

Biogeochemical Technology Application for the Full-Scale Treatment of an Aquifer Impacted with Chlorocarbons near a Salt Pond Ecosystem in Sardinia, Italy

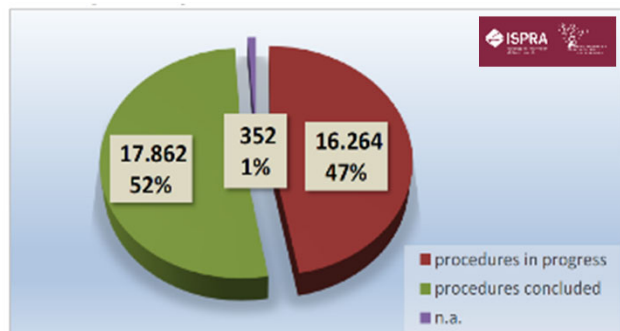
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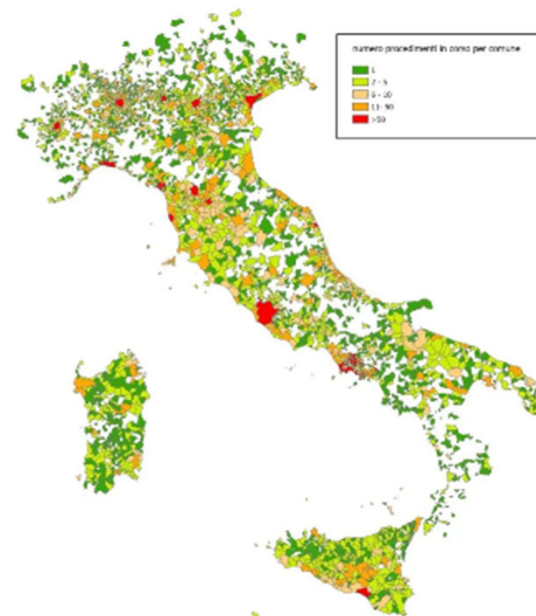


Discussion of Contaminated Sites in Italy

- Below the total number of sites subjected to an administrative procedure of local contamination management according to Legislative Decree n. 152/06.
 - The dataset covers all the procedures collected in regional registers in the period up to 2020, including those started and/or completed under the previous legislation (DM 471/99).



- Total number of contaminated sites was 34,478.
- In particular, 16,264 sites have ongoing procedures, and 17,862 sites have reached site closure.



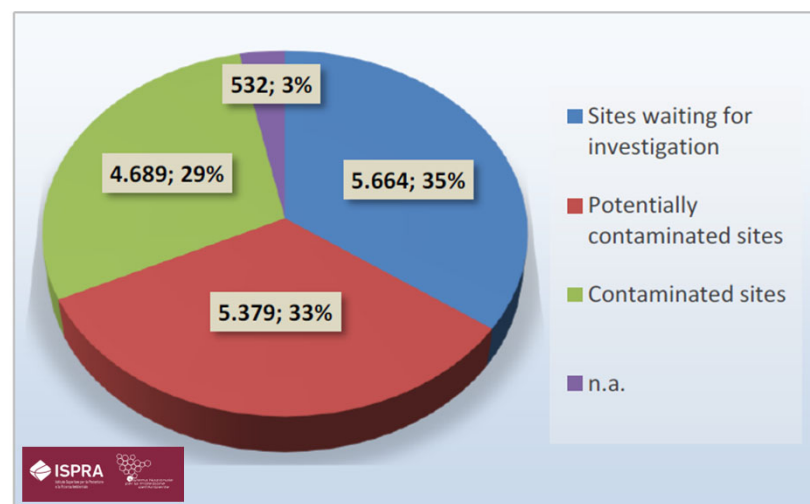
Number of OPEN contaminated site proceedings for each IT Municipality

(ISPRA - Italian Institute for Environmental Protection and Research, 2020)

Discussion of Contaminated Sites in Italy

Procedures in progress - The information on the contamination status is reported for 15,733 equal to 97% of the sites.

- Substantial balance between sites waiting for preliminary investigations (contamination not known – 35%), potentially contaminated sites (screening values exceeded – 33%) and contaminated sites (*unacceptable risks* – 29%).
- Where the contamination risk is not acceptable, remediation actions have been implemented or planned.
- Very typical of having *low remedial goals* (Legislative Decree n. 152/06) in GW for...
 - ✓ *TPH* = 0.35 mg/L
 - ✓ *MTBE, ETBE* = 0.04 mg/L
 - ✓ *Benzene* = 0.001 mg/L
 - ✓ *PAHs* = 0.0001 mg/L



Type of OPEN contaminated site proceedings

(ISPRA - Italian Institute for Environmental Protection and Research, 2020)

Chlorinated Compound Site Remediation Activities

Demand for an in-situ remedy for many reasons

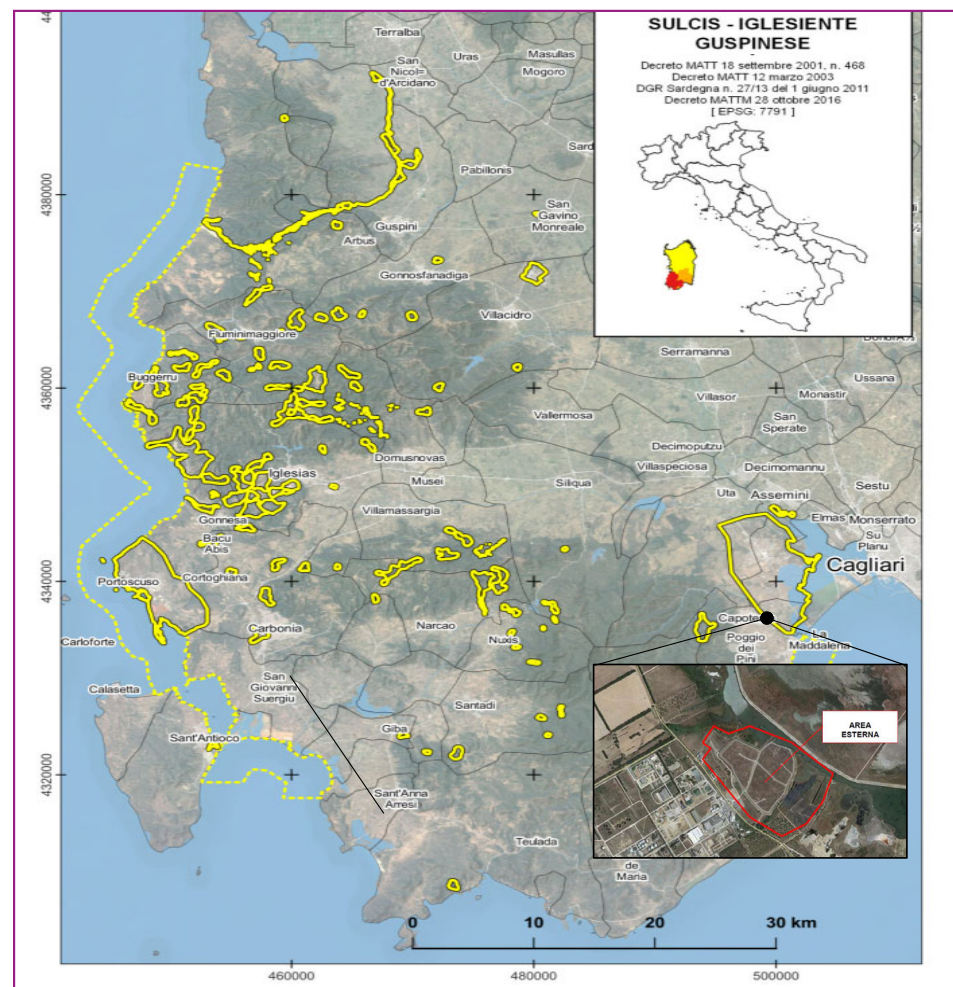
- Need for solution in areas that cannot be excavated – *i.e., active chemical plant*
- Existing in-situ remedies unsuccessful – *i.e., physical remedial approach such as P&T, SVE, other common reagents, etc.*
- Large portfolio of sites needed a safe and cost-effective approach that could be implemented throughout the country

In 2017, Evonik was contacted by several firms regarding our technologies

- Considering typical concentrations and characteristics of sites we reviewed, we generally recommended testing a combined ISCR & ERD approach on site, such as EHC[®] Liquid, in order to address the following main concerns:
 - ✓ Other common treatment reagents completely failed with CT, CF and DCA in groundwater treatment
 - ✓ Request of a reagent with a *very high stable molecule and long-lasting release profile*
 - ✓ Minimal formation of daughter products thanks to the combined ISCR & ERD approach
 - ✓ No disruption of daily site activities (*i.e., chemical plant*)
 - ✓ Effective in several site conditions, low-cost, safe, and easy to apply

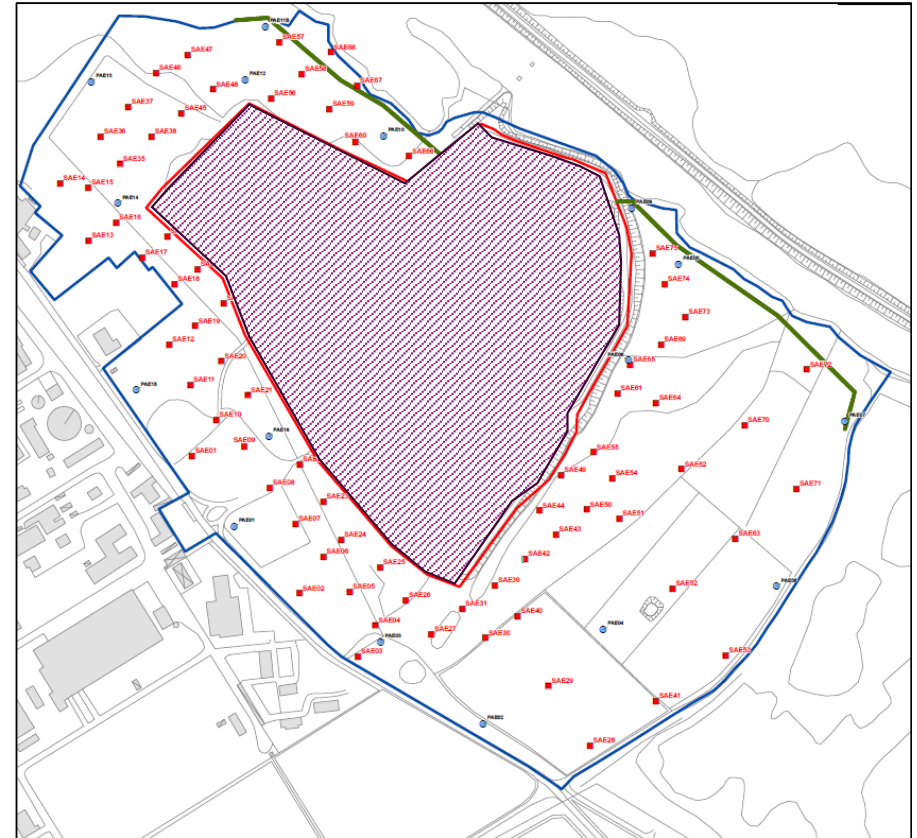
IT Case Study Background

- Active chemical plant with numerous facilities located in the National Interest Site “*Sulcis Iglesiente Guspinese*” in Sardinia Island (IT).
- Several Contractors have been supporting the client at this site for remediation solutions.
- Heavy contamination due to CHCs (mainly Tetrachloroethylene, 1,1,2-Trichloroethane and Chloroform) and, secondarily, VC for both capillary fringe and saturated zones.
- Hydrogeological setting consisting of two main silt and sand aquifers separated by clay level. The phreatic aquifer has been shown as the most contaminated.



External Area of Manufacturing Facility

- Total Contaminated Surface: approx. 39 ha
- Source area: Dump of about 207000 m², where VOCs-contaminated Industrial wastes were disposed in the past, has been confined with a 1900 m long plastic diafram until the depth of 40 m b.g.l.
- Capping on top the dump area in order to avoid rain infiltration
- Active P&T (6 wells) inside the source area to maintain the natural phreatimetric aquifer level 0.7-1 m lower than the external area
- Morphology of the area: Salt and Flat Pond Ecosystem

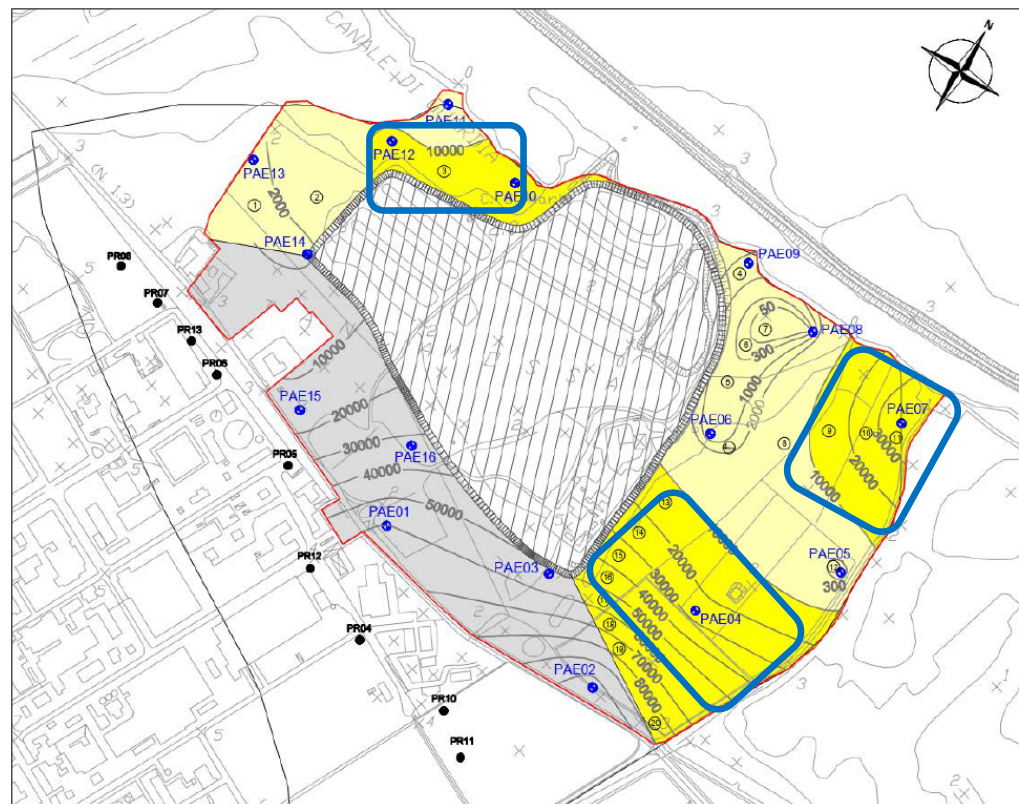


Enhanced Reductive Dechlorination (ERD)

- Three main contaminated areas (VOCs concentrations up to 10 mg/L) has been treated using EHC Liquid technology
- Contaminated zone: Shallow silty / sandy aquifer from 1 m b.g.l to 15 m b.g.l where a clay layer represents the bottom
- Phreatic aquifer characteristics: $K=5 \cdot 10^{-4}$ m/s, $i=4,3 \cdot 10^{-4}$ m/m, $\Phi_e=0.25$
- Natural geochemical conditions: Neutral pH, moderate anaerobic, High Sulfate (up to 2000 mg/L), High Nitrate (up to 600 mg/L)

➤ Site- Specific goals:

Contaminanti - Obiettivi di bonifica	U.M.	CSR
Cloroformio (Triclorometano)	µg/l	40
Cloruro di Vinile	µg/l	16
1,2 Dicloroetano	µg/l	99
Tricloroetilene	µg/l	104
Tetracloroetilene	µg/l	51
1,2 Dicloroetilene	µg/l	2.437
1,1,2 Tricloroetano	µg/l	215
1,2,3 Tricloropropano	µg/l	3
Benzene	µg/l	92
1,1,2,2 Tetracloroetano	µg/l	128
Esaclorobutadiene	µg/l	15
1,1 Dicloroetilene	µg/l	3



EHC[®] Liquid Overview

- Cold-water soluble ISCR & ERD product - injection via existing wells or hydraulic injection networks
- Composition: controlled-release organic carbon with an organo-iron compound, all food grade
- Delivered in two parts:
 1. ELS[®] Microemulsion or Concentrate
 2. EHC[®] Liquid Mix, an organo-iron powder (pH buffer, if needed, delivered as powder)
- Water content will vary with desired injection volume and physical conditions – typically 10% concentration in water

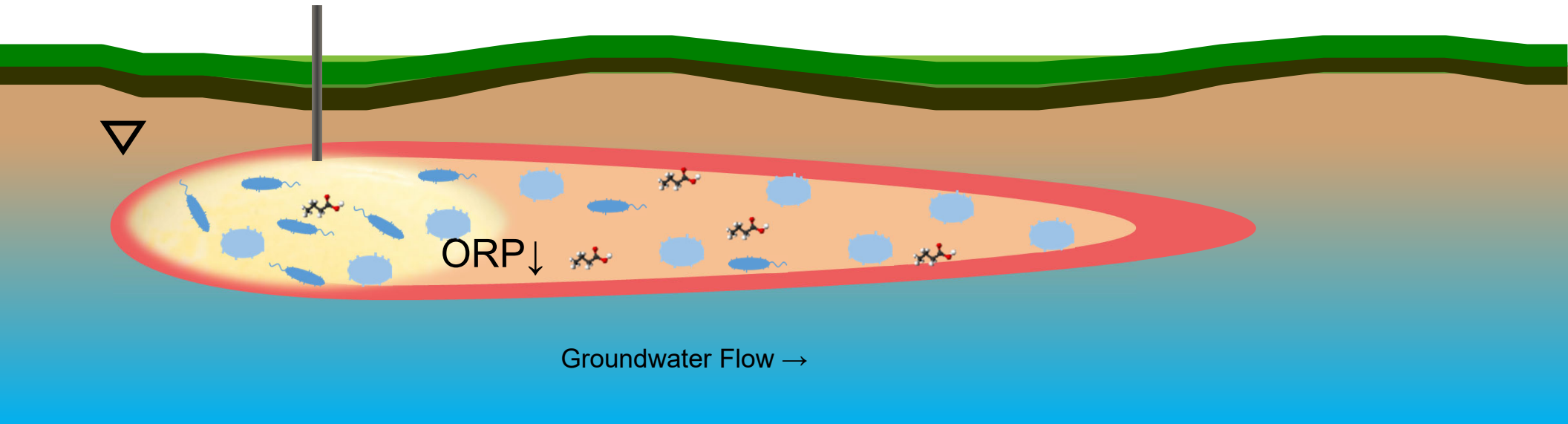


Overview of Reductive Mechanisms

Enhanced Reductive Dechlorination

After the addition of organic carbon (liquid or solid) to the subsurface:

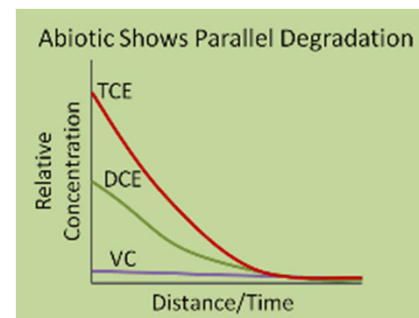
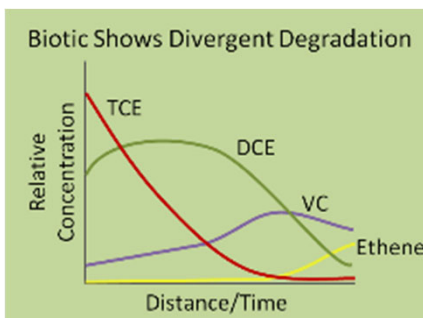
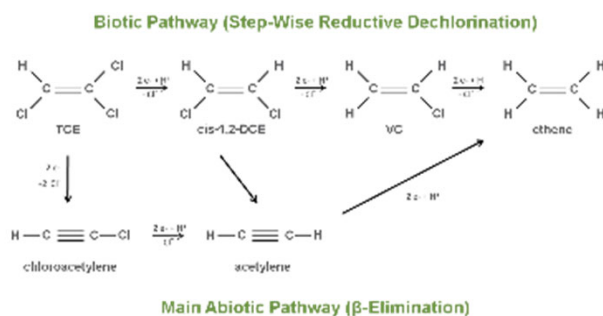
-  Heterotrophic bacteria feed on the organic carbon as an electron acceptors reducing the redox potential
-  Volatile fatty acids (VFAs) are generated through fermentation and released into the treatment area
-  Dehalogenators utilize the VFAs as electron donors and feed on the chlorinated organics



Overview of Reductive Mechanisms and Pathways

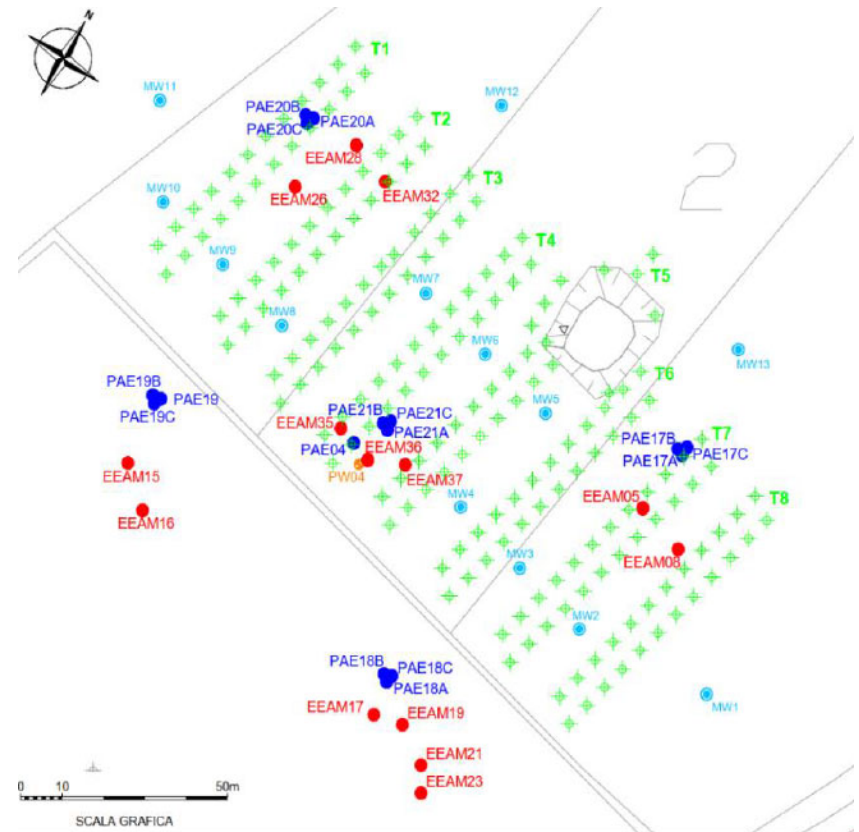
Indirect Chemical Reduction (Biogeochemical)

- Occurs when soluble ferrous iron along with >500 mg/L sulfate in subsurface precipitates out of solution as reduced iron minerals
 - Iron sulfides: pyrite, mackinawite, greigite
 - Iron oxides: magnetite, iron hydroxide / green rust
- These iron minerals support abiotic (biogeochemical) dichlorination
- Since soluble ferrous iron can migrate, indirect chemical reduction can occur beyond the placement zone



Full-scale application in area PAE04

- 8 sets of 2 rows of injection, 24 injection points each set (Grand total of 192 injection points) – Area 170 m X 75 m (12750 mq)
- Direct Push injection method has been selected for injecting just ELS™ substrate into the contaminated aquifer between 2 m and 15 m b.g.l
- 48000 kg of ELS™ Concentrate have been mixed at 10% concentration in water and injected bottom-up
- Injection pression between 1 and 15 bar, Injection rate between 20 and 50 Liters/min, Application March 2022



Full-scale Monitoring Results in area PAE04 (12 months)

Test pilota - Baseline (luglio/agosto 2018)

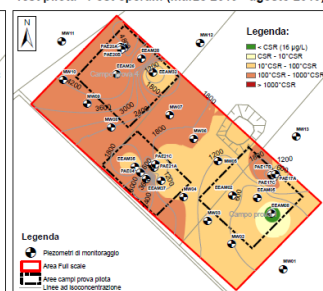
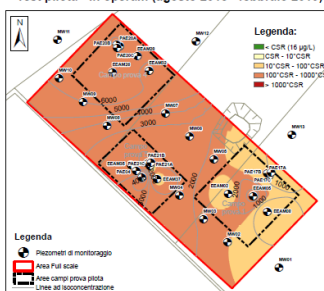
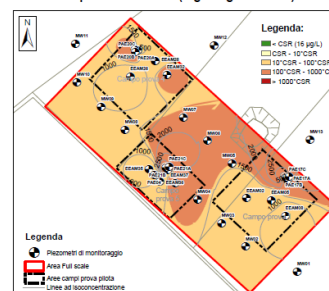
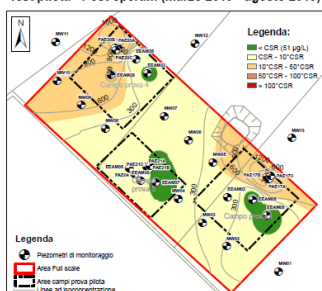
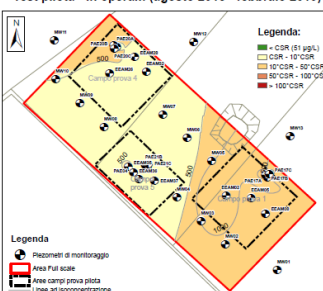
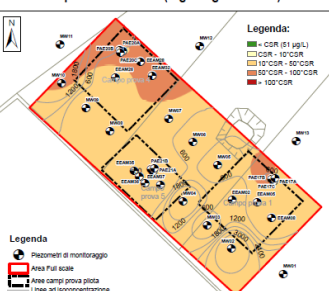
Test pilota - In operam (agosto 2018 - febbraio 2019)

Test pilota - Post operam (marzo 2019 - agosto 2019)

Test pilota - Baseline (luglio/agosto 2018)

Test pilota - In operam (agosto 2018 - febbraio 2019)

Test pilota - Post operam (marzo 2019 - agosto 2019)



Full scale - Baseline (gennaio 2022)

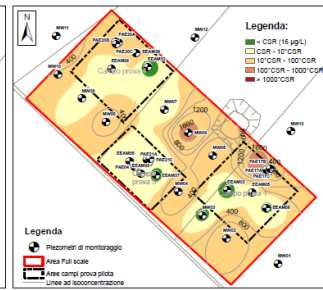
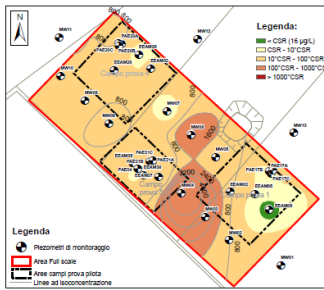
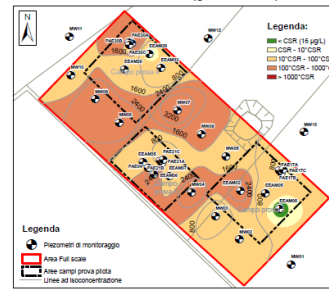
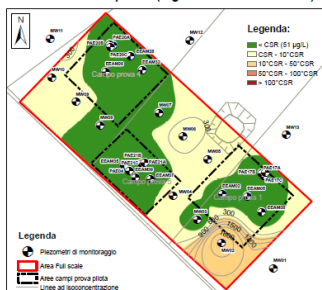
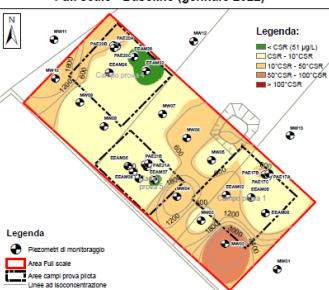
Full scale - In operam (gennaio 2022 - giugno 2022)

Full scale - Post operam (luglio 2022 - ottobre 2022)

Full scale - Baseline (gennaio 2022)

Full scale - In operam (gennaio 2022 - giugno 2022)

Full scale - Post operam (luglio 2022 - ottobre 2022)

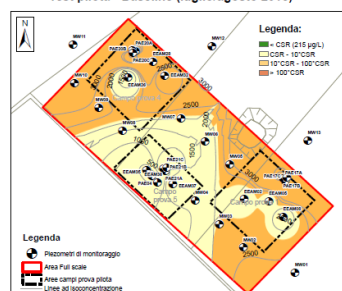


Tetrachloroethylene

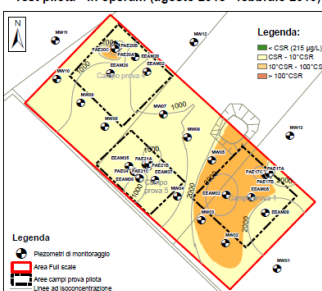
Vinyl chloride

Full-scale Monitoring Results in area PAE04 (12 months)

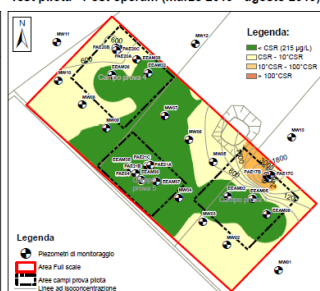
Test pilota - Baseline (luglio/agosto 2018)



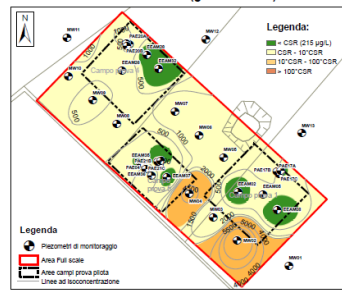
Test pilota - In operam (agosto 2018 - febbraio 2019)



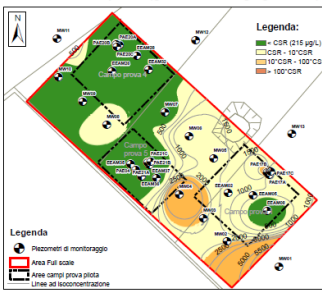
Test pilota - Post operam (marzo 2019 - agosto 2019)



Full scale - Baseline (gennaio 2022)



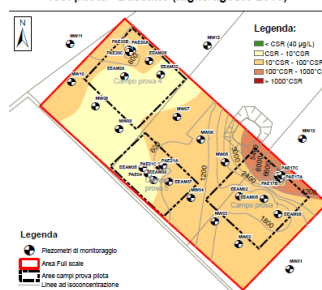
Full scale - In operam (gennaio 2022 - giugno 2022)



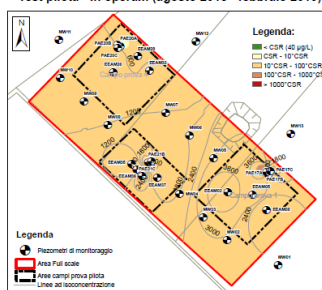
Full scale - Post operam (luglio 2022 - ottobre 2022)



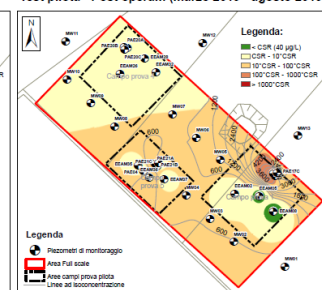
Test pilota - Baseline (luglio/agosto 2018)



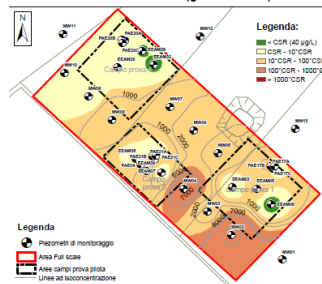
Test pilota - In operam (agosto 2018 - febbraio 2019)



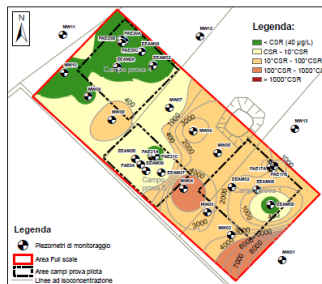
Test pilota - Post operam (marzo 2019 - agosto 2019)



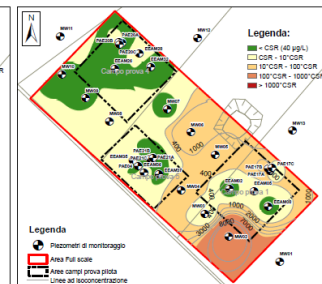
Full scale - Baseline (gennaio 2022)



Full scale - In operam (gennaio 2022 - giugno 2022)



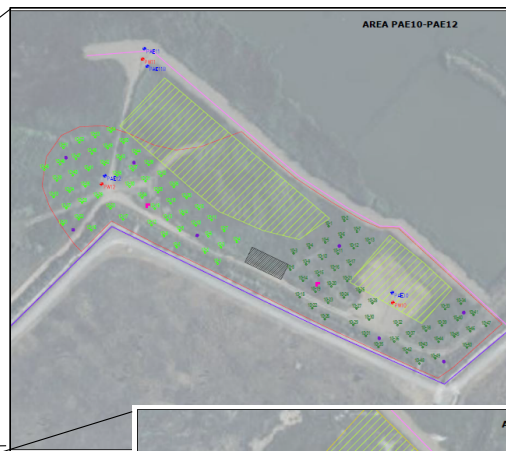
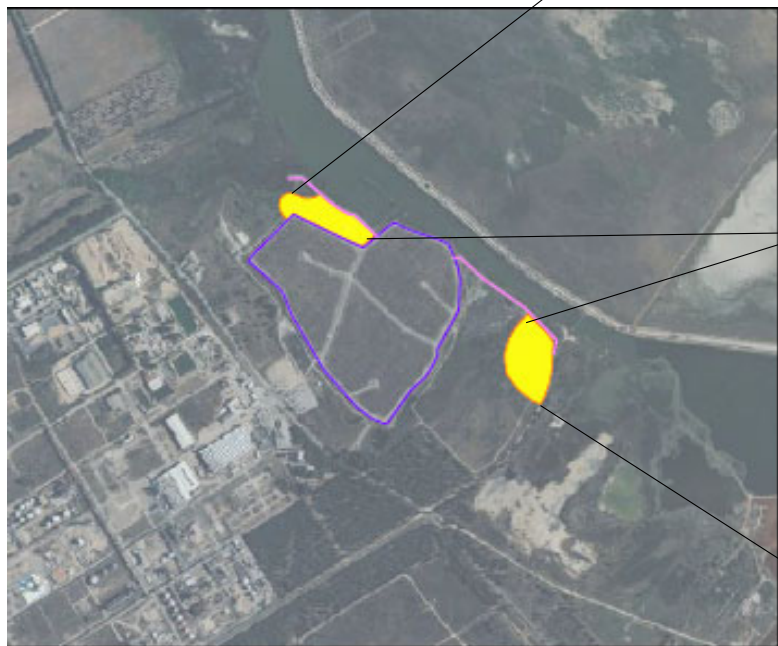
Full scale - Post operam (luglio 2022 - ottobre 2022)



1,1,2-Trichloroethane

Chloroform

Full-scale application in areas PAE07, PAE10 and PAE12



Area PAE10 and PAE12

- Approx. 10400 m²
- Injection between 2 m and 15 m b.g.l
- 104 Injection points, Direct Push
- 104520 kg ELS concentrate + 24000 kg EHC Liquid MIX at 10% concentration in water
- Application in January 2024



Area PAE7

- Approx. 10750 m²
- Injection between 2 m and 15 m b.g.l
- 196 injection points, Direct Push
- 95060 kg ELS concentrate + 21809 kg EHC Liquid MIX at 10% concentration in water
- Application in January 2024

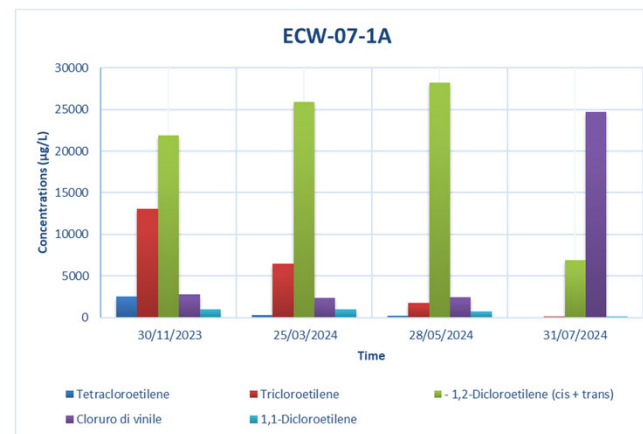
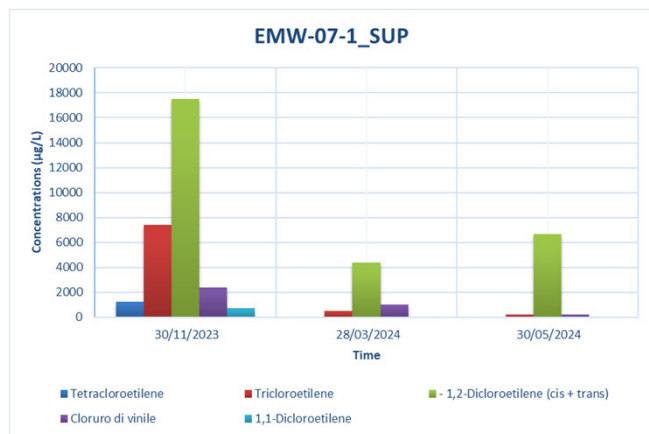
Pre-treatment geochemical conditions in areas PAE07, PAE10 and PAE12

Tabella 3: Parametri chimico-fisici e chimici per il dimensionamento dell'intervento full-scale nelle aree PAE06, PZE05A, PZE05B e PZE05C

			PAE06	PZE05A	PZE05B	PZE05C	Valore medio dei 3 piezometri
	CSC		Valore medio 2021 -2022				
Solfati	250000	ug/l	2888750,00	464190,75	850762,50	963418,75	1291780,50
Ferro	200	ug/l	5068,75	88,15	88,50	65,33	1327,68
Manganese	50	ug/l	12881,25	6270,00	16325,00	17300,00	13194,06
Benzene	1	ug/l	119,24	154,88	156,88	323,75	188,68
Idrocarburi clorurati cancerogeni							
Clorometano	1,5	ug/l	< 0,075	< 3,7	< 3,7	< 3,7	2,79
Triclorometano	0,15	ug/l	61,66	219,13	197,13	225,25	175,79
Cloruro di vinile	0,5	ug/l	259,45	74,88	233,13	270,88	209,58
1,2-Dicloroetano	3	ug/l	100,75	1103,75	516,00	3026,25	1186,69
1,1-Dicloroetilene	0,05	ug/l	107,69	646,25	453,00	432,00	409,73
Tricloroetilene	1,5	ug/l	1014,79	15575,00	7750,00	7212,50	7888,07
Tetracloroetilene	1,1	ug/l	618,74	12000,00	6602,50	6475,00	6424,06
Esaclorobutadiene	0,15	ug/l	21,46	110,50	153,50	165,88	112,83

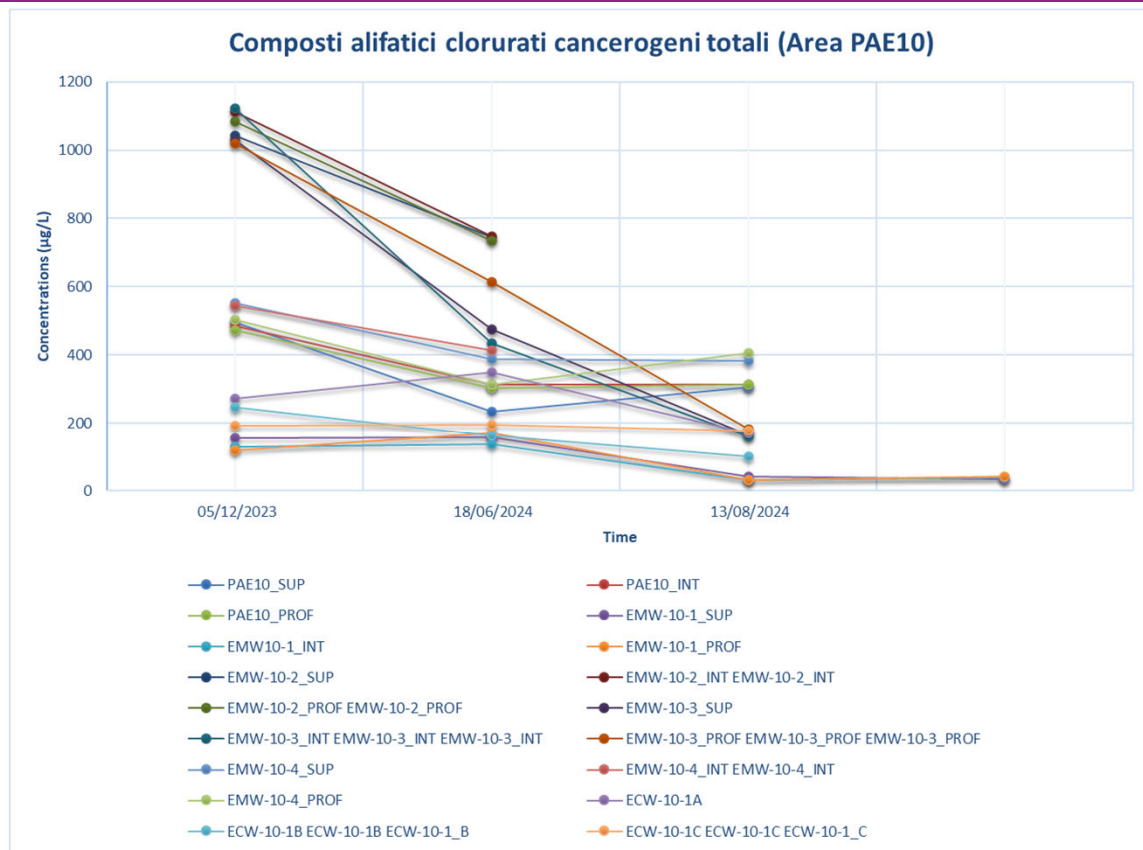
Full-scale Monitoring Results in area PAE07 (6 months)

- ✓ Fe and Mn concentration increase in GW as anaerobic cometabolites
- ✓ Sulfates and Nitrates decrease in GW as sulfate-reducing condition establishment
- ✓ Negative Redox, neutral pH, DO <1 mg/L
- ✓ Complete treatment of PCE and TCE in GW in all the main monitoring wells, minimal "Daughter product" accumulation in some wells but increase in some other wells due to desorption from saturated microporosity
- ✓ CF and TCA concentration reduction in GW



Full-scale Monitoring Results in area PAE10 (6 months)

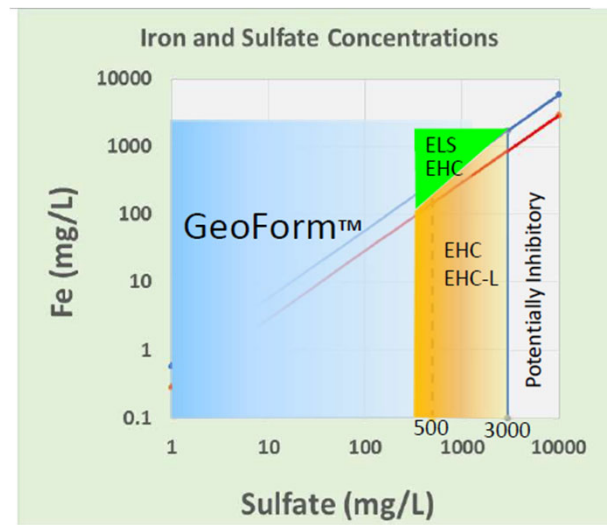
- ✓ Fe and Mn concentration increase in GW as anaerobic cometabolites
- ✓ Sulfates and Nitrates decrease in GW as sulfate-reducing condition establishment
- ✓ Negative Redox, neutral pH, DO <1 mg/L
- ✓ Complete treatment of PCE and TCE in GW in all the main monitoring wells
- ✓ CF and TCA concentration reduction in GW
- Minimal "Daughter product" accumulation in some wells showing a decay trend
- The VOCs sum tends to decrease over time in all the monitoring wells indicating complete dechlorination



Summary

- Client has been happy with approach combining ISCR with ERD (Enhanced Reductive Dechlorination); approach continues to be used by the client.
- This treatment approach was tailored for the site as it already had sulfur in GW. If the site didn't have sulfur, we'd recommend GeoForm[®] technology. If the site had iron and sulfur in GW, you could have used ELS Microemulsion only.
- EHC[®] Liquid is ideal for low to moderate levels of chlorinated compound contamination thanks to three possible treatment pathways from a single application:
 - In-situ chemical reduction with organo-iron powder
 - Anaerobic bioremediation with extended-release ELS[®] Microemulsion
 - Biogeochemical Dechlorination with reduced iron minerals
- Highly contaminated sites would favor more classic ISCR & ERD applications such as EHC[®], a ZVI – based reagent.
- Multiple sites planned for 2026

**Remedial goals achieved
Polishing ongoing!**



Questions?

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**Thank you for your attention.
We look forward to working
with you!**



