NANOIRON
FUTURE TECHNOLOGY

Properties, Application and Further Aspects of Zero-Valent Iron Nanoparticles used in Groundwater Remediation

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Applications of Nanotechnology for Safe and Sustainable Environmental Remediations
November 2nd, 2015

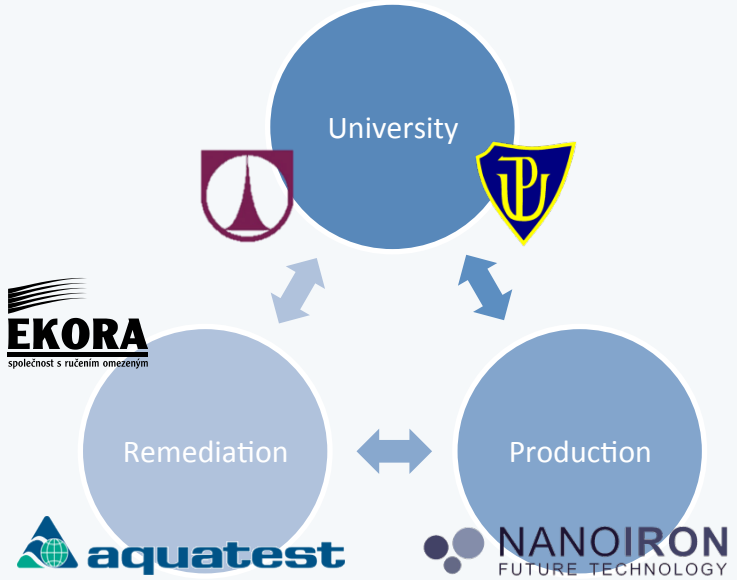
Presentation outline

- Introduction: nZVI products & characteristic
- nZVI processing and application
- QA/QC, Toxicity and Transport studies
- Technology implementation including field remediation experience: 2 sites example
- Conclusions

NANO IRON
company profile

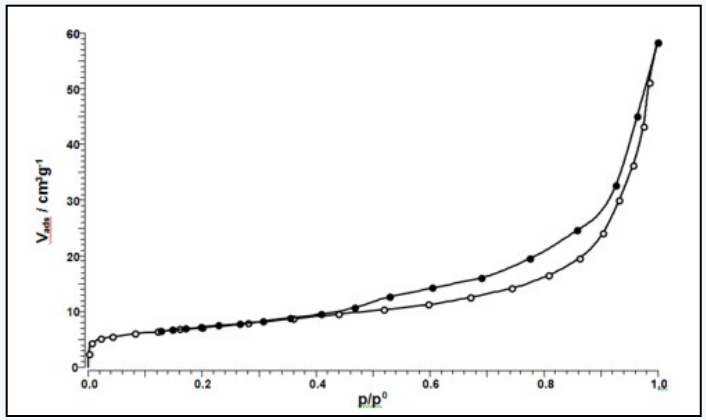
- NANO IRON, s.r.o. established in 2008
- Zero-Valent Iron nanoparticles (nZVI) industrial production in large quantities
- Worldwide distribution
- Technical support
- Technology development
- Scientific research

Laboratory dispersing unit

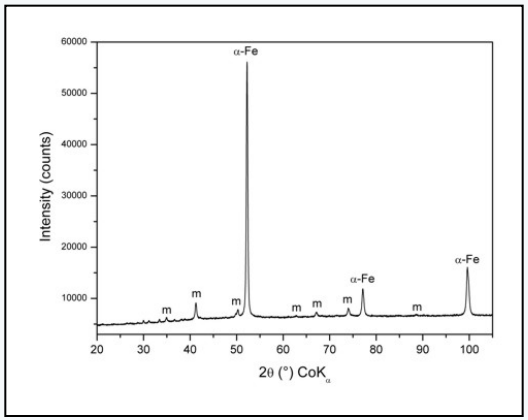


PRODUCTS CHARACTERISTICS

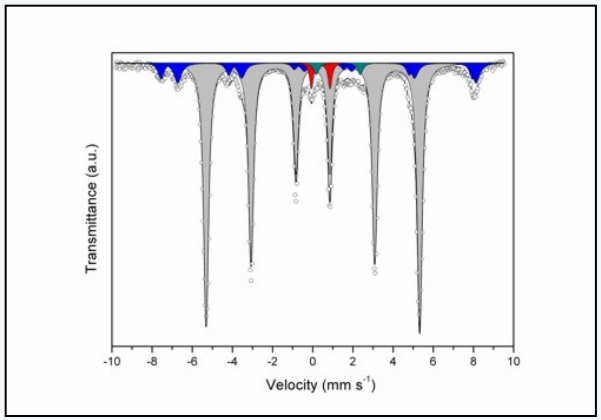
- Average particle size: 50nm
- Narrow particle size distribution: 20-100nm
- Average surface area: 20-25m^2/g



BET adsorption-desorption isotherms



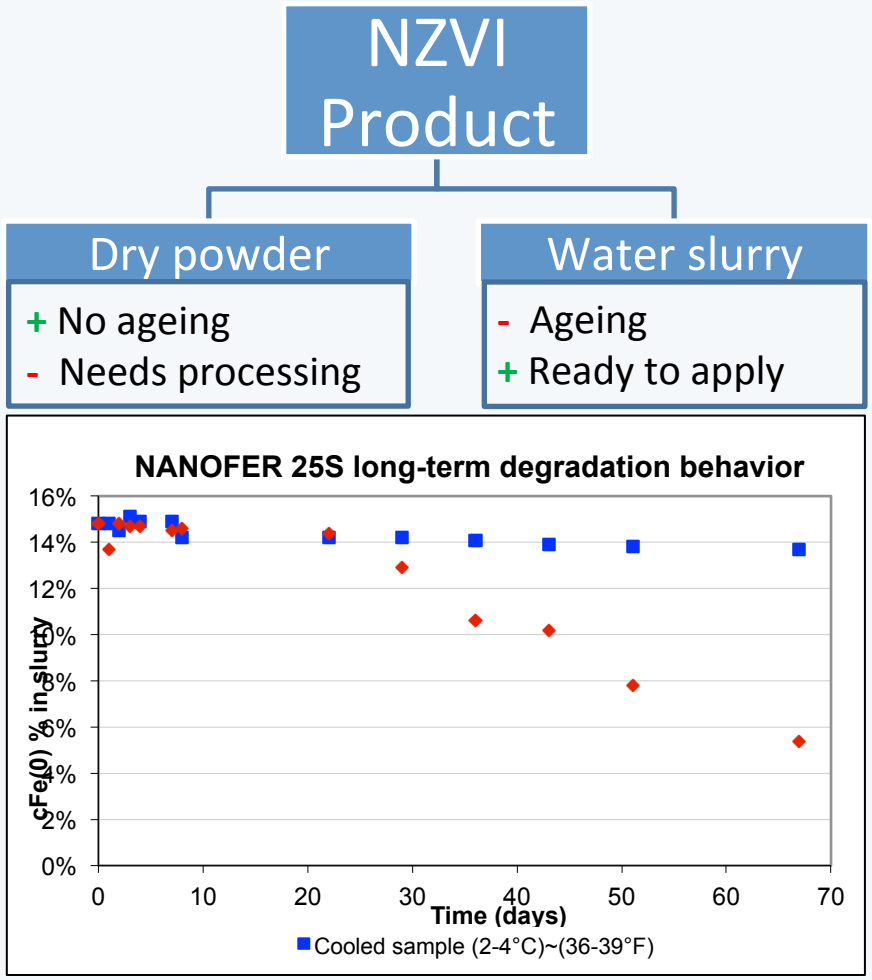
XRD pattern



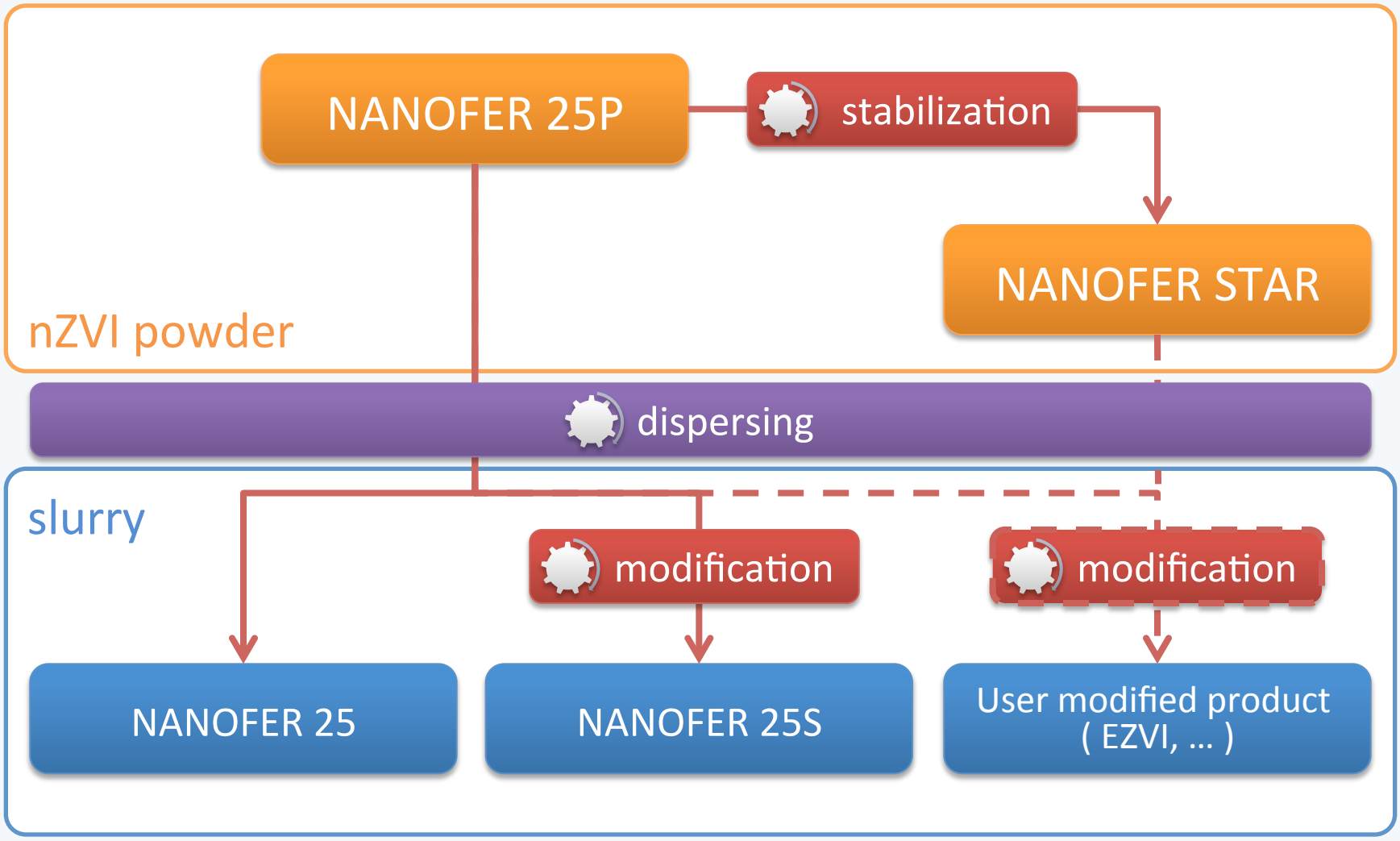
Mössbauer spectrum

nZVI manufacturing methods

- Liquid phase reduction (borohydride)
- Milling (ball, cryogenic)
- Plasma spraying
- Solid-state reduction
- Gas phase reduction
- Electrochemical
- Sonochemical
- Others + combinations



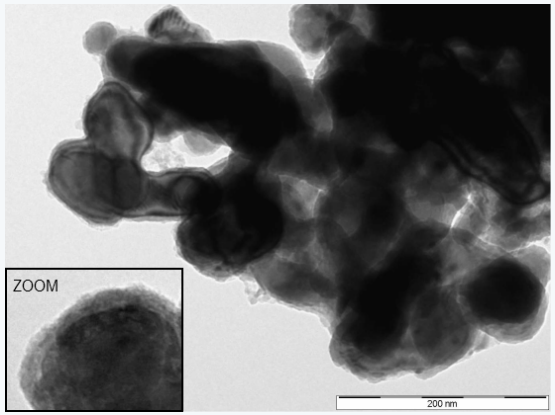
PRODUCTS


NANOFER 25P
stabilization
NANOFER STAR
nZVI powder
dispersing
slurry
modification
modification
NANOFER 25
NANOFER 25S
User modified product
(EZVI, …)

NANOFER STAR dry nanopowder

oxidic layer stabilized nZVI

- Product composition (weight):
  - 60-80% of nZVI
  - 40-20% of iron oxides



- Product is:
  - **S**urface stabilized
  - **T**ransportable
  - **A**ir-stable
  - **R**eactive

No degradation
(unlimited storage time)

High reactivity
(comparable to NANOFER 25P)

Even cheaper shipping
(comparing to NANOFER 25P)

Air stability

Dangerous classified
(UN 3089 - flammable)

Lower amount of nZVI
(comparing to NANOFER 25P)

nZVI APPLICATION

matter of time

SLURRY MANUFACTURING → SHIPPING → STORAGE → DILUTION → INJECTION

Conventional delivery and application process of nZVI

15-60 days

1 day

POWDER SHIPPING → STORAGE → SLURRY MANUFACTURING → DILUTION → INJECTION

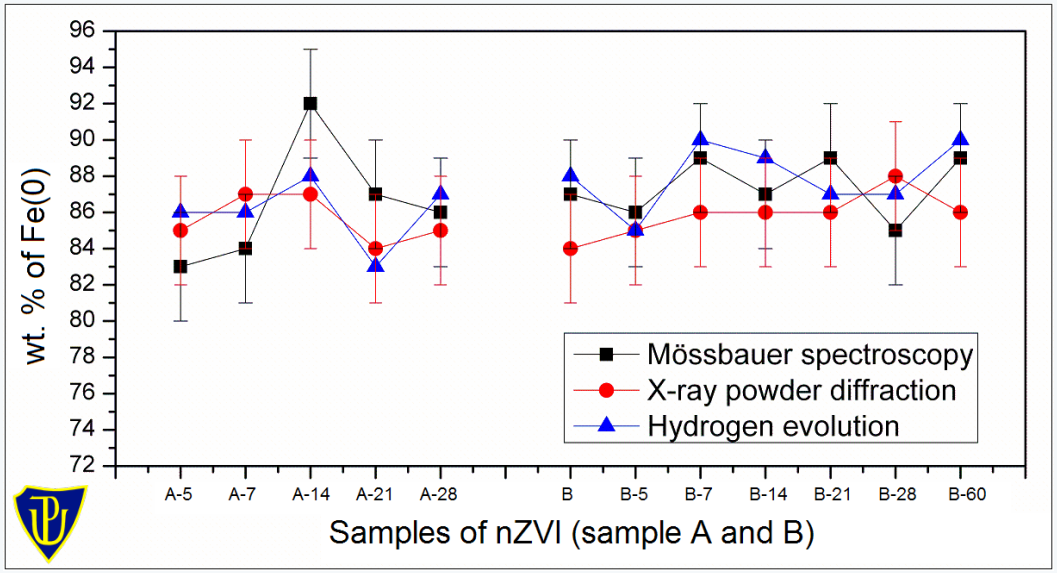
Innovative application process of nZVI

QA/QC
characterization techniques

- **Zeta potential analysis;**
- **Brunauer–Emmett–Teller method (BET);**
- **Electron microscopy (TEM, SEM);**
- **X-ray powder diffraction (XRD);**
- **^{57}Fe Mössbauer spectroscopy;**
- X-ray photoelectron spectroscopy (XPS);
- Auger electron spectroscopy (AES);
- Secondary ion mass spectroscopy (SIMS);
- X-ray absorption spectroscopy (XAS);
- Magnetic measurements (vibrating-sample or SQUID);
- Thermogravimetric analysis (TGA);
- Temperature-controlled oxidation (TPO);
- and many others…

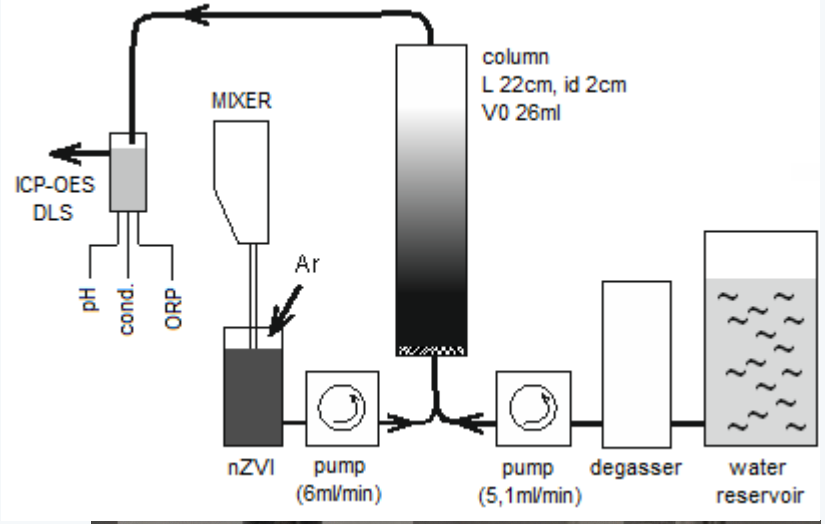
nZVI TESTER
slurry quality measurement

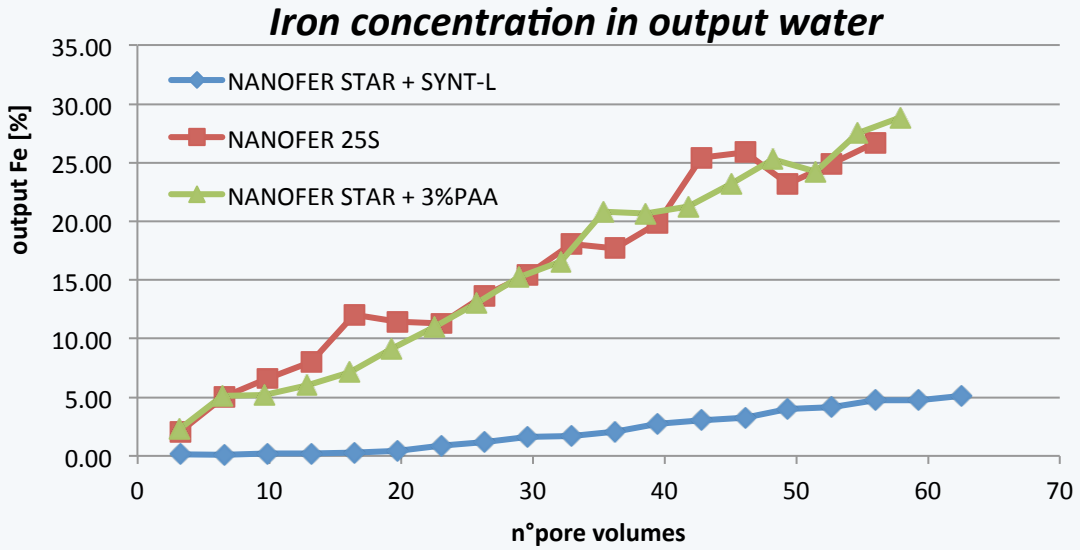
- Simple, cheap and fast measurement of nZVI content
- Principle: measurement of hydrogen volume, which is evolving during chemical reaction of nZVI and an acid
- The method is comparable to Mössbauer spectroscopy and X-ray powder diffraction

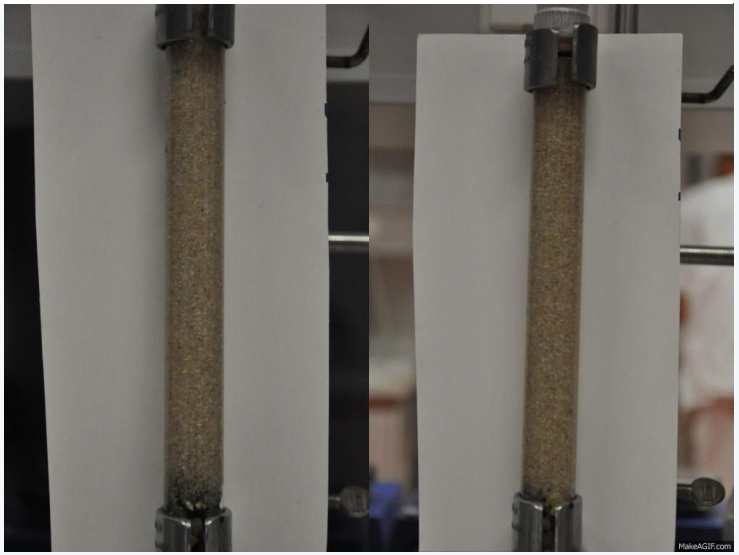


Column study
migration of nanoparticles

- Testing of various stabilizers under the same conditions (flow/ concentration/porosity/…)
- Testing various conditions (flow, nZVI dosing, …) with the same material
- Method used during product development for the comparision







Health & Safety

- Health and Safety is an important issue
  - Study and understand the product behaviour
  - Reduce risk, e.g. to minimize the contact with NPs (technology and equipment)
  - Possibility of controlled agglomeration in the subsurface ($CaCl_2$)
- Fate of nanoparticles in environment
- Current knowledge and future direction
  - Toxicity of nZVI towards water organisms, EU REACH legislation
- Iron oxides/hydroxides are final products after reaction of nZVI with water.
- Two recent studies including NANOFER product:

  Erik J. Joner at. al.: DDT degradation efficiency and ecotoxicological effects of two types of nanosized zero-valent iron (nZVI) in water and soil

  Arturo A. Keller at. al.: Toxicity of Nano-Zero Valent Iron to Freshwater and Marine Organisms
- US TSCA:

  "Although a nanoscale substance that has the same molecular identity as a non-nanoscale substance listed on the Inventory differs in particle size and may differ in certain physical and/or chemical properties resulting from the difference in particle size, EPA considers the two forms to be the same chemical substance because they have the same molecular identity. The inventory listing in this case is considered to represent both the nanoscale and non-nanoscale forms of the substance and, as such, does not distinguish between two forms having the same molecular identity that differ only in particle size and/or physical/chemical properties resulting from difference in particle size."

Toxicity of nZVI

Soil Slurry: ecotoxicological effects and DDT degradation					
Organism	Endpoint	nZVI-B		NANOFER 25S	
		Aqueous p.	Solid p.	Aqueous p.	Solid p.
Earthworms	Mortality	n.a.	+	n.a.	0
	Growth	n.a.	-	n.a.	+
	Reproduction	n.a.	-	n.a.	+
Ostracods	Mortality	-	-	0	0
	Growth	-	-	0	+
Bacteria	Growth	-	n.a.	0	n.a.
Barley	Germination	+	-	0	-
	Root growth	-	-	+	+
Flax	Germination	-	-	0	0
	Root growth	-	-	+	0
DDT reduction in 24h		92.4%		78.3%	

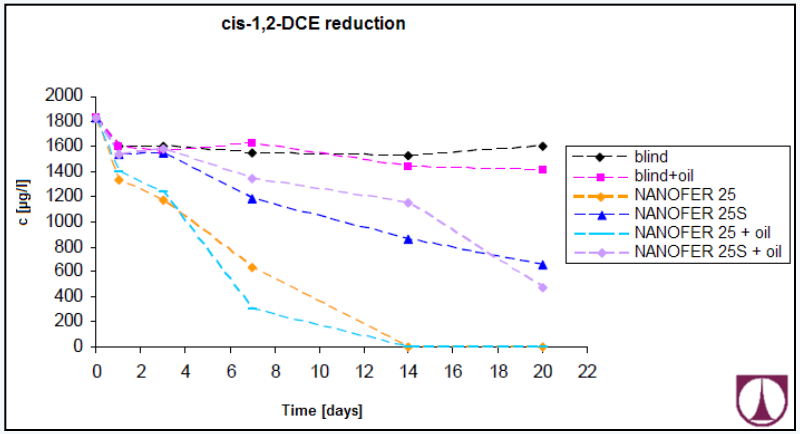
DDT degradation efficiency and ecotoxicological effects of two types of nanosized zero-valent iron (nZVI) in water and soil

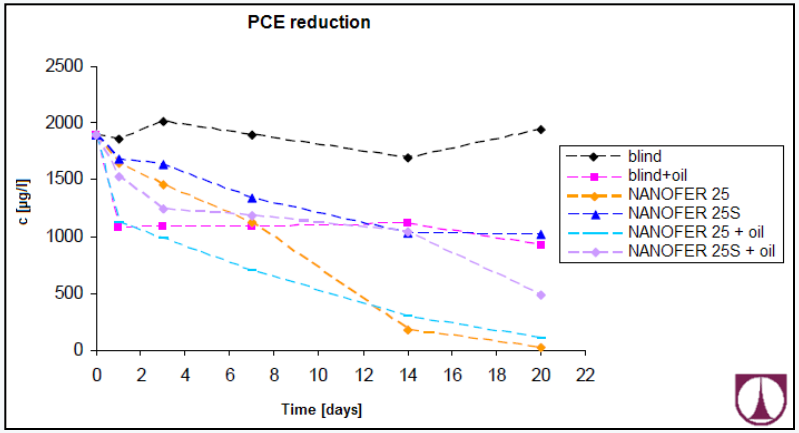
nZVI REMEDIATION CONCERNS

- Delivery and utilization of technology
- Implementation of technology
- Regulatory approval process

nZVI IMPLEMETATION

- LABORATORY EXPERIMENTS – feasibility approval
  - Batch experiments: groundwater + soil + nZVI concentration
  - Concentration dependency (efficient concentration) in g/L
  - Kinetic (reaction rate)
  - Comparison of different products
- REGULATORY APPROVAL
  - Subjected to decision of local authority
- FIELD PILOT STUDY
  - Usually 20-100kg of nZVI
- FULL SCALE REMEDIATION





nZVI REMEDIATION EXPERIENCE

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- Fur processing site
- Contamination: Chlorinated ethenes (PCE, TCE, DCE, VC) and chromium (Cr6+)
- Previous treatment: pump&treat, venting, vapor deposition, ISCO, sodium dithionite

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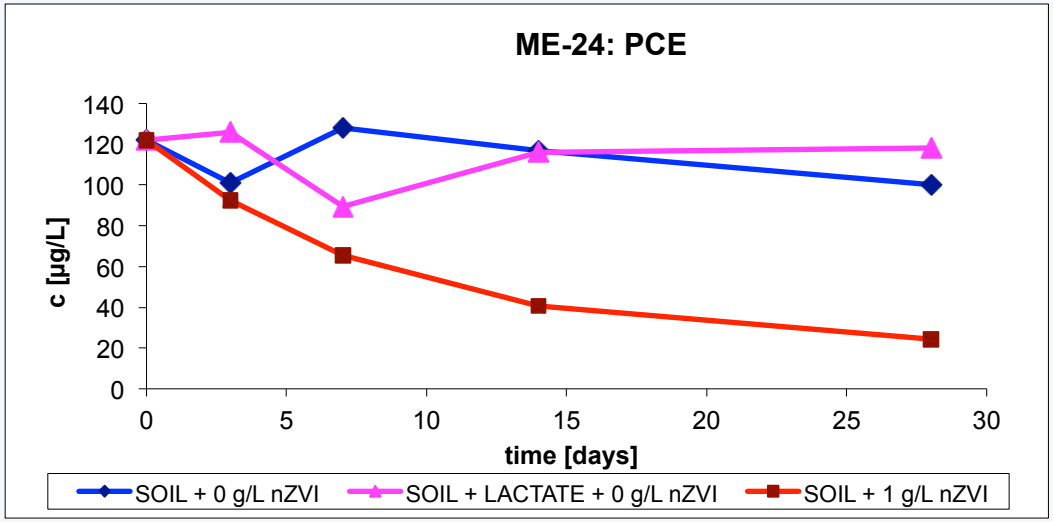
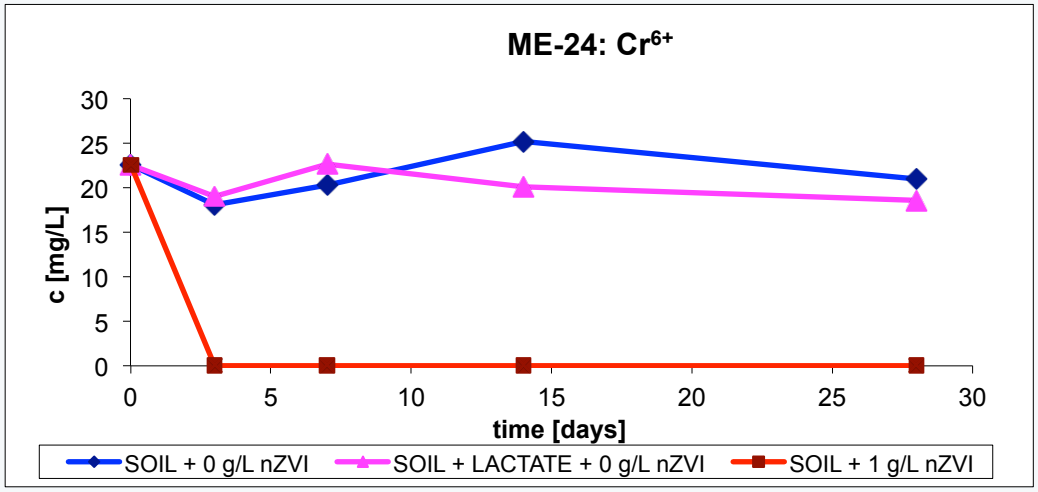
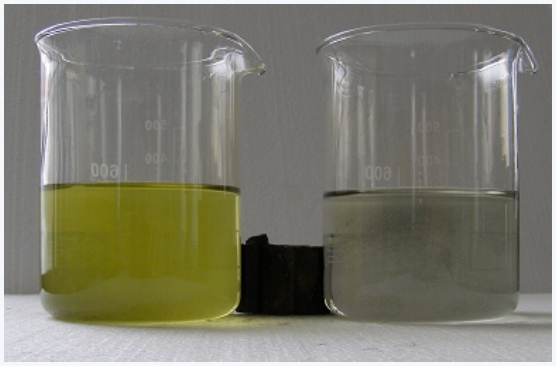
laboratory study

EKORA společnost s ručením omezeným







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pilot injection

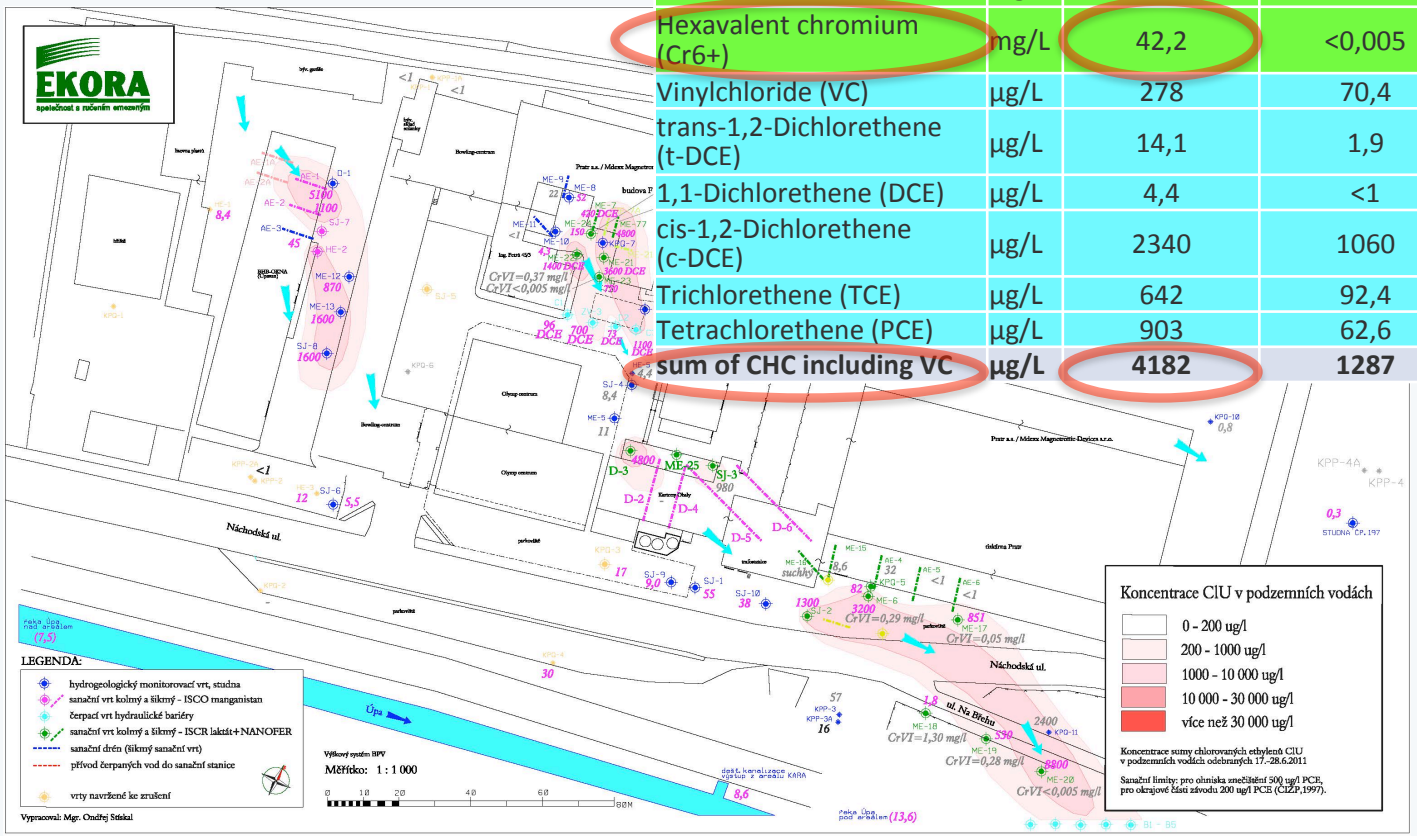
EKORA
společnost s ručením omezeným

NANOFER 25S

- 200kg
- 2 injection wells

Results after 2 months

Chemical composition of ground water - well ME-24					
parameter	*unit*	*September 8th*	*September 20th*	*October 22nd*	*October 31st*
pH	-	6,94	8,58	7,98	7,87
Total chromium (Cr tot.)	mg/L	42,5	<0,001	0,874	<0,001
Hexavalent chromium (Cr6+)	mg/L	42,2	<0,005	0,873	<0,005
Vinylchloride (VC)	µg/L	278	70,4	<4	<4
trans-1,2-Dichlorethene (t-DCE)	µg/L	14,1	1,9	<1	<1
1,1-Dichlorethene (DCE)	µg/L	4,4	<1	<1	<1
cis-1,2-Dichlorethene (c-DCE)	µg/L	2340	1060	3,1	18,9
Trichlorethene (TCE)	µg/L	642	92,4	1,64	<0,50
Tetrachlorethene (PCE)	µg/L	903	62,6	3,77	<0,50
sum of CHC including VC	**µg/L**	**4182**	**1287**	**8,5**	**18,9**



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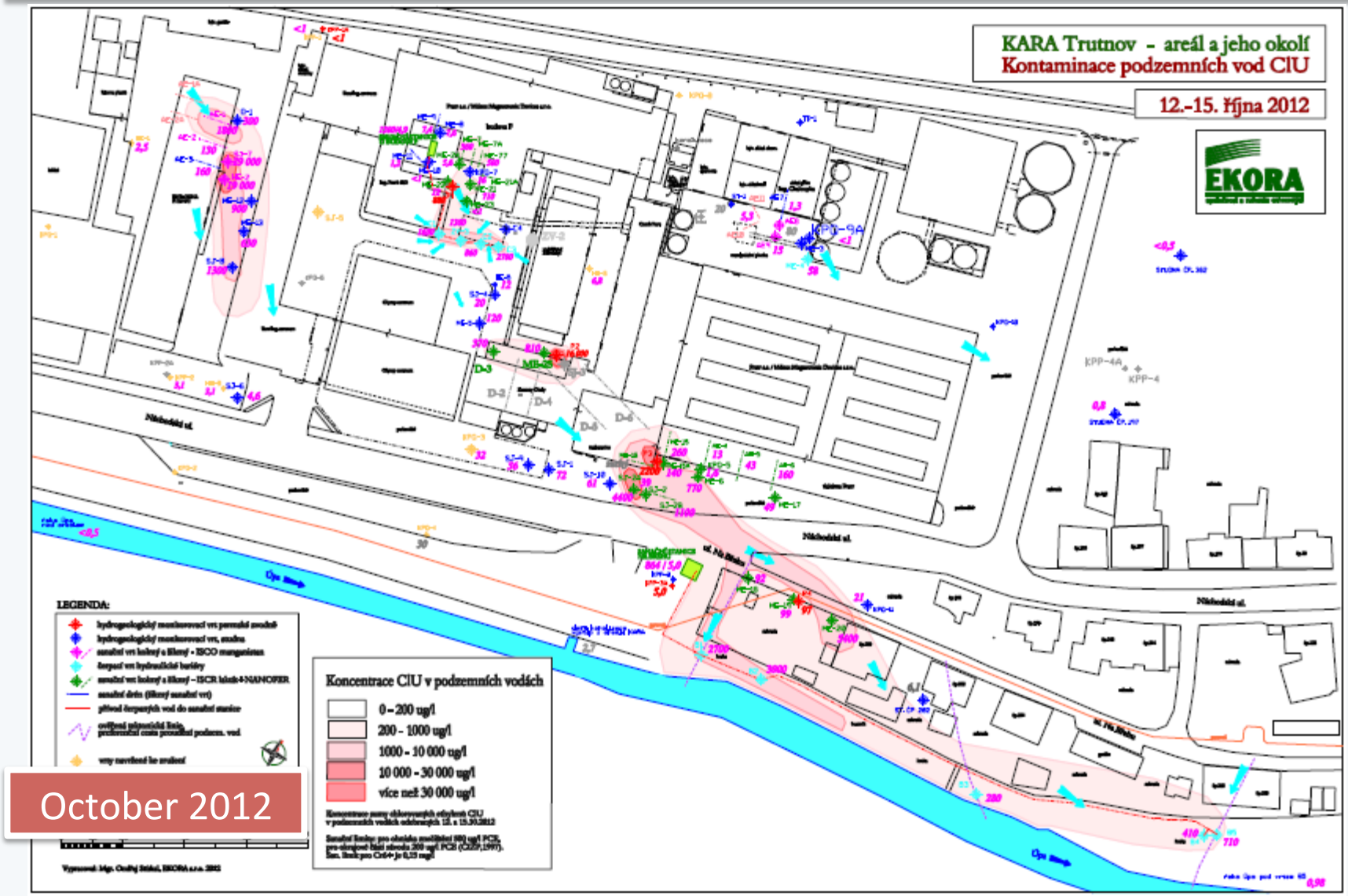
full-scale remediation

EKORA
společnost s ručením omezeným

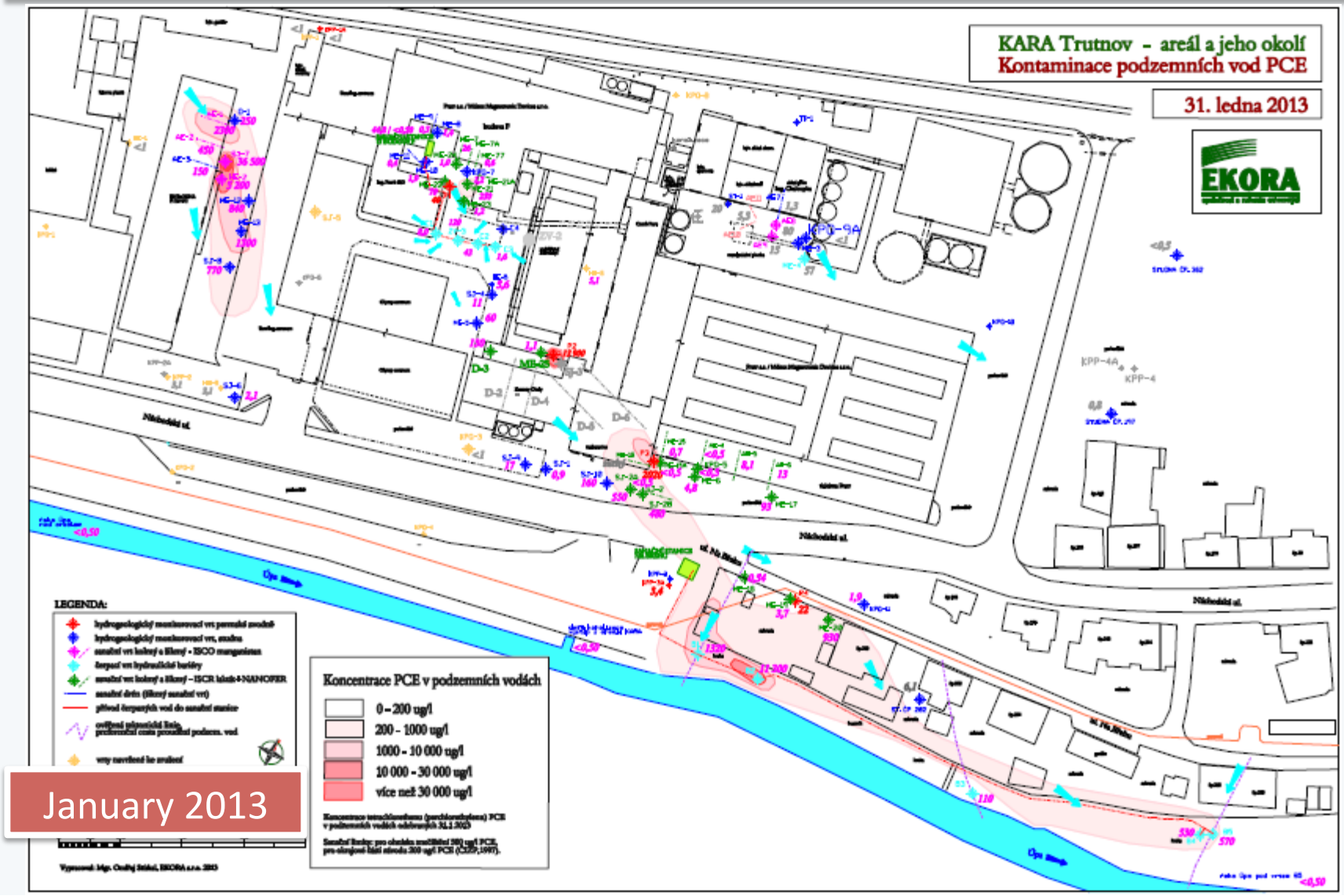


October 2012

KARA TRUTNOV

full-scale remediation

EKORA
společnost s ručením omezeným

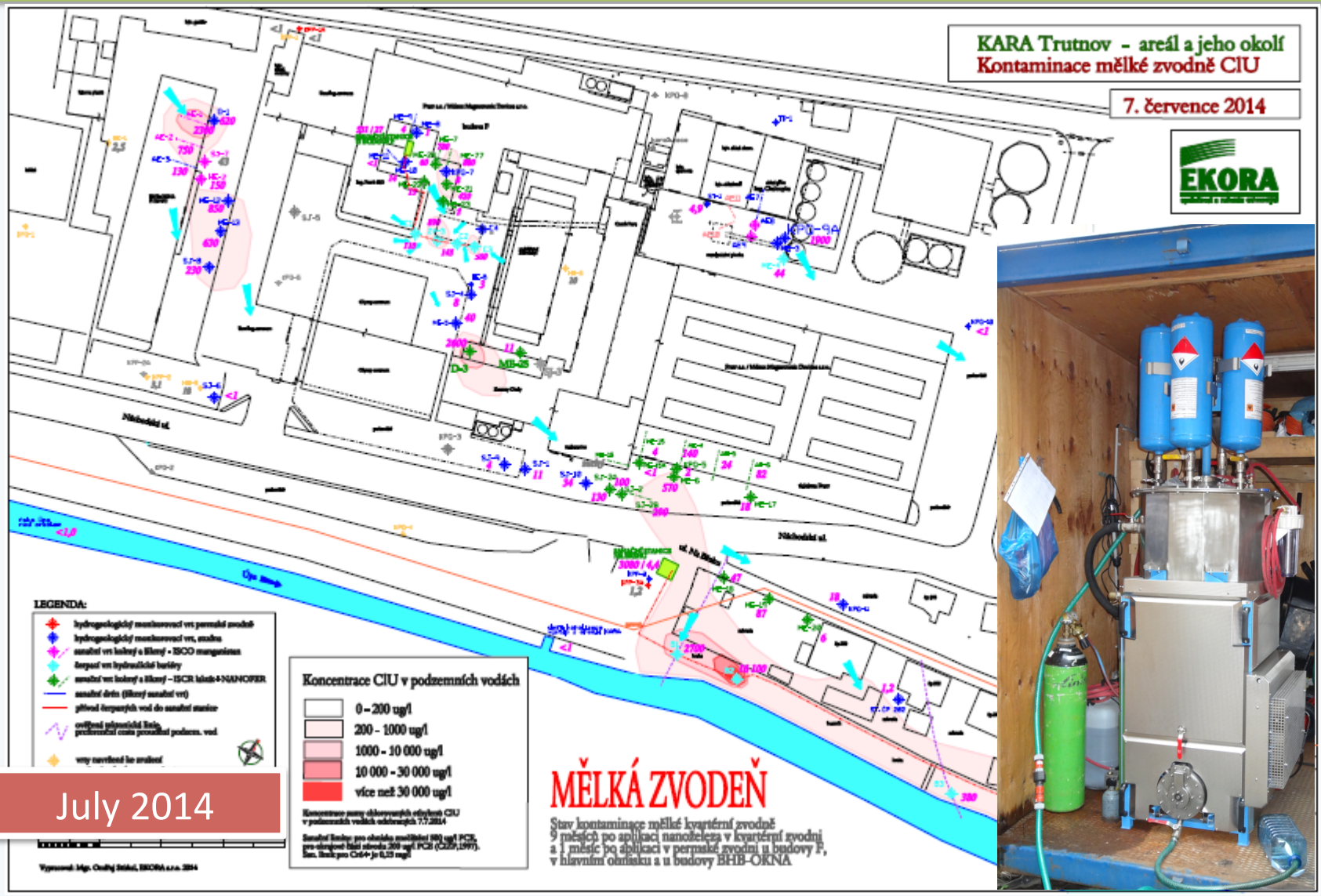


January 2013

KARA TRUTNOV

full-scale remediation

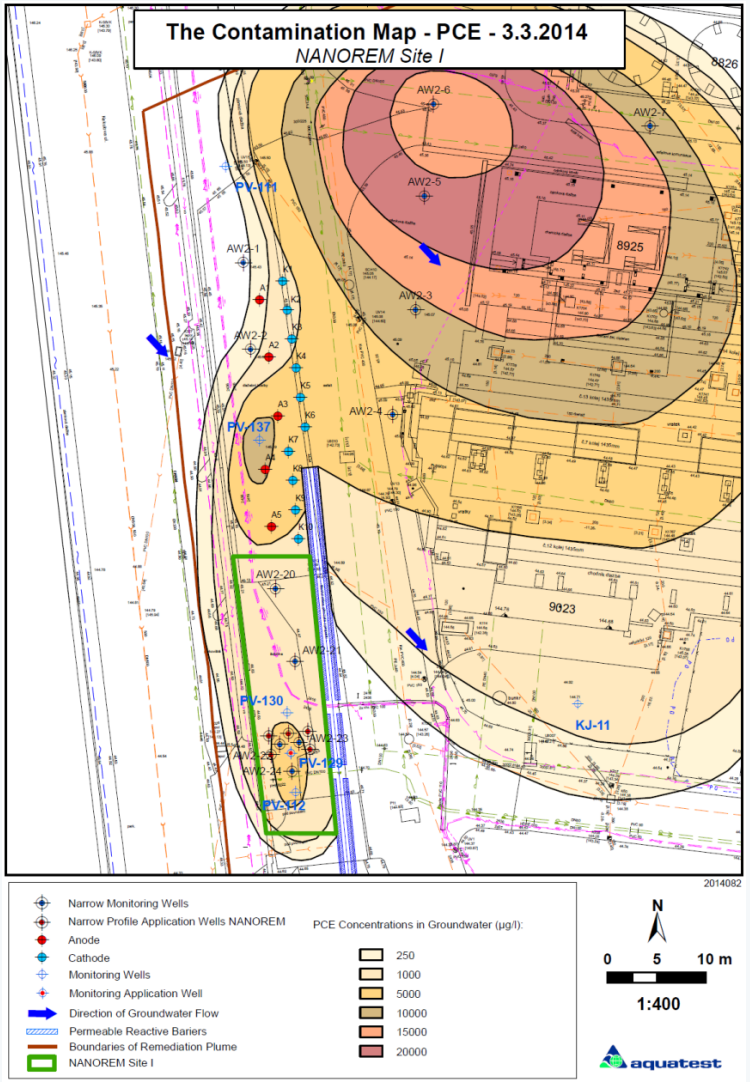
EKORA
společnost s ručením omezeným



July 2014

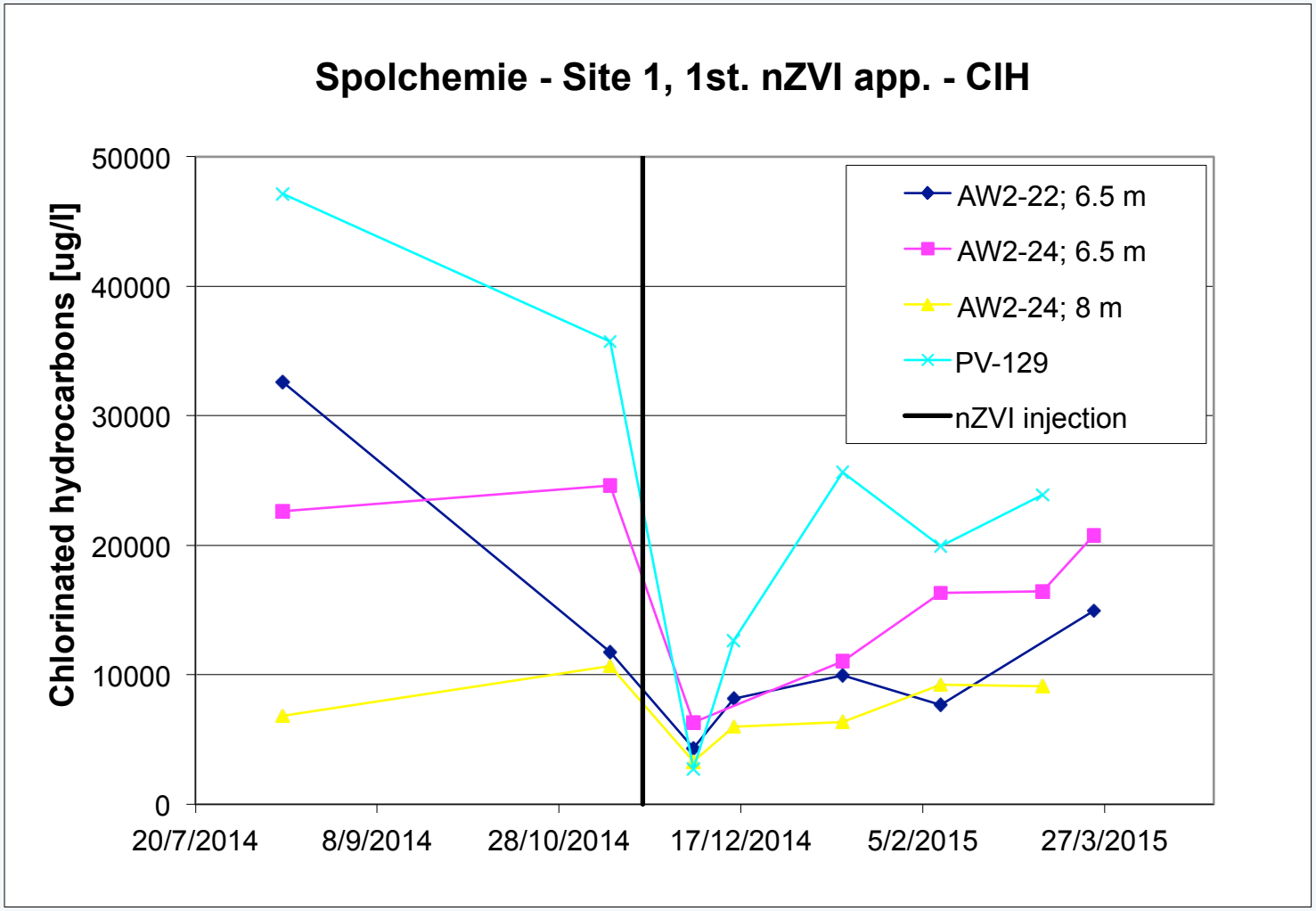
SPOLCHEMIE

- Chemical factory
- Aquifer, quarternary, sand, gravel, 6-7 m thickness
- Source: production, storage and distribution of DNAPL
  (PCE, PCM); bounded by Permeable Reactive Barrier
- Monitoring
  - Contamination
  - Migration and transformation of nZVI
  - Changes of toxicity
- Samples taken
  - Drill cores, water and sediments from monitoring wells, injected nanoparticles

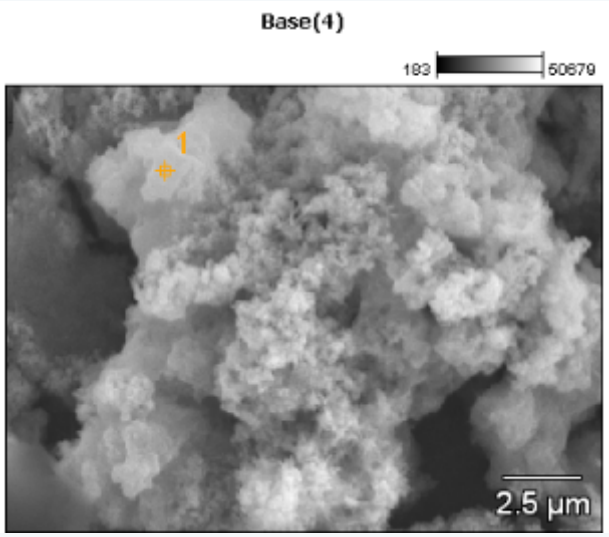


SPOLCHEMIE

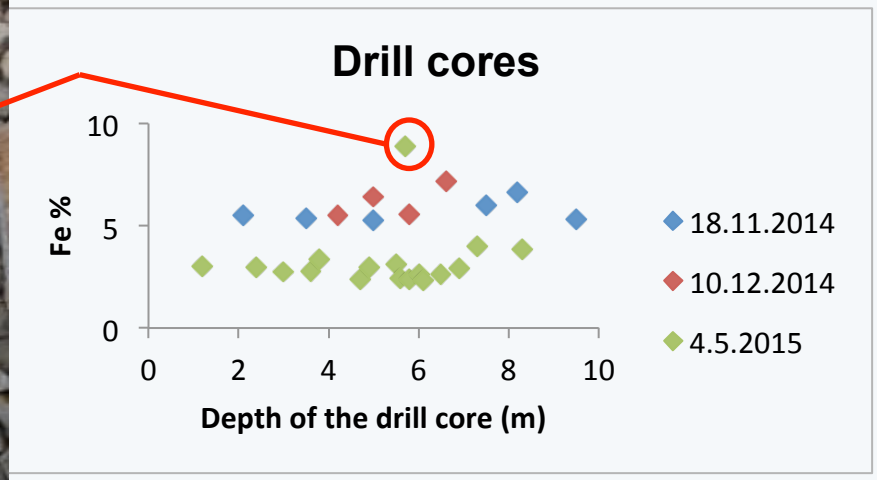
1st nZVI application results



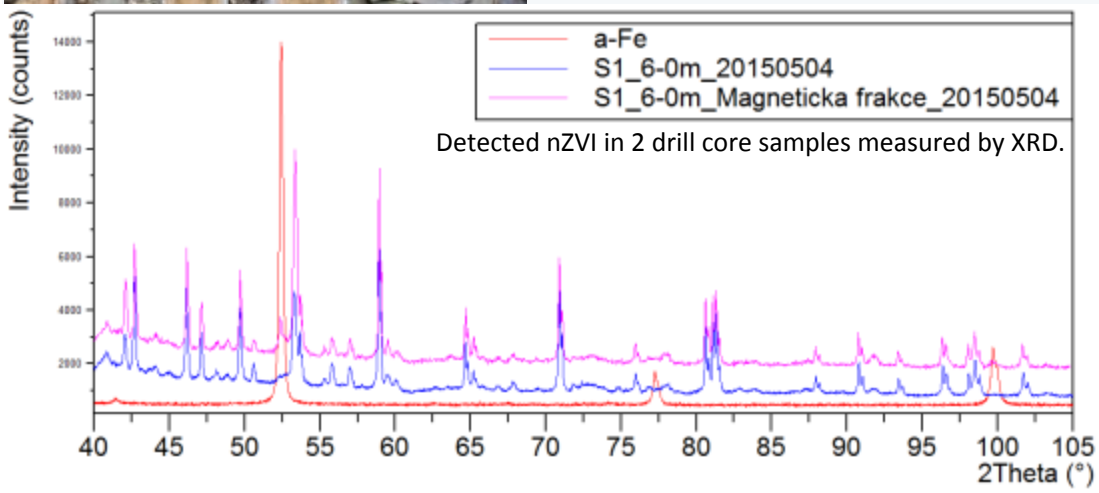
SPOLCHEMIE



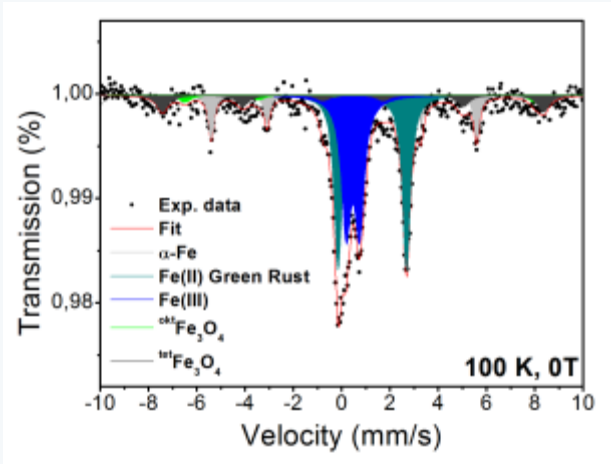
SPOLCHEMIE



Detected concentration of iron in % depending on depth of the drill core measured by XRF.



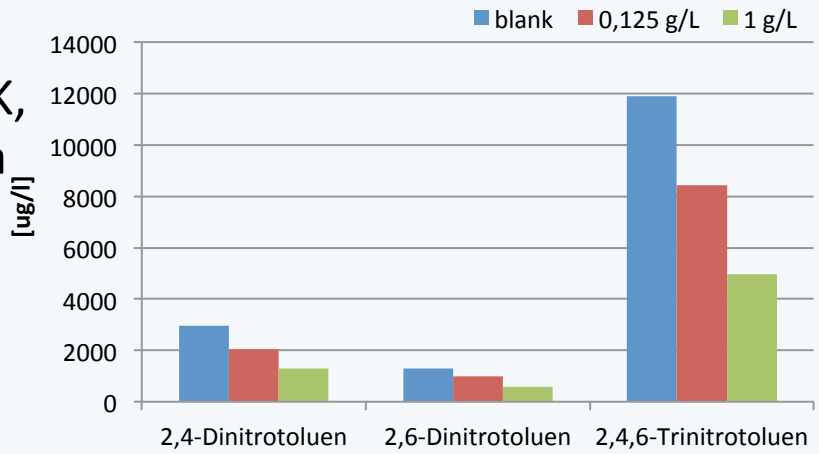
Detected nZVI in 2 drill core samples measured by XRD.



MS spectrum of drill core from 6m, 4th of May

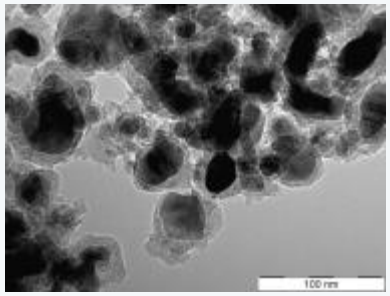
OTHER SITES and STUDIES

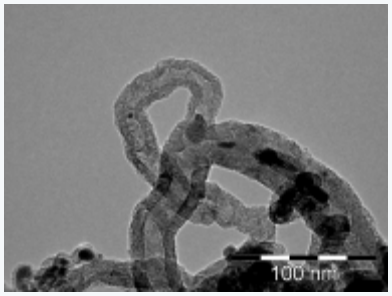
- CHC Pilot and full-scale injections
  - Netherlands, Belgium, France, CZ, SK, Denmark, USA, Canada, South Korea
- Pesticides pilot injection (CZ)
- TNT laboratory study (Portugal)
- Mine tailings remediation study



- Wastewater treatment studies (selenium, arsenic, chromium, …)
- More than 20 tons of NANOFER 25S applied on various sites around Europe.
- Others: 350 free-samples of NANOFER products shipped wordwide in past years, 75 to USA and Canada, mainly to universities, research institutes and remediation companies.

CONCLUSION





- nZVI works where others failed
- Product development
  - Air stable nZVI
  - nZVI based nanocomposites (Fe_3C-C having 80m^2/g)
  - Combined methods (lactates, vegetable oil, …)
  - Potassium Ferrate

- Comprehensive evaluation of NP's applied within NANOREM
- Understand product behaviour and take corresponding measures to achieve successful applications
  - Handling and proper application of reactive materials is important

Acknowledgement

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Thank you for your attention

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2011

2009

2013