Nanoremediation technologies – findings of the EU FP7 NanoRem Project

Paul Bardos

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NanoRem Funding

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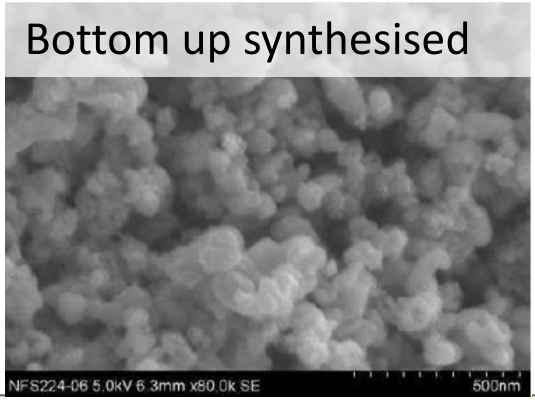
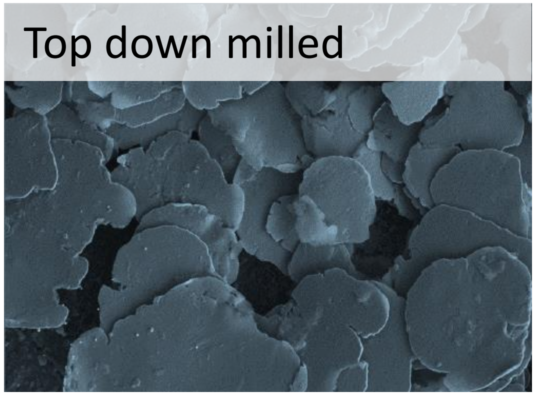
What is nanoremediation?

- The use of nanoparticles (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 <100nm.
- Can include larger composite particles with embedded nanoparticles.





Deployments

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- At source or in pathway
- Via wells, via direct injection
- "Naked" NPs have short lifetimes and limited travel distances
- Therefore:
  - NP modifiers (coatings, catalysts etc)
  - Co-injectants (carboxy methyl cellulose)
  - Composites

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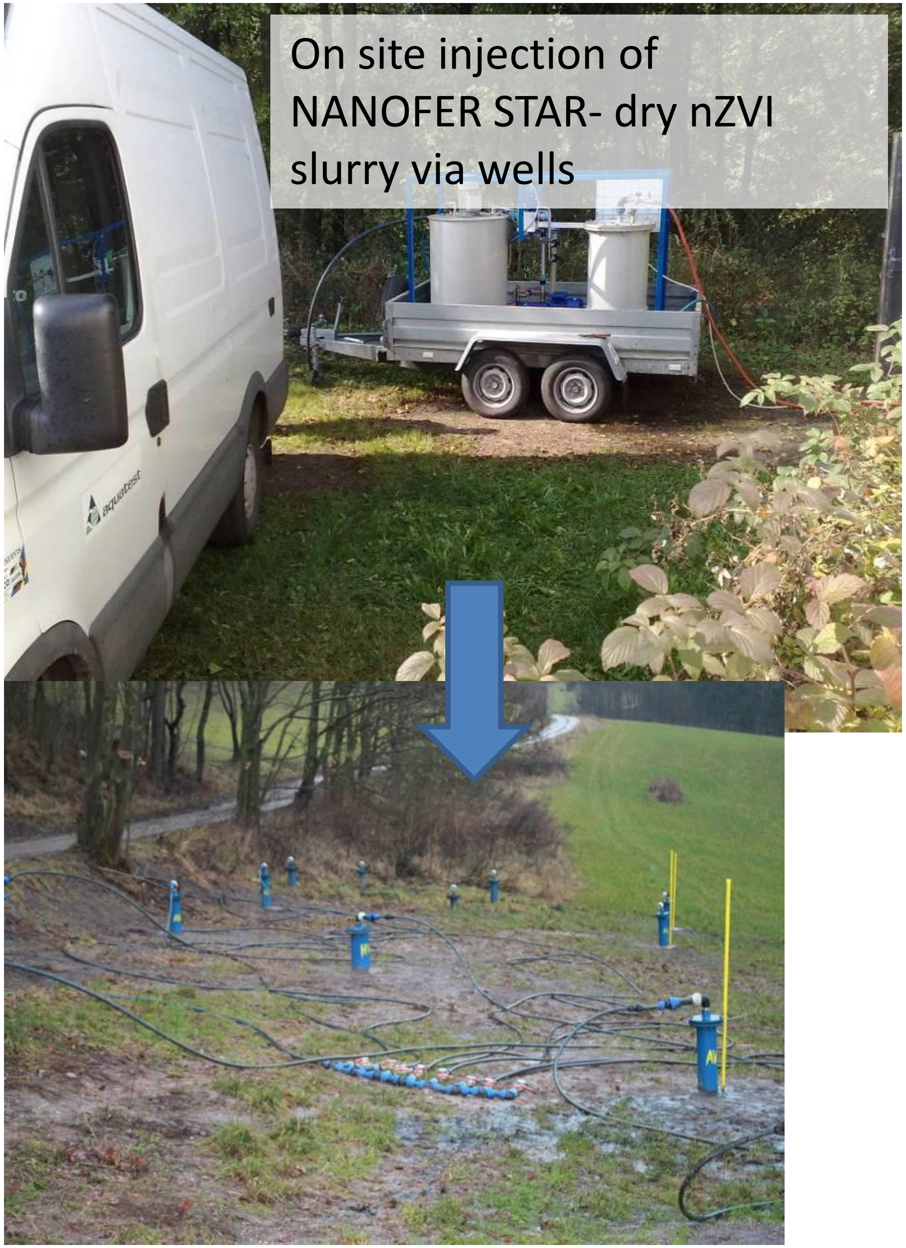
On site injection of NANOFER STAR- dry nZVI slurry via wells



Direct injection of NANOFER STAR- dry nZVI slurry

Worldwide use of nanoremediation

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- NanoRem has tracked ~ 90 field applications of nanoremediation worldwide since it was first used in Trenton New Jersey in 2000
- Primarily chlorinated solvent applications
- Limited uptake compared to the expansion of *in situ* bio and ISCO over the same period
- Main barriers: complexity, perceived cost, public opinion and regulatory hurdles
- And also: a lack of well validated field applications: which becomes an “invirtuous” circle

- NanoRem is a €14 million international collaborative project with 29 Partners from 13 countries, and an international Project Advisory Group (PAG) providing linkages to the USA and Asia.

- Industry, research, SMEs, public agencies, technology providers

NanoRem's Aims

- Unlock the true potential of nanoremediation
- Support appropriate use of nanotechnology in restoring land and aquifer resources
- Develop knowledge-based and economical remediation technology at a world leading level for the benefit of a wide range of users in the EU environmental sector
- Enhance the development of nanoremediation markets and its applications in the EU and beyond

Outcomes to be discussed

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- NanoRem particles
- Field tests
- Behaviour (lab, scale-up, field, modelling)
- Ecotoxicity
- Risks, benefits & sustainability of nanoremediation deployment

- This is a very very high level birds-eye view of what has been achieved by the project
  - May be as seen by Rüppell's vulture or a Bar-headed goose? (https://en.wikipedia.org/wiki/List_of_birds_by_flight_heights)

Particles: Field tested and commercially available NPs

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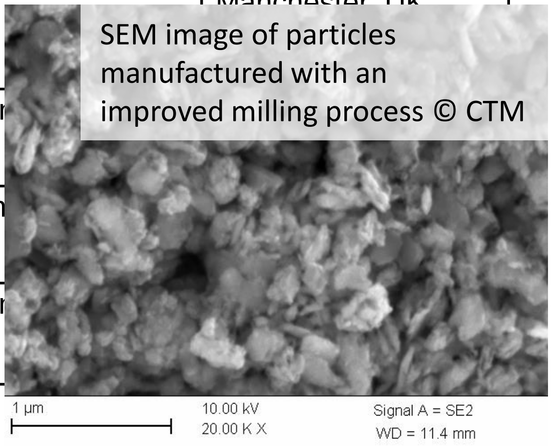
Particle name	Type of particle	Target contaminants	Process of contaminant removal	Manufacturer
Carbo-Iron® (industry)	Composite of nZVI) and activated carbon	Halogenated organics (contaminant spectrum as for nZVI)	Adsorption + Reduction	ScIDre GmbH, Germany
FerMEG12	Mechanically ground nZVI particles	Halogenated hydrocarbons	Reduction	UVR-FIA GmbH, Germany
NANOFER 25S	Nano scale zero valent iron (nZVI)	Halogenated hydrocarbons and heavy metals	Reduction	NANO IRON s.r.o., Czech Republic
NANOFER STAR	Air stable powder, nZVI	Halogenated hydrocarbons and heavy metals	Reduction	NANO IRON s.r.o., Czech Republic
Nano-Goethite	Pristine iron oxides stabilized with HA	Biodegradable (preferably non-halogenated) organics, such as BTEX; heavy metals	Oxidation (catalytic effect on bioremediation) + Adsorption of heavy metals	University of Duisburg-Essen, Germany

Particles: Lab and pre-market NPs

Particle name	Type of particle	Target contaminants	Process of contaminant removal	Manufacturer
Trap-Ox Fe-zeolites	Nanoporous alumosilicate loaded with Fe(III)	Small molecules (depending on pore size of zeolite) - e.g. BTEX, MTBE, dichloroethane, chloroform, dichlormethane…	Adsorbent + Oxidation (catalyst)	UFZ Leipzig, Germany
Bionanomagnetite	Produced from nano-Fe(III) minerales	Heavy metals, e.g. Cr(VI)	Reducing agent and adsorption of heavy metals	University of Manchester, UK
Palladized bionanomagnetite	Biomagnetite doped with palladium	E.g. Halogenated substances (contaminant spectrum broader than for nZVI)	Reduction (catalyst)	University of Manchester, UK
Abrasive Milling nZVI	Milled iron	Halogenated alifatics and Cr(VI)	Reductio	
Barium Ferrate	Fe(VI)	BTEX? (under investigation)	Oxidation	
Mg/Al particles	Zero valent metals	Halogenated hydrocarbons	Reductio	



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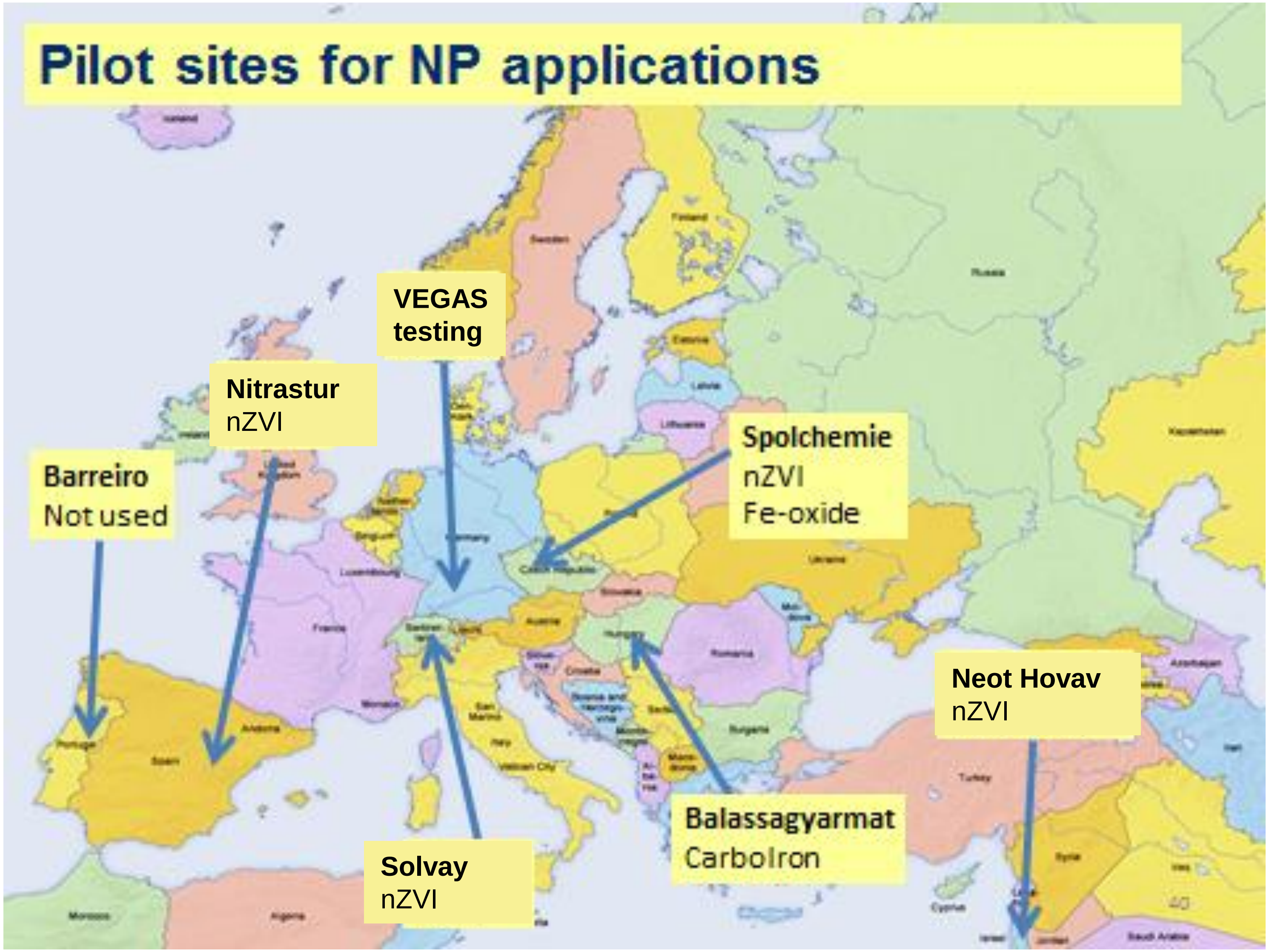
Pilot sites for NP applications



Field (pilot) tests

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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	CZ	CZ	CH	HU	IL	ES
Current use	Industry	Industry	Ind. brownfield	Ind. brownfield	Industry	Ind. 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	heavy metals
Main contaminant(s)	chlorinated hydrocarbons	BTEX, styrene	PCE, TCE	PCE, TCE, DCE	TCE, cis-DCE, toluene	As, Pb, Zn, Cu, Ba, Cd
Type of Aquifer	porous, unconf.	porous, unconf.	porous, unconf.	porous, unconf.	fractured	porous, unconf.
NP used	NANOFER 25S/ NANOFER STAR	Nano Goethite	FerMEG12	Carbo-Iron®	Carbo-Iron®	NANOFER STAR
NP provided by	Nano Iron, s.r.o.	UDE	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)

Generally NR did "what it said on the tin". A series of pilot site bulletins will be published on the CL:AIRE and NanoRem websites reviewed by the CL:AIRE "TRG"

Behaviour (lab, scale-up, field, and modelling studies) - 1

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- Bench scale studies suggest added nZVI lasts from 6 to 12 months, depending on particles and environmental conditions.
- Scale up studies (VEGAS) predict/confirm field results: It is a necessary to use the right amount of NP and the right concentration of stabiliser and the right injection technology to place particles in the intended reactive zone.
- A numerical modelling tool has been developed and is designed to be a module for *ModFlow* groundwater modelling tool and should be available soon to help predict migration of NP in predefined hydro-chemical environments.

Behaviour (lab, scale-up, field, and modelling studies) - 2

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- A number of field monitoring techniques have been tested, incl. micro pumps and susceptibility probes (i.e. magnetic arrays).
  - Micro pumps proved effective, even though the NP have a very high density and are not soluble.
  - Magnetic arrays showed very successfully the distribution of particles.
  - Obtaining a good picture of the distribution of both the injected slurry and its NPs needs a combination of micro-pumps, temperature sensors, and magnetic arrays.
- These field scale investigations show (travel distance) of up 5 meters, depending on particle type and stabilisers used.

Ecotoxicity

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- Benchmarking against standard test organisms
  - No evidence of sustained specific nano related toxicity for the NanoRem NPs
  - Possibly toxicity from milling process additives
- On site investigations
  - Emplacement environments are already highly disturbed
  - Transient effects from NP may occur
  - Effects may occur due to change in pH / redox
  - Dehalorespiration stimulated

Risks, benefits & sustainability of nanoremediation deployment

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- NanoRem provided a pre-deployment risk assessment appraisal method based on best available knowledge
  - A revised version will be available as a downloadable tool
- NanoRem has carried out aggregated LCA assessment of three of its commercially available NPs
- NanoRem has carried out two initial sustainability assessments
  - A retrospective on one of the Czech pilot sites
  - An initial assessment for a UK site with Vertase-FLI

Risks - Benefits

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Risks	Benefits
Human health • NPs may be pyrophoric and hazardous → comply with material safety datasheets (exposure once deployed unlikely) – ISCO agents also hazardous? Impacts on water environment and ecology • Limited travel distance • Limited lifetimes • No evidence of specific toxicity from tested NPs in the lab or on site • For iron based formulations ultimate fate is as oxides • Manage with pre-deployment RA	Breadth of solutions • Wide range of treatable problems (see following) • Potential for situations not treatable by *in situ* bio / facilitates *in situ* bio • Benefits of integrated systems (e.g. Carbo-Iron) Timescales • Fast, but travel distance limited (targeted measure) Costs • Really requires a site specific diagnosis and general rules of thumb not useful (akin to the early days of *in situ* biorem products)

Contaminant candidates for nanoremediation

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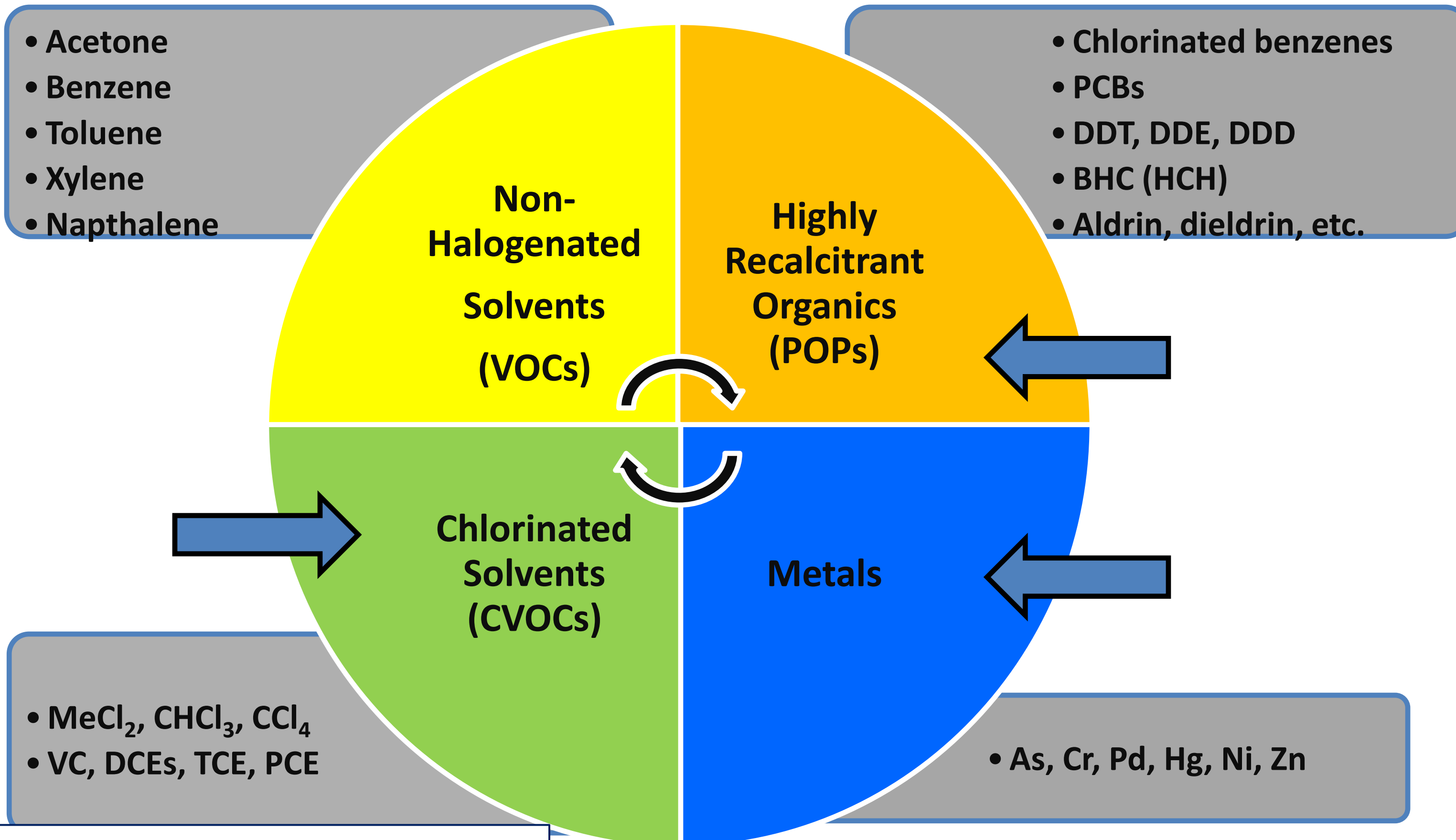

Others: MTBE, ClO_4^-, PFC

Deployment opportunities for nanoremediation

- Source and pathway applications
- NPs (in a carrier fluid) injected into saturated zone
- Portable (e.g. compared with pump and treat, SVE etc)
- Applicable below buildings
- “Independent” of application depth
- “Semi-passive” technology
- Transient aquifer impacts only

Therefore a “method of choice” for sensitive aquifers in the Czech Republic

The NanoRem Toolbox

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Nanoremediation Toolbox

The nanoremediation toolbox focuses on the needs of decision makers, consultants and site owners. It provides the respective output of NanoRem in three levels:

1) The bulletins include the most relevant information in a condensed and concise way.
2) More ... in the "Nanoparticles" and "Tools" sections.
3) Other dissemination products and selected project deliverables can found in the "Supporting Information" section.

Summary and detailed guidance

Bulletins: Project Results and Guidelines

Introduction
- Overall Project ...
- Appropriate Use of Nanoremediation

Application
- Generalised Guideline for Application
- Particle Bulletin
- Analytical Toolbox
- Nanoparticle simulation

Pilot Sites – Examples of Application and Results
- Spolchemie I, CZ
- Spolchemie II, CZ
- Solvay, CH
- ...
- ...sagyarma...
- ...astur, ES

Application guidance / appropriate use

Independently scrutinised European field tests

Nanoparticles

Particle Characterisation and Reactivity Studies
Links to Safety Data Sheets

Commercially Available Products
- Carbo-Iron®
- Biomagnetite
- FerMEG12
- NANOFER 25S
- NANOFER STAR
- Nano-Goethite
- Trap-Ox Fe-zeolites

Production Development
- Abrasive Milling nZVI
- Barium Ferrate particles
- Mg/Al particles
- NanoFerAl

Tools (Extracted From Deliverables)
- Generalised Guideline for Nanoremediation Application
- Risk Benefit Appraisal
- Deployment Risk Assessment
- Exploitation Strategy and Recommendations
- Sustainability Assessment and Life Cycle Assessment (LCA) Approaches

Deployment tools (e.g. RA, SA, field monitoring)

Commercially available systems

Supporting Information

Publications Catalogue*
(Journal Papers, Dissemination Activities and Other NanoRem Output)
Project Summary (final report)
Conference Proceedings

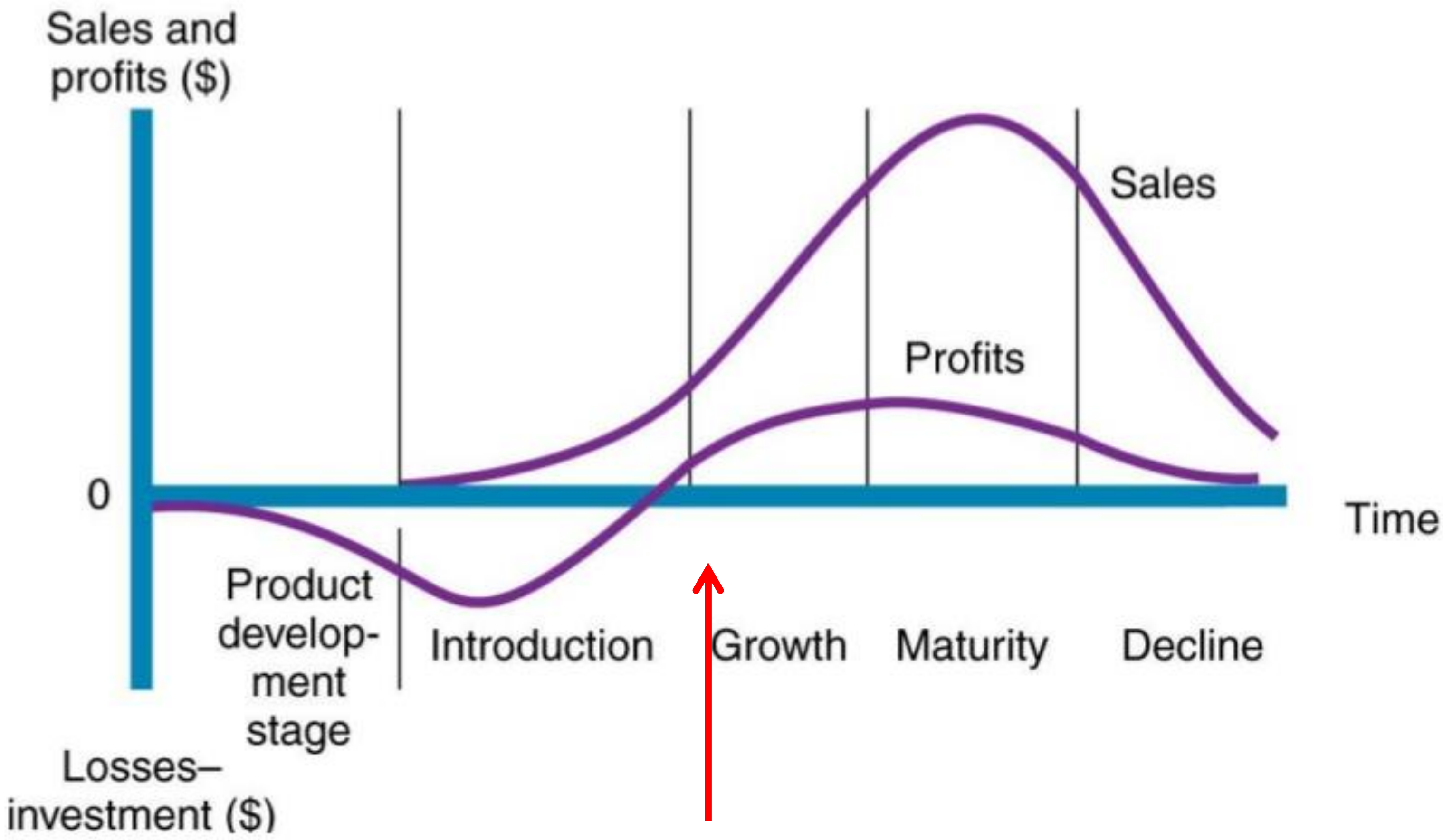
Selected Project Deliverables*
Newsletters
Thematic Pages
FAQs
* See reference list

Peer reviewed publications

Market prognosis and other tools

Draft

Conclusions



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Conclusions - continued

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- Through NanoRem there is now a comprehensive information resource in a European context (guidance, specific tools, field application trials); scaled up production and a broader range of technical options.
- Deployment risks are likely to have been overstated
- At this stage, benefits are niche and site specific rather than a step change but they may add significant value for some projects
- Reliable cost data from field deployments is still missing
- Just over the horizon there is the promise of improved benefits and lower costs from integrated approaches:
  - Nanoremediation + in situ bioremediation
  - Nanoremediation + electrokinetics
  - Managing recalcitrants

UK Moratorium

- The UK moratorium on environmental release of nanoparticles remains.
- We hope Defra will review this in the light of NanoRem outcomes, but this will be post-publication
  - But this is hindered by Brexit
- However, the moratorium does <u>not</u> prevent the regulator agreeing pilot deployments of nanoremediation in the field, which could ultimately support a case for the moratorium's removal.

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www.nanorem.eu

Thank you

NanoRem Final Conference

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Nanoremediation for Soil and Groundwater Clean-up - Possibilities and Future Trends

Date: 21st November 2016

Venue: DECHEMA, Haus Frankfurt, Theodor-Heuss-Allee 25, 60486 Frankfurt am Main, Germany

Directions: http://dechema.de/en/anfahrt.htm

Registration: www.dechema.de/nanorem2016

Costs: 90 € including catering and the NanoRem final reception

Topics:

1) What´s behind nanoremediation - technique, particles,…

2) Field application of nanoremediation tools and lessons learned from NanoRem

3) Operating windows and recommendations from NanoRem