Beginning of field experiments, 22. 2. 2022

Nanoremediation of contaminated soils

Technology implementation with respect to ecotoxicological aspects

The remediation of inorganic pollutants (metals and metalloids) is challenging due to their non-degradability and persistence in the environment.

Reducing their mobility and availability is a potential alternative to excavation and landfilling. Engineered iron nanoparticles are promising due to their high specific surface and reactivity.

SoilCon, Prague 2023

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Iceland Liechtenstein Norway grants

TACR

CZU Faculty of Environmental Sciences

dekonta

CHARLES UNIVERSITY IN PRAGUE

NIVA Norwegian Institute for Water Research

NTNU Norwegian University of Science and Technology

The *MetalRem* project benefits from a 1 496 360 € grant from Iceland, Liechtenstein and Norway through the EEA Grants and the Technology Agency of the Czech Republic within the KAPPA Programme.

Metal REM

Nanoremediation of contaminated soils

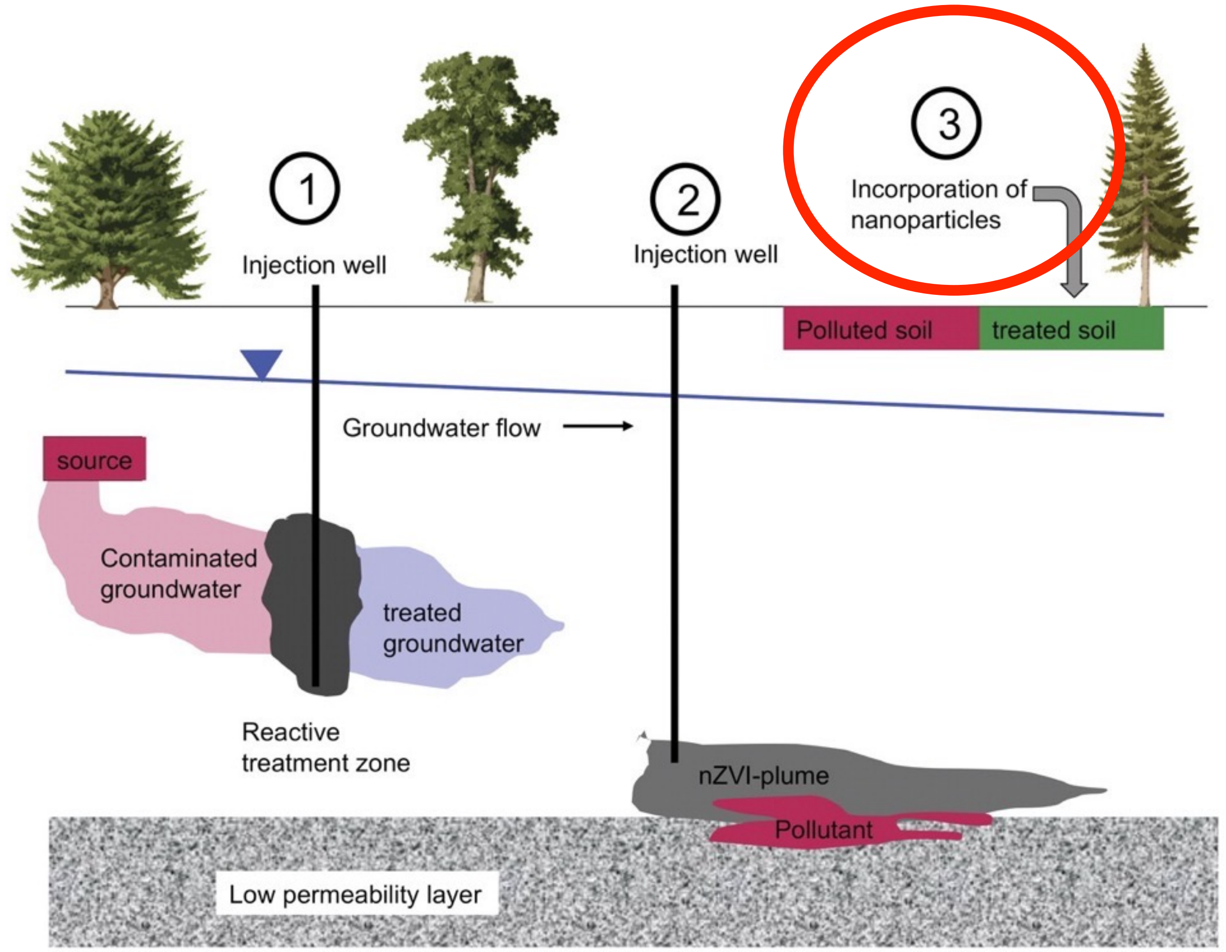
Michael Komárek (CZU Prague)

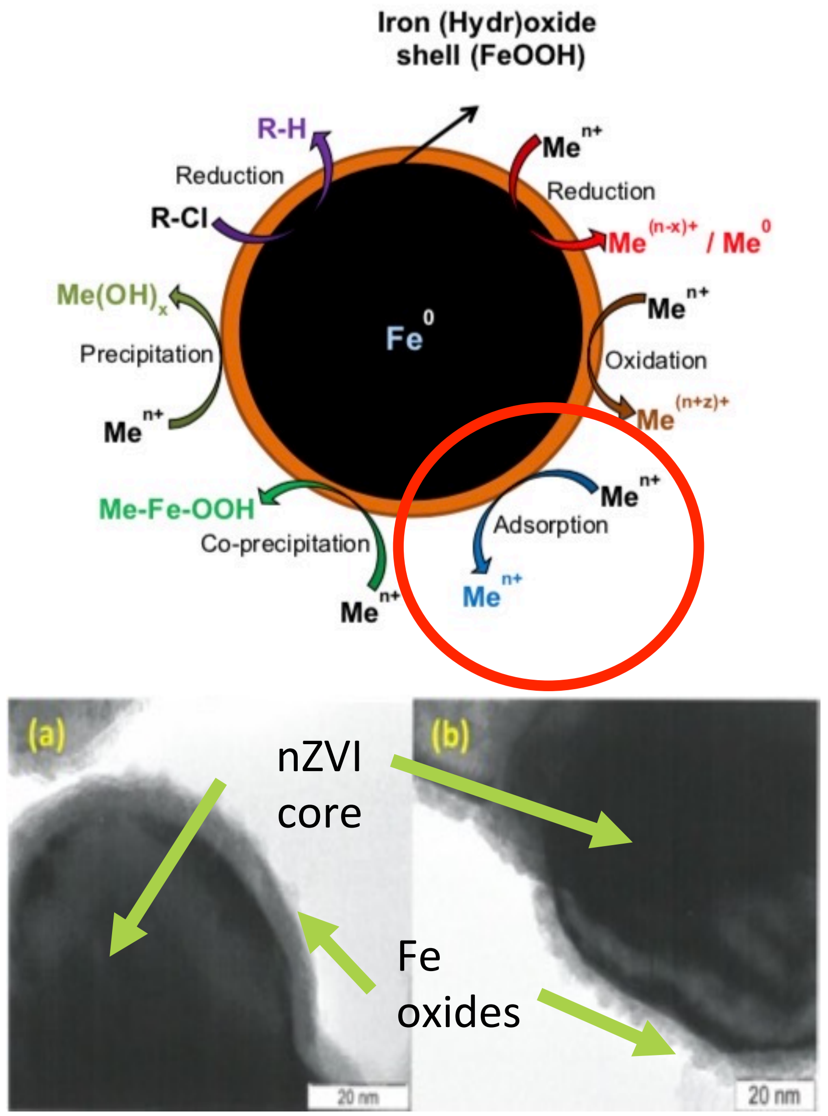
Ondřej Lhotský (Dekonta)

Tomáš Cajthaml (Charles University in Prague)

Solving big problems with tiny particles...

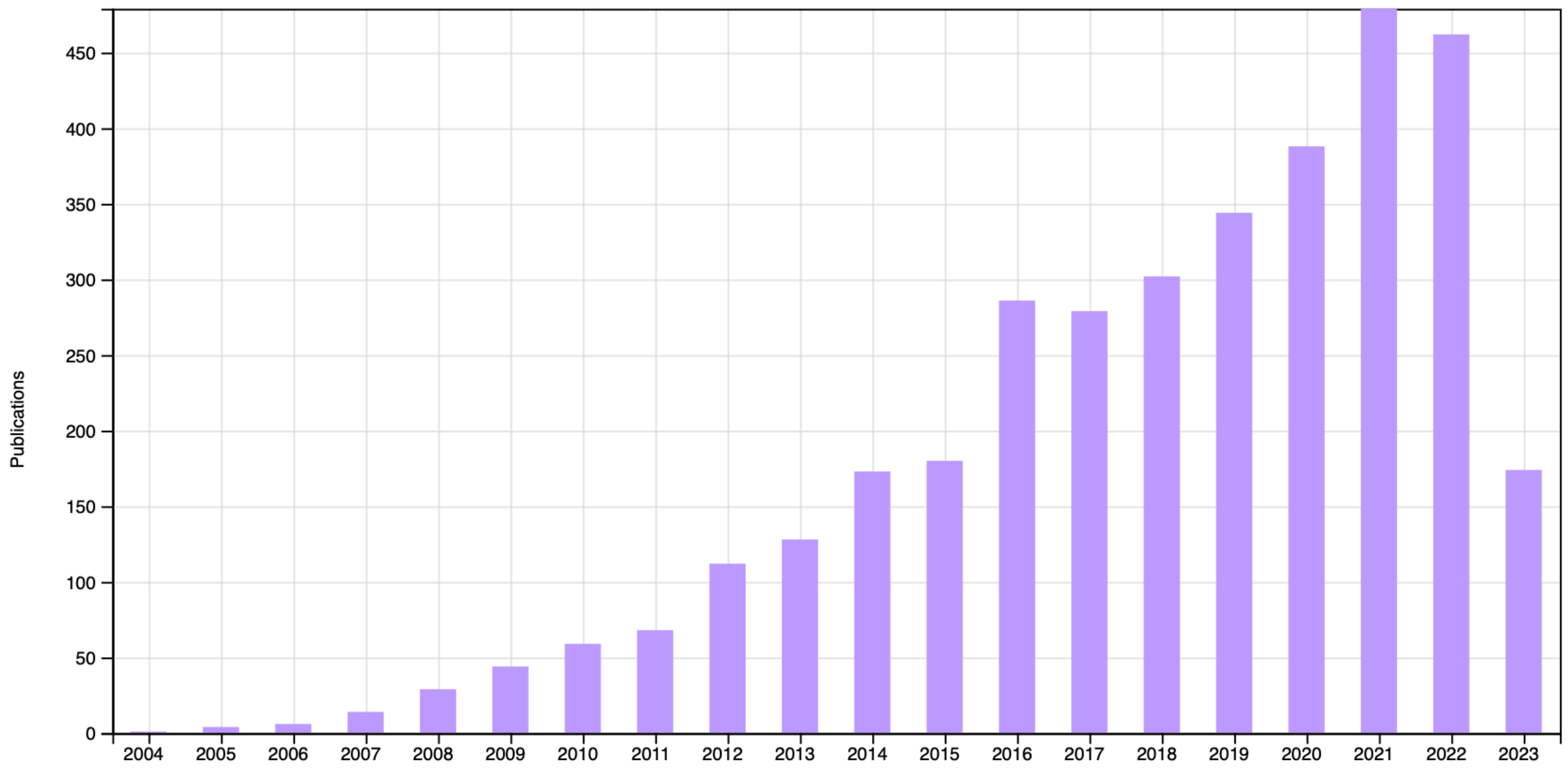
- soil oxides are natural components of soils influencing soil chemistry
- small particles (X0 nm–X00 μm) → large specific surface (X0–X00 m^2/g) → high reactivity → excellent adsorption characteristics
- combination with phytostabilization (aided phytostabilization), composites
- nZVI is commonly used for groundwater remediation

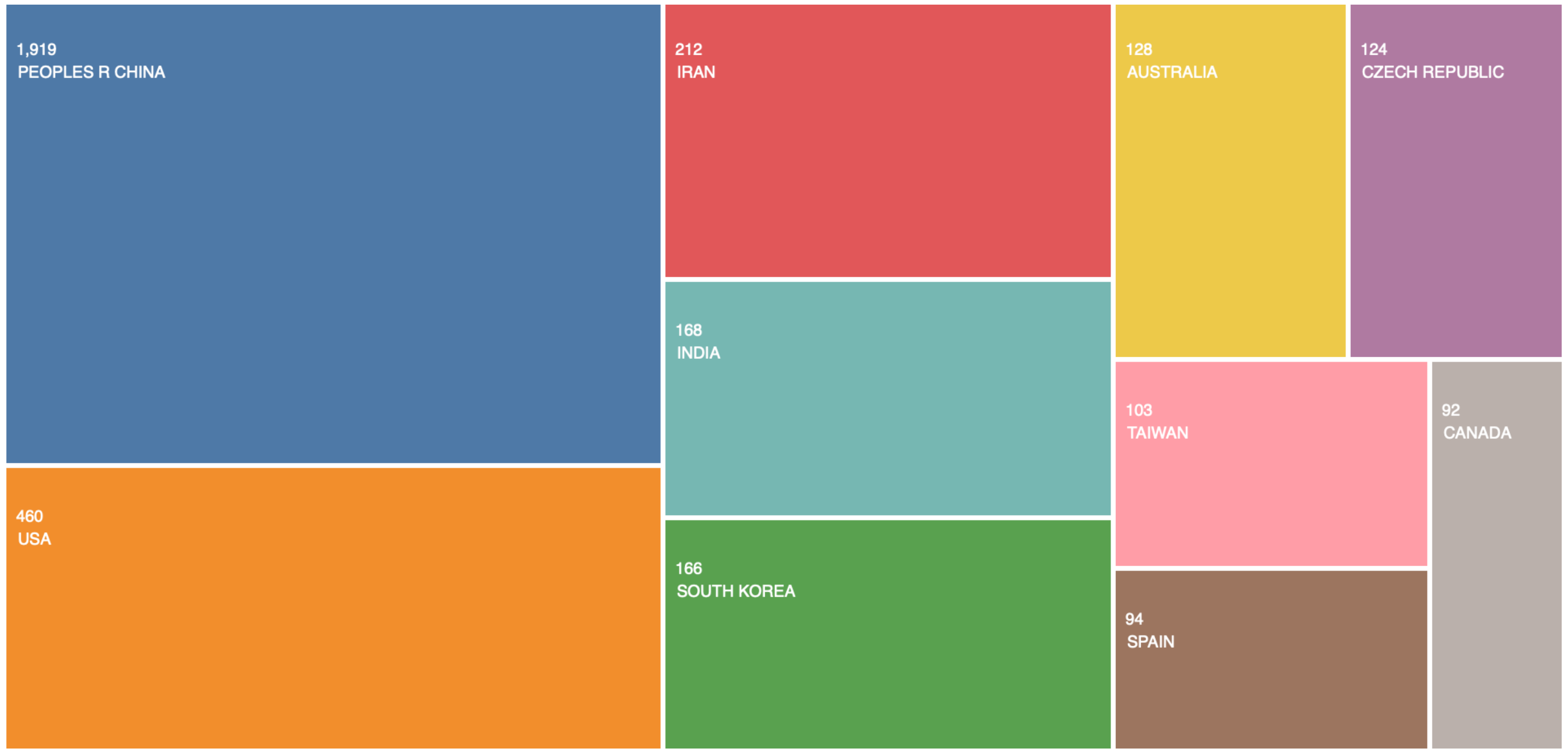




Mueller and Nowack, 2010, *Elements*
O'Caroll et al., 2013, *Adv. Water Res.*
Wu et al., 2018, *Environ. Sci. Technol.*

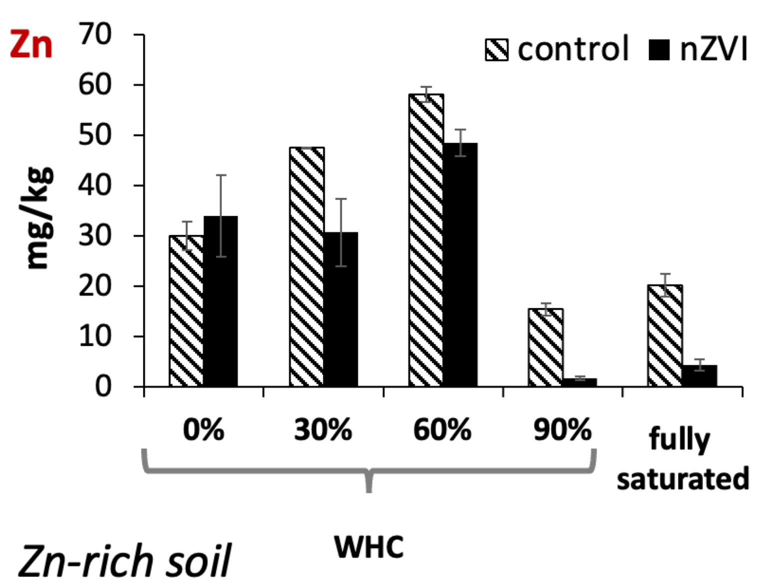
Over 3500 papers on nZVI in the last 19 years…



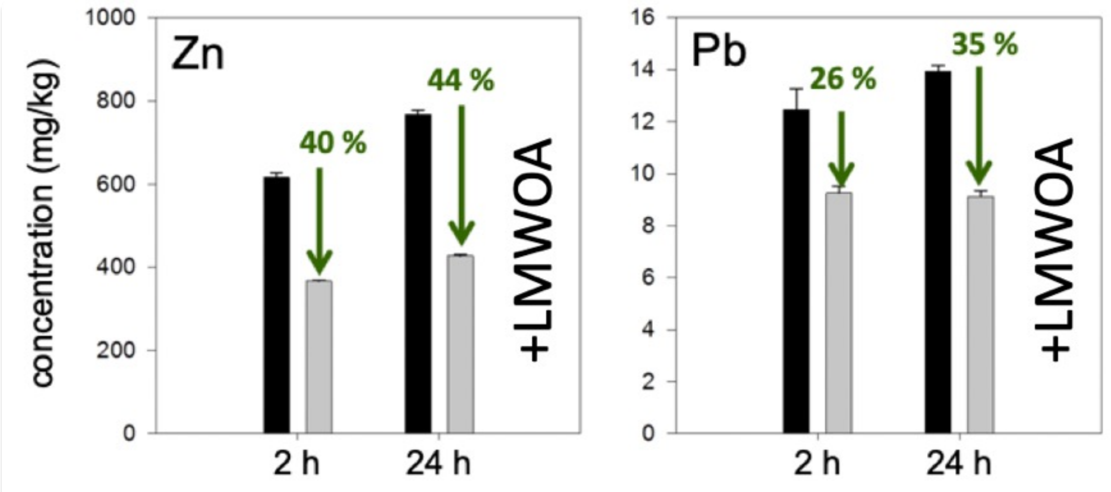


Data from the Web of Science (7/2023),
search string: *nZVI* OR *nanozerovalent iron*

Soil remediation



Zn-rich soil



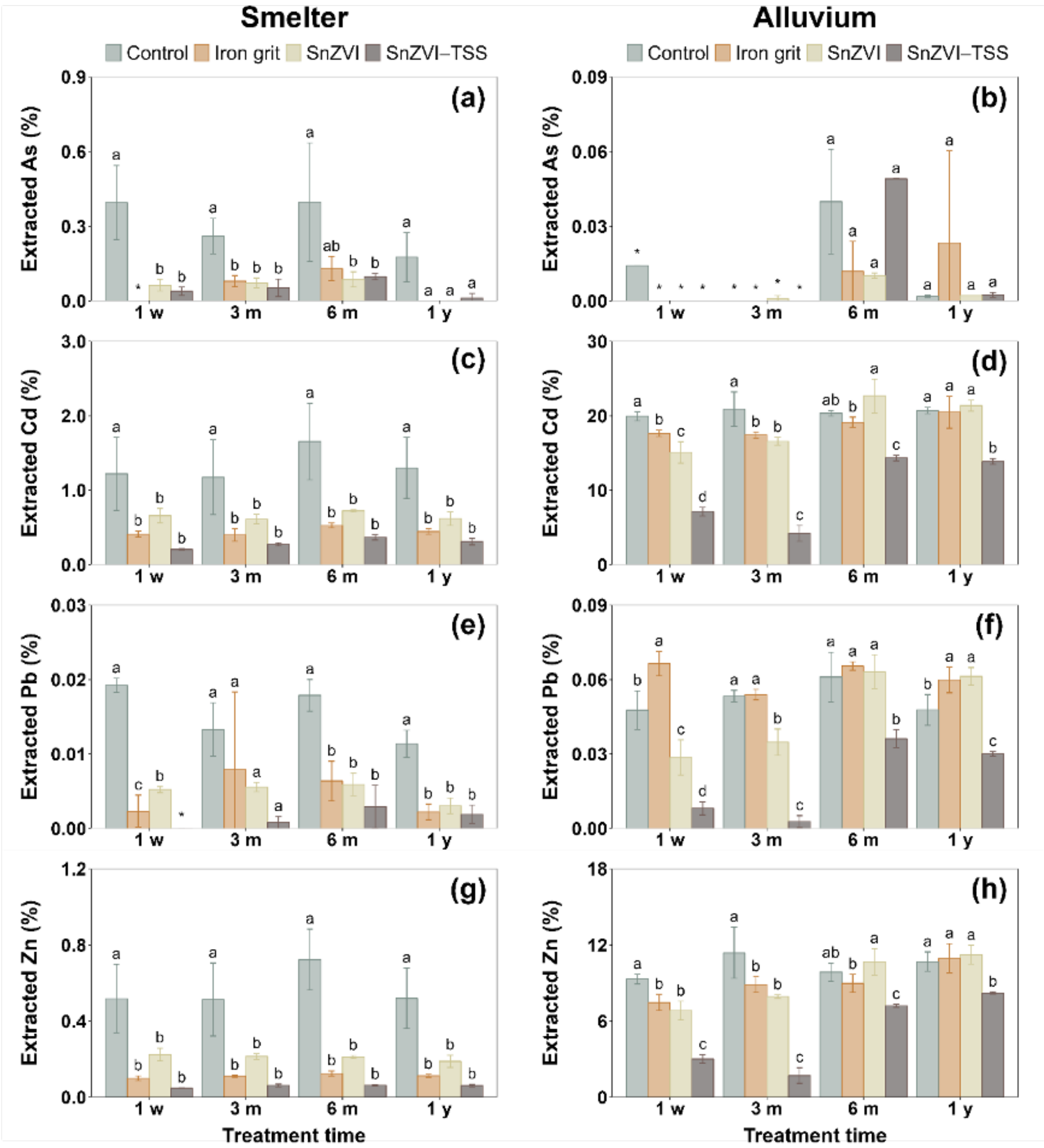
soil	time	pH	DOC (mg/l)	time	pH	DOC (mg/l)
control	2 h	3.90	380	24 h	4.50	400
nZVI	2 h	4.20	390	24 h	4.90	440

control soil
nZVI-stabilised soil

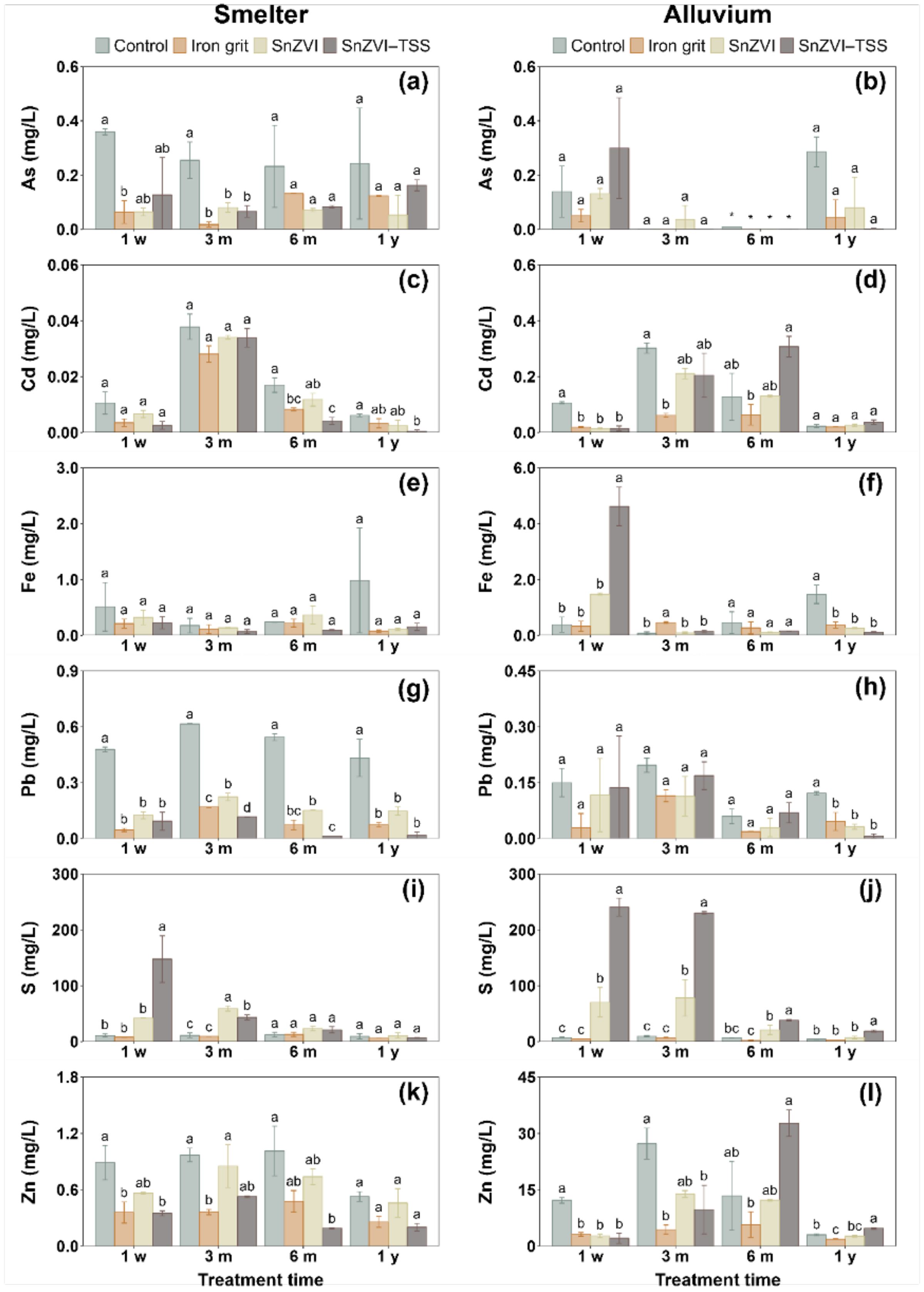
Vítková et al., 2017, J. *Environ. Manage.*

nZVI reduces soluble metals in the field in the long term …or not?

0.01 M $CaCl_2$ extractability of metal(loid)s

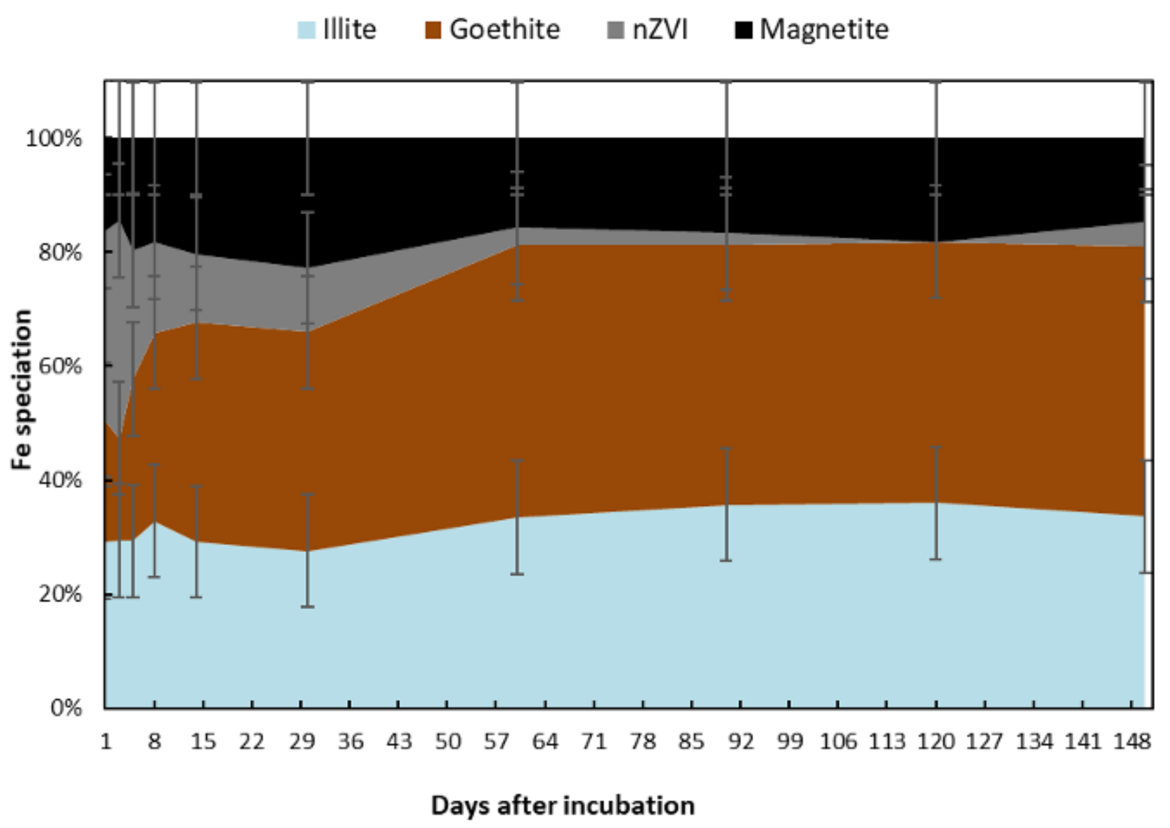


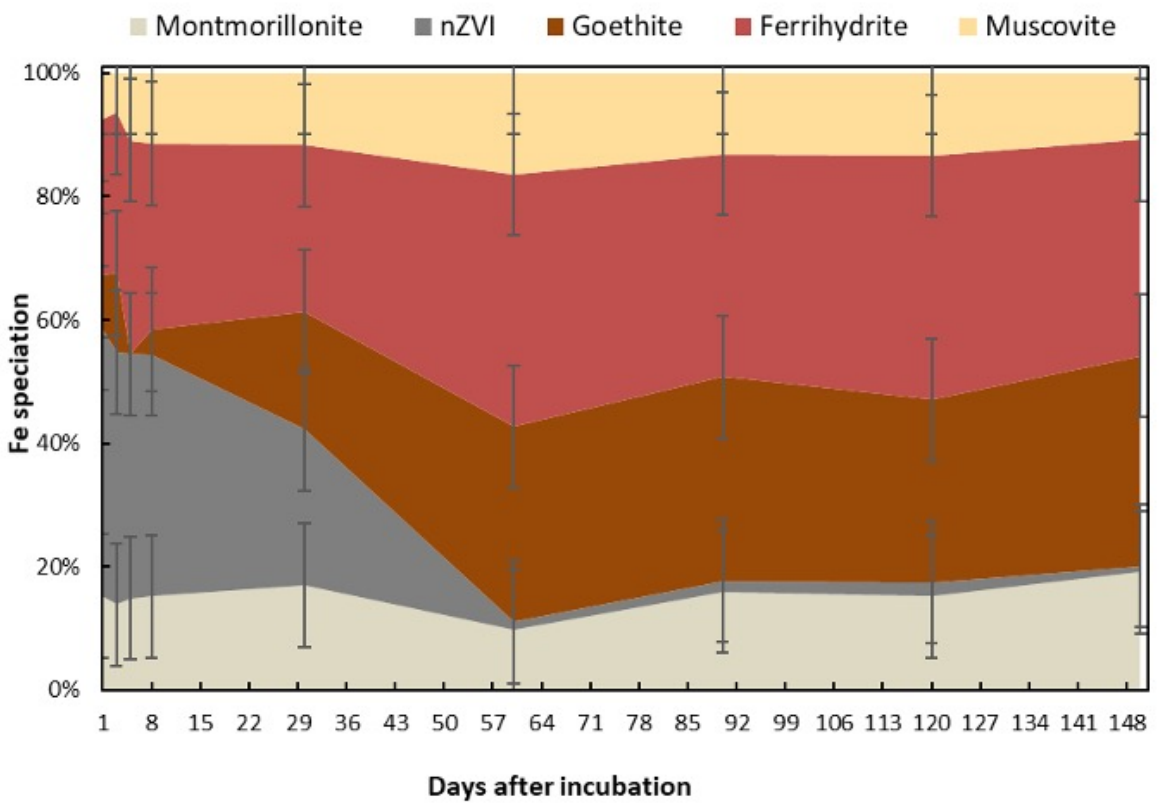
Metal(loid) concentration in soil solution

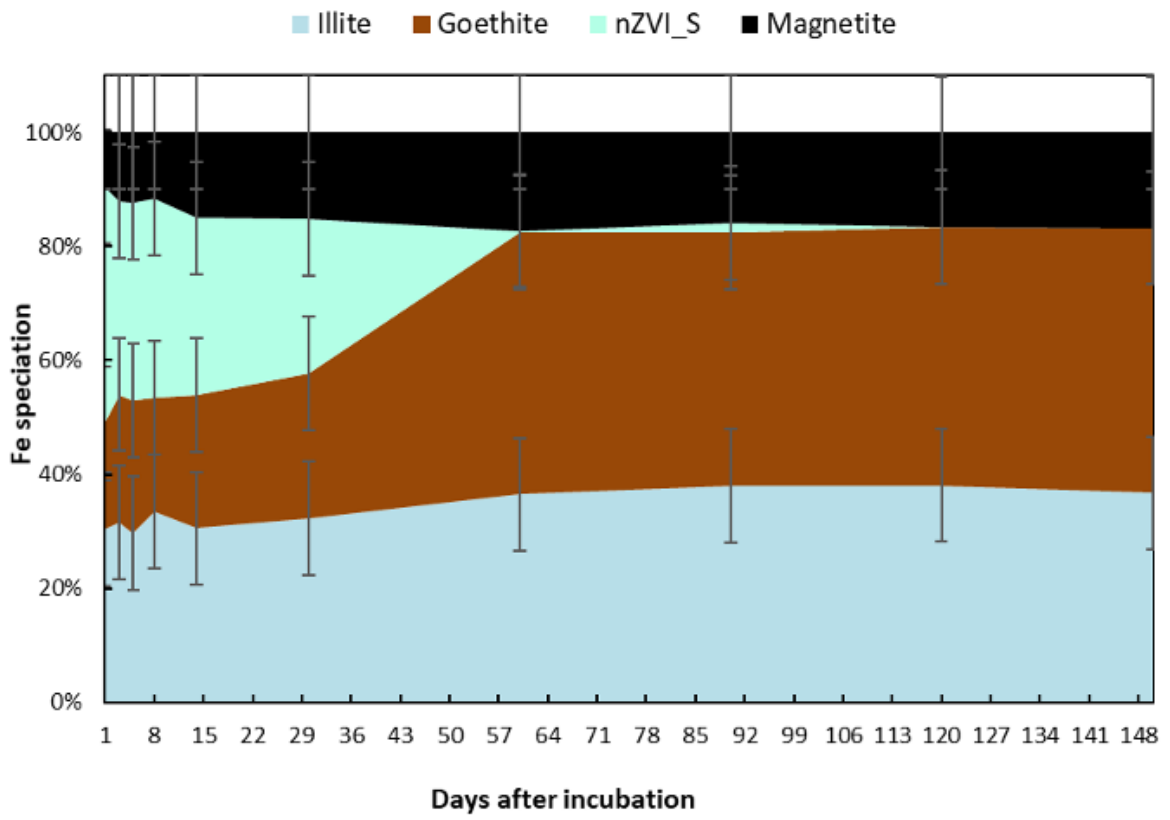


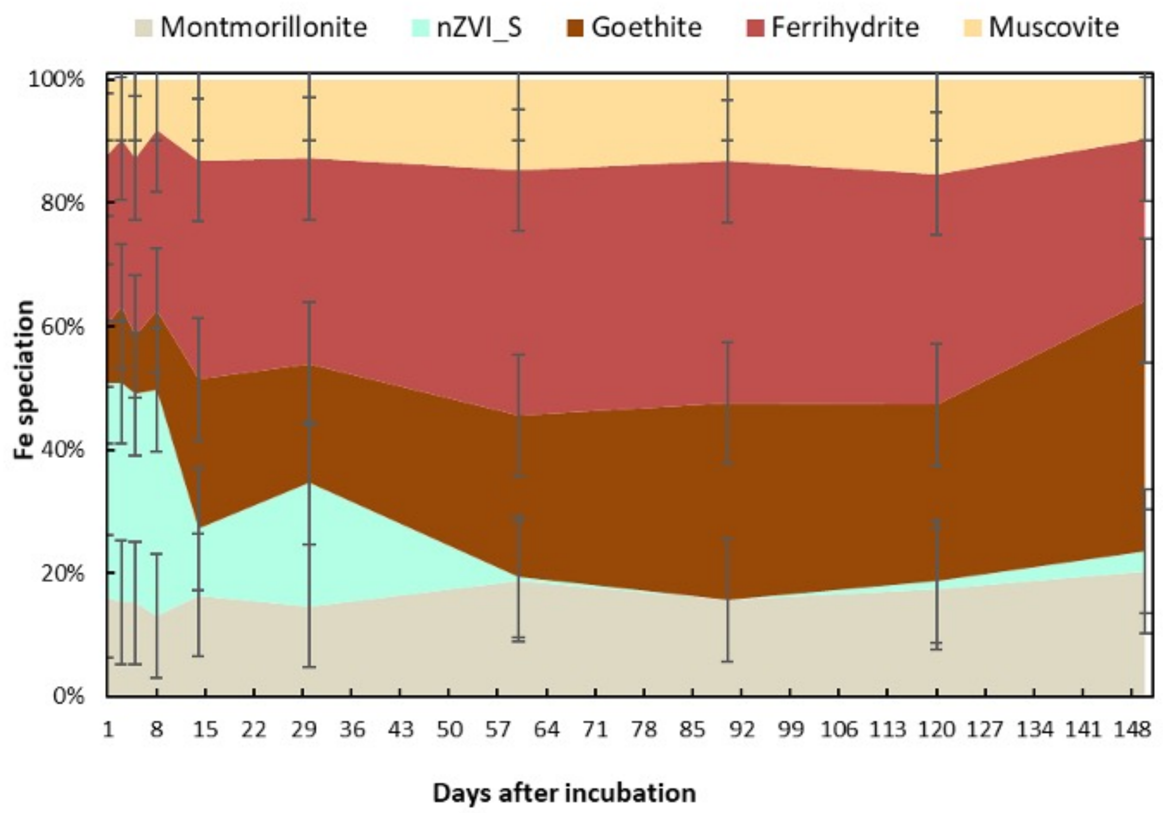
Lewandowská et al., 2023, to be submitted

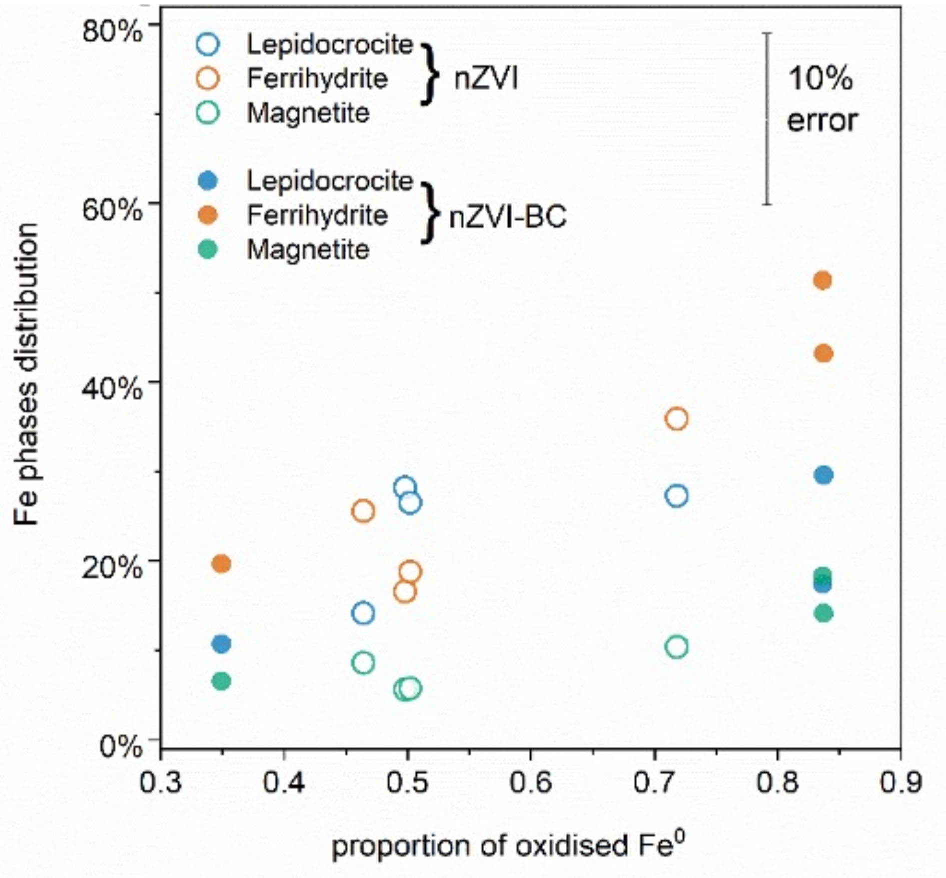
Mineralogical transformations







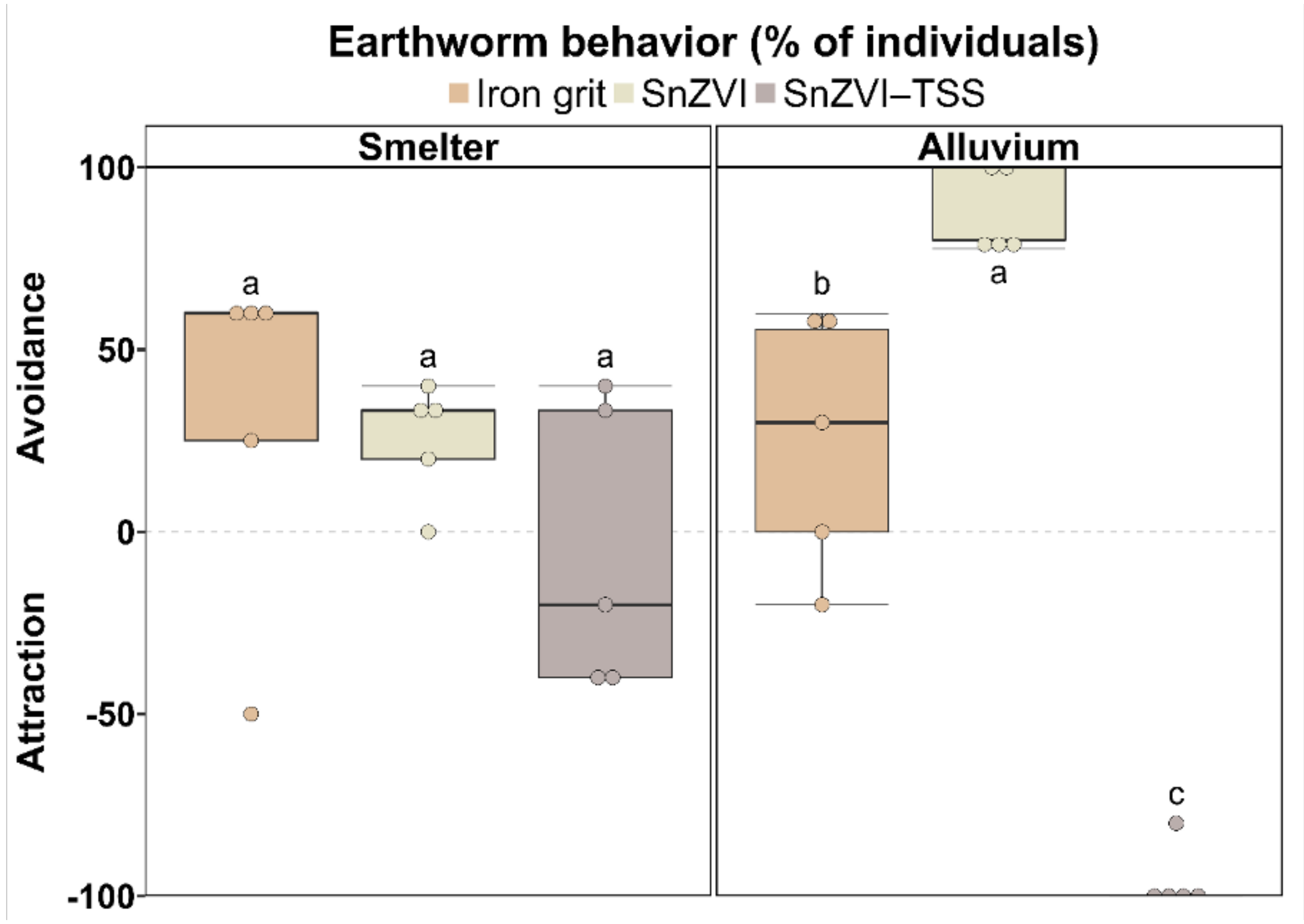


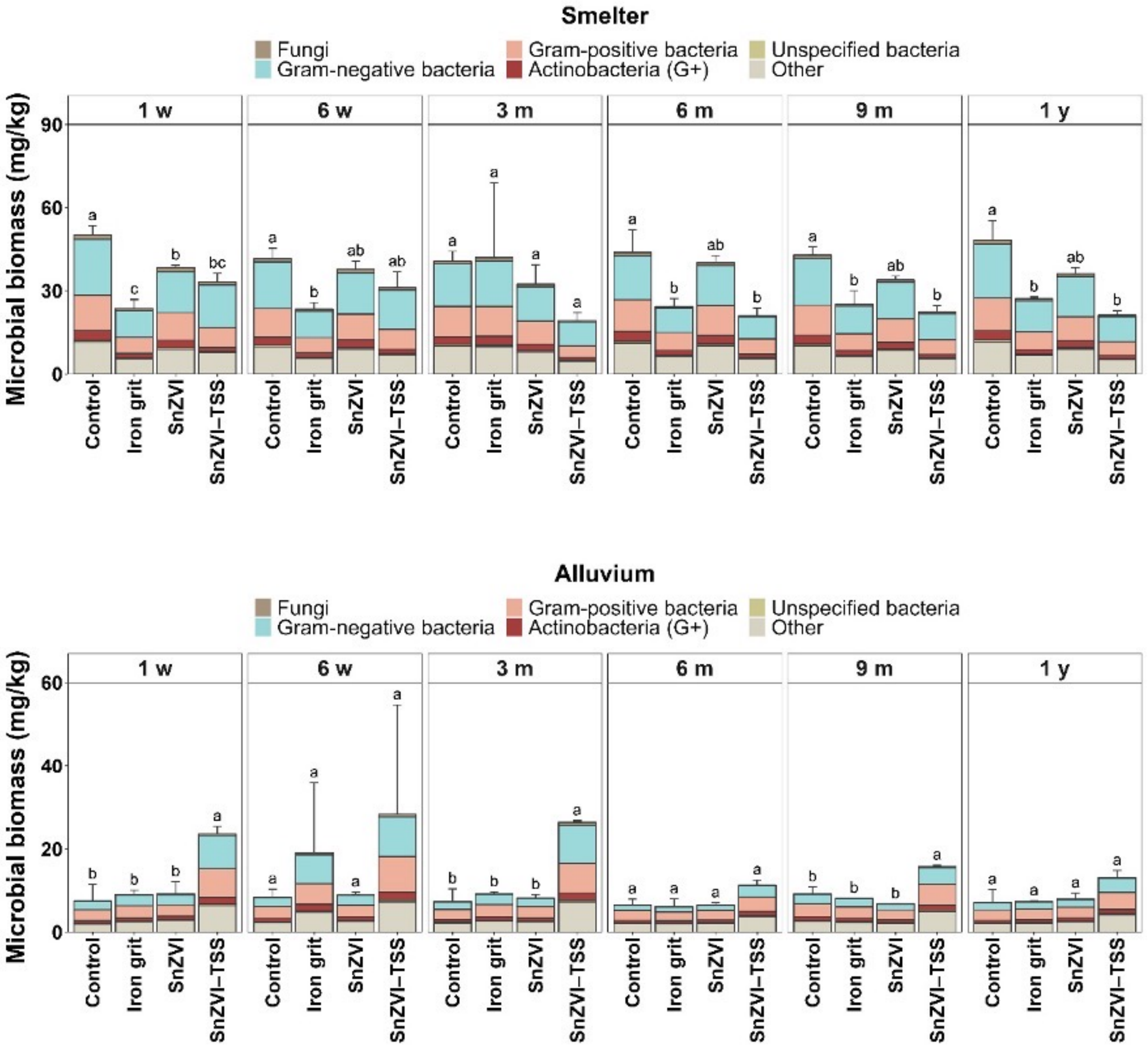


Mitzia et al., 2023, *Environ. Sci. Nano*

nZVI interacts with soil biota...

- earthworm avoidance test
- composition of microbial communities

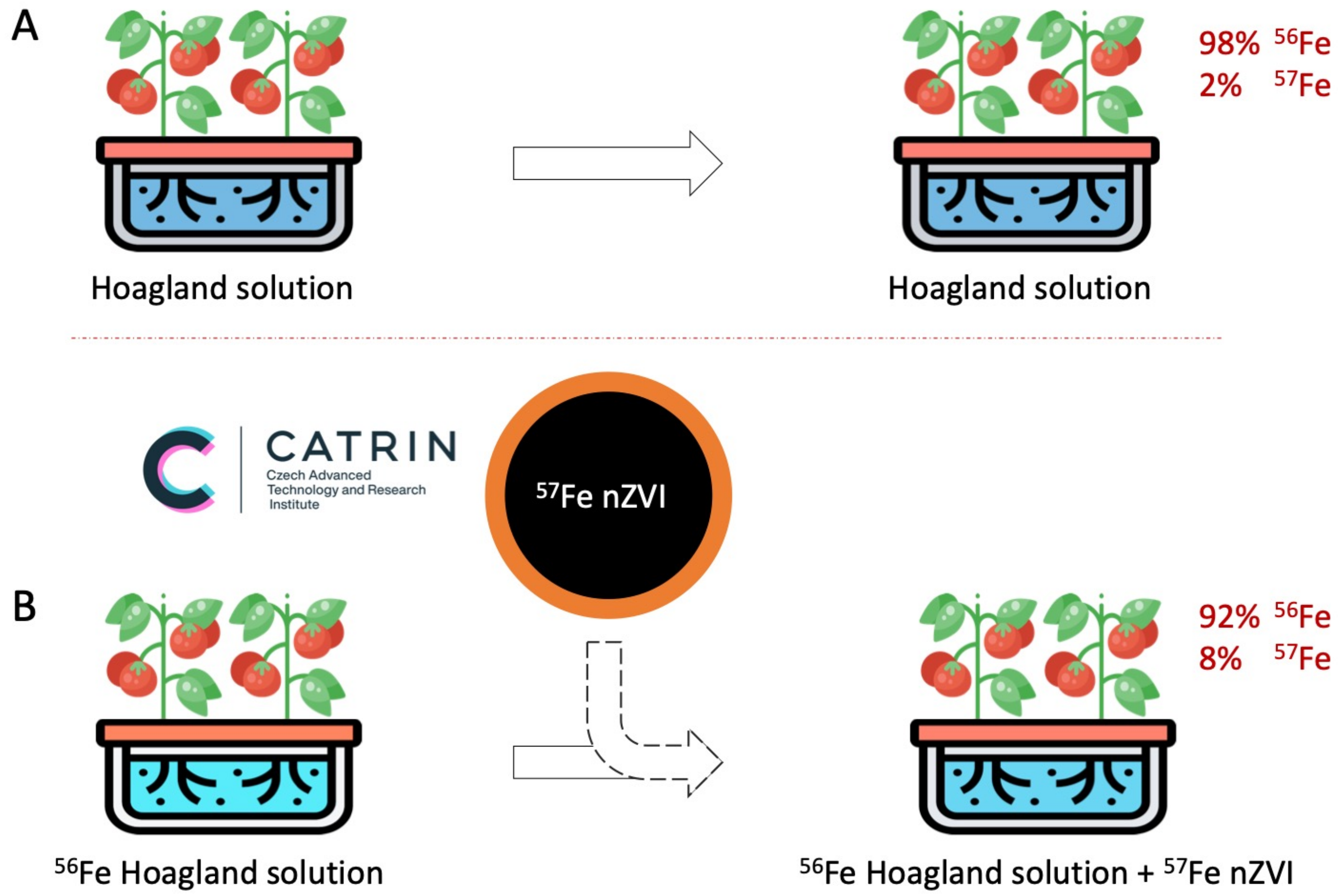


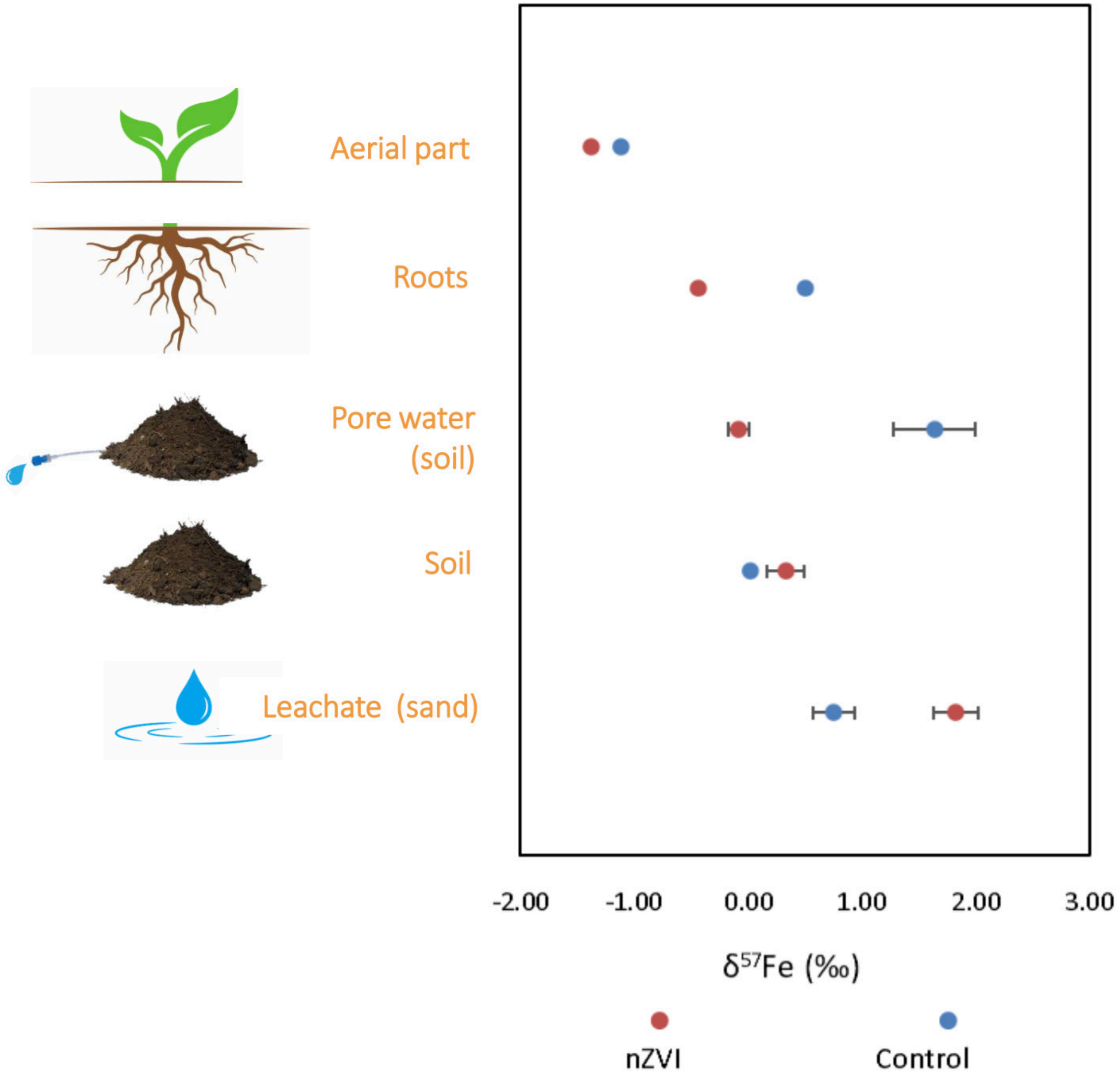


Lewandowská et al., 2023, to be submitted

Fe uptake from nZVI

$^{56}Fe/^{57}Fe$





Baragaño et al., 2023, in preparation

Fe uptake from nZVI

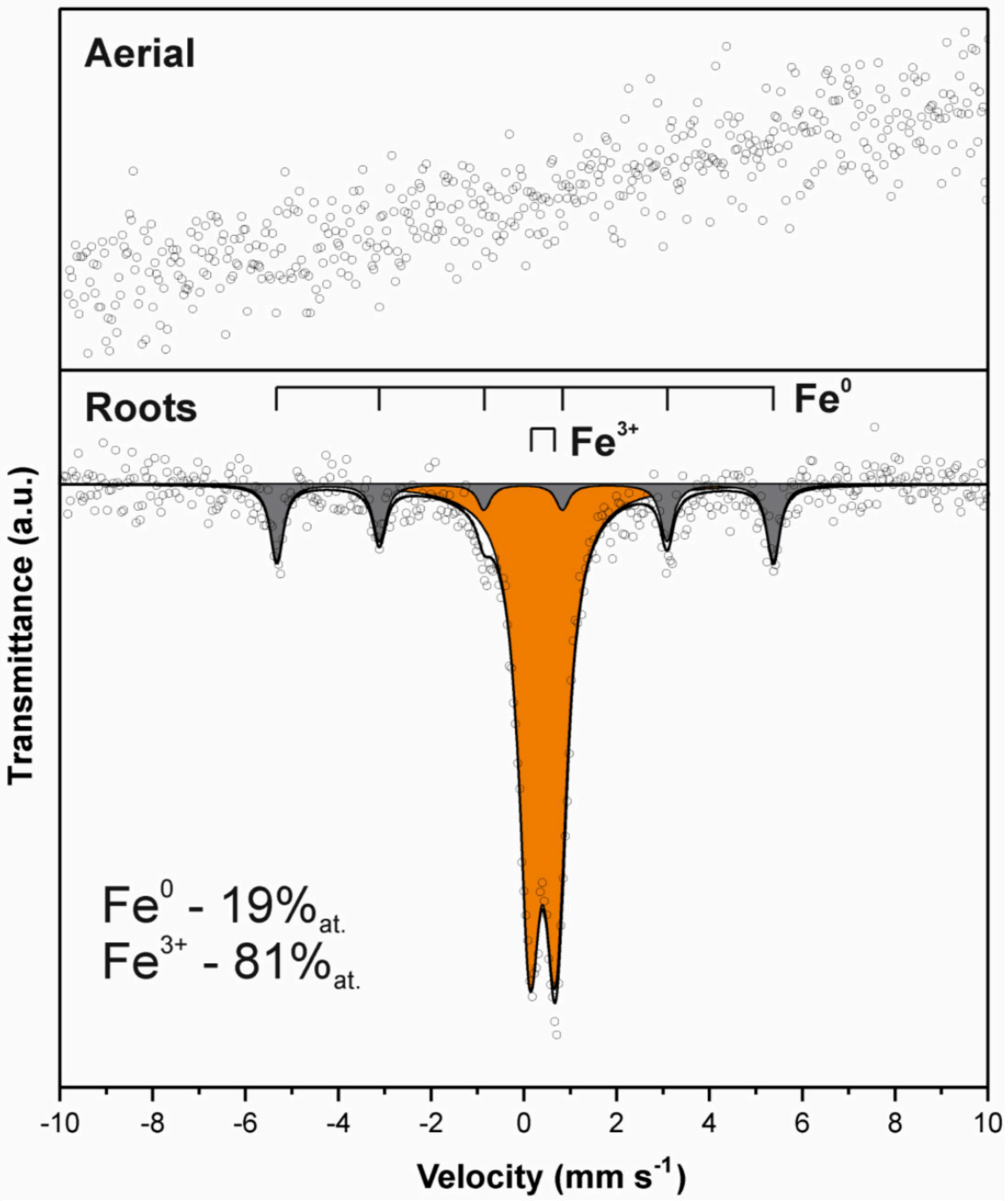
$^{56}Fe/^{57}Fe$

Mössbauer spectroscopy analysis

Conventional Mössbauer

Synchrotron Mössbauer Source spectroscopy
Beamline ID18

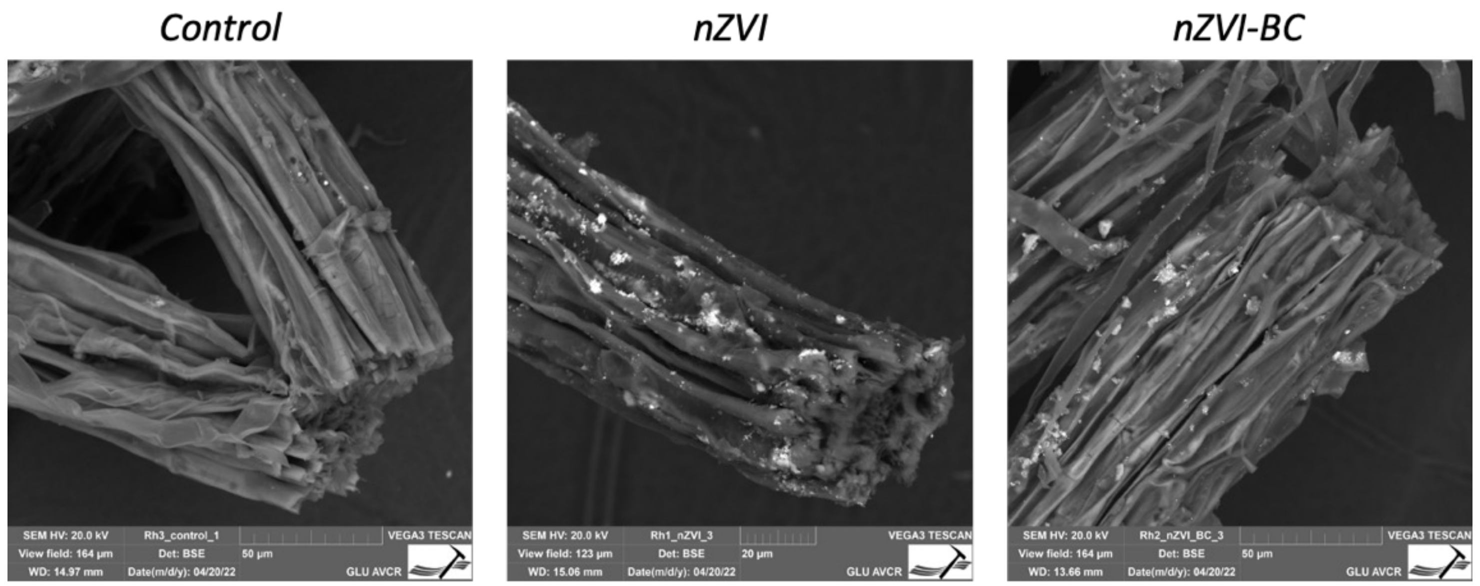
ESRF
The European Synchrotron

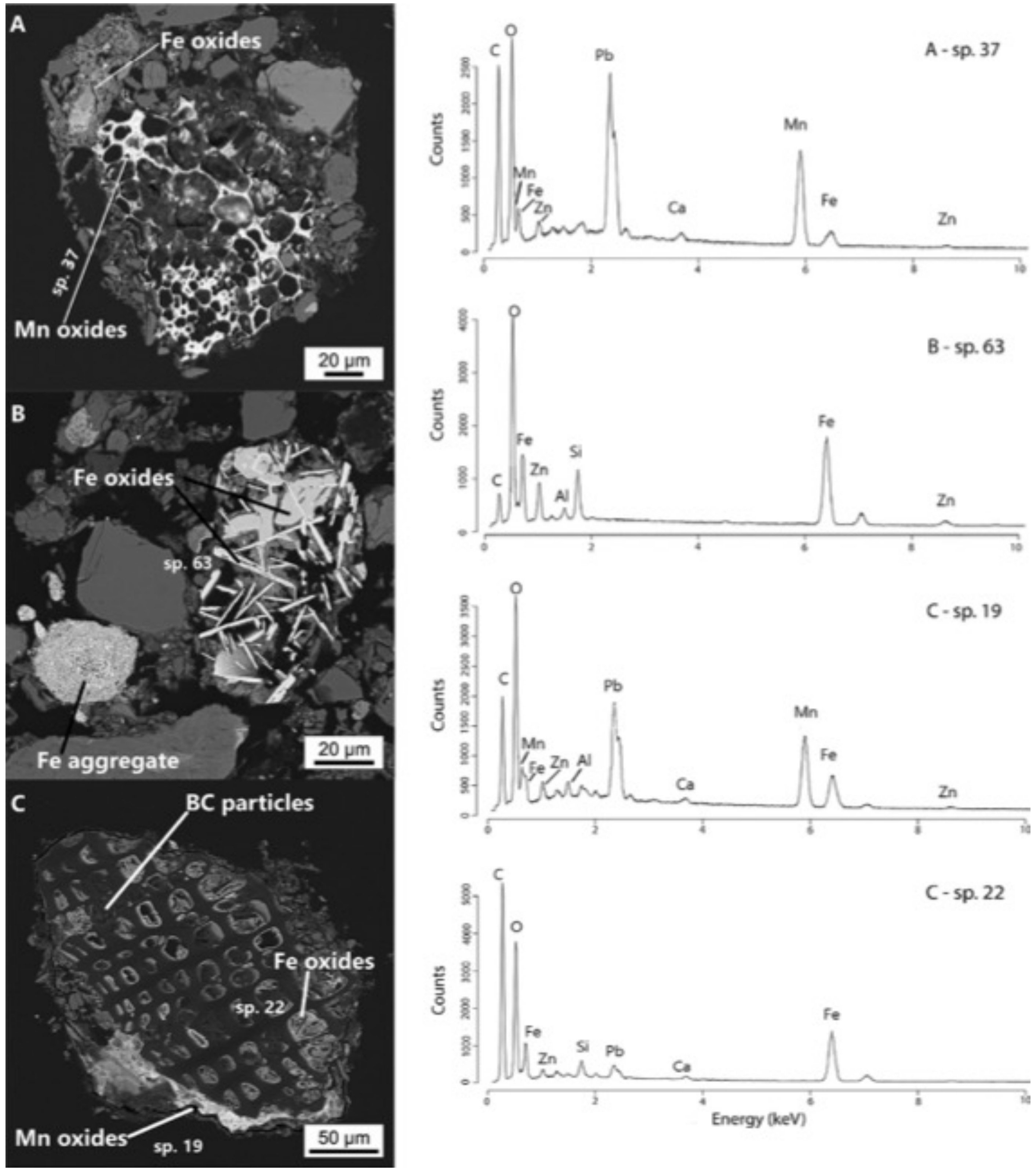


Baragaño et al., 2023, in preparation

Composites

- cost efficiency
- limiting nZVI aggregation and improving efficiency using nZVI-biochar composites
- composites were more efficient with regards to metal stabilization and pH conservation, nZVI was “more rapid”
- soil moisture content strongly affects metal and sorbent behavior over time, more pronounced with the BC-composites
- limiting potential toxicity and improving soil conditions (biochar, sewage sludge, compost etc.)





Mitzia et al., 2020, *Chemosphere*
Baragaño *et al.*, 2023, to be submitted

We still do not completely understand all the underlying mechanisms

- the combination of different methods and approaches, including chemical analysis, solid phase analysis, geochemical modeling, is crucial

Is nZVI perspective?

- various nZVI modifications and composites
- still missing additional practical field demonstrations at larger scale
- effect on hydraulic properties of soils and potential toxicity
- inclusion of private farmers and other relevant stakeholders
- perspective for emerging contaminants?
- perspective for other joint projects
- Soil Deal for Europe

Pilot scale testing of the metal/loids immobilization from groundwater
&
Experience with the R&D implementation in practice

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Development and pilot verification of technology for immobilization of metals from groundwater *in situ*

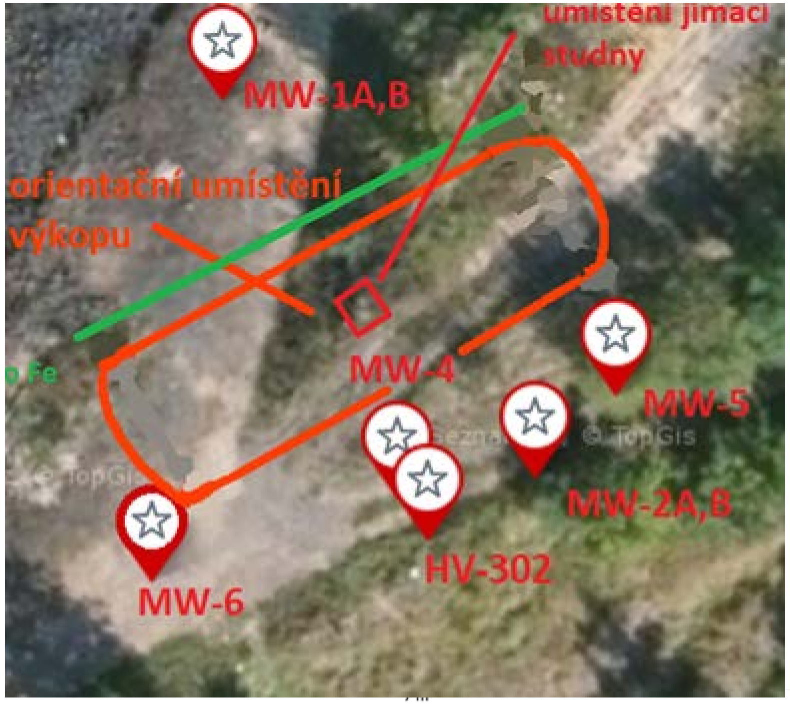
- Based on the application of iron particles to the aquifer and the immobilization of toxic metals from groundwater on these particles
- Immobilization of metals due to various mechanisms - adsorption, surface precipitation, structural incorporation and ion exchange
- Immobilized metals bound to supplied iron-based particles in the rock environment → decrease in their concentrations in groundwater → decrease in their mobility and associated risks
- The bond between the immobilized metal and the supplied particles is strong → metals are released back into the water only in the event of an extreme change in the character of the groundwater (most often as a result of an accident)

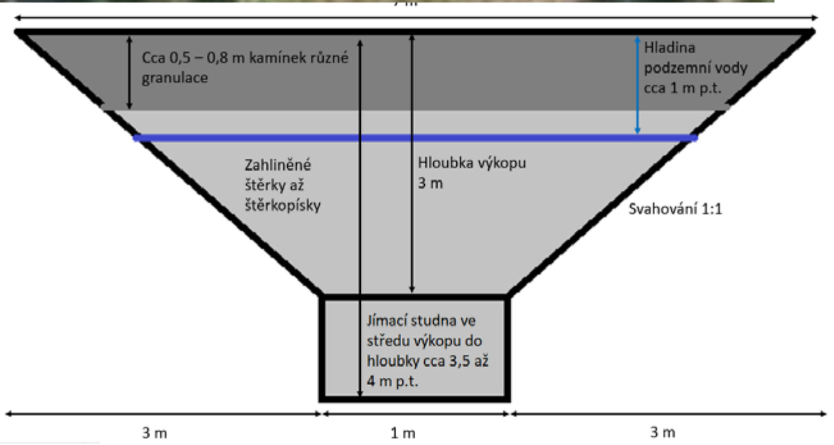
Pilot test - The site

- The site is located on the banks of small river Litavka close to the heaps with metallurgical waste.
- Main metals of interest are mainly Zn (conc. up to 42 mg/L) and Ni (conc. up to 2 mg/L)
- The mass transfer of metals to the stream must be lowered

Conceptual site model

Pilot test design





- The only feasible solution for the long-term reduction of the mass flow of metals into the stream is the application of a larger amount of cast iron
- Permeable reactive barrier 20 m long, perpendicular to the direction of groundwater flow installed
- Application of cast iron in the form of a shallow excavation to a depth of 3 m b.g.l. during backfilling – performed in January 23
- Deeper horizons below 3 m b.g.l. → injection of cast iron sawdust suspension – to be performed in late March
- Installation of additional monitoring wells and monitoring of the effects

PRB installation

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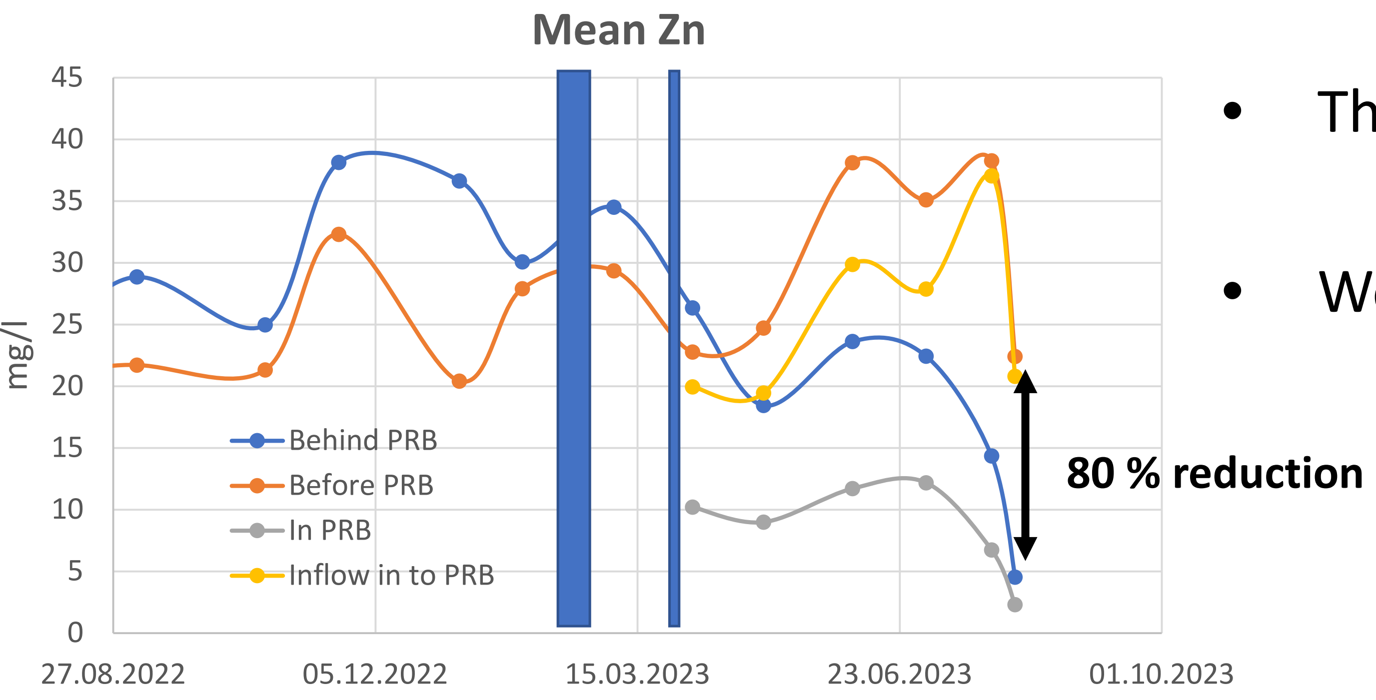
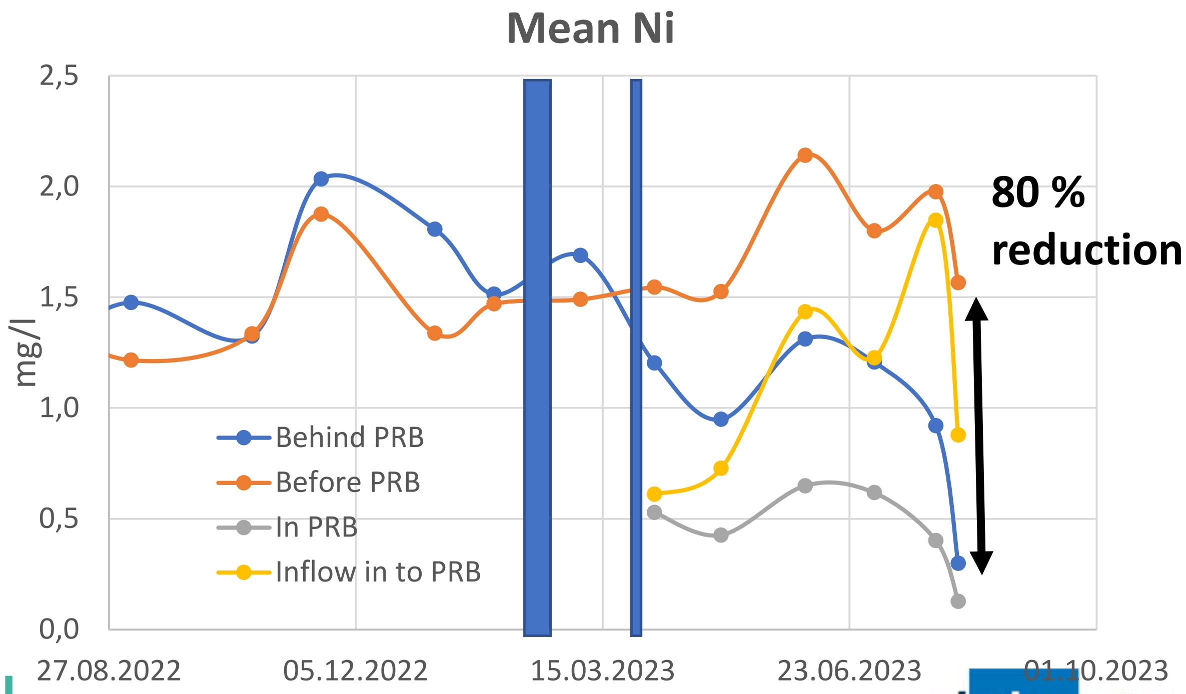
Pilot test design

- 7 injections of the cast iron sawdust in guar gum suspension in to horizons bellow 3 m b.g.l.
- Application of 600 L suspension/injection point
- 30 kg Fe/100L →in total 4200 L suspension with 1200 kg Fe
- Additional 5 monitoring wells
- Installation of passive samplers with cast iron in to the wells and their continuous sampling for assessment of the iron aging in the barrier → analyses on NTNU

Results



- The performance of the PRB in situ is slow as expected based on laboratory test
- We expect long lasting effect over next decades



- Post treatment iFlux mass flux measurement just finished – analytical data are not yet available
- Cast iron sawdust from passive samplers collected and prepared for analyses on NTNU

Conclusion

- Detailed evaluation of the results will be carried out in next months but it can be stated already that the immobilization of metals from groundwater *in situ* using iron particles is both environmentally and economically feasible solution for groundwater treatment

R&D implementation in practice

Co-Composting developed within the NANOBIOWAT Competence Center
Utilized for full scale remediation of Srní site

- Full-scale remediation of impregnation facility polluted by creosote oil using on-site co-composting developed within the project
- Site of historic impregnation of wood (railway sleepers) using creosote oil during 20th century close to water supply well for the city Česká Lípa
- Estimated quantity of contamination - 300 t of PAHs and 400 t of oil substances within the sandy soils in the unsaturated zone
- The contaminated sand is treated via so called co-composting technology

Old buried impregnation tank with creosote oil

The bottom of excavation pit

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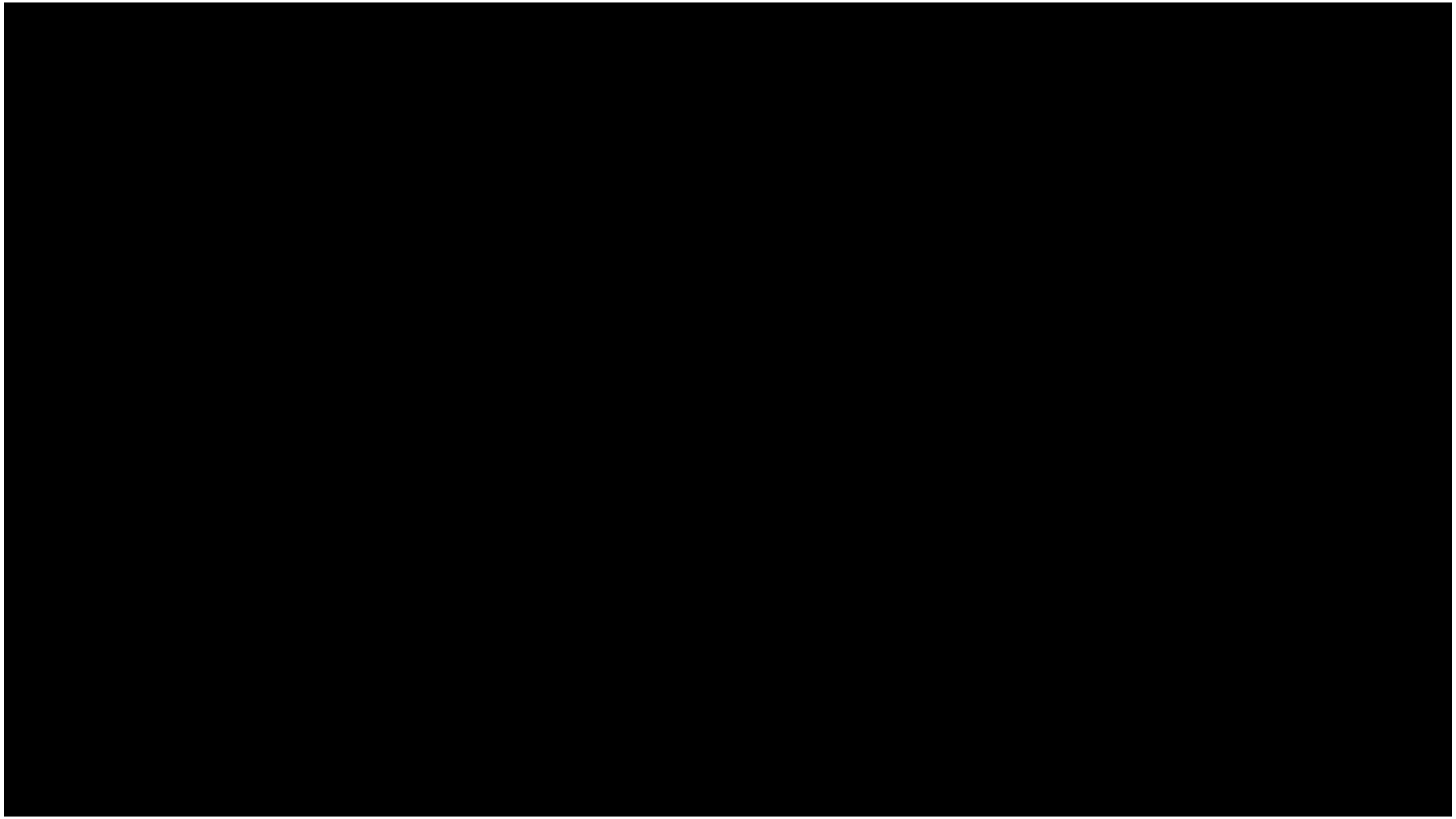
Co-Composting – Srní site

- Consists of mixing of polluted sand with organic substrate provided from local composting facility - mixture is moistened and regularly aerated
- The microbial consortia that develop during the process are responsible for the breakdown of organic matter as well as for the degradation of contaminants
- Almost 13 000 m^3 of contaminated sand was excavated and treated on-site
- The average degradation of monitored PAHs reached 85 % and the residual contamination is well below the remediation goals
- The treated soil is stabilized, free of odor and it was put back in to the excavation pit
- The remediation completed successfully this month

Homogenization of contaminated sandy soil

Homogenization of contaminated sandy soil

FRAC-IN technology developed within 2 EUROSTRS projects; currently used within EBioChem project and demonstrated within the LIFE FRAC-IN



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FRAC-IN technology

- The technology was utilized within a full scale remediation of the contamination source zone in the former premises of TDV Duchcov
- Used to treat the groundwater in low permeable clays contaminated by a mixture of chlorinated ethenes and hexavalent chromium
- More than 200 m^3 of a remediation suspension injected with about 15 t of ZVI and 6 m^3 of glycerol
- Thanks to FRAC-IN injections Cr^{6+} and ClE DNAPL disappeared
- The injections triggered the ClE biodegradation and other natural degradation processes that will in the future and lead to significant improvement of the GW quality
- The remediation completed successfully this month

The Results of the former Norwegian funded project applied in full scale

- DEKONTA collaborated earlier with Charles University on the Czech-Norwegian Research Programme CZ09 project project called PASSES.
- The project aimed to assess biodegradation potential for groundwater remediation
- Assessment conducted at the FARMAK site, significantly contaminated by organic solvents
- FARMAK site located near the Olomouc city's drinking water supply
- Bacteria present in the GW are capable of degradation of the contamination when supplied with sufficient oxygen
- Groundwater lacked the necessary oxygen for bacterial degradation

The Results of the former Norwegian funded project applied in full scale

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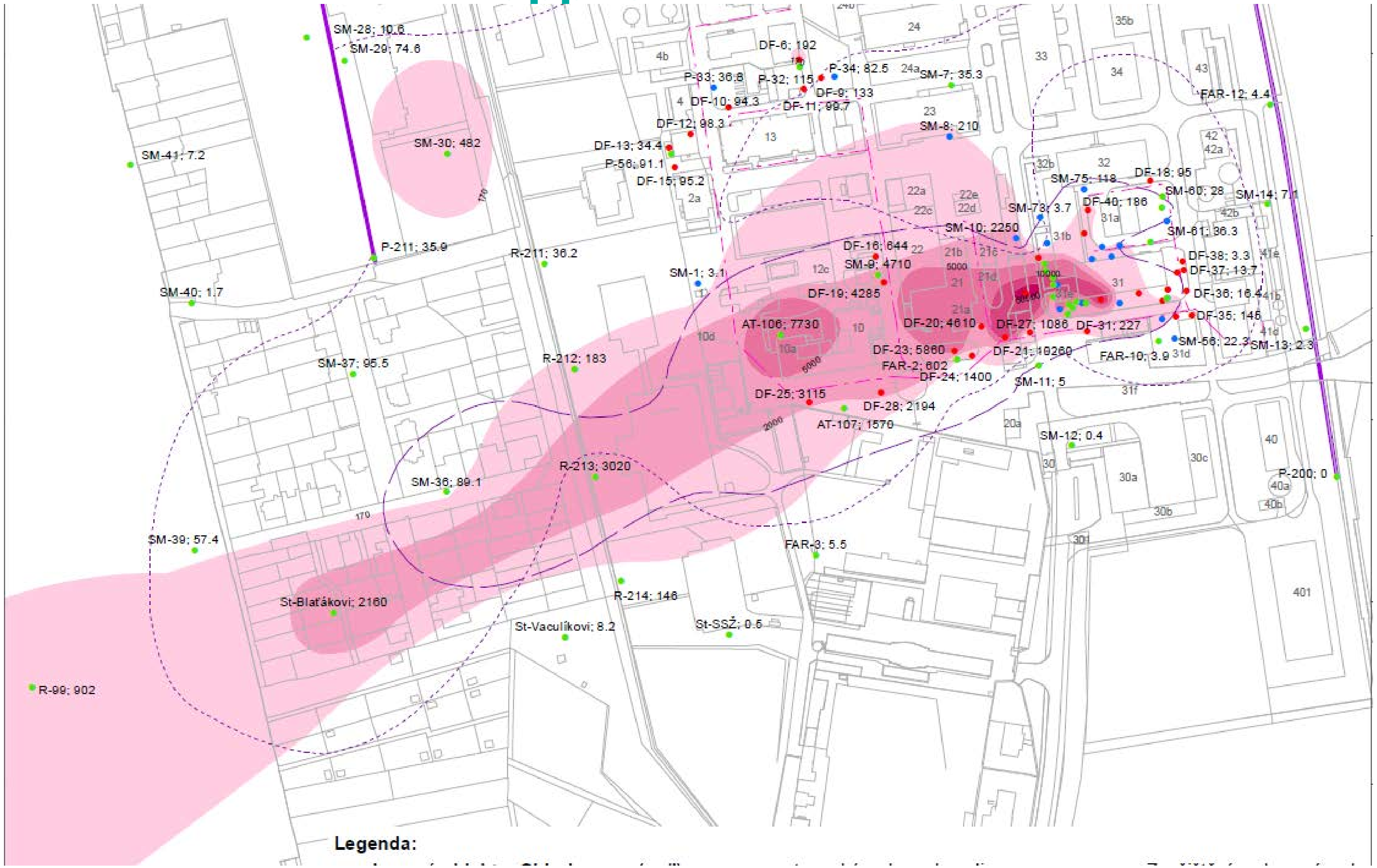
The Results of the former Norwegian funded project applied in full scale



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The Results of the former Norwegian funded project applied in full scale

- Direct push injections of calcium peroxide proved highly effective within the assessment
- It was proposed as the best technology for full-scale site remediation and later incorporated in to the full-scale remediation design
- Full-scale remediation funded by the Czech Ministry of Finance is currently in progress (it will last for 10 years)
- In addition 2 scientific papers about the assessment were published

ELSEVIER

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journal homepage: www.elsevier.com/locate/watres

Pharmaceuticals, benzene, toluene and chlorobenzene removal from contaminated groundwater by combined UV/H_2O_2 photo-oxidation and aeration

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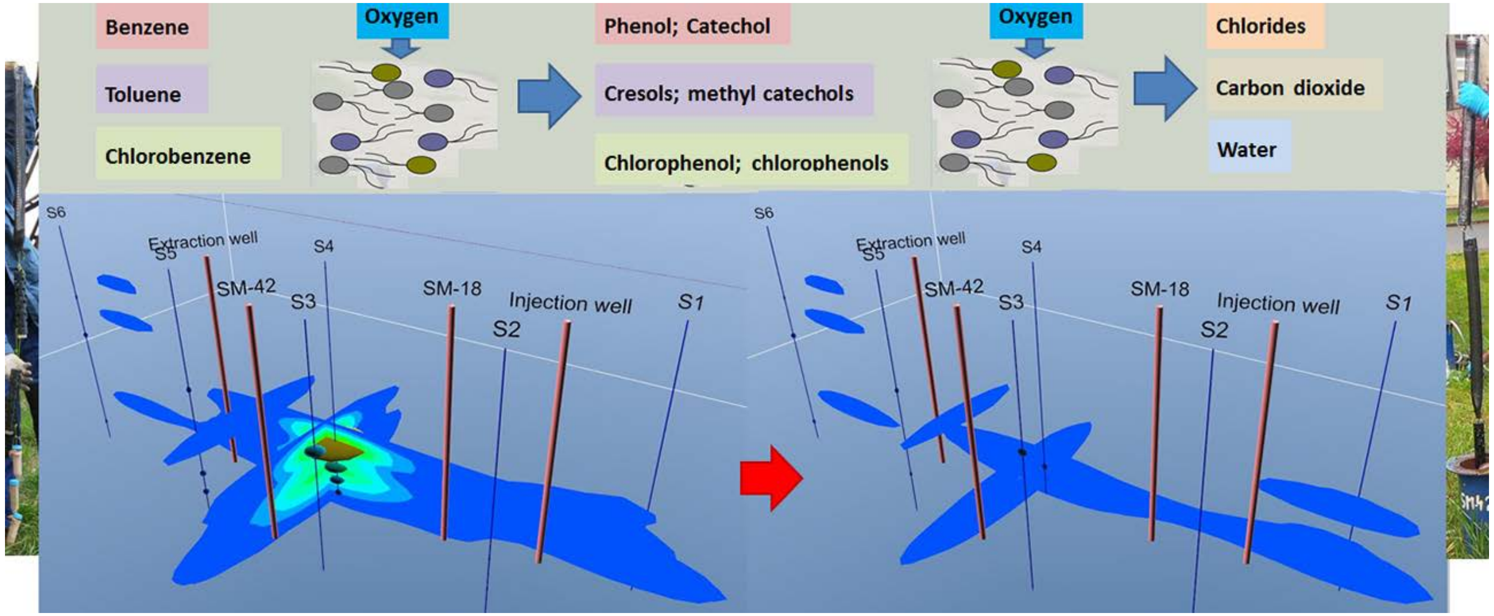

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Program Trend
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Thank you very much

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