14th International HCH and Pesticides Forum

FERNÁNDEZ CASCÁN, JESÚS

Technical staff (Geologist)

GOBIERNO DE ARAGON
Departamento de Agricultura, Ganadería y Medio Ambiente

LIFE SURFING PROJECT, ENHANCED SURFACTANTS EXTRACTION (SEAR) IN A FRACTURED AQUIFER

Fernández J.[1], Santos A.[2], Herranz C.[3], Net J.[1], Lorenzo D.[2], Arjol M.A.[3]

1 Gobierno de Aragón. *2 Universidad Complutense de Madrid* *3 SARGA*

GOBIERNO DE ARAGON
Departamento de Agricultura, Ganadería y Medio Ambiente

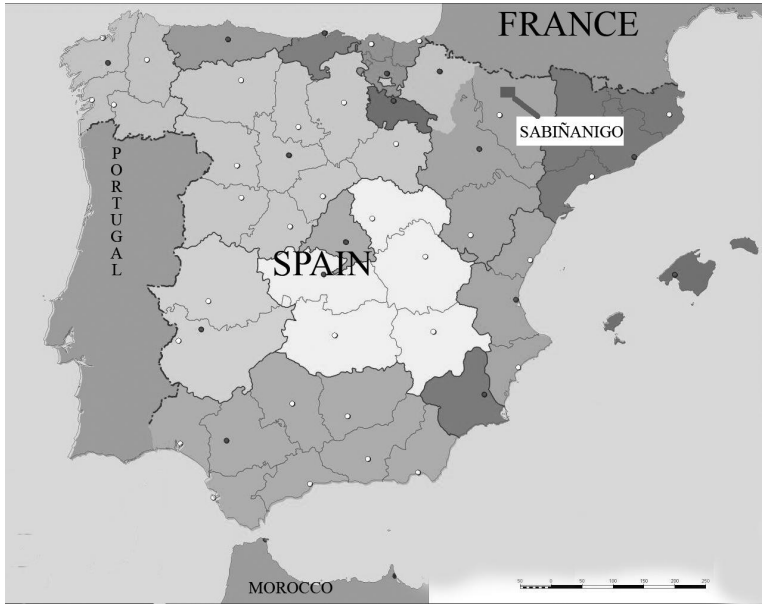
sarga

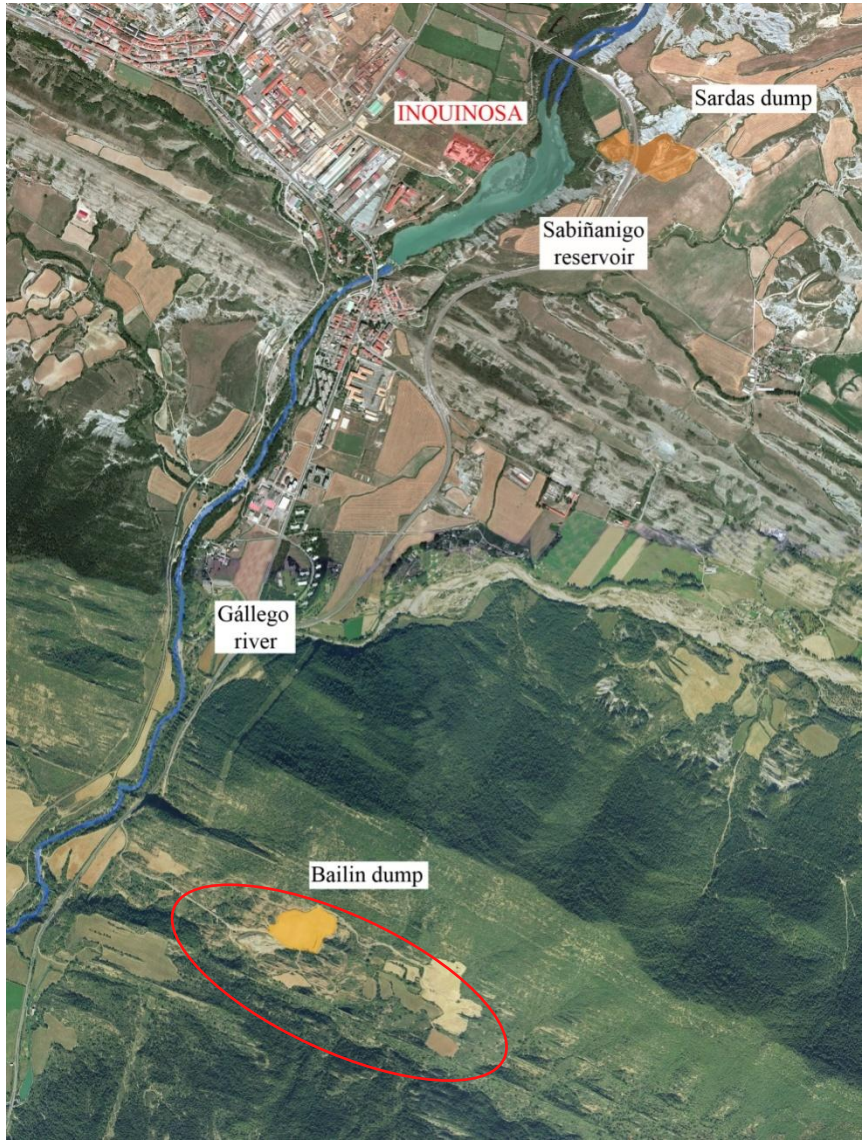
IHPA
International HCH & Pesticides Association

UNIVERSIDAD COMPLUTENSE MADRID

Universität Stuttgart

GEOGRAPHIC LOCATION



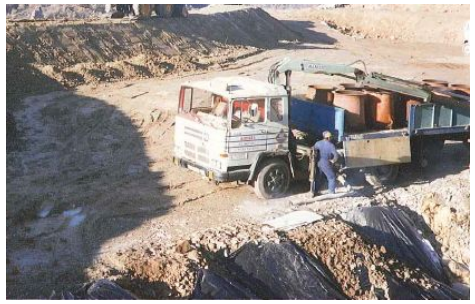


Main sources of lindane manufacturing waste:

- **OLD INQUINOSA FACTORY**
- **SARDAS LANDFILL**
- **BAILIN LANDFILL**

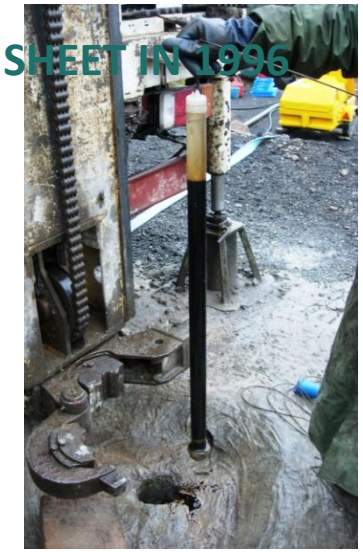
14th International HCH and Pesticides Forum

WE HAVE DNAPL. NOW WHAT?
TENEMOS DNAPL. ¿Y AHORA QUÉ?



BAILIN LANFILL. BASIC DATA:

* PERIOD OF OPERATION: 1984-1992
* TOTAL WASTE 200,000 m^3
  * SOLID WASTE OF HCH 64,000 t
  * CONTAMINATED LANDS 342,000 t
* WITHOUT INSULATION AT THE BASE
* SURFACE COVER WITH HDPE SHEET IN 1996
* DNAPL PRESENCE
* GÁLLEGO RIVER AT 800 M



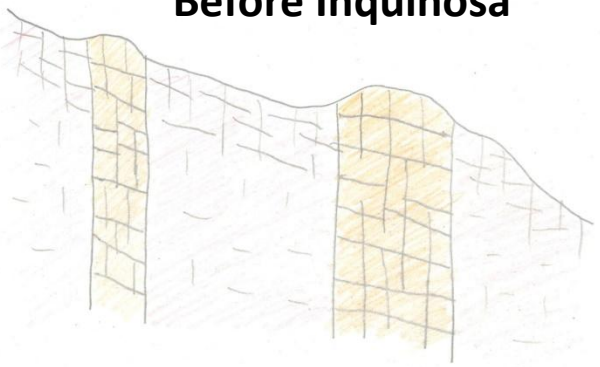
Composition of DNAPL samples from the Bailín landfill

		BAILIN-O1 (UCM)-2018	BAILIN-20 /03/19	BAILIN-11/ 09/19
Bencene	%	na	na	na
CB	%	10.40	11.19	11.26
1,3 DCB	%	0.20	0.39	0.31
1,4 DCB	%	2.10	2.60	2.46
1,2 DCB	%	1.70	1.78	1.57
1,3,5 TCB	%	0.00	0.06	0.07
1,2,4 TCB	%	5.50	6.07	5.73
1,2,3 TCB	%	0.50	0.77	0.56
TetraCB (1,2,3,5 + 1,2,4,5)	%	1.40	2.19	2.01
TetraCB (1,2,3,4)	%	2.40	2.70	2.54
PentaCB	%	0.20	0.46	0.32
∑-PentaCX	%	13.30	14.82	15.05
∑-HexaCX	%	5.20	3.71	3.17
∑-HeptaCH	%	26.70	25.50	28.22
α-HCH	%	4.40	4.47	4.43
β-HCH	%	0.03	0.00	0.00
γ-HCH	%	14.00	14.26	13.19
δ-HCH	%	10.70	7.72	7.87
ε-HCH	%	1.50	1.30	1.24

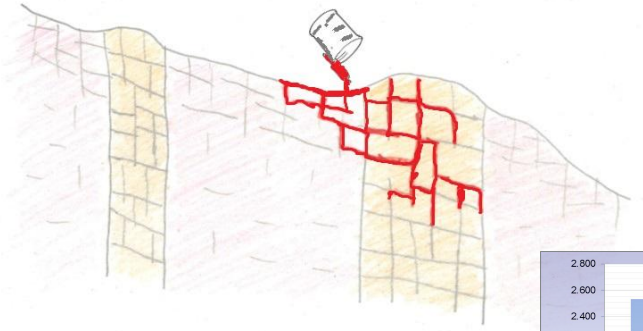
WHAT HAPPENED? WHERE WE ARE?

14th International HCH and Pesticides Forum

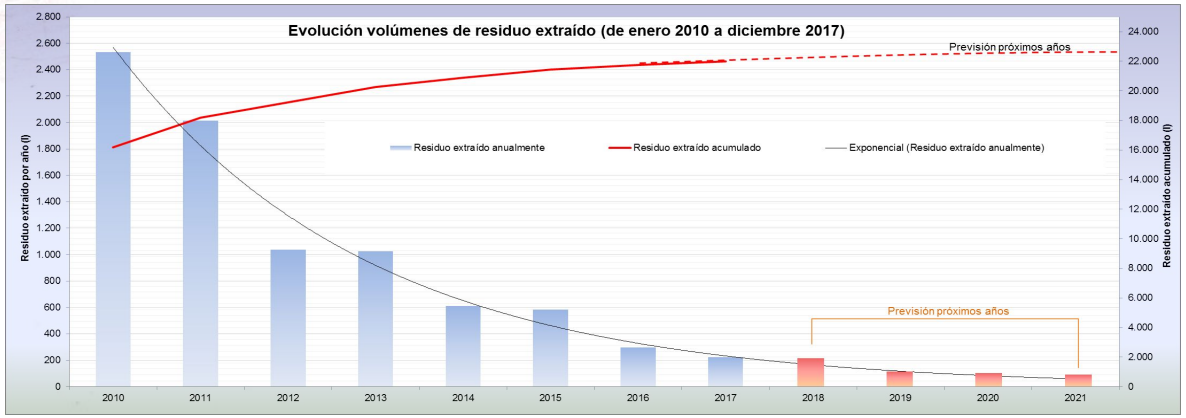
Before Inquinosa



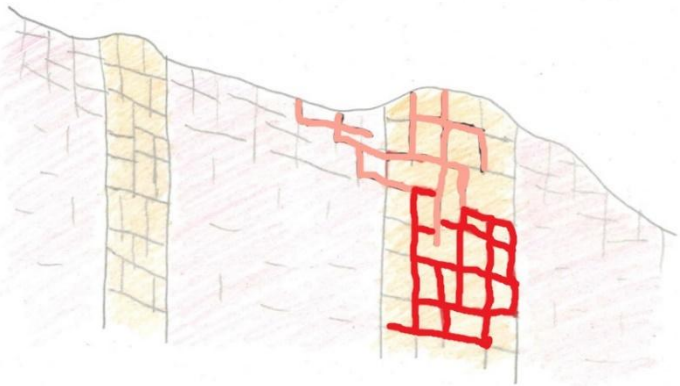
with INQUINOSA



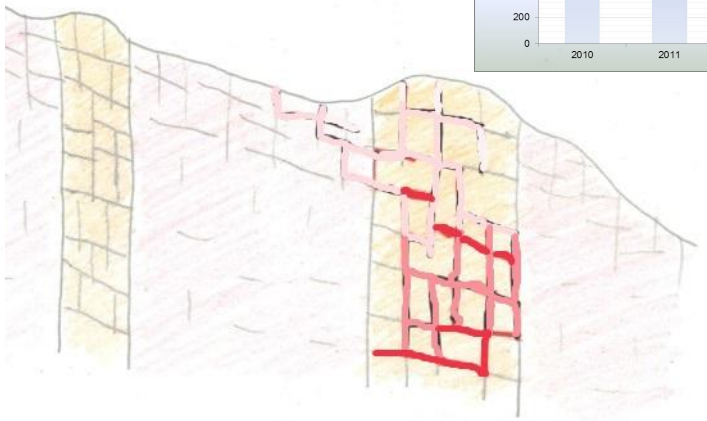
Evolution of DNAPL extraction



Before detecting DNAPL



In 2021



14th International HCH and Pesticides Forum

WHAT IS LIFE SURFING?

"SURFactant enhanced chemical oxidation for remediatING DNAPL"

Demonstration project for the application of S-ISCO techniques (combination of surfactants and oxidants) in fractured media with the presence of DNAPL

Proyecto demostrativo para la aplicación de técnicas S-ISCO (combinación de surfactantes y oxidantes) en medios fracturados con presencia de DNAPL

FLIX.NET

PRESENT: a LIFE production

Chap 1: Phase 0 - PREPARATORY WORK

Chap 2: Phase 1: Surfactant Enhanced Extraction (SEAR)

Chap 3: Phase 2: Surfactants + oxidants (S-ISCO)

Phase 0 - PREPARATORY WORK

- **Experimental design:**
  - ✔ Review of hydrogeological and geochemical data from the test area.
  - ✔ SEAR, S-ISCO research review carried out by the team.
  - ✔ Analysis of possible on-site treatment techniques
  - ✔ Tests of applicable barrier techniques
  - ✔ Definition of the test area

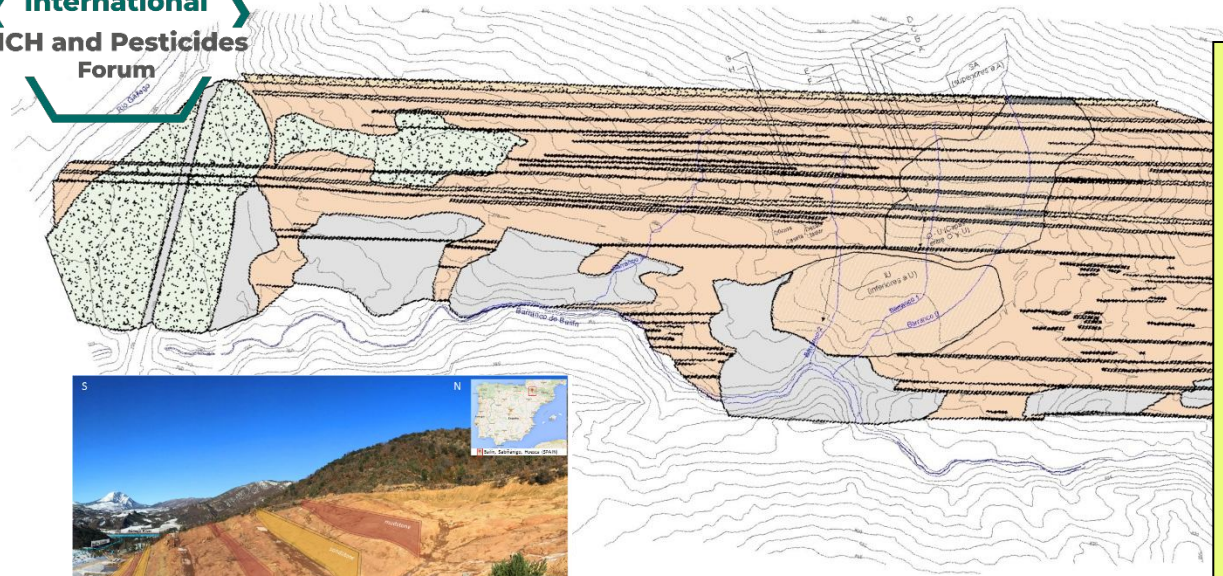
- **Execution of boreholes and infrastructures**

- **Base line of the test zone and layer M**
  - ✔ Hydrogeological tests: storage capacity, apparent permeability, connectivity, velocity, mass flow, etc.
  - ✔ Tracer test: Injection and Pump Strategies, Recovery Rates, Response Times.

TRACER TESTS – CONCLUSIONS

- **Injected flow rates are distributed mainly vertically, saturating the vadose zone.**
- **It is necessary to inject at P198** to reach some fractures with possible presence of dense phase between P195 and P198.
- The **useful permeability** in the cell zone above the water table at low water up to about 809 is **0.4%.** The **volume stored upstream of borehole P198** is approximately **2.4 m3,** with a **flow rate** of approximately **14 l/min downstream** to maintain equilibrium levels.
- The use of a **packer in P198** allows to decrease the downstream **flow rates** by at least **5 l/min.**
- The **recovery rate** is less than **30%** if no measures are taken. With the use of a **packer at P198 and pumping** (electric pump) **and recirculation at P171 and P172 it can approach 80%.**
- In the cell zone the flow is practically piston-like with increased downstream dispersion.
- The **flow velocity downstream** of the test cell, considering the first response in the level modification, varies between **40 and 180 m/h**, it does not respond to the real arrival of fluids but to an adjustment of pressures. Depending on the actual **arrival of the tracer**, the average **velocity** varies between **15 m/h for the first tracer flows** and **7 m/h for the concentration peak**.
- From the beginning of the injection, the **response time to adopt measures in the barrier zone** is approximately **27 hours**, **reaching the peak at 52 hours and prolonging the affected flow up to 5 days** from the beginning of the injection, always considering that no control measures are adopted upstream of the barrier zone.

GEOLOGICAL FRAMEWORK BY BAILIN

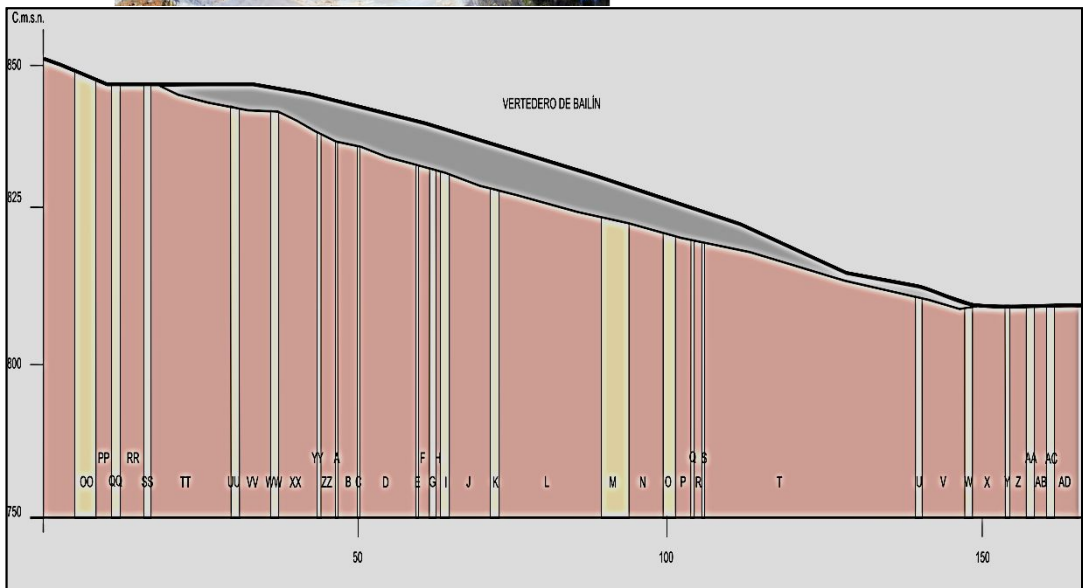


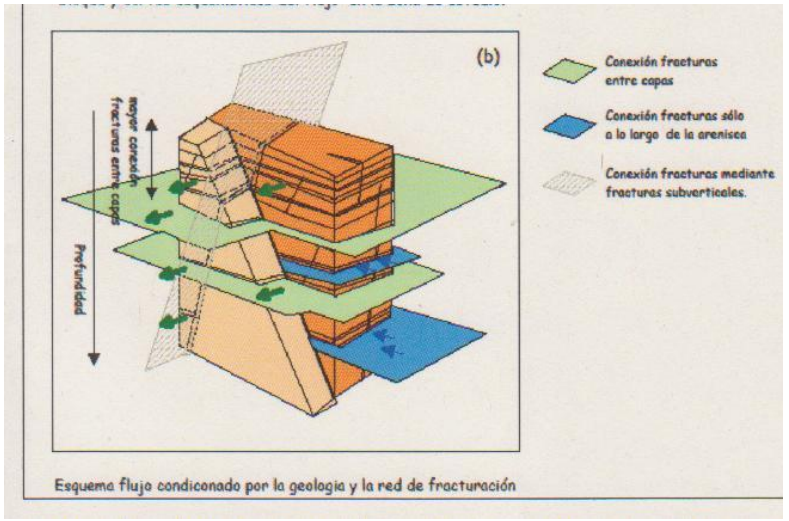
Lithology:

sandstones and conglomerates
siltstones

Structure:

subvertical layers
Faults transverse to the layers
More developed fracturing in sandstones



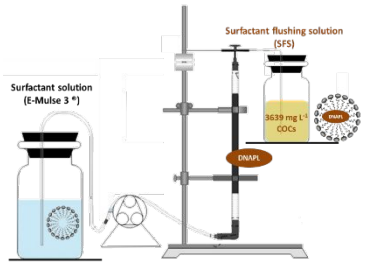


EXPERIMENTAL DESIGN: Selection of surfactant

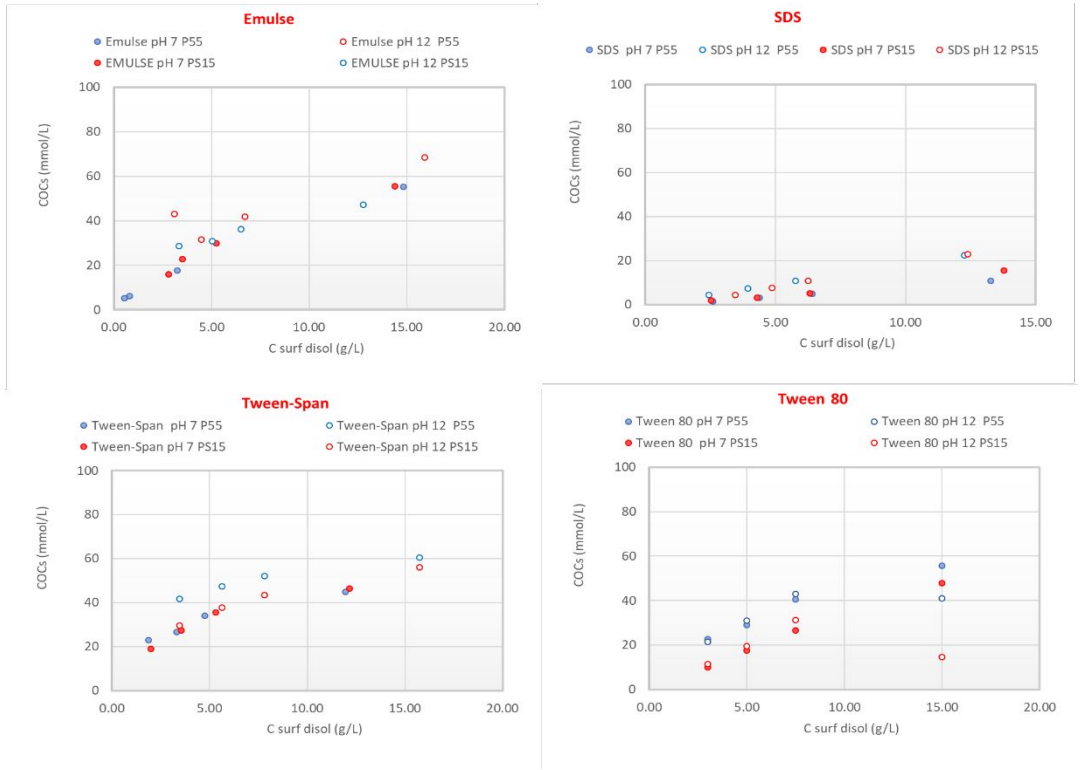
Previously selected surfactants in 2018 (Tween-Span, SDS) plus E-Mulse 3 ® proposed by UCM. Bacht and column tests: solubilization of DNAPL, CMC, behavior against pH, unproductive consumption with oxidants, stability of emulsions and demulsification, et.

COCs concentration (g/l) with and without surfactant for two DNAPL samples

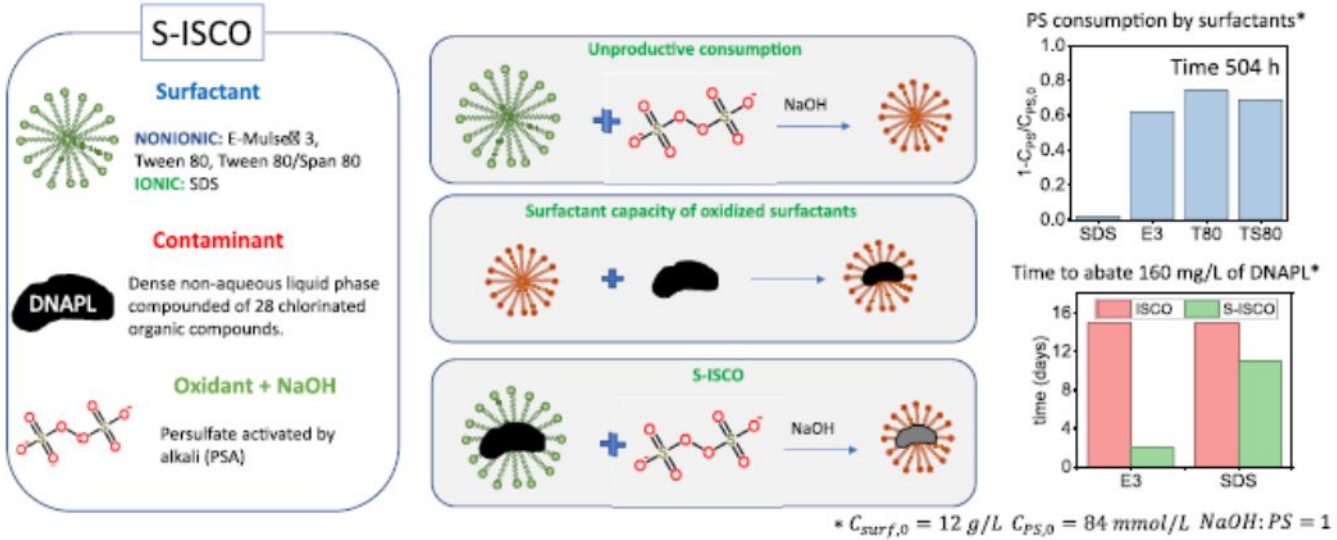
P55 (Bailin)			
Initial C Surfactant (g/L)	0 g/L	3 g/L	15 g/L
Emulse-3 ®	119	1182	13446
SDS	119	244	2560
Tween 80	119	5338	12829
Tween (35%)-Span (65%)	119	5549	7700
PS15 (Sardas)			
Initial C Surfactant (g/L)	0 g/L	3 g/L	15 g/L
Emulse-3 ®	130.2	3100	10906
SDS	130.2	300	2819
Tween 80	130.2	1830	8891
Tween (35%)-Span (65%)	130.2	3712	9188



Stability at alkaline pH



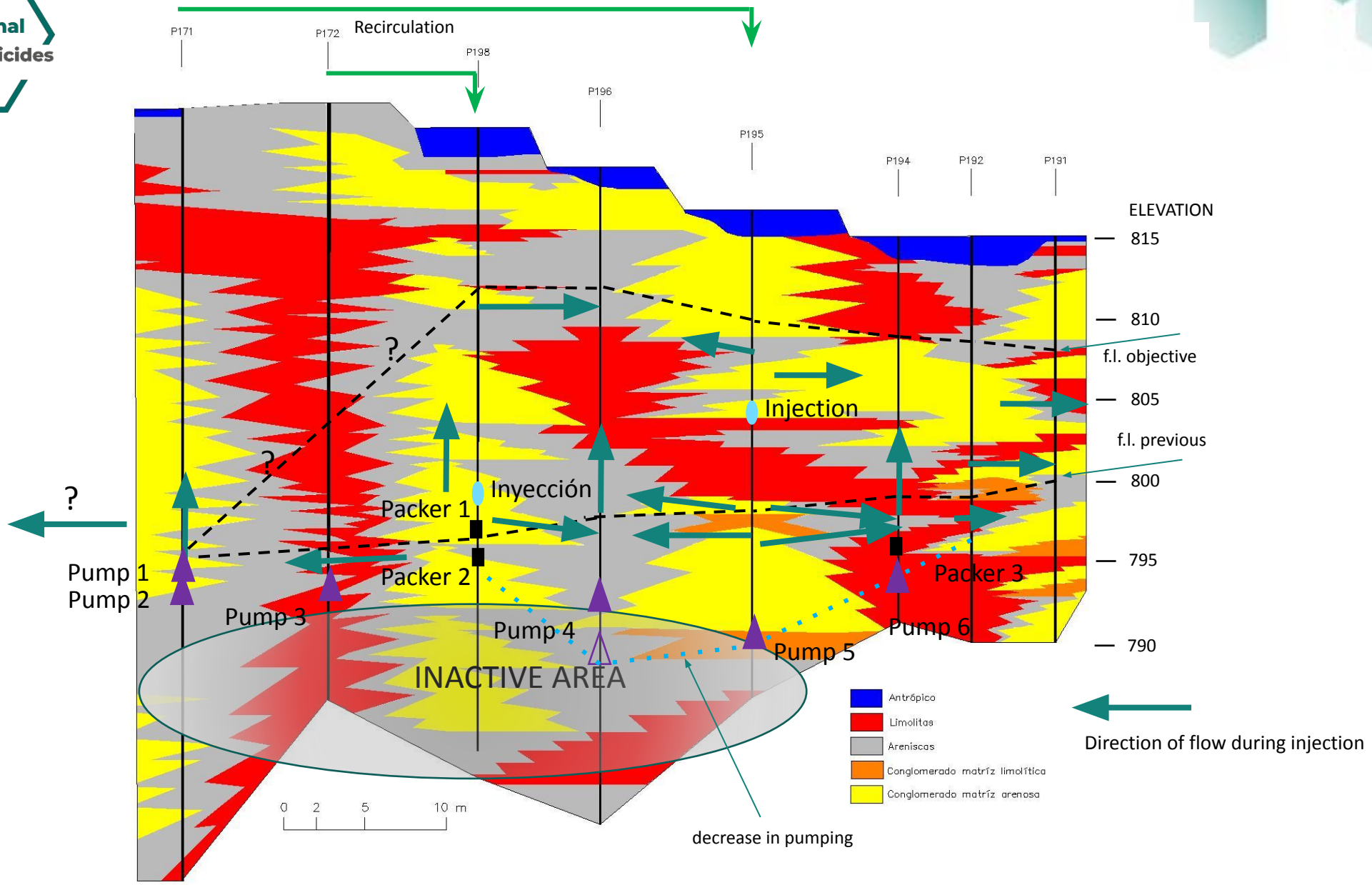
EXPERIMENTAL DESIGN: Selection of surfactant



$* C_{surf,0} = 12\ g/L\ \ C_{PS,0} = 84\ mmol/L\ \ NaOH{:}PS = 1$

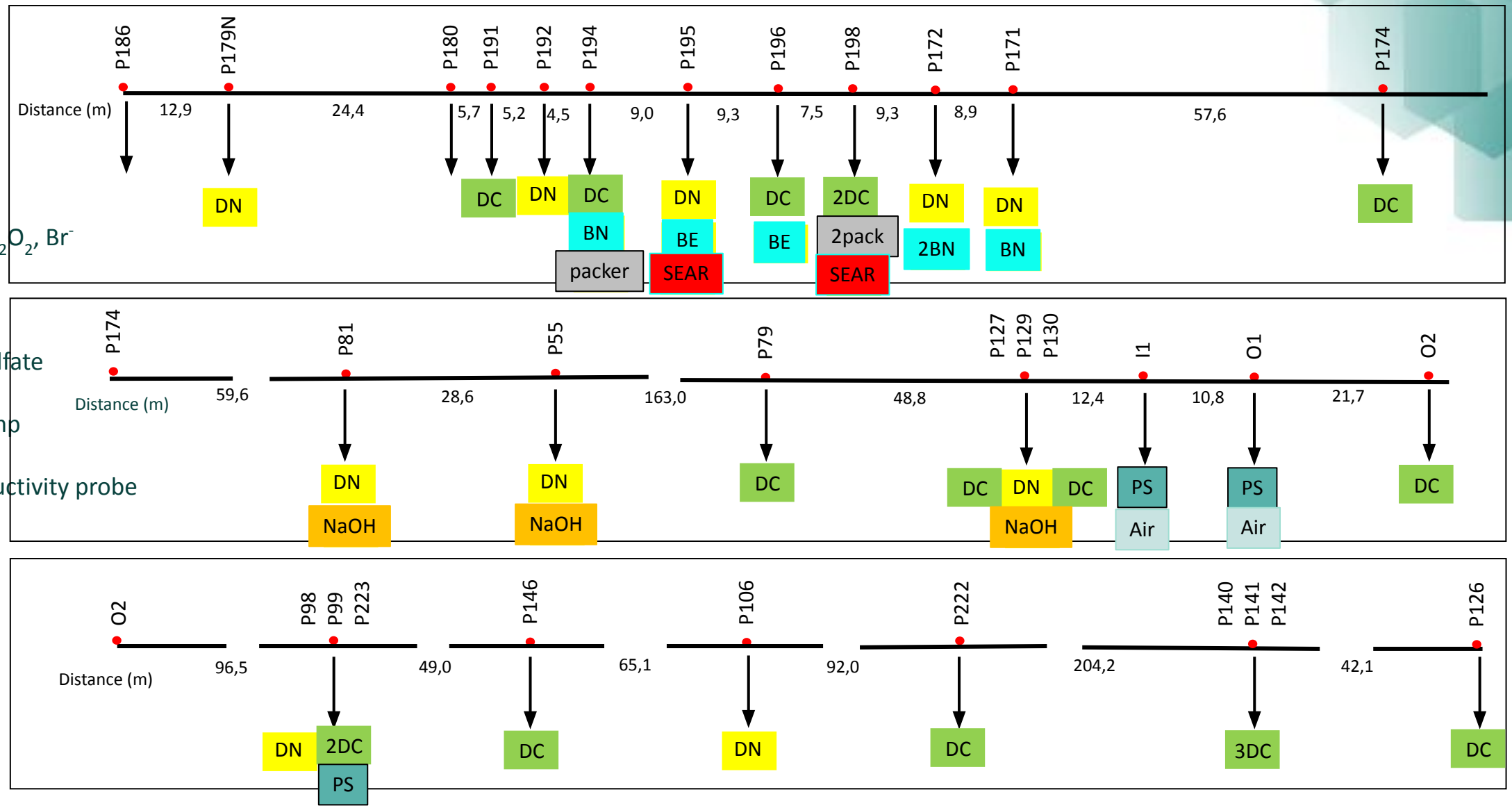
Taking into account the set of properties, the SDS is discarded, E-MULSE ® is selected for its good biodegradability, ease of handling and stability compared to Tween 80, Span 80 or mixtures of both.

SEAR 1 TEST SCHEME



SEAR 1 TEST - DISPOSAL OF REAGENTS AND EQUIPMENT

SEAR: surfactant, H_2O_2, Br^-
NaOH: soda 25 %
AE: defoamer
Air: aireation
PS: activated persulfate
BE: electric pump
BN: pneumatic pump
DN: level probe
DC: level and conductivity probe



SEAR 1

OBJECTIVES:

- ✔ Injection conditions to reach the target level and a residence time of several hours.
- ✔ Facilitate the mobilization and pumping of residual DNAPL.
- ✔ Solubilize the residual dense phase between boreholes P192 and P198.
- ✔ Recover as much emulsion volume as possible.
- ✔ Prevent surfactant and mobilized COCs from reaching sensitive receptors.

SURFACTANT SOLUTION

- E-Mulse-3®: 20 g/l.
- Bromide: 200 mg/l.
- H_2O_2: 1% v:v
- conductivity 6,5 mS/cm.
- Volume: 9,3 m^3
- Time 7:37 h
- Q med.: 20,4 l/min

REAGENTS for THE BARRIER ZONE:

OXIDIZING SOLUTION

- NaOH 25%: target pH > 12
- $H_2S_2O_8$: 80 g/l
- Volume: 10 m^3
- Time 54 h
- Q med.: 3 l/min

ALKALINE SOLUTION

- NaOH 25%: target pH > 12
- Volume: 104 l
- Q med.: 1,4 l/h

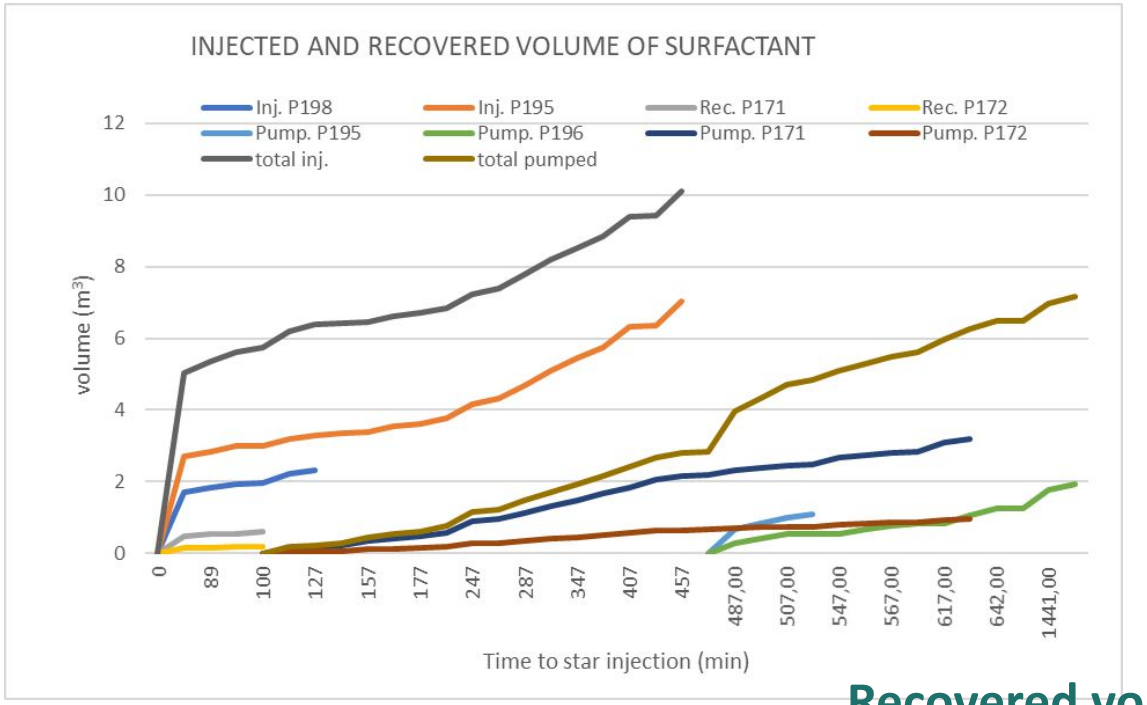
AERATION

- Injection 3,7 bar
- Q injection 29,5 m3/h
- Vacuum 31,6 mbar
- Defoamer 10%
- Time 10 jours

SEAR 1– TEST MONITORING

- Water level: fixed probes (divers), manual probe. **Evolution of the plume advance.**
- Conductivity: fixed probes (divers), manual probe (Vertical profiling). **Arrival time and dispersion rates.**
- pH: pH probe. **Target value for alkaline hydrolysis and oxidant activation.**
- Sampling: at target levels, bladder pump and discrete interval sampler
- Control of injected and pumped volumes/time
- Immediate in-lab determination:
  - Surfactant: FID-ECD (limonene, doped with 1-3 DCB). **Concentration along the M layer.**
  - Bromide: selective electrode, IC (ion chromatography). **Mass balance between injection and pumping. Dispersion rates.**
  - Persulfate: titration. **Oxidant evolution in the barrier zone.**
  - COCs: ECD – FID. **Mass of contaminants removed and evolution along the M layer.**

SEAR 1– INJECTION-PUMPING



SURFACTANT SOLUTION

- **E-Mulse®: 20 g/l.**
- **Bromide: 200 mg/l.**
- **H_2O_2: 1% v:v**
- **conductivity 6,5 mS/cm.**
- **Volume: 9,3 m^3**

Injected volume:

- **L1 (P198) 2.3 m^3 in 127 minutes**
- **L2 (P195) 7.0 m^3 in 457 minutes**
- **Recirculation P171-P195 0.6 m^3 in 100 minutes**
- **Recirculation P172-P198 0.18 m^3 in 100 minutes**

Recovered volume

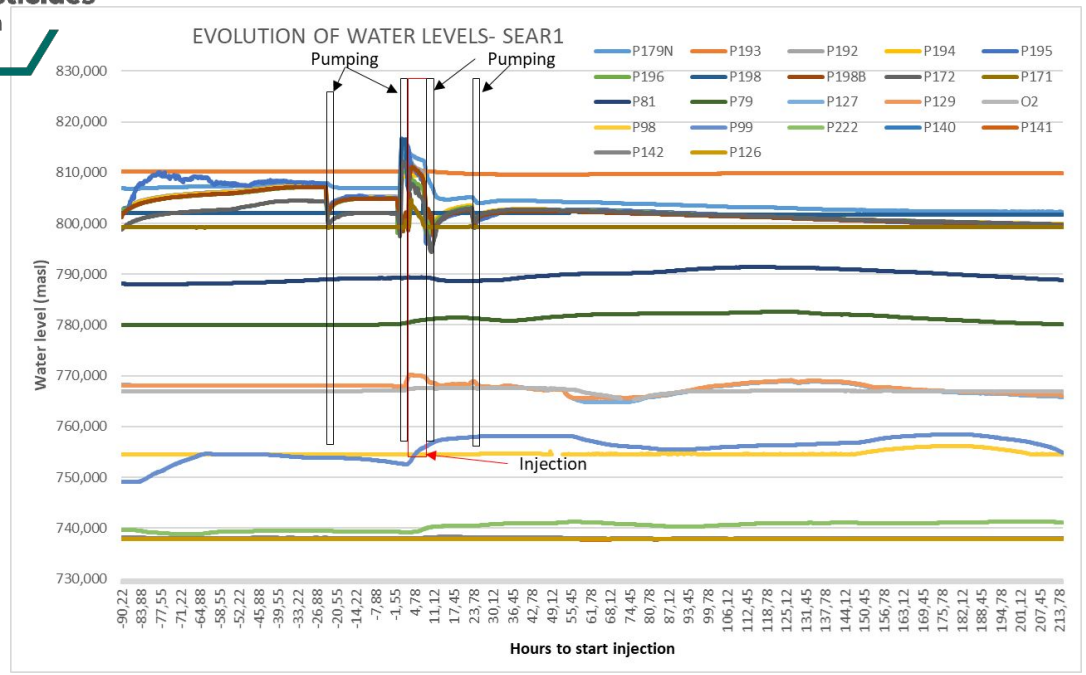
- **P195: 0,82 m^3**
- **P196: 2,17 m^3**
- **P171: 3,19 m^3**
- **P172: 0,96 m^3**
- **Total 7,14 m^3 (76,8 %)**

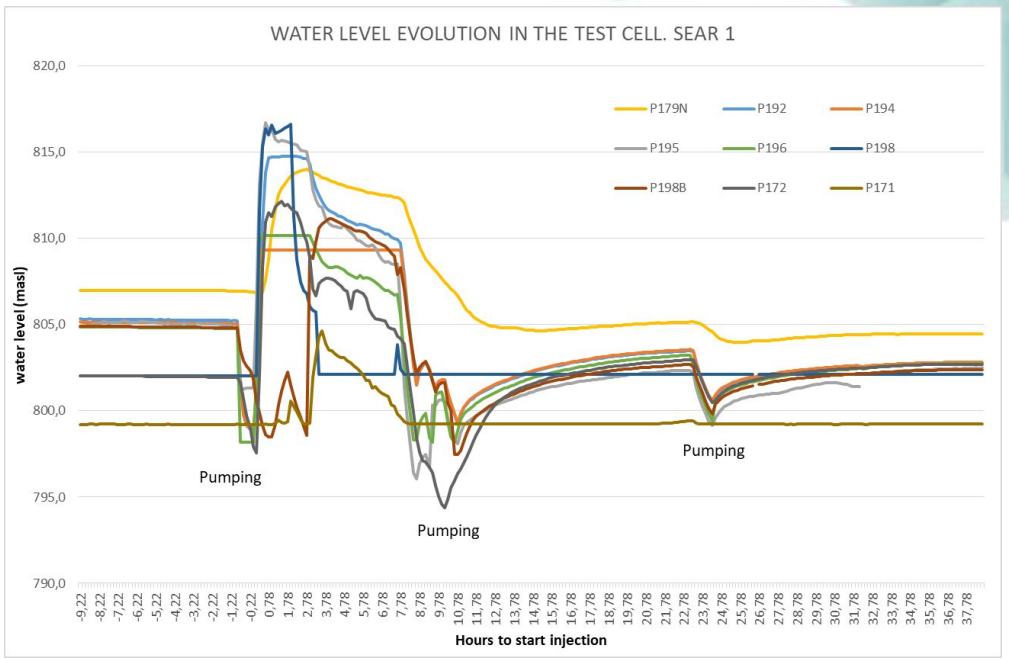
Recovered mass:

- **Bromide: 56 %.**
- **Conductivity: 57 %**
- **E-Mulse®: 29 %**

± 50 % of the tracer mass circulates downstream.
The surfactant is not conservative, about 25 % has been absorbed in the cell.

SEAR 1– WATER LEVEL

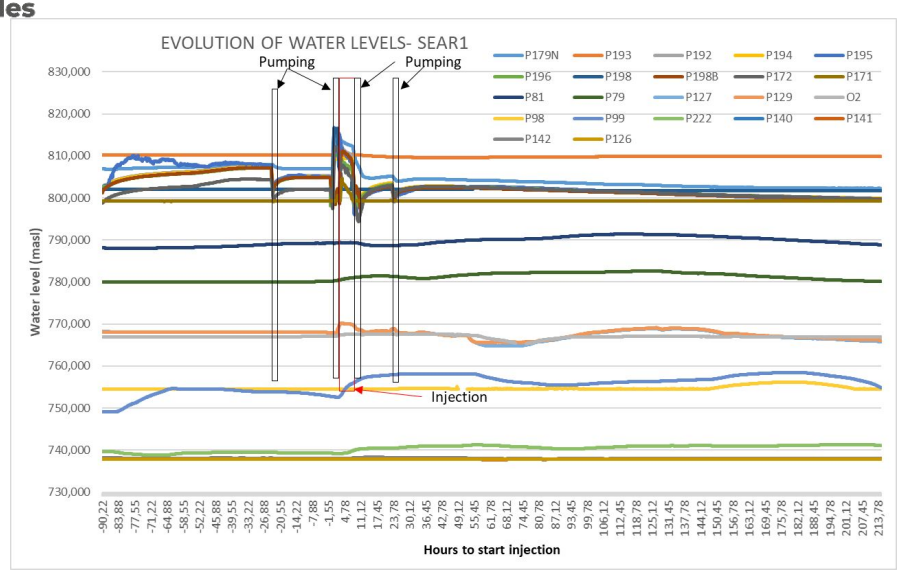


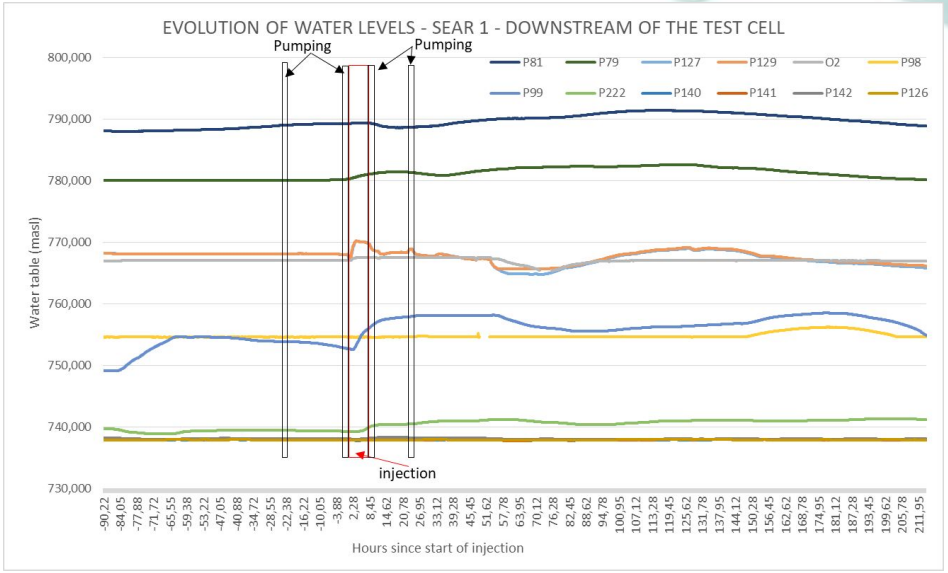


In the test Cell:

- **Rapid responses** to injection and pumping.
- **Target levels** have been **reached**
- **Foams** are generated reaching the **vadose zone with DNAPL**
- **Descent is prolonged for 9 days, level is below initial low water level**
- Significant mass of **fines mobilized with DNAPL**
- Partial effectiveness of pressure pulses at P194
- **The disconnection level** between P198 and P171-P172 **drops 3 meters.**

SEAR 1– WATER LEVEL

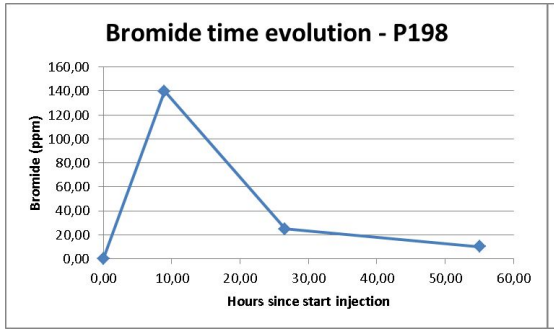


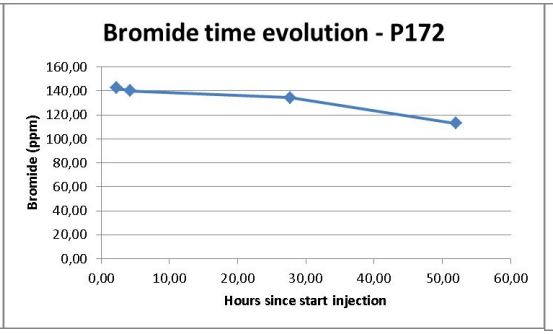


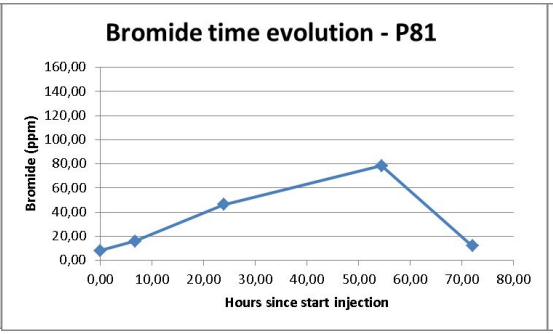
DOWNSTREAM:

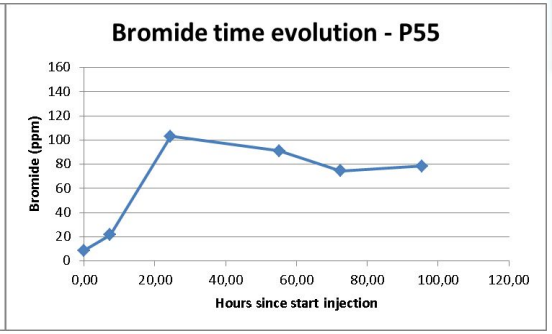
- **Rapid responses** to injection and pumping.
- **The ascent is heterogeneous**, depending on the recovery status of each well.
- **The ascent is moderate**, less than 3 meters.
- At the beginning of the **barrier zone** the **peak level** is reached in **5.5 days. Recovery** occurs in **9 days.**
- In the **boreholes near the river** there is an initial moderate response (30 cm) due to pressure adjustment, later it **is not detected.**
- The response is similar to that already observed in previous tests, with lower elevations due to lower circulating volume and similar passage times.

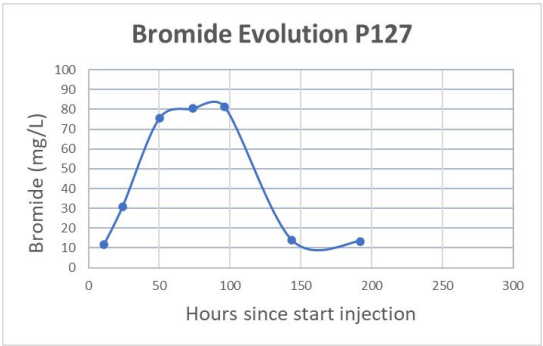
SEAR 1– BROMIDE EVOLUTION

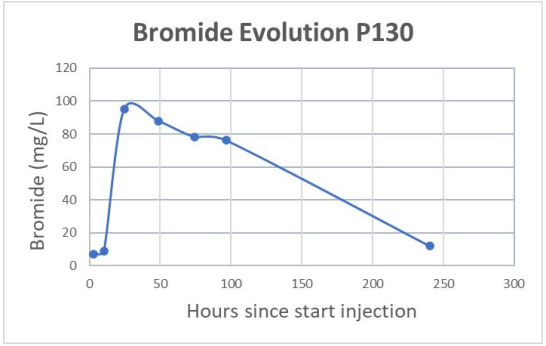


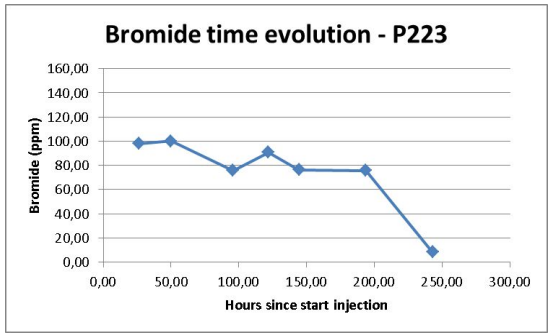


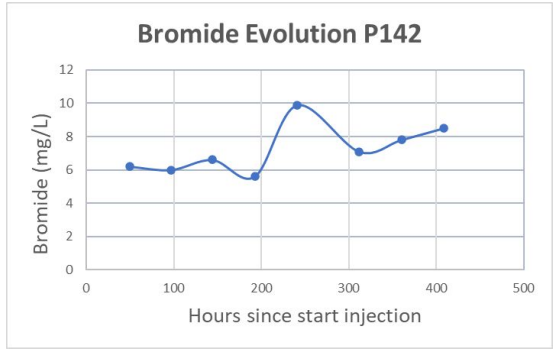






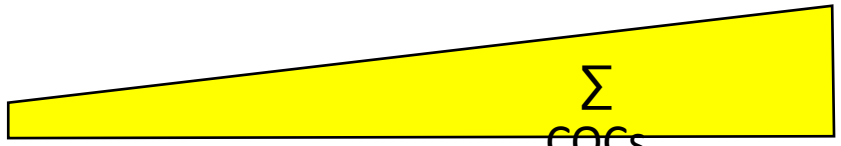




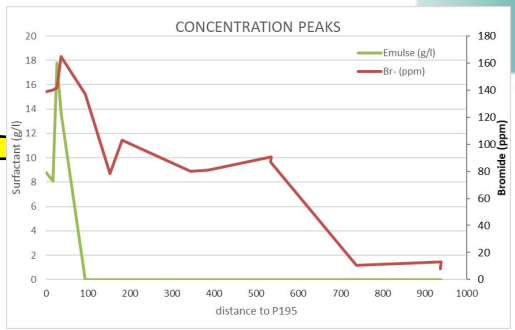


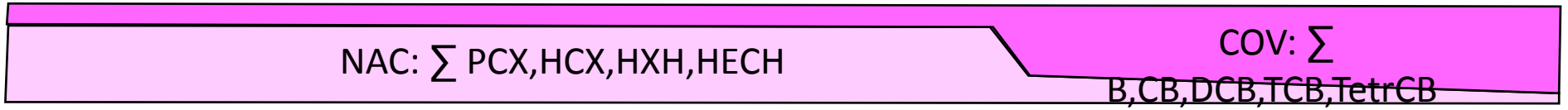
- ✔ In the injection cell, the bromide tends to baseline values when the injection is stopped.
- ✔ In poorly communicated boreholes in the lower part (P172) it is retained without being mobilized.
- ✔ Downstream the arrival of bromide at the beginning of the barrier zone occurs around 10 hours, the peak between 20 and 50 hours and the passage of the plume around 8 days.
- ✔ Not all the boreholes recover the baseline level; in some the bromide is immobilized in poorly communicated levels.
- ✔ The passage of the plume is slightly slower than that observed in previous tests.

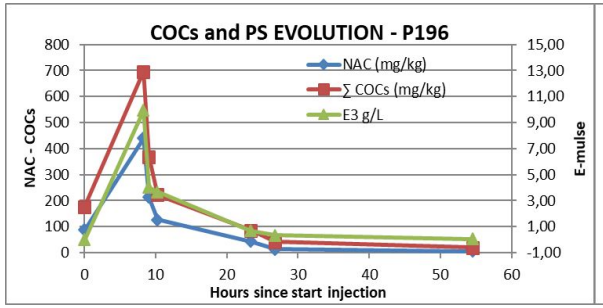
SEAR 1– COCs&REAGENTS EVOLUTION

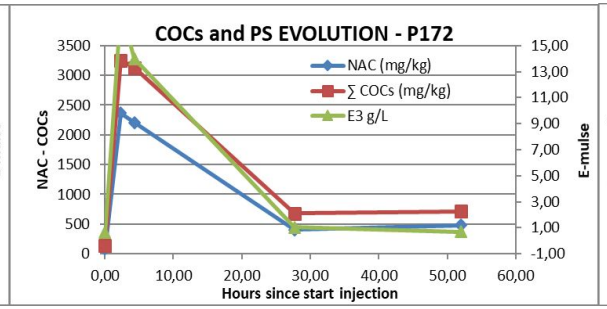


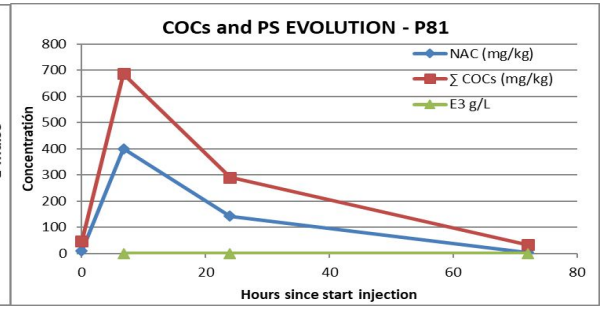
?

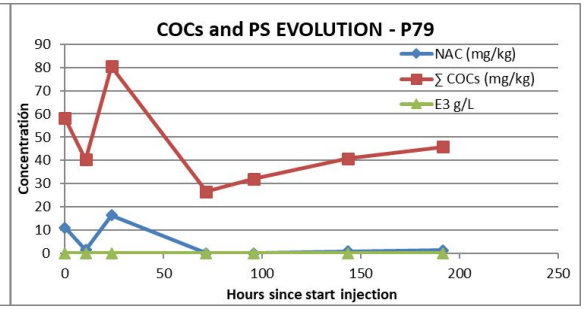




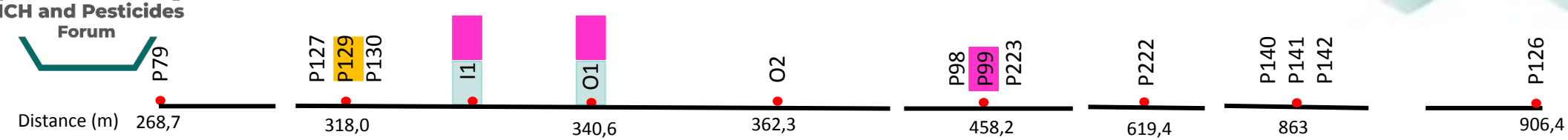








SEAR 1– COCs&REAGENTS EVOLUTION



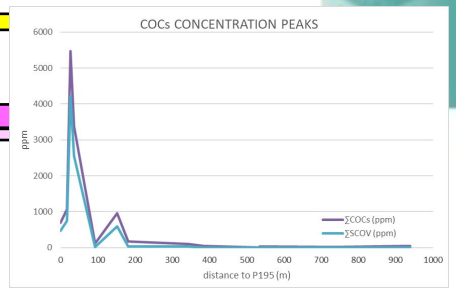
∑ COCs

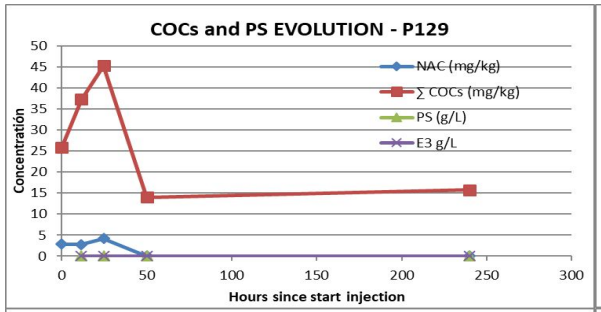
COV: ∑ B,CB,DCB,TCB,tetraCB

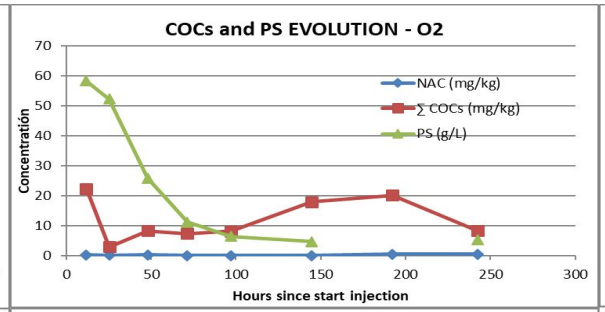
NAC: ∑ PCX,HCX,HXH,HECH

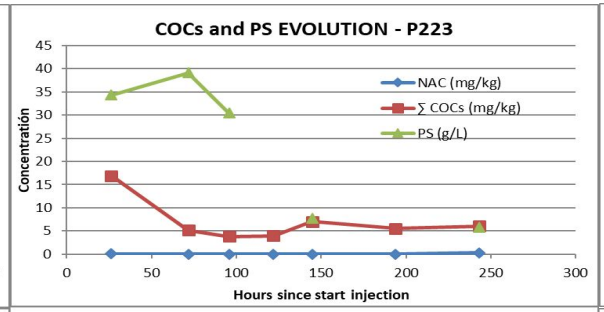
pH>11 ⟷ pH<8

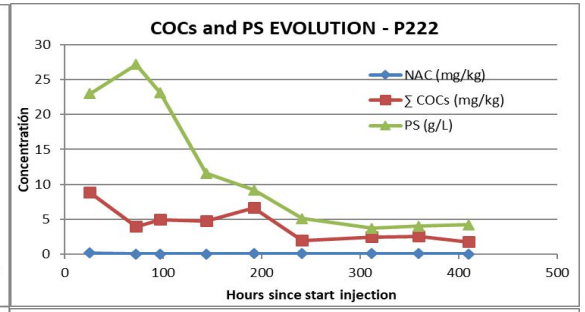
Persulfate

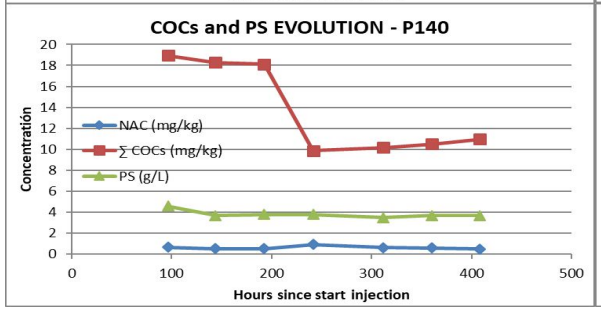


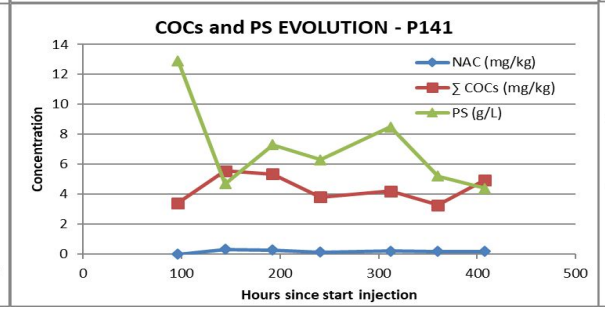


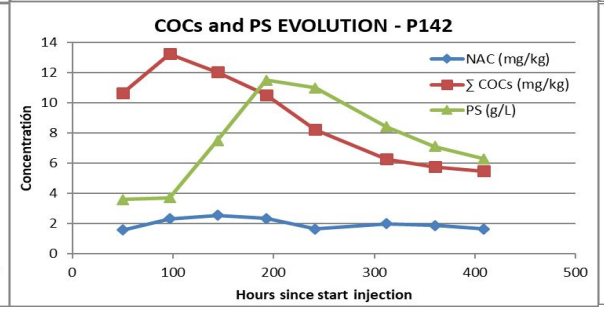


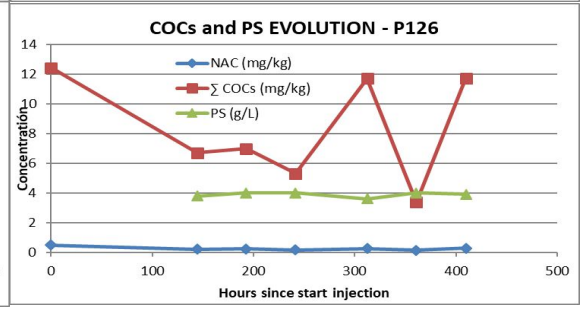












SEAR 2

OBJECTIVES:

- ✔ Conditions for a push and pull application of surfactant with a short residence time.
- ✔ Facilitate the mobilization and pumping of residual DNAPL.
- ✔ Solubilize the residual dense phase in P172 and P171 boreholes.
- ✔ Recover as much emulsion volume as possible.
- ✔ Prevent surfactant and mobilized COCs from reaching sensitive receptors.

REAGENTS:

SURFACTANT SOLUTION

- E-Mulse®: 20 g/l.
- Bromide: 200 mg/l.
- H_2O_2: 1% v:v
- conductivity 6,5 mS/cm.
- Volume: 6 m^3
- Time 6 h
- Q med.: 16,7 l/min

OXIDIZING SOLUTION

- NaOH 25%: target pH > 12
- $H_2S_2O_8$: 80 g/l
- Volume: 7,9 m^3
- Time 96 h
- Q med.: 1,4 l/min

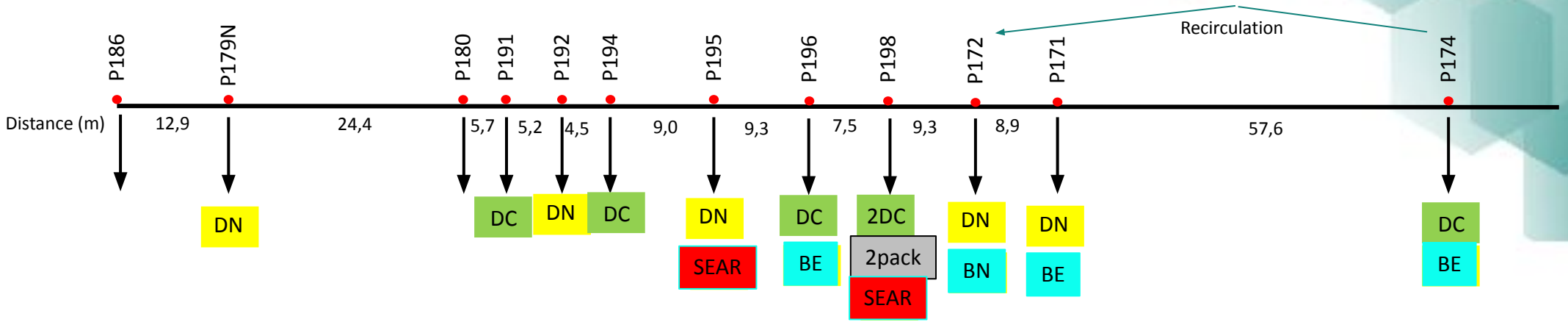
ALKALINE SOLUTION

- NaOH 25%: target pH > 12
- Volume: 200 l
- Q med.: 2,08 l/h

AERATION

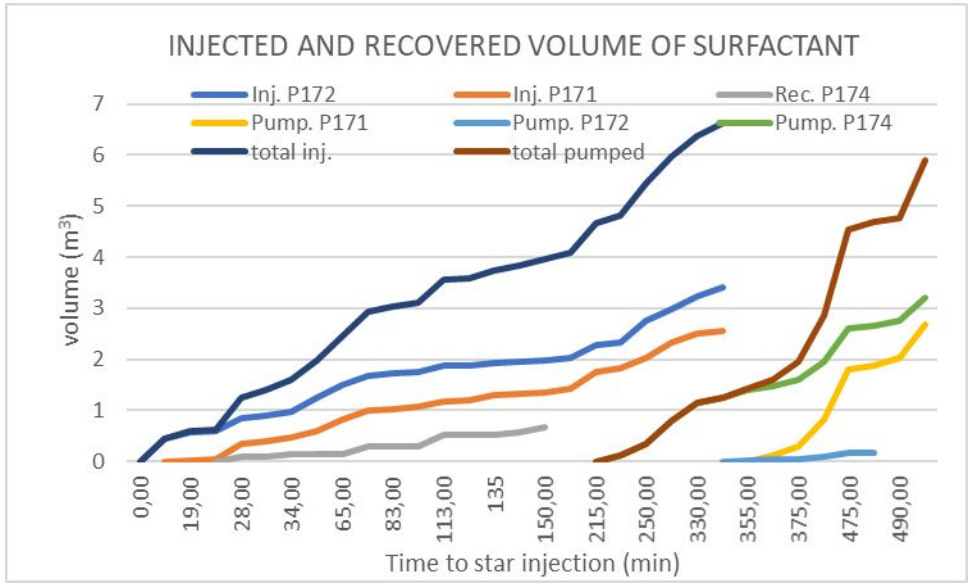
- Injection 3,7 bar
- Q injection 29,5 m3/h
- Vacuum 31,6 mbar
- Defoamer 10%
- Time 10 days

SEAR 2– INJECTION-PUMPING



SEAR: surfactant, H_2O_2, Br^-
NaOH: soda 25 %
AE: defoamer
Air: aireation
PS: activated persulfate
BE: electric pump
BN: pneumatic pump
DN: level probe
DC: level and conductivity probe

SEAR 2– INJECTION-PUMPING



SURFACTANT SOLUTION

- **E-Mulse®: 20 g/l.**
- **Bromide: 200 mg/l.**
- **H_2O_2: 1% v:v**
- **conductivity 6.5 mS/cm.**
- **Volume: 7.9 m^3**

Injected volume:

- **L1 (P172) 3.41 m^3 in 340 minutes**
- **L2 (P171) 7.0 m^3 in 340 minutes**
- **Recirculation P174-P171 0.66 m^3 in 130 minutes**

Recovered volume

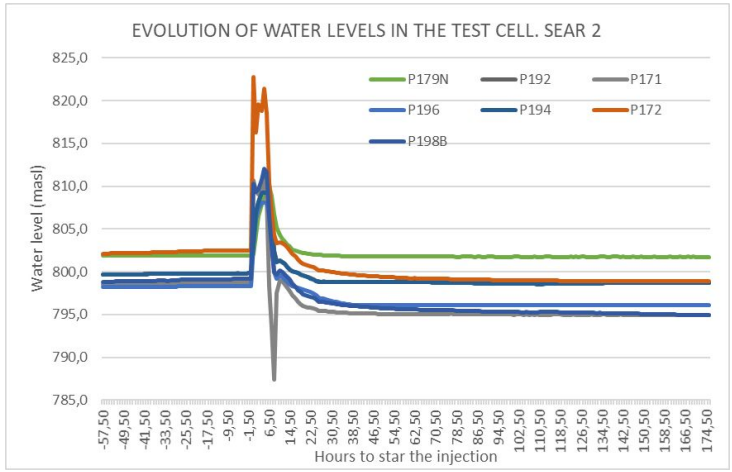
- **P172: 0.17 m^3**
- **P171: 2.68 m^3**
- **P174: 3.20 m^3**
- **Total 6.05 m^3 (100 %)**

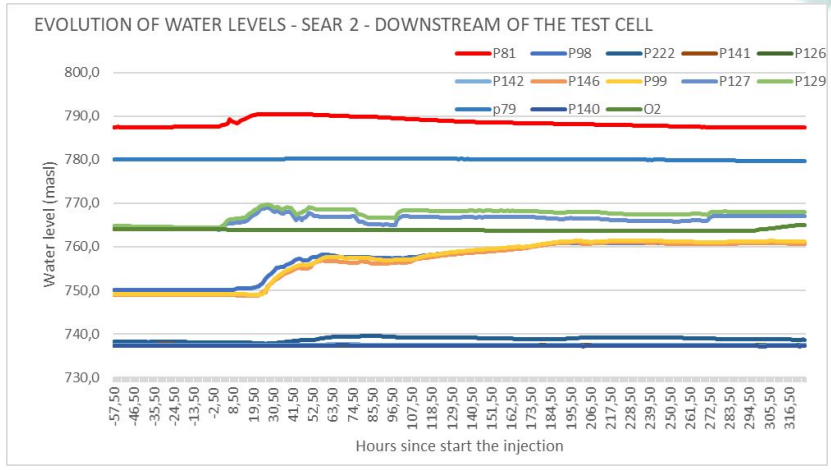
Recovered mass:

- **Bromide: 77 %.**
- **Conductivity: 83 %**
- **E-Mulse®: 46 %**

± 20-25 % of the tracer mass circulates downstream.
The surfactant is not conservative, about 30 % has been absorbed in the cell.

SEAR 2– WATER LEVEL





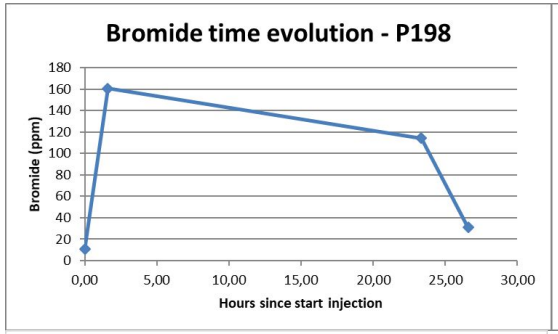
In the test Cell:

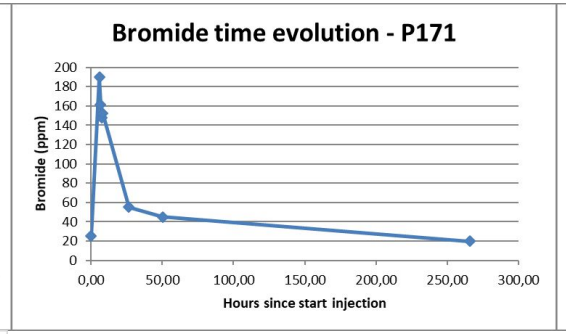
- **Similar a la del SER1: Rapid responses** to injection and pumping, t**arget levels** have been **reached, foams** are generated reaching the **vadose zone with DNAPL**
- **The descent is faster** than in the first test, between 24 and 72 hours. However, the **base level** is not recovered by going **4 meters deeper.**

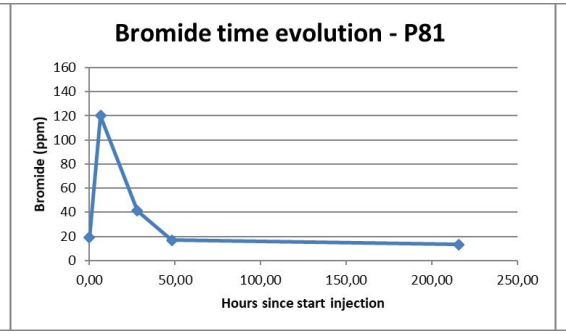
Downstream:

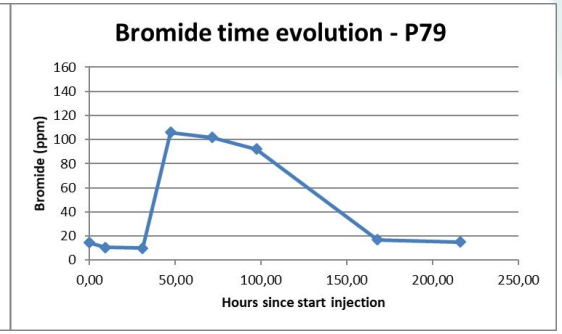
- **Rapid responses to injection and not appreciated when pumping.**
- The **ascent is heterogeneous**, depending on the recovery status of each well. It varies from a few centimeters to 12 meters.
- At the **beginning of the barrier zone**, the maximum level is reached in **24 hours** and the base level is not recovered.
- With the levels it is not possible to establish the time of passage of the plume.
- **In the wells near the river there is no response.**

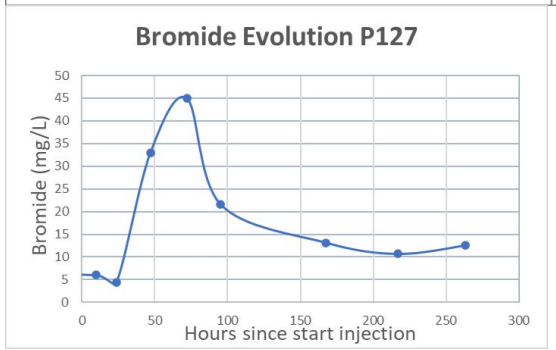
SEAR 2– BROMIDE EVOLUTION

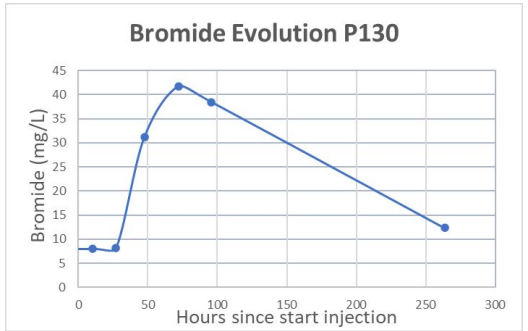


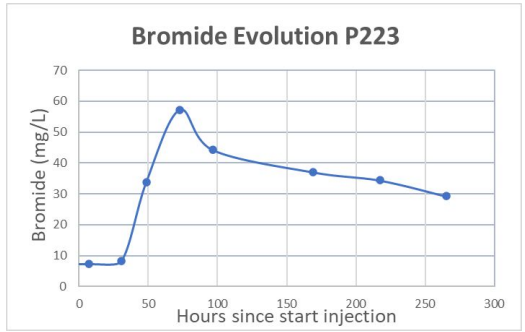


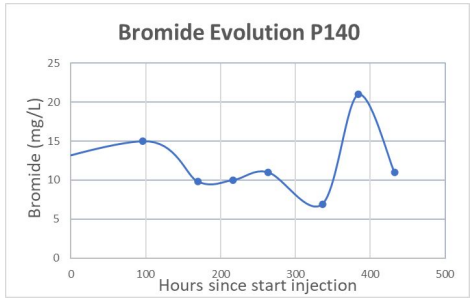






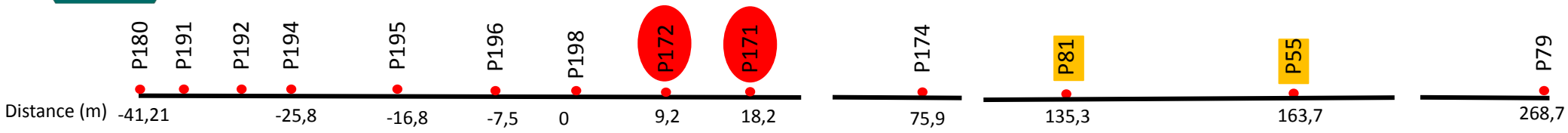


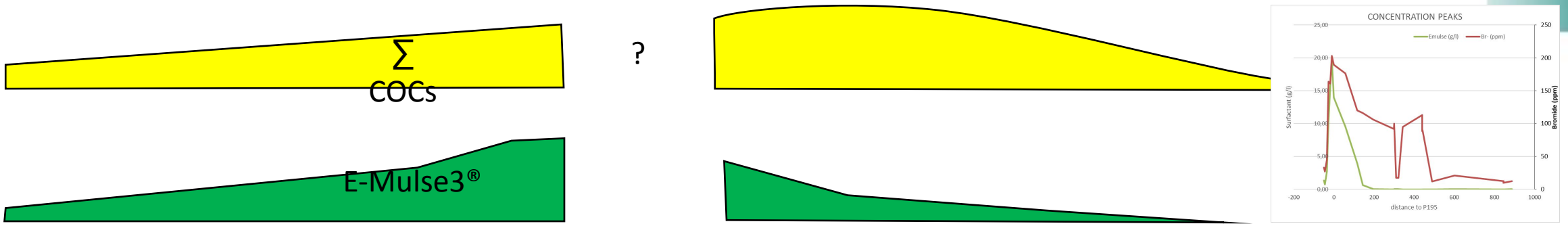


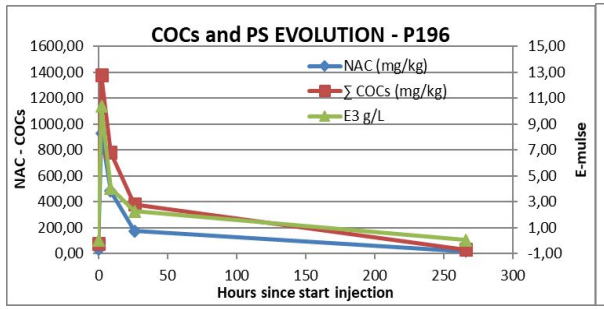


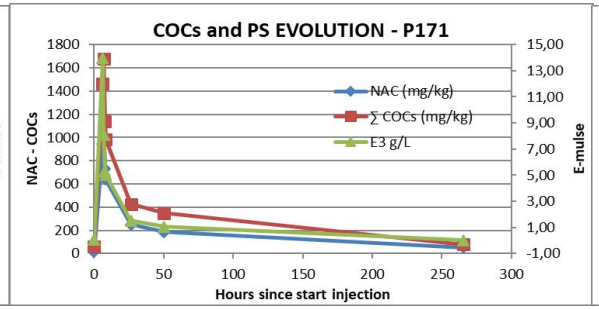
- ✔ In the injection cell, the bromide tends to baseline values when the injection is stopped.
- ✔ Downstream, the recovery of the base level is delayed. The arrival at the barrier zone is detected before 24 hours, the peak at 48 hours and the transit time between 7 and 9 days.
- ✔ Not all the boreholes recover the baseline level; in some the bromide is immobilized in poorly communicated levels.
- ✔ The plume passage time is similar to the previous SEAR.
- ✔ In the boreholes near the river, the base level is maintained.

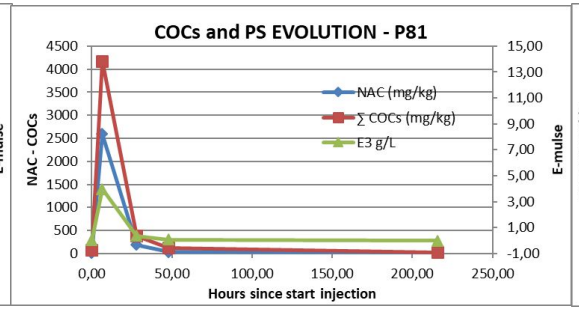
SEAR 2– COCs&REAGENTS EVOLUTION

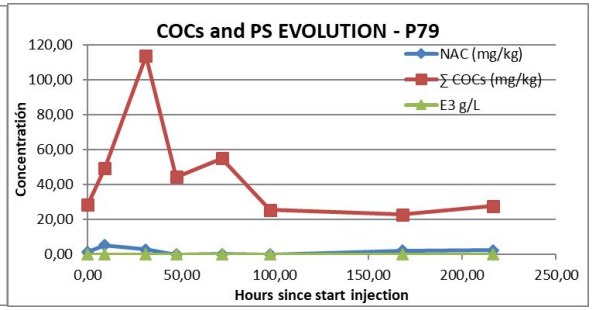




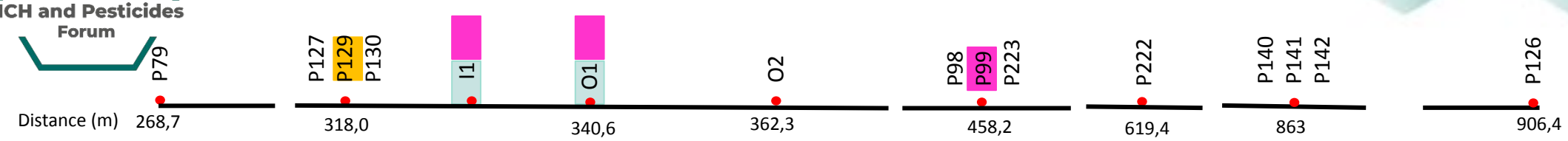


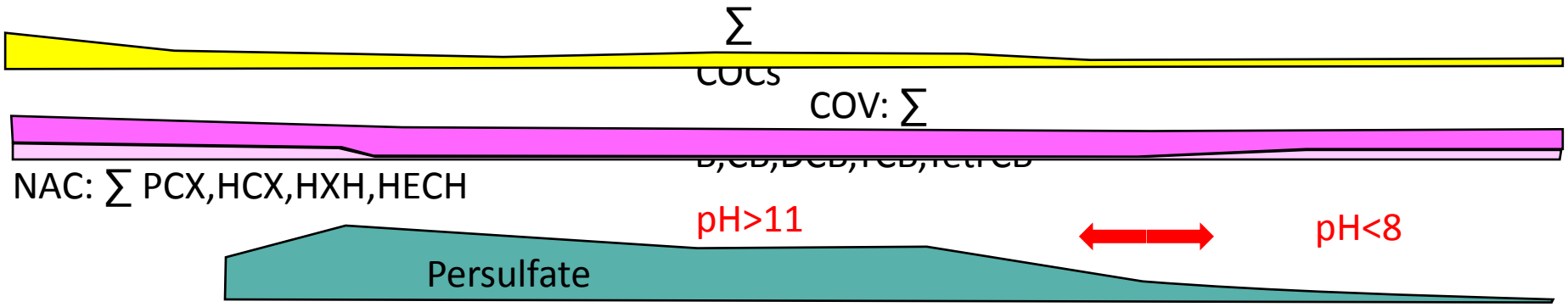


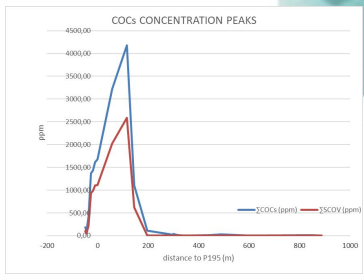


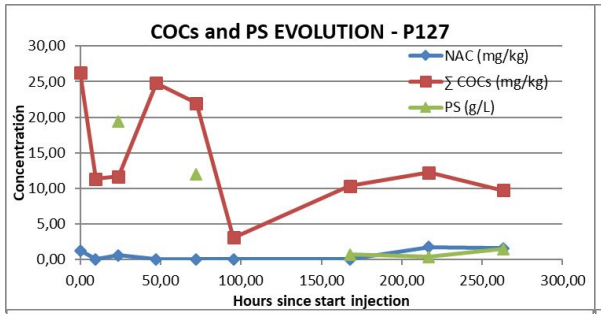


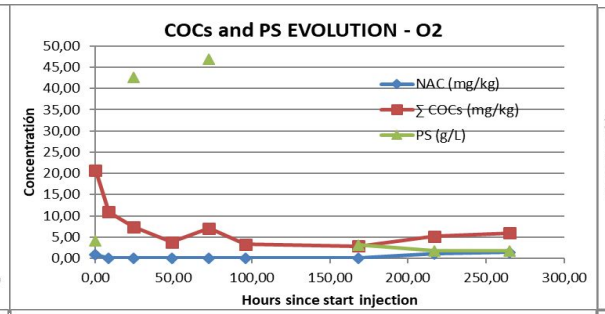
SEAR 2– COCs&REAGENTS EVOLUTION

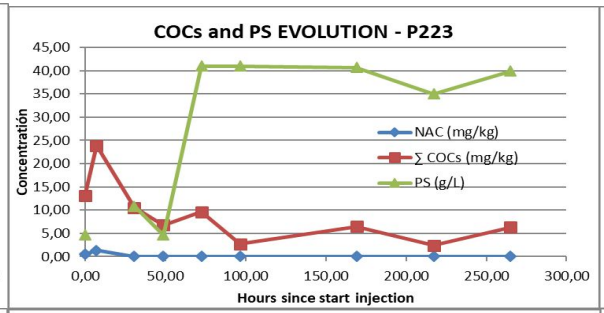


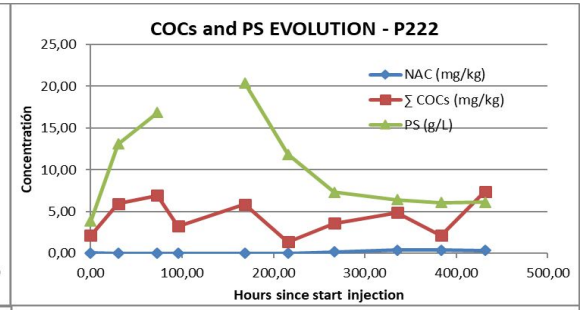


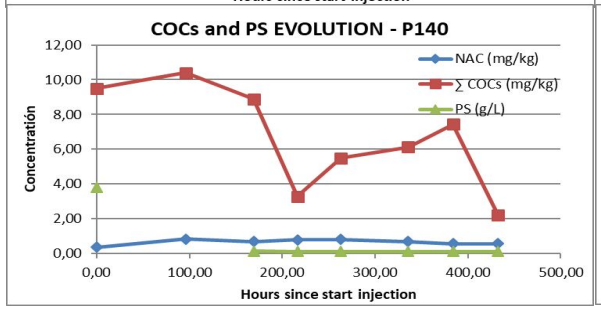


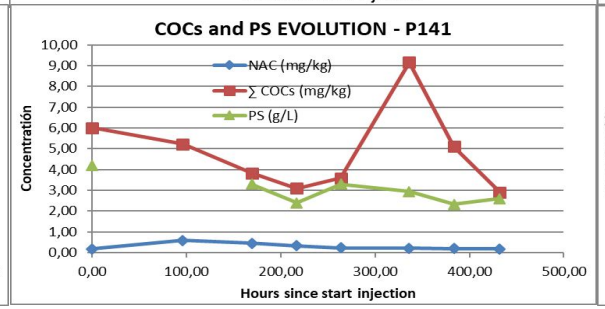


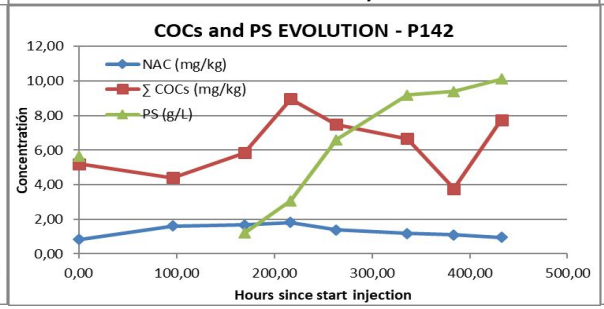


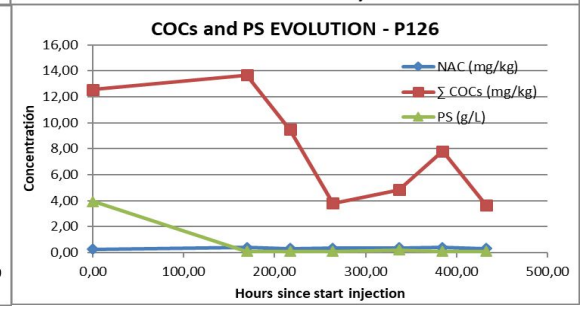












SEAR- CONCLUSIONS

- At the end of the two tests **100 kg of DNAPL were removed** (90 as DNAPL and 10 as dissolved DNAPL).
- Excluding the contaminant degraded during the test, the **productivity** obtained was **1:3.4 (DNAPL:Surfactant)**.
- **Surfactant-enhanced DNAPL extraction is a viable in heterogeneous fractured media.**
- A **detailed knowledge of the aquifer is necessary** to design the strategy for injection and recovery of the surfactant and contaminants.
- The **addition of hydrogen peroxide has generated foams** that have filled the vadose zone. The foams slow downstream flow and improve recovery of the contaminated emulsion by pumping.
- There has been a significant mobilization of fines and clays clogging the bottoms of the wells test cell and DNAPL with these particles.
- The **surfactant does not have a conservative behavior**, being adsorbed in the clays that fill fractures and absorbed in the DNAPL. Surfactant destabilizes at high pHs, preventing its arrival at the barrier zone.
- The addition of NaOH downstream and the combination of oxidation and aeration in barrier permit the practical disappearance of the heavy chlorates (PCX,HCX,HXH,HECH) and the degradation of the lighter ones at lower concentrations than the initial ones. The addition of NaOH is necessary to maintain persulfate activation due to the tendency to neutralize the pH in a carbonate medium.

14th International HCH and Pesticides Forum

THANK YOU FOR YOUR ATTENTION

jfernandezc@aragon.es

http://www.descontaminacionlindano.aragon.es

GOBIERNO DE ARAGON

GOBIERNO DE ARAGON
Departamento de Agricultura, Ganadería y Medio Ambiente

sarga

IHPA
International HCH & Pesticides Association

UNIVERSIDAD COMPLUTENSE MADRID

Universität Stuttgart