resulting from the NanoRem Project

Background

Nanotechnologies could offer a step-change in remediation capabilities: treating persistent contaminants which have limited remediation alternatives, avoiding degradation-related intermediates and increasing the speed at which degradation or stabilisation can take place. However, adoption of nanoremediation has been slower, with fewer than 100 field scale applications, since the first field application in 2000. However, the recent emergence of nanoremediation as a commercially-deployed remediation technology in several EU countries, notably the Czech Republic and Germany indicates that it is now time to look at nanoremediation as a technology in the European market-place.

Between 2013-2017, the NanoRem project (www.nanorem.eu) carried out an intensive development and optimisation programme for different nanoparticles (NPs), along with analysis and testing methods, investigations of fate and transport of the NPs and their environmental impact.

The aim of this bulletin is to provide an overview of NanoRem, its aims, structure and the main generic results. This overview provides links to other NanoRem outputs where a greater depth of detail can be found.

What is Nanoremediation?

Nanoremediation describes the *in situ* use of NPs in the treatment of contaminated groundwater and soil. Depending on the use of different particles nanoremediation processes generally involve reduction, oxidation, sorption or their combination. NPs are usually defined as particles with one or more dimensions of less than 100nm. In practice, nanoremediation may apply to particles which are larger, for example composites with embedded NPs. NPs used in remediation are mostly metals or metal oxides, most frequently nano-scale zerovalent iron (nZVI). They may be modified in various ways to improve their performance, for example inclusion of a catalyst (often palladium), use of coatings or modifiers, or emplacement on other materials such as activated carbon or zeolites (for iron oxides). They are generally applied *in situ* via various injection methods, which may include the use of viscosity control agents or other materials to facilitate targeted emplacement of nanoparticles in the subsurface.

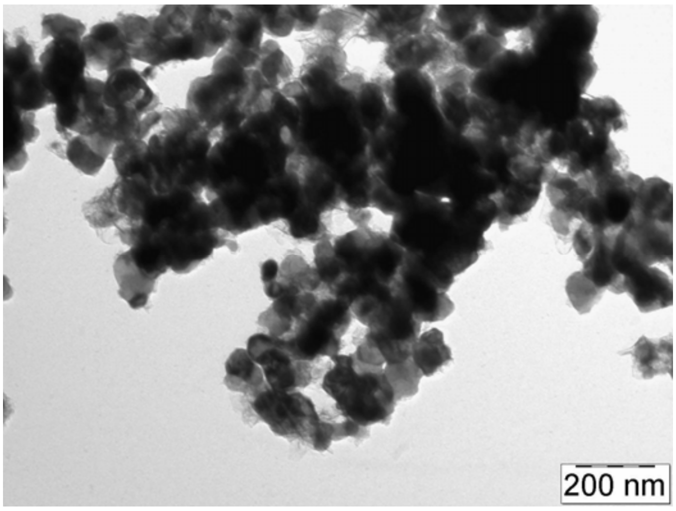

Figure 1. TEM image of nZVI particles injected at the Spolchemie I Site © J. Filip, UPOL, Palacký University in Olomouc, Czech Republic.

An Introduction to the NanoRem Project

NanoRem was a research project, funded through the European Union Seventh Framework Programme. The NanoRem project focused on facilitating practical, safe, economic and exploitable nanotechnology for *in situ* remediation. This was undertaken in parallel with developing a comprehensive understanding of the environmental risk-benefit for the use of NPs, market demand, overall sustainability, and stakeholder perceptions. The project was designed to unlock the potential of nanoremediation processes from laboratory-scale to end user applications and to support both the appropriate use of nanotechnology in restoring land and water resources and the development of the knowledge based economy at a world leading level for the benefit of a wide range of users in the EU environmental sector.

Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment.
This project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no. 309517.

The NanoRem consortium was multidisciplinary, cross-sectoral and transnational. It included 29 partners from 13 countries organised in 11 work packages. The consortium included 19 of the leading nanoremediation research groups in the EU, 9 industry and service providers (7 SMEs) and one organisation with policy and regulatory interest. The consortium was co-ordinated by the VEGAS team (Research Facility for Subsurface Remediation) from the University of Stuttgart in Germany. Figure 2 depicts the overall structure of the project.

The *Design and Production Group* comprised two work packages (WP2 & WP3) to facilitate the intense focus on different NPs and their corresponding production and application strengths.

The *Performance Group* was established to bridge the gap from production to application (WP4-WP7), to work closely together to ascertain potentials and limitations of NPs, and to extend the limits of economic and ecological NP application.

The *Application and Dissemination Group* was responsible for successfully transferring the technology to the end-user. This comprises the proof of concept in large-scale indoor experiments (WP8) and the demonstration at a number of pilot sites (i.e. field tests, WP10), risk assessment, sustainability and lifecycle assessment considerations (WP8 & WP9).

NanoRem Project Goals and Main Results

The overall aim of the NanoRem project was to demonstrate that the application of NPs is a practical and reliable method for the treatment of contaminated soil and groundwater. NanoRem provided a direct link between SME (small and medium sized enterprises) on the production side and SME on the application side of groundwater remediation using NPs. Six project goals were identified at the project outset. These are listed below along with brief text describing how these goals were met.

1. Identify the most appropriate nanoremediation technological approaches to achieve a step change in remediation practice.

Model systems (NPs + conditions mimicking real environmental conditions), both existing and novel, have been used to investigate mobility, reactivity (destruction, transformation or sorption of contaminants), functional lifetime and reaction products. For NP optimisation the influence of size, surface chemistry, structure and formulations on the performance was investigated leading to enhanced NPs as well as novel NP types. The step-change focus was to extend the range of practically treatable contaminants.

✓ NPs available are listed in Table 1. More information can be found within NanoRem Bulletin No.4 "A Guide to Nanoparticles for the Remediation of Contaminated Sites" and at www.nanorem.eu.

2. Develop lower cost production techniques and production at commercial scales of nanoparticles.

Laboratory-scale production processes were upscaled to the industrial level. The step-change focus was to produce substantially cheaper and more sustainable NPs.

✓ The production was upscaled successfully resulting in a commercially available and economically competitive technology.

✓ Nano-scale zerovalent iron particles (nZVI) have been improved via a new surface coating so that they are available as an air-stable dry powder in spite of a large specific surface. This allows for more convenient handling (transportation to the site, storable) - see also NanoRem Bulletin No.4 "A Guide to Nanoparticles for the Remediation of Contaminated Sites".

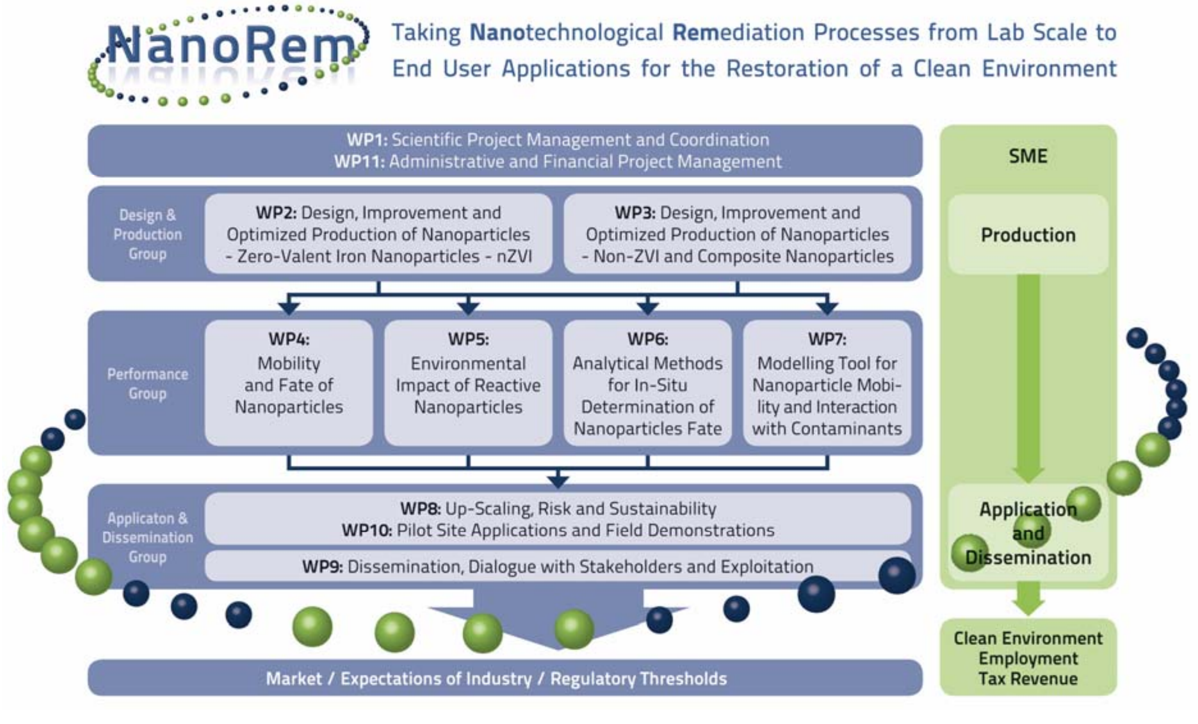

Figure 2. Structure of the NanoRem project.

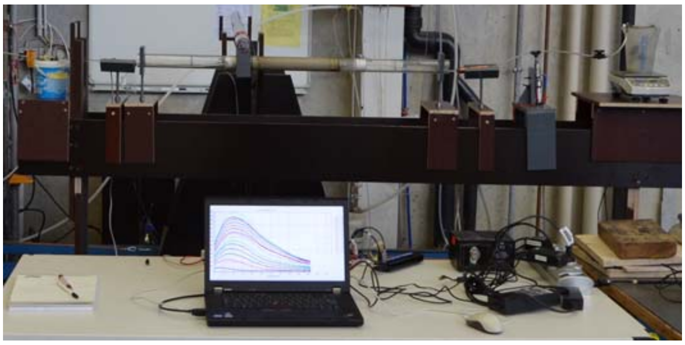

Figure 3. Cascading column experiments to investigate transport and sedimentation properties of different iron NPs. The computer shows time and space dependent distribution of iron NPs in the column during injection measured with a susceptibility sensor.© VEGAS/USTUTT, University of Stuttgart, Germany.

Figure 4. Spreading of Carbo-Iron® suspension in the large scale flume (LSF) experiment © VEGAS/USTUTT, University of Stuttgart, Germany.

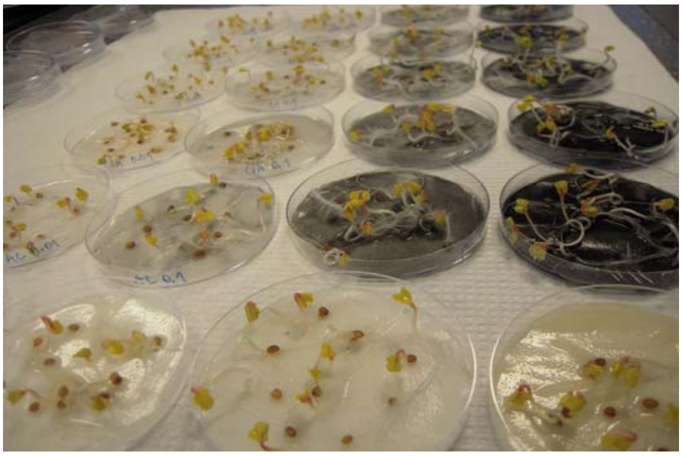

Figure 5. NPs developed during the project were tested for their potential effects on plant root elongation. The image shows an overview of the test after 6-days exposure of radish seeds *Raphanus sativus* to (from front to back) Fe-Zeolite, activated carbon, aged Carbo-Iron®, and Carbo-Iron® at 0.01, 0.1, 1 and 10 g/L. © Claire Coutris, NIBIO, Norway.

3. Determine the mobility and migration potential of nanoparticles in the subsurface, and relate these both to their potential usefulness and also their potential to cause harm.

Experiments for mobility and migration potential ranged from laboratory-scale (columns, Fig.3), over large-scale contained laboratory systems (Fig.4) to field tests. Furthermore, investigations included unintended secondary effects of NPs application on environment and ecosystems (Fig.5).

- ✓ Information on "*Stability, Mobility, Delivery and Fate of optimised NPs under Field Relevant Conditions*" can be found in the respective project deliverable, while results from the large-scale experiments are available in the project deliverable "*Final Report on Three Large-Scale Experiments and Generalised Guideline for Application*".
- ✓ Indications regarding the usefulness of NPs are given in NanoRem Pilot Site bulletins Nos 7-12.
- ✓ With regard to ecotoxicological aspects it was found that no significant toxic effects were observed on soil and water organisms when ecotoxicological tests were undertaken for a range of nanoparticles available for remediation (including with respect to the particles' interaction with contaminants and the resulting products).
- ✓ Furthermore, effects on selected soil and water organisms were monitored for up to nine months after NP treatments of the pilot sites. In three out of four sites investigated, no toxic effects were observed at concentrations applied in the field studies. A transient increase in toxicity was observed right after NP injection at the Solvay site. However, a positive effect of NP injection on indigenous microbial communities and more specifically, the apparition of organohalide-respiring bacteria after NP injection, was observed both at the Solvay and Balassagyarmat sites. More information can be found at www.nanorem.eu.

4. Develop a comprehensive set of tools for design, application and monitoring practical nanoremediation performance and determine the fate of nanoparticles in the subsurface.

The bulletins and tools described below can be downloaded from www.nanorem.eu.

- ✓ NanoRem Bulletin No.2 "Appropriate Use of Nanoremediation" aims to provide a concise and easily read overview of NanoRem's views on the appropriate use and application of nanoremediation technologies, and provide some clarity about how they are regulated in comparison with other forms of *in situ* reduction and oxidation remediation technologies.
- ✓ "Generalised Guideline for Application of Nanoremediation" (NanoRem Bulletin No.3 and Tool) gives a comprehensive overview on the implementation of nanoremediation. The aim of this guideline is to assist practitioners and consultants in screening nanoremediation as a possible remediation option for a given site and facilitate the communication between regulators and consultants.
- ✓ Numerical tools for "Forecasting Nanoparticle Transport for Soil Remediation" (NanoRem Bulletin No.6) include a 1D modelling tool (MNMs)[1] for the assisted quantitative analysis of laboratory-scale column tests and the preliminary design of pilot NP injections in simplified geometry (radial 1D simulations), and a full 3D transport module (MNM3D)[2] for the simulation of particle injection

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[1] Micro- and Nano-particles transport, filtration and clogging Model Suite, www.polito.it/groundwater/software

[2] Micro and Nanoparticle transport Model in 3D geometries

Bianco, C., Tosco, T., Sethi, R. (2016) A 3-dimensional micro- and nanoparticle transport and filtration model (MNM3D) applied to the migration of carbon-based nanomaterials in porous media. *Journal of Contaminant Hydrology*, 193, pp. 10-20. DOI: 10.1016/j.jconhyd.2016.08.006

Table 1: Overview of particles available from the NanoRem project.

Particle name	Type of particle	Manufacturer and website	Process of contaminant removal	Target contaminants	Development status as of January 2017
Carbo-Iron®	Composite of Fe^0 and activated carbon	SciDre GmbH, Germany www.carboiron.de/	Adsorption + Reduction	Halogenated organics (contaminant spectrum as for nZVI)	Field tested and commercially available
FerMEG12	Mechanically ground nZVI particles	UVR-FIA GmbH, Germany www.uvr-fia.de/	Reduction	Halogenated hydrocarbons	Field tested and commercially available
NANOFER 25S	Aqueous dispersion of nZVI	NANO IRON s.r.o., Czech Republic www.nanoiron.cz/en/nanofer-25s	Reduction	Halogenated hydrocarbons and heavy metals	Field tested and commercially available
NANOFER STAR	Air stable powder, nZVI	NANO IRON s.r.o., Czech Republic www.nanoiron.cz/en/nanofer-star	Reduction	Halogenated hydrocarbons and heavy metals	Field tested and commercially available
Nano-Goethite	Pristine iron oxides stabilised with humic acid	University of Duisburg-Essen, Germany www.uni-due.de/biofilm-centre	Oxidation (catalytic effect on bioremediation) + Adsorption of heavy metals	Biodegradable (preferably non-halogenated) organics, such as BTEX; heavy metals	Field tested and commercially available
Trap-Ox Fe-zeolites	Nanoporous alumosilicate loaded with Fe(III)	UFZ Leipzig, Germany www.ufz.de/index.php?en=2529	Adsorbent + Oxidation (catalyst)	Small molecules (depending on pore size of zeolite) - e.g. BTEX, MTBE, dichloroethane, chloroform, dichlormethane	Premarket
Bionanomagnetite	Produced from nano-Fe(III) minerals	University of Manchester, UK www.geomicrobiology.co.uk/	Reducing agent and adsorption of heavy metals	Heavy metals, e.g. Cr(VI)	Lab to premarket
Palladized bionanomagnetite	Biomagnetite doped with palladium	University of Manchester, UK www.geomicrobiology.co.uk/	Reduction (catalyst)	E.g. Halogenated substances (contaminant spectrum broader than for nZVI)	Lab and premarket
Abrasive Milling nZVI	Milled iron	Centre Tecnològic de Manresa, Spain www.ctm.com.es/en/index.php	Reduction	Halogenated aliphatics and Cr(VI)	Lab
Barium Ferrate	Fe(VI)	VEGAS, University of Stuttgart, Germany www.vegasinfo.de/	Oxidation	BTEX, nitroaromatic compounds (under investigation)	Lab
Mg/Al particles	Zero valent metals	Adaption of commercially available particles by VEGAS, University of Stuttgart, Germany www.vegasinfo.de/	Reduction (reagent)	Halogenated hydrocarbons	Lab
NanoFerAl	Composite of Fe and Al	UVR-FIA GmbH / VEGAS, University of Stuttgart, Germany http://www.vegasinfo.de/	Reduction (reagent)	Halogenated hydrocarbons	Lab

(in one or more injection points) in heterogeneous domains and prediction of NP fate and transport at the field scale. If coupled with MNMs, MNM3D can be used at the final stage of the remediation design process, as a support to estimate important operative parameters, including particles distribution around the injection well, influence radius for a target concentration, number of required injection wells, etc. The Bulletin gives details on how the tools can support the various stages of the design, implementation and evaluation of a nanoremediation.

- ✓ Analytical methods, field measurement devices (NanoRemBulletin No.5 "Development and Application of Analytical Methods for Monitoring Nanoparticles in Remediation") are needed to follow the fate of nanoparticles during and after injection, and to evaluate the efficiency of remediation. A variety of methods have been developed and tested at NanoRem field injections, ranging from on site sampling and measurement to *in situ* tracking using magnetic susceptibility.
- ✓ *Pre-Deployment risk assessment* (Tool) is used to establish whether NanoRem particles can be injected without causing pollution of groundwater or surface water.

Table 2: Listing of NanoRem field sites.

NanoRem Site Name	Spolchemie I	Spolchemie II	Solvay	Balassagyarmat	Neot Hovav	Nitrastur
Site Primary Investigator	AQUATEST	AQUATEST	Solvay	Golder	Ben Gurion University of the Negev	Tecnalia
Country	Czech Republic	Czech Republic	Switzerland	Hungary	Israel	Spain
Current use	Industry	Industry	Industrial brownfield, some subletting	Brownfield	Industry	Brownfield
Specification of contamination (source/plume)	dissolved plume	residual phase and dissolved plume	pooled phase and dissolved plume	dissolved plume	phase and plume in fractures	anthropogenic backfill containing heavy metals
Main contaminant(s)	chlorinated hydrocarbons	BTEX (mainly toluene and xylenes), styrene	chlorinated hydrocarbons	PCE, TCE, DCE	TCE, cis-DCE, toluene	As, Pb, Zn, Cu, Ba, Cd
Type of Aquifer	porous, unconfined	porous, unconfined	porous, unconfined	porous, unconfined	fractured	porous, unconfined
Hydraulic conductivity	10^{-4} to 10^{-6} m/s	10^{-4} to 10^{-6} m/s	8 10^{-3} to 2 10^{-5} m/s	5 10^{-3} to 2 10^{-8} m/s	n/a	2 10^{-4} to 10^{-5} m/s
Seepage velocity	0.2 m/d	0.9 m/d	5-20 m/d	0.3 m/d	not available	1 m/d
NP used	NANOFER 25S/ NANOFER STAR	Nano-Goethite	FerMEG12	Carbo-Iron®	Carbo-Iron®	NANOFER STAR
NP provided by	NANO IRON s.r.o.	University Duisburg Essen	UVR-FIA GmbH	ScIDre GmbH	UFZ	NANO IRON s.r.o.
Mass of NP injected	200 kg / 300 kg	300 kg	500 kg	176.8 kg	5 kg	250 kg
Injection System	Direct Push	Direct Push	Wells (with packers)	Direct Push	Wells (with packers)	Wells (with packers)
Remediation outcome	See NanoRem Bulletin #7	See NanoRem Bulletin #8	See NanoRem Bulletin #9	See NanoRem Bulletin #10	See NanoRem Bulletin #11	See NanoRem Bulletin #12

5. Engage in dialogue with key stakeholder and interest groups to ensure that research, development and demonstration meets their needs, is most sustainable and appropriate whilst balancing benefits against risks.

The main focus was on ensuring that research addresses real market and regulatory interests. Communicating findings regarding renegade particles and the relative sustainability of nanoremediation over the life cycle of a typical remediation project is vital. Information and knowledge is being shared widely across the Single Market so that advances in nanoremediation can be properly exploited.

The information described below can be downloaded from www.nanorem.eu.

- ✓ NanoRem's *Exploitation Strategy, Risk-Benefit Analysis and Standardisation Status* summarises NanoRem's findings regarding dissemination and exploitation.
- ✓ NanoRem applied an internationally recommended approach to *Life Cycle Assessment* (LCA) on the production process of three nanoparticles (see project deliverable *Final Report on Three Large-Scale Experiments and Generalised Guideline for Application*).
- ✓ Furthermore, the *NanoRem Case Study Sustainability Assessment Background and Workbook* has two broad purposes: to provide a background and NanoRem context for sustainable remediation and to provide a procedure to carry out a qualitative sustainability assessment of the nanoremediation technologies to be used at the field test sites.

6. Carry out a series of full-scale applications in several European countries to provide cost estimations and performance, fate and transport findings.

NPs were applied into both large-scale contained laboratory systems and during field trials on the pilot sites, to provide on-site validation of the results on a representative scale both in terms of the effectiveness of nanoremediation as well as the environmental fate of the NPs and their associated by-products (Fig. 6).

- ✓ A description of the applications and results can be found in the NanoRem Pilot Site Bulletins on www.nanorem.eu. All field trials within the project were carried out within a risk management regime for nanoparticle release that gained the required regulator approvals including where necessary using a pre-deployment risk assessment protocol. Qualitative sustainability assessments have been conducted in a retrospective sense for one of the Czech pilot sites and as part of remediation options appraisal for a separate UK based case study.

Figure 6. Heads of monitoring arrays for *in situ* susceptibility measurement (on Spolchemie I pilot site) connected to measuring hardware in protective box © VEGAS/USTUTT, University of Stuttgart, Germany.

Project Results Online – the NanoRem Toolbox

The NanoRem Toolbox (Fig.7), available on www.nanorem.eu, focuses on the needs of decision makers, consultants and site owners. It provides the respective outputs of NanoRem in three levels:

1) The bulletins include the most relevant information in a condensed and concise way.
2) More detailed information on nanoparticles and tools are located in the "Nanoparticles and Tools" shelf.
3) Other dissemination products and selected project deliverables can be found in the "Supporting Information" shelf.

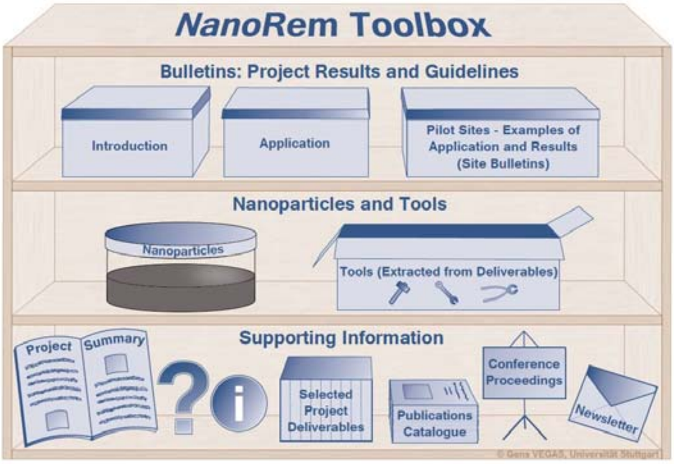

Figure 7. The NanoRem Toolbox.

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Table 3: List of NanoRem project partners.

Organisation Name	Country
University of Stuttgart (VEGAS) - Coordinator	DE
Karlsruhe Institute of Technology	DE
Solvay (Schweiz) AG	CH
Helmholtz-Zentrum für Umweltforschung GmbH, UFZ Centre for Environmental Research	DE
Ben-Gurion University of the Negev	IL
Fundació CTM Centre Tecnològic	ES
University of Vienna	AT
University of Manchester	UK
Fundacion Tecnalia Research & Innovation	ES
HMGU, Helmholtz Zentrum München *Left the consortium 31/03/2015*	DE
NIBIO, Norwegian Institute of Bioeconomy Research *Name change (formerly "Bioforsk")*	NO
Technical University of Liberec	CZ
NMBU, Norwegian University of Life Sciences	NO
Aquatest	CZ
Palacký University in Olomouc	CZ
CNRS, Centre National de la Recherche Scientifique	FR
Politecnico di Torino	IT
Geoplano Consultores, S.A.	PT
DTU, Technical University of Denmark	DK
Stichting Deltares	NL
r3 Environmental Technology Limited	UK
LQM, Land Quality Management Ltd.	UK
CL:AIRE	UK
NANO IRON, s.r.o.	CZ
Golder Associates GmbH	DE
BRGM, Bureau de Recherches Géologiques et Minières	FR
UVR-FIA GmbH	DE
ScIDre, Scientific Instruments Dresden GmbH	DE
University Duisburg-Essen *(Successor of HMGU)*	DE

For further information on NanoRem please visit www.nanorem.eu

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