Multiyear Temporal Changes in Chlorinated Solvent Concentrations at 23 Monitored Natural Attenuation Sites

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Abstract: Long-term (e.g., 5–15 years) groundwater concentration versus time records were compiled from 47 near-source zone monitoring wells at 23 chlorinated solvent sites (52 total records). Chlorinated volatile organic compound (CVOC) concentrations decreased significantly in most of the 52 temporal records, with a median reduction in concentration of 74%. A statistical method based on a Mann–Kendall analysis also showed that most sites had statistically significant decreasing concentration trends over time. Median point decay rate constants (k_{point}) values were calculated for nine sites containing tetrachloroethene (PCE); 13 sites containing trichloroethene (TCE); two sites containing cis-1,2-dichloroethene (DCE); and six sites containing 1,1,1-trichloroethane (TCA). The TCA sites had the highest k_{point} values (0.34/year) followed by PCE, DCE, and TCE (0.23/year, 0.16/year, and 0.11/year, respectively) (equal to decay half-lives of 2.0, 3.0, 4.3, and 6.1 years, respectively). If the median point decay rates from these sites are maintained over a 20 year period, the resulting reduction in concentration will be similar to the reported reduction in source zone concentrations achieved by active in situ source remediation technologies (typical project length: 1–2 years).

CE Database subject headings: Attenuation; Chlorination; TCE; PCE; Ground-water pollution; Water treatment.

Introduction

There is an increasing interest in predicting how long it will take natural attenuation processes to remediate groundwater plumes. The U.S Environmental Protection Agency (USEPA) Monitored Natural Attenuation (MNA) Directive (USEPA 1999) specifies that MNA relies on " . . . a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater." MNA involves data collection to estimate both the rate of attenuation processes and the "anticipated time required to achieve remediation objectives." The USEPA adds that " . . . determination of the most appropriate time frame is achieved through a comparison of estimates of remediation time frame for all appropriate remedy alternatives."

Some state regulatory programs also require a relative or absolute estimate of remedial time frame. For example, the Texas Commission on Environmental Quality (TCEQ) mandates all

MNA demonstrations address the requirement that remedial goals be achieved in a reasonable time frame by either: (1) comparing times required using other remedial alternatives at the same affected property under similar conditions; and/or (2) developing estimates of how long MNA will take to reach the cleanup goals (TCEQ 2001). The TCEQ program states that the simplest method to estimate a remediation time frame for MNA is to calculate a concentration versus time rate constant and then use the rate constant to determine the time when concentrations reach the required response goal.

Temporal Trend Studies

The potential lifetime of chlorinated solvent plumes and source zones has been evaluated using laboratory studies, mathematical models database studies, and heuristic judgement. Using laboratory data from Schwille (1998) and an analysis developed by Johnson and Pankow (1992), a hypothetical 50 L pool of dense nonaqueous phase liquids (DNAPL) would require at least 100 years to dissolve completely (Feenstra et al. 1996). Feenstra et al. (1996) concluded that source zones with considerable DNAPL mass " . . . will persist for many decades or centuries."

In 2003, a USEPA expert panel, based on their experience and judgment, stated that "the current default assumption is that DNAPL sites will require several decades to centuries of plume management with significant cost and future uncertainty" (Kavanaugh et al. 2003) and that contaminant mass in source zones can (except in rare cases) only be partially depleted (removed or destroyed) by active remediation. The expert panel's definition of a "DNAPL source zone" was the groundwater volume where DNAPL is in a separate phase or the volume where once-present DNAPL is now present only in the dissolved or sorbed phases or diffused into the matrix in fractured systems.

Other researchers have developed quantitative approaches to estimate source zone persistence. Newell et al. (1996) included a simple source decay term using a simple box model concept in

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the BIOSCREEN model, and Aziz et al. (2000) applied the same function in the BIOCHLOR model. Farhet et al. (2004) expanded the box model concept for the SourceDK software. Huntley and Beckett (2002a,b) applied a source decay term in the LNAST model that was based on the groundwater flux through the light nonaqueous phase liquid (LNAPL) zone and effective solubility relationships. Chapelle et al. (2003) applied a NAPL dissolution model in the Natural Attenuation Software (NAS) system so that the times of remediation for MNA could be estimated.

Only a few studies have analyzed temporal data from groundwater sites, the same approach used for this paper. Rice et al. (1995) and Mace et al. (1997) evaluated temporal trends for area-weighted average benzene, toluene, ethylbenzene, and xylene (BTEX) concentrations at fuel hydrocarbon release sites with plumes that were already shrinking (Newell and Connor 1998). In general, they found the median time for a 90% reduction in average BTEX plume concentrations was 1.4 years (Mace et al. 1997) and 3.2 years (Rice et al. 1995). Kampbell et al. (2000) and Parsons Engineering Science (1999, 2003) estimated natural LNAPL weathering and source-term reduction rates (k_{point}) at five JP-4 jet fuel sites. They reported maximum, median, and minimum total BTEX weathering half-lives (concentration versus time half-lives from wells in or near JP-4 LNAPL zones) of 23, 5.8, and 1.2 years, respectively.

Suarez and Rifai (2002) estimated a point decay rate constant of 0.046/year for a xylene and benzene source zone at a coastal chemical manufacturing facility. Suarez et al. (2004) calculated point decay rate constants (concentration versus time rate constants) for source zone wells at dry cleaner sites in Texas, and found median values of 0.26/year, 0.43/year, 0.15/year, and 0.39/year for tetrachloroethene (PCE) ($n=19$ sites); trichloroethene (TCE) ($n=19$); cis-1,2-dichloroethene (DCE) ($n=13$); and vinyl chloride ($n=13$). respectively. Only wells with decreasing concentrations trends were used in the analysis, however. McNab (2001) used linear regression techniques with a multisite chlorinated solvent database (McNab et al. 1999) and determined that 69% of 359 wells at 36 sites had a decreasing concentration trend. Each well had at least four sampling events and an $R^2 > 0.25$. Similar results were observed for PCE, 1,1-dichloroethane (1,1-DCA), and carbon tetrachloride.

In summary, there are different perspectives on how long source zones will persist. Some researchers have used heuristic approaches to suggest that source zones will persist for several decades or centuries. Other researchers have developed source models or have calculated source decay rates that can be used to estimate source persistence.

Objectives

The objective of this study was to determine if untreated chlorinated solvent plumes in a 23-site database were decaying, and if so, at what rate are concentrations decreasing. These sites were chosen on the basis of having data that could be compiled, long temporal records, and no source treatment. Because the nature and distribution of all chlorinated solvent sites is difficult to characterize, it is difficult to compare these 23 sites against an "average" or "typical" chlorinated solvent site. While the site selection criteria was not intentionally biased to exclude sites with any characteristics, the requirement that sites have untreated source zones likely removed high-risk sites from this study.

A total of 52 temporal records from 47 monitoring wells at 23 sites were collected from three sources and analyzed to:

1. Calculate the percentage concentration change from the first year to the last year of monitored data;
2. Determine if concentration trends were increasing, stable, or decreasing as defined by a nonparametric statistical trend analysis technique (i.e., a Mann–Kendall method);
3. Determine which of three simple mathematical models best fit the temporal records: a constant concentration, linear decay, or first order decay model; and
4. Calculate the actual rate of change (if any) in chlorinated solvent concentrations over time.

With trend and rate information from MNA sites, the time to achieve cleanup goals (e.g., the remediation time frame) under a MNA or containment alternative can be evaluated for the sites in this database and compared to the remediation time frame for partial source depletion projects (i.e., intensive source remediation technologies such as thermal treatment, chemical oxidation, enhanced in situ biodegradation) at these sites.

Methodology

Data Sources

Four sources were used to obtain the temporal data from monitoring wells at chlorinated volatile organic compound (CVOC) sites. A database developed by McNab (2001) from a research project performed by McNab et al. (1999) at the Lawrence Livermore National Laboratory (LLNL) provided 13 of the sites (Site Numbers 1–13). An additional two sites were supplied from GZA GeoEnvironmental (Manchester, N.H.) (Site Numbers 14 and 15), one site from the USGS in New Jersey (Site Number 16) and seven sites from the TCEQ Voluntray Cleanup Program (VCP) (Site Numbers 17–23) (Table 1). Wells that met the following criteria were retained for statistical analysis:

1. Had data for one or more of the following constituents: 1,1,1-trichloroethane (TCA); PCE; TCE; and cis-1,2-DCE (DCE) (note the majority of the cis-1,2-DCE is present as a degradation product of TCE);
2. Had at least 5 years of groundwater monitoring data;
3. Had no large gaps between data points (i.e., no periods greater than 50% of the monitoring period without data);
4. Had more than half of the data in the temporal record above detection limits; and
5. Had the highest or second highest concentration among all retained temporal records to represent source or near source wells.

Each site had between one and four temporal records that met these criteria, with a maximum of two wells per CVOC per site. These criteria were designed to represent long-term, relatively complete temporal records in source zone or near source wells at chlorinated solvent sites. The 52 temporal records had a median monitoring record of nine years. Two wells at two sites had 15 years of data. As described above, the minimum monitoring record for any well was 5 years (one well at one site). Fig. 1 shows four composite plots of normalized concentrations versus duration for the 52 temporal records sorted by constituent. Concentrations were normalized by dividing each value by the initial concentration of each individual temporal record, and by setting time zero as the date of the first sample of each record. While a large variation in concentration trends is evident for each constituent, most temporal records show concentrations decrease with time (values below 1.0), while some increase with time (values greater than 1.0).

Table 1. Percentage Change in Chlorinated Volatile Organic Compound

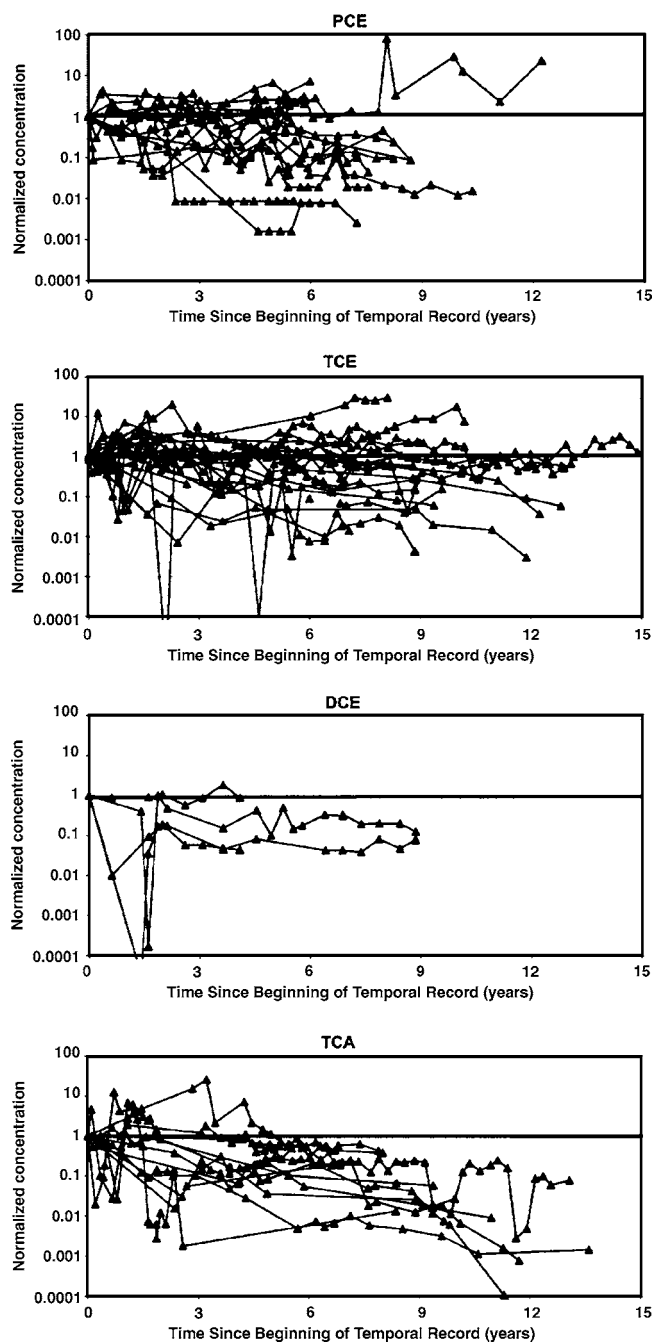| Temporal record	Site number	CVOC	Years of data	Geomean of CVOC concentration (mg/L) First year	Geomean of CVOC concentration (mg/L) Last year	Percent change (%)	Percent change per year (%)	Maximum CVOC concentration at site (mg/L)
1	1	TCE	10	0.054	0.025	−52.9	−5.5	0.8
2		TCE	10	0.630	0.329	−47.8	−5.0	
3	2	TCE	15	3.000	6.220	107.3	7.2	116
4		TCE	13	48.744	37.748	−22.6	−1.7	
5	3	TCE	8	0.004	0.055	1232.0	151.5	0.059
6	4	TCA	10	30.000	0.233	−99.2	−10.0	360
7		TCA	9	0.095	0.026	−72.8	−7.7	
8		TCE	10	360.000	6.465	−98.2	−9.9	
9		TCE	10	11.000	5.695	−48.2	−4.6	
10	5	PCE	12	0.068	0.379	458.6	37.5	100
11		PCE	12	0.350	0.005	−98.7	−8.1	
12		TCE	12	8.055	0.190	−97.6	−8.0	
13		TCE	9	8.045	7.200	−10.5	−1.1	
14	6	TCE	9	29.068	11.000	−62.2	−7.1	62.8
15		TCE	9	15.484	10.000	−35.4	−4.0	
16	7	TCA	12	18.100	0.020	−99.9	−8.5	22.8
17		TCA	12	22.800	0.002	−100.0	−8.5	
18	8	TCA	11	0.475	0.017	−96.4	−8.8	26.5
19		TCA	12	7.437	0.057	−99.2	−8.4	
20		TCE	13	6.121	0.732	−88.0	−6.9	
21		TCE	12	6.778	0.020	−99.7	−8.4	
22	9	TCA	9	25.509	4.490	−82.4	−8.8	85
23		TCE	9	9.402	1.977	−79.0	−8.4	
24	10	TCA	8	2.500	0.940	−62.4	−7.8	7.1
25	11	DCE	8	0.190	0.087	−53.9	−6.5	1.9
26		DCE	8	0.007	0.010	35.6	4.3	
27		PCE	8	0.090	0.009	−89.8	−10.9	
28		PCE	8	0.110	0.028	−74.3	−9.0	
29	12	TCE	12	0.005	0.046	850.0	71.0	0.077
30	13	TCA	14	0.704	0.001	−99.8	−7.1	25
31		TCA	15	0.497	0.076	−84.6	−5.8	
32		TCE	11	44.000	25.526	−42.0	−3.8	
33		TCE	9	215.777	122.959	−43.0	−4.7	
34	14	TCE	13	0.657	0.453	−31.1	−2.4	0.8
35	15	TCE	7	11.000	0.174	−98.4	−13.9	11
36	16	DCE	9	160.000	11.005	−93.1	−10.5	160
37		DCE	9	130.000	22.047	−83.0	−9.4	
38		TCE	9	0.270	0.003	−99.0	−11.2	
39		TCE	9	0.750	0.104	−86.2	−9.7	
40	17	PCE	6	0.863	0.005	−99.4	−17.9	1.4
41	18	PCE	9	22.495	6.454	−71.3	−8.2	36
42		PCE	6	0.112	0.039	−64.8	−11.0	
43	19	PCE	6	0.748	0.263	−64.9	−11.1	1.5
44		PCE	6	0.420	0.377	−10.3	−1.9	
45	20	PCE	6	0.766	0.105	−86.3	−14.4	9.4
46		PCE	6	2.165	0.978	−54.8	−9.1	
47	21	PCE	8	88.544	4.508	−94.9	−12.5	220
48		PCE	8	138.443	20.387	−85.3	−11.3	
49	22	PCE	6	1.173	0.565	−51.8	−9.3	3.3
50		PCE	5	0.047	0.017	−62.8	−11.5	
51	23	PCE	7	0.159	0.003	−97.8	−13.5	0.644
52		PCE	7	0.005	0.016	222.4	31.3	
		Median	9.0	1.669	0.212	−73.5	−8.3	11

Fig. 1. Standardized concentration versus time since beginning of record for each constituent. Concentrations were standardized by normalizing to initial concentration of each temporal record. Time zero was assigned to first observation at each temporal record.

The database was compared to other chlorinated solvent databases to determine if it was representative of chlorinated solvent sites now being managed under federal and state regulatory programs. The maximum concentrations of PCE, TCE, DCE, and TCA at each site ranged from 0.059 to 360 mg/L, with a median concentration of 11.0 mg/L (Table 1). The concentration data indicate that a wide range of site types is represented in the database, from highly impacted sites to less impacted sites.

The observed distribution in concentrations is similar to what has been observed in other CVOC database studies: Aziz et al. (2000) presented a 22-site TCE database with a median maximum TCE concentration of 3.2 mg/L. McNab et al. (1999) showed that of 55 TCE plumes with concentrations greater than 0.01 mg/L, 67% of the plumes had maximum plume concentrations greater than 0.10 mg/L, and 35% had maximum concentrations greater than 1 mg/L (note 13 of these sites were used for this study). McGuire et al. (2004) compiled data for 45 chlorinated solvent sites where MNA had been evaluated, and found the median maximum CVOC concentration fell between 1 and 10 mg/L. A literature survey of CVOC MNA sites found similar results (McGuire et al. 2003) (Table 2).

The fraction of sites in the database that could be classified as DNAPL sites was evaluated. The commonly applied "1% rule" (i.e., sites with chlorinated solvent concentrations >1% of effective solubility of the constituents indicates the presence of DNAPL) (Newell and Ross 1992) showed that 12 of the 23 sites had concentrations greater that 1% of the pure phase solubility of each constituent based on data shown in Table 1. Note this rule has no theoretical or fundamental basis, so that an exact determination of the number of sites with DNAPL cannot be made. However, it is likely that the majority of the sites in this database contain DNAPL or contain sorbed, dissolved, or diffused constituents from once-present DNAPL, thereby meeting the definition of a DNAPL source zone developed by Kavanaugh et al. (2003).

Percentage Change

Percentage concentration change over the monitoring record for each well was calculated by taking the geometric mean of the first year of monitoring data and comparing it to the geometric mean of the last year of monitoring data (Table 1).

Mann–Kendall Analysis

A temporal trend analysis based on the Mann–Kendall method approach (Aziz et al. 2003) was applied to the 52 temporal data sets. The method uses the Mann–Kendall S statistic (a nonparametric trend indicator), the confidence factor, and the coefficient

Table 2. Distribution of Maximum Site Concentration for Four Chlorinated Solvent Database Studies

Maximum CVOC concentration at site	Percentage of sites in maximum concentration category (%)			
	Technical survey	Literature compilation	Technical survey	This study
1 mg/L	29	20	29	22
1–10 mg/L	24	40	33	26
10–100 mg/L	29	24	33	27
>100 mg/L	18	16	4	22
Number of sites	45	17	24	23
Reference	McGuire et al. (2005)	McGuire et al. (2003)	Aziz et al. (2000)	This study

Table 3. Percent Change from First Year to Last year

CVOC	Median years of data	Median percent change (%)	Median percent change per year (%/year)
All CVOCs	9.0	−74	−8.2
PCE	7.1	−71	−10.0
TCE	10.0	−81	−8.1
DCE	8.9	−86	−9.7
TCA	11.0	−99	−9.0

of variation (COV) to categorize the trends as decreasing, probably decreasing, stable, no trend, probably increasing, or increasing. Criteria for each category are summarized below:

- "Increasing" trend: Mann–Kendall S statistic >0, confidence factor $>95\%$;
- "Probably increasing" trend: S statistic >0, confidence factor $>90\%$;
- "Stable" trend: S statistic <0, confidence factor $<90\%$, COV <1;
- "Probably decreasing" trend: S statistic <0, confidence factor $>90\%$;
- "Decreasing" trend: Mann–Kendall S statistic <0, confidence factor $>95\%$; and
- "No trend": S statistic <0, confidence factor $<90\%$, COV >1.

Trends were calculated for each well at each site. For sites with multiple wells a simple weighting system was used to determine an overall trend at the site (Aziz et al. 2000). Trend classification of "Decreasing," "Probably decreasing," "Stable," "No trend," "Probably increasing," and "Increasing" were assigned weighting values 1–6, respectively. The average weight was calculated for each site for all CVOCs. The resulting site weights were categorized as follows:

- Site weight <1.5=decreasing;
- $1.5<$ site weight ≤2.5=probably decreasing;
- $2.5<$ site weight ≤3.5=stable;
- $3.5<$ site weight ≤4.5=no trend;
- $4.5<$ site weight ≤5.5=probably increasing; and
- Site weight >5.5=increasing.

Simple Temporal Models

These simple concentration models: a first order decay model, linear decay model, and a constant concentration model, were compared to determine which best fit the CVOC concentration versus time data. The three models are expressed mathematically as:

Table 4. Mann–Kendall Based Trend Analysis by Site

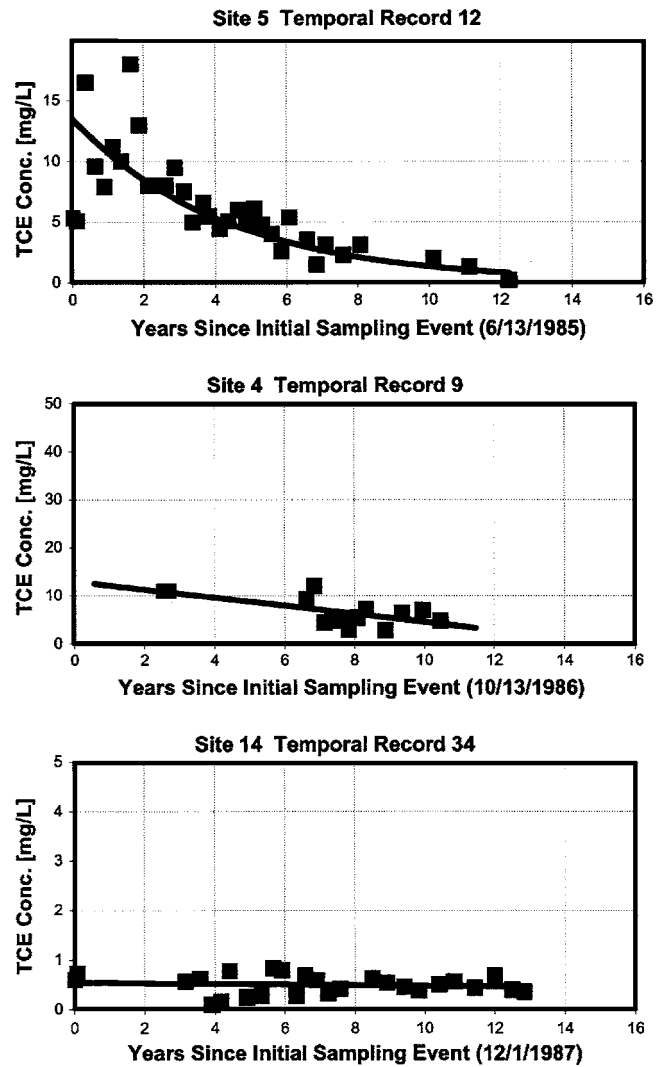| Trend	Number of sites				
	All	PCE	TCE	DCE	TCA
Increasing	2	0	2	0	0
Probably increasing	1	1	1	0	0
Stable	4	2	3	0	0
Probably decreasing	6	1	4	1	2
Decreasing	8	4	3	0	4
No trend	2	1	0	1	0
Number of sites	23	9	13	2	6

Fig. 2. Example of three temporal records with first order, linear, and constant concentration models

1. Constant concentration model: $C(t)$=geometric mean of the temporal record;
2. Linear decay model: $C(t)=m \cdot t+$ constant (m=slope of the best-fit line); and
3. First order decay model: $C(t)=$constant$\cdot \exp^{-k_{point} \cdot t}$ (k_{point}=slope of the natural log concentration versus time regression line).

The standard error and the coefficient of determination (R^2) were calculated for each of the three models using the data from the 52 temporal records. The standard error and R^2 were then compared to rank the models based on how well they fit the data.

Decay Rate Constant (k_{point})

To calculate decay rate constants (k_{point}), the natural log of concentration versus time for a single CVOC at a single well at a site was plotted and the k_{point} calculated as the slope of the best-fit line using simple regression (Newell et al. 2002). A positive (+) k_{point} indicated a decreasing trend in concentration, while a negative (−) k_{point} indicated an increasing concentration trend. Because the temporal records represent high-concentration wells at the site, the k_{point} values are likely to represent source zone or near-source zone locations at each site.

Table 5. Standard Error and R^2 for Three Models Fitted to Temporal Records

Record	Site	CVOC	First order Standard error	Rank	Linear Standard error	Rank	Step function Standard error	Rank	R^2 First order	Linear
1	1	TCE	0.024	(2)	0.023	(1)	0.024	(3)	0.17	0.13
2		TCE	0.118	(1)	0.123	(2)	0.179	(3)	0.45	0.53
3	2	TCE	2.867	(3)	2.579	(1)	2.617	(2)	0.08	0.03
4		TCE	44.204	(3)	23.949	(1)	24.449	(2)	0.01	0.04
5	3	TCE	0.006	(1)	0.010	(2)	0.025	(3)	0.93	0.85
6	4	TCA	8.435	(1)	7.496	(2)	9.730	(3)	0.31	0.41
7		TCA	0.022	(2)	0.022	(1)	0.035	(3)	0.39	0.63
8		TCE	98.013	(2)	88.284	(1)	115.119	(3)	0.30	0.41
9		TCE	2.384	(2)	2.373	(1)	3.144	(3)	0.33	0.43
10	5	PCE	1.036	(2)	0.957	(1)	1.053	(3)	0.49	0.17
11		PCE	0.033	(1)	0.053	(2)	0.099	(3)	0.81	0.71
12		TCE	2.987	(2)	2.746	(1)	4.104	(3)	0.73	0.55
13		TCE	33.609	(3)	30.276	(1)	30.335	(2)	0.00	0.00
14	6	TCE	21.060	(3)	16.846	(1)	17.236	(2)	0.02	0.04
15		TCE	15.891	(3)	10.459	(1)	10.470	(2)	0.02	0.00
16	7	TCA	3.536	(2)	3.119	(1)	4.759	(3)	0.92	0.57
17		TCA	2.105	(1)	4.217	(2)	5.247	(3)	0.63	0.35
18	8	TCA	3.357	(3)	2.885	(1)	2.999	(2)	0.16	0.07
19		TCA	7.758	(2)	6.858	(1)	8.941	(3)	0.87	0.41
20		TCE	4.778	(2)	4.357	(1)	5.624	(3)	0.57	0.40
21		TCE	2.964	(1)	3.057	(2)	4.220	(3)	0.90	0.48
22	9	TCA	27.640	(2)	23.628	(1)	33.587	(3)	0.44	0.51
23		TCE	21.062	(2)	18.222	(1)	21.833	(3)	0.38	0.30
24	10	TCA	1.105	(2)	1.044	(1)	1.596	(3)	0.70	0.57
25	11	DCE	0.662	(2)	0.531	(1)	0.682	(3)	0.13	0.39
26		DCE	0.003	(2)	0.003	(1)	0.003	(3)	0.03	0.06
27		PCE	0.019	(1)	0.020	(2)	0.030	(3)	0.61	0.54
28		PCE	0.038	(2)	0.027	(1)	0.047	(3)	0.75	0.67
29	12	TCE	0.010	(1)	0.011	(2)	0.017	(3)	0.59	0.54
30	13	TCA	0.165	(1)	0.186	(2)	0.228	(3)	0.89	0.34
31		TCA	4.705	(3)	4.288	(1)	4.699	(2)	0.38	0.17
32		TCE	0.947	(3)	0.185	(1)	0.217	(2)	0.52	0.28
33		TCE	0.911	(3)	0.168	(1)	0.187	(2)	0.12	0.20
34	14	TCE	0.212	(3)	0.203	(1)	0.204	(2)	0.00	0.02
35	15	TCE	2.485	(1)	2.534	(2)	4.784	(3)	0.77	0.72
36	16	DCE	6.285	(2)	5.983	(1)	6.597	(3)	0.33	0.23
37		DCE	5.026	(1)	5.039	(2)	6.045	(3)	0.40	0.31
38		TCE	0.068	(2)	0.064	(1)	0.080	(3)	0.66	0.36
39		TCE	2.325	(2)	2.009	(1)	2.347	(3)	0.28	0.27
40	17	PCE	0.191	(2)	0.151	(1)	0.193	(3)	0.61	0.52
41	18	PCE	10.034	(2)	9.200	(1)	10.830	(3)	0.39	0.28
42		PCE	0.258	(3)	0.242	(1)	0.244	(2)	0.12	0.01
43	19	PCE	0.430	(2)	0.375	(1)	0.459	(3)	0.33	0.33
44		PCE	0.191	(2)	0.186	(1)	0.198	(3)	0.15	0.12
45	20	PCE	0.443	(2)	0.429	(1)	0.480	(3)	0.19	0.20
46		PCE	2.551	(2)	2.419	(1)	2.667	(3)	0.26	0.18
47	21	PCE	25.989	(1)	27.562	(2)	45.747	(3)	0.72	0.64
48		PCE	32.618	(1)	34.707	(2)	52.185	(3)	0.54	0.56
49	22	PCE	0.893	(3)	0.767	(1)	0.889	(2)	0.12	0.25
50		PCE	1.029	(3)	0.036	(1)	0.040	(2)	0.25	0.20
51	23	PCE	0.155	(2)	0.143	(1)	0.184	(3)	0.09	0.40
52		PCE	0.012	(2)	0.011	(1)	0.012	(3)	0.12	0.12
			Ranked (1): 25%		Ranked (1): 75%		Ranked (1): 0%		Median: 0.38	0.33
			Ranked (2): 50%		Ranked (2): 25%		Ranked (2): 25%			
			Ranked (3): 25%		Ranked (3): 0%		Ranked (3): 75%			

Table 6. k_{point} by Temporal Record

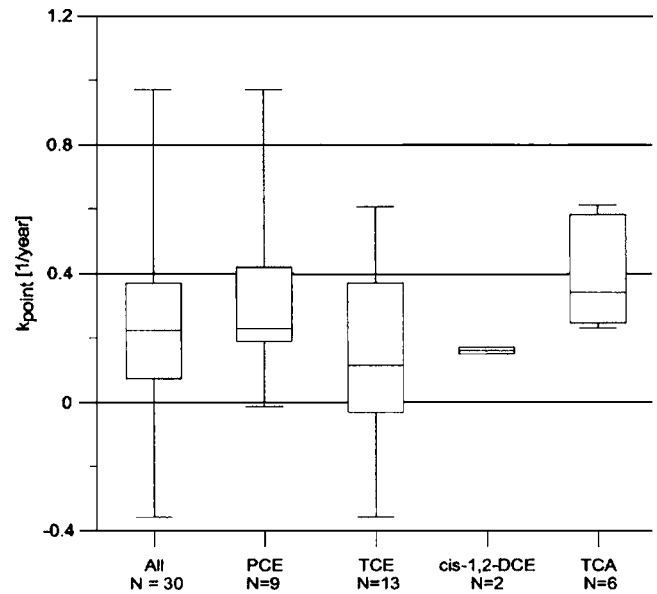| Temporal record	Site	CVOC	Value	Upper	Lower
			k_{point} (per year)		
				95% confidence limits	
1	1	TCE	0.08	0.20	−0.04
2		TCE	0.10	0.18	0.03
3	2	TCE	0.02	0.08	−0.05
4		TCE	−0.08	0.01	−0.17
5	3	TCE	−0.36	−0.29	−0.43
6	4	TCA	0.30	0.67	−0.07
7		TCE	0.25	0.55	−0.06
8		TCA	0.19	0.37	0.01
9		TCE	0.12	0.22	0.01
10	5	TCE	0.00	0.23	−0.24
11		PCE	−0.27	−0.12	−0.41
12		TCE	0.23	0.28	0.18
13		PCE	0.41	0.55	0.28
14	6	TCE	0.15	0.76	−0.46
15		TCE	−0.21	0.74	−1.17
16	7	TCA	0.56	0.66	0.47
17		TCA	0.60	0.83	0.36
18	8	TCA	0.64	1.41	−0.14
19		TCE	0.22	0.30	0.13
20		TCA	0.58	0.71	0.46
21		TCE	0.56	0.65	0.46
22	9	TCA	0.27	0.51	0.04
23		TCE	0.27	0.54	0.01
24	10	TCA	0.23	0.30	0.16
25	11	DCE	0.33	1.20	−0.53
26		PCE	0.24	0.35	0.12
27		DCE	−0.04	0.18	−0.26
28		PCE	0.23	0.32	0.14
29	12	TCE	−0.32	−0.21	−0.43
30	13	TCE	0.21	0.32	0.10
31		TCE	0.08	0.20	−0.04
32		TCA	0.51	0.60	0.42
33		TCA	0.31	0.44	0.19
34	14	TCE	0.00	0.05	−0.06
35	15	TCE	0.60	0.87	0.34
36	16	DCE	0.17	0.33	0.01
37		TCE	0.38	0.57	0.19
38		DCE	0.17	0.29	0.06
39		TCE	0.36	0.68	0.04
40	17	PCE	0.97	1.36	0.58
41	18	PCE	0.21	0.38	0.04
42		PCE	0.23	0.66	−0.20
43	19	PCE	0.27	0.50	0.04
44		PCE	0.10	0.26	−0.05
45	20	PCE	0.26	0.63	−0.12
46		PCE	0.20	0.44	−0.04
47	21	PCE	0.55	0.75	0.36
48		PCE	0.28	0.43	0.14
49	22	PCE	0.17	0.45	−0.11
50		PCE	0.30	0.61	−0.01
51	23	PCE	0.11	0.33	−0.11
52		PCE	−0.13	0.13	−0.40
	Median		0.23	0.43	0.01
	Number of k_{point} values>0		43	49	28
	Total records		52	52	52

Fig. 3. Box-whisker plot of k_{point} values by constituent

A statistical analysis was performed on all k_{point} values by temporal record. The 95% confidence limits of each k_{point} value were calculated by assuming that the residuals from the simple regression were normally and independently distributed with mean of zero and common variance.

Results

Percentage Change

For all CVOCs, the median change in concentration from the first year of recorded data to the last was a 74% reduction over a median record of 9 years (Table 3). This is a substantial decrease, due to natural attenuation alone, as no sites had any reported remediation or source depletion activities. The greatest reduction was seen for 1,1,1-TCA with a 99.2% reduction over 11 years. Dividing the percent change by the length of the temporal record yielded a median value of 8% decrease in concentration per year (Tables 1 and 3). Note that some sites showed increasing concentrations; for example 10% of the temporal records showed increases in concentration ranging from +35 to +1,200%.

Mann–Kendall Analysis

The Mann–Kendall approach showed that seven of the 13 TCE sites (54%) exhibited "Decreasing" or "Probably decreasing" trends in temporal near-source zone TCE concentrations, three of 13 sites (23%) were classified as "Stable" and three of 13 sites (23%) had "Increasing" or "Probably increasing" trends. In contrast, all of the TCA sites showed either "Decreasing" or "Probably decreasing" trends (Table 4).

Simple Temporal Models

Fig. 2 shows an example of the three models applied to three temporal records (note: these specific temporal records were selected to show good fits to each of the three models). When standard error was used to rank each model as first, second, or third best fit (Table 5), the linear model gave the best fit for 75%

Table 7. k_{point} Values by Site

Site	CVOC	k_{point} (per year)
1	TCE	0.09
2	TCE	−0.03
3	TCE	−0.36
4	TCA	0.25
4	TCE	0.18
5	PCE	0.07
5	TCE	0.11
6	TCE	−0.03
7	TCA	0.58
8	TCA	0.61
8	TCE	0.39
9	TCE	0.27
9	TCA	0.27
10	TCA	0.23
11	DCE	0.15
11	PCE	0.23
12	TCE	−0.32
13	TCA	0.41
13	TCE	0.15
14	TCE	0.00
15	TCE	0.60
16	DCE	0.00
16	TCE	0.37
17	PCE	0.97
18	PCE	0.22
19	PCE	0.19
20	PCE	0.23
21	PCE	0.42
22	PCE	0.24
23	PCE	−0.01
	Median	0.22
	Number	30
	Number > 0	24

Table 8. k_{point} by Site (per year)

	All	PCE	TCE	DCE	TCA
Maximum	0.97	0.97	0.60	0.17	0.61
75th percentile	0.37	0.24	0.27	—	0.54
Median	0.22	0.23	0.11	0.16	0.34
25th percentile	0.07	0.19	−0.03	—	0.25
Minimum	−0.36	−0.01	−0.36	0.15	0.23
Number of records	30	9	13	2	6

estimating how quickly remediation goals will be met at a site (Newell et al. 2002). Because of the statistical analysis, process knowledge, and the technical literature, further analysis of the temporal records was performed using the first order decay model.

Decay Rate Constant (k_{point})

Overall, 28 of 52 temporal data sets (54%) had k_{point} values with a 95% confidence interval greater than zero, indicating that the decreasing trend was statistically significant at the 95% level (Table 6). This indicates that CVOC concentration decay could only be measured in half of the temporal records. Fig. 3 shows the range of k_{point} calculated values by constituent. The temporal records with statistically significant decreasing trends in this study showed a median reduction in concentration of 84%. This result is in close agreement with Wilson (1998), who suggested that a decrease in contaminant concentrations of at least 1 order of magnitude is necessary to demonstrate that the estimated rate is statistically different from zero at a 95% level of confidence.

To evaluate trends by site, the average k_{point} values for sites with two temporal records for a CVOC per site were calculated (Table 7). A statistical summary of the decay rate data by site is presented in Tables 8 and 9, both as k_{point} and as a decay half-life (half-life = $0.693 \div k_{point}$).

First order decay rate constants (k_{point}) by site ranged from −0.36/year (increasing concentrations) to 0.97/year (decreasing concentrations) (Table 8). The median k_{point} ranged from 0.11/year for TCE (equivalent to a decay half-life of 6.1 years) to 0.34/year for TCA (equivalent to a decay half-life of 2.0 years). PCE and DCE had k_{point} values of 0.23/year (half-life of 3.0 years) and 0.16/year (half-life of 4.4 years). A total of nine 13 TCE sites (70%) had decaying concentrations compared to eight of nine PCE sites (88%) and two of two DCE and six of six TCA sites (100%). Overall, these results generally match the results from the Mann–Kendall analysis.

Attempts were made to correlate k_{point} values to site data. No correlation between k_{point} and hydraulic conductivity was observed for six TCE sites. No correlation was observed between k_{point} for each CVOC and CVOC solubility (Pankow and Cherry 1996) as indicated below:

Table 9. CVOC Concentration Half Lives Derived from Average k_{point} Values by Site (years)

	All	PCE	TCE	DCE	TCA
Maximum	0.7	0.7	1.1	2.0	1.1
75th percentile	1.9	2.9	2.5	—	1.3
Median	3.2	3.0	6.1	4.3	2.0
25th percentile	9.4	3.7	(I)	—	2.8
Minimum	(I)	(I)	(I)	4.7	3.0

of the temporal records and the constant concentration model exhibited the worst performance (worst fit for 75% of the temporal records).

When the coefficient of determination (R^2) was used to rank each model, the first order decay model had a better fit (median $R^2 = 0.38$ for 52 temporal records) than the linear model ($R^2 = 0.33$) (Table 5). R^2 could not be computed for the constant concentration model.

Based on the statistical evaluation, both the linear model and the first order decay model provided a better fit to the data than the constant concentration model, but the statistical methods diverged on which of these two models was better. However, process knowledge of source zone decay indicates that a first order decay model is likely to be more appropriate than either the linear or constant concentration model. Source zone decay is a combination of a variety of processes, such as DNAPL dissolution from fingers, DNAPL dissolution from pools, matrix diffusion, linear, and nonlinear desorption processes, resulting in significant tailing that would likely be best described by the first order decay model.

The USEPA evaluated the use of different types of attenuation rates for MNA studies (e.g., concentration versus distance; concentration versus time), and concluded that first order decay concentration versus time rate constants (k_{point}) should be used for

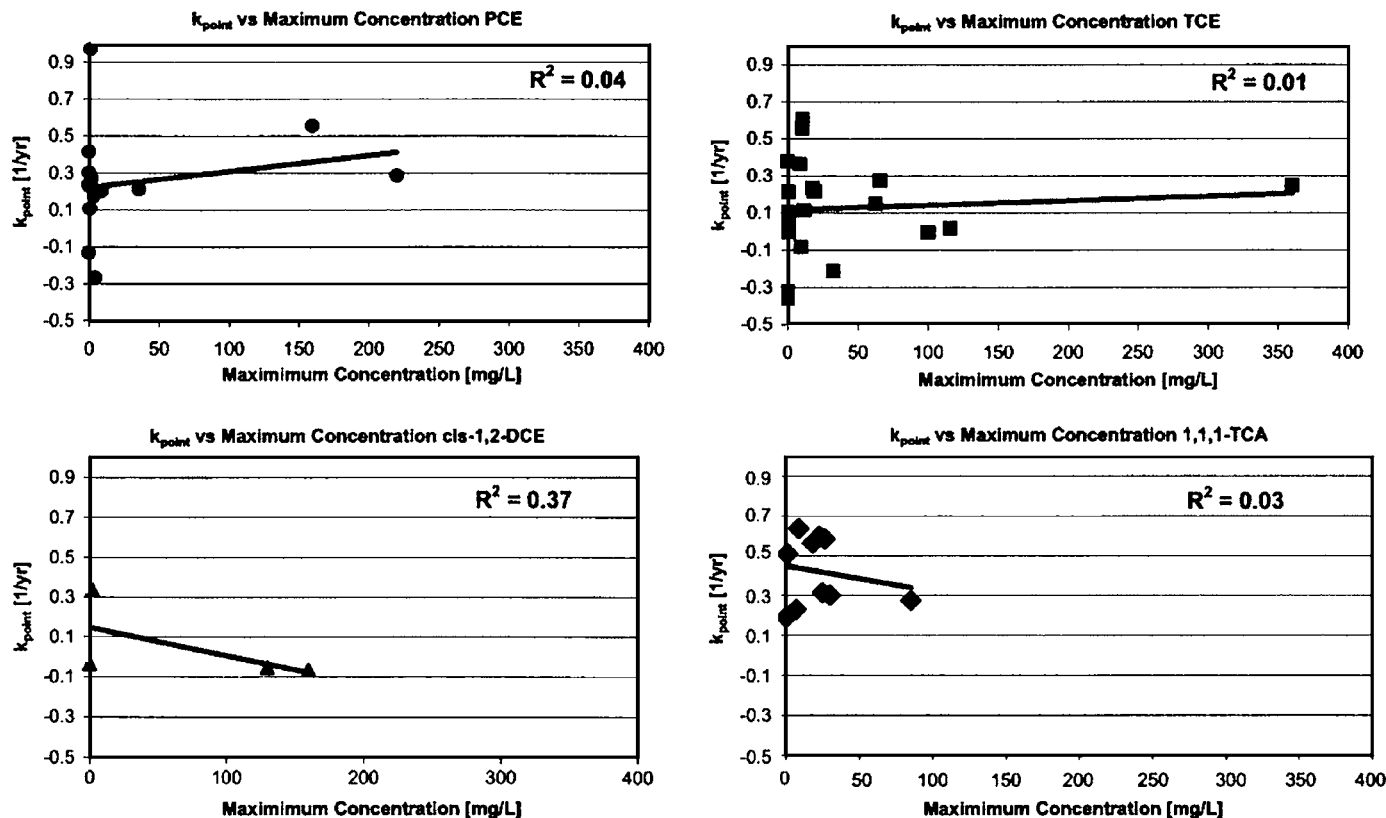**Fig. 4.** Point decay rate constant versus maximum concentration for each CVOC

- cis-1,2-DCE = 3,500 mg/L versus median k_{point} = 0.16 year^{-1};
- 1,1,1-TCA = 1,300 mg/L versus median k_{point} = 0.34 year^{-1};
- TCE = 1,100 mg/L versus median k_{point} = 0.11 year^{-1}; and
- PCE = 200 mg/L versus median k_{point} = 0.23 year^{-1}.

More importantly, no strong correlation was observed between k_{point} and maximum concentration during the temporal record as R^2 values (one for each CVOC) were all less than 0.04 (Fig. 4). A test for significance at the 95% confidence level showed that the R^2 was not significantly different from zero.

Conclusions

An analysis of long-term temporal trends (i.e., minimum record of 5 years and median record 9 years) from 47 source zone or near source zone groundwater monitoring wells at 23 sites shows that most of the wells exhibit decreasing CVOC concentrations over time. The median change for all four CVOCs analyzed (PCE, TCE, DCE, and TCA) was 74%, or an approximately 8% reduction per year.

A nonparametric trend analysis methodology was applied to the data set. Only three of 13 TCE sites showed "Increasing" or "Probably increasing" trends in concentrations over time, compared to one of nine PCE sites, zero of two DCE sites, and zero of six TCA sites. Three additional TCE sites were classified as "Stable," with seven sites showing "Decreasing" or "Probably decreasing" trends.

Both a linear regression model and a first order decay model fit the long-term concentration versus time better than a constant concentration model. The median first order decay coefficient (k_{point}) for 13 TCE sites was 0.11/year (half-life of 6.1 years). The median k_{point} value for TCA sites was highest (median value of

0.34/year, or a half-life of 2.0 years). Median k_{point} values for sites with PCE and DCE fell between the median values for TCE and TCA. Fifty-four percent of the temporal records had k_{point} values that were statistically greater than zero (at the 95% confidence level).

No correlation was observed between k_{point} and maximum concentration during the temporal record, indicating that the high-concentration plumes in this dataset appeared to be decaying as fast as low-concentration plumes. No correlation was observed between k_{point} and hydraulic conductivity ($n=6$) and median k_{point} and solubility ($n=4$).

The greater reduction in TCA concentrations over time (compared to PCE, TCE, and DCE) may be related to secondary degradation processes. TCA is quickly degraded in the aqueous phase via a hydrolysis reaction; this would tend to reduce TCA concentrations over time in plumes, and tend to increase the release rate from TCA source zones (e.g., DNAPL or matrix diffusion zones) because of increased concentration gradients between the source material and TCA in the aqueous phase groundwater. However, a detailed accounting of the specific contribution from various attenuation processes contributing to the reduction in TCA concentrations over time (abiotic degradation, biological degradation, DNAPL dissolution, diffusion from the matrix, dispersion) cannot be performed with the existing dataset.

The trend data, although they show considerable uncertainty, indicate that naturally occurring processes can significantly reduce CVOC plume concentrations over a span of a few years at some sites. Instead of CVOC sites being represented by unchanging concentrations over long periods of time (decades or centuries), this limited data set indicates that a more appropriate conceptual model of CVOCs includes source decay as an active process at CVOC sites, and that significant reductions in plume

concentrations can occur over relatively short timescales at some sites (i.e., median concentration versus time half-lives less than 10 years).

These results suggest untreated chlorinated solvent source zones in this 23-site database decay fast enough that active source depletion projects (e.g., thermal treatment, chemical oxidation, in situ enhanced biodegradation, or cosolvent flushing) will only achieve a reduction in remediation time frame of 20 years or less. A source depletion project is likely to reduce chlorinated solvent source zone concentrations by 75–90% (Stroo et al. 2003; McGuire et al. 2005), equivalent to two or three MNA decay half-lives (for sites where the concentration versus time response is represented by a first order decay process). Although the data are very limited, the results for DCE (cis-1,2-DCE, a daughter product of biodegradation processes) indicate that daughter product concentrations in source zones may be decaying as quickly as parent compounds at some sites.

Based on median source decay rate constants derived from this data set, the equivalent results (two half-lives) could be achieved by MNA alone after: 12 years for TCE; 8 years for DCE; 6 years for PCE, and 4 years for TCA. An 88% reduction could be achieved in 18, 12, 9, and 6 years for TCE, DCE, PCE, and TCA, respectively based on the median decay rate constants.

The question of partial source depletion is (in part) a question of the cost of source depletion versus the cost of MNA or long-term containment (Kavanaugh et al. 2003). The results of this work can be used to bound the potential life-cycle costs of MNA and/or containment alternatives at chlorinated solvent sites, which then can be compared to these costs of partial source depletion.

Acknowledgments

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