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From Discovery to Innovation...

The *eMaMoC* (electrolytic methanogenic-methanotrophic coupling) SYSTEM : A TOOL FOR BIOREMEDIATION OF CHLORINATED SOLVENTS

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Problem

- Environment contamination by chlorinated organic compounds including chlorinated solvents
- Since the 1940's, intensive use (as degreasers, solvents, reactants…) and disposal by a variety of industries
- Low rates of natural attenuation
- In Canada: over 1,000 tons per year of chlorinated solvents enter the Canadian environment
- Costly and difficult decontamination

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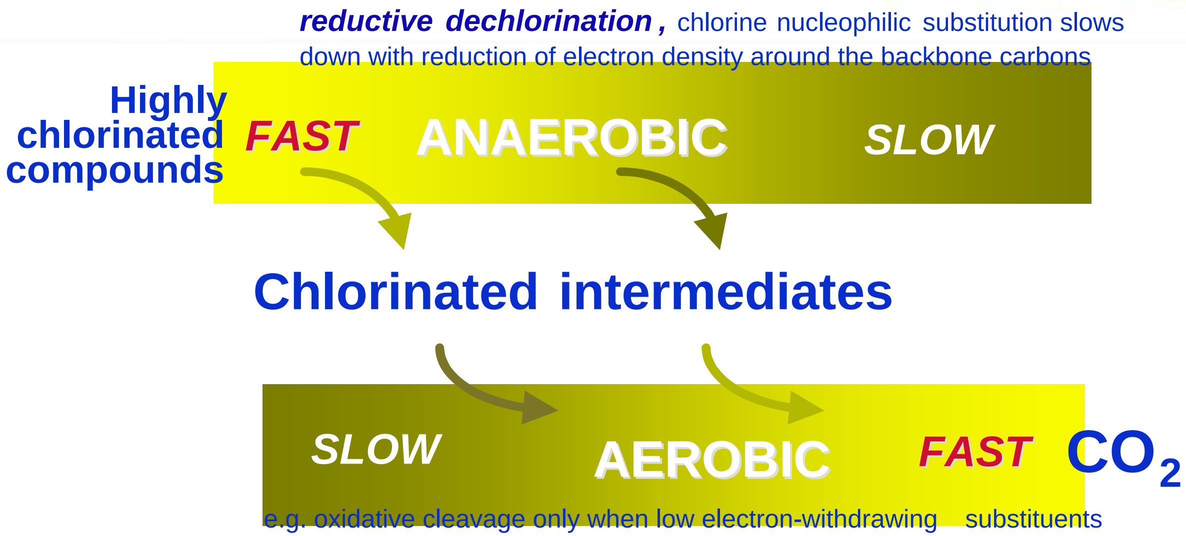
Approach



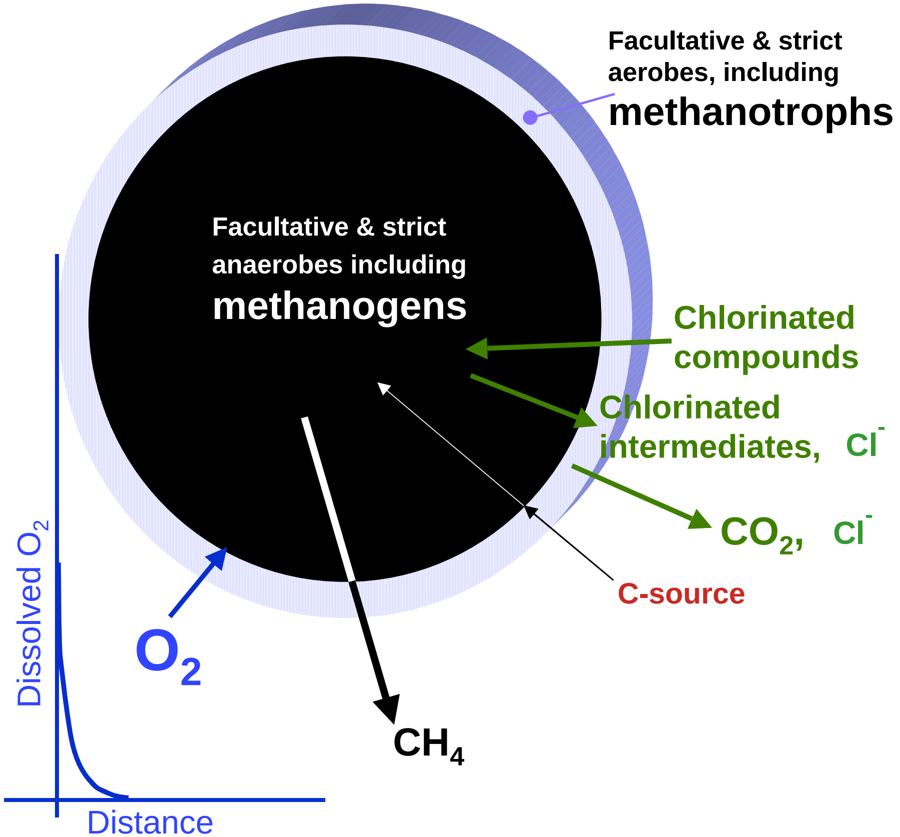
- reductive dechlorination by anaerobic bacteria, including methanogens, sequentially reduces the number of chlorines of highly chlorinated organic compounds (e.g. PCE)
- reductive dechlorination often results in accumulation of intermediates (e.g. DCE, vinyl chloride)
- in contrast aerobic microorganisms, methanotrophs in particular, are efficient degraders of less chlorinated compounds
- **complete biodegradation requires a combination of anaerobic and aerobic conditions (unless *Dehalococcoides* are present)**

Technology

- Coupled anaerobic-aerobic bioremediation is based on co-existence of anaerobic and aerobic bacteria in a biofilm

- Anaerobes can perform rapidly first dechlorination steps and produce methane

- Presence of O_2 and CH_4 is expected to promote the growth of methanotrophic bacteria, which may co-metabolically oxidize the less chlorinated intermediates left over by the anaerobic transformation



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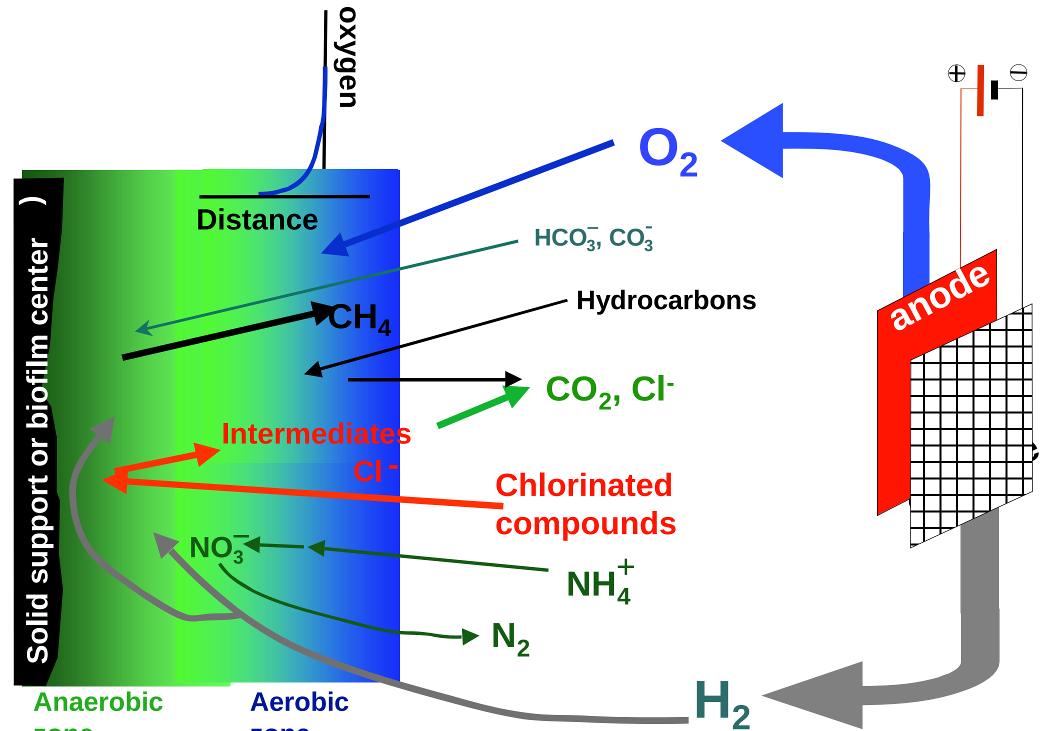
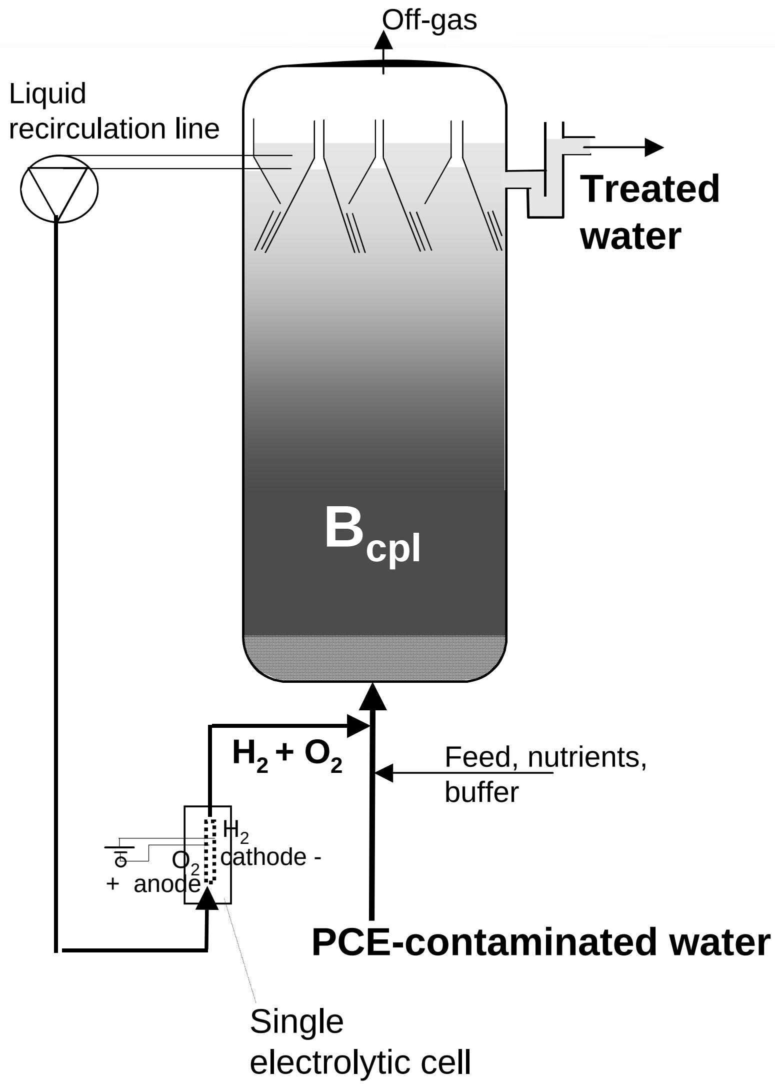
Technology (Cont'd)

- Recent development: use of water electrolysis
- Simultaneous supply of O_2 to aerobes and H_2 to methanogens and dechlorinators

⇒ Electrolytic Methanotrophic/ Methanogenic Coupling (**eMaMoC**) Technology



PROOF OF CONCEPT AT LAB-SCALE



Preliminary evaluation as a single-stage system

Experimental setup and conditions

- 5-L glass-made reactors (ID 10 cm)
- inoculated with unadapted anaerobic sludge granules
- v_{UP} between 0.4 and 2 m/h
- temperature : 22ºC
- electrodes (5 cmx10 cm) = titanium coated with iridium-dioxide
- electrical power applied : between 0.4 to 1.1 W (3 V x 140 mA - 4.5 V x 240 mA)
- oxygen generation rate : between 40 and 440 mg O_2/L_{rx}·d, with 20-95% transferred
- feed: PCE/EtOH-solution, nutrient solution (KH_2PO_4, K_2HPO_4, NH_4HCO_3), chloride-free trace metal solution

Abiotic tests: maximum 5% of dechlorination by the electrolysis alone

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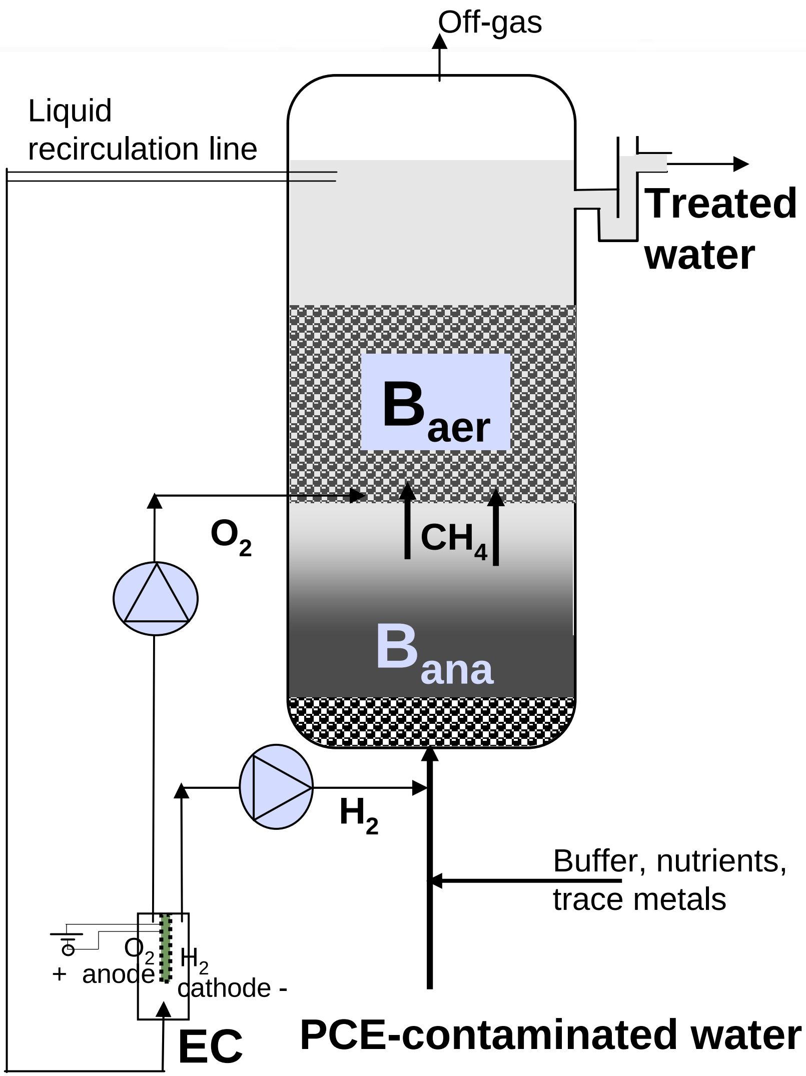
PCE degradation results of two single-stage 5-L eMaMoC reactors

Time (month)	Dissolved O_2 (DO) mg/L	v_{UP} m/h	PCE in mg/L	PCE in μM	PCE removed % [1]	1,2-*cis*-DCE out % [1]	Mineralization [3] %
Reactor I: HRT 1 d							
1	0	2	6.1	37	94	92	2
2-4	0.6-3	1	7.4	45	95	76	16±4
5	3-4	1	5.6	34	98	46	48±4
6	5-8	1	4.3	26	98	48	53±7
Reactor II: HRT 6.3 d							
1-3	1.5	0.43	8.6	52	98.1 [2]	65 [2]	31±17
4	2.3	0.75	8.6	52	99.5 [2]	40 [2]	58±8
5-6	2.2	0.75	5.5	33	98.5 [2]	14 [2]	83±5

temperature of 22-25°C
v_{UP} liquid upflow velocity in reactor
[1] includes off-gas loss : PCE <2 %; DCE <4%
[2] includes off-gas loss : PCE 0.1 %; DCE 0.02%
[3] based on mole balance between the inlet PCE and all products in the outlets (off gas and liquid)

- **higher DCE mineralization efficiency with an HRT of 6.3 days**
- **maximum mineralization efficiency = only 83%.**
- **mineralization limit probably related to oxidative degradation kinetics and/or DCE-oxidizing microorganisms content**

Kinetics study of the eMaMoC system in the two-stage mode



- two-stage assembly ⇒ to segregate methanogens and methanotrophs
- bottom methanogenic zone, inoculated with unadapted industrial anaerobic granules
- upper methanotrophic zone, packed with perlite (granulated silicate), inoculated with activated sludge
- temperature : 25ºC
- liquid upflow velocity : 0.5 – 2 m/h
- nutrients as above (ethanol load: 50 mg COD/L_{rx}-d)
- electrical power applied : 0.25-1.25 W

  (2.5 V x 100 mA - 5 V x 250 mA)
- O_2 generated & transferred : 100-500 mg O_2/L_{rxr}-d, 80% transferred

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Performance of the two-stage eMaMoC reactor,

under various operational conditions, for an operational period of 24 months.

HRT d	PCE load mg/L$_{rx}$ád	PCE$_{in}$ µM	PCE degrad. % (1)	DCE$_{out}$ % (1)	Mineral-ization % (3)	X_{rx}^{aer}	k_{max}^{DCE}
1	6.2±1.3	34±6.6	98 ±0.1	49±3	49 ±5	~ 0.8	n.d.
4	0.9±0.2	22±5	95 ±3	34±10	62 ±10	~ 0.9	1.15
8	1.1 ±0.2	50±6	97 ±3	32±4	64 ±4		2.3
24	0.35 ±0.04	46±9	100 ±0	15±5	85 ±5	1.4	3.9
47	0.24 ±0.09	59±19	100 ±1 (2)	5±6 (2)	95 ±5		
9	0.79 ±0.4	42±13	97 ±4	7 ±2	89 ±3	1.65	4.5
5	1.3 ±0.5	41±11	100 ±0.1	23 ±19	77 ±19		
2 (4)	*4.82 ±0.2*	*53±1.2*	*99.5 ±0.5*	*98 ±8*	*0 ±8*	1.33	

X_{rx}^{aer}: biomass content in the aerobic upper compartment, reported to the overall reactor volume
k_{max}^{DCE}: maximum specific DCE mineralization rate
(1) includes off gas losses : PCE <1 %; DCE <1%
(2) PCE, DCE not detected in off gas
(3) based on mole balance between the inlet PCE and all products in the outlets (off gas and liquid)
(4) no electrolysis, only H_2 supply
VSS : volatile suspended solids

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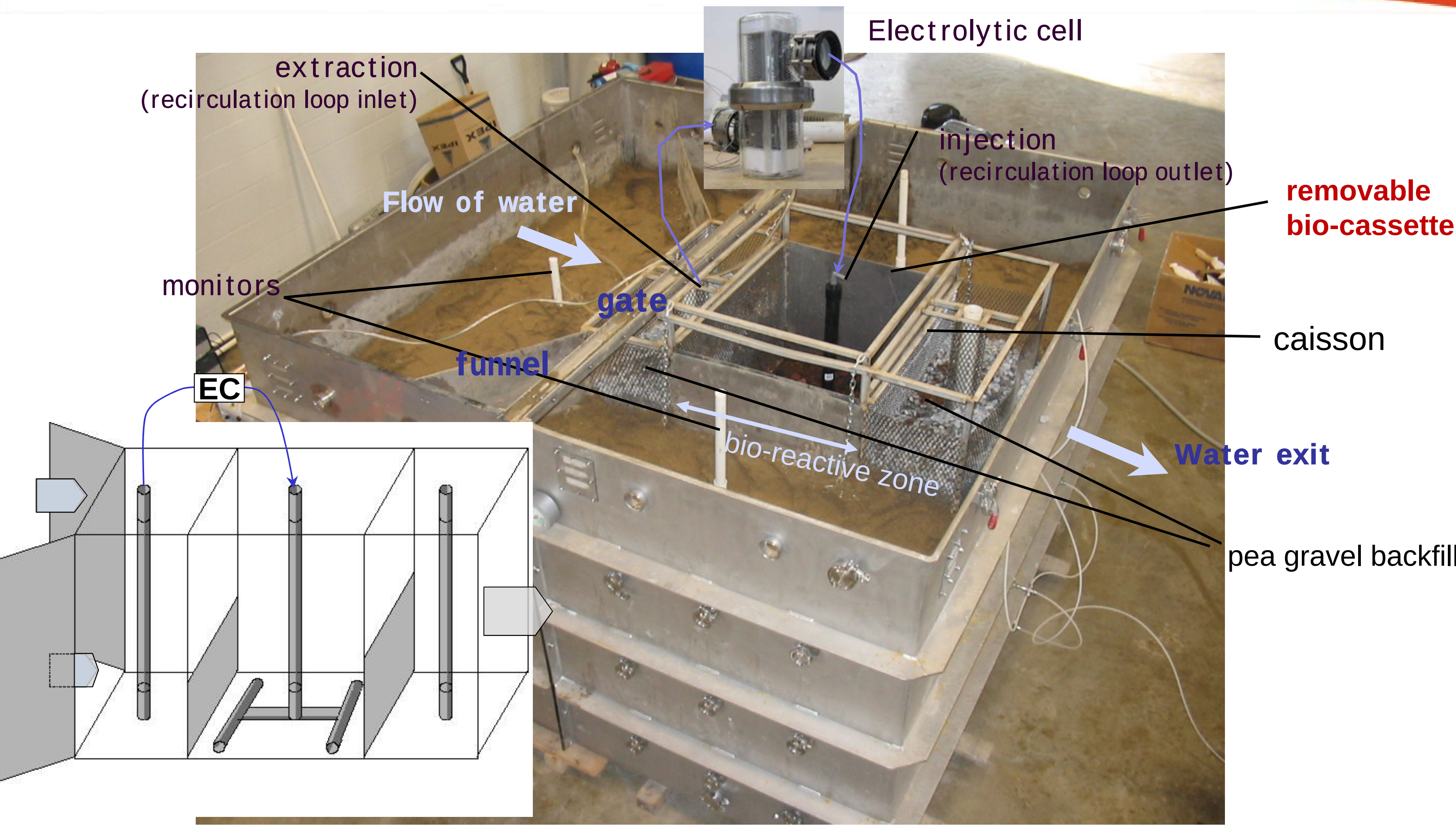
Pilot Scale : eMaMoC-based biobarrier within a funnel-&-gate remediation system



Pilot Scale : conditions and performance

- Linear velocity of groundwater : ~ 15 cm/day.
- Temperature: 15-20 ^{o}C.
- Hydraulic retention time (HRT): between 4 and 6 days
- Amendments: grass fertilizer, sodium bicarbonate, ethanol (200 mg COD/L, pulse mode)
- Electrical power applied to the electrolytic cell : between 10 and 30 W
- Oxygen generated: between 30 and 100 g O_2 / m^3 reactive barrier-d, with 20 to 70% transferred to the liquid phase
- Dissolved O_2 in the recirculating liquid: between 1.8 and 3.5 mg/L
- Dissolved CH_4 in the recirculating liquid: between 1 and 12 mg/L

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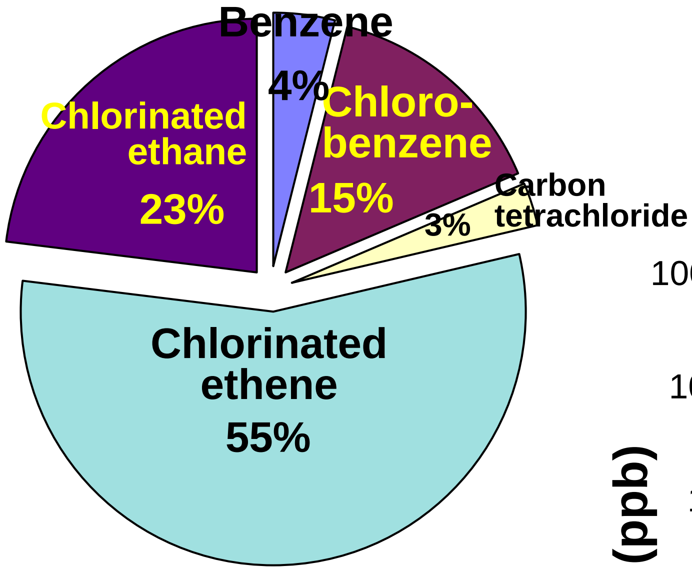
Pilot Scale : conditions and performance

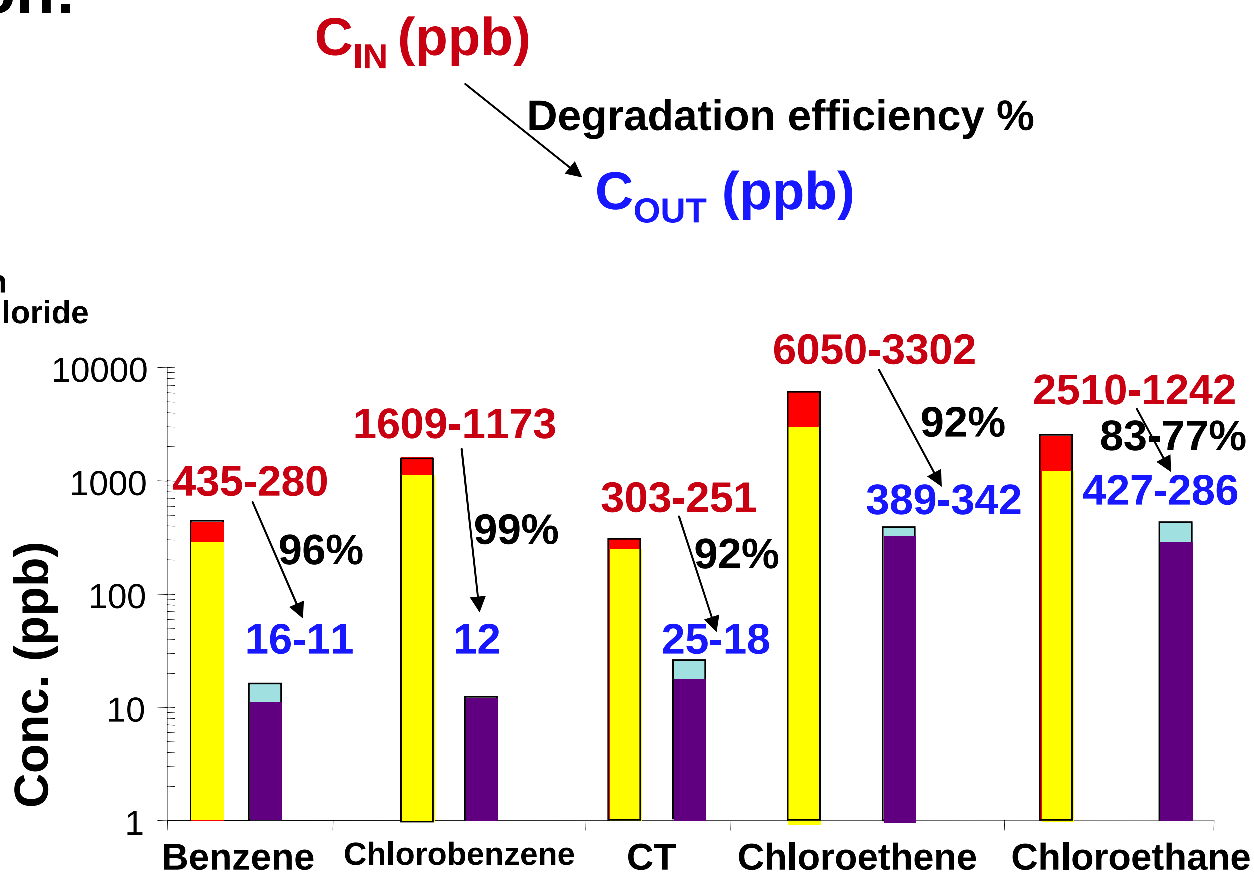
- Inlet PCE concentration: between 1 to 22 µM (0.2 to 3.7 mg/L)
- PCE removal and mineralization, between 38 and 68% after 40 days of operation, then over 98% after 80 days
- Incidental increase of the PCE inlet concentration to 14 mg/L $\Rightarrow$ still removal efficiency of over 97%, with effluent concentrations inferior to 50 ppb, for PCE, TCE and DCE, and of 157±33 ppb, for VC
- Inorganic chlorine balance between inlet and effluent: 9±4 mg/L for 14 mg PCE/L removed: i.e. 75±33% indicating a stoichiometric recovery

Pilot Scale :

performance with mixed DNAPL from a real site

- **DNAPL composition:**





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Pilot Scale : enhanced bioremediation

- Recirculation by a submersible pump
- No amendments
- Inlet PCE concentration: 2 to 3.7 mg/L
- PCE removal and mineralization over 98%

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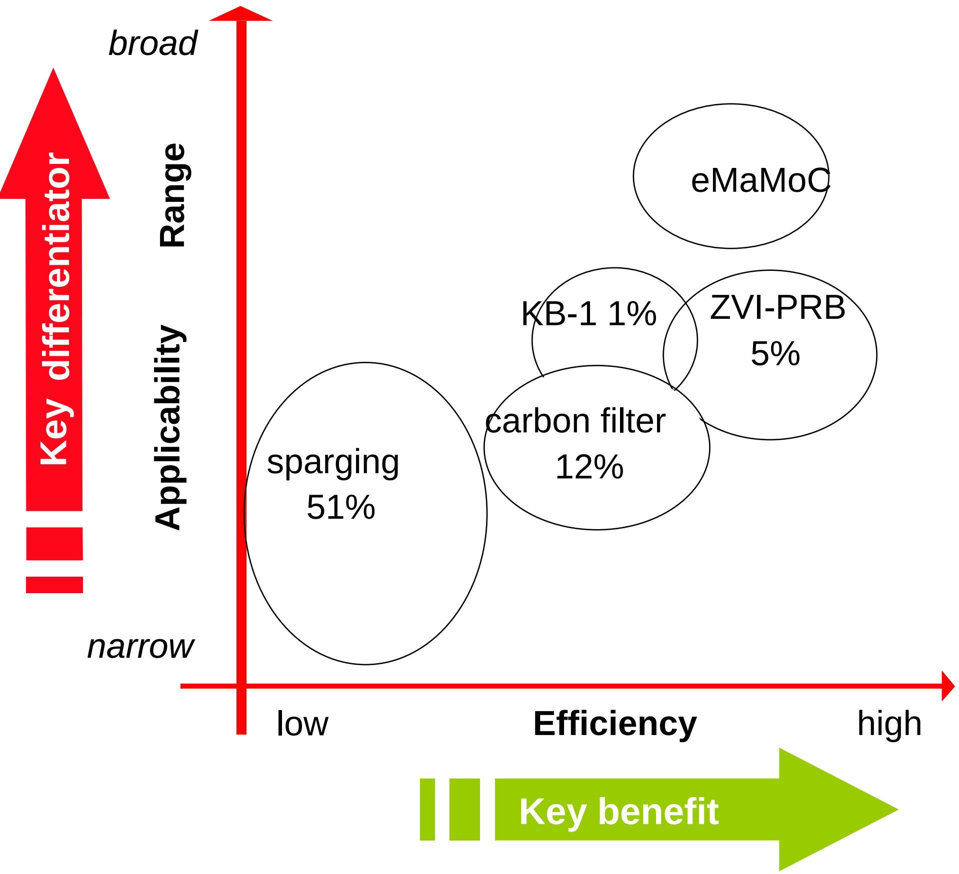
Advantages



- **Cost reduction**: single-stage operation, efficient oxygen supply and transfer by electrolysis
- **Hydrogen** simultaneously produced at **no extra cost**
- **Beneficial mutualism** between anaerobes and aerobes
- Potential for **complete degradation** of a **broad range of contaminants**