





Replacing Pump and Treat System with Sustainable In Situ Bioremediation Strategy for Chlorinated Solvent Plume

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- Summary of Historical Remedial Procedure (Hydraulic Containment)
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- Lessons Learned



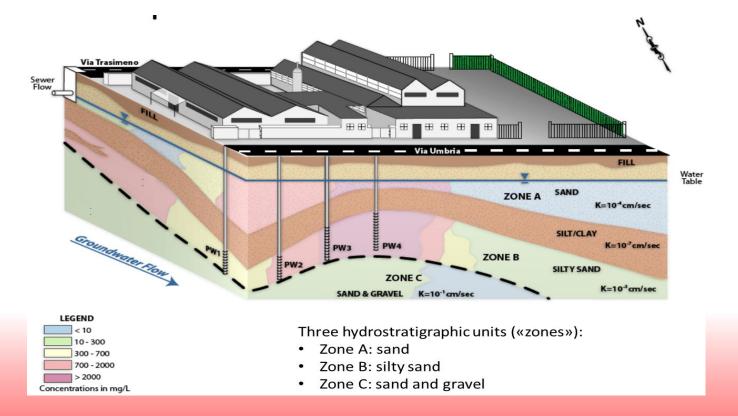


Background

- Chemical Manufacturing site operating since the early 1980's in industrial area of northern Italy
- Experienced release of chlorinated solvents, primarily PCE and TCE to shallow soil and groundwater
- Hydraulic containment installed to capture both shallow and intermediate zones to mitigate off site migration in 2005



Historical Conceptual Site Model





Hydraulic Containment

- Continuously operated as operational safety measure (MISO)
- Mass removal rates decreased to asymptotic
- Treated water discharge to public sewer required permit and annual fees
- Weekly O&M, wastes generation and electric costs with elevated carbon footprint



Summary of Supplemental Activities

- Risk Assessment (RA) approved in April 2008 with prescriptions
- Updated RA approved in March 2011
- In 2014, discharge authority limited the total further amount of water that could be discharged to the sewer to 15,000 cubic meters, equal to approx. 3 years at current flow rates
- High Resolution Site Characterization (HRSC) performed in 2015 (MIP)
- Treatability tests (Bio-traps[®]) performed in 2015 to evaluate effectiveness of in situ remediation via Anaerobic Reductive Dechlorination (ARD)



Remediation Technology

- Several technologies were analysed (ZVI PRB, P&T, ISCO, SVE)
- Remediation technology screening indicated In Situ Anaerobic reductive (ARD) Dechlorination as the most appropriate remedial technology to:
 - **Biobarrier** to mitigate off-site migration (replace hydraulic containment)
 - Remediate **source area** for both zones A and B to reduce migrating mass flux and shorten timeframe to maintain biobarrier
- To better understand rate limiting factors for implementation of ARD, bioremediation tests through *Bio-traps®* were performed in October 2015 to identify if indigenous microbial population is present and active



Bio-traps[®]

- Passive sampling tools that collect microbes over time for the purpose of better understanding biodegradation potential
- 9 Bio-traps deployed for ~ 30 days in monitoring wells (in each aquifer Zone) and analysed at the Microbial Insights, Knoxville, Tennessee, USA laboratories
- Biotraps are designed to attract indigenous microbes to surface area within the traps (biosep beads)
- Beads are then analyzed to using quantitative polymerase chain reaction (qPCR) to identify *dehalococcoides sp.* (known dechlorinating bacteria)





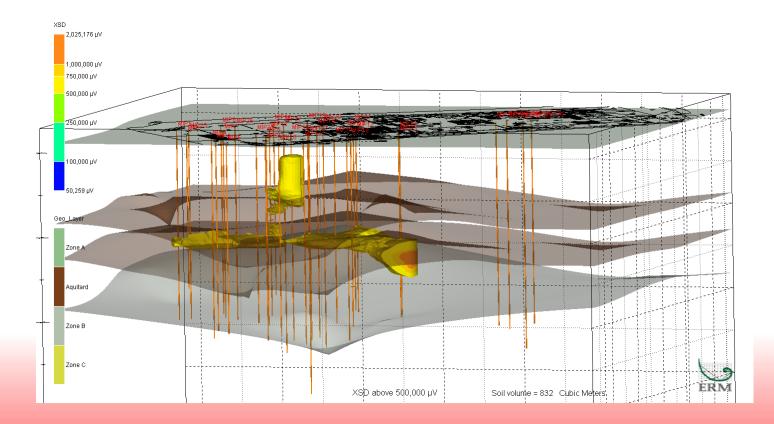


Bio-traps[®]

- 4 traps indicated **low detections of DHC** (*Dehalococcoides sp.*, a known dechlorinating bacteria)
- 5 traps indicated **moderate detection of DHC**
- DHC identified indicating that carbon source / electron donor is rate limiting factor for complete anaerobic reductive dechlorination to innocuous end products ethene / ethane

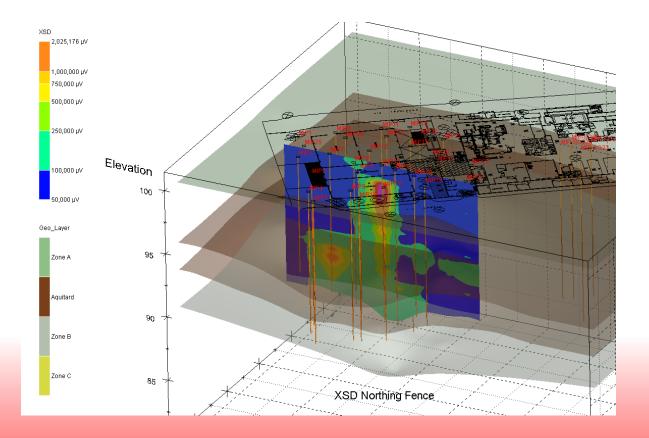


High Resolution Site Characterization (MIP)





High Resolution Site Characterization (MIP) Cont'd





Sustainable Remediation Technology Selection

- Several technologies were evaluated (ZVI PRB, P&T, ISCO, SVE and In Situ Bioremediation)
- Semi-quantitative assessment considering environmental, economic and social aspects of remediation
 - Remedy still has to effectively mitigate migration of COCs in GW
 - Reduce long term cost to client
 - Reduce burden of discharge water and removal of GW from aquifer





In Situ Bioremediation (ARD)

- Selected In Situ Bioremediation through Emulsified Vegetable Oil (EVO, soybean oil based) as Sustainable Remediation
 - Mitigate off-site migration (replace existing hydraulic containment system with a injection biobarrier)
 - Remediate the source areas identified in zones A and B, thereby reducing mass flux and shortening the operating timeframe for the biobarrier
 - Significantly reduce operating costs by >50%
 - Reduce burden to local POTW

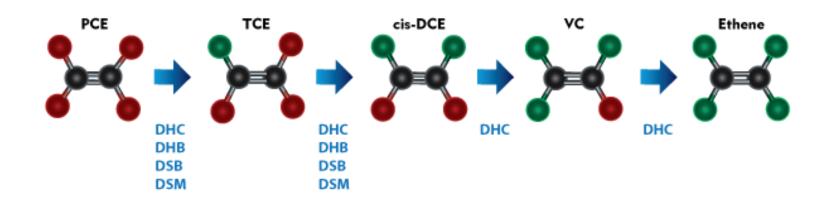
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 Significant reduction of carbon footprint of remediation (no electricity, significantly less O&M)





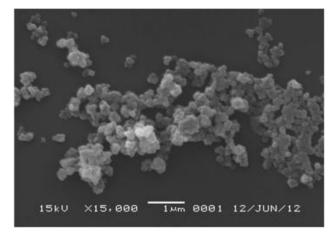
Chloroethene Degradation Pathway





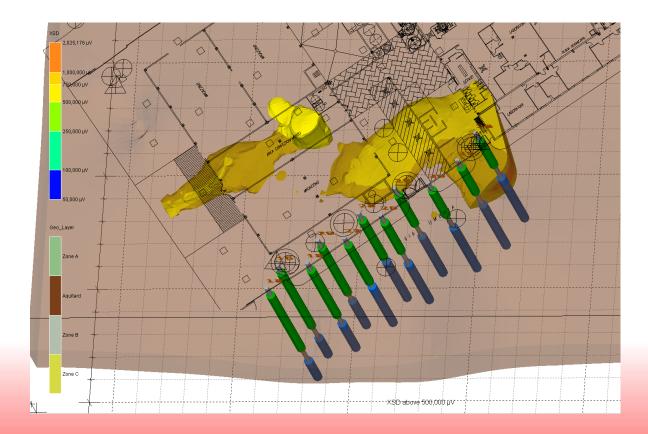
Complete Reductive Dechlorination

- Stall at cis-1,2-DCE or VC typically a result of insufficient substrate (carbon/electron donor source) and/or lack of *dehalococcoides sp. (DHC)*
- By generating sufficient reducing conditions and with the appropriate microbial population complete anaerobic reductive dechlorination to innocuous end products ethene/ethane will occur
- Injection of fluid EVO solutions (biostimulation) in injecton wells at pressures <2-3 bar and low volumes (<20% of available pore space) does not change geophysical nature of soils
- Bioaugmentation includes the <u>addition of a DHC microbial</u> <u>consortium to augment the indigenous population to</u> <u>completely reduce COCs and outcompete methanogens</u>



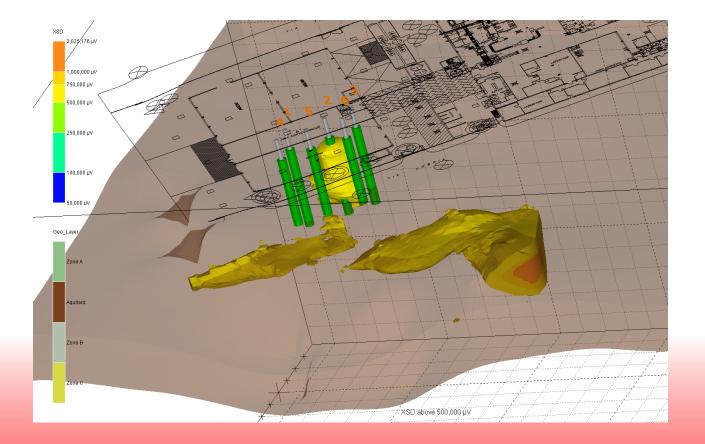


Biobarrier Remediation Approach



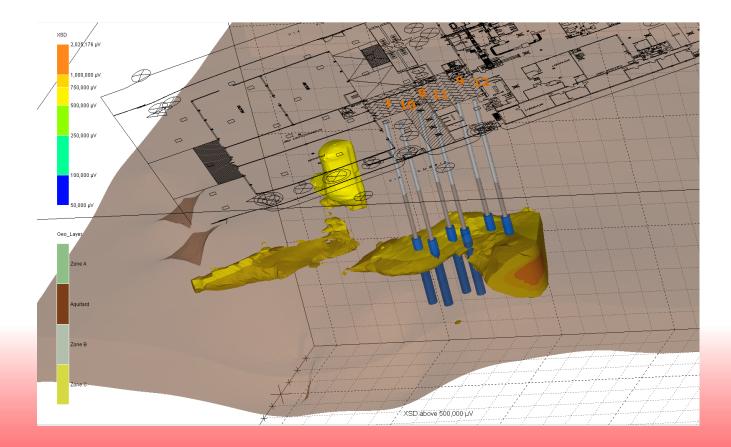


• Source Area A Conceptual Design





• Source Area B Conceptual Design



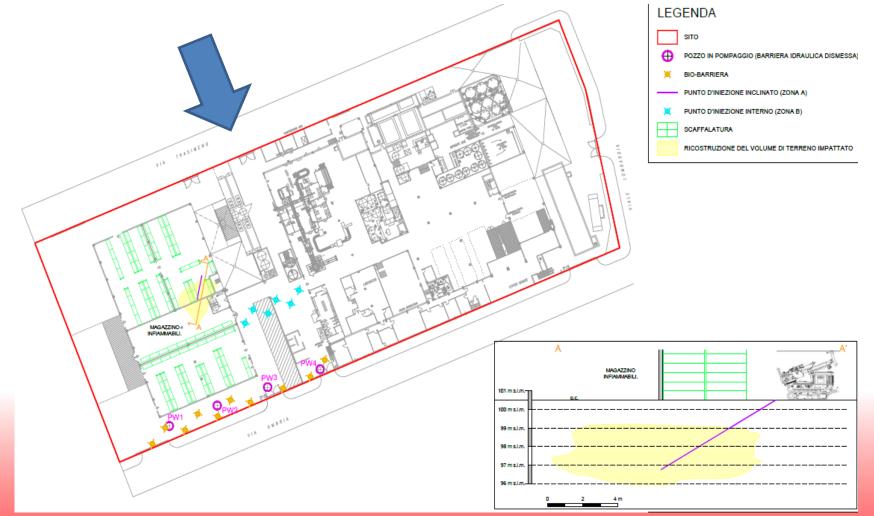


Property Owner Concerns

- 1. A warehouse building in the "zone A" is used as flammable storage and not accessible for drilling inside the building at any time. *Response: Directional drilling*.
- 2. Possibility of impacts on structures/foundations of pressure injection of oil emulsion. *Response: low pressure injection.*
- 3. Possible degradation by products vapor production under building, i.e. methane, vinyl chloride. *Response: Low concentration substrate solution and specific degrading microbial consortium has been shown to mitigate methane production and allow for complete anaerobic reductive dechlorination all the way to ethene and ethane. Monitor soil gases quarterly.*



Amendment Injection Final Layout



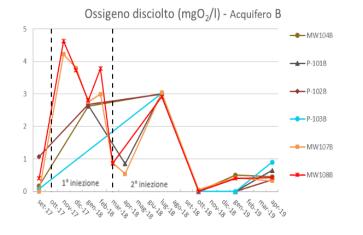


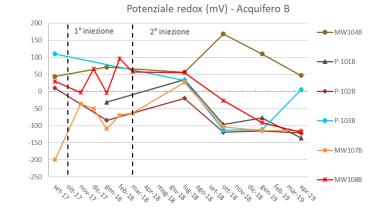
Quarterly Monitoring

- COCs and daughter products primarily (PCE, TCE, cis-1,2-DCE VC)
- Dissolved gases (ethene, ethane and methane)
- Field parameters (DO, pH, ORP)
- Geochemical data (dissolved iron, nitrate, sulfate)

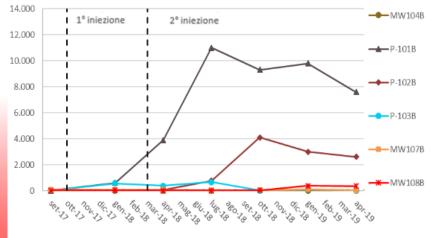


Biogeochemical indicators – Zone B



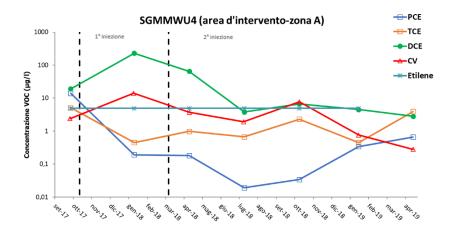


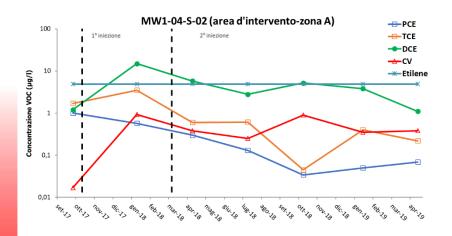
Metano disciolto (µg/l) - Acquifero B





Bioremediation evaluation 1/2

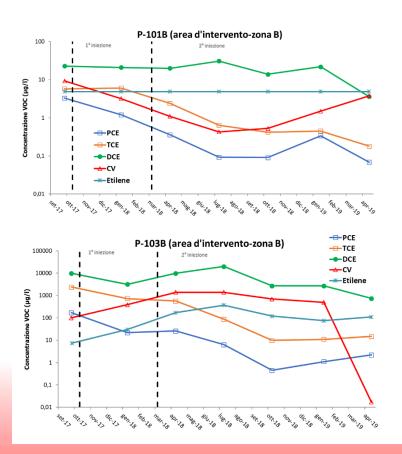








Bioremediation evaluation 2/2







ZONE A

composto e punto	settembre 2017	aprile 2019	riduzione
SGMMWU4			
tetracloroetilene	14,0	0,66	95,3 %
tricloroetilene	5,10	3,9	23,5 %
cloruro di vinile	2,40	0,28	88,3 %
cloroformio	0,41	0,042	89,8 %
sommatoria degli organoalogenati	22	4,9	77,7 %
MW1-04-S-02			
tricloroetilene	1,70	0,22	87,1 %
cloroformio	0,76	0,029	96,2 %



ZONE B

composto	settembre 2017	aprile 2019	riduzione (%)
	(µg/l)	(µg/l)	
cloruro di vinile (P-101B)	9,3	3,8	59,1
1,1,2,2-tetracloroetano (P-102B)	7,6	4,3	43,4
tricloroetilene (P-103B)	2400	15	99,4
cloruro di vinile (MW-107B)	940	210	77,7
cloroformio (MW-108B)	1,4	0,21	85,0
1,2-dicloroetilene (MW-108B)	3300	530	83,9
1,2-dicloropropano (MW-108B)	1,90	0,15	92,1



Results & Conclusions

- Shut-off of P&T system
- The Data shows biogeochemical conditions conducive to anaerobic reductive dechlorination with elevated total organic carbon and ferrous iron at several key monitoring wells.
- Data from monitoring wells in the source areas and downgradient continue to indicate primarily reducing trends in total CVOCs including continued detections of innocuous end product ethene at several locations.
- Monitoring points downgradient of injection biobarrier indicate lowest detections of parent compounds (PCE and TCE) since wells installed
- Source treatment and significant reduction of carbon footprint and O&M costs over P&T system





Thank you

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