

## **Rapid In Situ Dechlorination of Solvents by Abiotic and Biotic Mechanisms**

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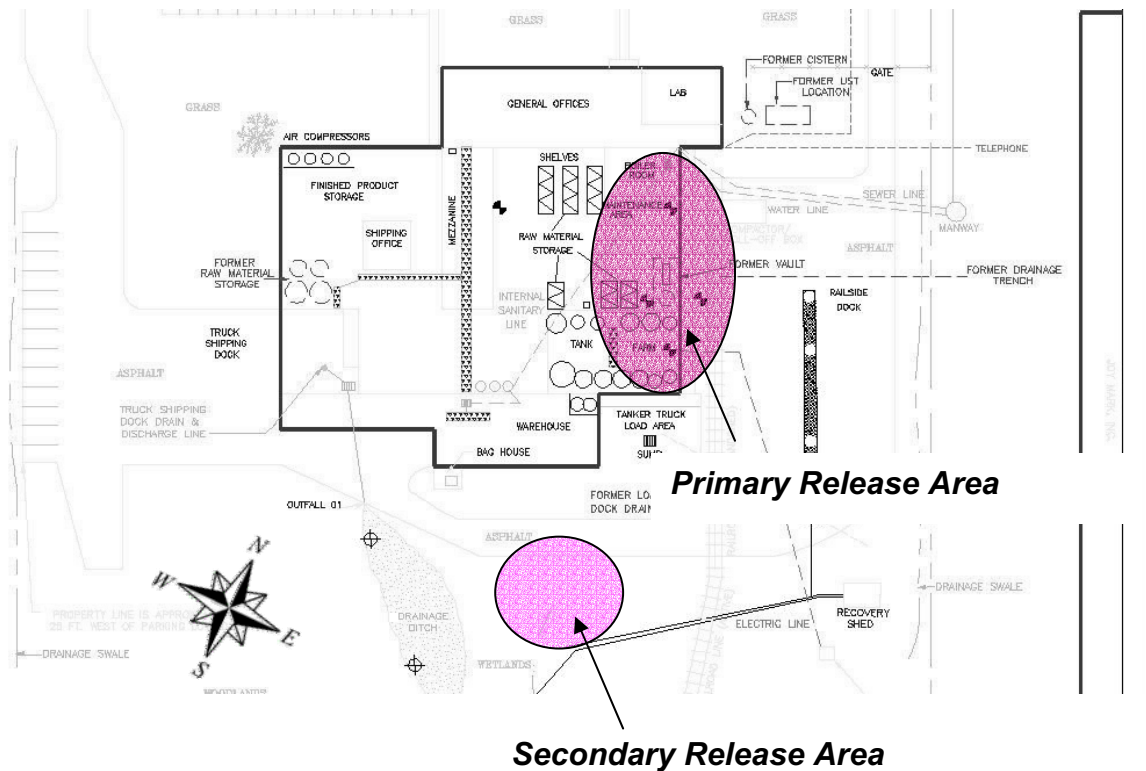
**ABSTRACT:** A combined abiotic/biotic field pilot study was performed at an industrial site with high concentrations of chlorinated solvents in a fractured bedrock groundwater system. The primary groundwater contaminants consist of 1,1,1-trichloroethane (TCA) and related degradation products, including 1,1-dichloroethane (DCA), 1,1-dichloroethene (DCE), chloroethane (CA), and vinyl chloride (VC). The pilot study consisted of a co-injection of submicron zero-valent iron (ZVI) powder and a biological enhancement amendment into the source area within the bedrock formation. The ZVI catalyzes a rapid abiotic reductive dechlorination reaction, resulting in complete degradation of the chlorinated compounds to ethane and ethene. The biological enhancement amendment consists of emulsified soybean oil and sodium lactate that provides a combination of fast and slow-release electron donors to enhance and support biological degradation of the chlorinated solvents for long periods of time. There is clear evidence of biological degradation by the bacteria *Dehalococcoides ethenogenes* (*D. ethenogenes*) and TCA-degrading microorganisms, with no inhibition of *D. ethenogenes* activity by the presence of TCA. Groundwater monitoring was performed for 13 months subsequent to the injection, and results indicate rapid dechlorination of all of the chlorinated compounds both by abiotic and biotic mechanisms. Specifically, TCA concentrations decreased from 10,000 µg/L to below detection limits within seven months and continue to be below detection limits more than one year after the pilot study.

### **INTRODUCTION**

The site is a former adhesives manufacturing facility located within an industrial area of Edison, New Jersey. Adhesives were manufactured between 1967 and 2002. 1,1,1-Trichloroethane (TCA) was used in the manufacturing process up to about 1990 and was delivered to the site by tanker rail car and tanker truck and off-loaded into aboveground storage tanks (AST) located within the manufacturing building. The facility ceased operation in October 2002 and has been fully decommissioned.

Subsurface investigations performed since 1995 indicate the presence of several chlorinated volatile organic compounds (VOCs) in groundwater above New Jersey groundwater protection standards. The primary contaminants detected at the site are TCA, trichloroethene (TCE) and associated degradation products, including 1,1-dichloroethane (DCA), 1,1-dichloroethene (DCE), chloroethane (CA), and vinyl chloride. No specific release or catastrophic failure was recorded during the operation of the adhesives manufacturing facility, and it is believed that the groundwater and soil contamination resulted

from a number of small spills that occurred during transfer of the solvents from the rail cars and tanker trucks to the storage tanks (Primary Release Area) and a separate release(s) within the wetland buffer zone (Secondary Release Area), as shown in Figure 1.



**FIGURE 1. Site plan**

A pump and treat system has been in operation since July 2001 as an interim remedial measure. The system has been effective in minimizing further off-site migration of contaminants.

### **SITE GEOLOGY AND CONTAMINANT DISTRIBUTION**

Surface elevation at the site ranges from approximately 95 feet above mean sea level (amsl) to approximately 85 feet amsl. Surface water generally drains to the south and collects in an undeveloped portion of the property that occasionally floods. The site is located in the Piedmont Plateau physiographic province. Bedrock underlying the site is the Brunswick Shale, the upper formation of the Newark Group (Triassic). Bedding in the Brunswick Shale beneath the site strikes about North 50° East and dips about 9-12° northwest. The fractures observed in site borings in the Brunswick Shale fall into two sets, both striking more or less parallel to bedding. One fracture set dips roughly parallel to bedding (a few degrees toward the northwest), while the other set dips steeply (around 70° northwest).

Site soil consists of a thin layer (4 to 6 feet) of unconsolidated materials, predominantly silt and clay that has been weathered from the underlying Brunswick Shale. Results of bedrock coring conducted at the site show that the red shale underlying the unconsolidated materials continues to beyond 100 feet below ground surface (bgs) at the

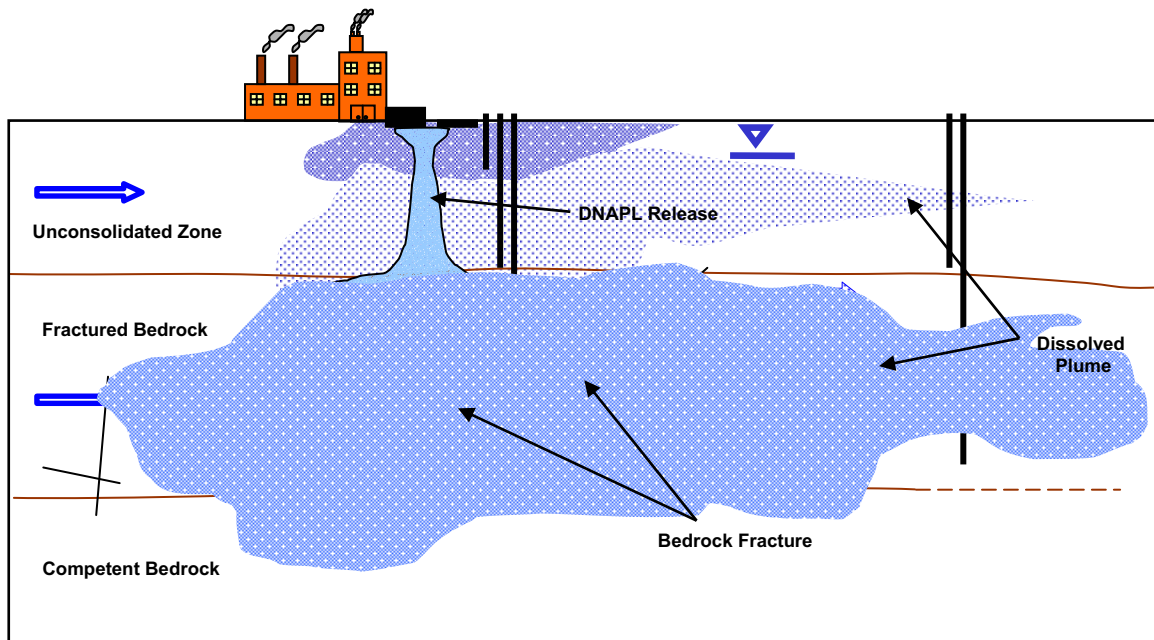
site. The shale is highly fractured to a depth of 80 feet bgs. The frequency of observed fractures decreases between 80 and 100 feet bgs.

Three water-bearing depth ranges or zones are presently monitored at the Site. A shallow unconfined perched zone (depths ranging from 8 to 11 feet bgs) is present south and east of the building. This zone includes the unconsolidated material above the top of bedrock. The shallow bedrock aquifer, which is highly weathered, is the uppermost continuous water-bearing zone beneath the site. The deep bedrock zone is monitored at depths of 65 to 85 feet bgs. Based on historical groundwater elevations, an east-northeasterly groundwater flow direction is evident in the perched zone and shallow bedrock aquifer. The vertical hydraulic gradient at the Site is generally downward.

There are two distinct release areas at the site: (1) Primary Source Area located along the loading dock and (2) Secondary Release Area located within a wetland buffer zone in the southern undeveloped portion of the property (see Figure 1). Higher concentrations (up to 37,000 mg/L TCA) are located within the Primary Source Area and indicate the likely presence of dense, nonaqueous-phase liquid (DNAPL). The DNAPL appears to have migrated through the bedrock fractures to locations beneath the building. Lower concentrations (up to 10,000  $\mu\text{g/L}$  TCA) are located with the Secondary Source Area and suggest possible, but not probably, presence of DNAPL. In both release areas, the highest groundwater concentrations are detected in the shallow bedrock aquifer, indicating that the decrease in fracturing has mitigated the downward migration of contaminants. A conceptual model of the DNAPL migration and resulting groundwater contamination is presented as Figure 2.

## TREATMENT MATERIALS AND BENCH-SCALE TESTING

The treatment materials used in the pilot study consists of zero-valent iron (ZVI) powder and an emulsified vegetable oil amendment. The use of ZVI to degrade chlorinated



**FIGURE 2. Conceptual site model of DNAPL migration and groundwater contamination.**

VOCs was first identified around 1992 and has been demonstrated in several studies (Tratnvek, 1996). The ZVI powder used in the pilot study is manufactured by OnMaterials, LLC. The iron is a sub-micron powder with average particle diameters equivalent to about 0.3 to 0.6 micron with surface areas of about 1 square meter per gram (m<sup>2</sup>/g). The small particle size allows for transport in the subsurface, and the high surface area creates a very reactive material.

Various studies have demonstrated that vegetable oil is a slow release electron donor that can be used to stimulate microbial growth and reductive dechlorination of chlorinated VOCs (Skladany et al, 2001). The emulsified vegetable oil amendment used in the pilot study is manufactured by Remediation and Natural Attenuation Services, Inc. under the name of Newman Zone. The amendment is a blend of emulsified soybean oil (50% by volume) and sodium lactate (4% by weight) to provide a balance of fast and slow-release electron donors. The emulsion has a very small oil droplet size, less than 0.5 micron, and a very tight distribution of droplet sizes. Food-grade stabilizing agents are used to create an extremely stable emulsion in the environment.

Several bench-scale studies were performed by Bioremediation Consulting Inc. (BCI) prior to designing the pilot study. The bench-scale studies indicated that:

- The dechlorinating bacteria *Dehalococcoides ethenogenes* (*D. ethenogenes*) is present at the site, and the presence of TCA does not inhibit *D. ethenogenes* activity.
- Both abiotic and biotic reductive dechlorination is naturally occurring.
- ZVI catalyzes rapid abiotic reductive dechlorination of the chlorinated contaminants to ethane and ethane.
- DCE and VC degraded more rapidly than DCA and CA.
- The emulsified vegetable oil amendment is supportive of biological reductive dechlorination of the chlorinated contaminants.
- The emulsified vegetable oil amendment, in conjunction with ZVI, does not inhibit the ZVI activity.
- Specific alkanes and alkenes (propane, propene, butane, butane, and pentane) were identified as byproducts of ZVI degradation.

## **PILOT STUDY IMPLEMENTATION**

The pilot study was implemented within the Secondary Source Area (see Figure 1). This area is located away from the site building and site utilities, and contamination in this area is relatively localized. A groundwater extraction well was located in this area. This extraction well was turned off for the pilot study and subsequent groundwater monitoring and converted into a shallow injection well, corresponding to the shallow unconfined perched zone. An adjacent shallow bedrock monitoring well located within the Secondary Source Area was also converted into an injection well for the pilot study.

For the pilot study, ZVI concentrate (powder and oil) was delivered to the site and blended on site with emulsified vegetable oil amendment and water to create a dilute ZVI/oil injection solution with a density and viscosity very similar to water. The ZVI/oil solution was pumped into the injection wells at pressures ranging from 25 to 50 pounds per square inch (psi). A total of 300 pounds of ZVI and 1,500 gallons of emulsified vegetable oil amendment were injected into the two injection wells over a two-day period.

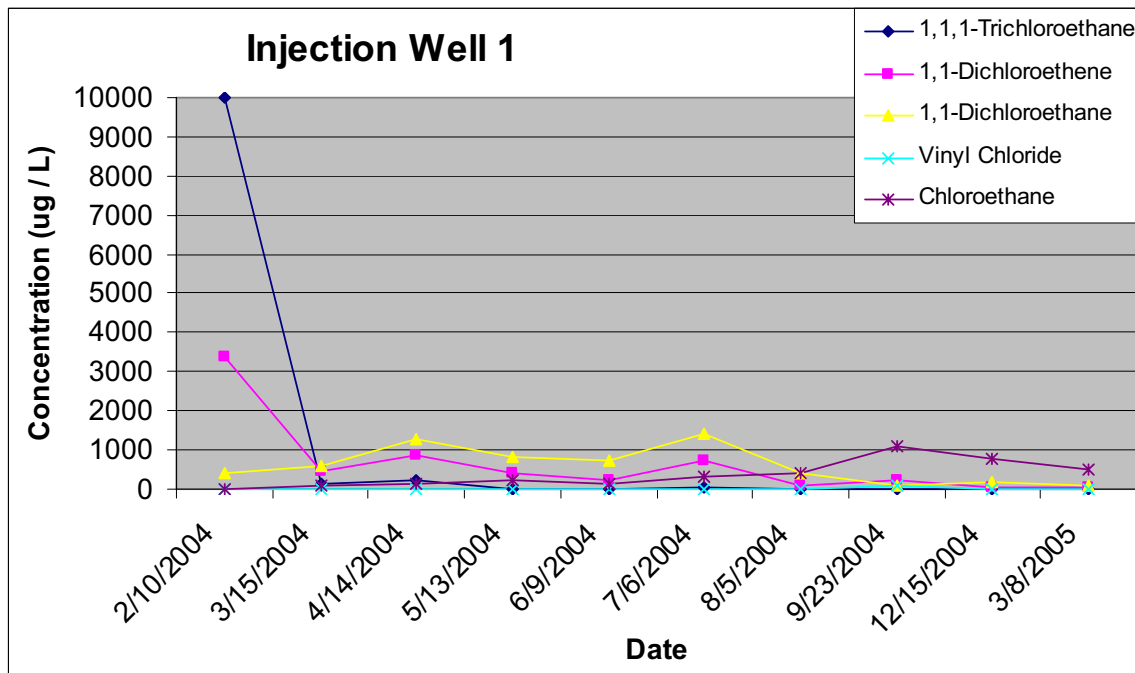
Groundwater monitoring was performed one month prior to and 13 months subsequent to the pilot study injection. Groundwater samples were collected and analyzed for VOCs, total organic carbon, total iron, volatile fatty acids, dissolved gases, pH, temperature, conductivity, dissolved oxygen, and oxygen reduction potential (ORP). Selected groundwater samples were also analyzed for alkanes/alkenes (propane, propene, butane, butane, and pentane) and molecular hydrogen as indicators of ZVI activity.

**RESULTS AND DISCUSSION**

VOC concentrations are graphically presented in Figures 3 and 4 for one of the two injection wells and two downgradient monitoring wells, and results are discussed below.



**FIGURE 3. Concentrated emulsified vegetable oil amendment and zero-valent iron slurry.**



**FIGURE 4. VOC concentrations in Injection Well 1.**

**Injection Well 1.** Injection Well 1 received approximately half of the total amount of ZVI and emulsified oil injected in the pilot study. VOC concentrations for Injection Well 1 are presented in Figure 4 and Table 1. Vigorous ZVI activity is observed in this well through several parameters. TCA concentrations decreased from 10,000 micrograms per liter ( $\mu\text{g/L}$ ) prior to the injection to below the minimum detection limit. DCA concentrations initially increased, reflecting the ZVI degradation of TCA to DCA and then the DCA concentrations decreased beyond levels observed prior to the injection. Concentrations of CA, which is created from the ZVI degradation of DCA, steadily increased in Injection Well 1 and have slowly been decreasing in the past two sampling events, indicating that the CA degradation is occurring more slowly. Concentrations of ethane, which is created from the ZVI degradation of CA and the reduction of ethene, have steadily increased and reflect the vigorous ZVI degradation reactions in this well.

**TABLE 1. VOC Concentrations in Injection Well 1 ( $\mu\text{g/L}$ ).**

DATE	TCA	DCE	DCA	VC	CA	Ethene	Ethane
2/10/2004	10000	3400	390	ND	ND	NA	NA
3/15/2004	130	450	610	16	93	41	285
4/14/2004	230	860	1300	12	130	73	512
5/13/2004	12	430	820	11	230	54	706
6/9/2004	7.2	240	740	ND	130	36	600
7/6/2004	29	720	1400	ND	330	67	780
8/5/2004	ND	100	420	ND	410	12	874
9/23/2004	ND	250	100	69	1100	64	1600
12/15/2004	ND	34	190	11	760	24	1530
3/8/2005	ND	48	100	ND	520	13	1470

DCE concentrations have decreased by over an order of magnitude and no significant accumulation of VC or ethene has been observed in this well, indicating complete reduction to ethane.

The highest concentrations of alkanes/alkenes and molecular hydrogen were observed in Injection Well 1. Alkanes/alkenes and molecular hydrogen were still observed in this injection well in Month 7, indicating that ZVI is still active seven months after the injection.

Elevated concentrations of acetate, propionate, and butyrate are observed in this injection well, which would be indicative that the oil amendment is undergoing degradation. The presence of volatile fatty acids, molecular hydrogen, and low ORP in this well are also favorable indicators and conditions for biological reductive dechlorination. However, the pH is slightly acidic and may inhibit activity of the *D. ethenogenes* bacteria.

**Downgradient Monitoring Well 1.** A key monitoring well for the pilot study is screened in the same zone as the injection wells and is located approximately 60 feet downgradient from the injection wells. VOC concentrations for downgradient Monitoring Well 1 are presented in Figure 5 and Table 2. TCA and DCE concentrations have decreased dramatically in this well over the past year. DCA concentrations increased but now appear to be decreasing. VC and CA concentrations appear to be accumulating. Ethene concentrations have increased significantly, consistent with degradation of DCE and VC.

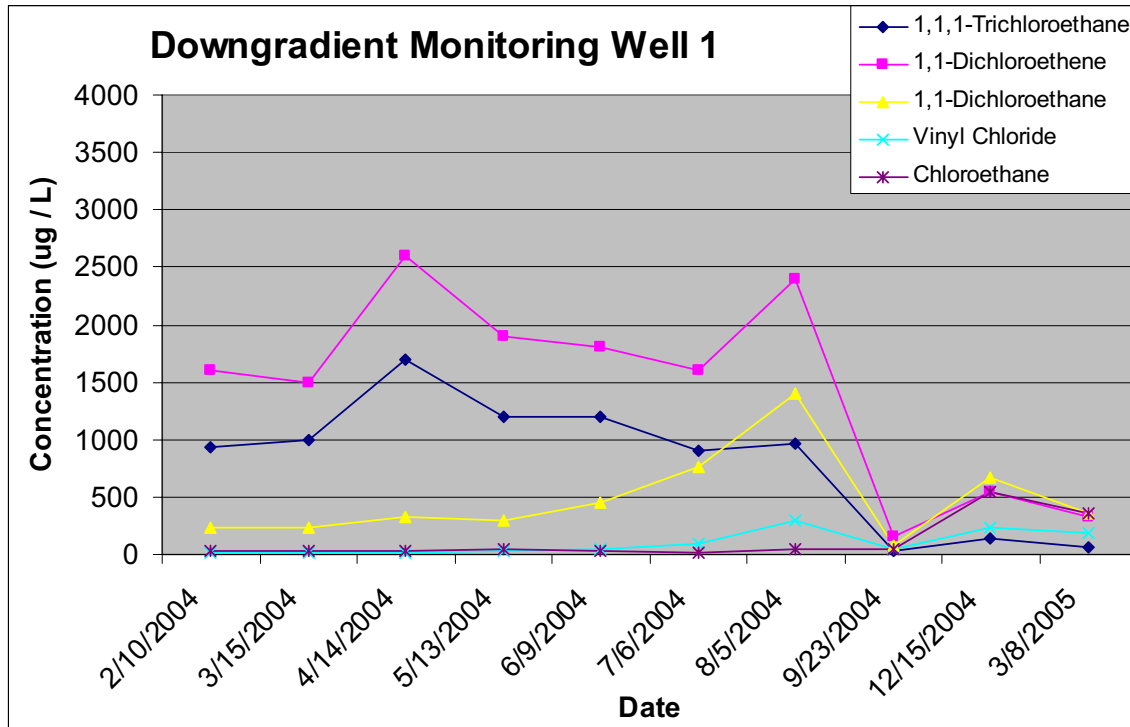


FIGURE 5. VOC concentrations in downgradient Monitoring Well 1

TABLE 2. VOC concentrations in downgradient Monitoring Well 1 (µg/L).

DATE	TCA	DCE	DCA	VC	CA	Ethene	Ethane
2/10/2004	940	1600	230	7.9	26	NA	NA
3/15/2004	1000	1500	240	14	26	ND	ND
4/14/2004	1700	2600	330	19	36	0.9	1.6
5/13/2004	1200	1900	300	38	44	0.9	2.0
6/9/2004	1200	1800	450	43	28	0.9	0.7
7/6/2004	910	1600	770	94	22	6.0	2.0
8/5/2004	970	2400	1400	290	39	ND	0.8
9/23/2004	25	160	75	41	48	23	1.1
12/15/2004	140	550	670	240	550	230	2
3/8/2005	66	330	360	180	360	156	2

There is no evidence of ZVI activity in this well. Specifically, limited alkanes/alkenes have been observed in this well. Therefore, the observed degradation of chlorinated compounds is attributed to biological reductive dechlorination. The decreasing TCA and DCA concentrations, accumulation of CA, and lack of ethane are clear indicators of a TCA-degrading microorganism. The decreasing DCE concentrations and increasing ethene concentrations are clear indicators of *D. ethenogenes* activity. The presence of TCA does not appear to affect the *D. ethenogenes*.

Low concentrations of acetate and propionate are observed in this monitoring well, indicating emulsified oil degradation products have migrated to this location. The presence

of volatile fatty acids and low ORP in this well are favorable conditions for biological reductive dechlorination.

## CONCLUSIONS

A field pilot study injection of ZVI and emulsified vegetable oil amendment has proved successful in quickly remediating a bedrock aquifer contaminated with TCA and degradation products. The ZVI catalyzes rapid abiotic degradation of TCA and the degradation products, while the emulsified vegetable oil supports long-term biological reductive dechlorination by *D. ethenogenes* and TCA-degrading microorganisms. Groundwater monitoring for 13 months subsequent to the injection indicates that TCA concentrations decreased from 10,000 µg/L to below detection limits within seven months and continue to be below detection limits more than one year after the pilot study. There is clear evidence of ZVI-catalyzed abiotic degradation of TCA and degradation products in the injection well, and clear evidence of biological degradation by *D. ethenogenes* and TCA-degrading microorganisms in a downgradient monitoring well, with no inhibition of *D. ethenogenes* activity by the presence of TCA. Ethene and ethane gases continue to be generated, indicating continuing reductive dechlorination processes are still occurring 13 months after the injection.

## REFERENCES

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