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6824

Evaluating the Degradation of Chlorinated Hydrocarbons in Contaminated Groundwater

W. W. McNab, Jr., and T. N. Narasimhan

Since 1983, it has become known that groundwater beneath the site of the Lawrence Livermore National Laboratory (LLNL) has been contaminated with volatile organic compounds (VOCs), notably PCE, TCE, 1,1- and 1,2-DCE, 1,1,1-TCA, and 1,1- and 1,2-DCA. The Environmental Restoration Division (ERD) of LLNL is exploring many alternatives to remove the VOCs from groundwater so as to comply with the regulations of the Environmental Protection Agency (EPA). In evaluating the relative merits of these strategies, an important issue concerns whether the dissolved organic compounds undergo degradation into

daughter products and, if so, determining the half-lives of such degradation reactions.

The purpose of this study is to analyze the water quality data already collected from the site by the ERD for evidence of degradation. This work is based on the premise that dissolved organic compounds may follow a variety of degradation pathways, determined largely by the overall groundwater geochemistry, notably redox conditions. Therefore, it is rational to commence the evaluation effort with a study of the thermodynamic state of groundwater at the site. A detailed report of this study is presented in McNab and Narasimhan (1992).

THERMODYNAMIC CONSTRAINTS ON DEGRADATION REACTIONS IN GROUND-WATER

Highly halogenated VOCs, such as those found at LLNL, primarily tend to degrade through reduction reactions (reductive dehalogenation), whereas their less chlorinated counterparts tend to be more susceptible to oxidation. The contaminants of greatest concern at LLNL—PCE and TCE—are highly chlorinated and hence would be expected to degrade primarily through reduction. One way to quantify the susceptibility of VOCs in LLNL groundwater to reductive dehalogenation is to follow the lead of Vogel et al. (1987) and calculate the equilibrium pE value at which a particular degradation path will be favored. Such values, relevant to the chlorinated ethanes and ethenes at the site, are given in Table 1. These estimates assume a mean pH of 7.6 and a mean Cl^- concentration of 2.8×10^{-3} mol/l, approximately representative of conditions in LLNL groundwater. Potential reductive dehalogenation pathways involving VOCs found in LLNL groundwater are shown in Figure 1. Clearly, whether degradation by reductive dehalogenation does or does not occur at the site depends on redox conditions in local groundwater.

LOCAL HYDROGEOCHEMISTRY

Geochemical evidence strongly suggests that the local subsurface environment at LLNL is highly oxidizing in nature and hence is highly unfavorable for the reductive dehalogenations shown in Figure 1. The prevalent oxidizing state is manifested in (a) the presence of dissolved oxygen up to 8 mg/l in a large number of groundwater samples, (b) the presence of iron oxide stains in Holocene alluvium, (c) the presence of solid phase MnO_2 and low Mn^{2+} concentrations in the aqueous state, and (d) the dominance of Cr^{6+} over Cr^{3+} . On the basis of the mean pH value and the speciation of Mn and Cr, it has been estimated that effective pE values in groundwater are at least 9.0 or 10.0.

Table 1. Redox constraints on common reductive VOC-degradation reactions in LLNL groundwater.

Reaction ¹	Maximum pE	Remarks
PCE → TCE	9.3	
TCE → 1,2-DCE	8.6	
1,2-DCE → VC	6.1	
1,1,1-TCA → 1,1-DCA	9.0	
1,1-DCA → CA	8.3	Product not observed ²
1,1-DCE → VC	6.3	Product not observed

¹CA = chloroethane; VC = vinyl chloride.

²Chloroethane has been detected only twice out of 2019 samples.

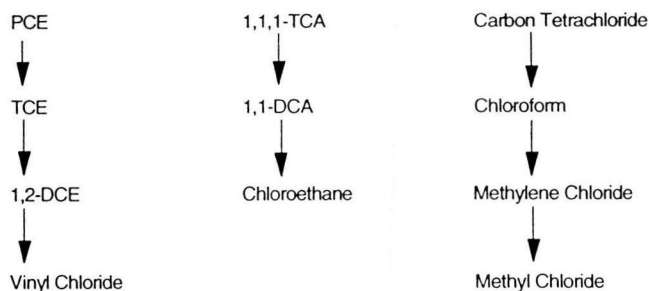


Figure 1. Reductive dehalogenation pathways for VOCs in LLNL groundwater. [XBL 935-797]

NONREDOX PROCESSES

Apart from redox-dependent reactions, many other degradation reactions are known that do not involve electron transfer (i.e., nonredox reactions). These reactions need not depend on the presence of microbial agents to proceed at measurable rates. Such reactions would therefore not be as strongly system-dependent as redox degradation reactions. As a result, abiotic degradation rates measured in the laboratory might sometimes be qualitatively extended to actual field conditions. Studies of hydrolysis rates for a variety of compounds of environmental concern were conducted by Mabey and Mill (1978), Vogel et al., (1987), and Jeffers et al. (1989). These studies indicate that chlorinated ethenes generally do not hydrolyze at significant rates. Estimated hydrolysis half-lives for chlorinated ethenes found in LLNL groundwater (PCE, TCE, 1,1-DCE and 1,2-DCE) range from millions to hundreds of millions of years and are thus insignificant. Halogenated ethanes, as a group, appear to be more susceptible to hydrolysis. 1,1,1-TCA is the most reactive of the group, with an effective half-life on the order of 0.5 to 2.5 years under neutral pH conditions, with 1,1-DCE and acetic acid noted as possible daughter products. Because 1,1,1-TCA is among the VOCs present in LLNL groundwater, its degradation is perhaps the most likely to be detected.

DATA ANALYSIS

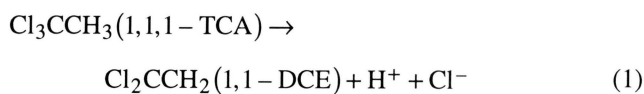
The most intuitive approach for ascertaining whether a given chemical is degrading is to measure the change in its total mass as a function of time. However, the existing spatial and temporal resolution of the LLNL groundwater chemistry database does not readily permit accurate estimates of such changes. The error associated with integrating under inferred concentration contour intervals may be greater than the degradation effects being measured. A more suitable method for searching for field evidence for degradation reactions is to qualitatively compare the behavior of suspected parent compound-daughter compound pairs. Such an evaluation may include examining spatial

and temporal trends in the ratio of concentrations of the daughter and parent compounds.

To test the various degradation hypotheses, two scenarios were considered. The first was the degradation of 1,1,1-TCA to 1,1-DCE, perhaps the most likely degradation reaction in LLNL groundwater. For comparative purposes, the second considered the reductive degradation of PCE to TCE. From thermodynamic considerations, we concluded that for the redox conditions prevalent at the site, the most plausible dehalogenation path would be that of PCE transforming to TCE.

1,1,1-TCA AND 1,1-DCE

The abiotic transformation of 1,1,1-TCA into 1,1-DCE through dehydrohalogenation may be expressed as



If 1,1,1-TCA does indeed transform into 1,1-DCE at some measurable rate, it should be expected that the ratio of the concentration of 1,1-DCE to that of 1,1,1-TCA would tend to increase over time wherever both chemicals are detected. However, 1,1,1-TCA is more hydrophobic than 1,1-DCE (Mercer et al., 1990) and thus is likely to be less mobile in groundwater. Retardation effects alone should therefore result in a decrease in the [1,1-DCE] to [1,1,1-TCA]¹ ratio over time in regions where 1,1,1-TCA is detectable (as 1,1-DCE would tend to escape such regions at a faster rate). Thus the superimposed effects of both degradation and adsorption may influence the [1,1-DCE] to [1,1,1-TCA] ratio in a complex manner. To qualitatively evaluate the expected variation in the [1,1-DCE] to [1,1,1-TCA] ratio influenced by both degradation and sorption, a numerical solute transport model was used to compare two possible scenarios: chemical degradation effects combined with retardation, and retardation alone. Both scenarios are based upon hydrologic data collected from the LLNL facility. Modeling results indicate that the primary difference between the two scenarios is an increase in the [1,1-DCE] to [1,1,1-TCA] ratio associated with degradation contrasted by a decrease in the ratio in the absence of degradation. Figure 2 shows measured temporal trends in the [1,1-DCE] to [1,1,1-TCA] ratio for a number of wells located on the major longitudinal axis of the 1,1,1-TCA plume along Arroyo Seco on the LLNL site. An increase in this ratio in the data is clearly evident. This is qualitatively consistent with the degradation scenario and entirely inconsistent with the nonreactive scenario.

¹ Square brackets, [], refer to chemical concentration.

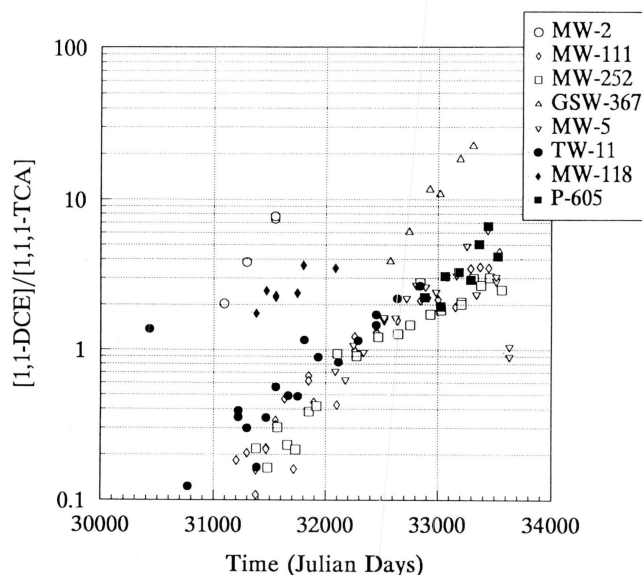


Figure 2. Temporal variation of the [1,1-DCE] to [1,1,1-TCA] ratio (mol/l) with distance in select Arroyo Seco area wells. [XBL 935-798]

Semiquantitative evidence for the degradation of 1,1,1-TCA to 1,1-DCE was also obtained by examining apparent changes in their respective total masses in a given area over time. Although this calculation was not feasible over the entire LLNL site, the relatively well-defined plumes in the Arroyo Seco area allowed such a calculation on a local level. The relative total masses of dissolved 1,1,1-TCA and 1,1-DCE along the Arroyo Seco Creek for each year were calculated by integrating the spatial distribution of the concentrations. The implied variation of the relative total masses of 1,1,1-TCA and 1,1-DCE shows a pronounced decline in 1,1,1-TCA concentrations compared with 1,1-DCE (Figure 3). It is unlikely that this relative decrease in the total mass of 1,1,1-TCA compared with 1,1-DCE is due to preferential transport of 1,1,1-TCA, as it is likely less mobile than 1,1-DCE (based upon hydrophobicity). The decline in the concentration of 1,1,1-TCA is equivalent to an effective half-life of approximately 2 yr, which agrees very well with published values ranging from 0.5 yr to 2.5 yr (Vogel et al., 1987, Jeffers et al., 1989). However, the degree to which other mechanisms, such as advection and dispersion, influence the observed decline is difficult to establish. Unfortunately, it is not possible to establish a direct mass-balance relationship between the observed relative masses of 1,1,1-TCA and 1,1-DCE. This is not just due to transport effects, because other degradation products, particularly acetic acid, may also be produced from 1,1,1-TCA.

To gain further insight into the behavior of 1,1-DCE with respect to 1,1,1-TCA across the entire LLNL facility, temporal trends in the [1,1-DCE] to [1,1,1-TCA] ratio were

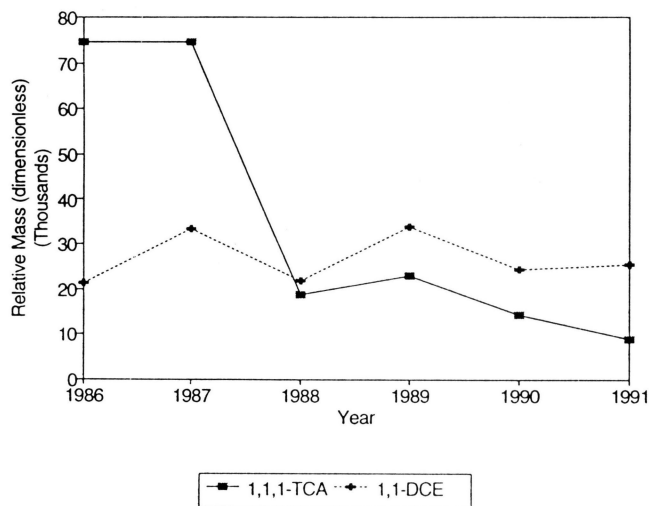
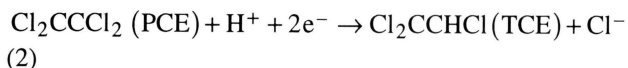


Figure 3. Relative total masses of 1,1,1-TCA and 1,1-DCE in the Arroyo Seco area over time. [XBL 935-799]

studied in 64 individual wells located in different areas and screened in different water-bearing zones. These results also corroborated the inference that 1,1,1-TCA is indeed degrading to 1,1-DCE.

PCE AND TCE

The evidence presented for the 1,1,1-TCA degradation illustrates how observations of patterns in correlated concentration data for suspected reaction pairs may be used to assess possible degradation. The same general methodology was also used to search for evidence of the transformation of PCE to TCE, a reaction that is probably unlikely to occur in LLNL groundwater for thermodynamic reasons. The reductive dehalogenation of PCE to TCE may be expressed as



The ratio of the concentration of TCE to PCE (mol/l) over time for a number of wells in the Arroyo Seco area is illustrated in Figure 4. This information is equivalent to that in Figure 2 for 1,1-DCE and 1,1,1-TCA in that the data points represent sampling locations along the major axis of a presumed localized plume. Unlike the same graph for 1,1-DCE and 1,1,1-TCA, however, no apparent overall increase in the daughter-to-parent product ratio over time is observable. We conclude that field evidence at the LLNL site does not support the degradation of PCE to TCE.

As with 1,1-DCE and 1,1,1-TCA, temporal trends in the concentration ratio of 1,1-DCE to 1,1,1-TCA were evaluated in wells across the LLNL facility in an effort to establish an overall behavior in the ratio (i.e., increasing or

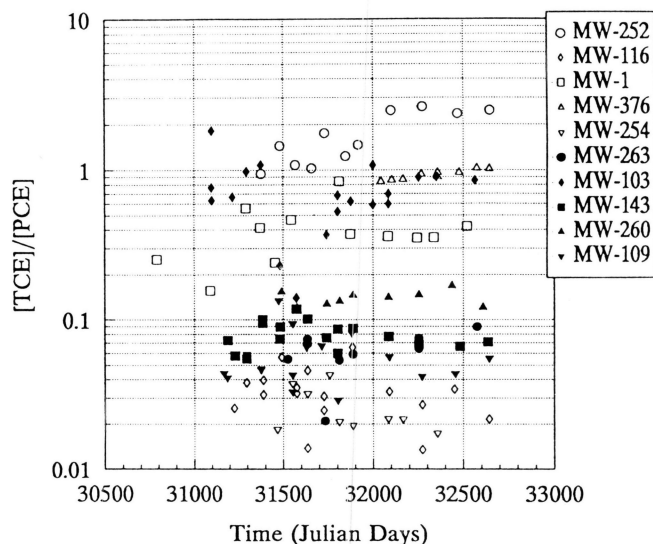


Figure 4. Temporal variation of the [TCE] to [PCE] ratio (mol/l) with distance in select Arroyo Seco area wells. [XBL 935-800]

decreasing with time). This analysis also corroborated the inference that PCE is not degrading to TCE at the site.

A final comparison with the 1,1-DCE/1,1,1-TCA case was based on the overall association of the suspected daughter and parent compounds by well. Out of approximately 400 individual groundwater samples collected from the Arroyo Seco area and included in our evaluation, approximately 18% contained detectable concentrations of PCE but no detectable concentrations of TCE. In contrast, out of approximately 5600 individual samples evaluated for 1,1,1-TCA and 1,1-DCE across the entire LLNL facility, less than 3% of the samples contained detectable 1,1,1-TCA concentrations but no detectable 1,1-DCE concentrations. A strong correlation between detections of two given chemicals does not necessarily imply degradation, as the two may have been introduced into the groundwater environment as co-contaminants. However, a significant number of samples containing detectable amounts of the suspected parent compound without the daughter compound calls into question the suspected degradation relationship. This appears to be the case with respect to PCE and TCE.

SUMMARY

Careful cross-correlation of aqueous VOC concentrations at the LLNL facility indicates evidence for the degradation of 1,1,1-TCA to 1,1-DCE with a half-life of about 2 yr. No such evidence has been found for the degradation of PCE to TCE. These findings are consistent with the highly oxidizing state of the local groundwater and the paucity of anaerobic organisms in the aquifer environment. Both of these factors do not favor the reductive dehalogenation of chlorine-rich PCE.

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6825

Multiple-Peak Response to Tracer Injection Tests in Single Fractures: A Numerical Study

L. Moreno and C.F. Tsang*

In experimental tracer tests carried out in a single fracture zone in crystalline rock, the breakthrough curves obtained using pulse tracer injection have multiple peaks in some situations (Steffen and Steiger, 1988; J. Hadermann, Paul Scherrer Inst., Switzerland, private communication, 1989; Hoehn et al., 1989). In some cases, it is observed that the shape of these breakthrough curves changes when the injection flow rate is varied. Moreover, the behavior of these multi-peaked curves is observed only for a limited range of injection flow rates.

This article presents some recent simulations of tracer tests in a single fracture with variable apertures. The aim of the work is to study the conditions under which the breakthrough curve may present multiple peaks and to determine how the injection flow rate modifies the shape of the curves in different situations. Although the study focuses on multiple peaks observed during tracer tests with pulse injection, the results can be applied to the case of continuous injection. The breakthrough curve for the latter case would show multiple steps, where each step corresponds to the arrival of a pulse in the pulse test.

DESCRIPTION OF THE MODEL

The apertures of a fracture are not constant in magnitude but vary spatially in the fracture plane. Fluid flowing through the fracture seeks out the least resistive pathways. The main flow is expected to occur through a few channels

in the fracture plane (Abelin et al., 1985; Neretnieks, 1987). In defining channels, we mean preferred flow paths in the fracture. If the direction of the pressure gradient is changed, then a new pattern of channel networks would emerge, depending on pressure gradients. Tsang and Tsang (1989) demonstrated that they can be characterized stochastically by the same set of parameters as long as the anisotropy of the spatial correlation of the apertures remains relatively small.

Let us assume that we have a fracture with an overall flow under a “regional” pressure gradient. A solution containing the solute is then injected with a given flow rate at a point in the fracture plane. The injection pressure increases the local pressure profile and hence modifies the original flow pattern around the injection point. For a given distribution of the variable apertures, the injection feeds the solute into flow paths that are in the neighborhood of the injection point. The larger the injection flow, the larger the local pressure profile and the larger the number of paths that may be reached by the solute. However, the pattern of these flow paths depends strongly on the variable apertures near the injection point.

More specifically, the spatial distribution of fracture apertures is obtained by using a grid to partition the fracture and assigning a different aperture to each node enclosed by grid lines. The aperture values used are defined by an aperture density distribution (mean aperture $b = 80 \mu\text{m}$ and spread $\sigma_{\text{inb}} = 0.5$) and a spatial correlation length (λ/L). A lognormal distribution for these apertures and an exponential fraction for the spatial covariance of the apertures were chosen. Details may be found in Moreno et al. (1988). For the

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