Where are our Nanoparticles?

At site and *in situ* monitoring

Deborah Oughton and WP6/8/10

NanoRem Final Conference

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

Frankfurt am Main, 21st November 2016

Overall WP objectives

- ..the development and application of analytical methods and protocols for in-situ measurement, detection and studies of the fate of nanoparticles.

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

WP 6: Analytical Methods for *In-situ* Determination of Nanoparticles Fate.

DL 6.1 Feasibility and Applicability of Monitoring Methods

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March 31st 2015

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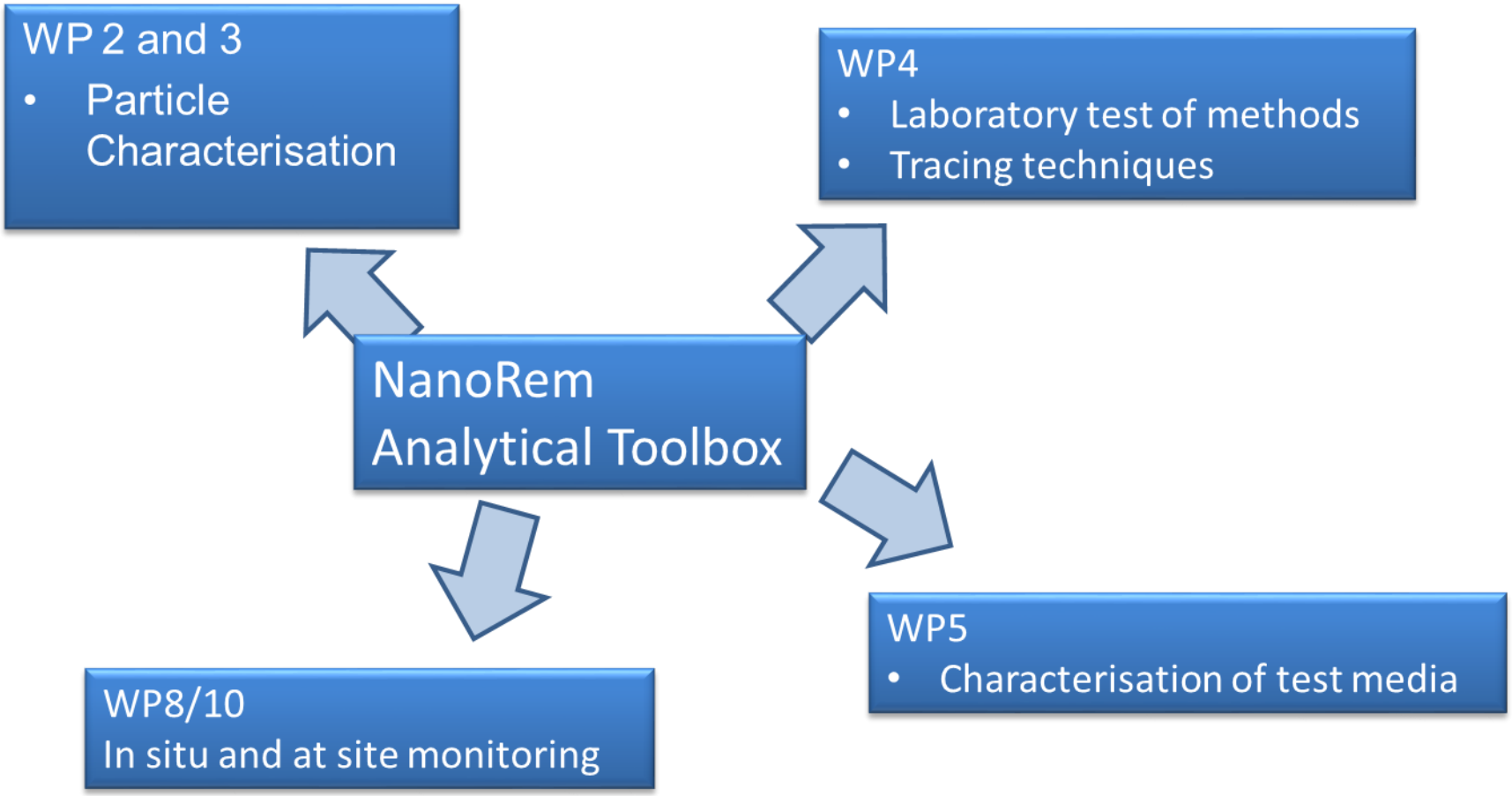
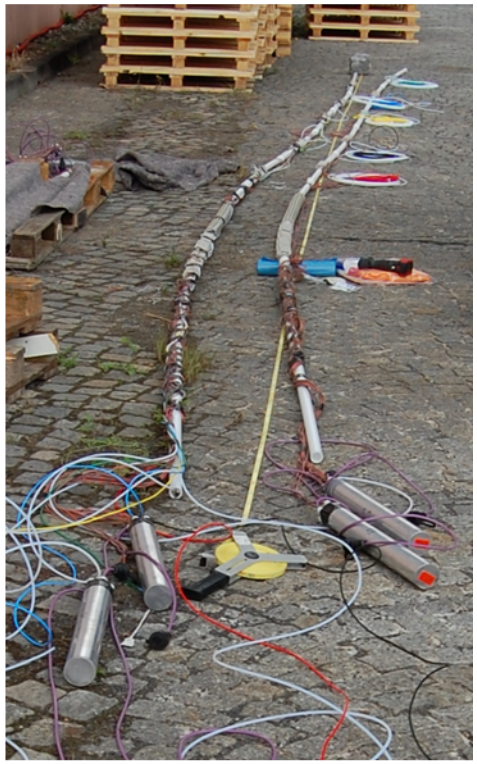
Analytical Toolbox



At site *and In situ* measurement

- Definition of *in situ* measurement. In principle, a true *in situ* measurement means putting the measuring device in the aquifer. At present, only magnetic susceptibility, and possibly some of the redox/H_2 methods would qualify. But field methods can also make use of a range of *in situ* sampling techniques. The approach means that we can study the particles' behaviour *in situ* rather than relying on laboratory studies.

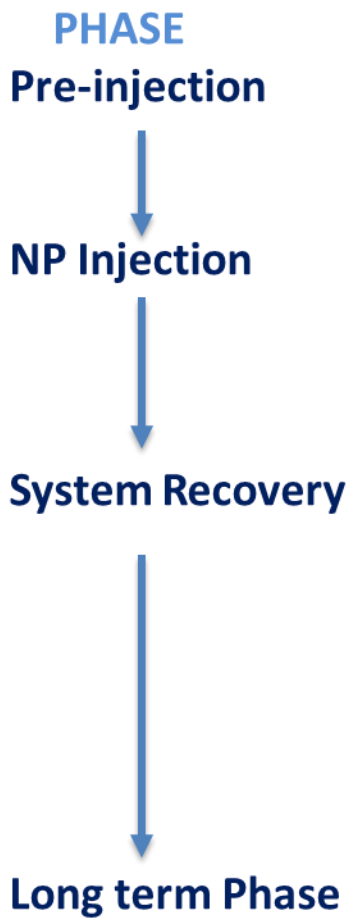
- Need to see all methods as complimentary; there is no one method that can answer all questions, at all sampling points.



Field arrays VEGAS

For All Field Sites: Data Needs at Different Phases

1. Field characterisation studies prior to injection
2. Monitoring the movement and distribution of particles during injection. Is the particle suspension reaching the required location, with the required concentration and state?
3. Monitoring for transport of “fine” or “renegade” particles out of the core application area during and after injection. Low NP concentrations give rise to challenges with detection against background levels of colloids.
4. Post injection behaviour. Transformation and reactivity of the particles. Need for reinjection.



Tank tests VEGAS, October 2014

UNVIE
Turbidity
Fe content
ICP-MS
Zetasizer
EM
Redox/pH

NMBU
Ultrafiltration
Fe-content (on site spectrophotometry)
ICP-MS
SEM/TEM
pH/conductivity

USTUTT
Fe content
Gravametric
Redox/pH/temp
+++

UDE
Conductivity
Fe content
Sediment/core sampling

Monitoring Method Tests: Field Sites

Spolchemie I and Spolchemie II, CZ
NANOFER STAR, NANOFER 25S and Nano-Goethite
2014, 2016

UPOL: Mössbauer, H_2 production, Fe and REE fingerprint, XRD
USTUTT: *In situ* magnetic susceptability, temperature
NMBU: Ultrafiltration, Fe spectrophotometry (Fe II/ Fe III), Rare Earth Element Fingerprint Stable Fe-isotope, EM, redox,
UNVIE: Turbidity, ICP-MS
UDE: Conductivity, Fe content
Aquatest: Pollutant monitoring, chemistry, tracer

Balassagyarmat, HU
Carbo-Iron®
UFZ
USTUTT
NMBU

Solvay, CH
FerMEG12
NANOFER STAR
2015, 2016

USTUTT
NMBU

Field activities at the Spolchemie site (© Jan Filip, UPOL)

Neot Hovav, IL
Carbo-Iron®

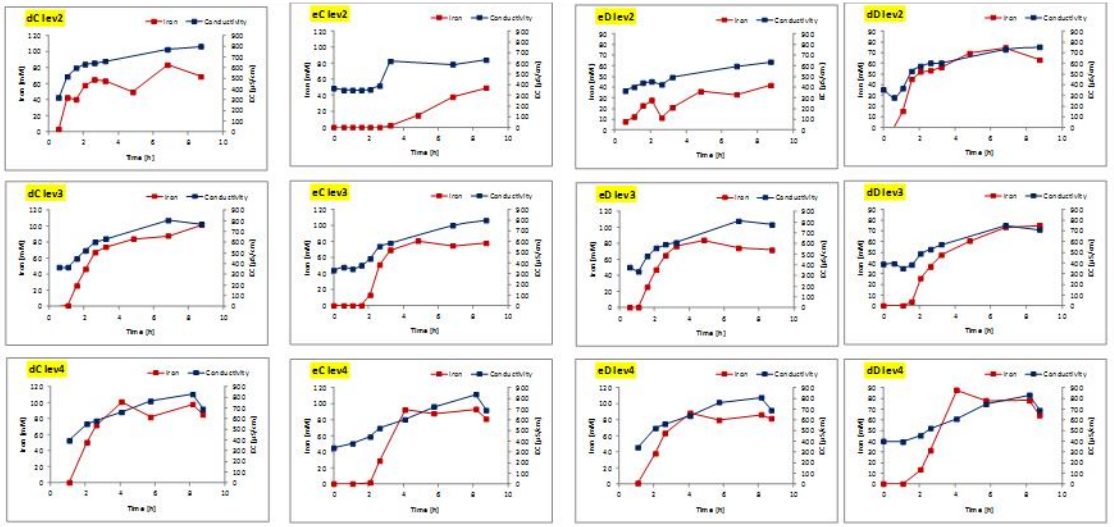
NMBU

What Works?

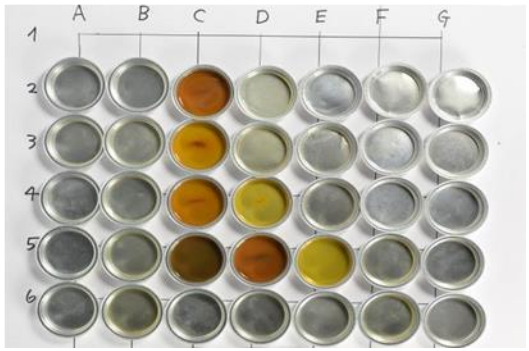
What Works During Injection?

Spatial and Temporal distribution

- Turbidity, Fe content (including on site using spectrophotometry), conductivity, gravimetric, filtration/ultrafiltration, … at concentrations of mg/L - g/L

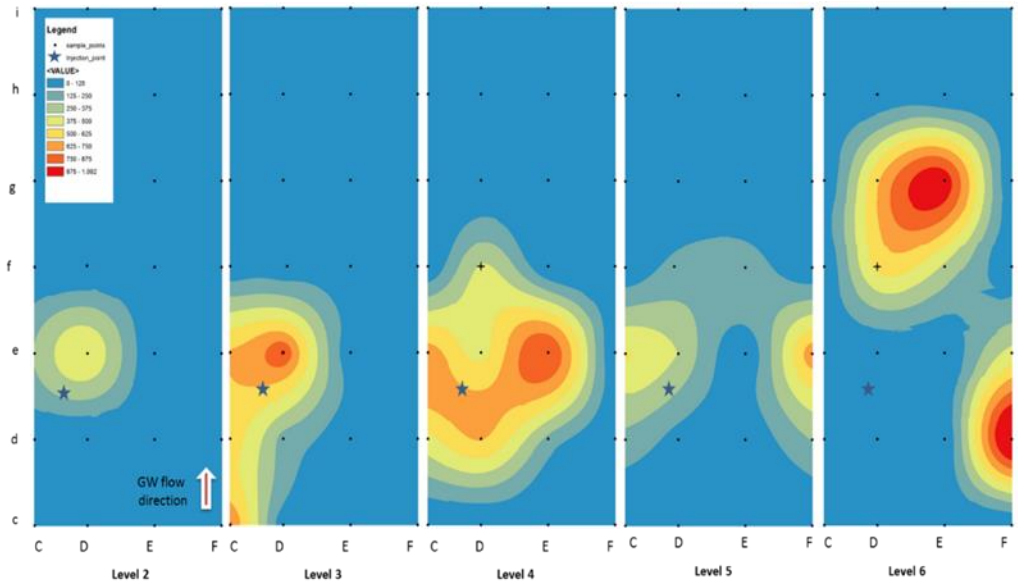


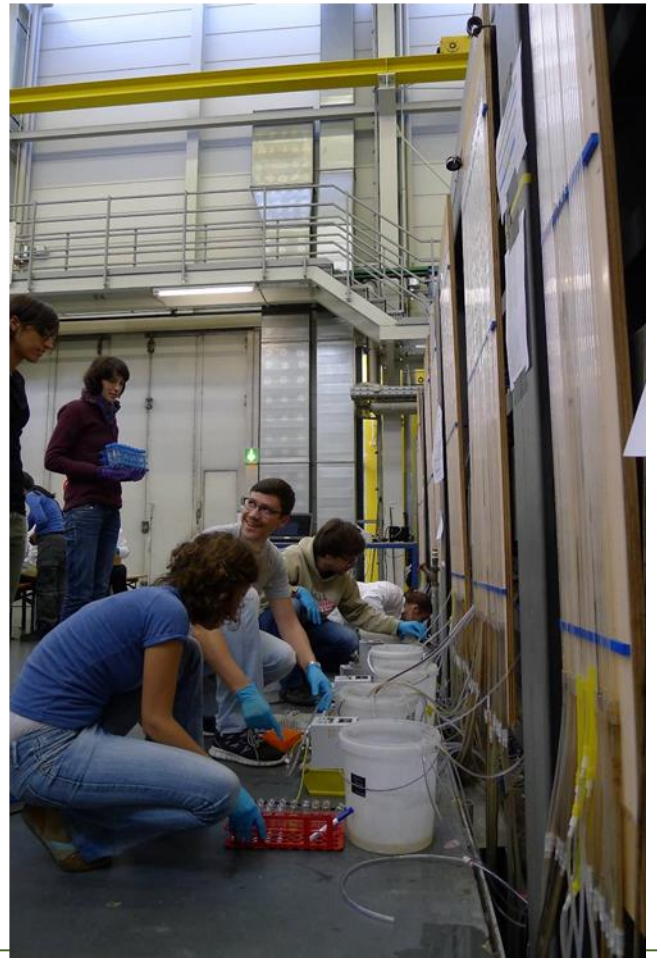
Fe content and conductivity measurements (D 6.1)



What Works During Injection?

Turbidity measurements 20 hr post FeOx injection.





What Works During Injection?

In situ measurement methods for nZVI

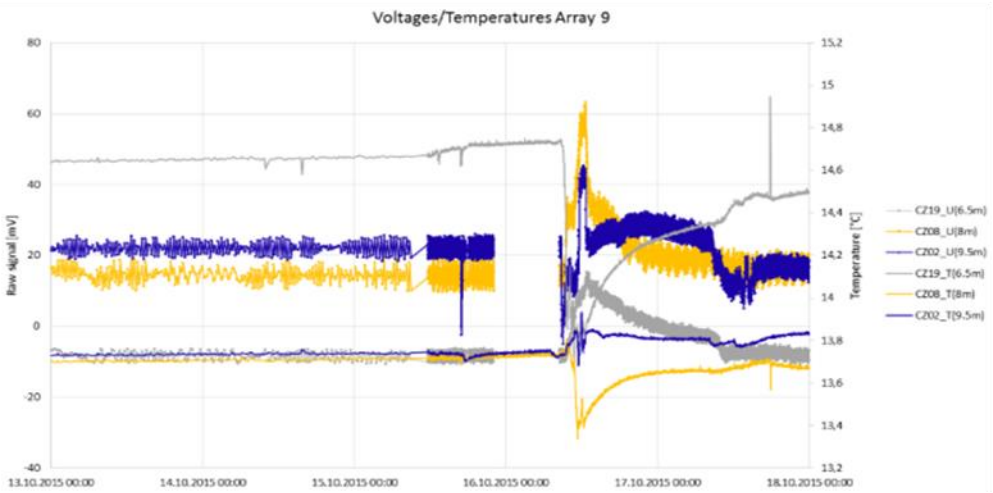
– Magnetic susceptibility arrays installed and tested at Spolchemie (nZVI) and Solvay (milled Fe).

Replacing arrays at Spolchemie, November 2015 (left); installing arrays at Solvay (right): Photo USTUTT

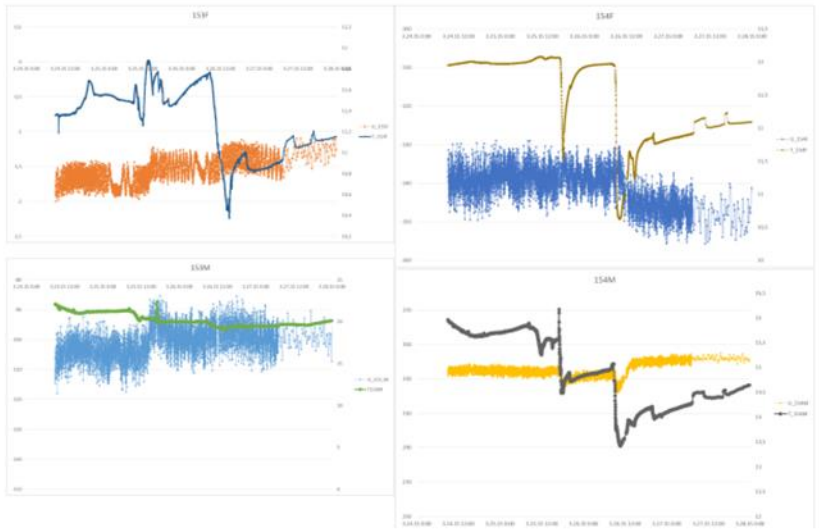
What Works During Injection?

In situ measurement methods for nZVI and milled Fe

– Positive detection of signals at both sites (susceptibility and temperature)



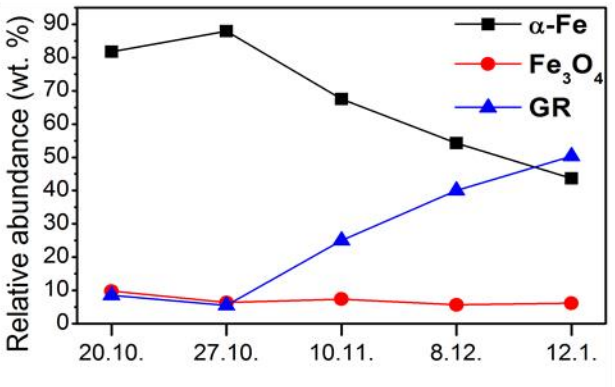
Spolchemie (USTUTT)



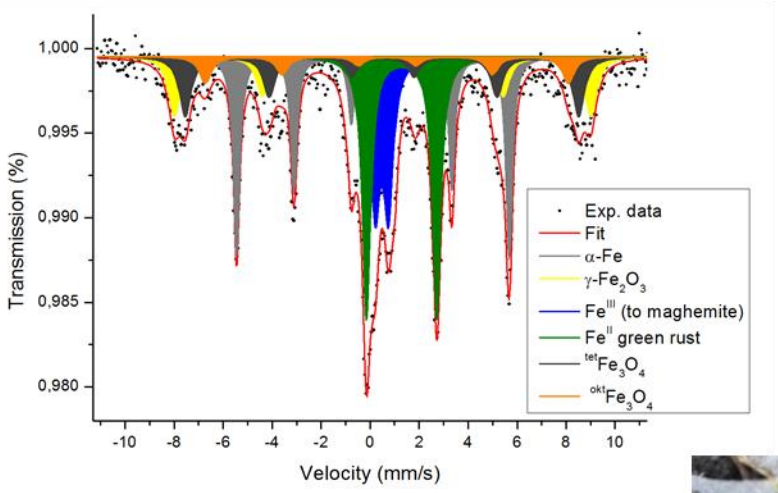
Solvay (USTUTT)

What Works for Post Injection Fate

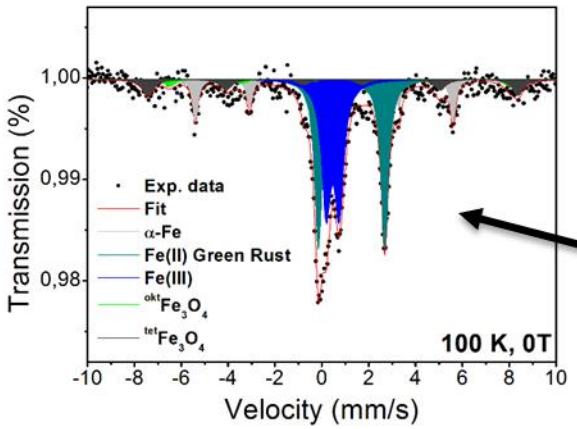
- Mössbauer (nZVI), EM, redox measurements, Fe content sediments, XRD, (synchrotron ++, if more information is needed)



Structural changes during 4 months after second injection (2015 and 2016) investigate using XRD; GR = green rust (UPOL)



Mössbauer spectrum of sediment from well PV-129 in 29th June 2015 (UPOL)

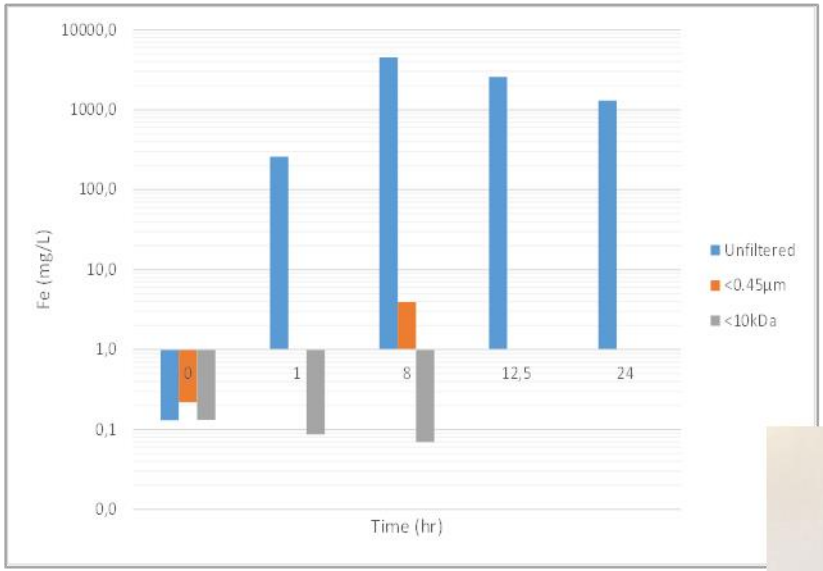


Mössbauer spectrum of drill core from from well PV-129 in 29th June 2015

Where are our Nanoparticles

What Works for Tracing Renegades?

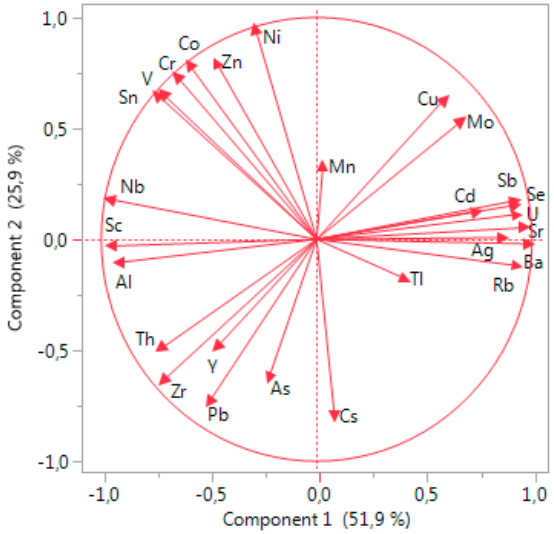
- Turbidity (FeOx, CarboIron a few mg/l)
- Ultrafiltration (demarking dissolved Fe, from colloidal Fe, ug-mg/L)

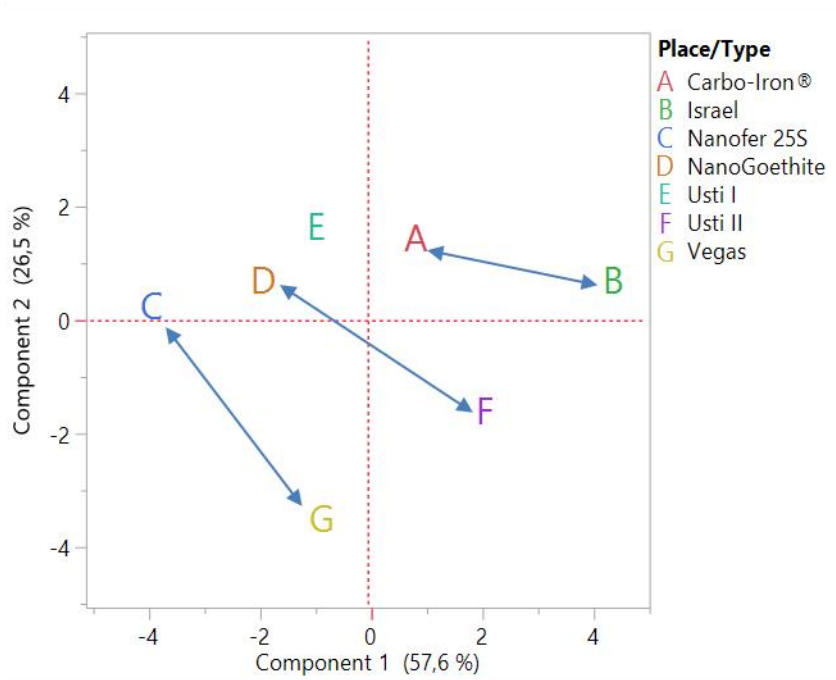


Figures from NMBU:

What Works for Tracing Renegades?

– Lanthanide and multi-element fingerprinting combined with principle component analysis

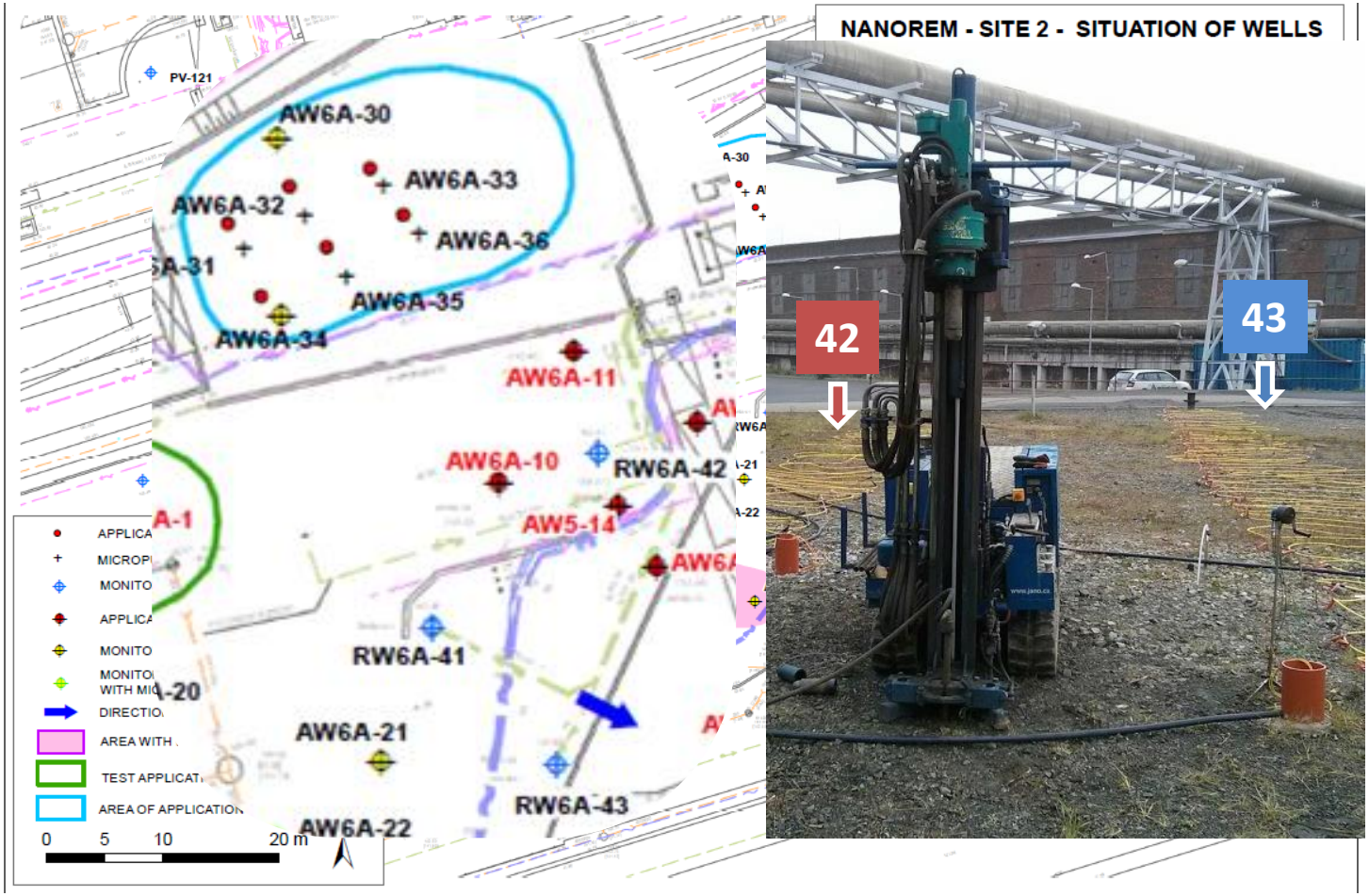




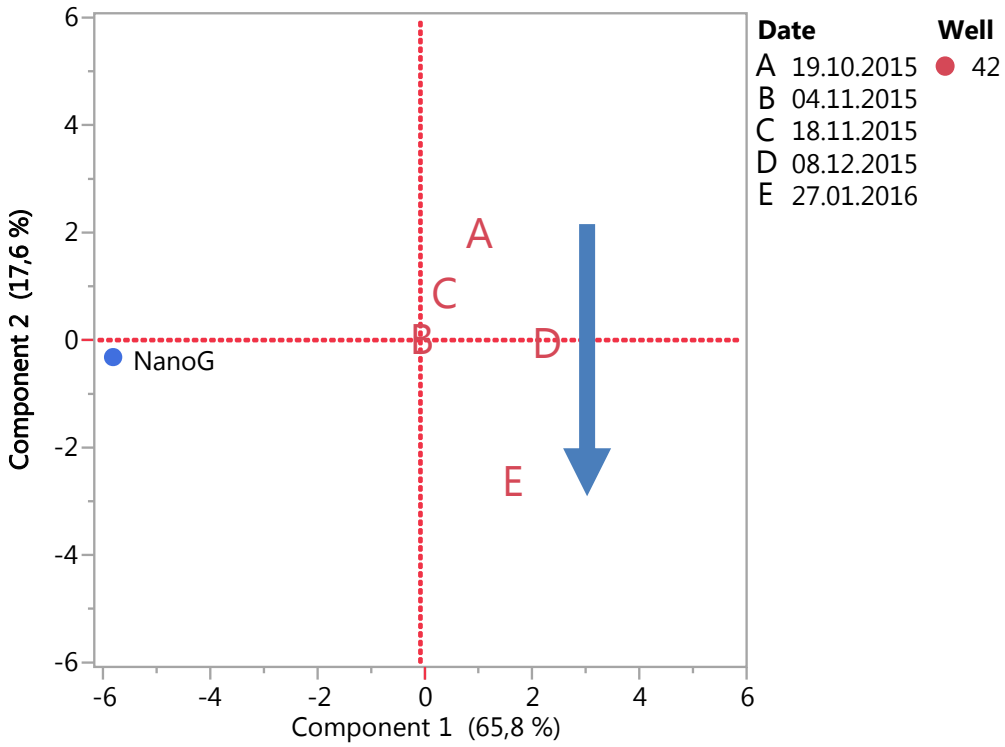
See Lebed et al. Poster this meeting

Priniciple Component analysis of REE signature in NP and sites: NMBU

Case study: Usti II - distant wells



Case study: Usti II - distant wells

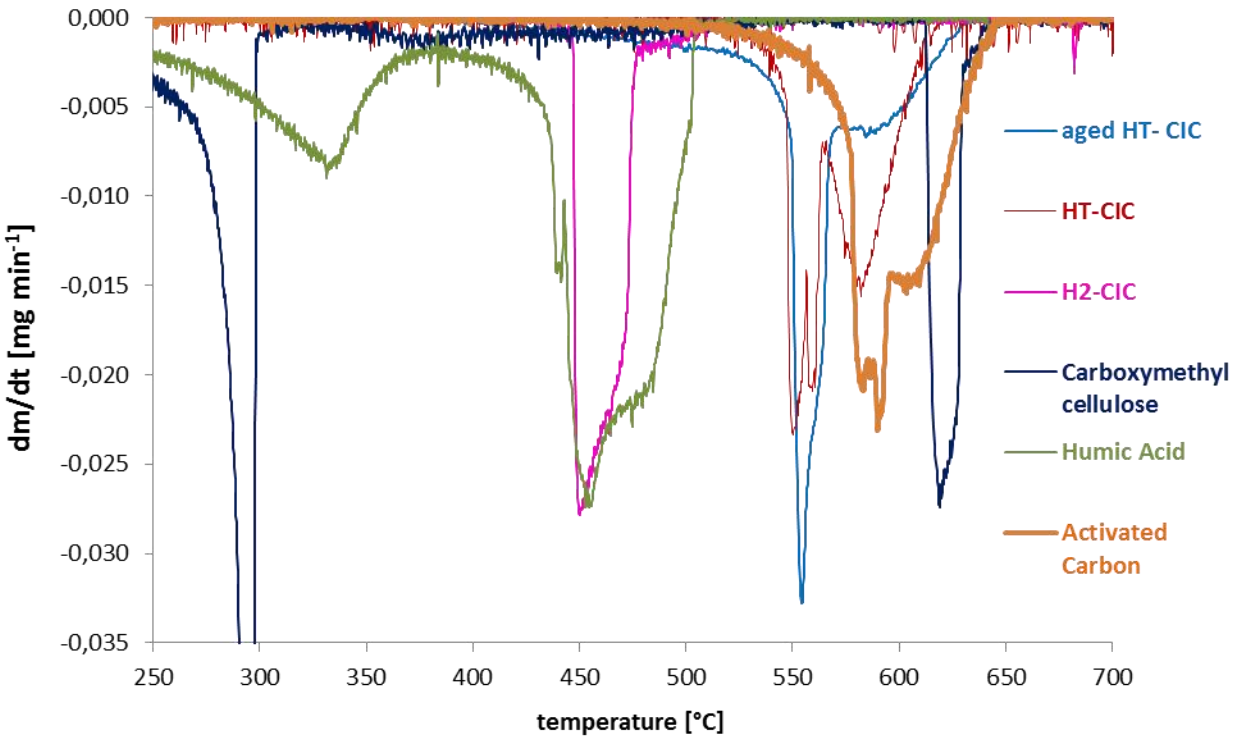


No detectable Nano-goethite (<1 mg/L)

What works for CarboIron?

Temperature-programmed oxidation (TPO) coupled with IR gas analysis (TPO-IR)

– Lab and field tests indicate LOD at 0.03% wt in sediments



TPO of carbonaceous materials in a thermogravimetric balance

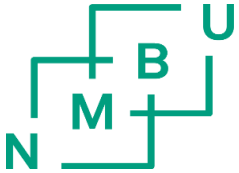
Core samples from Balassagyarmaat field site

Highlights

- Magnetic susceptability arrays successfully tested for *in-situ* monitoring of nZVI - Nanofer STAR, Nanofer 25S - and milled Fe -FerMEG12. (€1000 per array, detection limits g/L Fe)
- Variety of techniques applicable for simple on site tracing of Fe-based NPs – redox, Fe/Fe^{2+}, turbidity (€10's per sample; mg-g/L)
- Multi-elemental fingerprinting developed and tested at different NanoRem field sites (€2000- €10000 for monitoring renegades; µg-mg/L)
- New methods developed and tested for Carbo-Iron®

Thank you for your attention

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



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