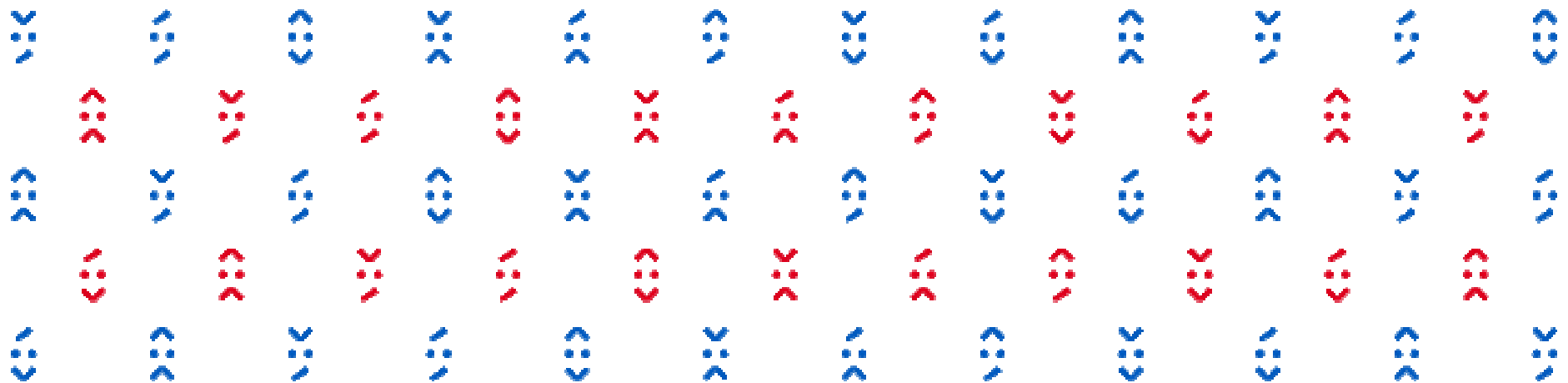


SK EU2016

Slovak Presidency of the Council
of the European Union



EXPLOSIVE ZONE (EX-1) GROUNDWATER REMEDIATION: MONITORING, CONTROL, AND SAFETY MANAGEMENT

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International Conference CONTAMINATED SITES 2016
Bratislava, 12. – 13. 09. 2016

Introduction

ISCO

PCR

Site

Pollution

Lab

Pilot

EU2016

Take-home message:

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

2. Molecular Microbiology techniques provide boundary conditions for bioremediation finish.

Summary

EX-1 ZONE GROUNDWATER REMEDIATION: MONITORING, CONTROL, AND SAFETY MANAGEMENT,
Bratislava, 12./13. 09. 2016

Introduction

ISCO

PCR

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Pilot

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Summary

Acknowledgements

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

In situ chemical oxidation

Intro

ISCO

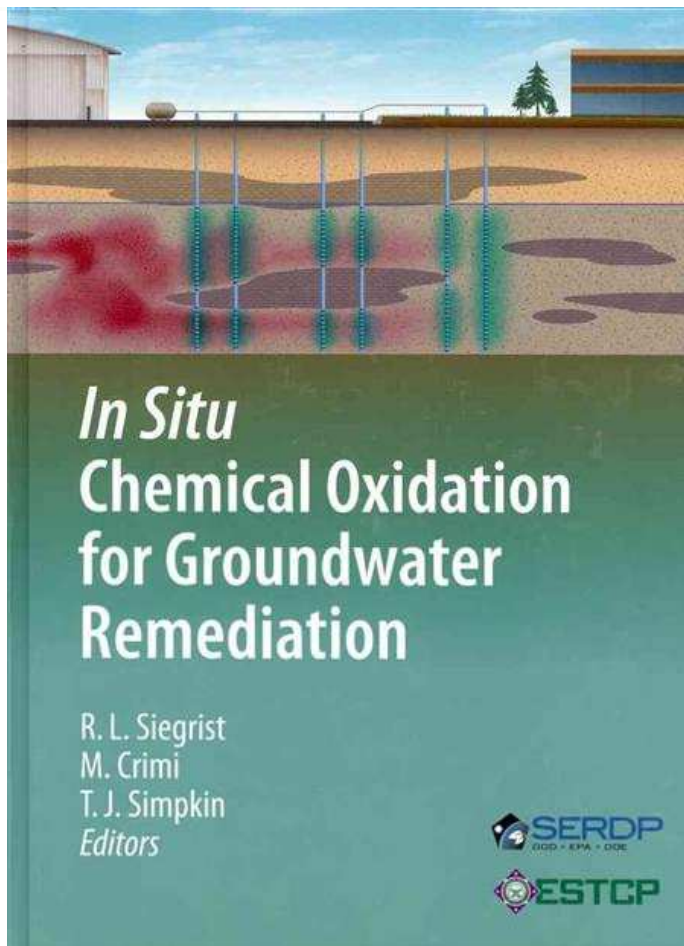
PCR

Site

Pollution

Lab

Pilot



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

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Summary

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Intro

Why ISCO??

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Cost:

Often most effective alternative

PCR

Time:

Quick results, usually within weeks or months

Site

Target pollutants:

Wide spectrum = chlorinated solvents, petroleum-derived hydrocarbons, ...

Pollution

Lab

Contamination range:

Broad range of concentration levels including heavily impacted sites (biodegradation processes inhibited)

Pilot

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Summary

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Intro

Fenton's Reagent

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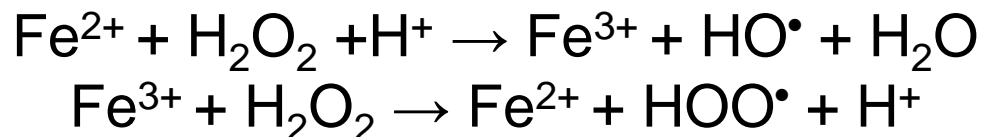
Fenton's reaction:

- Described in mammal heart cells (*Ischemic heart disease)
- Reaction between hydrogen peroxide and ferrous ions generating OH• radicals:

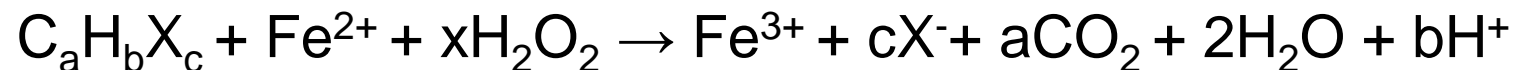
PCR

Site

Pollution



Lab



Exothermal reaction !!!

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Summary

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Intro

Modified Fenton?

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- Cheap, very strong oxidant (ROS)

Site

- **INSTABILITY**

- Fast disintegration, **exothermic decay (!!)**
- Produces large amounts of gas: O₂ & VOCs

Pollution

Lab

- **STABILIZATION** = critical know-how:
 - Addition of stabilizer (phosphates, chelates, organic acids = pH drops)

Pilot



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Intro

Polymerase Chain Reaction

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= photocopying of target gene sequences

PCR

- Living or dead cells (no cultivation bias)

Site

- Real-Time qPCR

- Quantification of target gene sequences => comparison among samples:

- Whole genome screening – 16S rDNA
- Denitrification coding genes – NirK, NirS

Pollution

Lab

Pilot

- For enhanced attenuation potential assessment

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Summary

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Summary



Google Earth



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Bratislava, 12./13. 09. 2016

Intro

Sandy gravel aquifer

ISCO

- $K \approx 10^{-5} - 10^{-4} \text{ m/s}$

PCR

- Aquifer thickness ~1,5 m

Site

Pollution

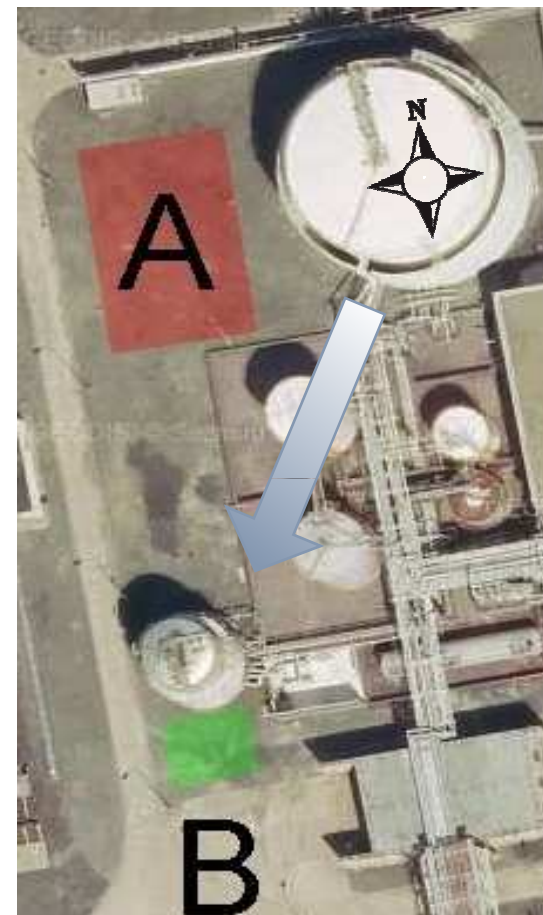
- Porosity $n = 0,15$
Field A

Lab

- 530 m^2

Pilot

- $V \sim 120 \text{ m}^3$



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Explosive zone EX-1

Intro

ISCO



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Summary

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Bratislava, 12./13. 09. 2016

Intro

Primary pilot test objectives

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1. To verify technology functionality and usability,
2. to reduce contamination levels,

PCR

3. to comply with rigorous safety regulations (EX-1), and

Site

to optimize on site process and reaction control tools (real time monitoring).

Pollution

Studied risk factors

Lab

1. Exothermic reaction course,
2. reagent corrosiveness (maintain $\text{pH} \geq 4,5$ and g.w. level below the depth of utility networks), and

Pilot

3. generation of VOCs as daughter products.

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Summary

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Intro

Wide range of petrochemical operations

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

PCR

HV-8857: pollutant evolution

Site

Date

Benzene[$\mu\text{g/l}$]

Naphthalene[$\mu\text{g/l}$]

NOC[mg/l]

Pollution

RC

400

1700

no FPLH

TC

2500

2500

10

Lab

2004

-

-

FPLH

2006

125 000

<0,5

>200

2013*

10 300

162

13,2

Pilot

*(pre-pilot)

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Summary

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Bratislava, 12./13. 09. 2016

Intro

Soil & g.w. matrix – buffering capacity

ISCO

PCR

Site

Pollution

Lab

Pilot

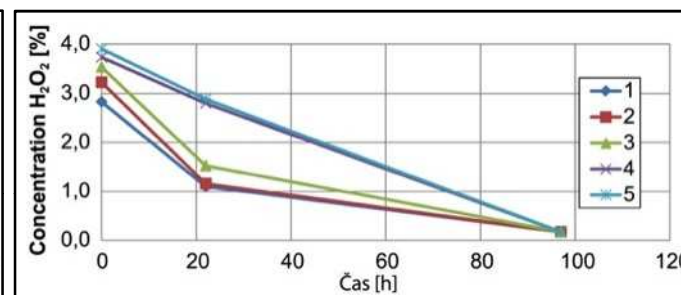
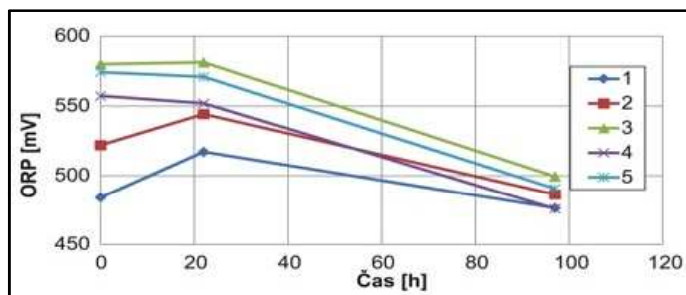
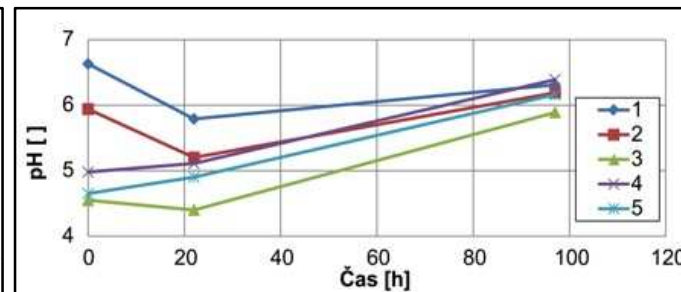
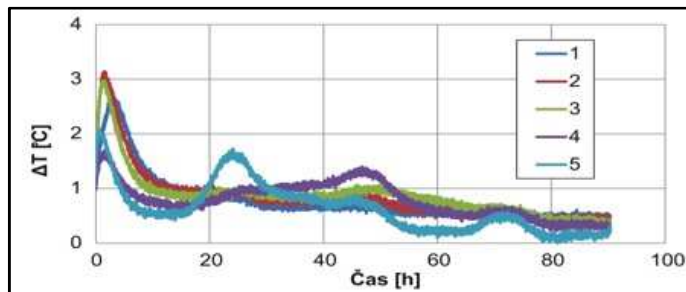
- 5% hydrogen peroxide (H_2O_2)
- $FeSO_4 \cdot n H_2O$
- $C_6H_8O_7$ (Citric acid) => Temperature increase < 4°C

The option for biodegradation finish was verified...

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Summary

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Bratislava, 12./13. 09. 2016





12.11.2013 – 28.1.2014:

Intro

ISCO

PCR

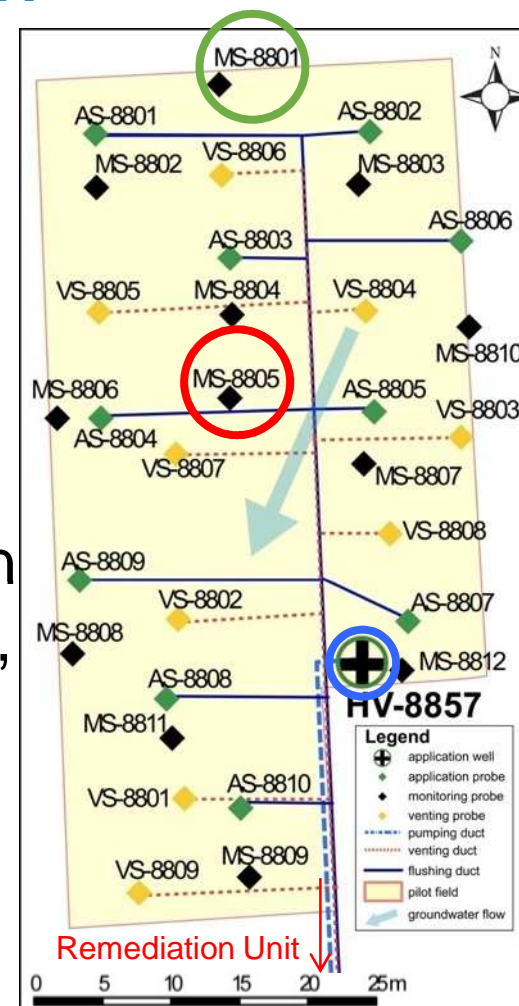
Site

Pollution

Lab

Pilot

- 7 phases:
- 77 m³ (5% H₂O₂): areal & pointed injection
- Gw. pump-and-treat between the phases (after rxn' fade out) => filtration & recirculation
- Soil air pump-and-treat => filtration
- *In situ* real-time monitoring: Temp., gw. level, EC
- Field on site monitoring: Physicochemical parameters, COCs & H₂O₂ concentrations



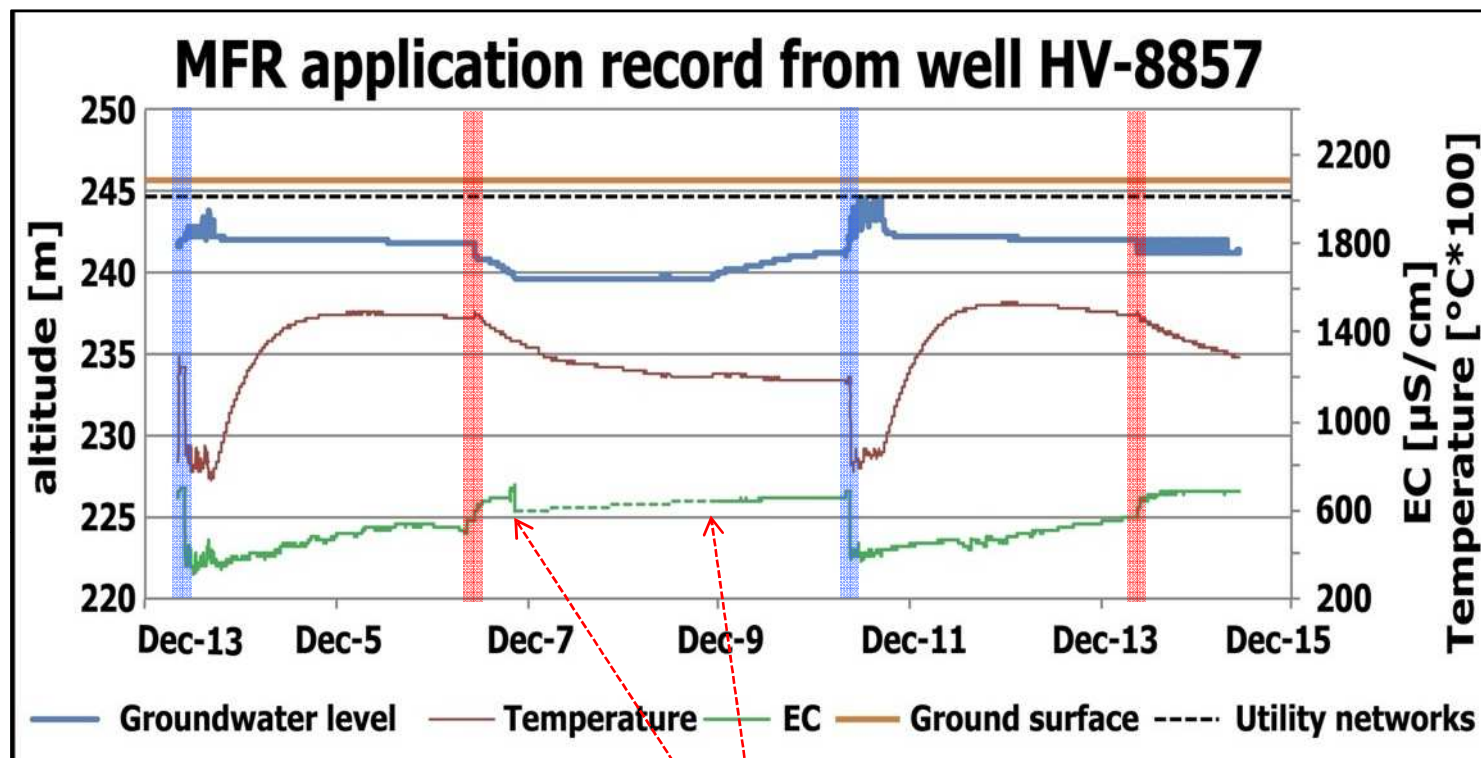
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Summary

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Temp. and g.w. level - Safety

- Intro
- ISCO
- PCR
- Site
- Pollution
- Lab
- Pilot**
- Summary

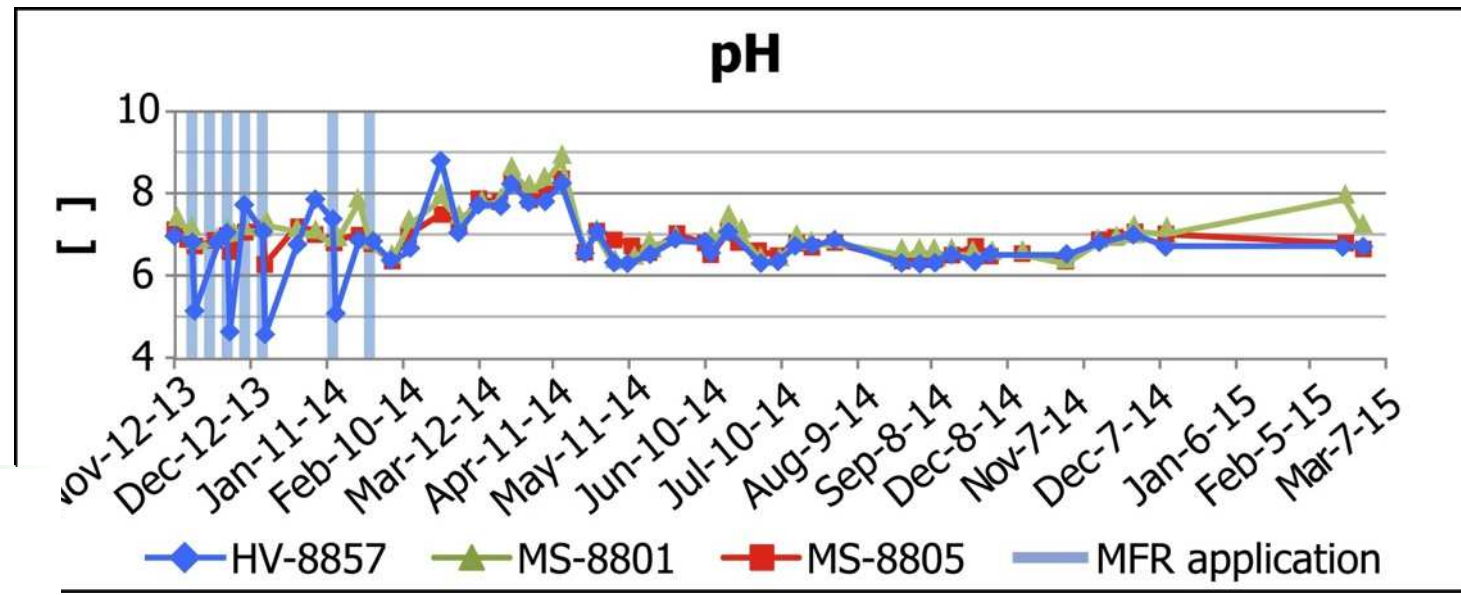
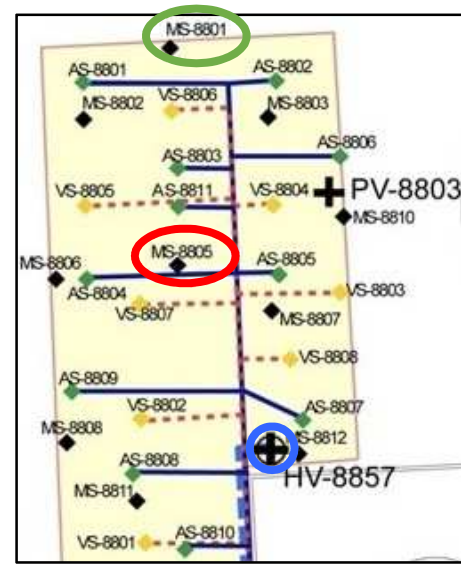


MFR application Well empty G.w. pumping

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- Intro
- ISCO
- PCR
- Site
- Pollution
- Lab
- Pilot
- Summary

pH – Safety



Intro

ISCO

PCR

Site

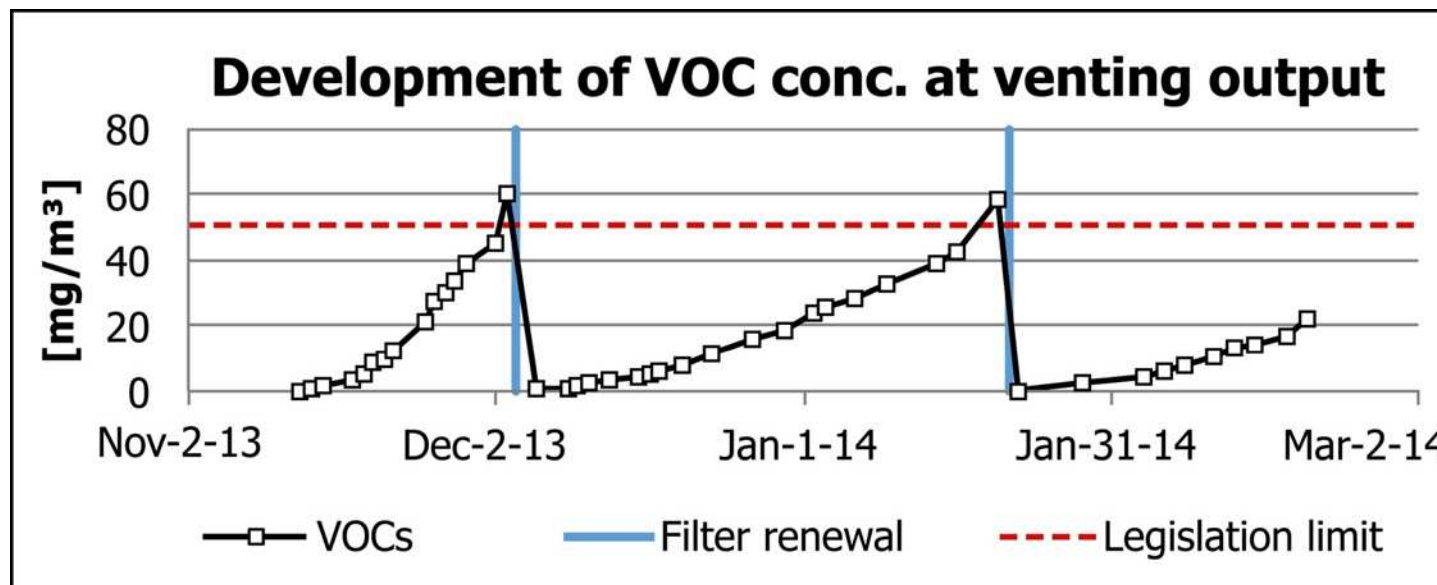
Pollution

Lab

Pilot

Summary

VOCs – Safety



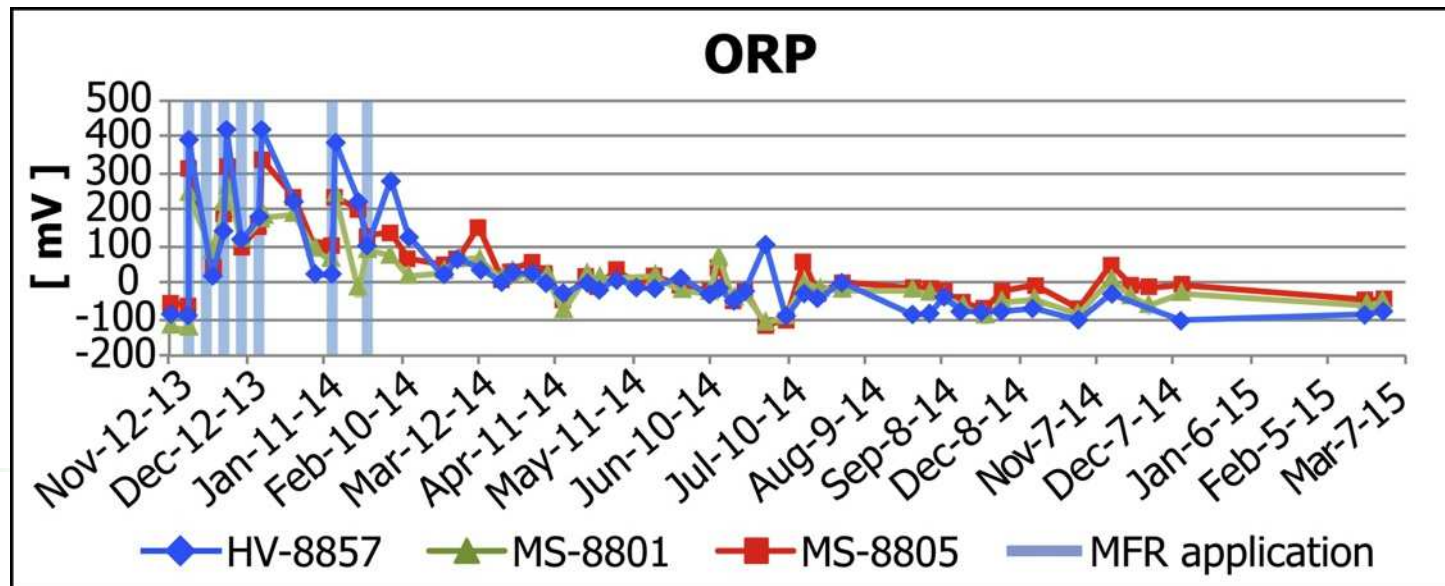
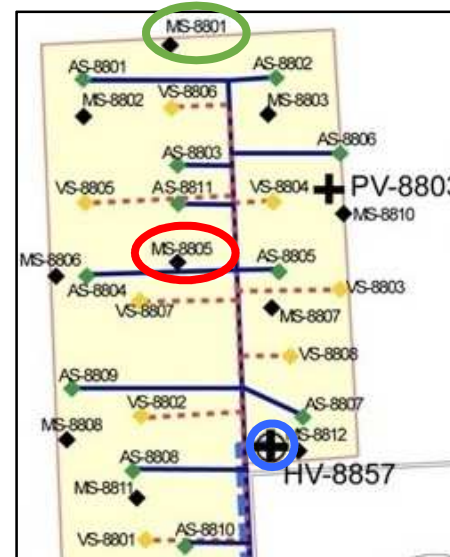
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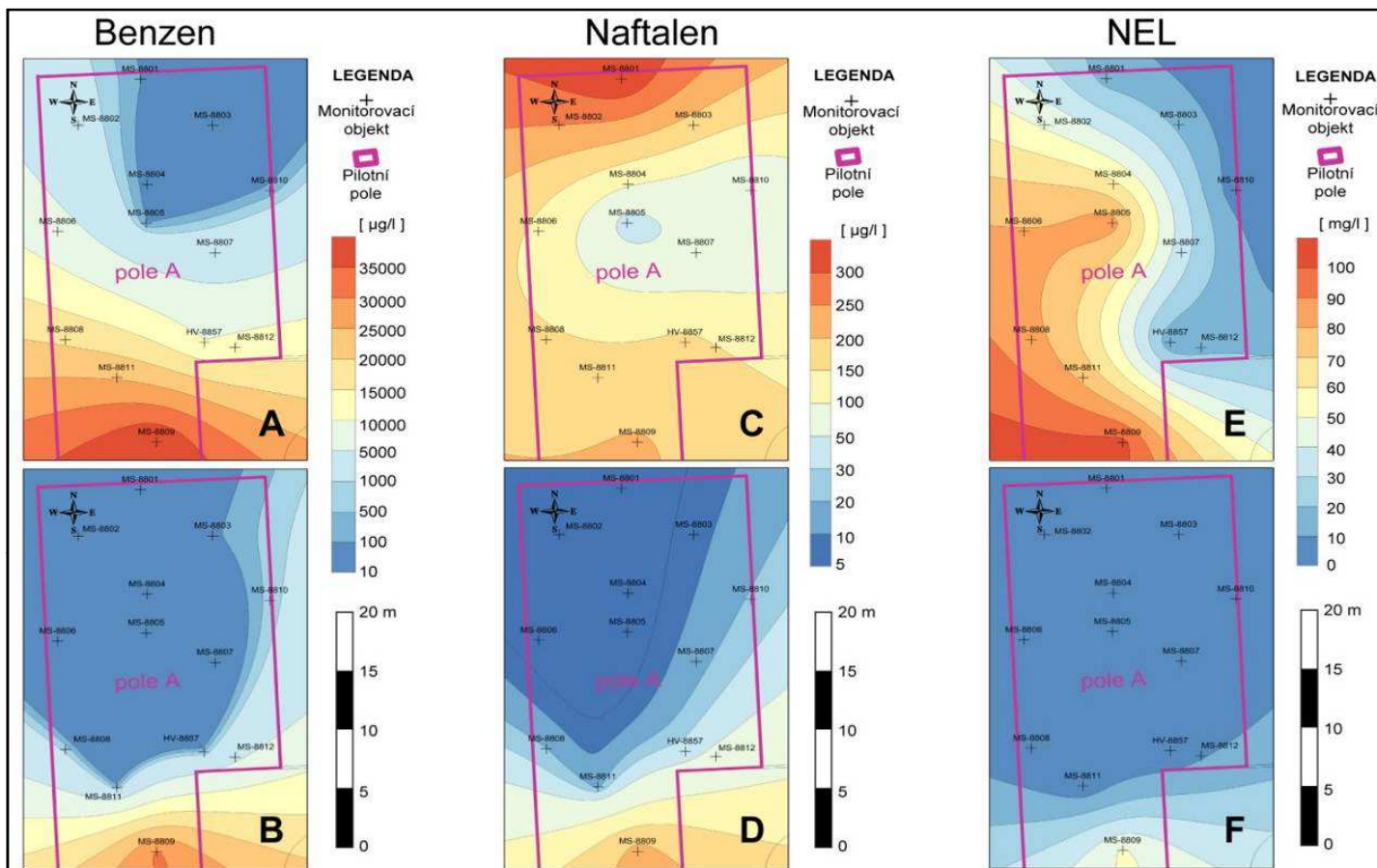
ORP – Effectiveness

Parallel with the DO parameter



Pollutant destruction

- Intro
- ISCO
- PCR
- Site
- Pollution
- Lab
- Pilot**
- Summary



**Before pilot test – A, C, E*
After pilot test – B, D, F

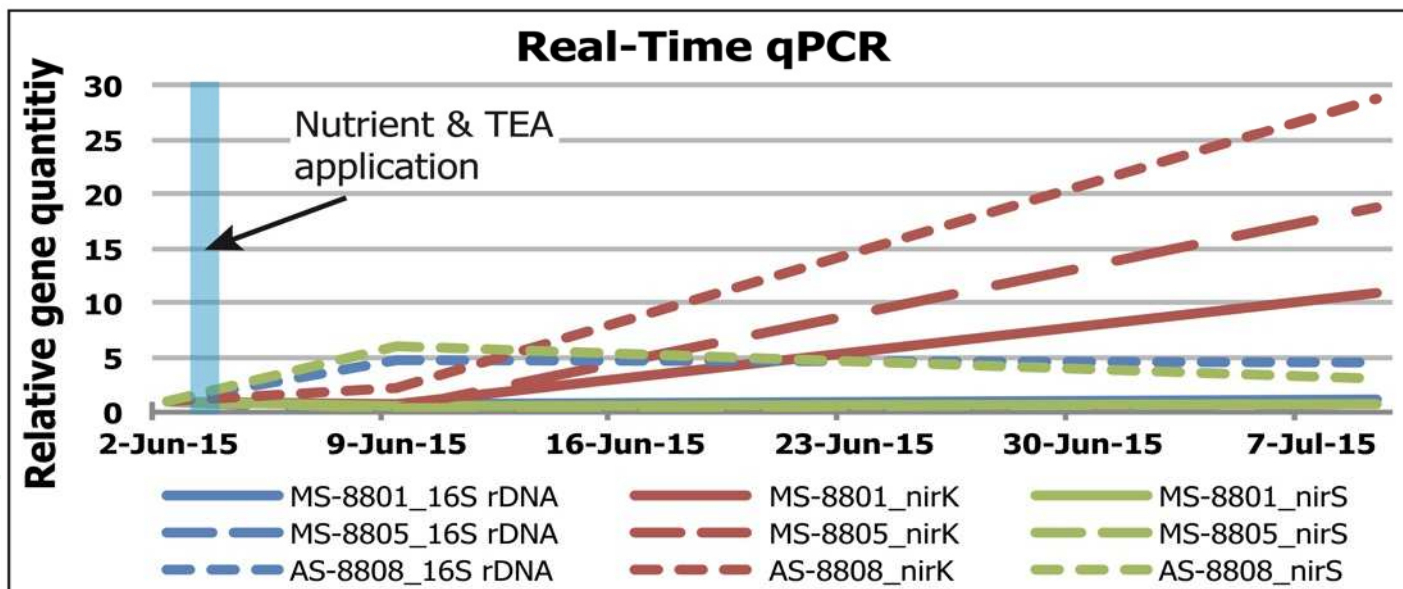
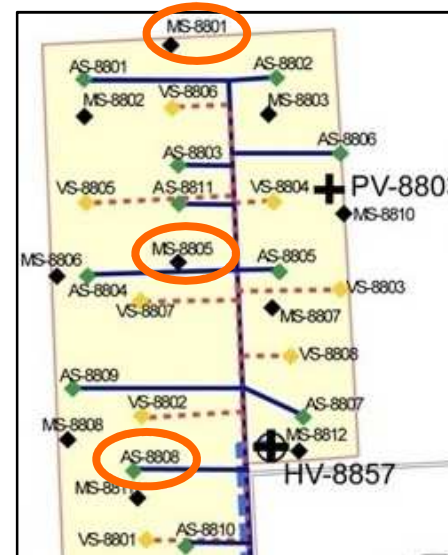
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Bratislava, 12./13. 09. 2016

- Intro
- ISCO
- PCR
- Site
- Pollution
- Lab
- Pilot
- Summary

Microbial Metabolic Potential

- Enhanced attenuation:
- Nutrients and TEA



Intro

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).

Site

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

Pollution

Lab

Pilot

Enhanced attenuation potential => denitrification

Summary

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Bratislava, 12./13. 09. 2016