Long-Term Evaluation of Chlorinated Solvent Attenuation Rates in Ground Water

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Background

The former Twin Cities Army Ammunition Plant (TCAAP) is located north of St. Paul, Minnesota. Disposal of trichloroethylene (TCE) at the site resulted in extensive ground water contamination. Remediation efforts included a soil vapor extraction system at the source area and a system of extraction wells at the site boundary.

In 1999, ground water contaminant modelling showed that natural attenuation was an important factor in limiting the magnitude and extent of the ground water contamination. Microcosm studies with aquifer sediment revealed that abiotic degradation of the contaminants could explain the observed attenuation of cis-DCE with distance along the flow path.

In monitoring wells along the vertical axis of the plume, the average point rate of attenuation over time was 0.3 yr^{-1}.
Annual ground water contaminant monitoring has continued at the TCAAP as part of the Record of Decision at the site. Contaminant concentration data was re-evaluated to determine whether the point rate of attenuation has stayed the same.

Figure 1. Location of the former TCAAP facility and the ground water contaminant plume.

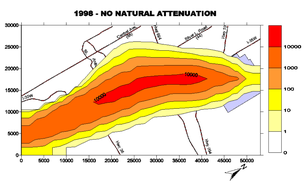
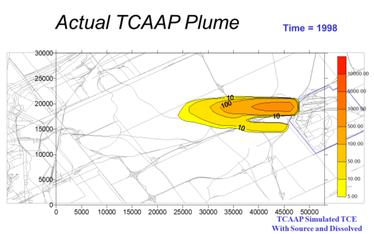


Figure 2. Modeling indicated that considerable destruction of contaminants must be occurring in ground water to account for the current plume size



Microcosm studies showed abiotic degradation of TCE and cis-DCE in groundwater associated with the presence of magnetite.

The data from ground water monitoring wells show a change in the rate of contaminant attenuation since it was first measured in 1999

Figure 3. Observations of degradation breakpoints in three monitoring wells downgradient of the source area.

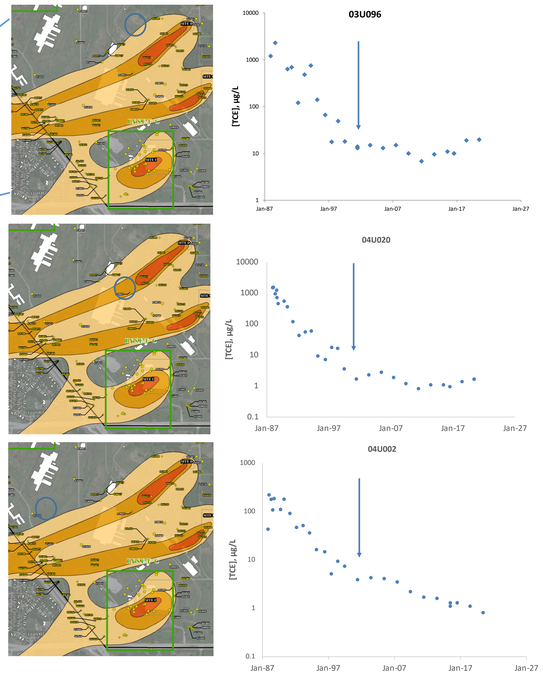


Table 1. Rates of attenuation observed in 1999 for several monitoring wells at TCAAP

Well No.	Time interval (years)	Number of observations	Apparent attenuation rate of TCE (per day)	Upper 95% confidence interval (per day)	Apparent attenuation rate of TCE (per year)	Upper 95% confidence interval (per year)	P-value
03U096	10	10	-0.0010	-0.0006	-0.3650	-0.2018	1.64E-03
03U094	10	9	-0.0010	-0.0007	-0.3590	-0.2452	1.42E-04
03U003	7	21	-0.0008	-0.0006	-0.2780	-0.2059	1.46E-07
03U079	10	16	-0.0010	-0.0008	-0.3530	-0.2765	1.07E-07
03U093	9	27	-0.0019	-0.0016	-0.6913	-0.5743	5.33E-12
03U094	10	9	-0.0010	-0.0007	-0.3590	-0.2452	1.42E-04
03L002	10	14	-0.0010	-0.0008	-0.3828	-0.2963	5.30E-07
03L020	10	4	-0.0012	-0.0006	-0.4296	-0.2180	1.29E-02
03L883	4	13	-0.0010	-0.0007	-0.3761	-0.2388	8.57E-05
04U002	9	13	-0.0010	-0.0008	-0.3476	-0.2827	1.40E-07
04U020	10	15	-0.0015	-0.0013	-0.5556	-0.4573	1.69E-08
04U848	10	18	-0.0016	-0.0013	-0.5736	-0.4858	2.51E-10
TGRS	7	8	-0.0006	-0.0005	-0.2288	-0.1847	1.45E-05
Mean			-0.0011	-0.0008	-0.4076	-0.3010	

Changepoint statistical analysis of long-term attenuation rates

- Data from monitoring wells at TCAAP was analyzed to determine long-term attenuation rates. These wells included those that were used in the EPA natural attenuation study in 1999 together with additional data up to 2020.

- Piecewise regressions ("segmented" function (R v4.2.2; segmented package (Muggeo 2008)) were fit to the relationship between days from the start of monitoring in1987 and the natural log of TCE (Figure 4). Significant models ($p < 0.05$) were fit to data for 18 of the 22 wells with adjusted R-squared values ranging from 0.74-0.99 in the significant models (Table 2). The most common relationship observed (13 wells) was a rapid decline in TCE with a slower decline following the determined changepoint. Other patterns observed were a decline with multiple breakpoints (3 wells), a decline in TCE with no lower breakpoint (3 wells), an increase in TCE (2 wells), and no pattern (1 well). For the wells with a rapid then slower decline, the breakpoint was observed from 2662-8432 days with an average of 4724 days.

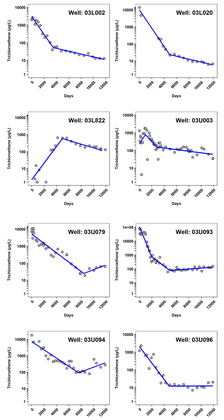


Figure 4. Graphs of calculated breakpoints in TCE degradation rates for several TCAAP monitoring wells.

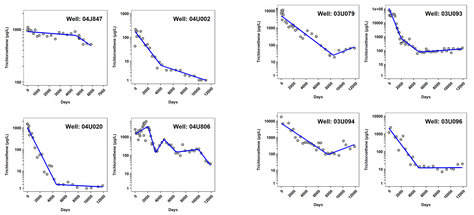
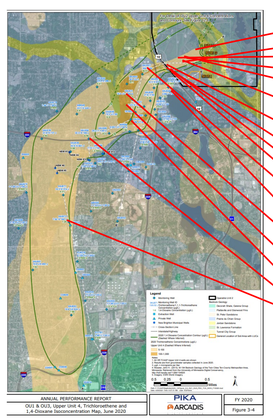


Figure 5. Location of monitoring wells in the TCAAP contaminant plume.



Well	Breakpoint (days)	p value	Adjusted R-squared	Category
03U096	4810	4.48E-08	0.90	Declining, 1 breakpoint
03U314	4277	<2.00E-16	0.99	Declining, 1 breakpoint
03U317	6287	<2.00E-16	0.81	Declining, 1 breakpoint
03U094	7579	9.13E-11	0.84	Declining, 1 breakpoint
03U093	4888	<2.00E-16	0.95	Declining, 2+ breakpoints
03L020	4876	6.57E-12	1.00	Declining, 1 breakpoint
04U020	4566	2.68E-13	0.96	Declining, 1 breakpoint
03L002	3486	7.10E-13	0.98	Declining, 1 breakpoint
04U002	4088	7.12E-10	0.95	Declining, 1 breakpoint
04U806	multiple	0.02	0.89	Declining, no lower breakpoint
03U079	8432	1.63E-14	0.92	Declining, 1 breakpoint
03U003	multiple	0.26	0.32	Declining, 2+ breakpoints
04J847	4456	0.05	0.68	Declining, no lower breakpoint
04U847	1572	0.15	0.05	No relationship
04U848	3002	4.92E-13	0.95	Declining, 1 breakpoint
04U823	2662	4.80E-06	0.91	Declining, 1 breakpoint
04U823	3129	2.68E-07	0.93	Declining, 1 breakpoint
04U827	5359	3.65E-07	0.82	Increasing
04U822	4732	6.01E-05	0.74	Increasing
04U844	4212	0.06	0.38	Declining, 1 breakpoint
04U850	682	0.56	0.52	Declining, no lower breakpoint
04U872	9064	0.04	0.76	Declining, 2+ breakpoints

Table 2: Piecewise regression model results. Highlighted wells comprise monitoring well nests. (03- and 04- wells are screened in the glacial outwash sand and the dolomite bedrock aquifers, respectively. U = upper aquifer; L= lower aquifer screen interval)

Conclusions

- The change in attenuation rates are statistically significant. Changepoint analysis is an effective tool to evaluate site remediation efforts.

- The change in rate may reflect exhaustion of magnetite in outwash sands that is responsible for degradation of TCE and DCE.

- The change in the rate constant may reflect disappearance of the TCE from the outwash sands, making more apparent the contribution of TCE that moves to the well from flow paths in the deeper bedrock aquifer without magnetite.

- The initial concentration of TCE in wells 03U096 and 04U020 is higher (near 3000 ug/L) than in 04U002 (near 300 ug/L). The reduction in rate constant is much stronger in wells 03U096 and 04U020 compared to well 04U002, supporting the idea that consumption of TCE is reducing the rate constant.

- The change in attenuation rates might reflect the effect of active remedies at the site.

- The results show the importance of continued monitoring at sites for changes in natural attenuation rates.

Observed changes in the rate of contaminant attenuation may alter the original estimates of the time needed for ground water cleanup, the possible need for evaluation of additional remediation measures, and might change the conceptual model of contaminant transport in the aquifer.

References
Muggeo, V.M.R. (2008). segmented: an R Package to Fit Regression Models with Broken-Line Relationships. R News, 8/1, 20-25. https://cran.r-project.org/doc/Rnews/.