This project has received funding from the European Horizon2020 research and innovation programme under Grant Agreement No. 826312

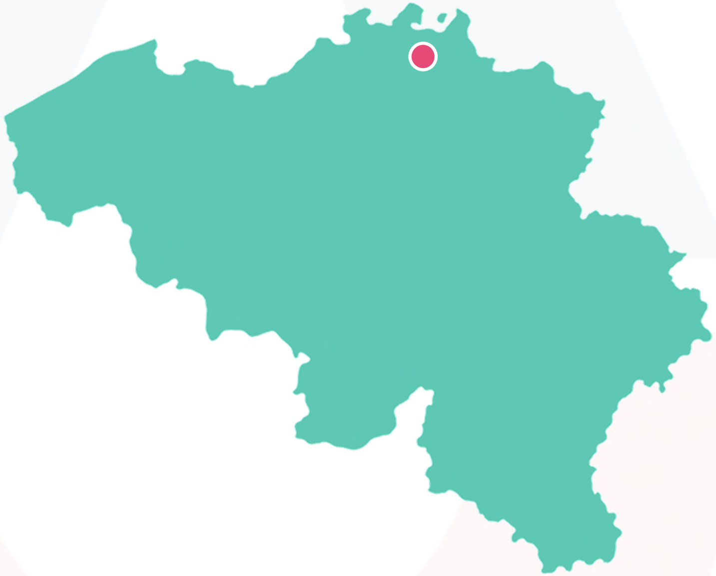
In Situ Metal Precipitation:

A pilot test on In Situ Metal Precipitation (ISMP) at an industrial site in Flanders

AquaConSoil2023

Dirk Paulus, TAUW Belgium

Background



Industrial activities

Smelting and refining > 350,000 tons of raw materials / year

Smelting complex metallic and oxidic secondary raw materials to feed their furnaces

Industrial activities since 1908

Calamities

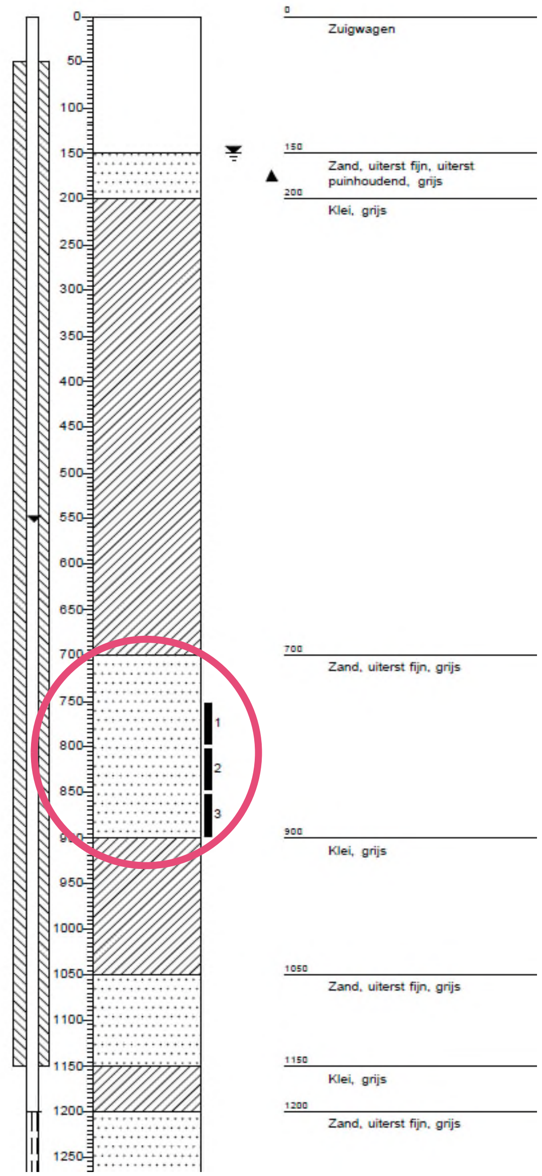
- Destruction of sulfuric acid depot during World War I
- In 1933 a fire destroyed the copper sulfation unit

Local (hydro)geology

Local geology:

- 0 – 2,0 m-bgl: Antropogenic (sand + rubble, 1ste perched aquifer)
- 2 - 6,5 m-bgl: Clay
- 6,5 – 8,0 m-bgl: Sand (2nd aquifer)
- 8,0 – 10 m-bgl: Clay
- > 10 m-bgl: Sand (3th aquifer)

- Groundwater table: 4,0 – 4,5 m-bgl
- Hydraulic conductivity of the 2nd aquifer: $5{,}22 \times 10^{-5}$ m/s
- Groundwater streams towards the south



Contamination

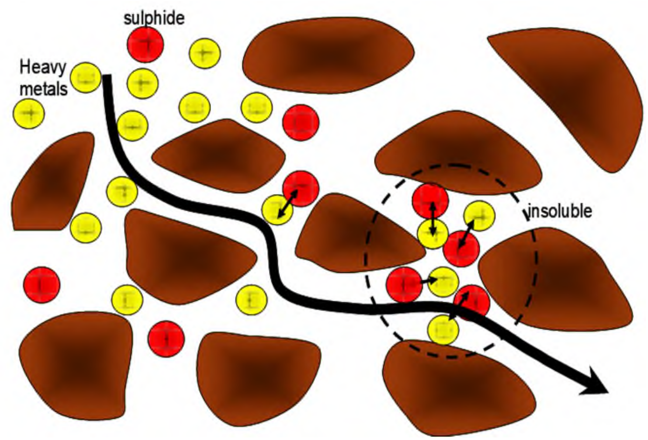
- Brine: Heavy metals (Cu, Ni, Zn) and As, ammonia, potassium and sulphate
- Acidity of groundwater: pH = 1 in core zone

	Sulphate (mg/l)	As (mg/l)	Cd (mg/l)	Cr (mg/l)	Cu (mg/l)	Hg (mg/l)	Pb (mg/l)	Ni (mg/l)	Zn (mg/l)
Average	11,241	28	5	1	1,086	0	0	879	104
Min	650	0.5	0.3	0	0	0	0	0	9.1
Max	40,000	210	26	6.7	6,000	0	0.5	5,800	330

TAUW

Principle of In Situ Metal Precipitation (ISMP)

- Injection of a fermentable C source to boost the growth of anaerobic microorganisms including sulfate-reducing bacteria (SRB)
- SRB use sulfate as terminal electron acceptor
- Sulfate is reduced to sulfide
- Sulfide binds to metal(loid)s forming stable insoluble sulfide minerals



- org. substrate → $H^+ + e^-$
- $SO_4^{2-} + 4H_2 \rightarrow 4H_2O + S^{2-}$
- $S^{2-} + Hg^{2+} \rightarrow HgS\downarrow$

Black precipitate
(insoluble metal sulfides)

Remediation: Lab testing

ISMP: lab test (chemical vs biological approach)

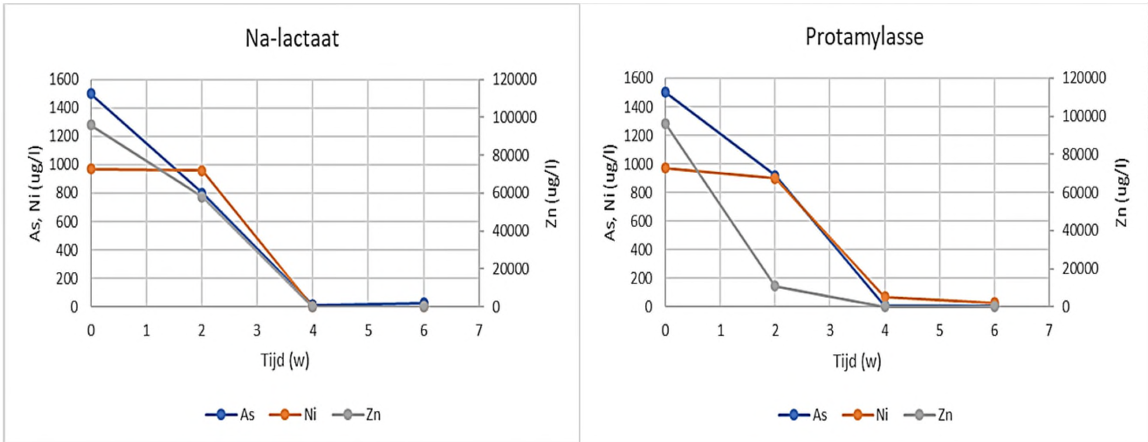
Adsorption of metals into iron(hydr)oxide

- Addition of ferrous sulphate
- pH correction

Test	pH	EC (µS/cm)	As (µg/l)	Ni (µg/l)	Zn (µg/l)
Initial	4,7	2570	1500	970	96000
Fe 0,2%	7,3	3390	<5,0	95	2300
Fe 1%	7,5	6380	<5,0	27	170

Precipitation of metals as metal sulphides

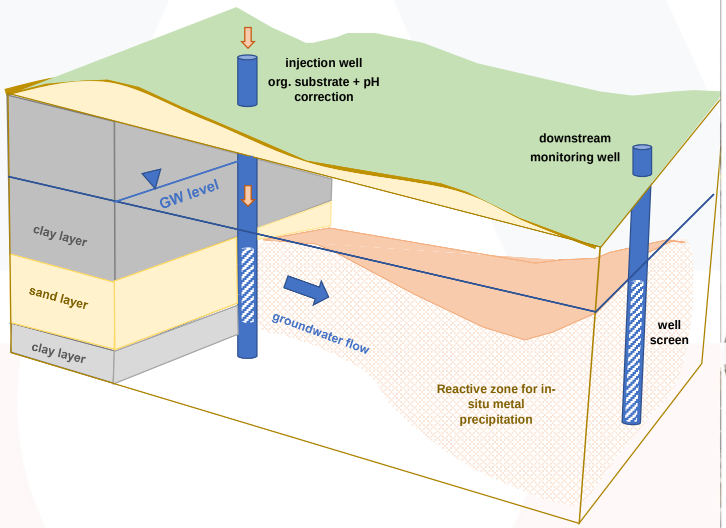
- Addition of protamylasse
- Addition of sodium lactate



TAUW

Field Testing

Field testing

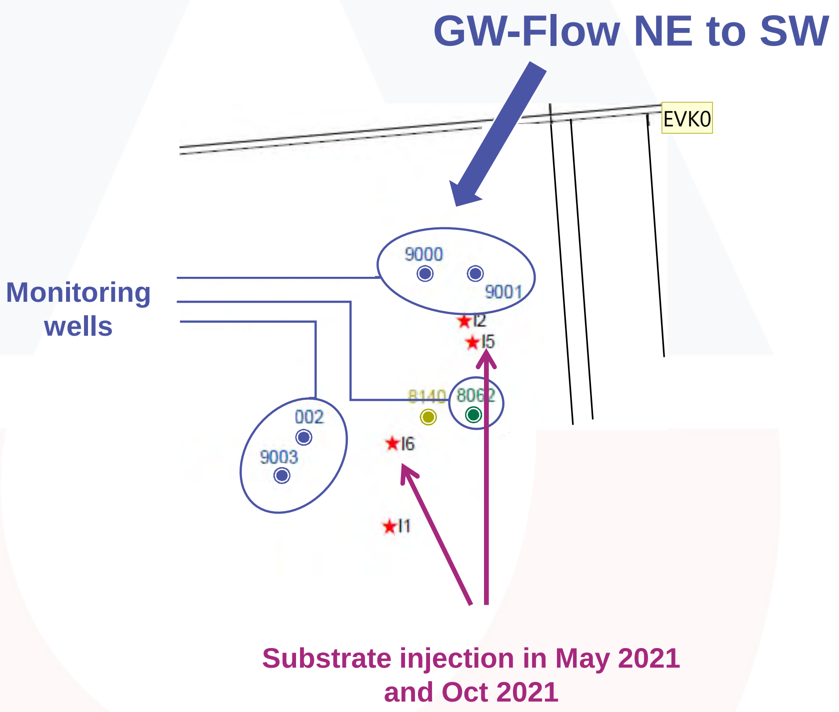


1. **Core zone (close to brine zone):** Chemical approach with direct injection of a Ca-polysulphide solution

2. **Plume zone (further downstream of brine zone)** Biological approach with injection of a carbon source (emulsified vegetable oil EOSPro) with a potassium bicarbonate (K_2CO_3) solution to increase the pH

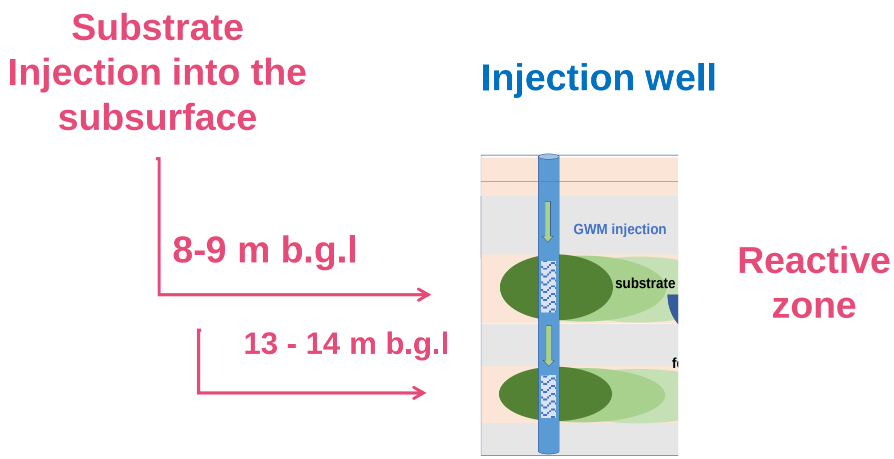
TAUW

Fieldtest setup: plume zone



Monitoring wells

1. **8062A** at a distance of 2 m of injection point I5
2. **9001** at a distance of 2 m of injection point I5
3. **9003** at a distance of 3,5 m of injection point I6



TAUW

Slide 10

EVK0 Tabellen verbergen
Ellen Van Kelst; 2023-09-08T11:48:31.500

Field test results

Field test results

Core zone (nearby brine zone):

Not very successful:

- Due to strong oxidative conditions sulphide rapidly was oxidised to sulphate
- No metal sulphide precipitation possible

Plume zone (further downstream of brine zone):

- **First injection** in June 2021

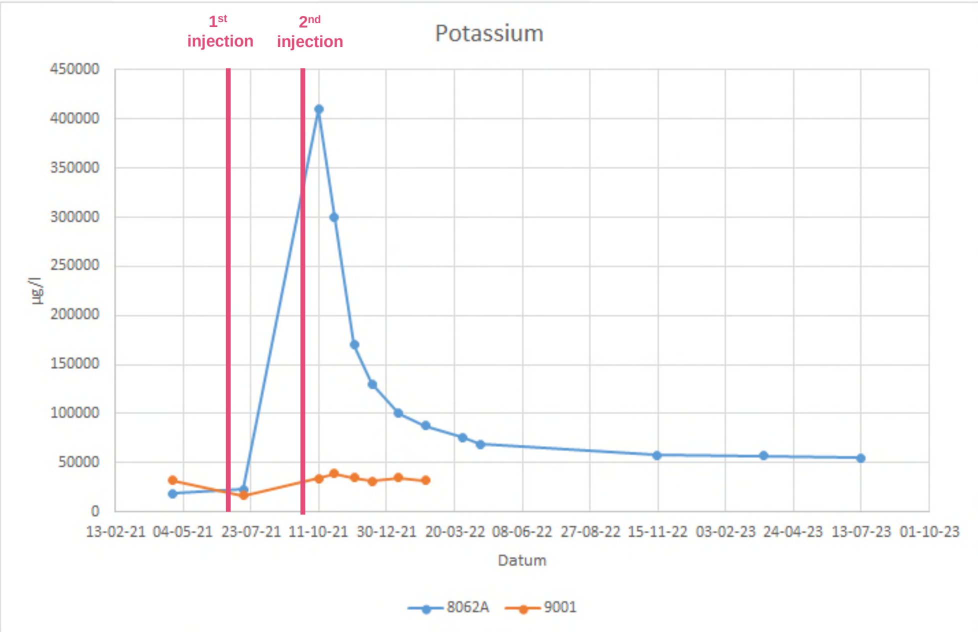
  Not very successful because the injected carbon source concentration was too low

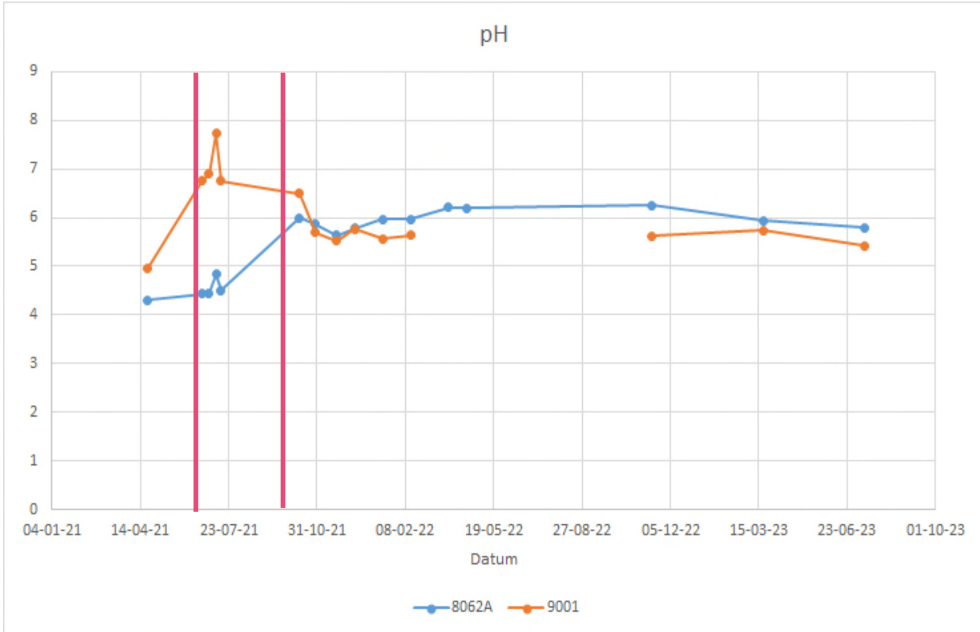
- **Second injection** in September 2021

  Doubled the doses of emulsified vegetable oil:

  - 50 kg of emulsified oil in a 6,6% solution
  - 1500 litres /m depth interval
  - Better results

Potassium bicarbonate: Effect as a tracer and pH correction

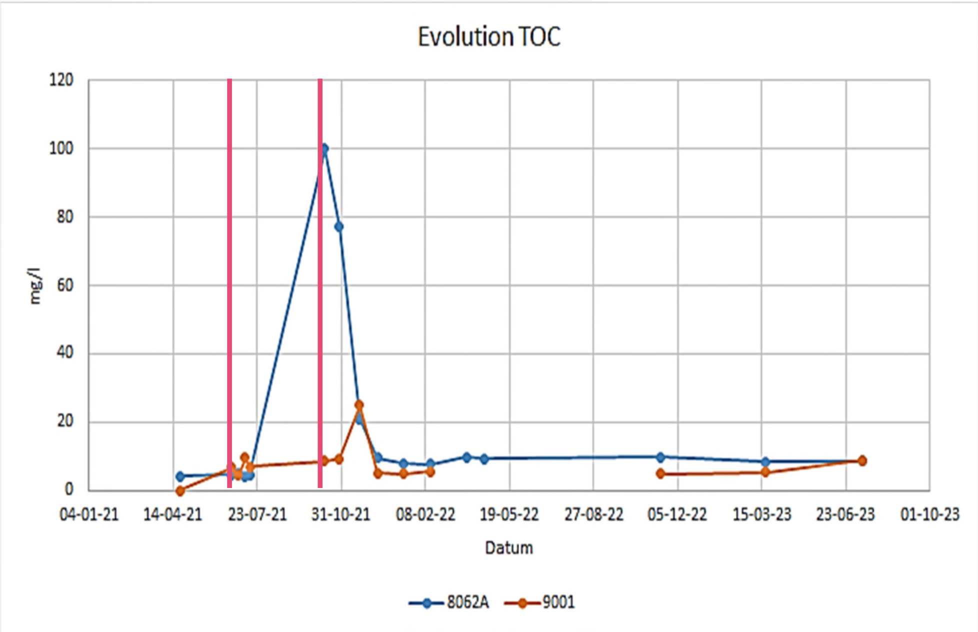


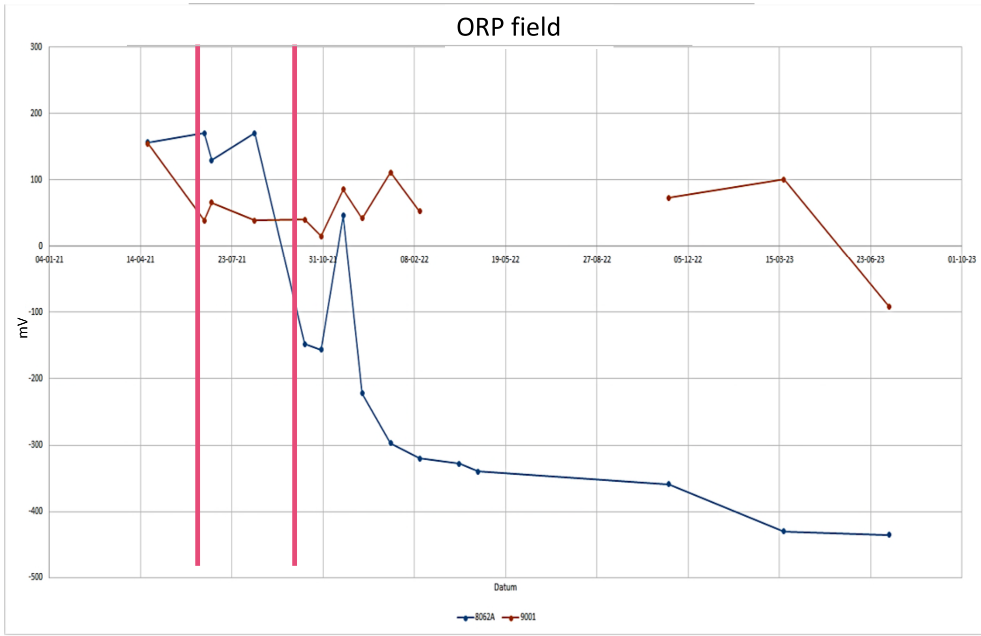


AquaConSoil2023

TAUW

Geochemical result after the carbon source injection: Effect on TOC and ORP

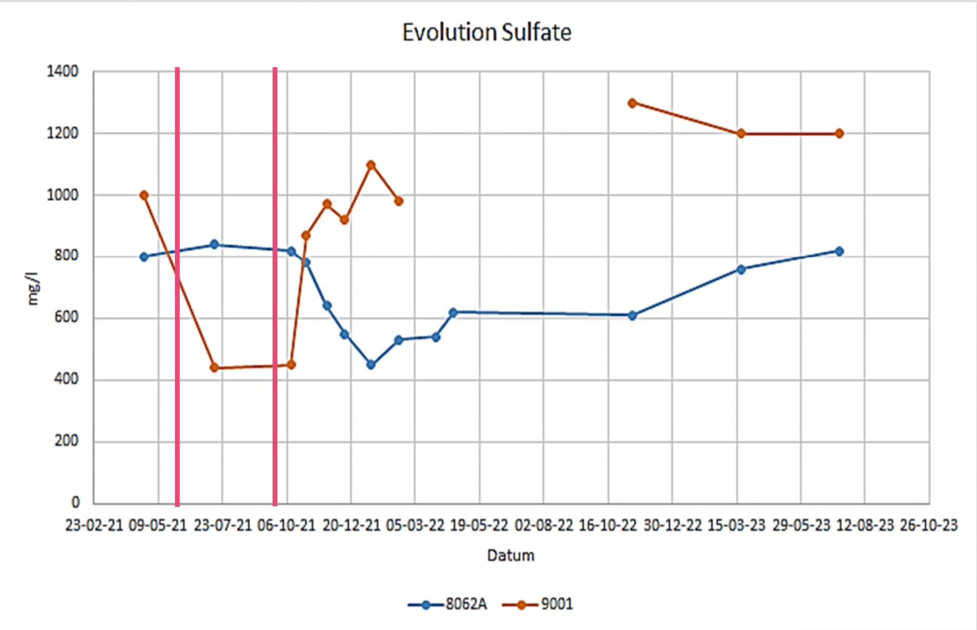


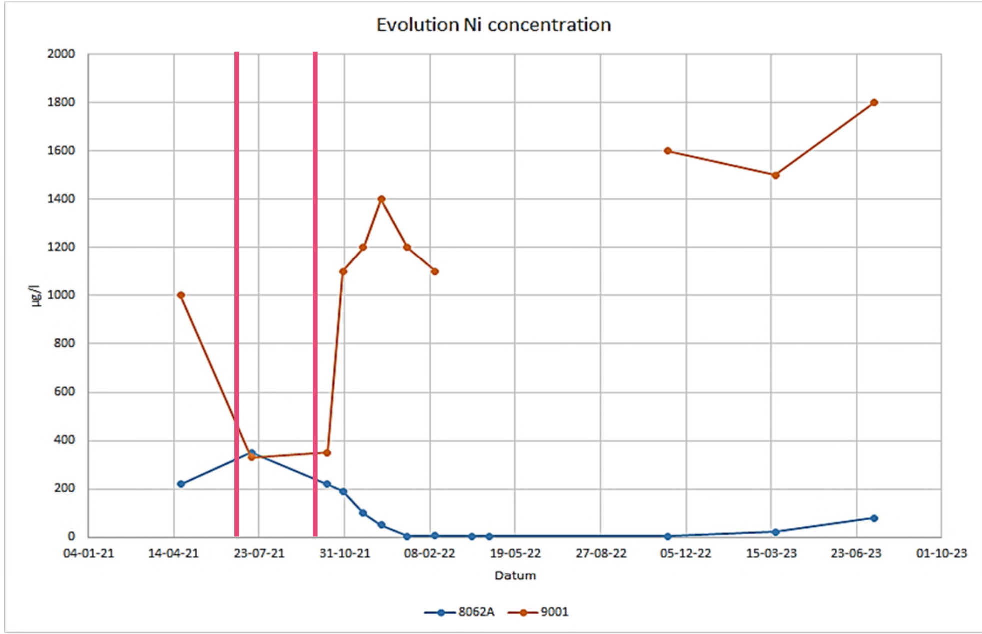


AquaConSoil2023

TAUW

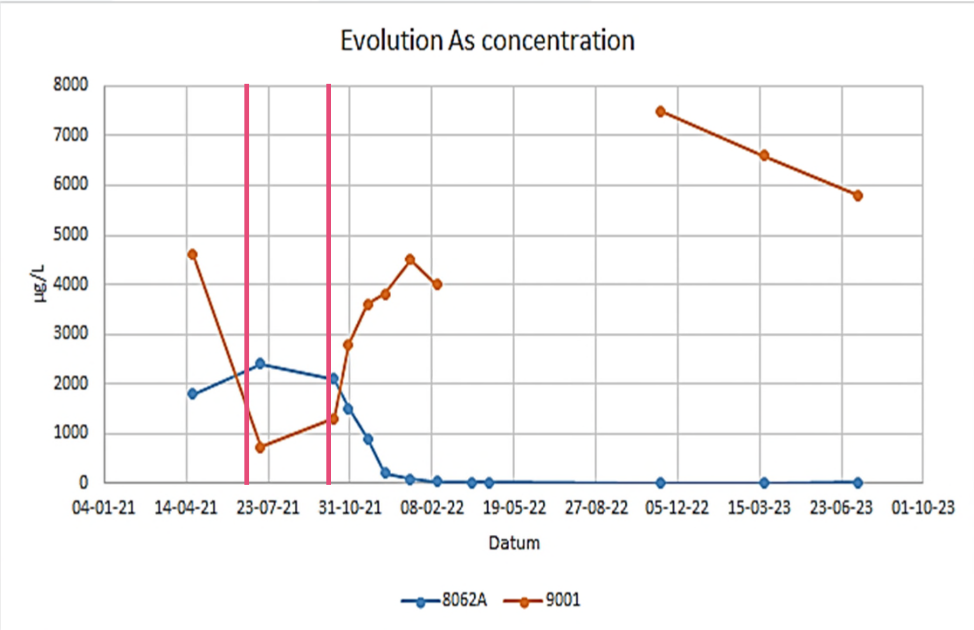
Field results

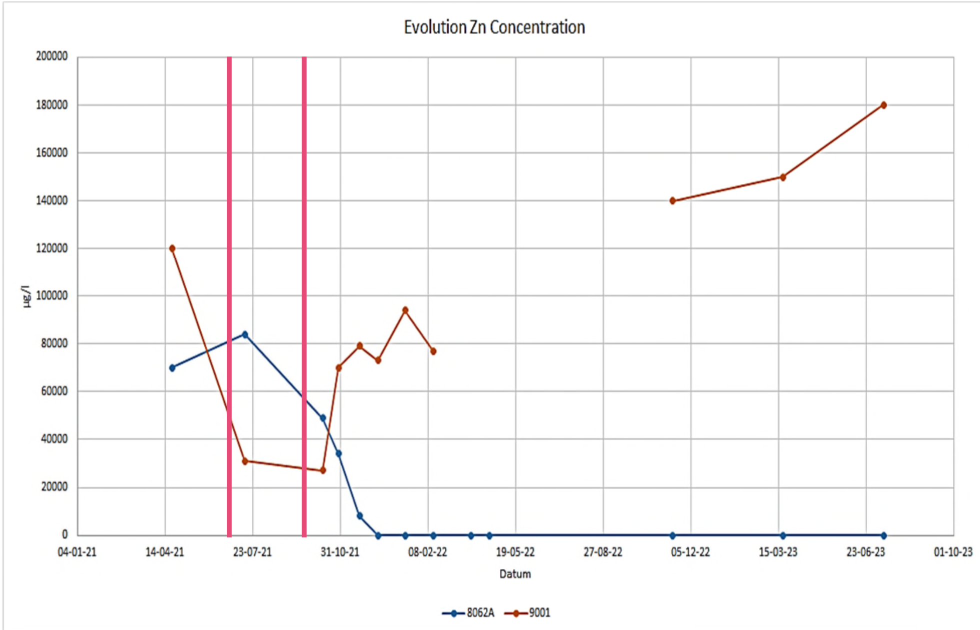




AquaConSoil2023

Pilot testing of ISMP



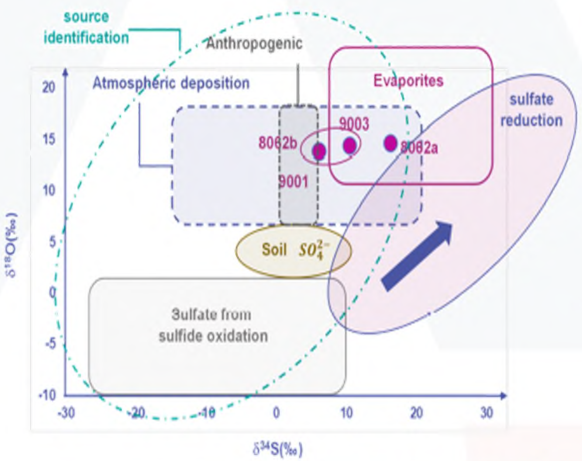


AquaConSoil2023

TAUW

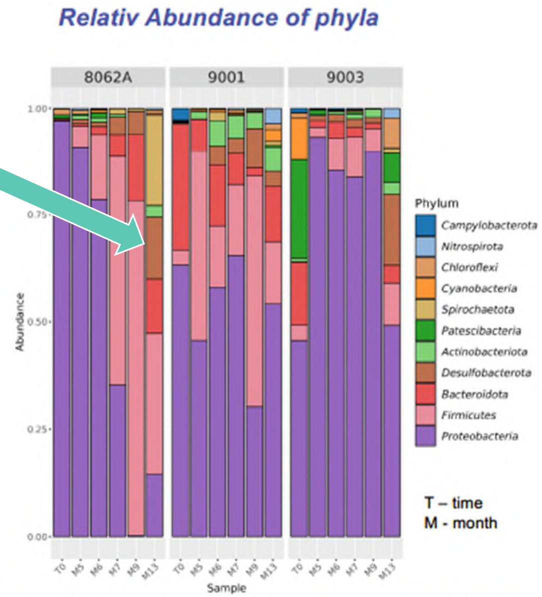
CSIA and DNA Analysis

CSIA – Compound Specific Isotope Analysis for sulfate and Microbial diversity analysis



		9001	9003	8062A	8062b
T13 (May 2022)	$^{34}S/^{32}S$	6.1 (0.2)	10.4 (0.2)	16.3 (0.3)	8.2
T13 (May 2022)	$^{18}O/^{16}O$	13.9 (0.6)	14.4 (0.5)	14.7 (0.6)	14.8
T0 (Apr 2021)	SO_4^{2-} [mg/L]	1.000	660	800	1.000
T13 (May 2022)	SO_4^{2-} [mg/L]	980	660	600	1.200
fraction SO_4^{2-} reduced		-	0.3 - 0.5	0.5 - 0.8	0.1 - 0.3

- For quantification of sulfate reduction an enrichment factor (ε_s) range of -14.8 and -6.2 ‰ was considered
- The S-signature of 9001 (+6.1 ‰) was used as source value
- A net change in sulfate concentration from 800 to 600 mg/L was observed for well 8062a
- A shift in δ34S of +10.2 ‰ was observed for well 8062a
- Sulfate reduction to sulfide by SRB in well 8260a ranged from 50 to 80 % according to stable isotope data



- **Microbial community gradually changed in 8062a as treatment progressed**
- ***Proteobacteria* were largely replaced by fermentative *Firmicutes*, later also by *Bacteroidota* and *Spirochaeta***
- ***Desulfobacteroidota (SRB) also thrived in 8062a***
- ***For wells 9001 and 9003 Proteobacteria* dominated over time**

TAUW

AquaConSoil2023

Conclusions

Lessons learned and conclusions

- Technique of ISMP not applicable in core zones with extreme geochemical conditions
- ISMP is applicable in plume zone areas with “gentle” geochemical conditions
- High C-doses might be required to manipulate the local geochemistry
- Injection with multiple rods is strongly advised to overcome soil heterogeneities
- In case of favourable geochemical conditions a clear shift of bacterial populations towards SRB was measured
- Long term stability of heavy metal precipitates (at least 2 years)
- ISMP is a low-cost technique and more sustainable compared to a classic P&T
  - Cost savings are in the range of 80% on CAPEX and 50% on the yearly OPEX cost

TAUW

TAUW

Acknowledgements

1. *Jaap Steketee, TAUW Netherlands, TAUW Test lab, Deventer Netherlands*
2. *Marian Langevoort, TAUW Netherlands, TAUW Test lab, Deventer Netherlands*
3. *A. Pérez-de-Mora, TAUW Gmbh, Dept. of Soil & Groundwater, Munich Germany*
4. *Herwig De Wilde, TAUW Belgium, Dept. of Soil & Groundwater, Lokeren Belgium*
5. *Dirk Paulus, TAUW Belgium, Dept. of Soil & Groundwater, Wijgmaal Belgium*

The authors also acknowledge funding by H2020 EU-GREENER (Grant Agreement No. 826312)

Horizon 2020
European Union Funding
for Research & Innovation

greener

Microbial analysis

Rob Onderwater

MATERIA NOVA Materials R&D Center

Daniel Farkas

UNIVERSITY OF SURREY

AquaConSoil2023

This project has received funding from the European Horizon2020 research and innovation programme under Grant Agreement No. 826312

greener

TAUW

Thank you for your attention

Dirk Paulus and Herwig De Wilde

Email: dirk.paulus@tauw.com and herwig.dewilde@tauw.com
Phone number: +32 498 87 61 09 and + 32 498 87 61 12

Deltares

Photon Water

Photon Remediation

Albemarle

ALL THE ELEMENTS FOR A BETTER WORLD

CARUS®

CZU Czech University of Life Sciences Prague