



## Whose Chlorinated Solvent is it?

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Chlorinated solvents such as perchloroethylene (PCE), trichloroethylene (TCE) and 1,1,1-trichloroethane (TCA) are among the most common contaminants found at hazardous waste sites. In an industrial or commercial area, there may have been multiple facilities that used any of these compounds for vapor degreasing or that used PCE for drycleaning. There may also have been successive users of the same chlorinated solvent at the same facility. Thus a frequent forensic issue is: "whose chlorinated solvent is it?"

This is an important question for cost allocation because a spill of chlorinated solvents can result in dense, nonaqueous-phase liquids (DNAPLs) below the water table. This makes sites contaminated with chlorinated solvents particularly difficult and expensive to remediate.

This is also an important question in defending a toxic tort. Several other factors have recently raised the importance of chlorinated solvents in a toxic tort context. First, the TCA additive 1,4-dioxane, is an "emerging" contaminant observed to have properties similar to the gasoline additive methyl tertiary-butyl ether (MTBE), in that it is persistent, mobile, probably carcinogenic, and may require special remedial techniques. Second, TCE has emerged as the chemical of concern at numerous soil vapor intrusion sites where buildings overlie a groundwater plume. Third, EPA's National Environmental Investigation Center has produced a recent widely used draft reassessment for TCE that significantly increases its cancer slope factor and hence the likelihood that it will determine risk assessment results.

Two ways of answering the question: "whose chlorinated solvent is it?" are to identify the location where the plume originates and to age-date the plume. In this newsletter, we discuss identification of chlorinated solvent sources by backward extrapolation of groundwater plumes. We also discuss several plume age-dating methods.

### Background

Background information and additional forensic methods, both for the chemicals discussed in this newsletter and for additional chlorinated solvents, can be found in this link (Morrison and Murphy 2006).

TCE has been the vapor degreasing solvent of choice except for a period from the mid-1970s until the mid-1980s, when TCA was more popular for a variety of economic, environmental, and regulatory factors. PCE can also be used for vapor degreasing, primarily of small metal parts, but its primary use is as a drycleaning fluid.

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A central factor in forensic analysis for all three solvents is that in the environment they degrade to other chemicals, termed daughter products. All three solvents biodegrade under anaerobic (absence of oxygen) conditions. In addition, the hydrolysis degradation pathway is important for TCA. Hydrolysis is a chemical reaction between a chemical and water, as opposed to a biological reaction; for TCA, it occurs at a fairly predictable rate that depends only on groundwater temperature. Some of the biodegradation daughter products, such as vinyl chloride, can biodegrade aerobically (in the presence of oxygen) as well.

In order to estimate the location of groundwater plume origin as well as plume size, data from monitoring wells is contoured. Because of degradation, it is not sufficient to base the analysis on just the parent compound. Instead, it is necessary to estimate what the plume would have looked like if there had been no degradation, a procedure we term “plume reconstruction.” This is done using the measured concentrations of degradation daughter products. We can do this because we know the relevant degradation pathways. (For example, PCE degrades to TCE. If we find 1  $\mu\text{g/L}$  TCE in groundwater at a PCE release site, this indicates that an additional 1.26  $\mu\text{g/L}$  of PCE would have been present if there had been no degradation. This is because a PCE molecule has a mass 26 percent greater than a TCE molecule.)

A second factor in forensic analysis of groundwater contaminant data is that groundwater flow direction needs to be considered in order to sort out what may be overlapping plumes. The basic physical idea is that a downgradient concentration is much more related to upgradient concentrations than to cross-gradient concentrations. Thus, when concentrations are contoured to provide lines of equal concentration (isopleths), the influence of cross-gradient concentrations should be lessened. The amount of lessening that is appropriate will vary from site to site. At some sites the groundwater flow direction is nearly constant and plumes have “pencil” shapes. In that case, severe discounting of cross-gradient locations is appropriate. At other sites, groundwater flow direction may vary seasonally and plumes will have “fan” shapes. In that case, a lesser degree of discounting of cross-gradient locations is appropriate. In either case, when the proper amount of cross-gradient restriction is imposed, distinct and separate plumes can emerge.

## Case Study: Source Identification

A Midwest manufacturing operation, like many facilities, first used TCE, then TCA, for vapor degreasing. Four manufacturing buildings were built sequentially from west to east. Thus, identifying the specific building that was a source of TCE or TCA effectively dates the release to after the construction of the building. For brevity, and because it is the more common groundwater contaminant, we illustrate the plume reconstruction method only for TCE.

The TCE concentration contours shown in Figure 1 demonstrate contouring without taking into account any cross-gradient restriction or plume reconstruction. This plume has an east-west extent similar to the north-south extent, which results from multiple sources under and along the southern edge of the buildings.

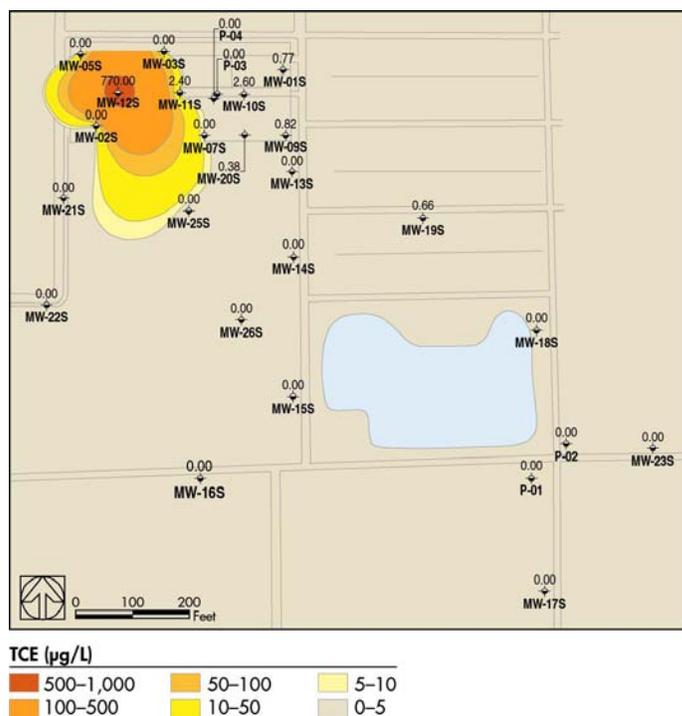


Figure 1.  
TCE contours

Next, we use a contouring program that weights the distance perpendicular to the direction of groundwater flow by a factor of four relative to the distance along the direction of groundwater flow (known to flow from northwest to southeast). This effectively makes cross-flow locations more distant from the location of interest, and therefore of lesser influence. In addition, we use daughter product concentrations to determine what the plume would

look like if there had been no degradation. The difference between Figure 2 and the previous figure is that almost all of the measurements at various shallow wells are now incorporated into plume-like structures. Thus, a greater proportion of the data is explained.

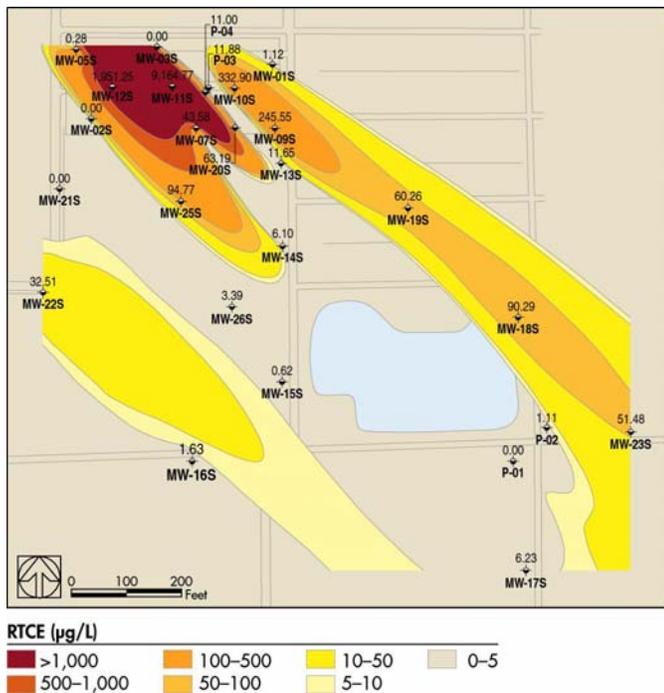


Figure 2. Reconstructed TCE contours taking groundwater flow direction into account

In Figure 2, several distinct plumes are now apparent. The plume furthest to the southwest emanates from a street corner where a sanitary sewer changes direction. Also, in Figure 2, individual plumes can be associated with specific buildings. Because the buildings were constructed at various times, this also helps age-date the plumes. More general age-dating methods are discussed below.

### Relevance for Plume Age-Dating

TCA plumes are a special case compared to other chlorinated solvents. As noted above, hydrolysis is an abiotic chemical process with the rate of degradation at a given groundwater temperature being constant. Thus, the amount of 1,1-DCE formed relative to the amount of TCA present serves as a “clock.” The age of a TCA plume can thus be estimated from the 1,1-DCE to TCA ratio, as shown in Figure 3. Further details may be found in (Gauthier and Murphy 2003).

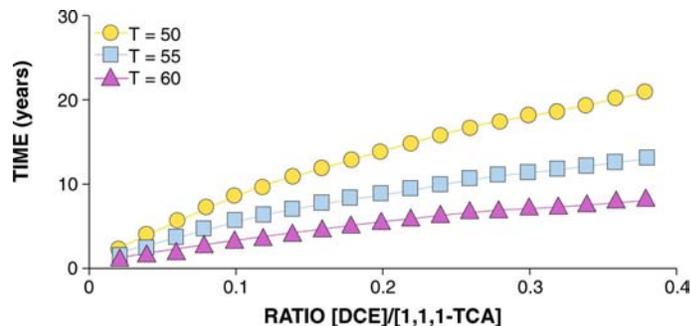


Figure 3. Plume age as a function of groundwater temperature and ration of [DCE]/[1,1,1-TCA]

Estimating the age of a PCE or TCE spill is more complex than for a TCA spill because biodegradation is not necessarily uniform in space or time. Furthermore, biodegradation rates can vary, depending on, among other factors, the microbial colonies and nutrients present, and solvent concentrations. Thus, the “clock” can be unreliable and estimating spill dates based on the extent of biodegradation together with literature half-life values is fraught with peril. A better dating method can be to base the age on the extent of the reconstructed plume, that is, the plume that would have been present without biodegradation. For example, at the Midwestern manufacturing site discussed above, the upper range of the groundwater velocity estimate is 2 ft/day. We estimated that the TCE velocity is about 20 percent less than that because of retardation and that the TCE daughter products were retarded by 10 percent or less. The distance from the buildings to the furthest contaminated well is about 1,530 feet. Thus, taking an average retardation factor of 10 percent, we estimate that the plume originated at least 2 years earlier than the monitoring date. (Morrison and Murphy 2006) discusses the uncertainties involved in this approach.

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