

Predicting the Fate of Trichloroethylene and Its Daughters in a Heterogeneous Environment

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Introduction

The T2VOC model (Falta, et al., 1995) was used to simulate the motion of chlorinated hydrocarbons released to the groundwater over a period of years from an industrial plant. This included thousands of kilograms of trichloroethylene (TCE) as well as other solvents and several kinds of alcohol. Anaerobic dehalogenation of chlorinated alkenes is favored in the presence of alcohol. All three isomers of dichloroethylene (DCE) and vinyl chloride were detected in the analytical field data. Using T2VOC in its standard form would allow one to estimate the motion of TCE and its daughters as a single species. However, to account for TCE and the daughter constituents in an individual way required two code modifications.

Code Modifications

First, the biodegradation rate of TCE differed from one part of the domain to another. Dehalogenation was fastest in the presence of high concentrations of dissolved-phase alcohol that occurred in a zone from 10 m upgradient to more than 200 m downgradient from the point of discharge. In the rest of the saturated zone, as well as in the entire vadose zone, the rate of dehalogenation was about one-tenth as great. In the underlying bedrock, the biodegradation rate was virtually zero. In the presence of nonaqueous phase liquids (NAPL) or at very high dissolved-phase concentrations of solvents, the biodegradation rates were likewise zero due to the toxicity of these constituents to the microorganisms that perform the biotransformation work. Thus, it was desirable to be able to assign more than one biodegradation rate to the constituent and to let it vary by grid block. Such a modification was accomplished in this study. In the CHEMP block, the parameter ALAM was replaced by six decay constants, ALAM-1 through ALAM-6. In ELEME, a new input was added for every grid block. This integer variable assigned the appropriate ALAM value to the specific grid block to be the local degradation rate. With this modification, the fate and transport of the parent constituent could be better modeled.

To allow for the modeling of the daughters, a second modification was needed. This modification counted the number of parent molecules destroyed in each grid block and recorded

them in a file named DAUGTR. In the code modification, the molecular weight of the daughter constituent was a new input in the CHEMP module. Thus, the mass reported in DAUGTR was the created mass of the daughter. For example, if TCE was converted to DCE, the ratio of the two molecular weights was used to account for the mass loss from the chlorine atom that was lost from each transformed TCE molecule. The DAUGTR file also contained the length of time of the T2VOC run. After the model run, a new program was used to calculate generation rates for the daughter in each grid block. These values were printed in GENER format and added to the data in a separate file that represented deep percolation of water into the domain, thus creating a GENER file for the next T2VOC run. In that run, there was a source of the daughter constituent in every grid block in which biotransformation had occurred in the last run. The rate of generation was determined such that the creation rate would match the decay from the previous run by mole.

Procedure

To solve a practical problem of an industrial release of TCE, a three-dimensional grid was devised. The grid represented a tilted system of rectangular blocks. Because the entry of soil gas into residences was a potential issue, every column of grid blocks had an atmospheric block at its top. The stratigraphy was relatively simple, with a sandy soil underlain by fractured bedrock. The petrophysical parameters for each layer were determined by a field study. Dynamic steady state was obtained for this grid. The source and its history were determined from records kept by the management of the industrial plant. The subsurface emission occurred at several locations and the amount of the loss differed from year to year. Therefore, separate T2VOC runs were needed for each year with different values for the sources in GENER for the given year of the release. Following this, runs were conducted for the subsequent years to study the evolution of the plume.

A preliminary run was conducted for the release of TCE without accounting for biodegradation. This run helped to determine which grid blocks would have NAPL. Blocks containing the NAPL were recorded on a list. A second preliminary run was conducted in which alcohol was released for two years at its maximum rate. The purpose of this run was to determine which grid blocks were likely to contain sufficient levels of alcohol to more rapidly degrade TCE. Any block with an alcohol concentration of 100 mg/L at the end of two years was recorded on a list (Figure 1). It was experimentally determined that the biodegradation of TCE at this site was enhanced by a factor of ten when alcohol was present at about 100 mg/L. Now the TCE release could be simulated. Three biodegradation rates were assigned. Any block within the bedrock was assigned a biodegradation rate of zero. Any grid block in which a NAPL was recorded to be present was also assigned a zero biodegradation rate. Grid blocks below the water table with more than 100 mg/L alcohol in the special alcohol run discussed above were given a high degradation rate, unless NAPL was present. All other blocks were assigned a biodegradation rate one order of magnitude lower than the experimental value. Field data revealed the presence of DCE even though there were no records of DCE ever being used at the plant in large quantities. This suggested that the DCE being detected in monitor wells was a daughter of TCE degradation. The predominant isomer detected was *cis*-1,2-dichloroethylene. Thus, to simplify the modeling procedure, all TCE destroyed by biodegradation was assumed to have been transformed into *cis*-1,2-dichloroethylene, which will be referred to as DCE in the remainder of this paper.

The modified code produced a new file that gave the mass of the DCE produced in each grid block. The new file was converted into GENER format. Thus a GENER file was produced for each year of the TCE simulation. Thus a set of DCE runs could be undertaken with the DCE created from the biodegradation of TCE being the unique source of DCE. From these runs, an experimentally determined value was used for the biodegradation of DCE into vinyl chloride. The same set of years was modeled to give a history of the motion of DCE and a set of GENER files that would allow the modeling of vinyl chloride. Lastly, a set of runs was conducted to give a history of the transport of vinyl chloride.

Results

The first simulations with this code modification did not succeed. There were problems in grid blocks with very high concentrations of the parent constituent, leading to unrealistically high generation rates of the daughter compound. To correct this problem, the biodegradation/biogenesis rates were reduced in these specific grid blocks. The model behaved much better with a low value for degradation in such grid blocks. Eventually, it was considered simpler to set the decay constant to zero for these blocks.

A second concern was the build-up of vinyl chloride. The biodegradation rate had initially been set to a very low rate. Any degradation rate for vinyl chloride that was lower than that for DCE seemed to lead to an increase in concentration that was hard to believe. Vinyl chloride did not seem to be volatilizing and migrating out of the domain as quickly as expected. Thus, the degradation rate of vinyl chloride was increased to that of DCE.

With these adjustments, the simulation was run to completion (Figures 2 – 4). After just nine years, the T2VOC model predicted groundwater concentrations of TCE at the ppm level 700 m from the source. The model predicted groundwater concentrations of TCE and DCE at the level of parts per million (ppm) more than one kilometer from the source several years later. It also predicted unacceptably high fluxes of soil gas into the dwellings of residents nearly one mile from the release. Predictions of TCE and DCE at later times when data were available were consistent with soil gas and groundwater monitoring data. However, the predicted vinyl chloride concentrations were too high. Some of the problem could be due to the age of the data and the possibility that there were inaccuracies in measuring this highly volatile species.

Discussion

Attempts to calibrate a model like T2VOC to groundwater analytical data are always difficult due to variability in soil conditions on a scale that is often too fine to simulate in a model. The problem is even more difficult in a multiconstituent simulation with the generation of daughters. In a one-species simulation, the biodegradation rate and the source term may be among the most important calibration parameters. If a model over-predicts field-measured concentrations, one can obtain the same result by lowering the estimate of the source term or by increasing the biodegradation rate. In a multichemical simulation with daughter generation, the method of calibration makes a large difference. Reducing the estimate of a source term to calibrate for TCE may reduce the strength of the DCE below field measurements. Increasing biodegradation will reduce TCE concentrations while increasing DCE and vinyl chloride.

The biodegradation rates were such that the constituents had half-lives in the presence of alcohol of 70 to 100 days. The time step in a model run one-year long can approach one month

in length or longer depending on how the maximum time step is limited. Thus it would be possible to have a time step that was more than half of the biological half-life of a constituent. To prevent too much error from entering into the computation, it is recommended that the maximum time step (DELTMX) be limited to one-fourth of the shortest constituent half-life of the six implied by the decay constants presented in the ALAM array.

Another potential source of error in this methodology is introduced by the linearity of the daughter generation function. The first-order degradation of an organic chemical is modeled by T2VOC as an exponential function of time. Although the total moles of parent destroyed in a runtime unit (one year) was set equal to that which was created, it should be noted that the total number of moles in the domain during a simulation will be less than the expected total in the middle of a run. For example, if you have two functions,

$$y_1 = e^{-t}$$

and

$$y_2 = at$$

where t is time and a is the reciprocal of e , the sum of y_1 and y_2 is always less than one over the range of zero to one except at the endpoints. It reaches a minimum at $t = 0.459$ of 0.922. This error may be acceptable given the uncertainties in the inputs. However, it may be possible under some set of circumstances for this small amount of error to lead to underestimates of the transport of the daughter.

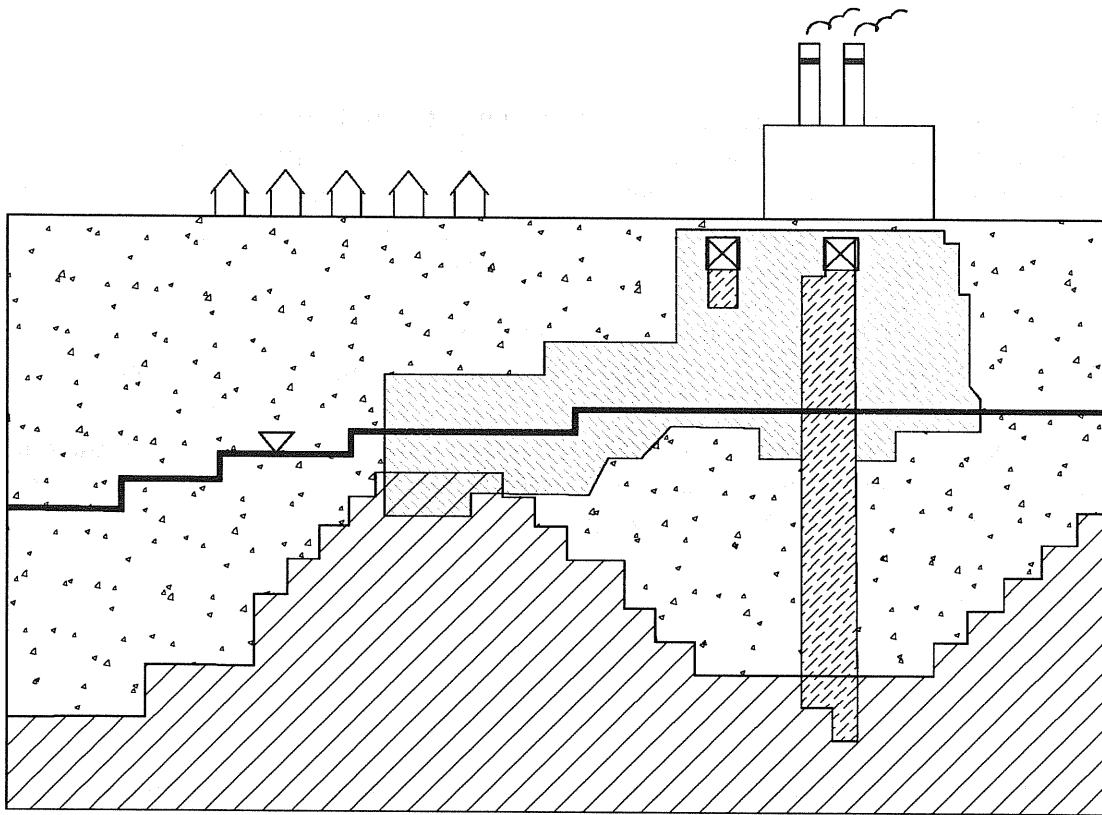
Conclusion

Simulations were run with this modified code for TCE, DCE, and vinyl chloride in sequence. Each of the simulations was composed of a set of model runs, each one-year long. Given the limitations in the field data, there was a good match for the TCE and the DCE data with the T2VOC output. Vinyl chloride generated in the model exceeded the values measured in the field, but this could be due in large part to the difficulties in accurately measuring this extremely volatile species.

Successfully predicting the concentration of a degradable constituent and a string of daughter compounds places a high demand on the quality of the biodegradation data. However, without the ability to vary the degradation rate in a large domain, or the ability to allow the generation at continuous points in time, it could be impossible to simulate the fate and transport of a daughter constituent with accuracy of T2VOC in its simultaneous handling of several phases, components, and transport mechanisms. These two code modifications bring this goal within the reach of a mathematical modeler.

References

Falta, R. W., K. Pruess, S. Finsterle, and A. Battistelli, 1995, T2VOC User's Guide, Lawrence Berkeley Laboratory, Berkeley, CA, LBL-36400.



Not to Scale

- | | |
|---------|------------------------------------|
| Sand | NAPL present |
| Bedrock | Alcohol present at 100 ppm or more |
| Source | Water table |

Figure 1. Schematic of the Site Grid.

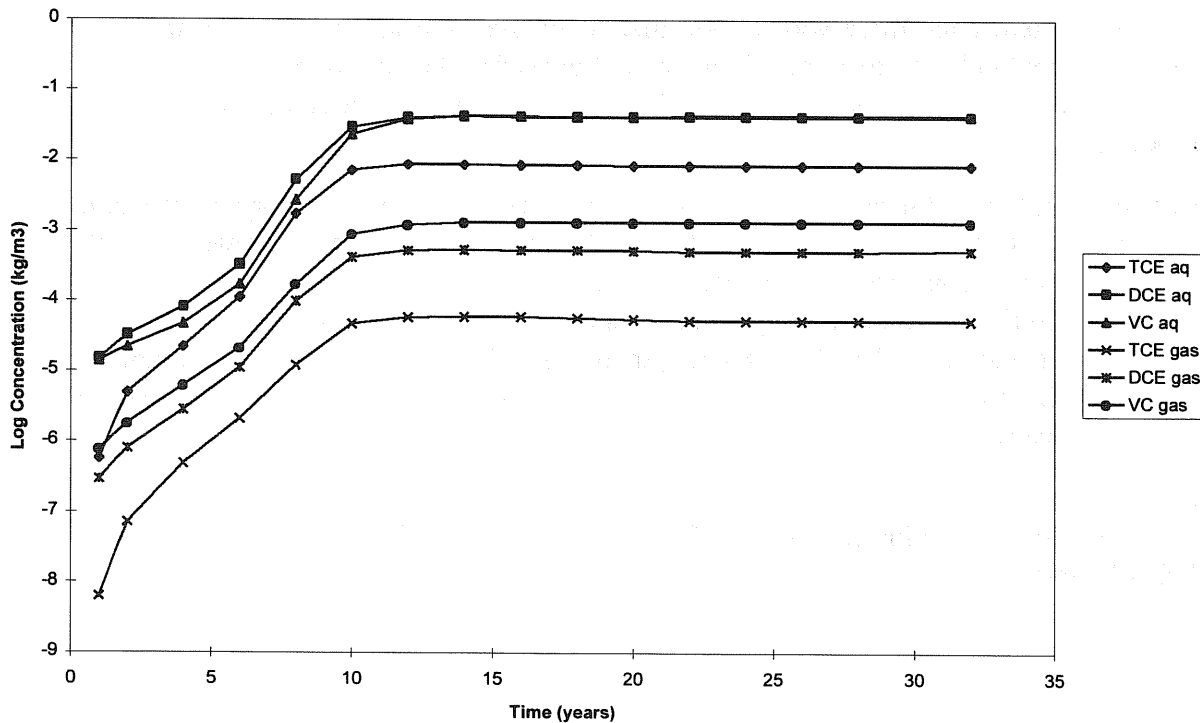


Figure 2. Groundwater Concentration History of a Water Table Grid Block 200 m from the Source with Soil Gas Concentration at the Surface.

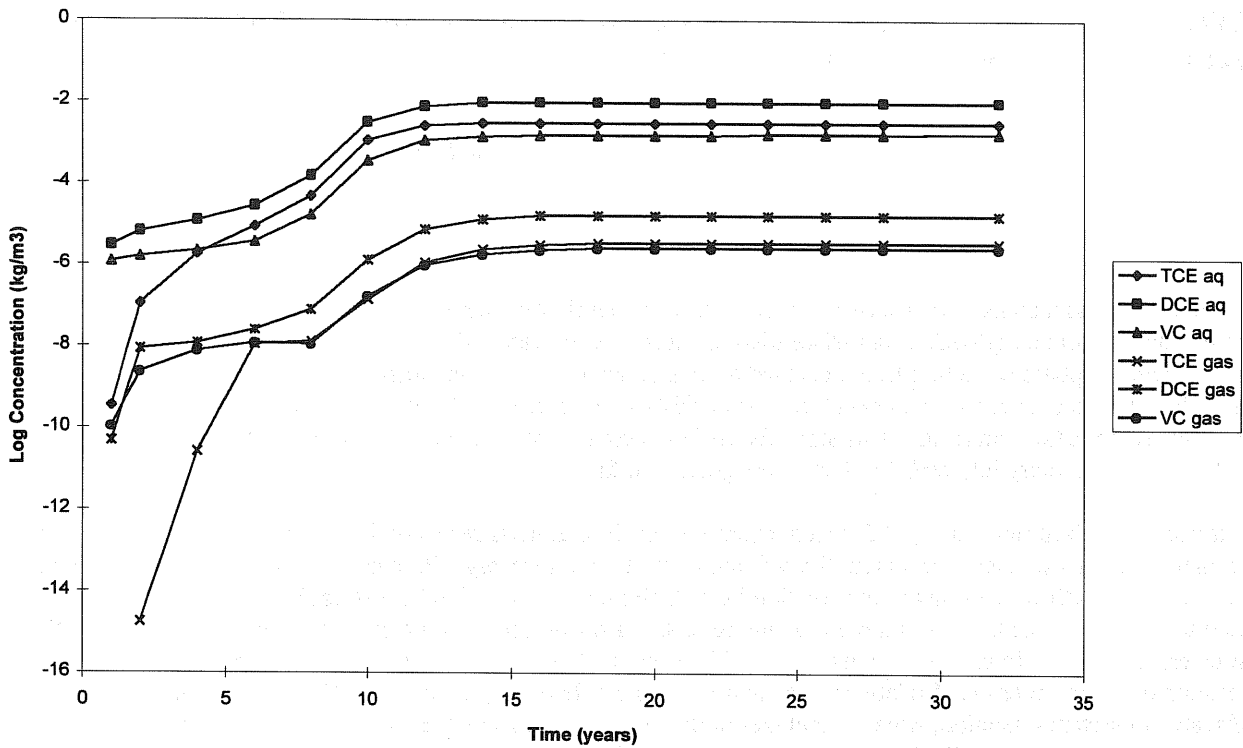


Figure 3. Groundwater Concentration History of a Water Table Grid Block 500 m from the Source with Soil Gas Concentration at the Surface.

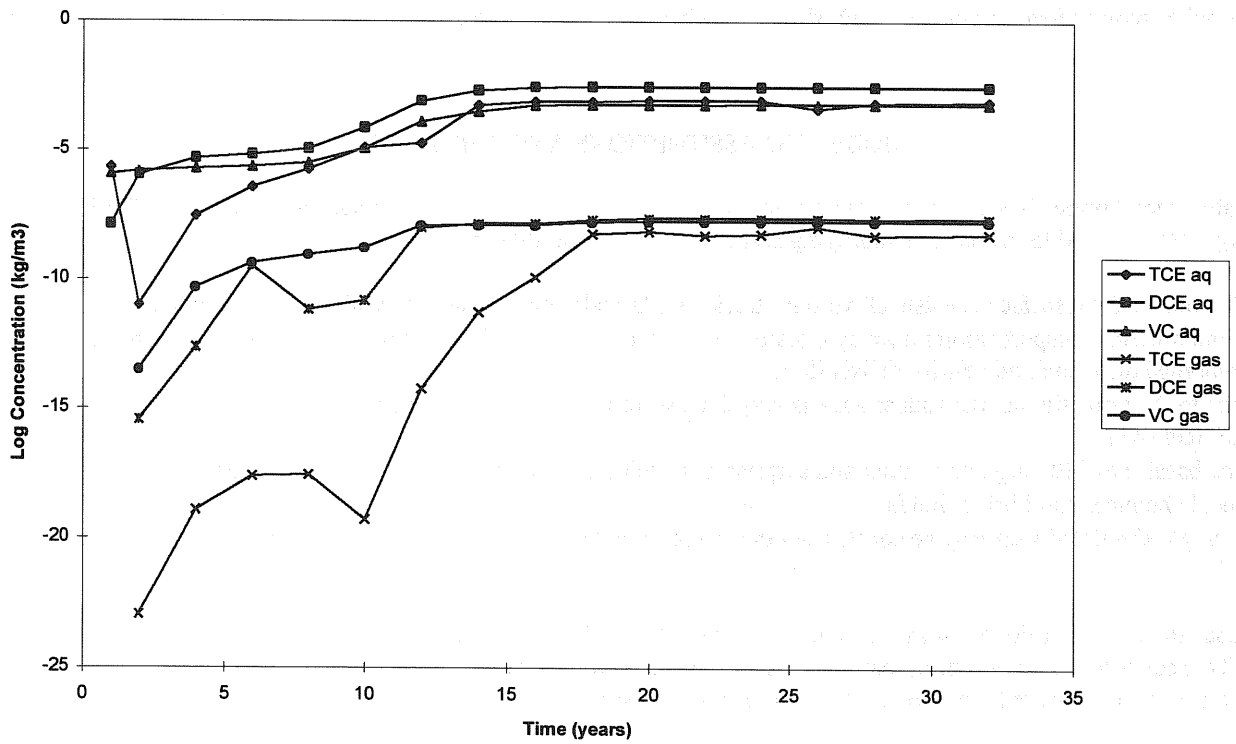


Figure 4. Groundwater Concentration History of a Water Table Grid Block 700 m from the Source with Soil Gas Concentration at the Surface.