Summer school on Advanced Oxidation processes
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ISCO - Fenton-like treatment of MtBE contaminated groundwater

Renato Baciocchi

Laboratory of Environmental Engineering
University of Rome “Tor Vergata”

Outline

- What is ISCO?
- Basics of ISCO design
- Why do we need to cleanup MtBE ?
- Case study

  - Feasibility study of ISCO treatment of MtBE (Lab + Modeling)

  - ISCO pilot-scale test on a MtBE contaminated site

  - Lesson learned and conclusions

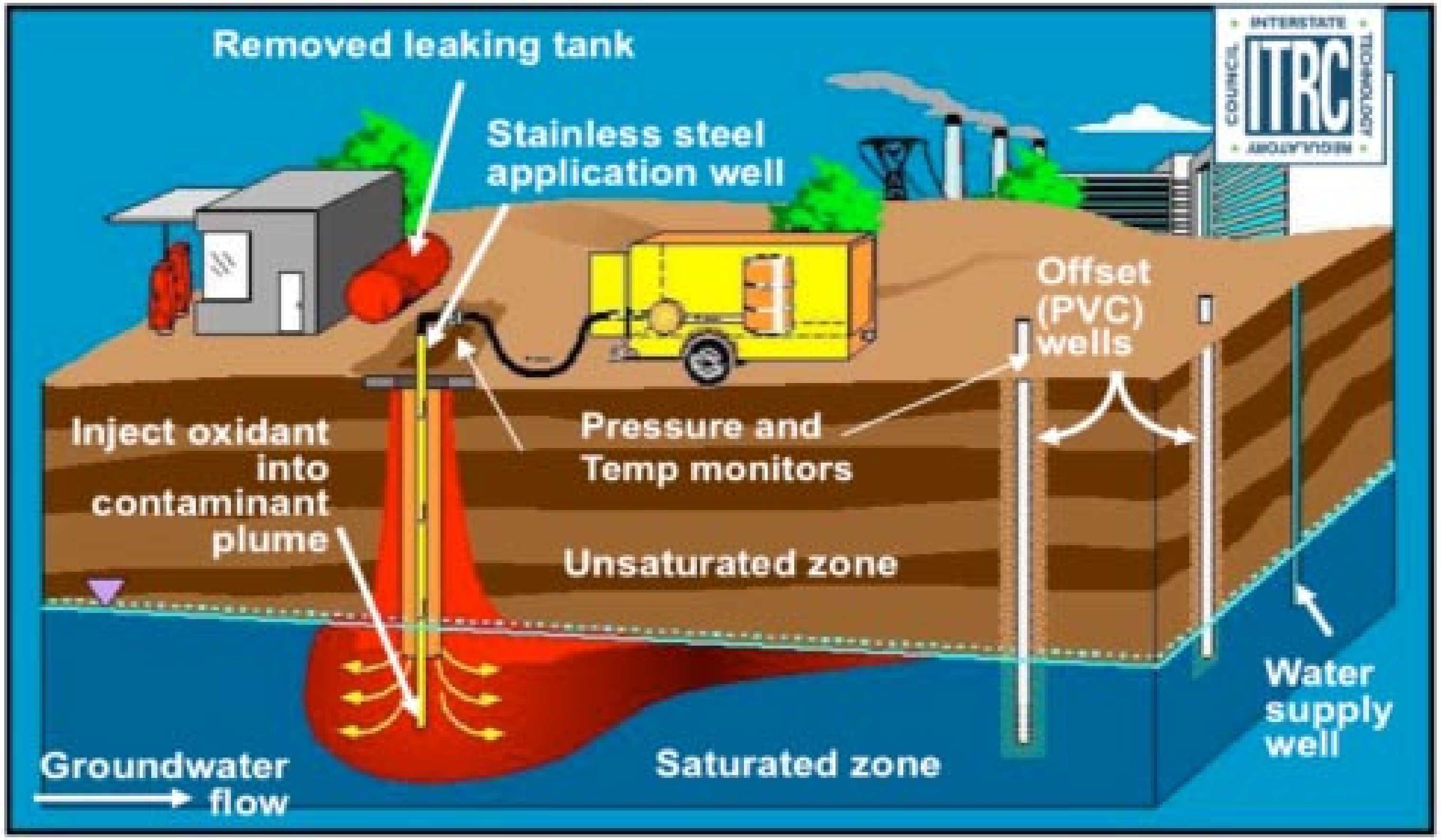
What is ISCO

ISCO = In-Situ Chemical Oxidation

Application of an AOP to the subsoil

- Hydrogen peroxide (Fenton’s reagent)
- Potassium permanganate
- Sodium persulfate (activated)
- Ozone

What is ISCO



In-Situ Chemical Oxidation (ISCO)

What is ISCO

Oxidant	Reactive Species	Form	Persistence (1)
Permanganate	MnO_4^-	powder/liquid	>3 months
Fenton's	$\cdot OH$, $\cdot O_2^-$, $\cdot HO_2$, HO_2^-	liquid	minutes - hours
Ozone	O_3, $\cdot OH$	gas	minutes - hours
Persulfate	$\cdot SO_4^{2-}$	powder/liquid	hours - weeks

from: EPA/600/R-06/072 August, 2006

What is ISCO

Oxidant	Redox potential (E^o) (V)
Hydroxyl radical	2.8
Sulfate radical	2.6
Ozone	2.07
Persulfate ion	2.01
Hydrogen peroxide	1.70
Permanganate ion	1.68

What is ISCO

$$H_2O_2 + Fe^{2+} \Rightarrow Fe^{3+} + OH^- + OH^\bullet$$

$Fe^{3+} + H_2O_2 \Rightarrow Fe^{2+} + HO_2^\bullet + H^+$

Redox cycle Fe^{2+}/Fe^{3+}

$HO_2^\bullet + Fe^{3+} \Rightarrow O_2 + H^+ + Fe^{2+}$

$HO_2^\bullet \Leftrightarrow O_2^{-\bullet} + H^+$

Hydroperoxide radical

$O_2^{-\bullet} + Fe^{3+} \Rightarrow Fe^{2+} + O_2$

$O_2^{-\bullet} + Fe^{2+} + 2H^+ \Rightarrow Fe^{3+} + H_2O_2$

$O_2^{-\bullet} + HO_2^\bullet + 2H^+ \Rightarrow HO_2^- + O_2$

Superoxide radical

$OH^\bullet + Fe^{2+} \Rightarrow Fe^{3+} + OH^-$

$OH^\bullet + H_2O_2 \Rightarrow HO_2^\bullet + H_2O$

$H_2O_2 \Leftrightarrow H_2O + ½ O_2$

Non productive consumption

What is ISCO

Fenton process:

- Reaction in aqueous phase
- $[H_2O_2]$ low ($< 10^{-2}$M)
- Acid pH (2 – 3)
- Catalyst (Fe^{2+}, Fe^{3+})

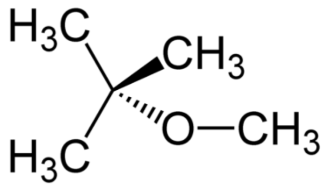
Modified Fenton's process:

- Soil + Water;
- $[H_2O_2]$ high ($> 10^{-2}$ M);
- "natural" pH(6 – 8);
- Catalyst (Fe^{2+}, Fe^{3+});
- Chelants (for Fe) or stabilizers of H_2O_2

Fenton-like process:

- Soil + Water;
- $[H_2O_2]$ high ($> 10^{-2}$ M);
- "natural" pH (6 – 8);
- Use of Fe present in the soil;
- Chelates (for Fe) + Stabilizers of H_2O_2

Why do we need to cleanup MtBE?



- **Methyl-t-butil ether (MtBE)**
- is used as an additive for gasoline to improve combustion efficiency and to increase the octane rating as replacement for tetra-ethyl lead

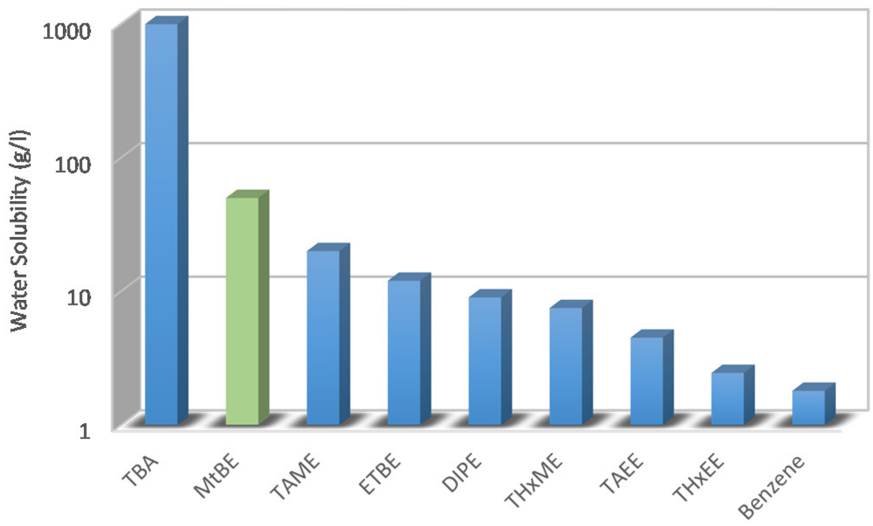
In Europe MtBE is added to gasoline in the range 5 -20% (mean values around 5%)

	Ether Oxygenates				
	MTBE	**ETBE**	**TAME**	**DIPE**	**TBA**
Total number of sampling events (n)					
	1,239	1,239	650	650	1,239
Mean (average) concentration in all European gasoline samples in 2000-2009 (m/m%)					
	5.39	0.91	0.29	0.00	0.03
Median concentration in all European gasoline samples in 2000-2009 (m/m%)					
	4.25	0.00	0.00	0.00	0.01
Maximum concentration observed in individual sampling rounds (m/m%)					
Concentration (m/m%)	20.43	15.50	11.22	0.88	1.03
Gasoline type	PULP	PUL	PUL	PULP	PULP
Period	Summer 2001	Winter 2008/2009	Winter 2007/2008	Winter 2002/2003	Winter 2000/2001
Country	Romania	France	Finland	Greece	Switzerland

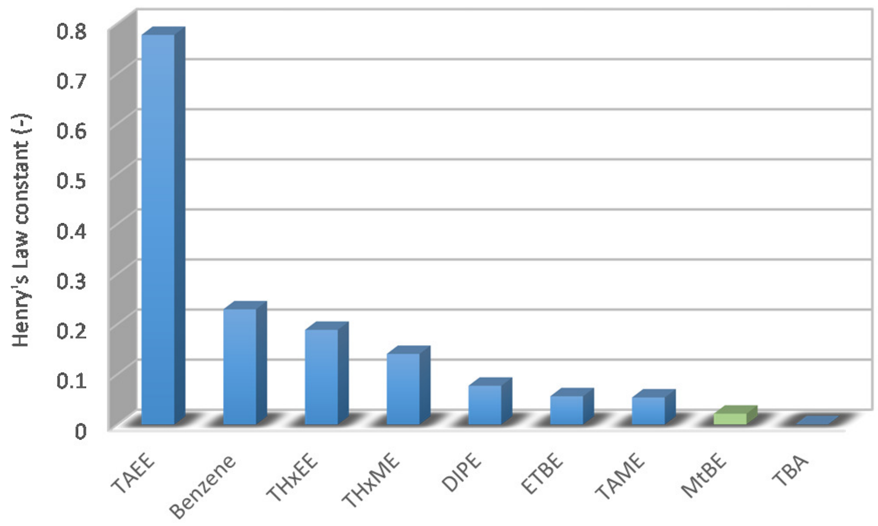
Concawe, 2010

Why do we need to cleanup MtBE?

Solubility in water (g/l)



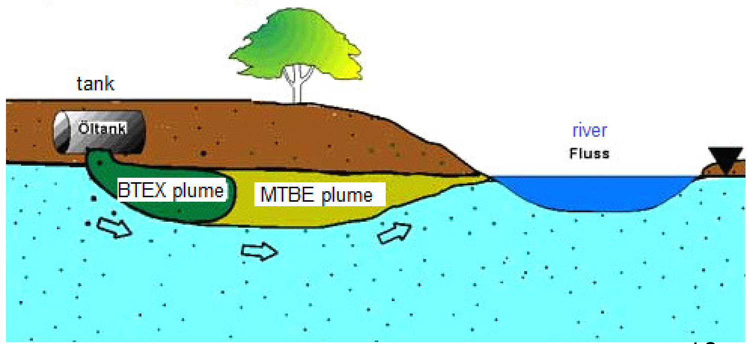
Henry's constant (-)



+ **Highly soluble**
+ **Poorly volatile**
+ **Poorly biodegradable**

= **Effects on groundwater quality**

Groundwater contamination with gasoline mixture: MTBE plume is reaching the river first



Basics of ISCO design

- ✓ **Lab-scale feasibility study**
  - selection of the most efficient oxidant
  - oxidant lifetime/ decomposition kinetics
  - optimization of oxidant dosage

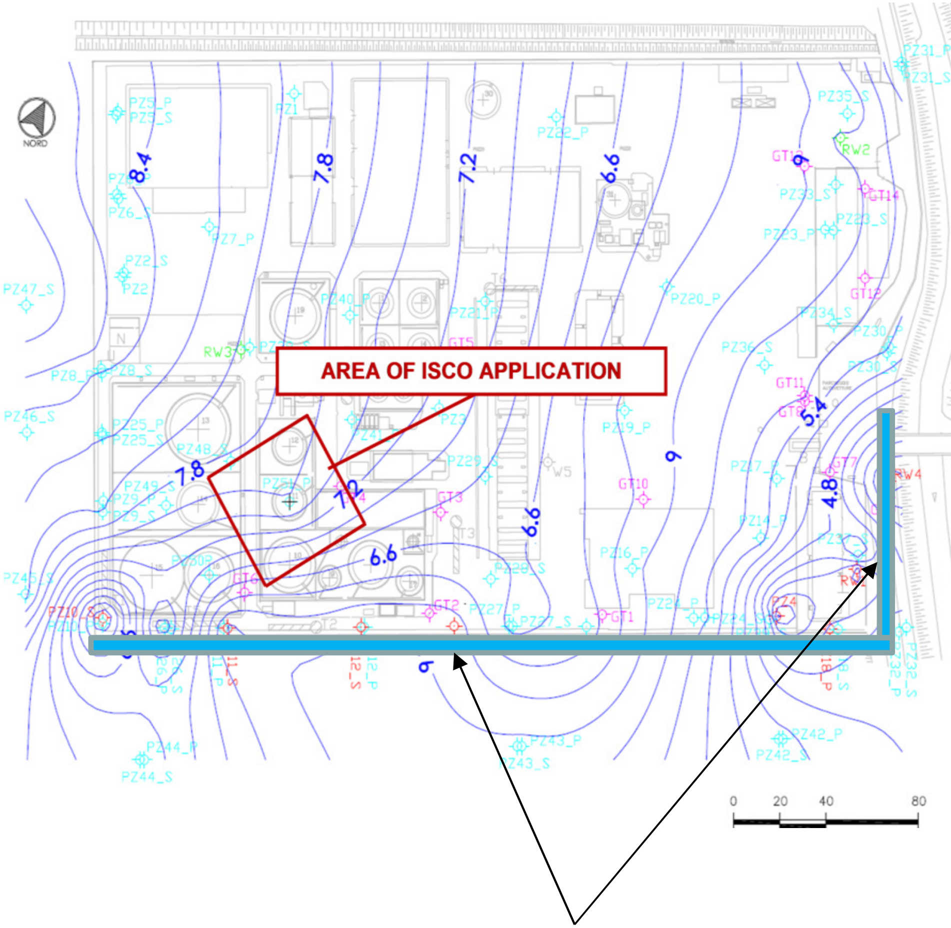
- ✓ **Hydrogeological characterization**
  - indirect estimate of geological characterisitics
  - pumping tests (eventually slug tests)
  - test with tracers: transmissivity of the aquifer

- ✓ **Modelling and design of the pilot test**

- ✓ **ISCO Pilot test operation**

- ✓ **Design of full scale ISCO remediation**

Case study: former petroleum storage tank site



Hydraulic barrier of Pump &Treat

- Only groundwater contamination:
  - MtBE: 2000 ÷ 5000 μg/l;

- Confined aquifer (5 ÷ 6 m depth from ground level);
- Artificial groundwater’s gradient ~ 3%

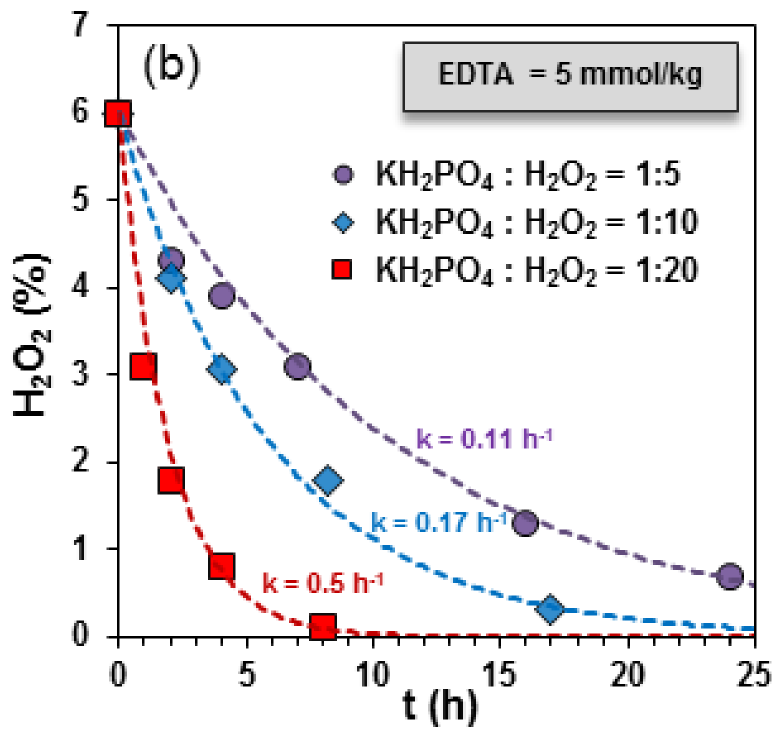
- Fine sand and silt;
- Heterogeneous soil (each meter presents different texture).

Lab-scale feasibility test

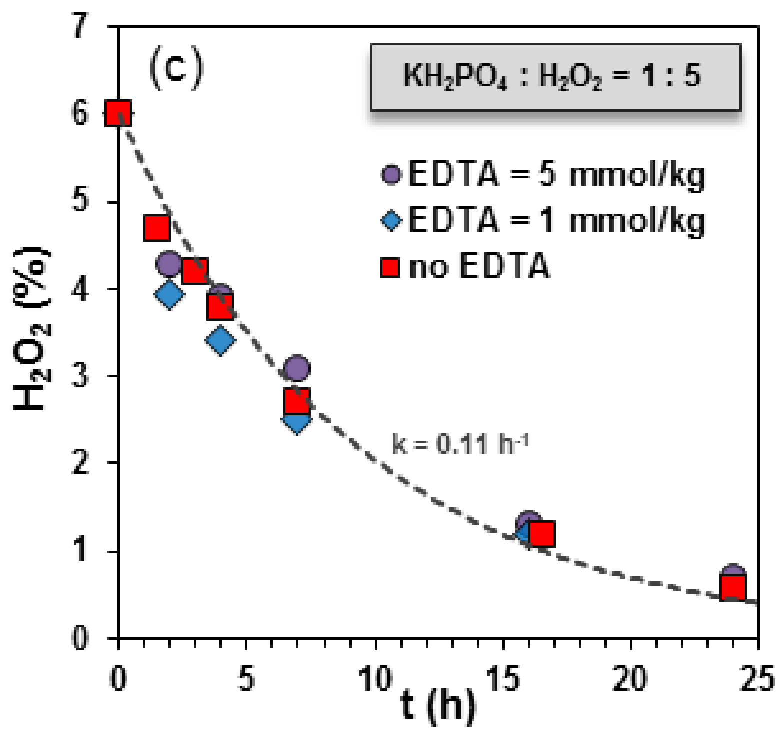
- Selection of best oxidant: H_2O_2 (based on preliminary tests)
- Oxidant dosage: concentration 6 % (based on preliminary tests)

- Oxidant lifetime/decomposition kinetics

Effect of stabilizer



Effect of chelate



Hydrogeological characterization

- Aquifer Transmissivity (pumping test) = 4.97×10^{-4} m^2/s;
- Porosity = 35%.

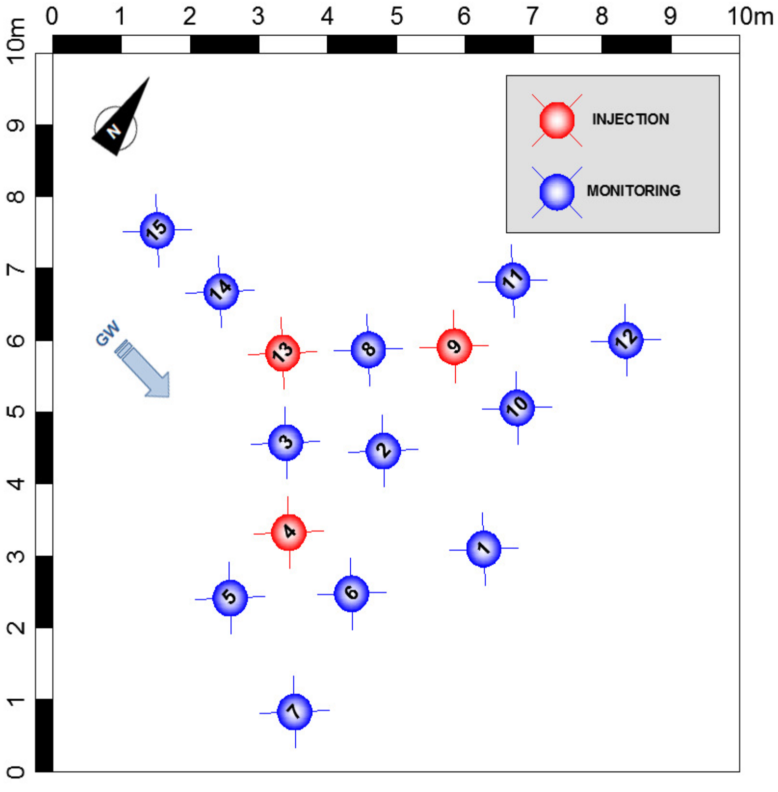
Modelling study 2D

- Pilot scale layout selection;
- Identification of the most suitable injection rate;

Parameter	Units	Value
Injection flow rate	m^3/day	2- 10
Hydrogen peroxide concentration	%wt	6
Aquifer trasmissivity	m^2/s	5×10^{-4}
Aquifer thickness	m	2 - 4
Hydraulic gradient (with P&T in operation)	%	3
Porosity	-	0.35
H_2O_2 decomposition rate constant (1st order)	h^{-1}	0.11
H_2O_2 injection time	h	15

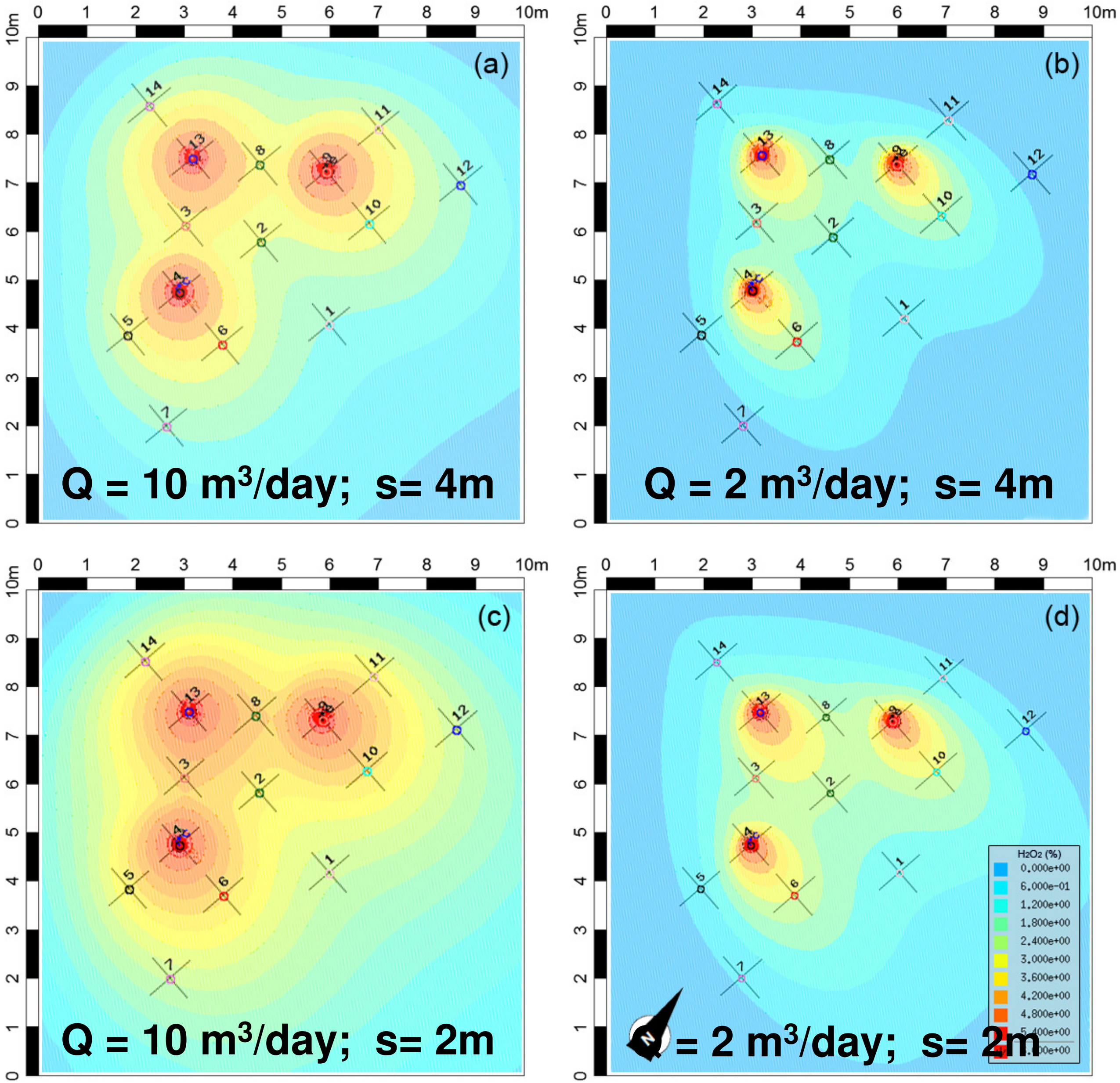
Design of the pilot test layout

- ✓ N. 3 injection wells
- ✓ N.10 monitoring wells
- ✓ Depth of about 10 meters below ground



Off gases from each well are collected and treated with GAC before venting.

Modeling of the ISCO pilot test (H_2O_2 delivery)



Hydrogen peroxide distribution of hydrogen peroxide after 15 hours injection

Different flow rates and thickness of the target aquifer were assumed

Modeling of the ISCO pilot test (H_2O_2 ROI)

Modelling study 2D

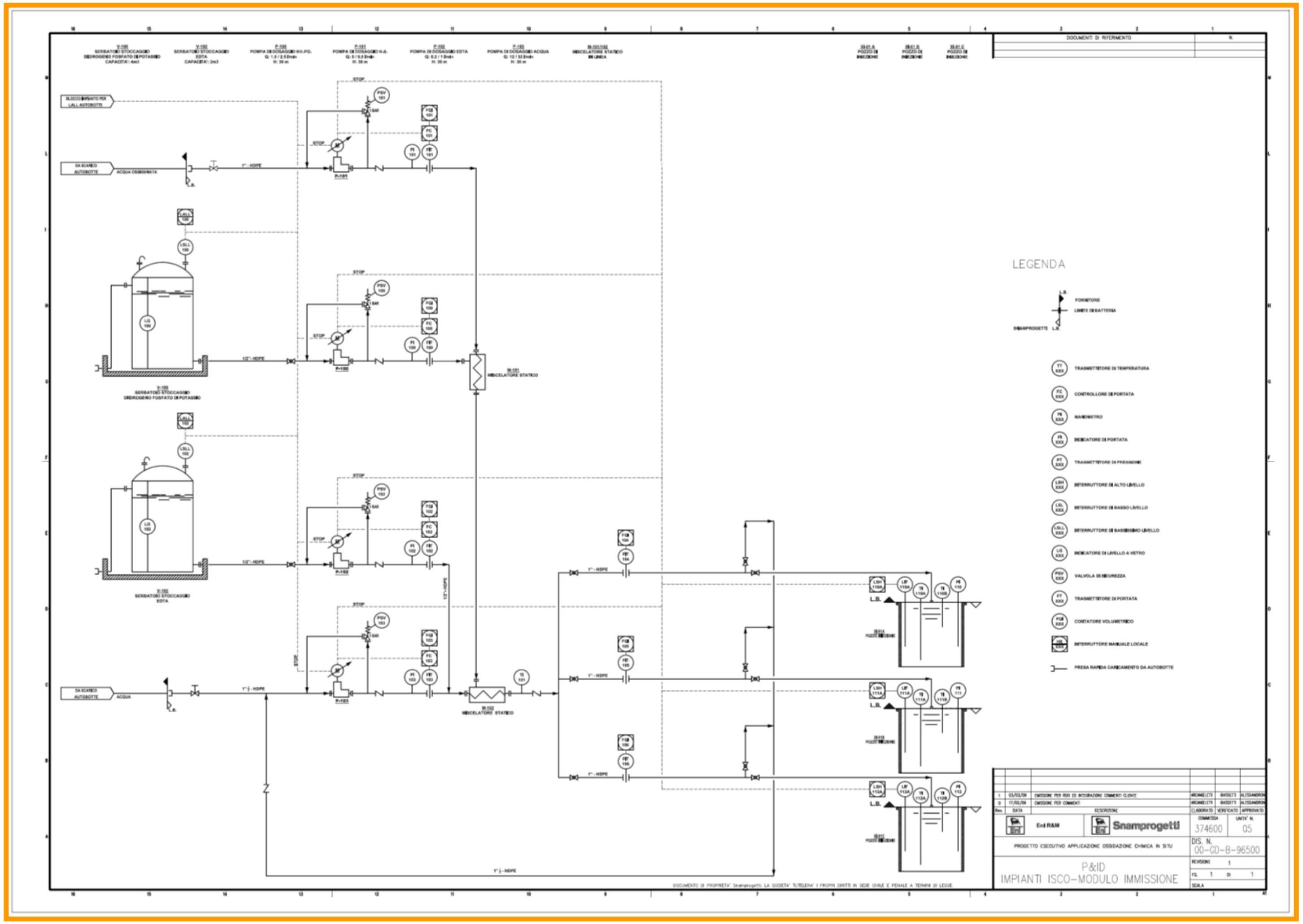
Conditions simulated with FEFLOW	ROI (m)	O_{2max} (m^3/h)	Δh (m)
Q = 10 m^3/day for 15 h (k = 0.11 h^{-1}; thickness 4 m)	2.5 – 4	9	0.6
Q = 2 m^3/day for 15 h (k = 0.11 h^{-1}; thickness 4 m)	1.2 – 2.5	1.8	0.15
Q = 10 m^3/day for 15 h (k = 0.11 h^{-1}; thickness 2 m)	3.3 – 5.5	9	0.6
Q = 2 m^3/day for 15 h (k = 0.11 h^{-1}; thickness 2 m)	1.5 – 3.5	1.8	0.15

ROI = Radius of Influence
O_{2max} = Maximum stoichiometric O_2 production by H_2O_2 decomposition
Δh = Estimated increase of water head near the injection well

Pilot plant

Injection skid

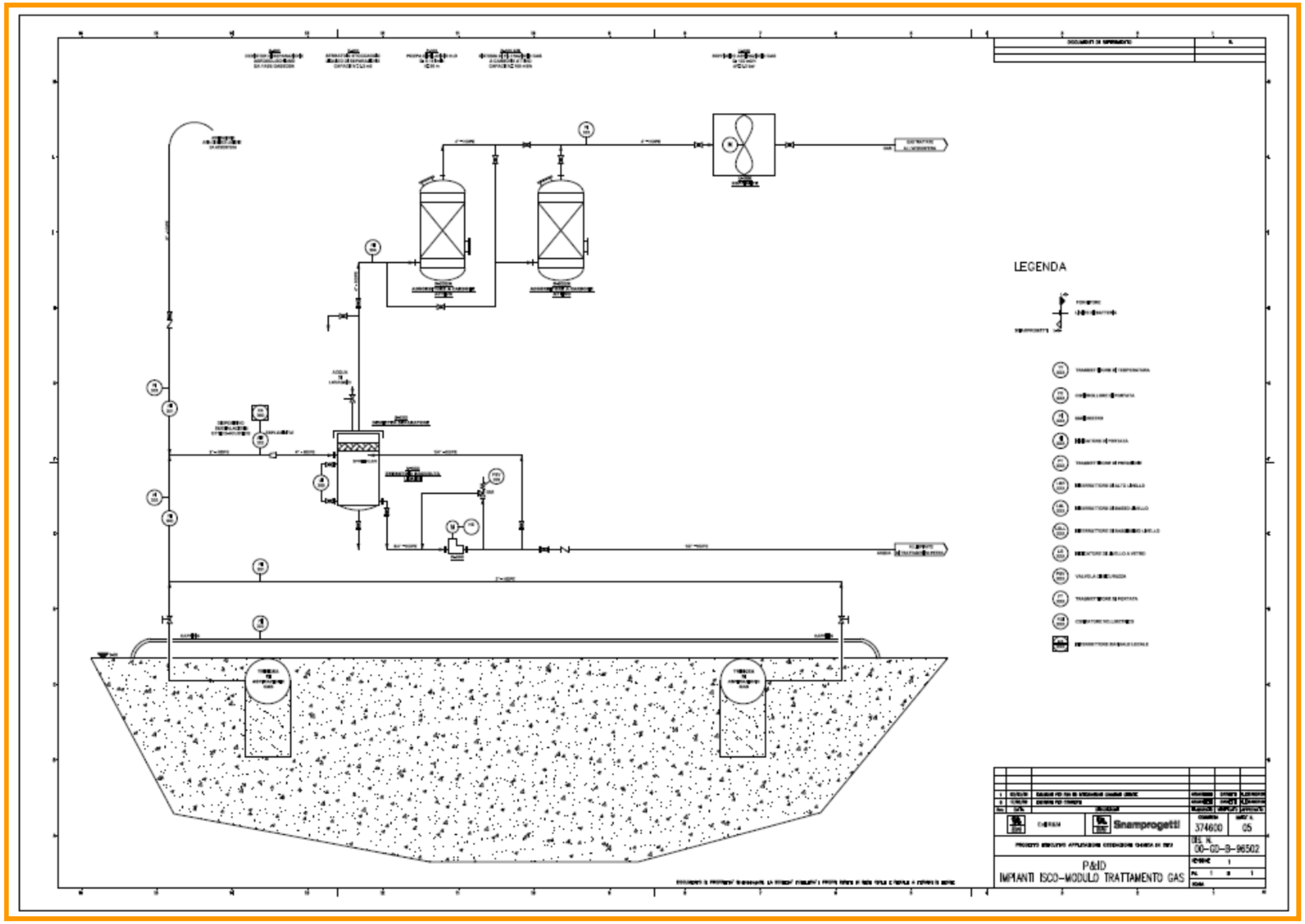
Q_{inj}= 2 ÷10 m^3/d for each injection well



Pilot plant

Soil vapor extraction

$Q_{off\text{-}gas} = 20 \div 100\ m^3/h$



Pilot plant and injection/monitoring wells

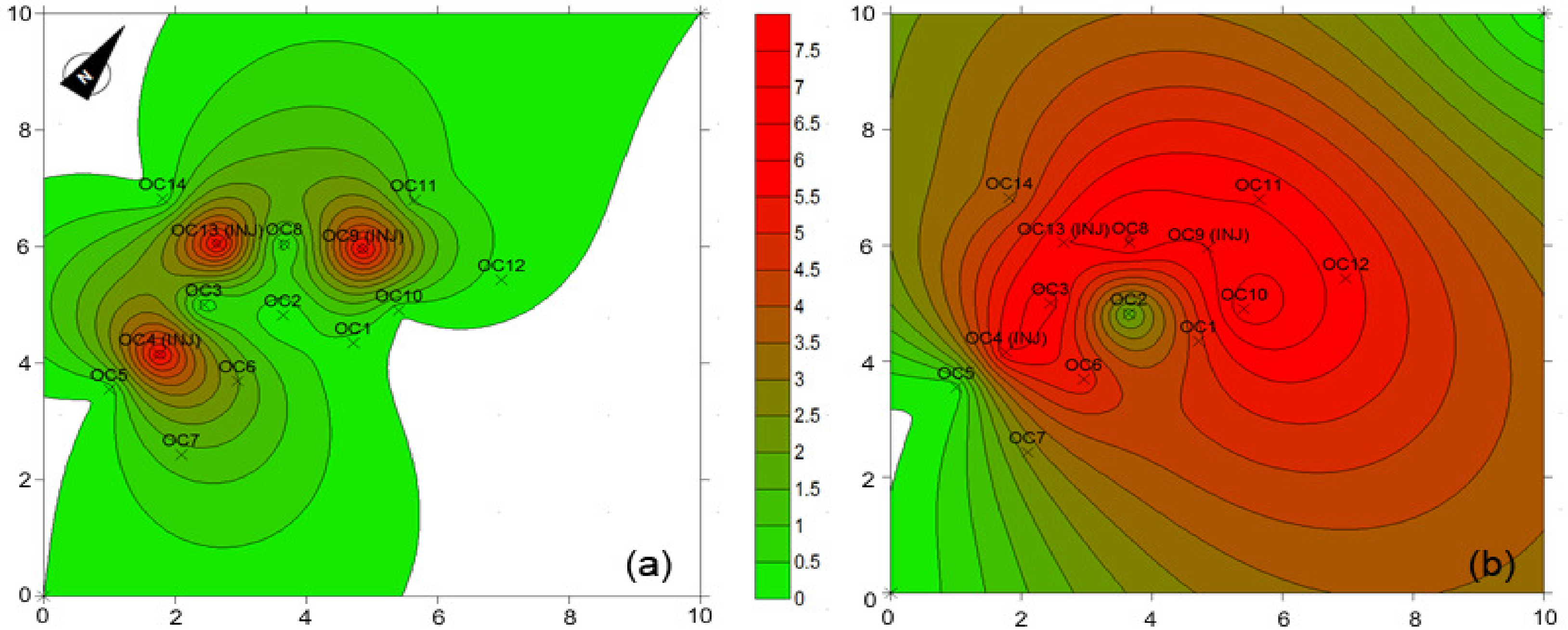
- Pilot plant

- Injection and monitoring wells

Pilot plant management

- **Before H_2O_2 injection, a chelating agent (EDTA) solution was injected**;
- **One injection cycle was completed (16h of injection):**
  - H_2O_2 6%, Q_{inj} = 2 m^3/d (for each inj. well)

Groundwater monitoring during injection (H_2O_2)

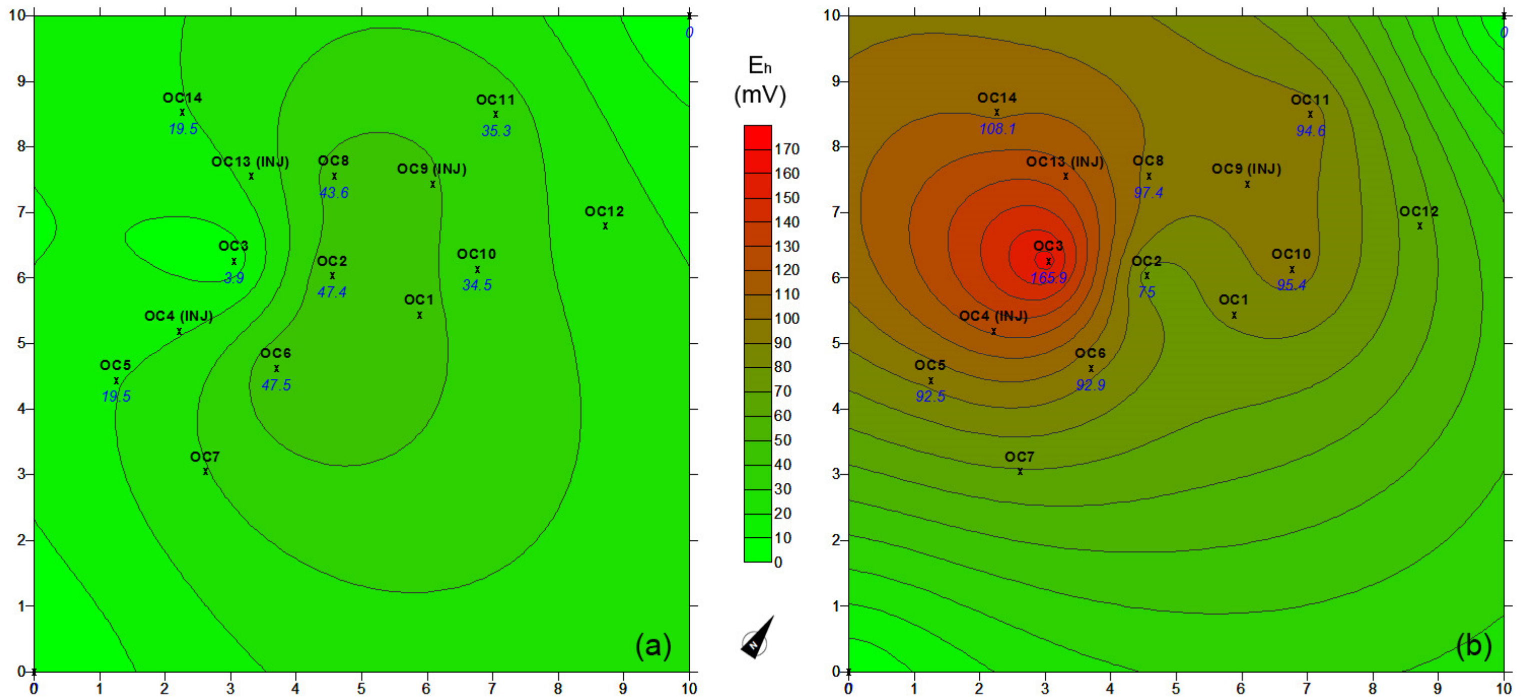


Results of the pilot-scale test - H_2O_2 (%wt) contour lines (axis scale in m):

(a) after 6h injection;

(b) after 11h injection.

Groundwater monitoring during injection (Redox)

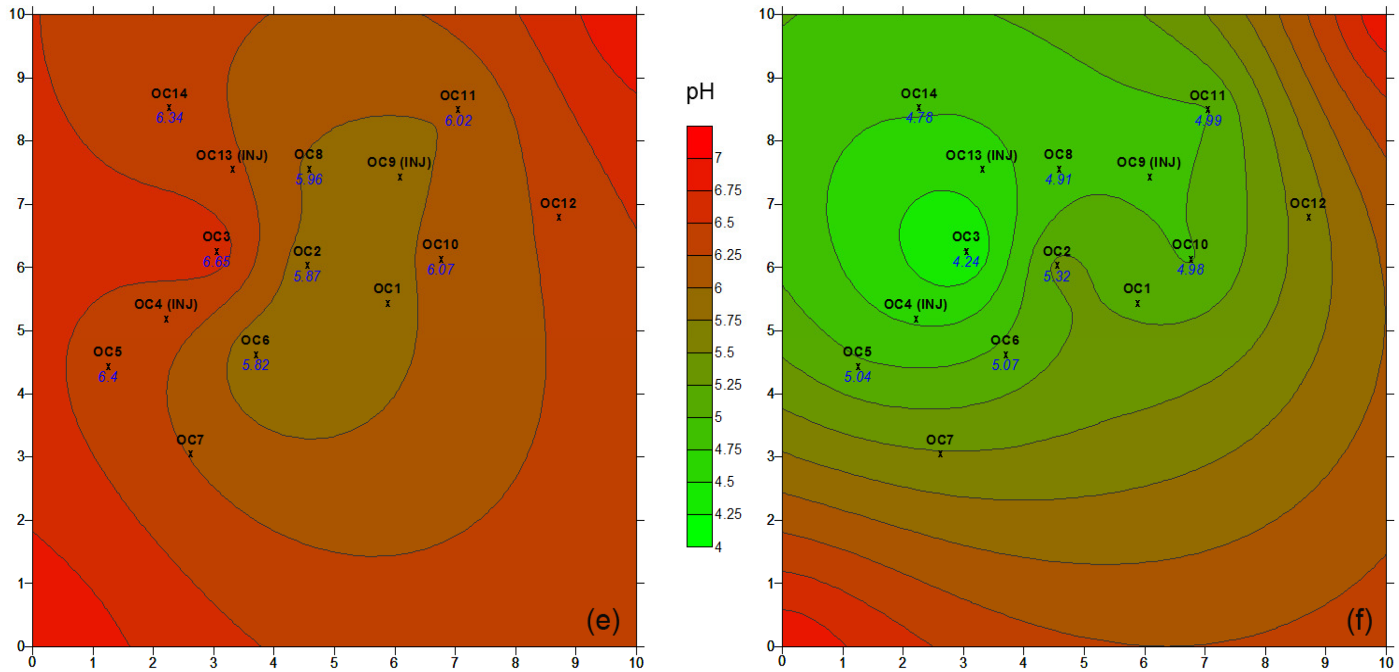


Results of the pilot-scale test - Redox (mV) contour lines (axis scale in m):

(a) after 6h injection;

(b) after 12h injection.

Groundwater monitoring during injection (pH)

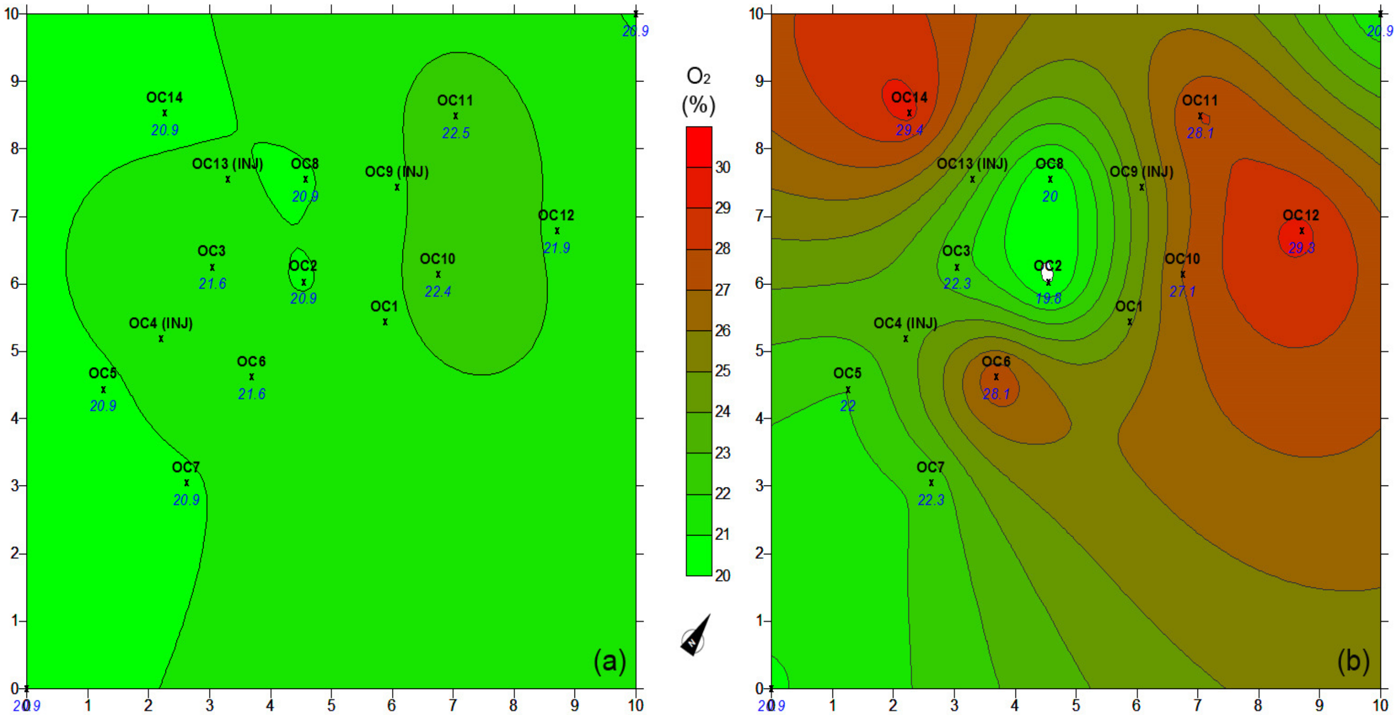


Results of the pilot-scale test - pH contour lines (axis scale in m):

(a) after 6h injection;

(b) after 12h injection.

Off-gas monitoring during injection (O_2)

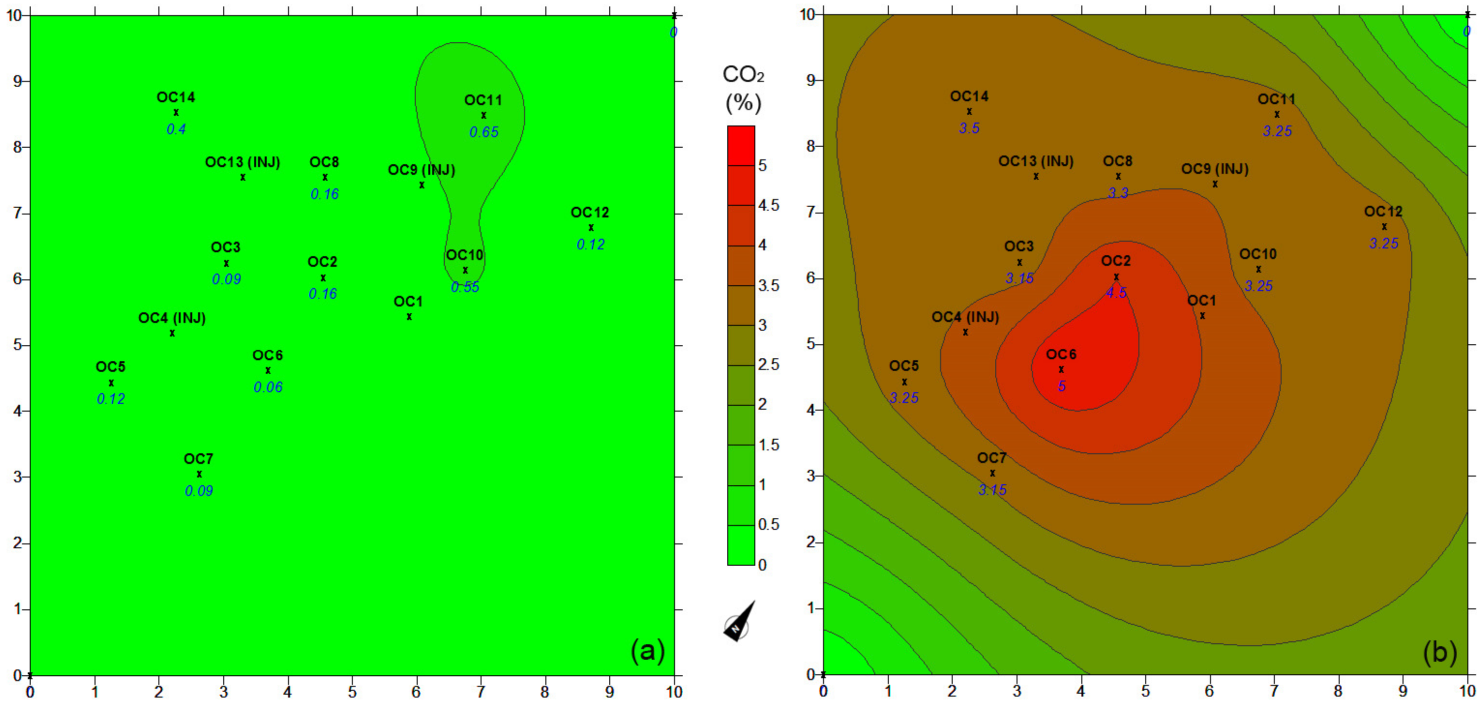


Results of the pilot-scale test - O_2 (%) contour lines (axis scale in m):

(a) after 6h injection;

(b) after 12h injection.

Off-gas monitoring during injection (CO_2)

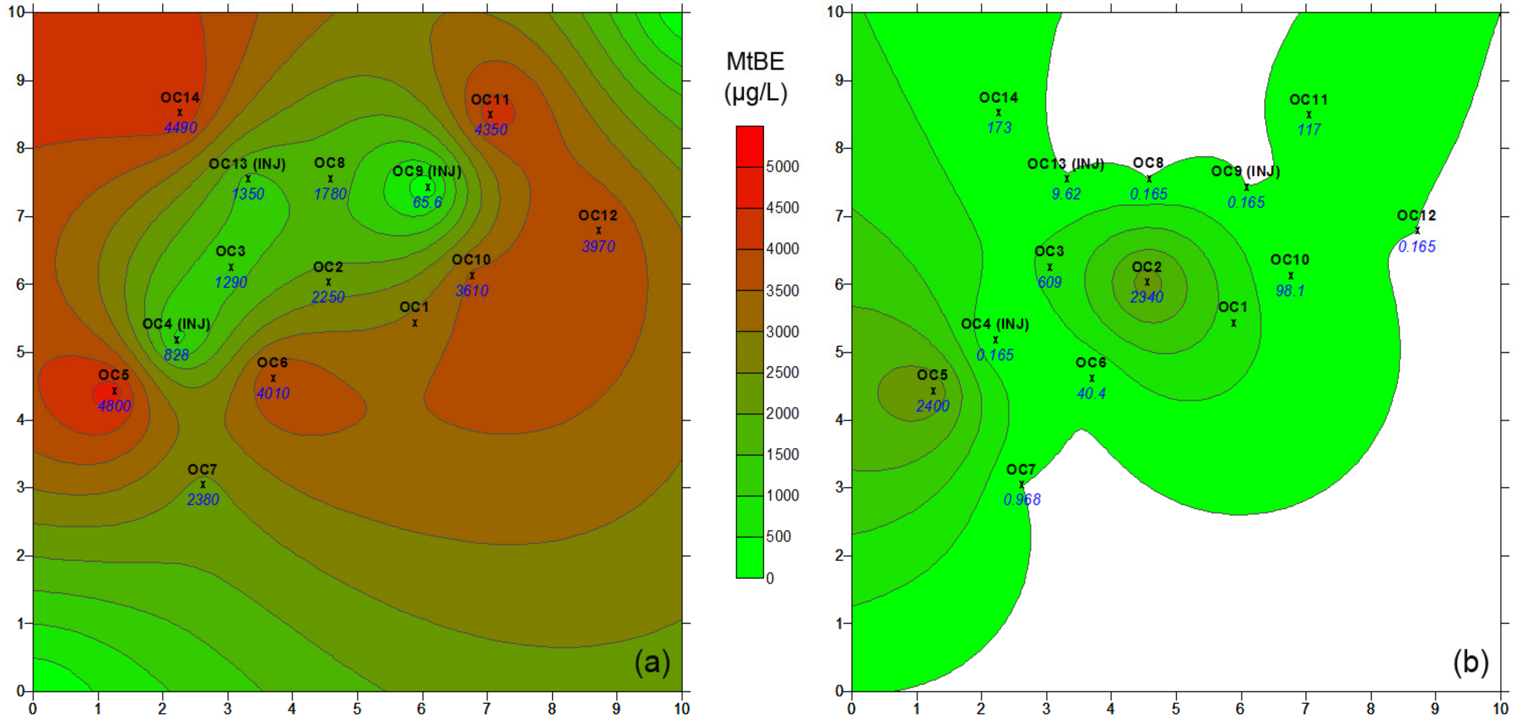


Results of the pilot-scale test - CO_2 (%) contour lines (axis scale in m):

(a) after 6h injection;

(b) after 30h injection.

Groundwater analysis (MtBE)

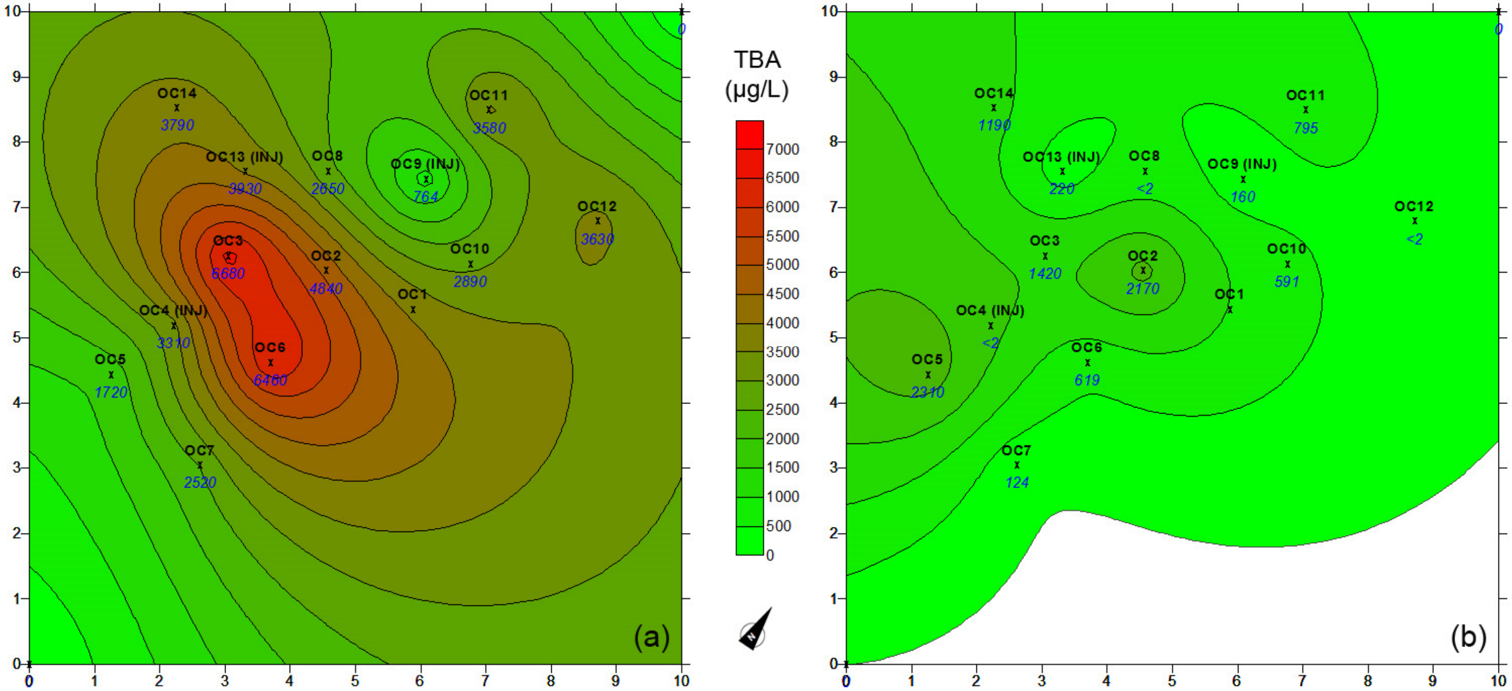


Results of the pilot-scale test -- MtBE (µg/L) contour lines (axis scale in m):

(a) after chelating agent injection;

(b) after H_2O_2 injection.

Groundwater analysis (TBA)

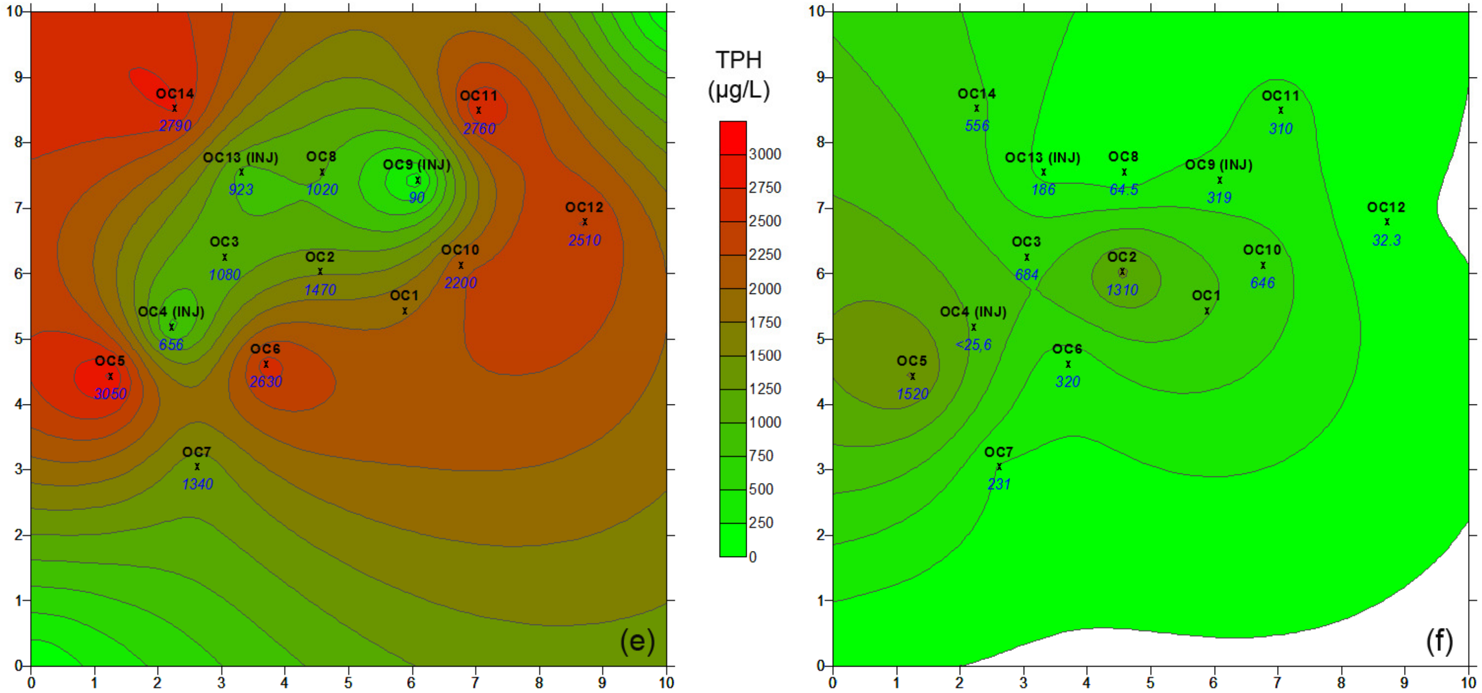


Results of the pilot-scale test -- TBA (µg/L) contour lines (axis scale in m) :

(a) after chelating agent injection;

(b) after H_2O_2 injection.

Groundwater analysis (TPH)



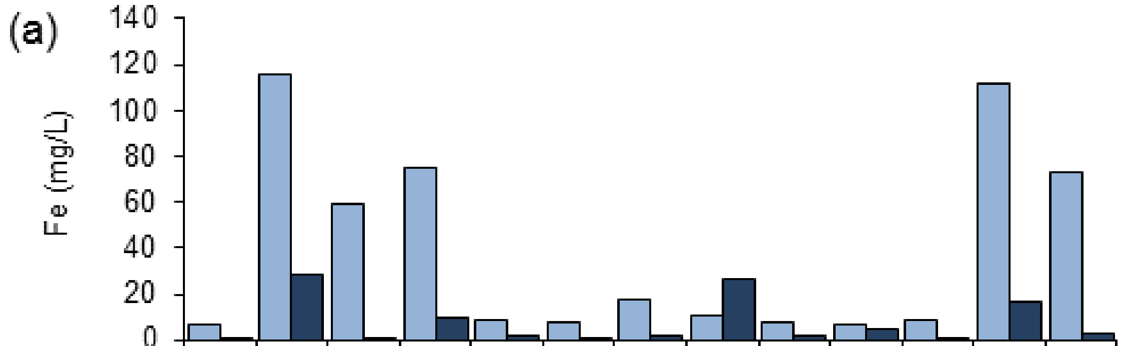
Results of the pilot-scale test -- TPH (µg/L) contour lines (axis scale in m) :

(a) after chelating agent injection;

(b) after H_2O_2 injection.

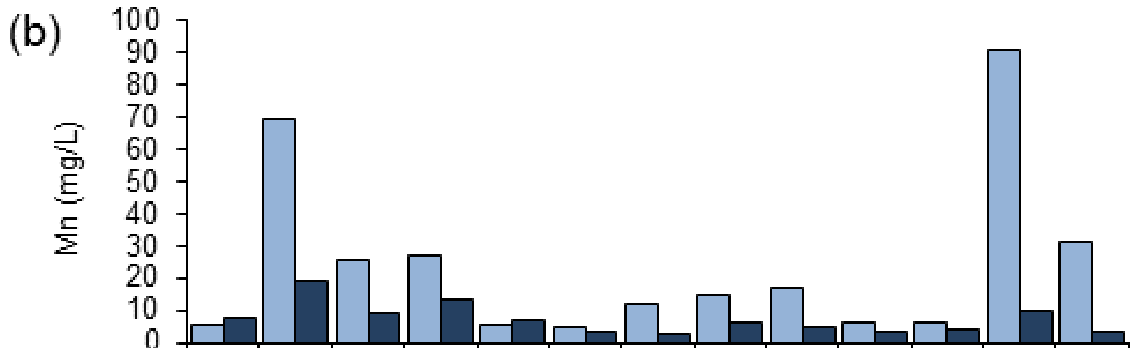
Secondary effects: metal mobilization

Fe



	2	3	4 (INJ)	5	6	7	8	9 (INJ)	10	11	12	13 (INJ)	14
After EDTA	7,0	116,0	59,0	74,7	8,4	8,1	17,2	10,5	7,7	6,7	8,5	112,0	73,5
After ISCO	0,7	28,7	0,7	9,8	1,6	0,2	1,6	26,7	1,6	4,3	0,1	16,7	3,1

Mn



	2	3	4 (INJ)	5	6	7	8	9 (INJ)	10	11	12	13 (INJ)	14
After EDTA	5,4	69,3	25,9	27,1	5,2	5,0	11,7	14,8	16,7	6,4	6,2	90,8	31,3
After ISCO	7,6	18,9	9,1	13,3	6,6	3,7	2,9	6,5	5,0	3,3	4,2	9,7	3,4

Mass balance

It was performed on the carbon dioxide produced by MtBE mineralization

Measured CO_2: estimated from the flow rate of each off-gas extraction well (approximately 1.5 m3/h) and the corresponding CO_2 concentration measured at different time intervals.

Calculated CO_2:

$$CO_2 = \gamma_i \cdot \frac{M_{in,i} - M_{out,i}}{MW_i}$$

MtBE

$$C_5H_{12}O + \frac{15}{2}O_2 \rightarrow 5CO_2 + 6H_2O$$

TBA

$$C_4H_{10}O + 6O_2 \rightarrow 4CO_2 + 5H_2O$$

TPH

$$C_nH_m + \left(n + \frac{m}{4}\right)O_2 \rightarrow nCO_2 + \frac{m}{2}H_2O$$

Mass balance

Two assumptions were made

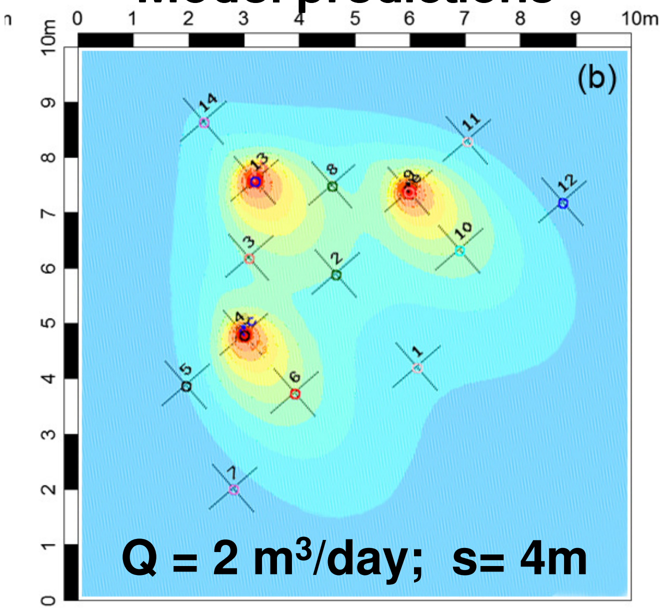
W: MtBE only in the water phase

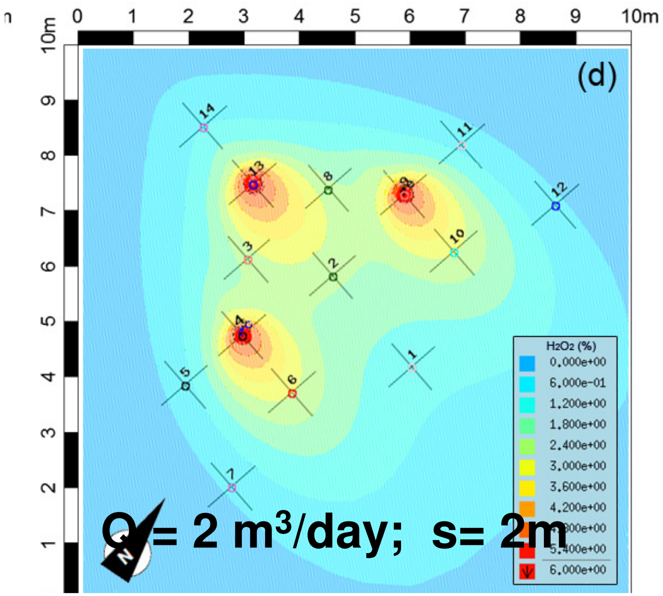
W+S: MtBE both in the water and soil phase $$C_s = C_w \cdot k_{oc} \cdot f_{oc}$$

Compound	Initial Mass (g)		Mass after ISCO (g)		Mass removed (g)		Calculated CO_2 (mol)		Measured CO_2 (mol)
	W	W + S	W	W + S	W	W + S	W	W + S	
MtBE	169	171	26.1	26.4	143	145	8.1	8.2	**78**
TBA	184	185	41.2	41.3	143	143	7.7	7.7	
TPH	108	1499	24.7	343.9	83	1155	5.8	79.8	
Total	**461**	**1855**	**92**	**412**	**369**	**1443**	**22**	**96**	

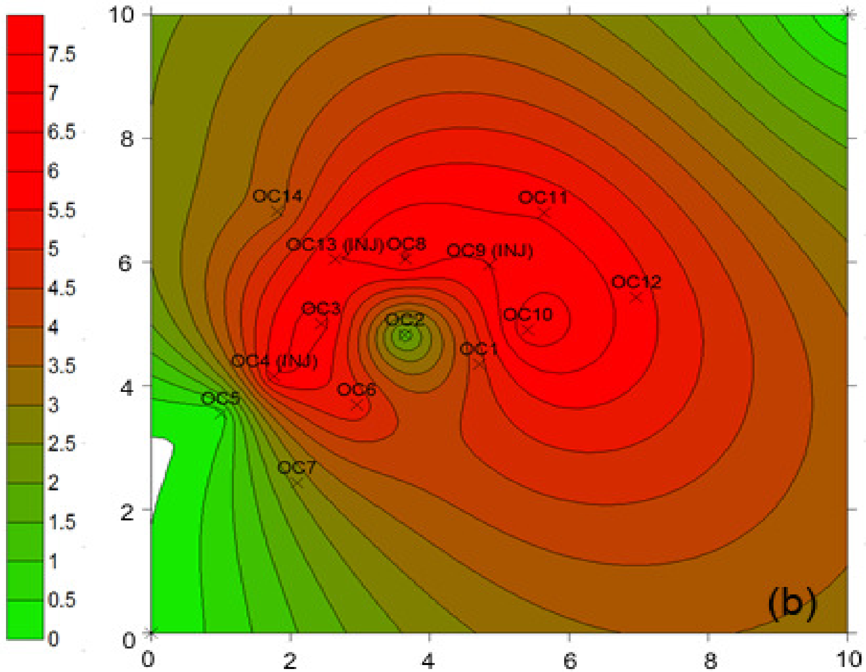
Lessons learned: H_2O_2 delivery

Model predictions





Field data



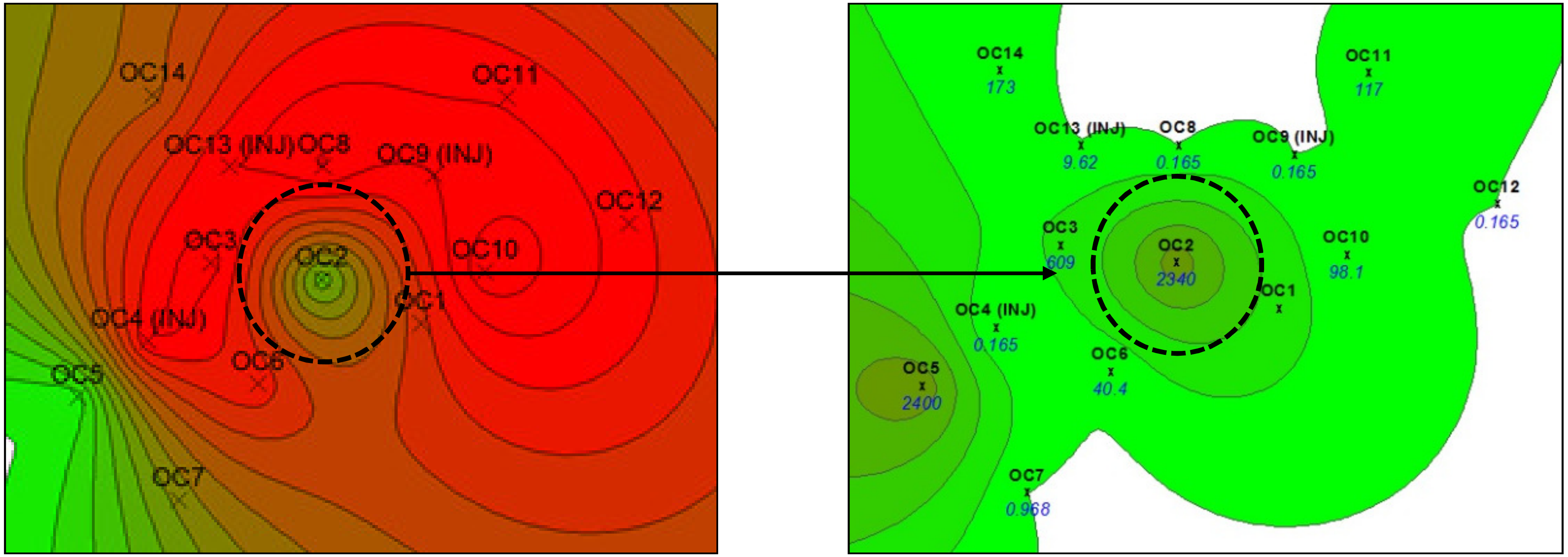
Possibly the oxidant propagation could have addressed only the more permeable layer, where probably most of MtBE contaminated groundwater should be present.

Lessons learned (H_2O_2 delivery vs. MtBE degradation)

Good MtBE removal by 1 peroxide injection (8 wells about 13 monitored wells have met the cleanup goals).

H_2O_2 propagation

Residual MtBE



No problem with gas production or local overheating.

Conclusions

- The feasibility test and the modeling activitied allowed for a proper design of the ISCO pilot-scale tests
- Where hydrogen peroxide delivery was effective, MtBE, TBA and TPH were effectively oxidised by ISCO using Fenton's reagent and mostly mineralized
- Issues related to soil heterogeneity probably affected the delivery of the oxidant and the effectiveness of the ISCO treatment

Acknowledgements

- Iason Verginelli, Daniela Zingaretti post-docs in our group
- Eni, for supporting this research and for pilot plant data