14th International HCH and Pesticides Forum

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LIFE SURFING PROJECT, IN SITU CHEMICAL OXIDATION ENHANCED WITH SURFACTANTS (SISCO) IN A FRACTURED AQUIFER

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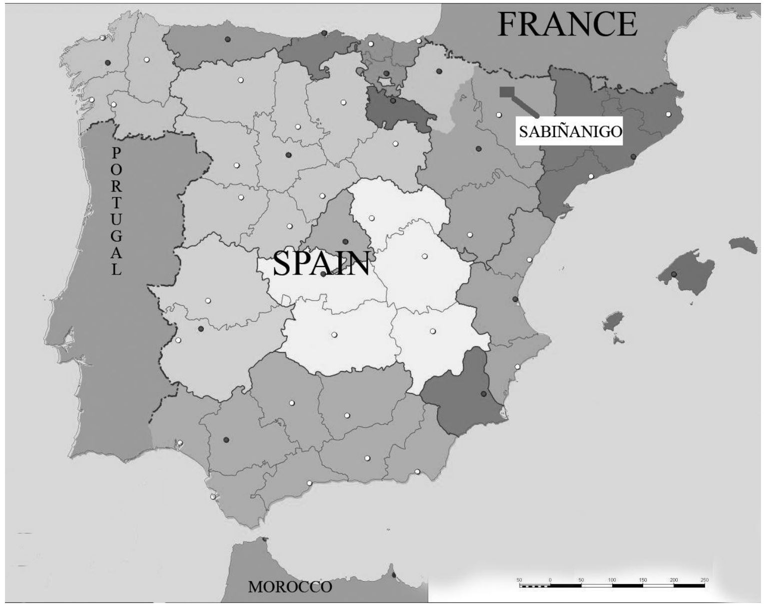
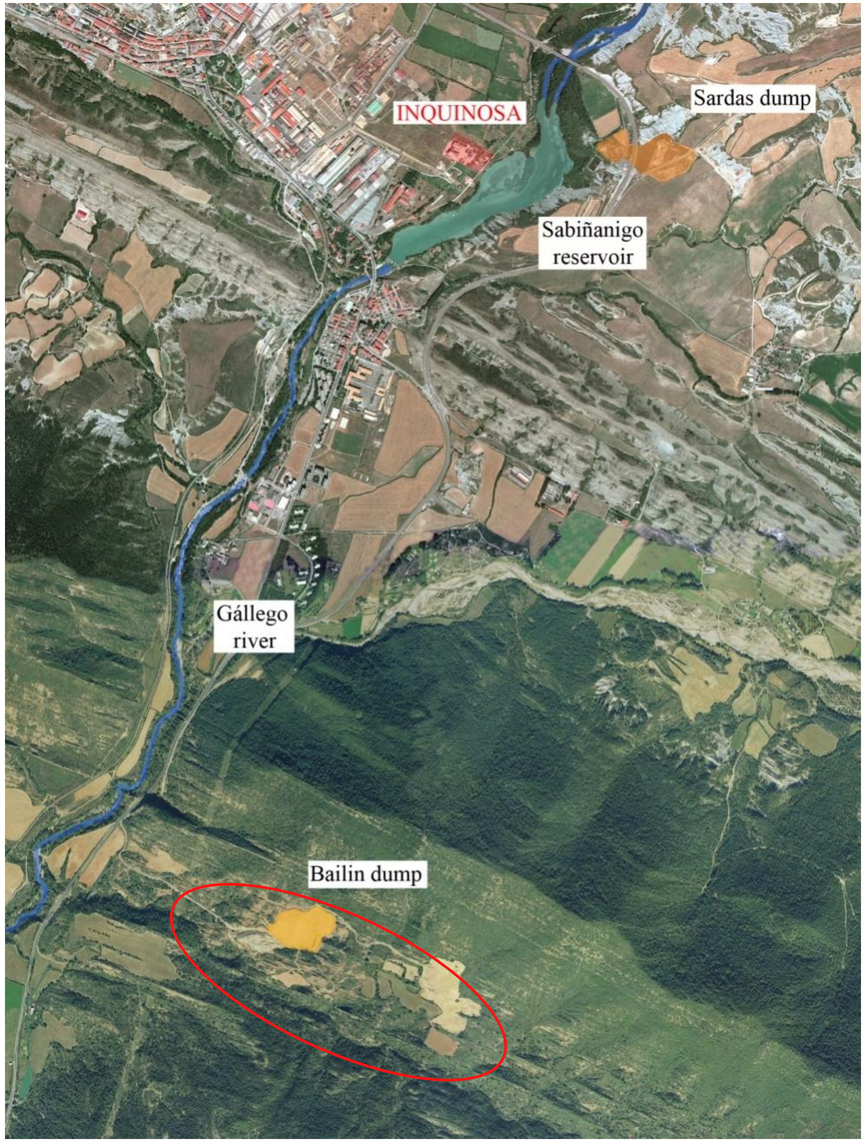
IHPA
International HCH & Pesticides Association

UNIVERSIDAD COMPLUTENSE MADRID

Universität Stuttgart

GEOGRAPHIC LOCATION





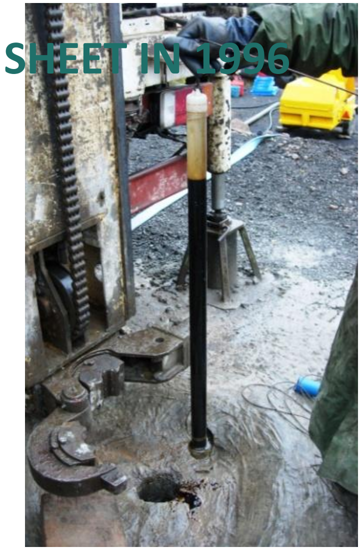
Main sources of lindane manufacturing waste:

- OLD INQUINOSA FACTORY
- SARDAS LANDFILL
- BAILIN LANDFILL

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

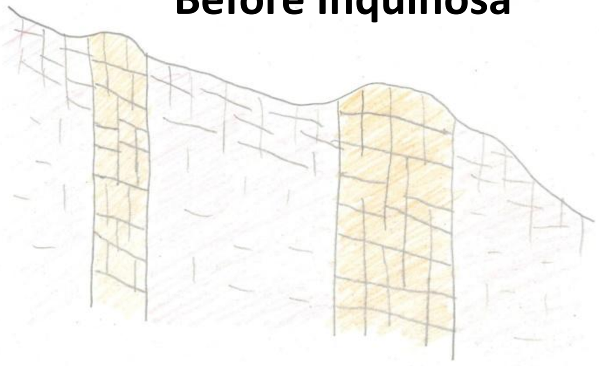


Composition of DNAPL samples from the Bailín landfill

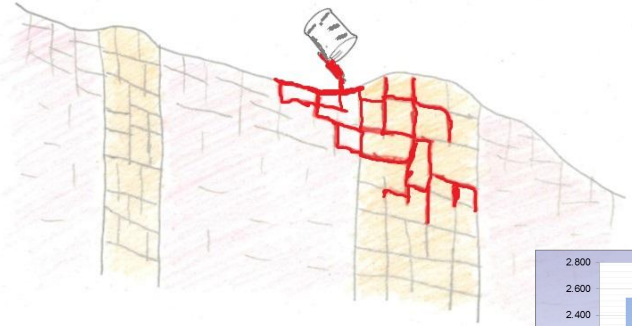
		BAILIN-O1 (UCM)-2018	BAILIN-20 /03/19	BAILIN-11/ 09/19
Bencene	%	na	na	na
CB	%	10.40	11.19	11.26
1,3 DCB	%	0.20	0.39	0.31
1,4 DCB	%	2.10	2.60	2.46
1,2 DCB	%	1.70	1.78	1.57
1,3,5 TCB	%	0.00	0.06	0.07
1,2,4 TCB	%	5.50	6.07	5.73
1,2,3 TCB	%	0.50	0.77	0.56
TetraCB (1,2,3,5 + 1,2,4,5)	%	1.40	2.19	2.01
TetraCB (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?

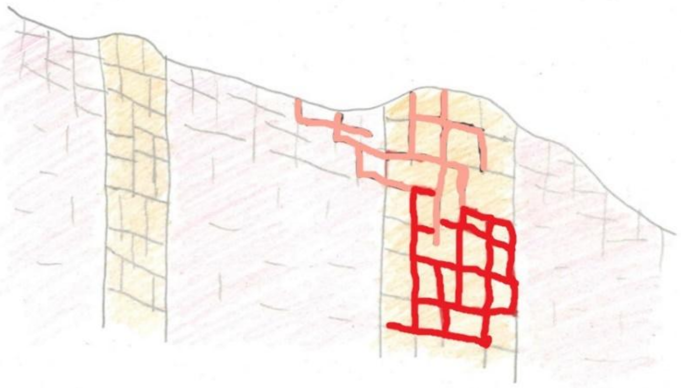
Before Inquinosa



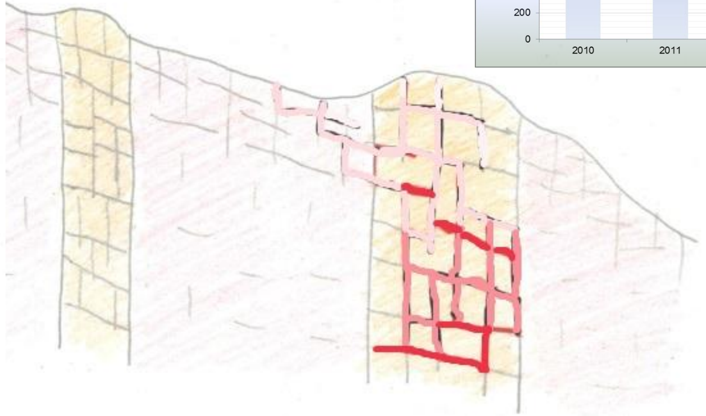
with INQUINOSA



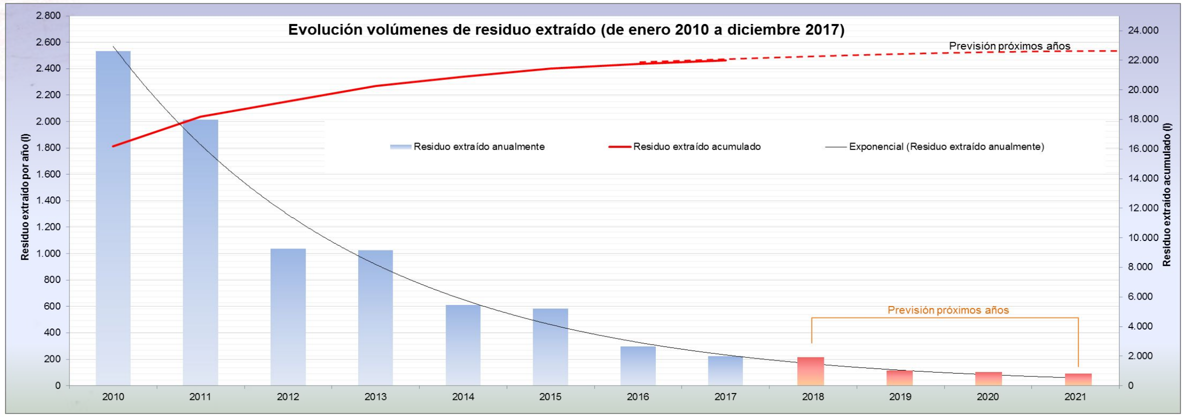
Before detecting DNAPL



In 2021



Evolution of DNAPL extraction



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

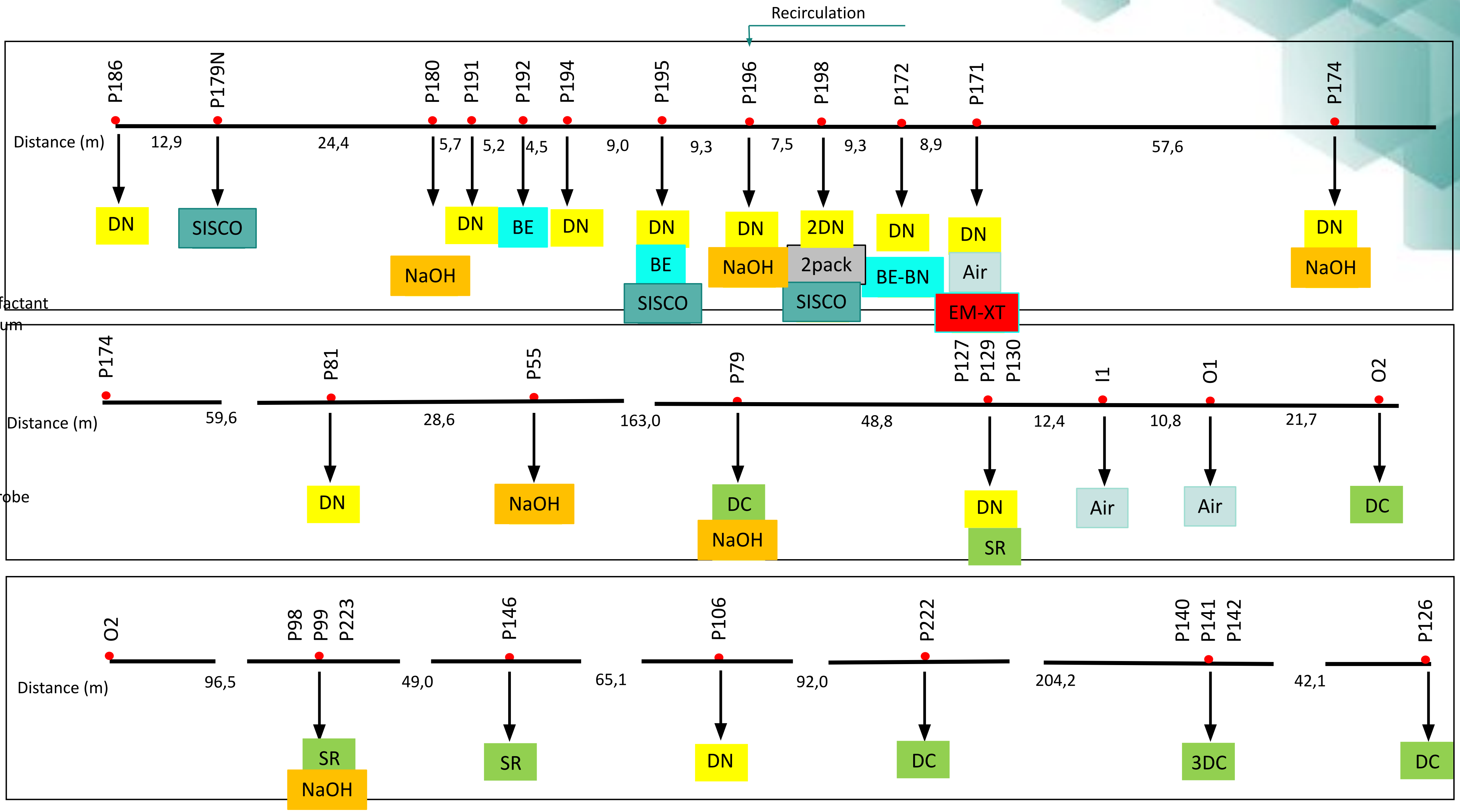
FLIX.NET **PRESENT: a LIFE production**

Chap 1: Phase 0 - PREPARATORY WORK

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

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

SISCO - DISPOSAL OF REAGENTS AND EQUIPMENT



SISCO: persulfate, NaOH,surfactant
EM-XT: surfactant-xanthan gum
NaOH: soda 25 %
AE: defoamer
Air: aireation
PS: activated persulfate
BE: electric pump
BN: pneumatic pump
DN: level probe
DC: level and conductivity probe
SR: remote probe

SISCO

OBJECTIVES:

- ✔ Injection conditions to reach the target level and a residence time of several hours.
- ✔ Increase, between boreholes P192 and P198, the availability of wet COCs to improve in situ oxidation yields.
- ✔ Maintain downstream oxidant activation to degrade mobilized COCs before they reach sensitive receptors.

REAGENTS:

OXIDANT SOLUTION
- E-Mulse®: 4 g/l.
- Persulfate: 40 g/l
- NaOH 25%: 41.37 g/l
- Target pH 12
- Volume: 20 m^3
- Time 2 days

FOAM SOLUTION
- E-Mulse®: 5 g/l.
- Xanthan Gum: 2 g/l
- Volume: 2 m^3
- Time 48 h

ALKALINE SOLUTION
- NaOH 25%: target pH > 12
- Volume: 200 l
- Q med.: 1,4 l/h

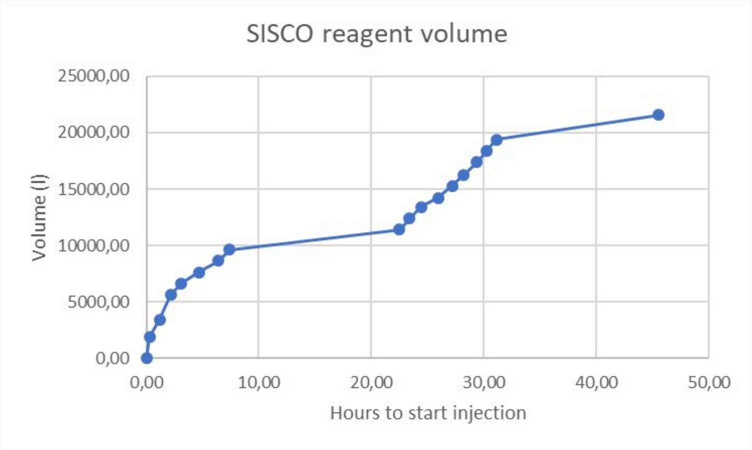
AERATION
- Injection 3,7 bar
- Q injection 29,5 m3/h
- Vacuum 31,6 mbar
- Defoamer 10%
- Time 10 jours

SISCO– TEST MONITORING

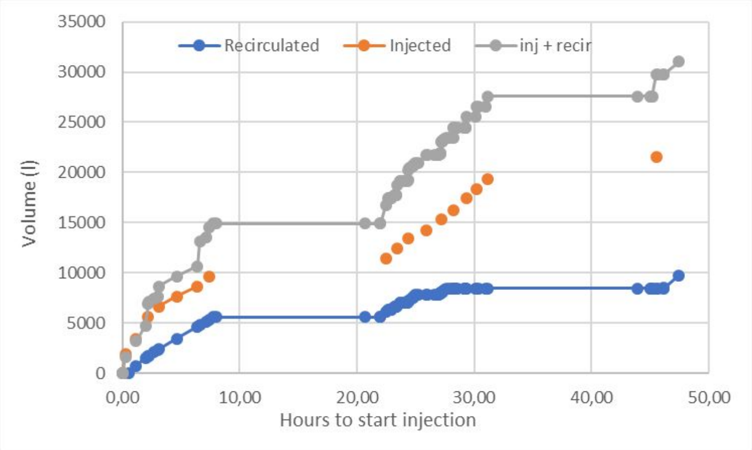
- Water level: fixed probes (divers), manual probe. Evolution of the plume advance.
- Conductivity: fixed probes (divers), manual probe (Vertical profiling). Arrival time and dispersion rates.
- pH: pH probe. Target value for acaline hydrolysis and oxidant activation.
- Sampling: at target levels, bladder 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 layer.
  - Persulfate: titration. Oxidant evolution in the barrier zone.
  - COCs: ECD – FID. Mass of contaminants removed and evolution along the layer.

SISCO– INJECTION

INJECTION: P198 and P195
RECIRCULATION: FROM P172 TO P196



Date	Start (h)	End (h)	Pulse time (min)	pulse	V 198 (m3 injected)	V195 (m3 injected)	Vtot. pulse (m3)
04/10/2022	13:00	13:16	16,00	1	0,93	0,93	1,86
04/10/2022	13:25	14:10	45,00	2	0,79	0,79	1,58
04/10/2022	14:10	15:10	60,00	3	1,09	1,09	2,18
04/10/2022	16:00	16:06	6,00	4	0,50	0,50	1,00
04/10/2022	17:28	17:39	11,00	5	0,50	0,50	1,00
04/10/2022	19:13	19:24	11,00	6	0,50	0,50	1,00
04/10/2022	20:14	20:24	10,00	7	0,50	0,50	1,00
05/10/2022	11:11	11:29	18,00	8	0,89	0,89	1,78
05/10/2022	12:14	12:24	10,00	9	0,51	0,50	1,01
05/10/2022	13:12	13:24	12,00	10	0,52	0,49	1,01
05/10/2022	14:45	14:56	11,00	11	0,41	0,40	0,81
05/10/2022	16:00	16:10	10,00	12	0,50	0,56	1,06
05/10/2022	17:02	17:12	10,00	13	0,49	0,50	0,99
05/10/2022	17:58	18:22	24,00	14	0,15	0,96	1,11
05/10/2022	19:00	19:12	12,00	15	0,50	0,50	1,00
05/10/2022	20:00	20:07	7,00	16	0,51	0,49	1,00
06/10/2022	9:55	10:33	38,00	17	1,10	1,10	2,20
						TOTAL	21,58

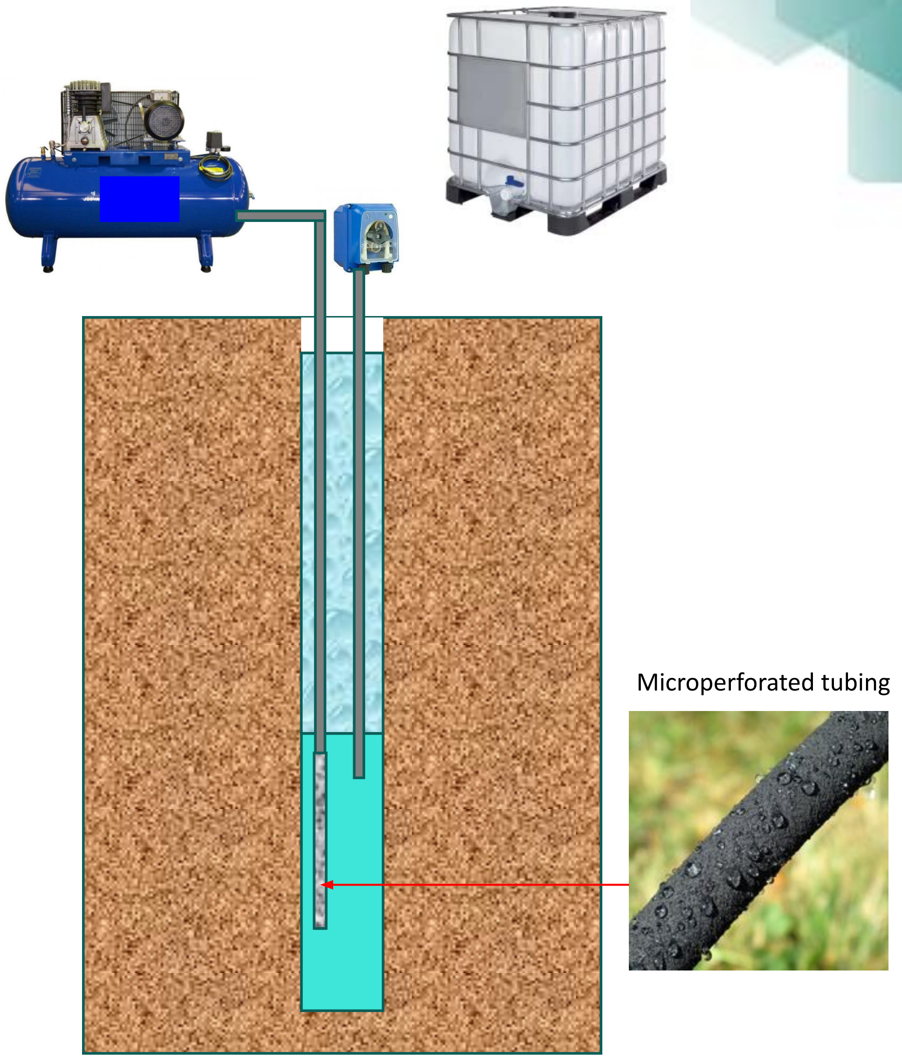


RECIRCULATION: Poor performance. Operational problems. Pneumatic pumps give low performance (100 l/h). The electric pump (1000 l/h) exhausts the well and does not allow continuous operation. It is necessary to obtain a system with electric pump and variator to adjust pumping flow rates and work continuously.

SISCO– INJECTION

FOAM BARRIER

- Aqueous solution with 2 g/l Xanthan Gum and 5 g/l Emulse.
- Aeration: field compressor, plant compressor, diffusion through microperforated irrigation pipe (11 meters).
- Foam is only generated above the phreatic when aeration is initiated.
- RECOMMENDATIONS:
  - Improve foam durability (e.g. add starch).
  - Generate foam in plant and inject it into borehole without equipping under packer at different heights.
  - Objective: create a barrier along the entire length of the borehole (below and above the water table), promote its infiltration over the width of the layer (infiltrate under packer under pressure).



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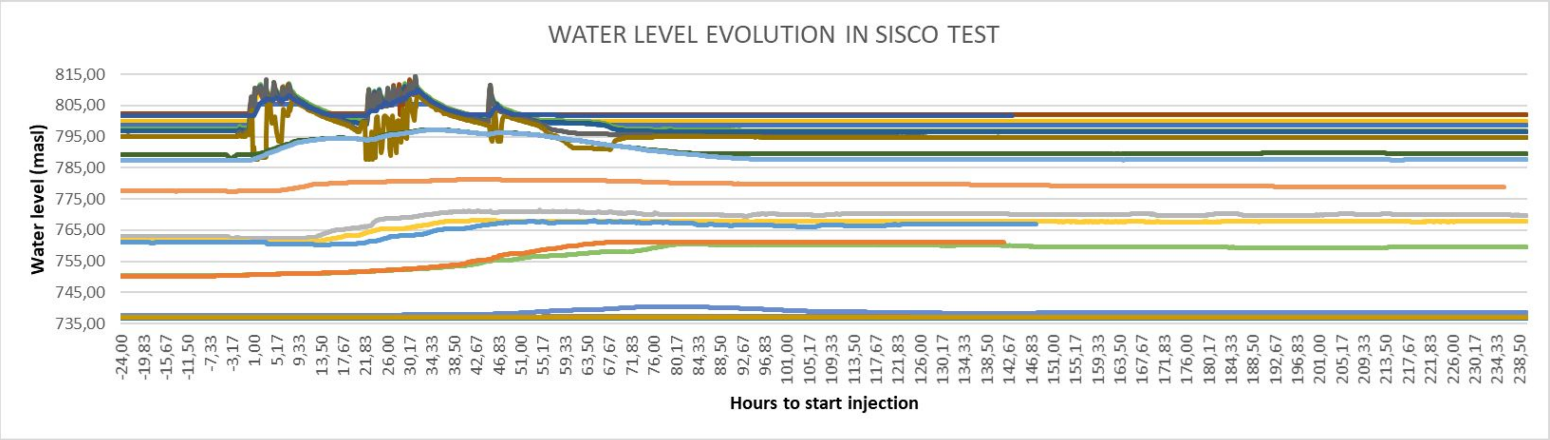
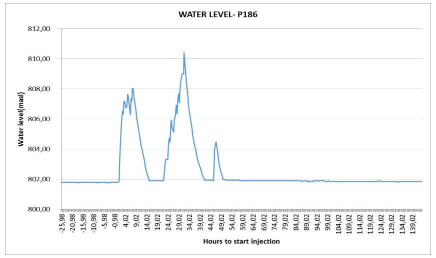
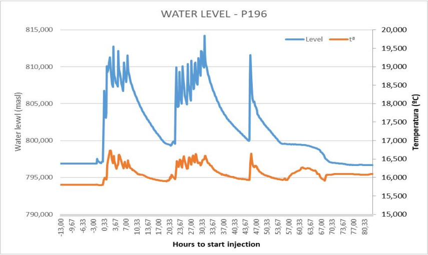
SISCO– WATER LEVEL

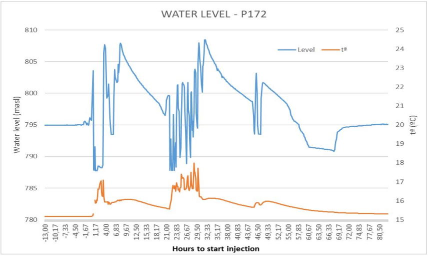




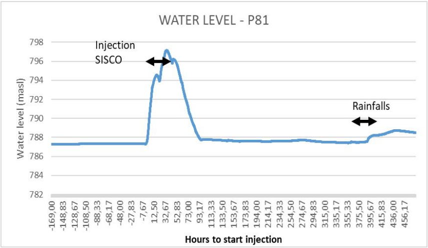
Upstream of the cell, immediate response, gradient reversal



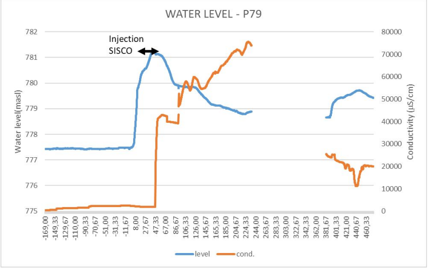
Test cell, target levels are reached



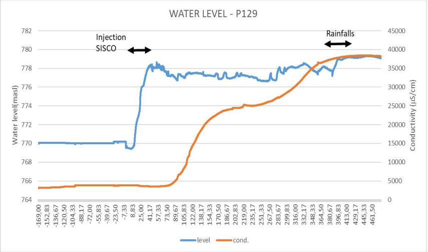
Pumping and recirculation. Poor function of the pumping system



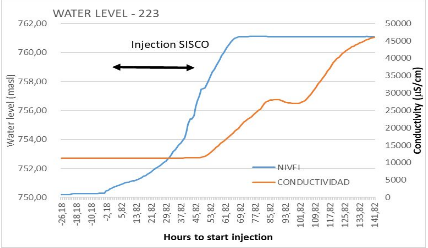
Downstream of the cell, immediate response. Pulses are grouped. Base level recovers in 4 days.



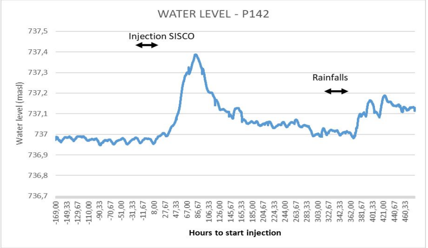
Before barrier zone, immediate response (2.5 hours), no base level recovery



Beginning of barrier zone, response at 11h, no recovery of base level

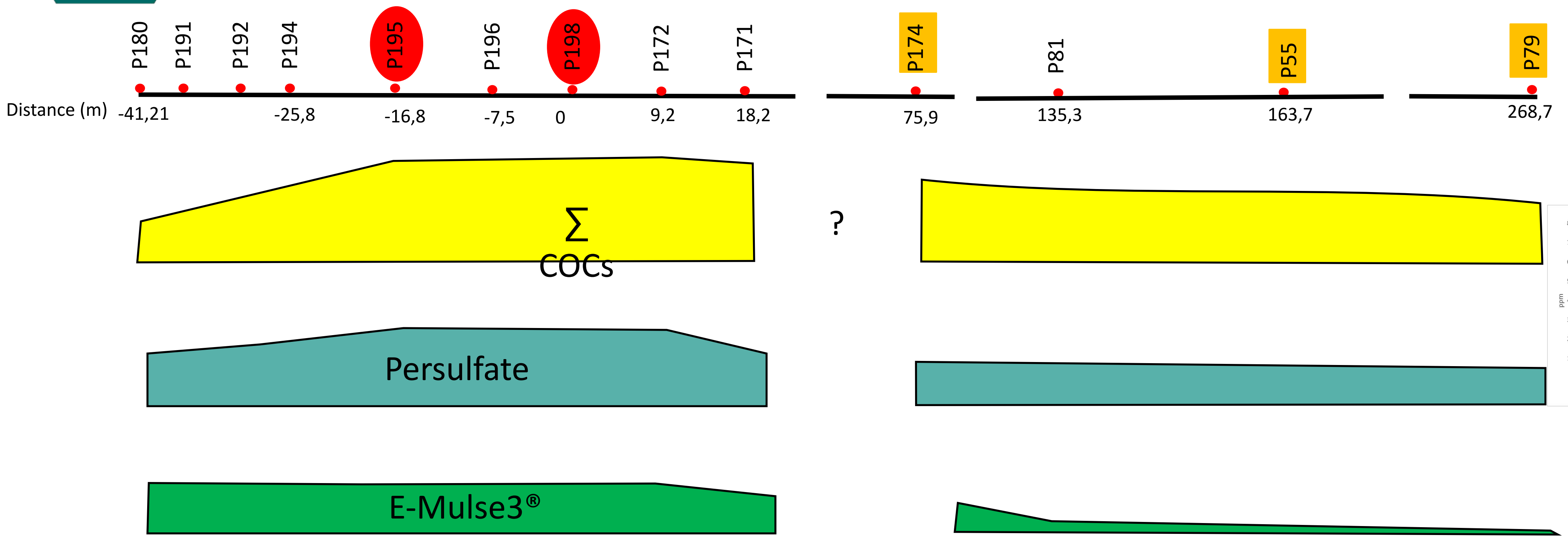


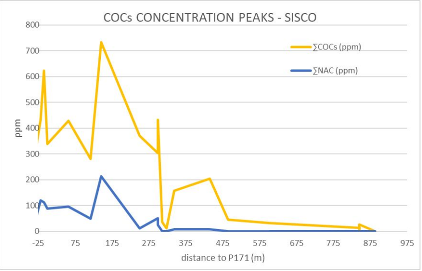
End of barrier zone, immediate level response. 56 hour delay in conductivity, no recovery of the base level.

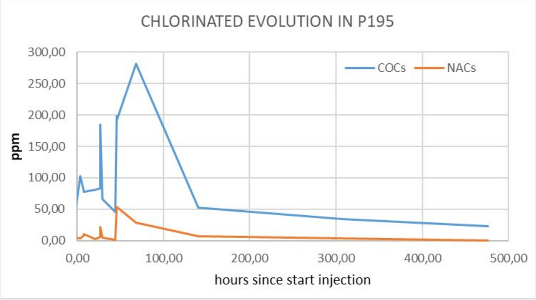


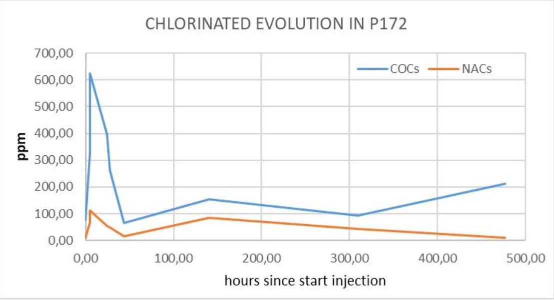
Near river, minimum level response at 31 hours, conductivity responds slightly at 13 days.

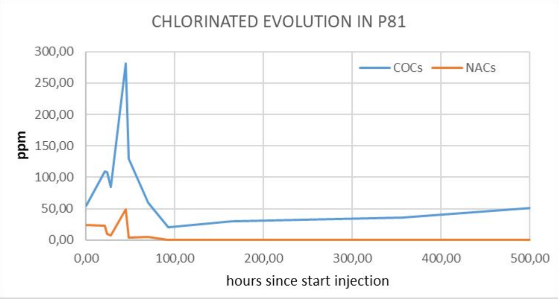
SISCO– COCs&REAGENTS EVOLUTION

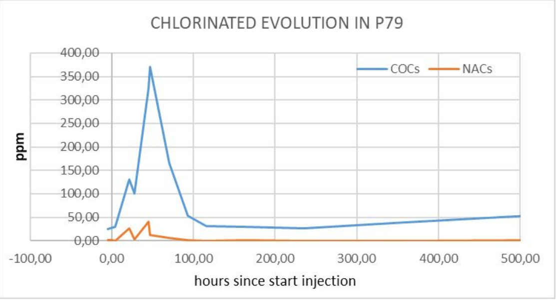




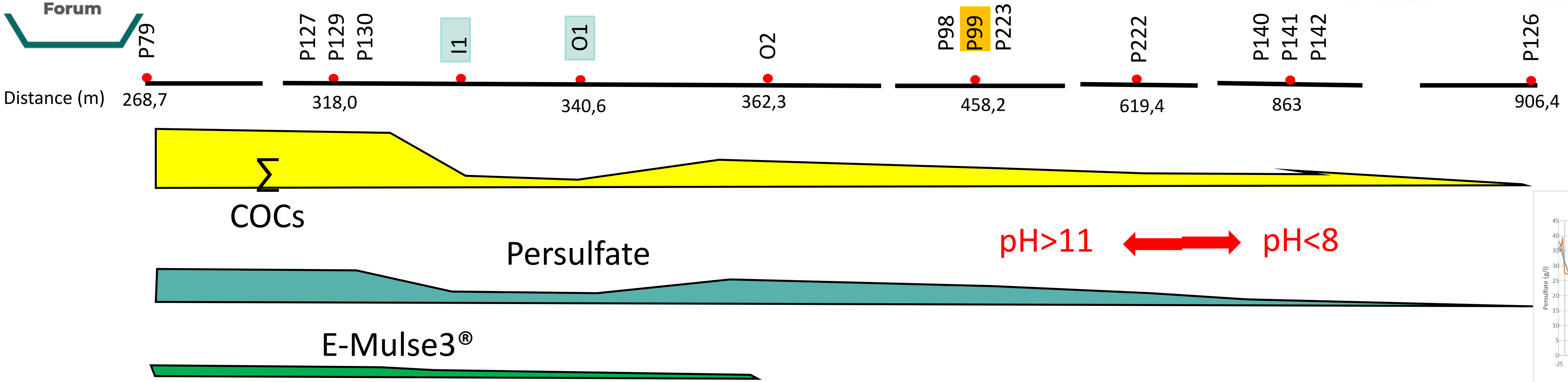


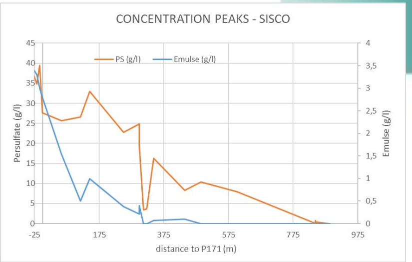


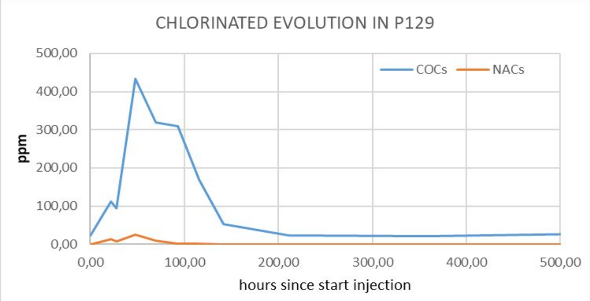


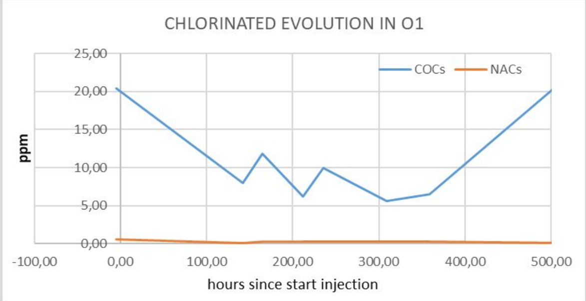


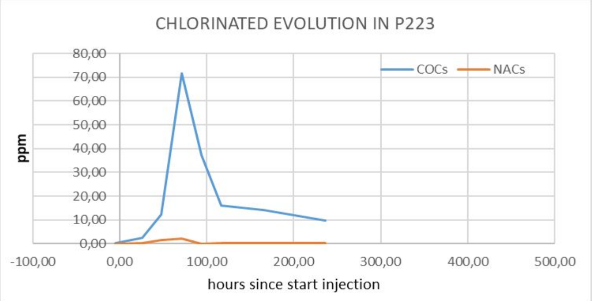
SISCO– COCs&REAGENTS EVOLUTION

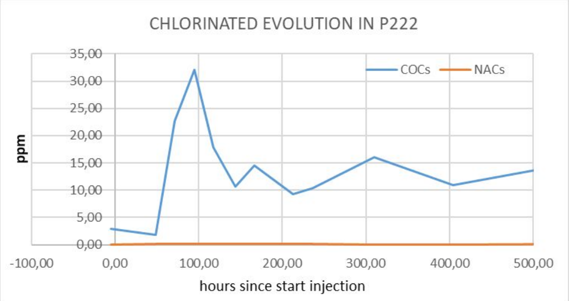


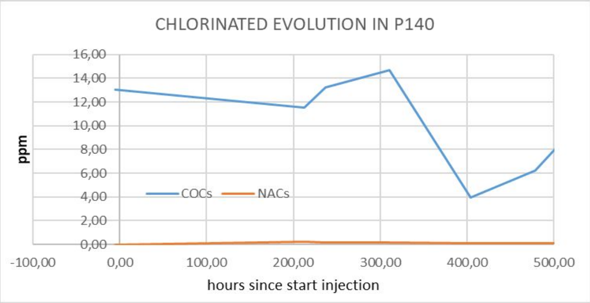


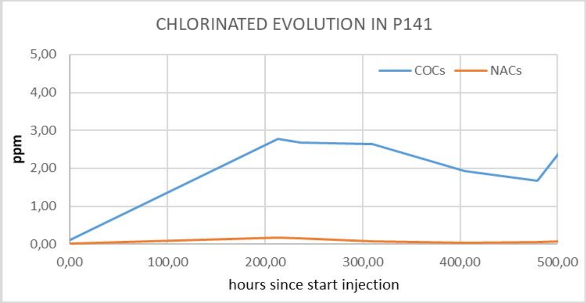


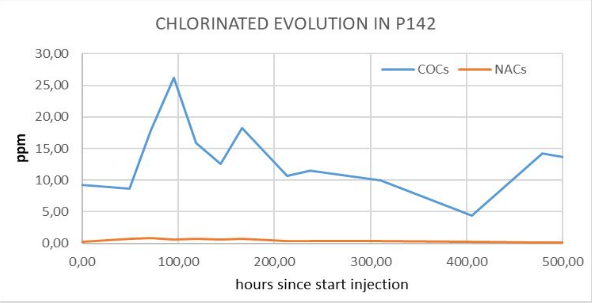


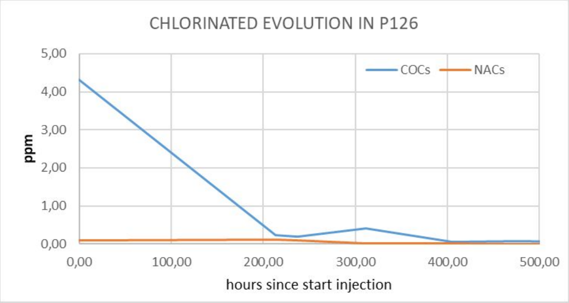




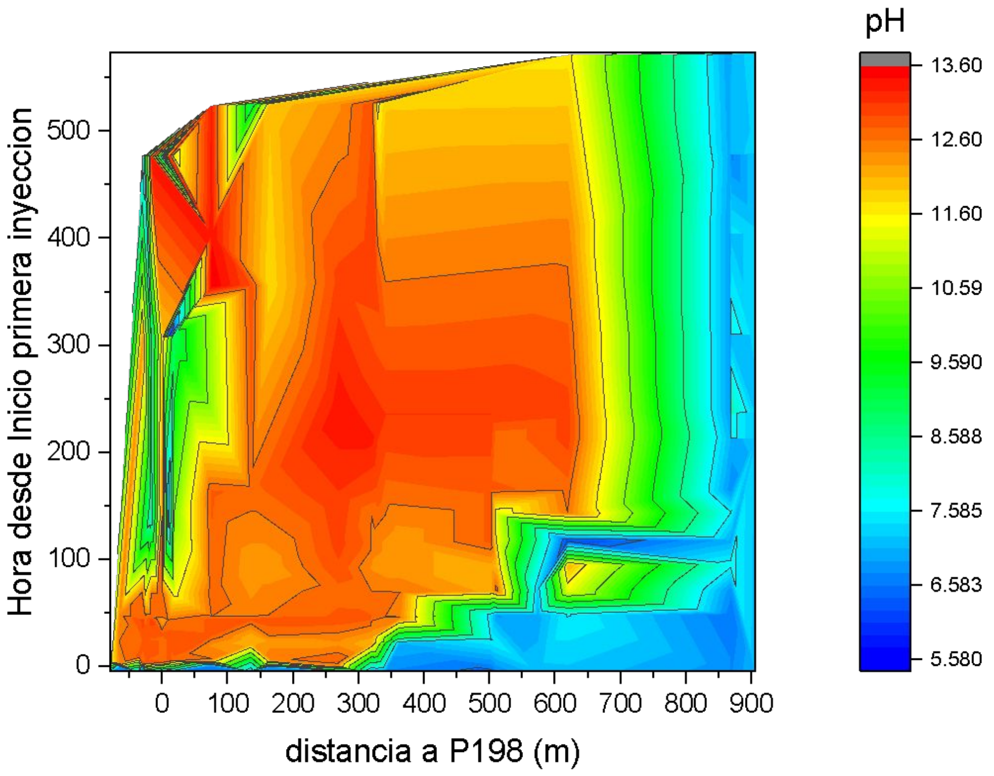


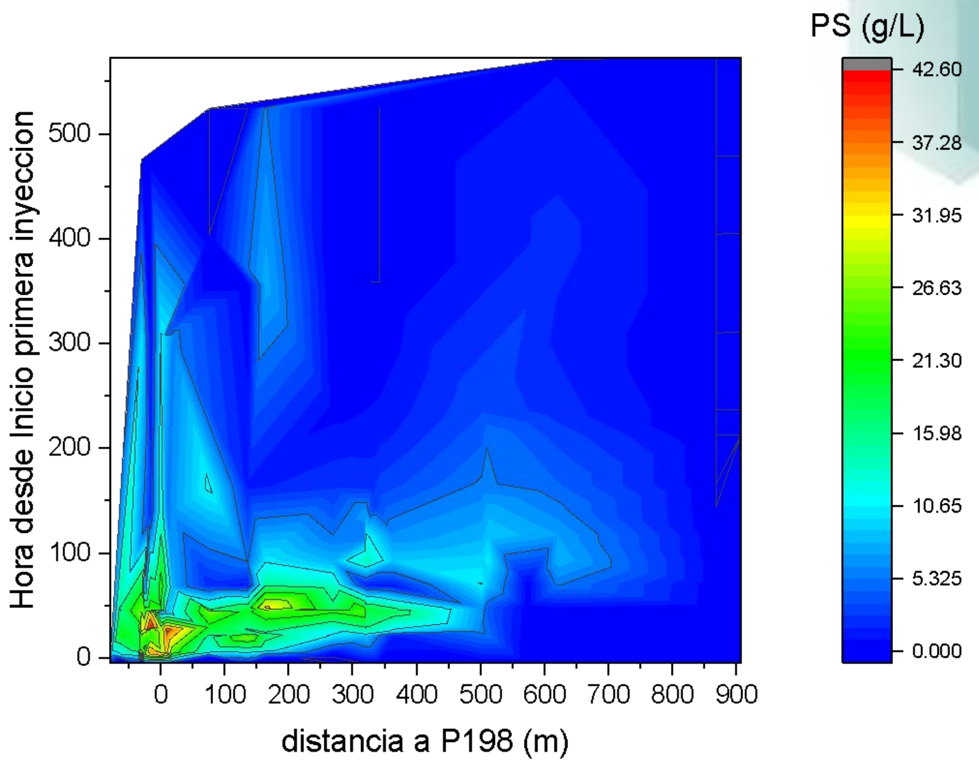






SISCO– COCs&REAGENTS EVOLUTION

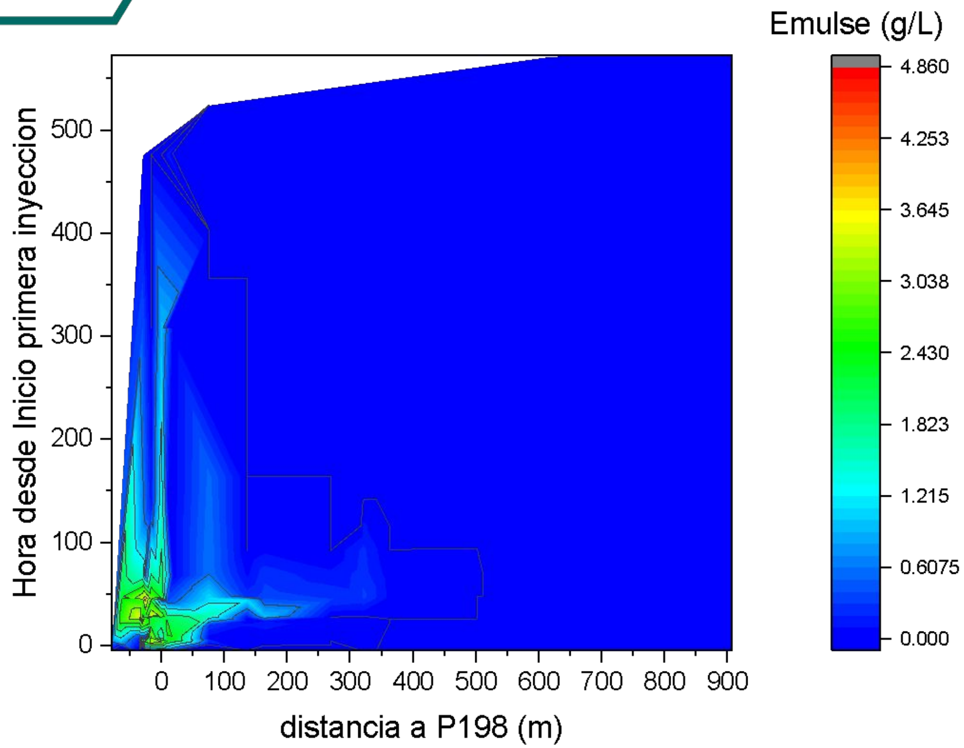


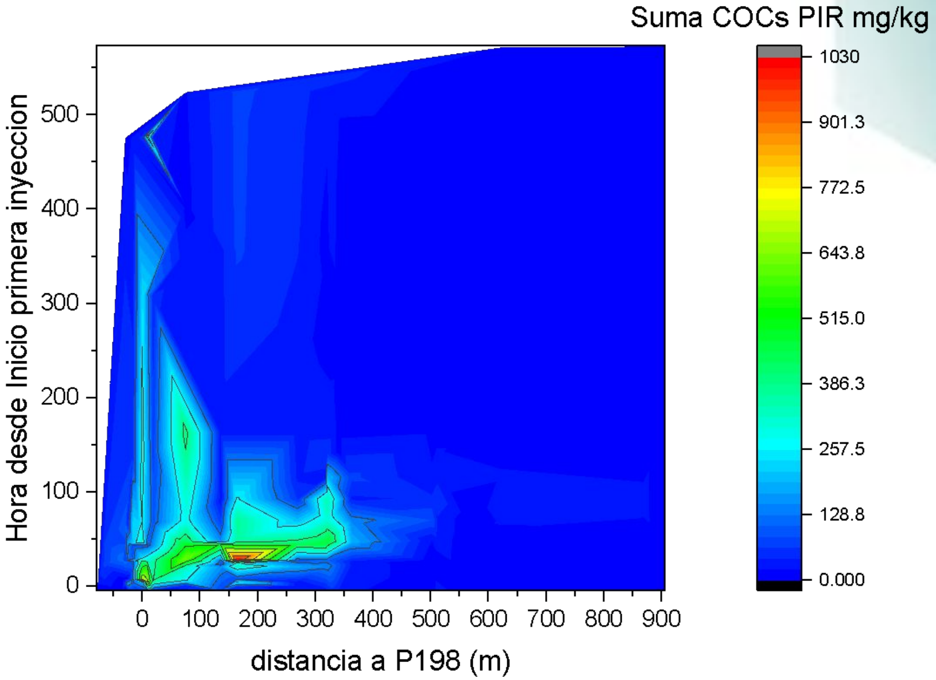


The pH has been maintained at suitable conditions to favor alkaline hydrolysis and persulfate activation during most of the test.

Persulfate maintained significant concentrations for the first 4 days, reaching concentrations of more than 5 g/l up to borehole P222. The persulfate has accumulated in the wells in zones of very slow communication, functioning as continuous tanks until the exhaustion of the persulfate.

SISCO– COCs&REAGENTS EVOLUTION

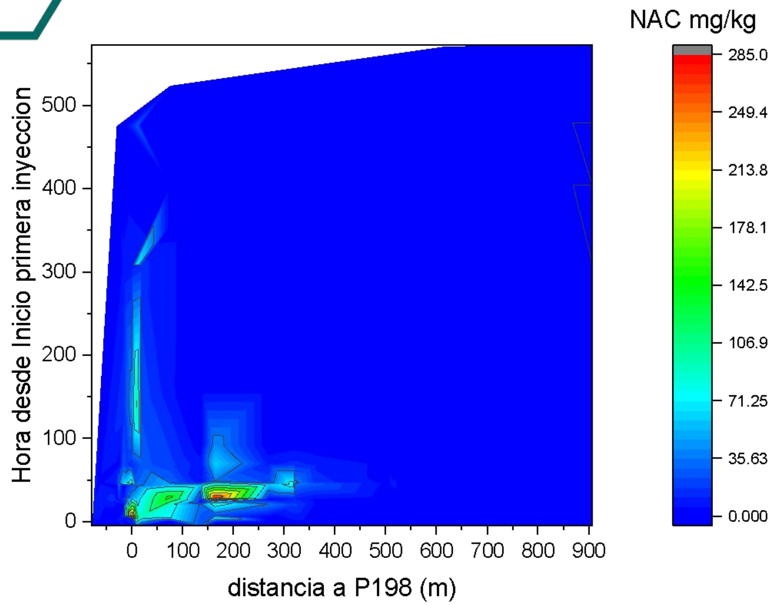


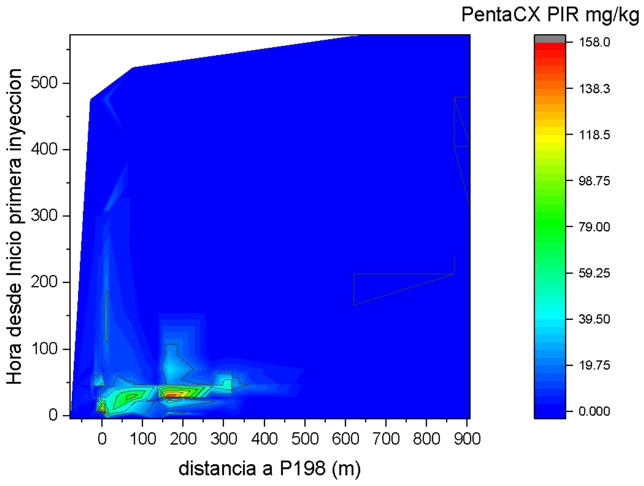


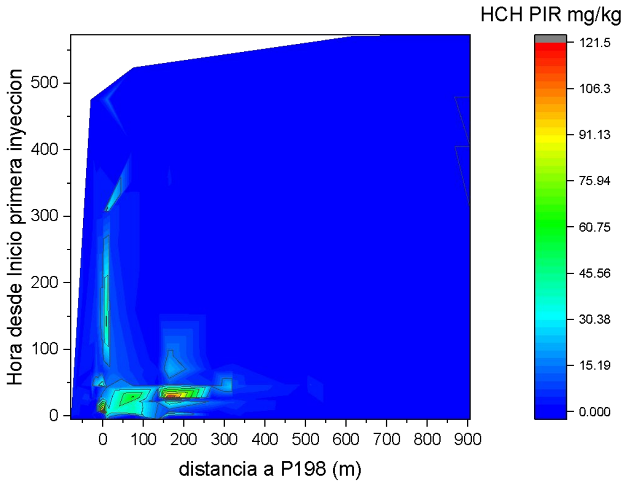
The surfactant concentration decreases by diffusion, adsorption and reaction with PS. In the test cell, the presence of surfactant has been maintained for some time in the dead zone of the boreholes, until its degradation by persulfate.

The sum of contaminants increases above the baseline level, reaching peak concentrations of 1 g/l in the boreholes where DNAPL still remains. In the barrier zone the increase over the initial concentration is negligible. Upstream of the barrier zone the concentration decreases progressively due to the processes of alkaline hydrolysis and oxidation by persulfate.

SISCO– COCs&REAGENTS EVOLUTION

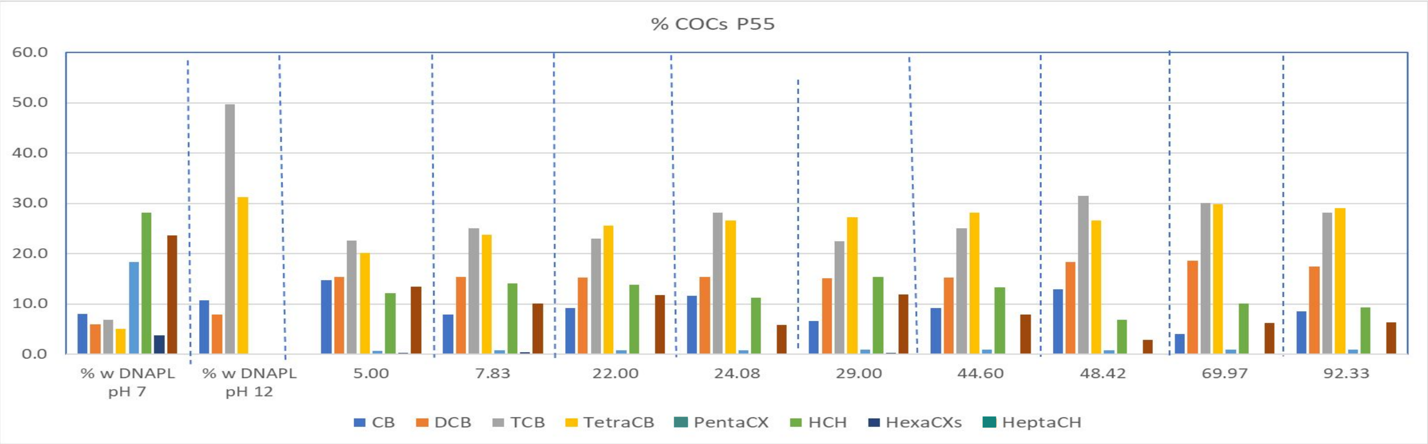


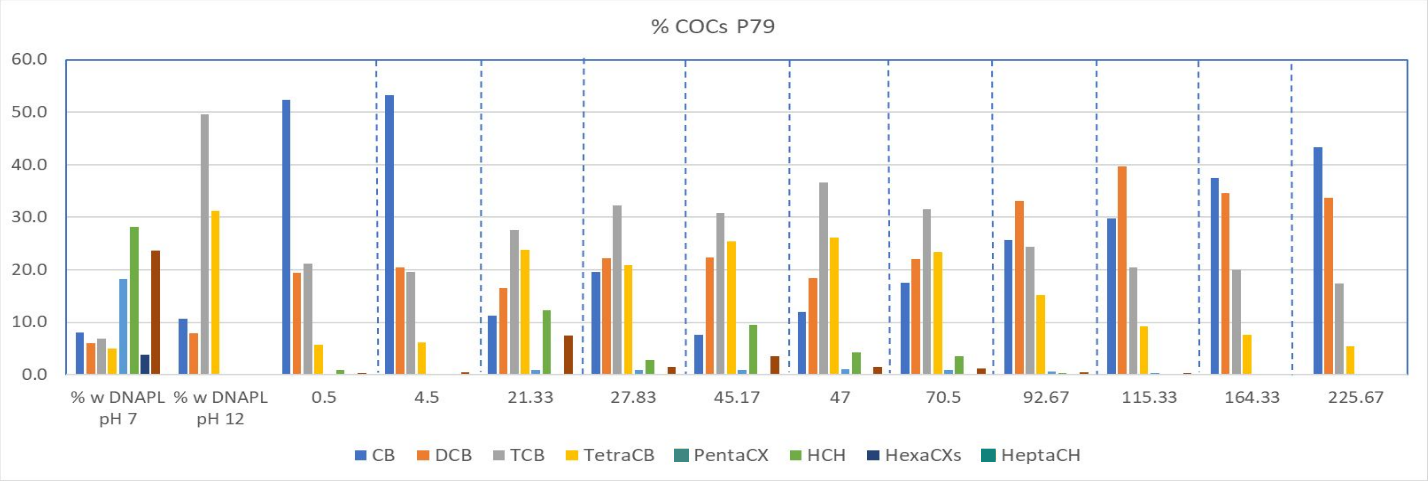




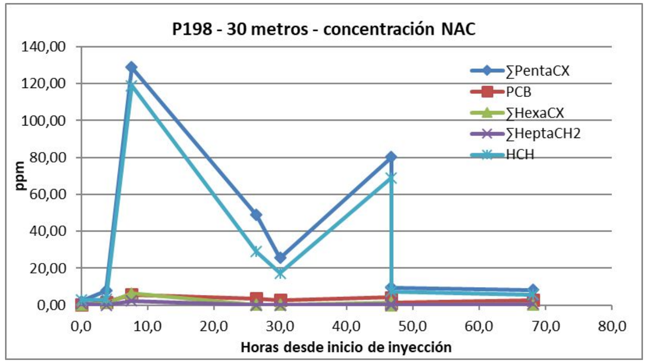
The evolution of the non-aromatic NAC compounds (sum of PentaCX, HCH, HexaCX and HeptaCH) is very rapid. There is an initial increase due to solubilization of residual DNAPL up to probe P55. However, the decline is equally rapid, mainly due to alkaline hydrolysis. The concentrations of these compounds are lower than the baseline downstream of borehole P79.

SISCO– COCs&REAGENTS EVOLUTION



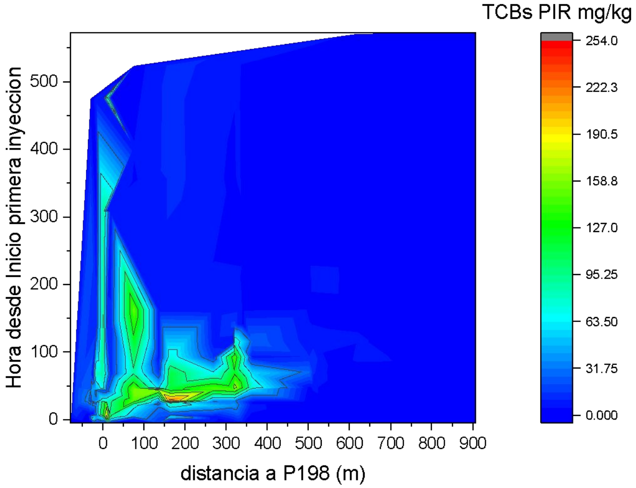


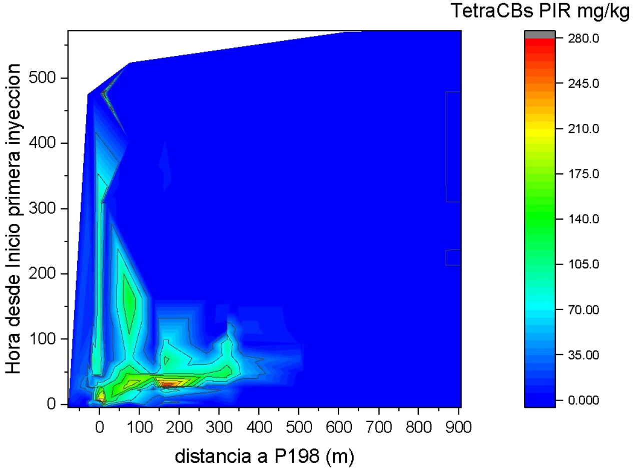
	DNAPL Bailin %	
HCH	30,57	26,7
PentaCX	15,52	13,3
HexaCX	6,69	5,2
HeptaCH	30,20	30,6
TCB	6,41	9,8
TtCB	3,00	-
COV	16,79	24,2

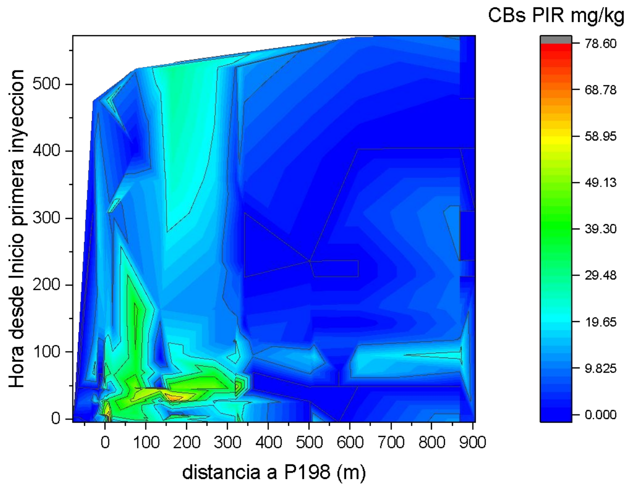


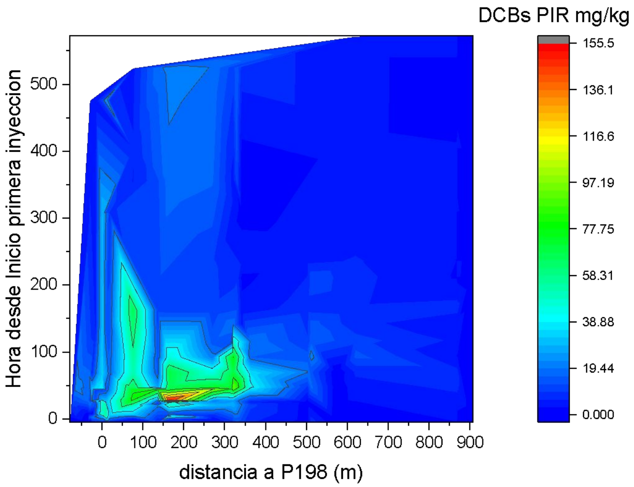
HeptaCH and HexaCX with a very high percentage in DNAPL at pH 7 almost disappear in the solubilization of DNAPL under alkaline conditions. The hydrodechlorination kinetics is very fast for these two compounds. HCH initially maintains higher values with slower hydrolysis and oxidation kinetics, although it practically disappears. On the other hand, PentaCX initially have a higher weight, which is associated with their generation as intermediates in the hydrolysis and oxidation pathway of HCH and Heptas.

SISCO– COCs&REAGENTS EVOLUTION









In the alkaline hydrolysis process, a rapid generation of TCB and TtraCB is observed, which continues in the cell until the precursors disappear. Subsequently, these compounds decay by oxidation, increasing DCB CB, which eventually disappear by oxidation and volatilization.In the alkaline hydrolysis process, not only TCBs are generated, but also hydrodechlorination reaches the DCBs. However, we have not been able to verify this in the laboratory, but it has been observed in more field tests.

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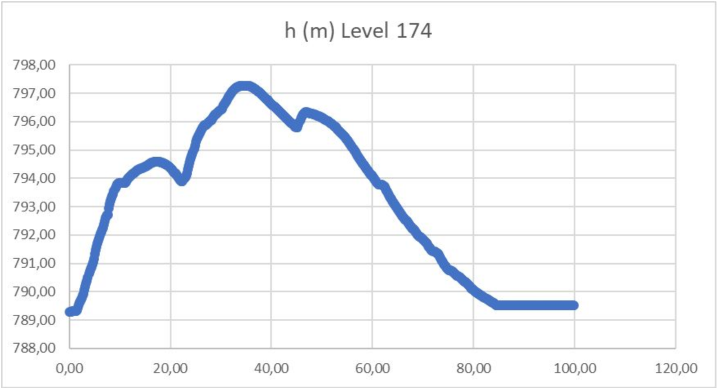
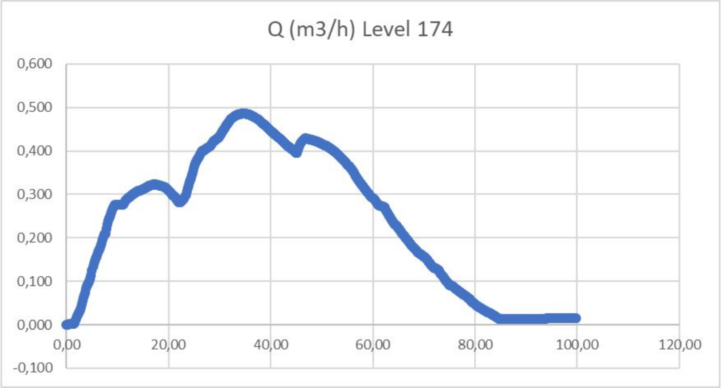
COCS, PS AND EMULSE BALANCE DOWNSTREAM OF THE CELL



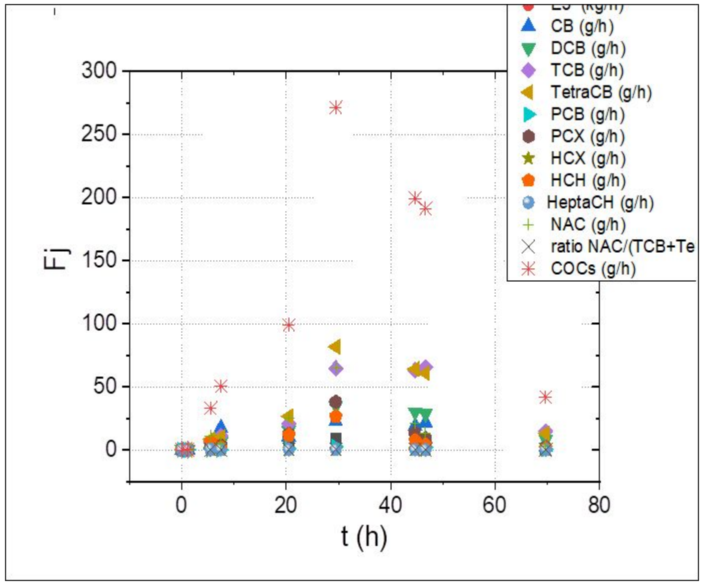


$$Q_t = k\Delta h_t \qquad \bar{Q} = \frac{1}{t_f}\int_{t_i}^{t_f} k\Delta h dt = \frac{V_{iny}}{t_f}$$

$$\frac{Q_t}{\bar{Q}} = \left(\frac{k\Delta h}{\frac{1}{t_f}\int_{t_i}^{t_f} k\Delta h dt}\right) = \left(t_f \frac{\Delta h}{\int_{t_i}^{t_f} \Delta h dt}\right)$$

$$Q_t = \left(t_f \frac{\Delta h_t}{\int_{t_i}^{t_f} \Delta h dt}\right)\bar{Q} \qquad V_t = \int_{t_i}^{t_f} Q_t dt$$

$$F_{j_t} = Q_t C_{j_t} \qquad m_j = \int_{t_i}^{t_f} F_{j_t} dt$$



In the section of the layer where the volumes are conservative we can assume that the level rise is proportional to the flow rate passing through a given point (Qt = KΔht), so the total volume (the injected one) will be the sum of the flow rates passing at each moment. Moreover, taking into account the analysis over time at these points, we can consider that the mass at each moment will be equal to the flow rate and the concentrations at that time (Fjt = QtCjt) and the sum of these masses will be the total mass that has passed through a given point.

Below the base level, the aquifer behaves like a discontinuous reactor and evolves according to the persulfate mass, pH and COCs concentration. Therefore, the estimate of the mass circulating through each borehole is a downward approximation.

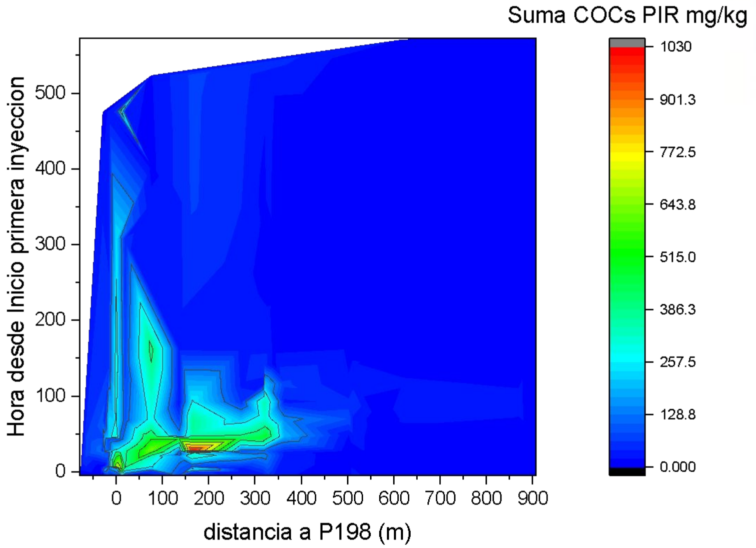
SISCO– COCs&REAGENTS EVOLUTION

SISCO– COCs&REAGENTS EVOLUTION

Mass of compounds passing through wells downstream of the test cell during S-ISCO.

Compuesto	P174	P81	P55	P79	P222*
PS (kg)	355	347	568	213	35
Emulse (kg)	21.0	6.6	10.3	1.6	0.0
CBs (g)	911	402	1017	516	53
CBs (g)	1362	651	2016	753	66
TCBs (g)	2636	1217	3205	1026	42
TetraCBs (g)	2884	1325	3387	748	10
PentaCX (g)	918	268	1531	177	1
HexaCX (g)	9.1	1.1	20.5	0.8	0.1
HCH (g)	662	163	1054	74	1
HeptaCH (g)	7.7	2.0	26.8	0.8	0.2
NAC (g)	1597	434	2633	252	2
Suma COCs (g)	9475	4075	12365	3322	173

(*) in P222 it has been assumed that 10 m3 are passed in the time analyzed in S-ISCO



- The concentration of reagents and COCs decreases downstream.
- At P55 the surfactant concentration is sufficient to solubilize the DNAPL present in the zone, increasing the concentration of COCs.
- The presence of persulfate and the alkaline conditions degrade the pollutants, so that after passing the barrier zone we are practically at the initial conditions and the NACs have disappeared.
- Without considering the degraded contaminant mass in the test cell itself and below the base water table, between 12 and 17 kg of solubilized COCs have been eliminated.

SISCO- CONCLUSIONS

- The reagent dosage (40 g/l PS, 4 g/l Emulse®) and the set point pH (> 12) are adequate to solubilize the COCs and degrade them without generating risks.
- Pulsed injection allows target levels to be reached and maintained for a longer period of time, favoring agitation.
- Reagent recirculation and the temporary barrier effect of the foam just downstream of the recirculation cell need to be improved.
- The contact time in the cell is insufficient for oxidative degradation to occur in this zone, mobilizing a large part of the solubilized COCs downstream.
- It is necessary to add NaOH along the layer and over time to maintain the pH at set point conditions, compensating for the tendency to neutrality due to the carbonate condition of the aquifer.
- The solubilized COCs and surfactant degrade before the barrier zone, without generating a risk to the river.
- The solubilized Heptachloros are hydrolyzed very quickly, within hours. HCHs have slower hydrodechlorination kinetics, although they are eliminated in the circulation time before the barrier zone.
- Alkaline hydrolysis generates TCB and TetraCB and appears to go as far as the generation of DCB.
- The kinetics of oxidation by persulfate is slower but is efficient if the alkaline pH is maintained, degrading the COCs in approximately 4 days.
- Excluding degradation in the test cell and below the base water table, between 12 and 17 kg of COCs were degraded.

LIFE SURFING- GENERAL CONCLUSIONS

- Enhanced extraction with surfactants and the combination of oxidants and surfactants in a heterogeneous fractured aquifer is feasible.
- The selection of reagents (oxidants, surfactants, activators, etc.) at laboratory scale is important not only to establish dosages and yields, but also to take into account the compatibility between them.
- A detailed knowledge of hydrogeological performance is essential. Preliminary hydrogeological and tracer tests must be adapted to the characteristics of the aquifer and focused on establishing injection strategies and actual flow rates.
- Reagent dosages should be adapted to the available contact time (distance to the receptor) or measures should be taken to slow down the flow or degrade the contaminants.
- In the overall pilot test 120 kg of DNAPL have been removed in the hydrogeological and tracer tests, 100 kg in the two SEAR tests and approximately 20 kg in the SISCO test, in total about 240 KG.
- The treatment developed and applied in Bailín to eliminate the residual DNAPL in a fractured medium using surfactants and oxidants is not a fixed protocol but a methodology that must be adapted to each case. A detailed characterisation of the aquifer behaviour is critical for the success of SEAR and S-ISCO trials. Moreover, the injection strategy design should allow for reaching the target zones and achieving a sufficient contact time. Implementation of downstream measures to control the advance of the plume with dissolved COCs and reagents must also be carefully considered.

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THANK YOU FOR YOUR ATTENTION

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