Modified Fenton's Reagent: Explosive Zone (EX-1) Application control and safety management

Karel Waska

Contaminated Sites, 2015

EPS biotechnologie

Introduction

Take-home message:

When the time and complex surface conditions limit the remediation efforts, ISCO offers a quick and definite solution.

EPS biotechnologie

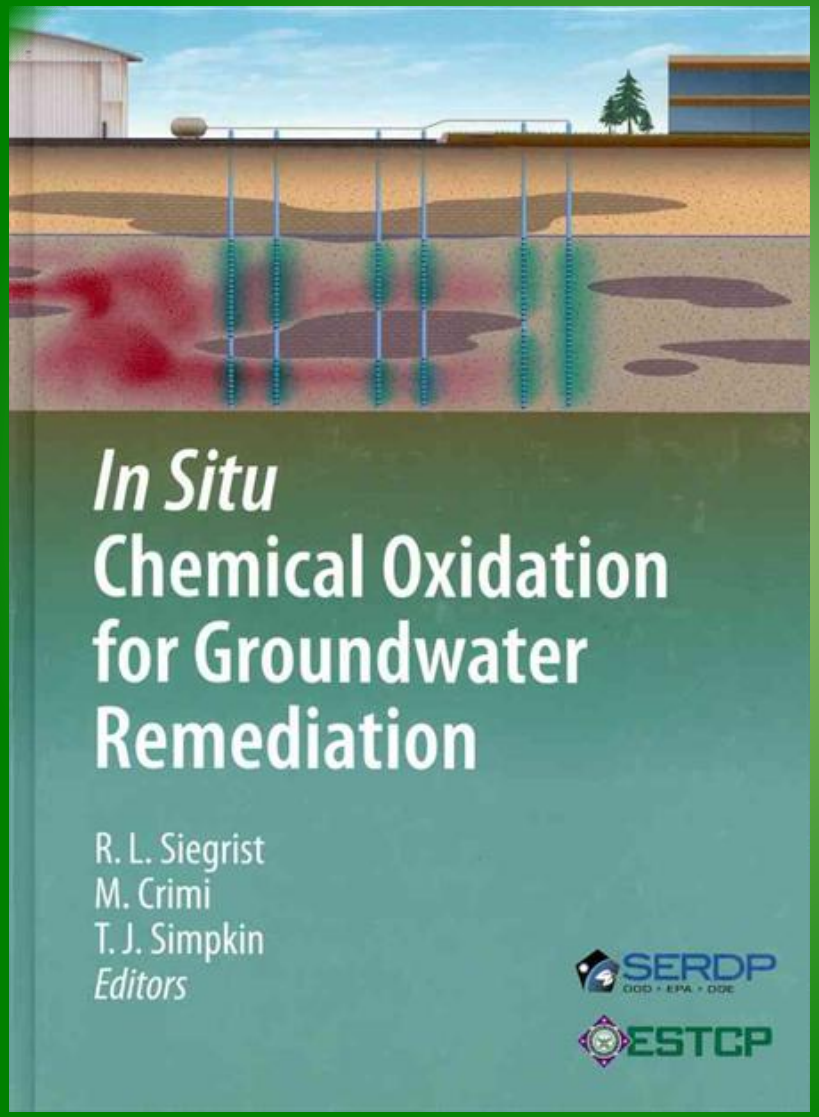
Introduction

Acknowledgements

- *Mgr.* **Jiří Kamas**
- *Ing.* **Petr Beneš,** *Ph.D.*
- *Ing.* **Karel Horák**
- *Ing.* **Miroslav Minařík**
- *Ing.* **Vlastimil Píštěk**

EPS biotechnologie

In situ chemical oxidation



Siegrist, R. L., Crimi, M., Simpkin, T. J.: *In Situ* Chemical Oxidation for Groundwater Remediation, Springer 2011, ISBN: 978-1-4419-7825-7

EPS biotechnologie

Why ISCO??

Cost:
Often most effective alternative

Time:
Quick results, usually within weeks or months

Target pollutants:
Wide spectrum = chlorinated solvents, petroleum-derived hydrocarbons, …

Contamination range:
Broad range of concentration levels including heavily impacted sites (inhibition of biodegradation processes)

EPS biotechnologie

Fenton's Reagent

Fenton's reaction:

- Described in mammal heart cells (*Ischemic heart dissease)
- **Reaction between hydrogen peroxide and ferrous ions generating $OH^{\bullet}$ radicals:**

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + HO^{\bullet} + H_2O$$

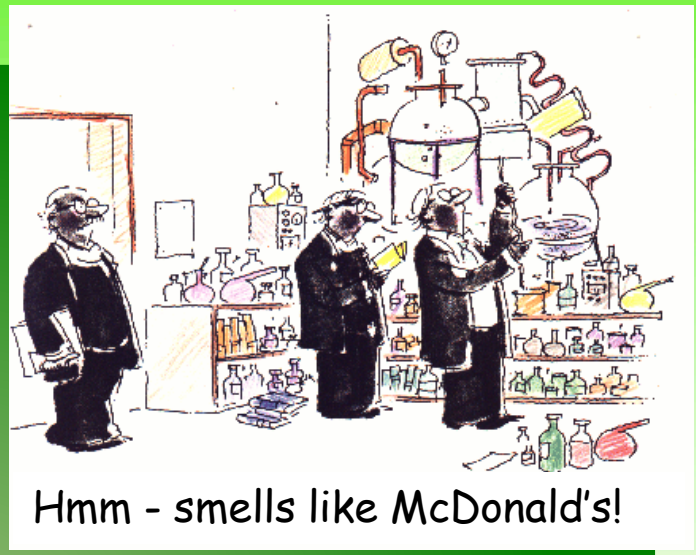
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^{\bullet} + H^+$$

$$C_aH_bX_c + Fe^{2+} + xH_2O_2 \rightarrow Fe^{3+} + cX^- + aCO_2 + 2H_2O + bH^+$$

Exothermal reaction !!!

EPS biotechnologie

Why modify? H_2O_2 =>



- Cheap, very strong oxidant (ROS)
- Main property = **INSTABILITY=>**
- Fast disintegration, exothermic decay
- Releases large amounts of O_2 => 1 L of 5% H_2O_2 generates up to 20 L of O_2
- **STABILIZATION** = critical know-how:
  - Addition of stabilizer (phosphates, chelates, organic acids = pH drops)

EPS biotechnologie

Google Earth

EPS biotechnologie

Sandy gravel aquifer

- K ≈ 10^{-5} – 10^{-4} m/s
- Aquifer thickness ~1,5 m
- Porosity n = 0,15

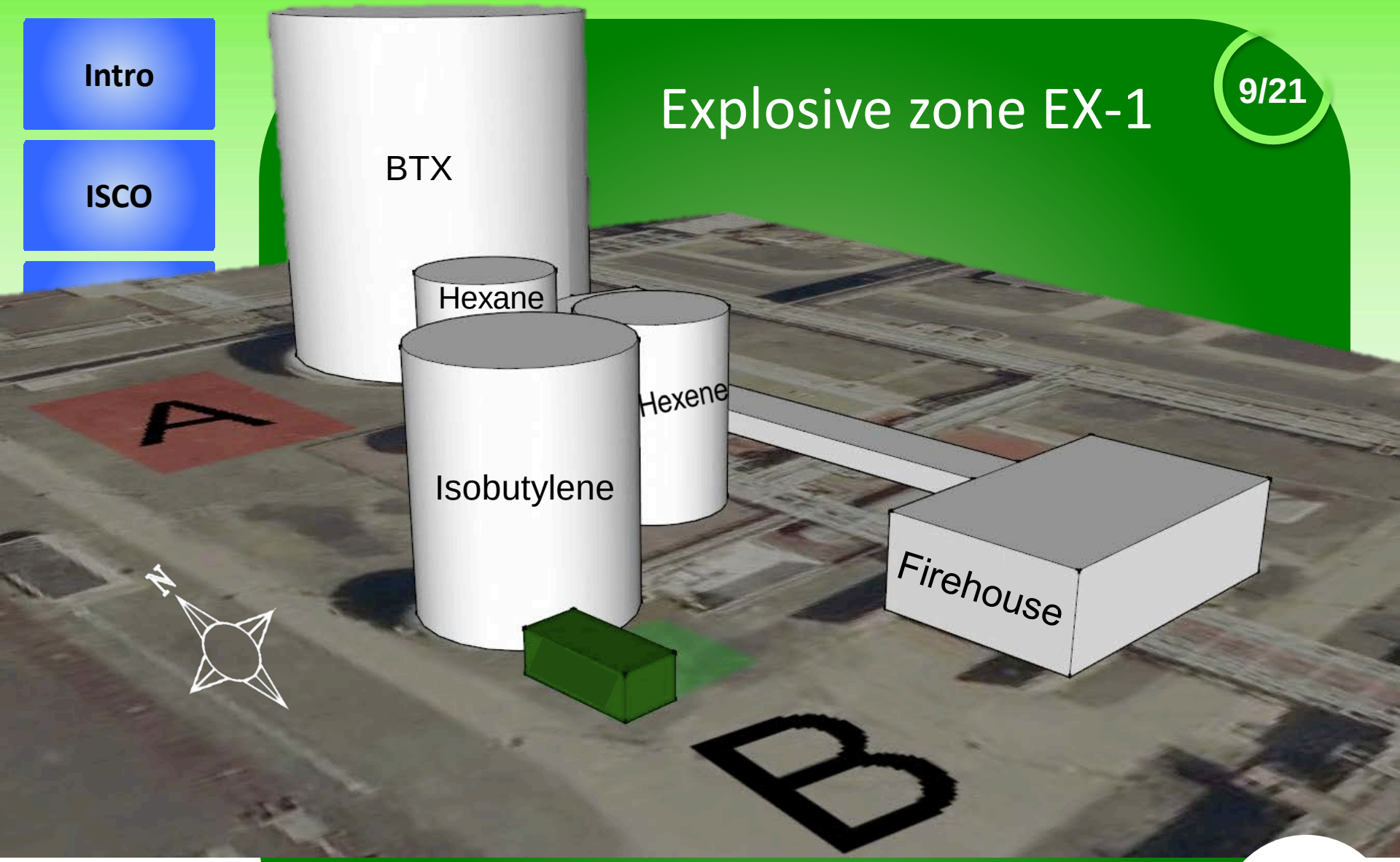
Field A

- 530 m^2
- V~120 m^3

Google Earth

EPS biotechnologie

Explosive zone EX-1



Google Earth

EPS biotechnologie

Primary pilot test objectives:

1. To verify technology functionality and usability,
2. to reduce contamination levels,
3. to comply with rigorous safety regulations (EX-1), and
4. to optimize on site process and reaction control tools (real time monitoring).

Studied risk factors:

1. Exothermic reaction course,
2. reagent corrosiveness (maintain pH ≥ 4,5 and g.w. level below the depth of utility networks), and
3. generation of VOCs as daughter products.

EPS biotechnologie

Wide range of petrochemical operations

- Ethylene production => pollutants:
  - BTEX, Naphthalene, Non-polar organics

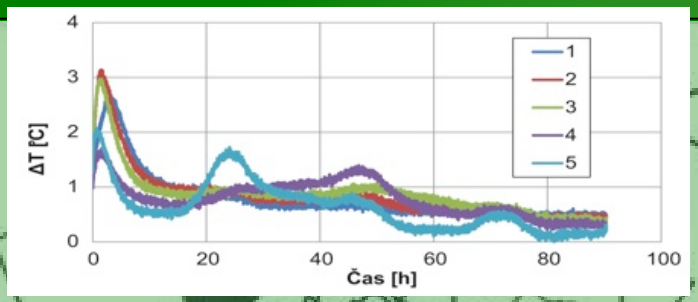
HV-8857: pollutant evolution

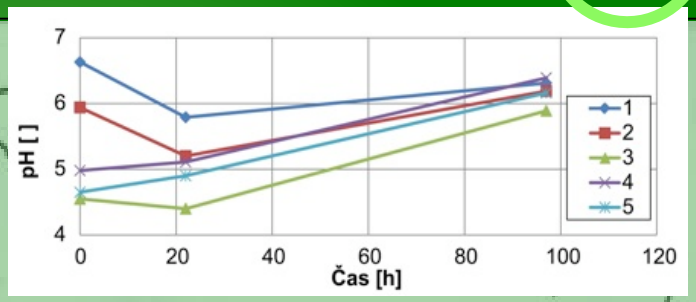
CONT.	Benzene[µg/l]	Naphthalene[µg/l]	NOC[mg/l]
RC	400	1700	no FPLH
TC	2500	2500	10
2004	-	-	FPLH
2006	125 000	<0,5	>200
2013*	10 300	162	13,2

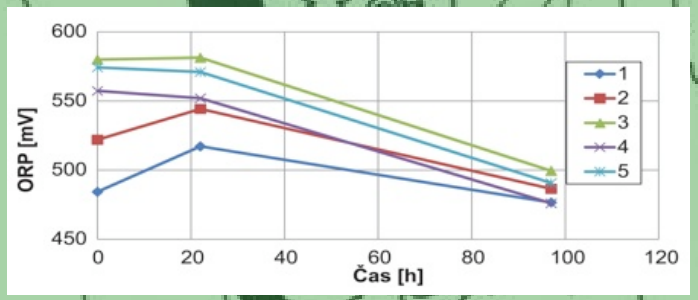
*(before pilot)

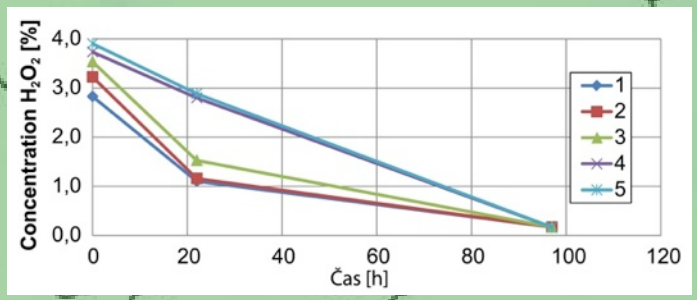
EPS biotechnologie

Soil & g.w. matrix – buffering capacity









- 5% hydrogen peroxide (H_2O_2)
- $FeSO_4 \cdot n\ H_2O$
- $C_6H_8O_7$ (Citric acid)

=> Temperature increase < 4°C

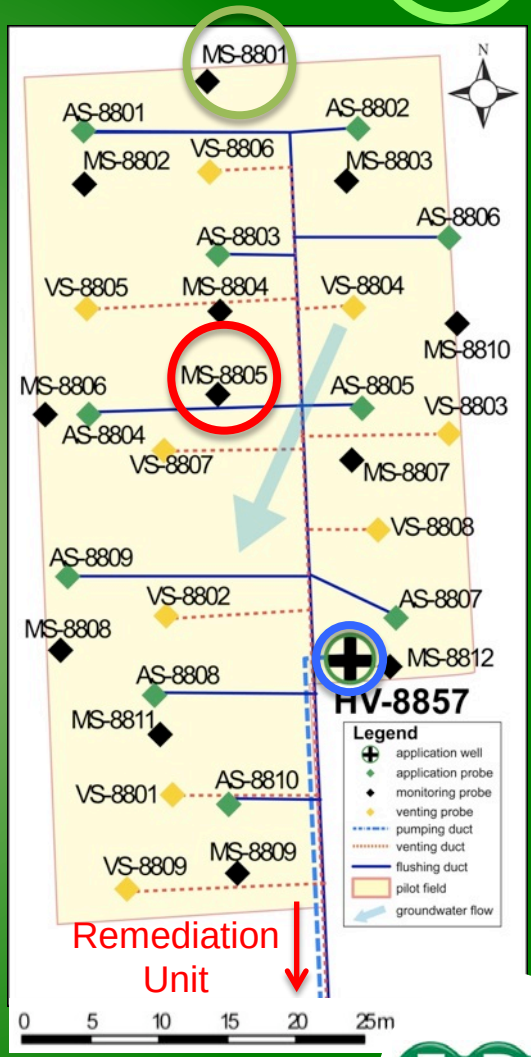
The option for biodegradation finish was verified…

EPS biotechnologie


13/21
AUTOLÉKÁRNIČKA
EPS
biotechnologie

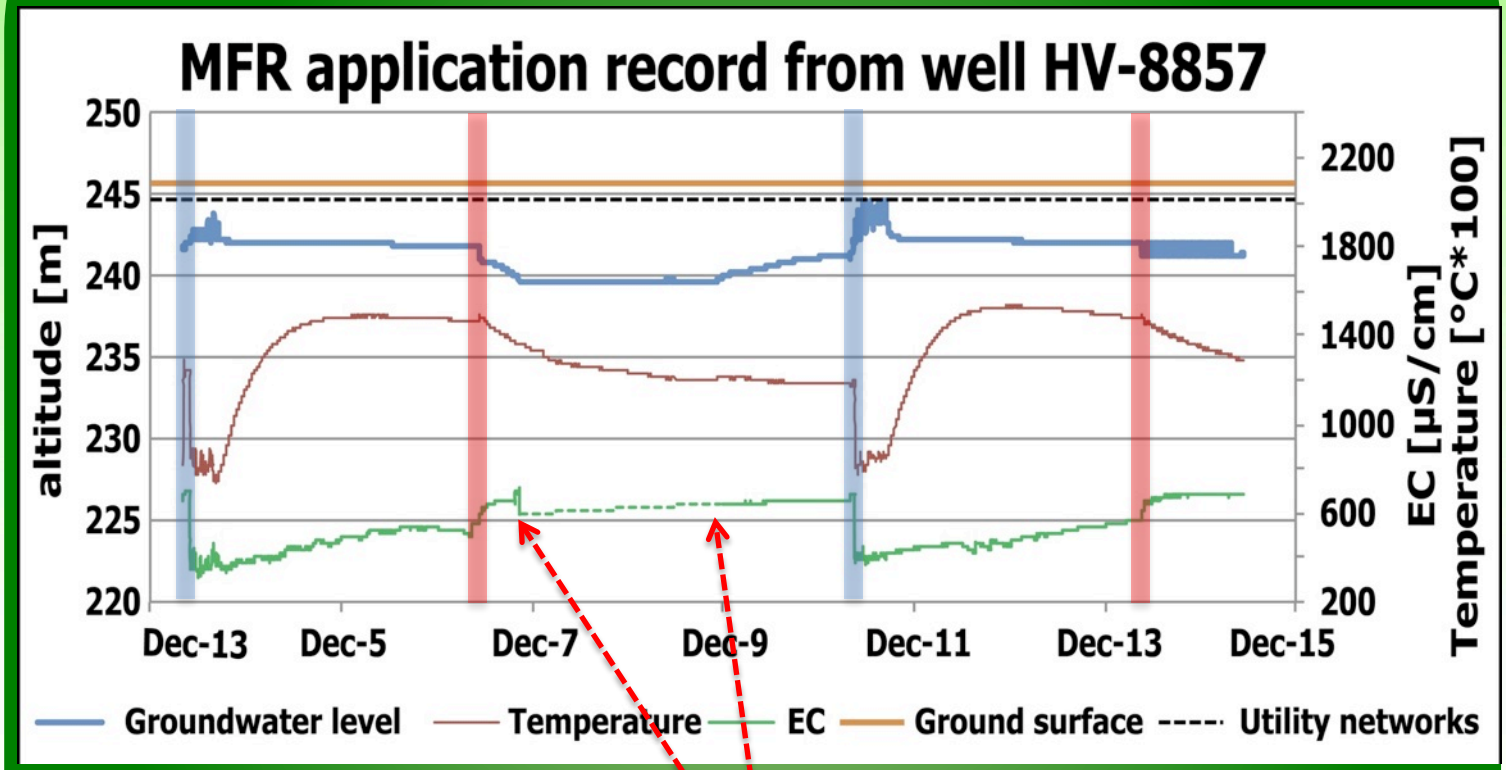
12.11.2013 – 28.1.2014:

- 7 phases
- 77 m^3 (5% H_2O_2): areal & pointed injection
- G.w. pump-and-treat between the phases (after rxn fade out) => filtration & recirculation
- Soil air pump-and-treat => filtration
- *In situ* real-time monitoring: Temp., g.w. level, EC
- Field on site monitoring: Physicochemical parameters, VOCs & H_2O_2 concentrations



EPS biotechnologie

Temp. and g.w. level - Safety



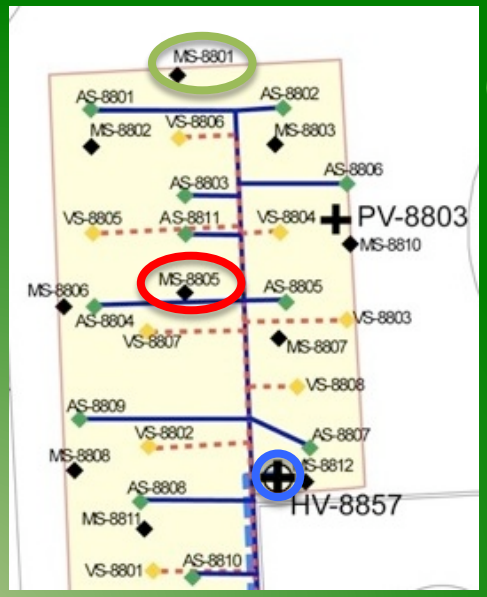
MFR application

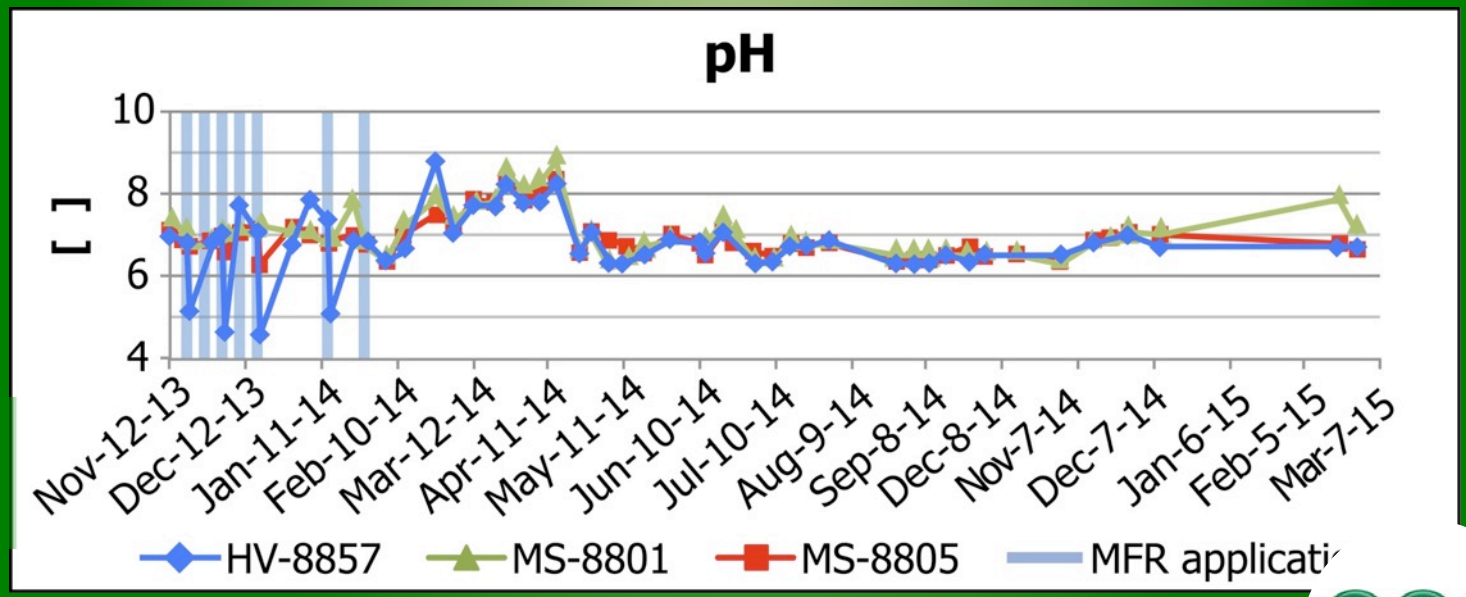
Well empty

G.w. pumping

EPS biotechnologie

pH – Safety

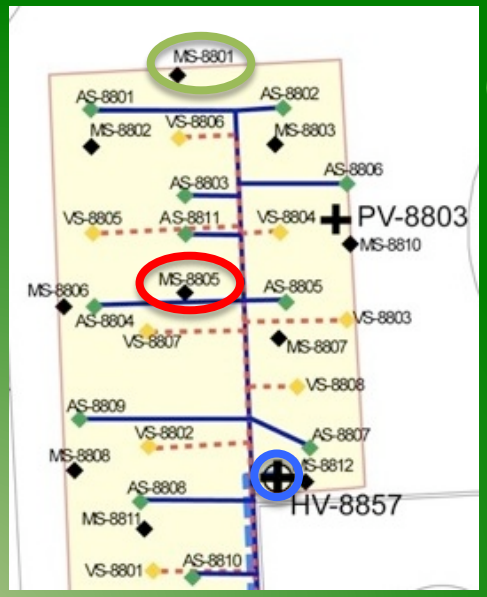


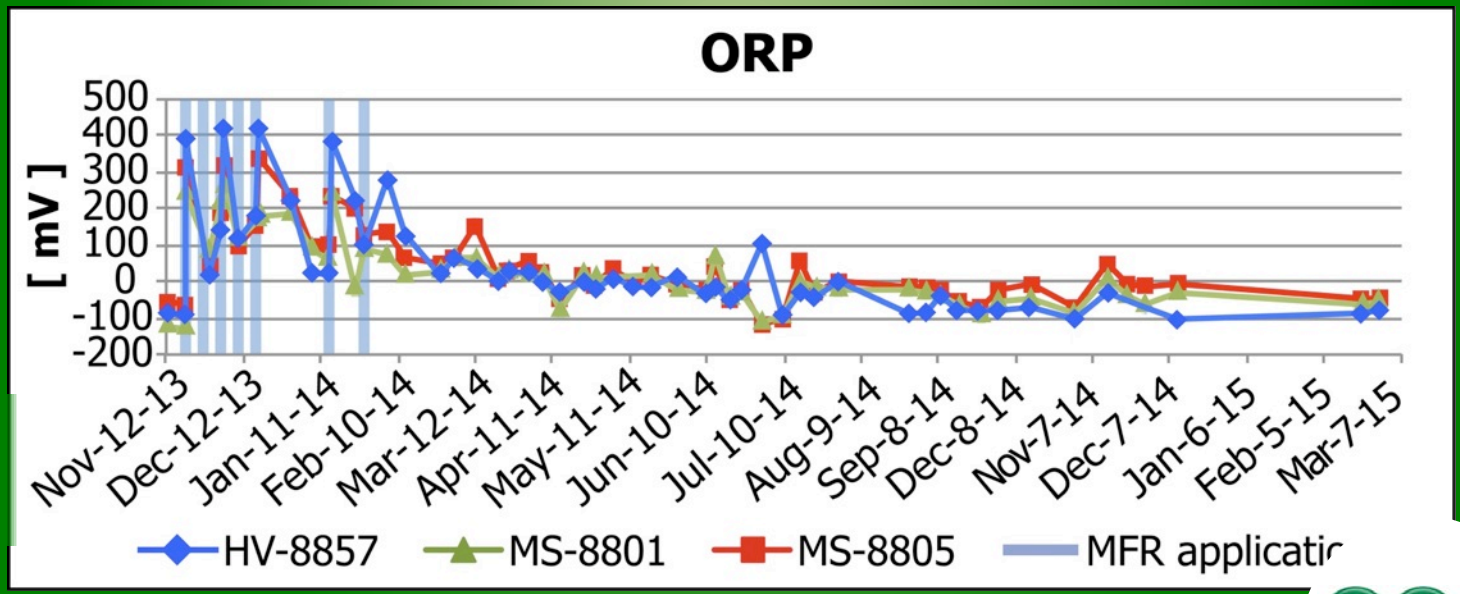


EPS biotechnologie

Intro
ISCO
MFR
Site
Pollution
Lab
Pilot
Conclusion

ORP – Effectiveness

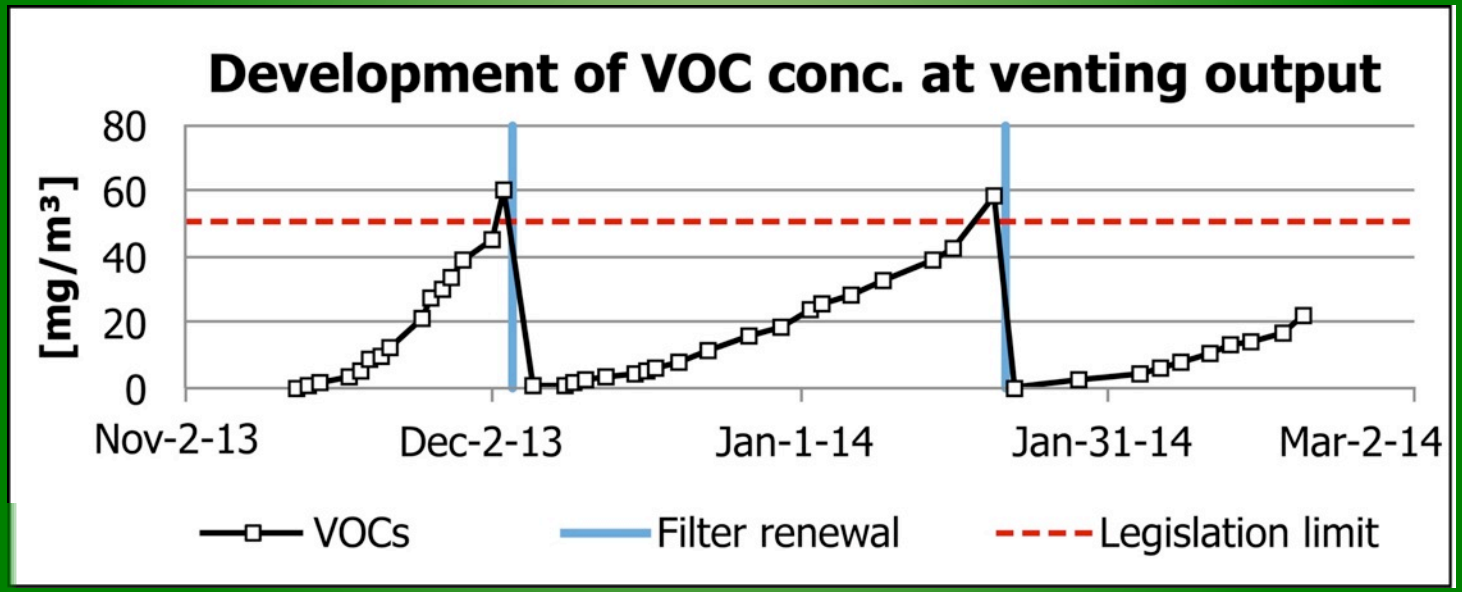




Parallel with the DO parameter

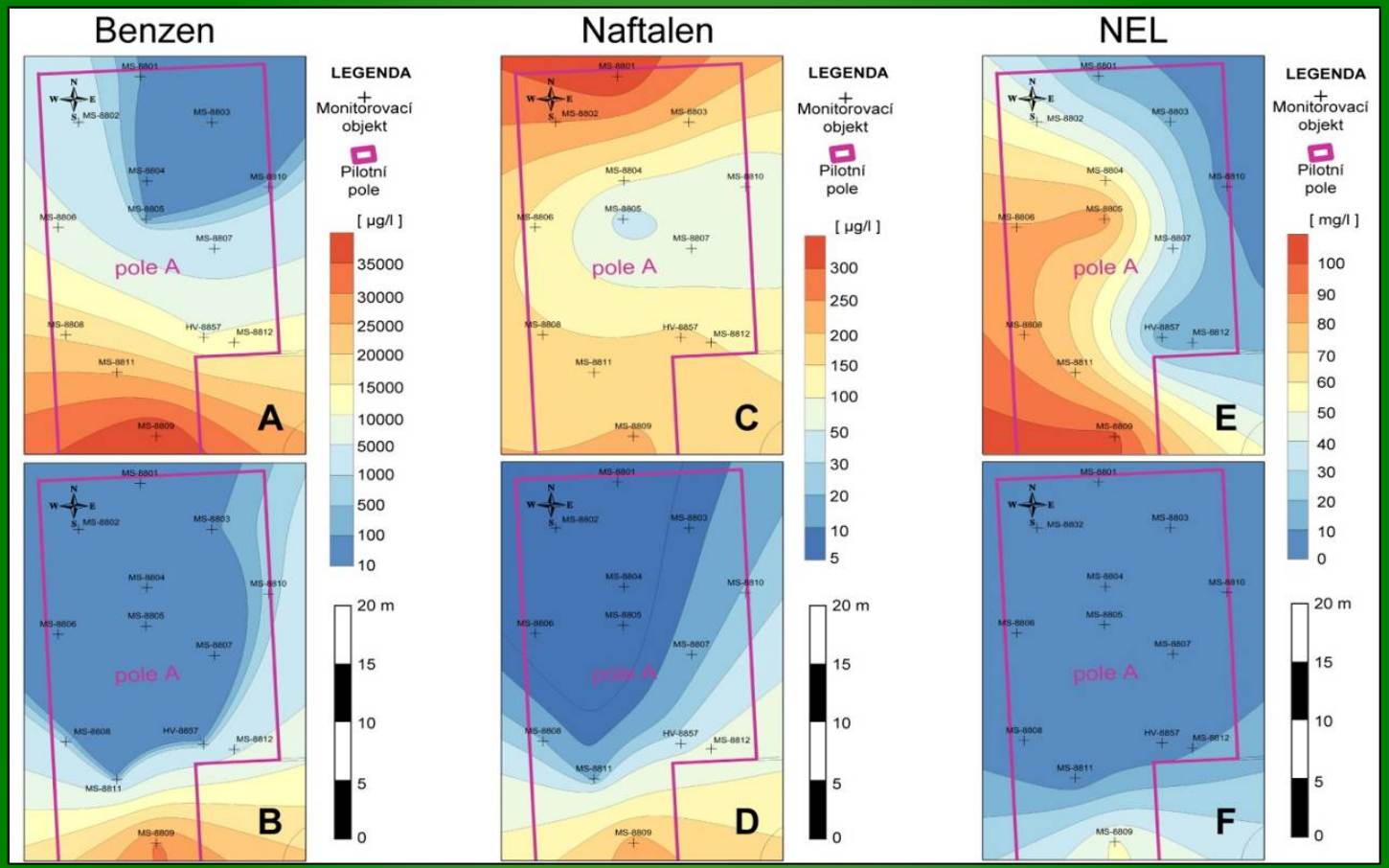
EPS biotechnologie

VOCs – Safety



EPS biotechnologie

Pollutant destruction



**Before pilot test – A, C, E*

After pilot test – B, D, F

EPS biotechnologie

Primary pilot test objectives:

- ✔ 1. Technology verification,
- ✔ 2. reduction of contamination levels,
- ✔ 3. rigorous safety regulations (zone EX-1), and
- ✔ 4. Control tools optimisation (real time monitoring).

Studied risk factors:

1. Exothermic rxn: Temp. increase less than 5°C
2. Corrosiveness: pH > 4,5 & g.w. level below the level of utility networks
3. VOCs generation: concentration decrease along time

Conclusion

Enhanced attenuation potential => anaerobic biodegradation…

EPS biotechnologie

Happy Fenton…?