Aerobic biological remediation design of a complex pollution in unfavorable conditions

Carole Marcon

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La dépollution sur mesure

The context

- Former Industrial plant near Paris
- Historic chemical storage (1933 to 2013)=> soil and groundwater impacted by acetone, 1,2-DCA, isopropyl alcool, ammonium, pH10…and extension on the downstream neighboring site (strained relations)
- Geology: brown clay (0-1,5m), beige marl (1,5-9m), Monceau sandy clay (9-12m – aquifer layer)
- Groundwater table between 9m and 11m

Groundwater contamination (µg/l)		
	South area	North area
pH	**10**	**10**
Acétone	15 000	200 000
Alcool Isopropylique	1 900	2 400
1,2 DCA	55 000	20 000
1,2 DCP	3 900	3 100
Chloroforme	1 900	310
Ammonium	1 100 000	2 900 000

The challenge

- **A technical challenge**
  Complex pollution cocktail in groundwater

- **In a complex environment**
  Unfavorable conditions (pH10)
  Clayed aquifer

- **With specific constraints**

  Customer timing constraints (land for sale)

  Strained relations with the neighboring

→ **Need to design a tailor made rehabilitation solution**

Previous feasibility tests : laboratory

ISCO laboratory tests

- ISCO laboratory tests with NaOH activated sodium persulfate ($Na_2S_2O_8$)
- Extrem chemical conditions necessary to obtain good resultts in laboratory (NaOH excess = 10% mass)
- NaOH essential to activate radical mechanisms decomposition of persulfate
- High decrease of polluant concentration whatever the persulfate concentration but with high concentration of NaOH : acetone (82,7 to 98,9%), 1,2-DCA (55,1 to 94,9%) and DCM (58,3 et 95,2%)
- No direct link with oxydation : hydrogenolysis ?

→ **ISCO must be tested on the field**

Previous feasibility tests : field pilot

ISCO field pilot test

- ISCO field pilot test showed contaminant increase, mainly due to geochemical environment modification
- No durability of the product due to hight and fast dissolution of the reagent
- Significant release of metals and metalloids

ISCO with this reagent is not adapted to this site

Pump and treat test

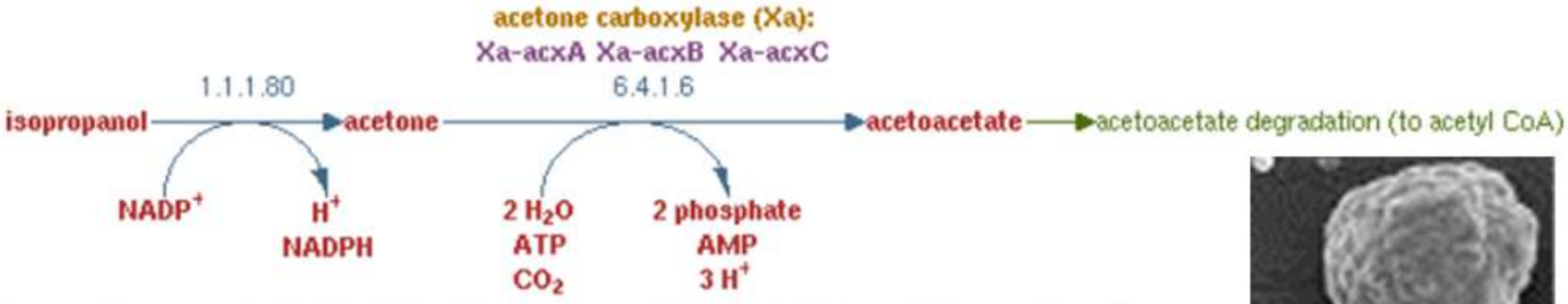
- Acetone (main contaminant) : essentially dissolved and highly soluble, no free phase

Pumping is not efficient enough to recover pollution

Other technics study – bibliography step

Acetone biodegradation

- Several strains able to use isopropanol as the sole source of carbon and energy. *Sphingobacterium mizutaii* => acetone as an intermediate
- Isopropanol-producing bacteria => alcohol dehydrogenase enzymes that catalyze the reversible conversion of acetone to isopropanol
- Much more is known about the conversion of acetone to acetoacetate. Mostly know is obligate aerobe *Xanthobacter autotrophicus Py2* => inducible acetone carboxylase (25% of solubles proteins after induction)

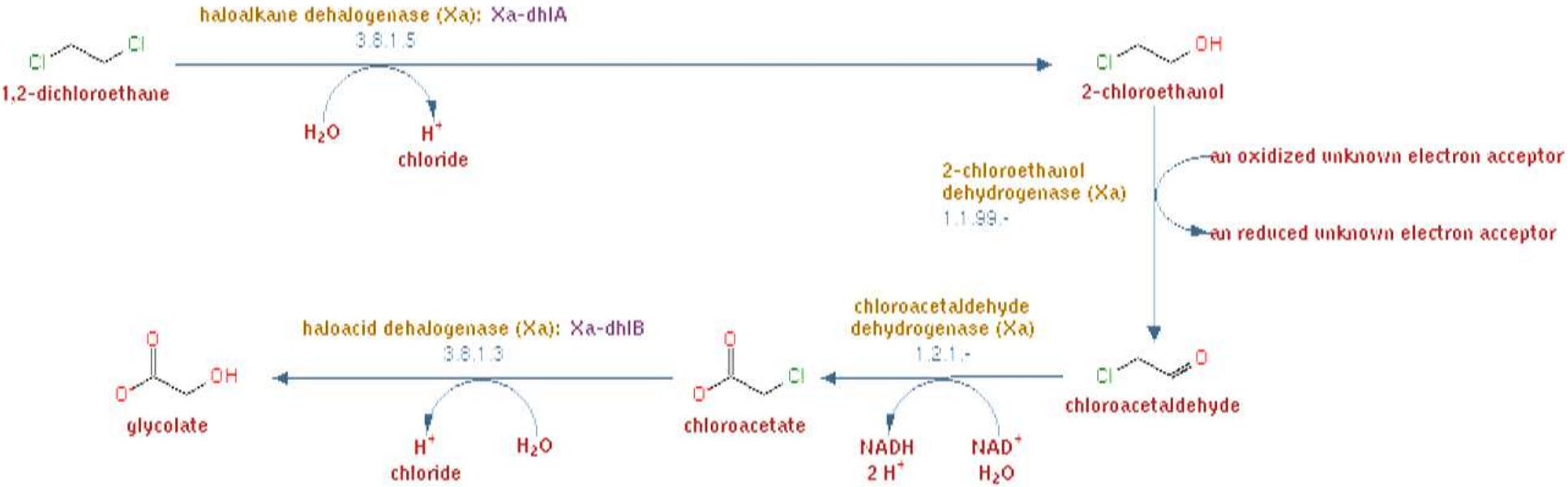


Exemple de voie de biodégradation de l'isopropanol et de l'acétone par la bactérie aérobie *Xanthobacter autotrophicus Py2*

Other technics study – bibliography step

1,2 dichloroethane biodegradation

Xanthobacter autotrophicus GJ10 is able to utilize 1,2-dichloroethane as a carbon source. The pathway proceeds through four reactions ending with glycolate which then enters the central metabolic pathway



Other technics study – bibliography step

Oxidation

- Permanganate : not the strongest oxidant but the longer life time (>3 months)
- Searching much more long term efficiency than fast acting (kinetic effect)

Oxydants et réactions	Electrode Potential (Eh)	Persistance
Permanganate (liquide)		
MnO4- + 4 H+ + 3 e- ->MnO2 + 2 H2O	1.7 V (permanganate ion)	>3mois
Fenton's (H_2O_2 Derived Reactants) (liquide)		
H2O2 + 2 H+ + 2 e- ->2 H2O	1.8 V (hydrogen peroxide)	minutes/heures
Ozone (gaz)		
O3 + 2 H+ + 2 e- ->O2 + H2O	2.1 V (ozone)	minutes/heures
Persulfate (liquide)		
S2O82- + 2 e□ 2 SO42-	2.1 V (persulfate)	semaines

Source: EPA Engineering issue- In-situ chemical oxidation

New approach design

- Biodegradation and oxidation feasibility must be tested in laboratory regarding to the specific and unfavorable environmental conditions
- This mainly concerns biodegradation (pH10)
- New approach design

Biodegradation

LABORATORY TESTS

Best results

FIELD PILOT TEST

Oxidation

Biodegradation laboratory tests

- If it works, this technology could give the most interesting ratio cost/efficiency
- Microbial communities are specifically adapted to this very specific environment
- **2 questions:**

→ **Is it possible to enhance biodegradation?**

→ **Is it necessary to buffer or dilute water?**

Biodegradation laboratory tests

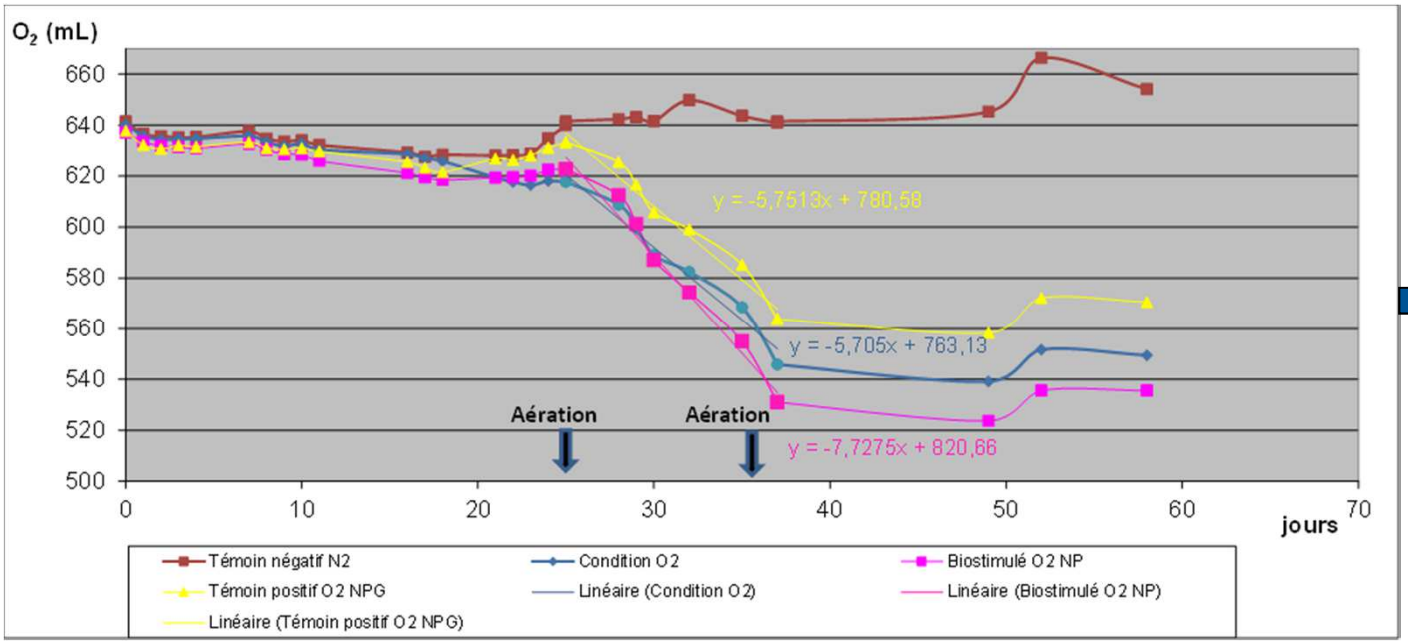
Batches conditions

- N_2 (negative control)
- O_2
- O_2 + HCl buffer (pH7)
- O_2+ HCl buffer (pH7) + nutrients
- O_2 + HCl buffer (pH7) + nutrients + glucose (positive control**)**
- O_2 + 1/2 dilution
- O_2 + HCl buffer (pH7) + 1/2 dilution
- O_2 + 1/10 dilution
- O_2 + HCl buffer (pH7) + 1/10 dilution

Biodegradation laboratory tests

Respirometric monitoring during 57 days with O_2 renewal , at 20° C

- No O_2 consumption during the first 25 days: microorganism need an adaptation time
- After 1st aeration, begining of O_2 consumption until day 37 and then no more: resource depletion in the batches (confined without cellular and nutrients renewal)
- O_2 consumption in the negative control didn't change : respiratory activity is 20 to 27 times more important in O_2 conditions



- ✓ **Biostimulation possible**
- ✓ **No toxic effect of water**
- ✓ **Nutrients not necessary**

Biodegradation laboratory tests

Results

- >96% 1,2 DCA decrease in all conditions
- > 99% 1,2 DCP decrease in all conditions
- >79% isopropyl alcool decrease in all conditions but O2 + 1/10 dilution and O_2 + 1/10 dilution + HCl buffer (pH7)
- > 98% acetone decrease in conditions O_2 + HCl buffer (pH7) + 1/2 dilution and O_2 + HCl buffer (pH7) + 1/10 dilution
- 35% to 45% acetone decrease in conditions O_2, O_2 + HCl buffer (pH7), O_2 + 1/2 dilution, O_2 + 1/10 dilution

For acetone only

- ✓ **No impact of buffering or diluting alone**
- ✓ **Better results when dilution + buffering**

For the contaminant cocktail

- ✓ **Biodegradation is effective for all compounds**
- ✓ **Contaminant decrease look good without dilution or buffering**

Oxidation laboratory tests

Soil oxidant demand (SOD)

- Minimal amount of oxidant (sodium permanganate) required to oxidize all the oxidable matter in soil + groundwater :

Contaminant oxidation + Organic matter/Metals oxidation => Global SOD

→ 35g/kg SOD in the mixing soil + site groundwater

→ 1g/kg SOD in the mixing soil + distilled water

→ 97% SOD comes from contaminants in water: essentially disolved pollution

Oxidation laboratory tests

Oxidation tests

35g/kg SOD ⇔ 1,7% NaMnO4 in groundwater

Batches conditions: 0%, 0,1%, 0,5%, 1% et 2%, 72h at 20° C

Results (2% condition: remaining oxidant)

- 57% 1,2 DCA decrease
- 86% 1,2 DCP decrease
- >99% acetone decrease
- >94% isopropyl alcool decrease

➡ **Oxidation is efficient for all contaminants**

➡ **Better results with highter oxidant concentration (2%)**

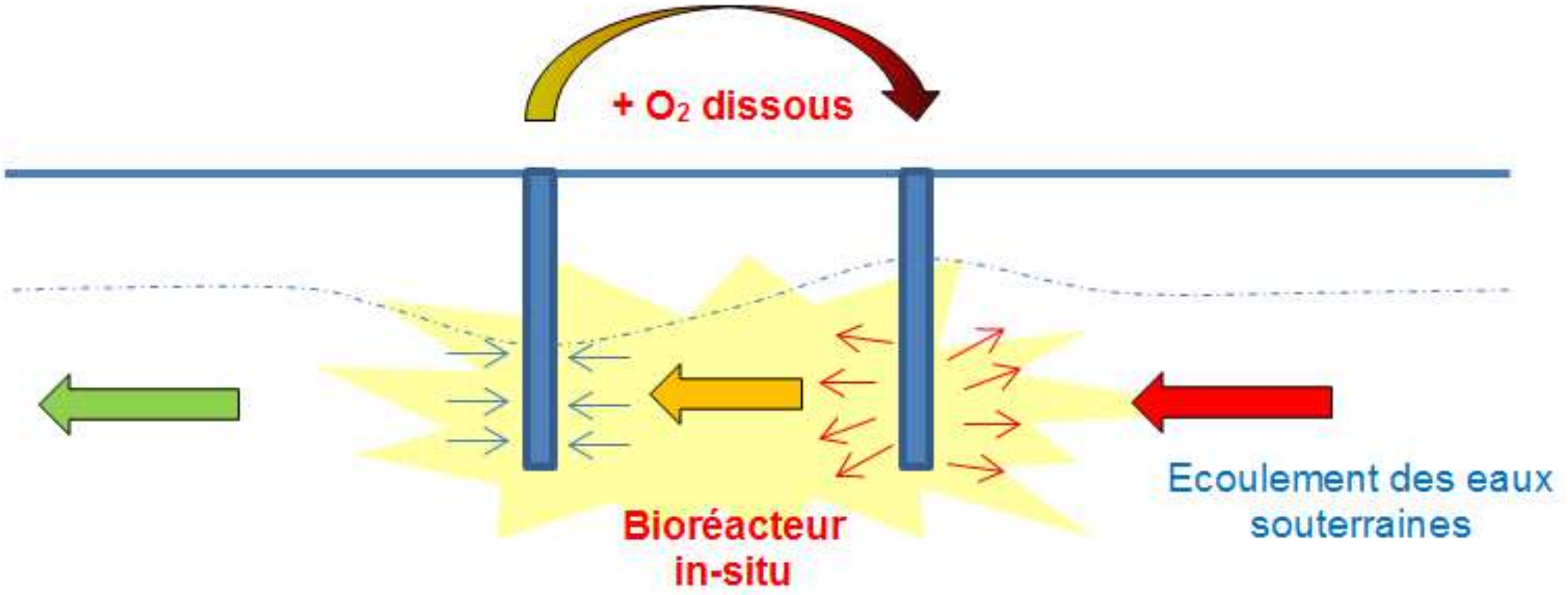
Laboratory tests conclusions

- Biodegradation and oxidation are effective
- Biological treatment must be privileged mainly regarding to the important amount of oxidant required for oxidation and reagent costs
- Pollution is mainly disolved, so pumping and reinjecting water seams necessary in order to avoid pushing pollution downstream

- A biological field pilot test is necessary to validate this technology
- The pilot will begin without buffering, with possibility to add some if necessary

Field pilot test

3 months pilot (feb-apr 2016)

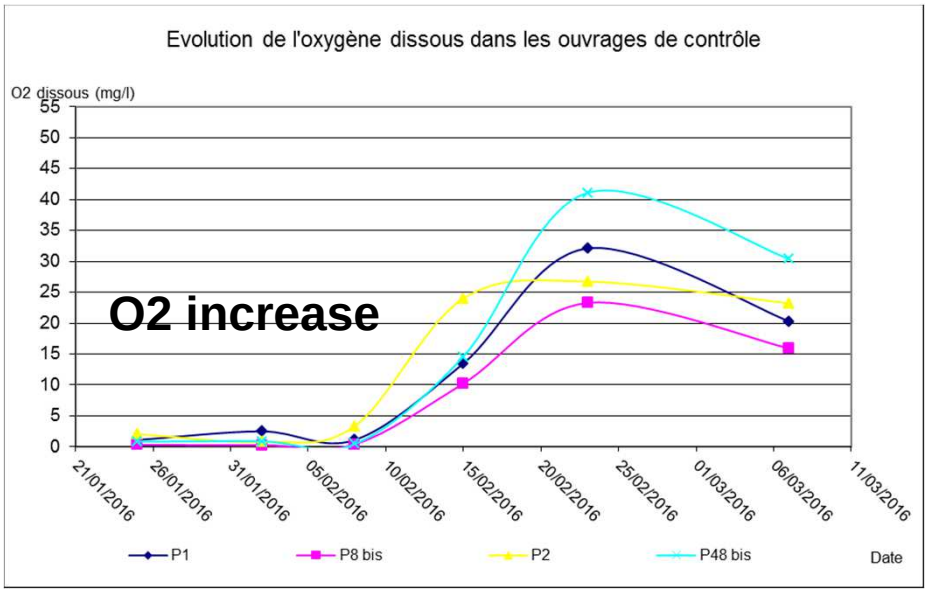


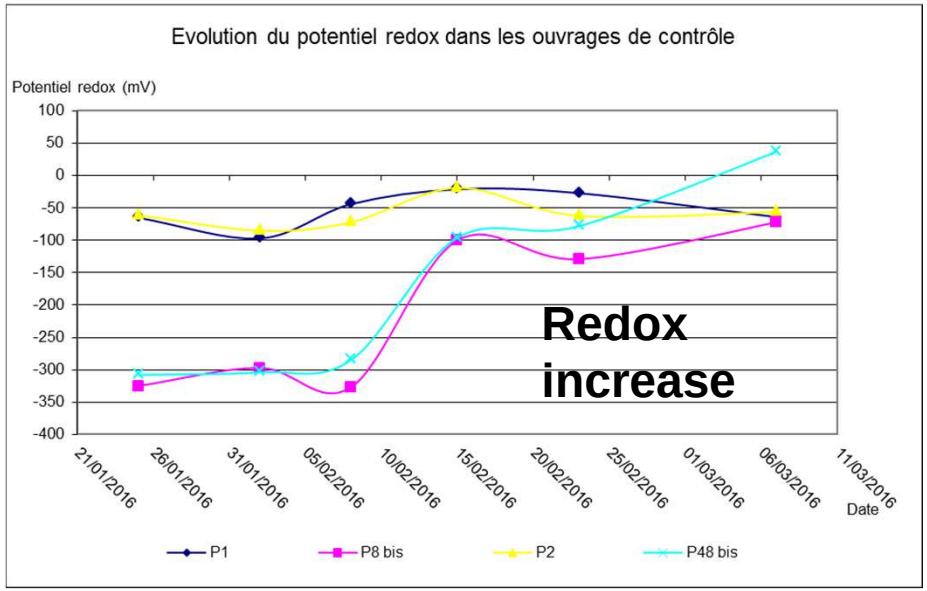
- Pumping water in 2 zones with 2 different range of concentration
- Treatment on an aerobic bioreactor
- Reinjection in the 2 zones after dissolved O_2 enrichment

Field pilot test

Field pilot test

1st results in control wells

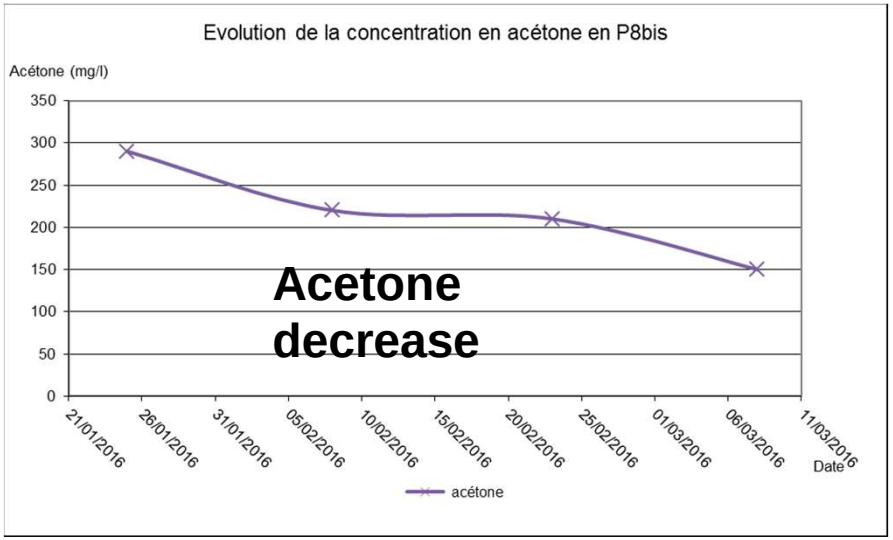


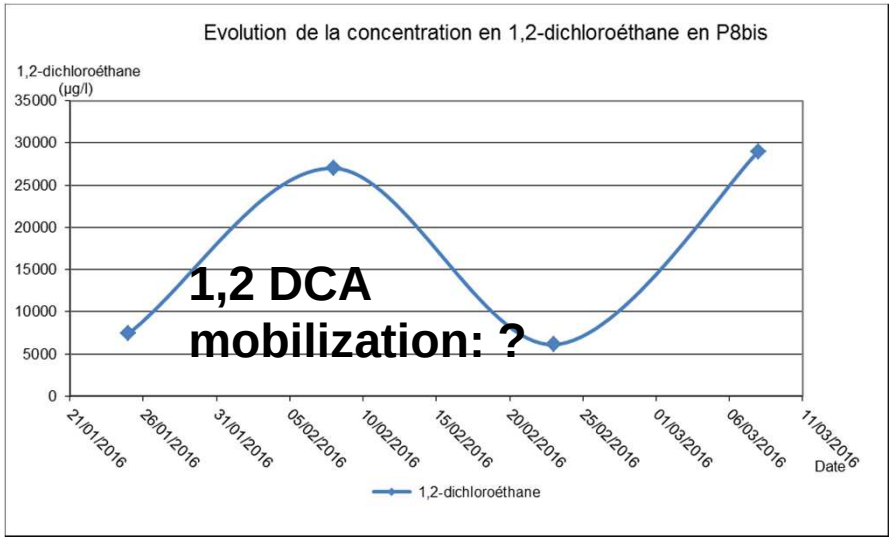


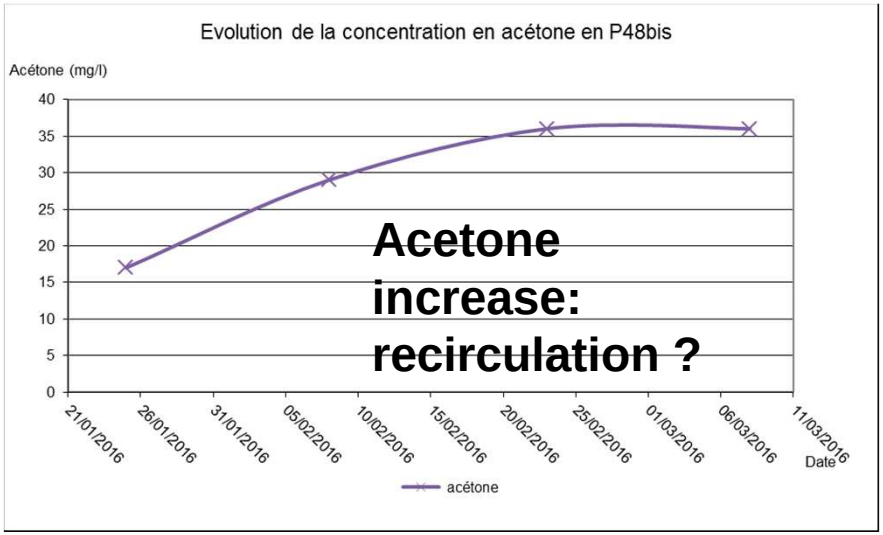
Efficient oxygenation

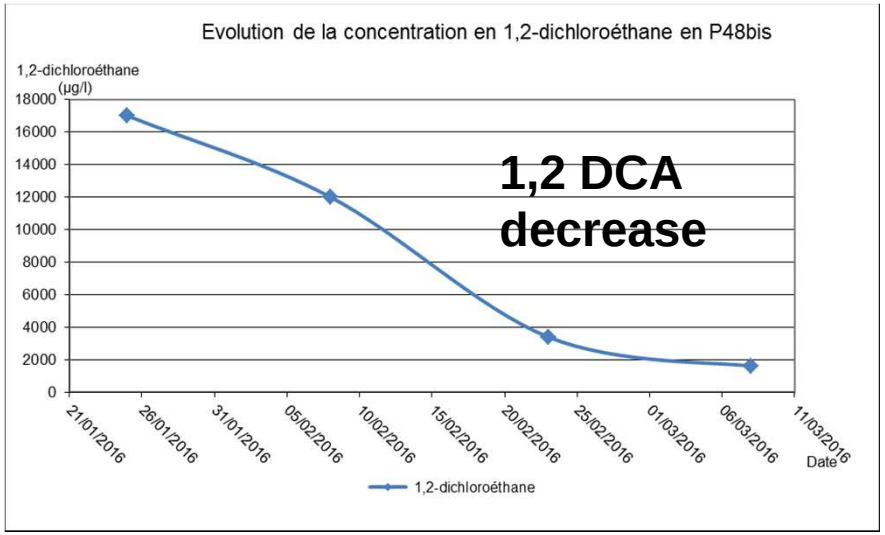
Field pilot test

1st results in control wells









Field pilot test

Biomolecular analysis

Molécules d'intérêt	Biomarqueurs	Métabolismes	Gènes cibles	Voie de dégradation ciblée
--	EP2019		16S	Comptage bactéries totales
acétone	EP2107	AE	mimA	binuclear iron monooygenase (BIM)
acétone	EP2108	AE	acmA	acétone monooxygénase (BVMO)
acétone	EP2109	AE	acxA	acétone carboxylase (AC)
DCA (dichloroethane)	EP1337	AE	dhlA	déhalogenase

- T0+ T3 months:

  Specific acetone and 1,2 DCA biodegradation genes (ADN + ARN)

- T0+T1+T2+T3 months:

  Total bacteria

ENOVEO

Field pilot test

Results

Tableau 3: Tableau des résultats d'analyses par qPCR et RT-qPCR

			T0	T1	T0	T1
			Copies ADN par litre		Copies ARN par litre	
	Bactéries totales	--	4,66E+08	3,83E+07	n.r.	n.r.
Acétone	EC2107	BIM	n.d.	n.r.	n.d.	n.r.
	EC2108	BVMO	<L.Q.	n.r.	n.d.	n.r.
	EC2109	AC	2,22E+06	n.r.	<L.Q.	n.r.
1,2-DCA	EC1337	dehalogenase	n.d.	n.r.	n.d.	n.r.

n.d. : non détecté ; <L.Q. : inférieur à la limite de quantification ; n.r. : non réalisé

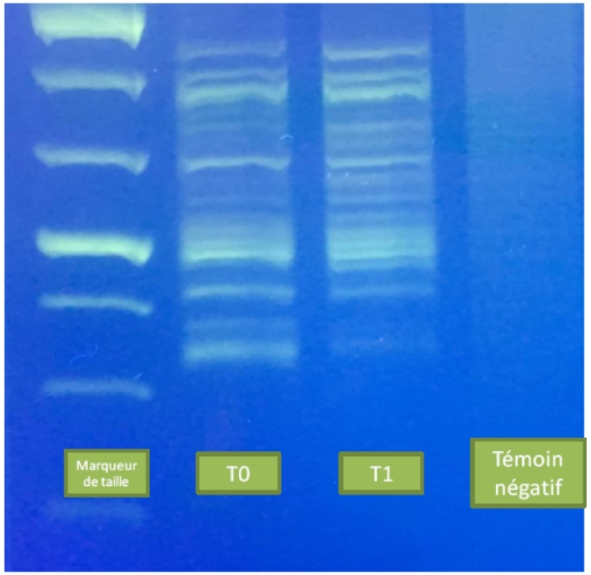


Figure 5 : Gel d'agarose présentant les structures des communautés révélées par RISA.

T0:
presence of acetone biodegradation gene, not 1,2 DCA

T1 month:
No significant bacterial community change

Conclusions

- Tailor made treatment design need a scientific approach

- Each design step of the treatment must be validated by corresponding tests (laboratory, field pilot…)

- Such an approach allows to :
  - Save money 1,5 M€ => 0,5 M€
  - Give more confidence in the efficiency of the treatment
  - At least, propose guaranteed results to the client

- This study also shows that biological treatments, even if less powerfull, can compete and give better results than much more agressive ones like chemical oxidation

Agence Ile-de-France et Siège
ZAC des Chevries- 11, rue des Chevries - 78 410 Aubergenville
Tél : 01 39 29 75 70 - Fax : 01 39 29 72 03

Agence Rhône-Alpes
8 ter avenue du Dr Schweitzer - 69330 Meyzieu
Tél : 04 72 45 32 70 - Fax : 04 72 05 81 84

Agence Normandie
ZA route de Fécamp – RD 925 – 76 110 Goderville
Tél : 02 35 10 18 14 - Fax : 02 35 10 18 17

Agence PACA
645, rue Mayor De Montricher - Tech'Indus A3 - Pôle d'activités – 13 854 Aix en Provence
Tél : 04 42 27 30 52 - Fax : 09 70 61 35 03

Contact
information@soleo-services.fr

www.soleo-services.fr