

Appendix A

Analysis of Field Data

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A-1. Physical Variables and Plume Length

A-1.1. Source Strength

Non-aqueous phase liquids (DNAPLs), present in the subsurface as ganglia or droplets above or below the water table, often constitute a source of new dissolved-phase contaminants to the expanding plume. In practice, because of its elusive nature, any DNAPL present at a site is extremely difficult to identify or quantify (Feenstra et al., 1996). As a result, rules-of-thumb pertaining to the maximum concentrations observed at a site are often used to flag the possible occurrence of DNAPL. For example, Feenstra and Cherry (1988) proposed that measured concentrations of a given CVOC in groundwater monitoring wells at a site that exceed 10% of its solubility may be reflective of DNAPL. Newell and Ross (1991) proposed a more conservative threshold of 1% of the solubility limit.

Taking these rules-of-thumb at face value, maximum observed historical concentrations may be used to define three levels of confidence as to the possibility that DNAPL material is contributing to a dissolved plume. In cases where maximum concentration of a given CVOC exceeds 10% of its solubility, DNAPL may be assumed as likely to contribute to the plume. If the maximum concentration falls between 1% and 10% of the solubility, DNAPL may be assumed as possibly contributing to the plume. Finally, if the maximum concentration is less than 1% of the solubility, DNAPL may be assumed to not be present or else not be contributing significantly to the plume.

Using these definitions, the association of potential DNAPL sources with plumes representing the most common CVOCs in the data set (i.e., CVOCs represented by 10 or more plumes) are given in Table A-1. There appears to be some distinction between the presumed presence of DNAPLs with regard to likely original contaminants – TCE, PCE, and 1,1,1-TCA – and potential transformation daughter products – *cis*-1,2-DCE, 1,1-DCE, 1,1-DCA, and vinyl chloride. However, this observation simply be a reflection of greater use of the former group as opposed to the latter in industrial operations, hence a greater likelihood of encountering high concentrations indicative of DNAPL.

A more general analysis of the relationship between plume length and the maximum observed historical concentration would assume that the latter simply reflects the overall strength of the source term. This source strength term entails not only the presence or absence of DNAPL but also the potential for high concentrations of a CVOC (which may or may not be associated with DNAPL) to leach into the monitored portion of the aquifer. Correlation relationships between plume length and maximum historical concentrations for all CVOCs across all of the sites are shown on Figure A-1. Although a great deal of scatter is present in these relationships, statistically significant correlations are apparent. The scatter in these relationships is produced

by: (1) dependence of plume length on other variables beside source strength, and (2) variability among the sites as to how well the high concentrations immediately associated with the source are reflected in water quality measurements. The greater correlation between plume length and maximum concentration apparent with 100- and 1000-ppb plumes in comparison to 10-ppb plumes may be associated with the greater proximity of the higher concentration contours to the source area. In the case of 10-ppb-defined plumes, with the leading edge far downgradient of the source area, variability in groundwater velocity and other factors may reduce the impact of source strength variability (McNab and Doohar, 1998).

A-1.2. Advection

Among the 65 sites that provided data for this study, hydraulic conductivity values were available from 46 sites at the time of analysis. In some cases, these were provided as a table of conductivity estimates derived from pumping tests or slug tests in multiple groundwater monitoring wells. In other cases, a range of values consisting of a minimum and maximum value for the site was provided. In both of these situations, given the lognormal distribution of hydraulic conductivity values characterizing most hydrogeologic settings, a representative hydraulic conductivity was estimated for the site using the geometric mean. In still other cases, some sites provided only a single interpreted mean hydraulic conductivity value for a site.

Of the sites that supplied hydraulic conductivity estimates, mean hydraulic gradient estimates were given in the hydrogeologic data from 34 sites. This permitted the calculation of a mean groundwater velocity at each of these sites using Darcy's law (assuming a universal average porosity of 0.25). The resulting probability distribution of groundwater velocities from these sites is shown on Figure A-2. This velocity distribution is reasonable in terms of groundwater velocities generally reported in shallow sedimentary materials. For example, Mackay et al. (1985) provided an estimate range of typical groundwater velocities on the order of 1 to 100 m/yr (0.009 ft/day to 0.9 ft/day).

The relationship between the maximum CVOC plume length at each site and the groundwater velocity is shown on Figure A-3. Maximum plume length at each site was used for this analysis, rather than all site plume lengths, because the longest plumes presumably reflect a better average of site conditions than small plumes which may attenuate as a result of insufficient mass. Furthermore, including all of the CVOC plume lengths at a given site in this analysis would result in a bias toward those sites with more plumes. At sites where ranges of hydraulic conductivity values were provided, the error bars denote the minimum and maximum groundwater velocities, assuming a single value for both hydraulic gradient and porosity. The scatter plot is shown with the independent variable (log groundwater velocity) on the y-axis to facilitate inspection of the error bars. A positive correlation clearly exists between the mean groundwater velocity and maximum site plume length. Some degree of mutual correlation between minimum groundwater velocity, maximum groundwater velocity, and maximum site plume length is also apparent.

Although a relationship between plume length and groundwater velocity is intuitive in a mechanistic sense, the identification of this relationship in field data is not immediately straightforward. Hydraulic conductivity and groundwater velocity are well known to vary greatly across a given site, thus defining a mean hydraulic conductivity and velocity may be problematic at first glance. Relying on only the maximum velocity at each site as an indicator of

advection, based on the assumption that the plume will travel only through the most permeable channels, may not be an acceptable substitute. This is because, without further information, the continuity of the most permeable bodies and their mutual inter-connectiveness cannot be ascertained. In contrast, the mean hydraulic conductivity and hence mean groundwater velocity may reflect the preponderance of a certain lithology at a given site (i.e., a generally coarse-grained sedimentary environment versus a fine-grained one) and thus provide a better qualitative guide to the potential for plume migration.

A-1.3. Additional Factors: Plume Age and Macrodispersion

Intuitively, the overall age of a plume would be expected to exert an effect on plume length. Clearly, the longer a source of contamination is active, or the longer the elapsed time since an instantaneous release had occurred, the longer advective and dispersive transport mechanisms have had the opportunity to act on the plume. The obvious expectation is that older plumes should be longer than younger ones. Unfortunately, precise quantification of release history associated with typical CVOC groundwater contamination sites is not usually possible. However, there is likely to be some correlation between the age of a CVOC plume and the duration of industrial operations at a release site. Thus, the variability in plume age may be reflected in the distribution of site operation times observed in the project data set (Fig. A-4).

The relationship between plume length, calculated groundwater velocity, and the elapsed time of site operations for 30 TCE plumes is shown on Figure A-5. The size of the circles indicates the elapsed period of site operations, and the shade of the disk represents the range of maximum historical TCE concentration. The longest plume (A) shown on Figure A-5 exhibits a maximum historical concentration of less than 1,000 ppb, but is characterized by an elapsed site operation period of 48 years and corresponds to the second highest pore water velocity (34 ft/day). The next longest plume (B) exhibits a pore water velocity of 0.27 ft/day and a relatively large maximum concentration (56,330 ppb). An adjacent plume on the figure, Plume C, is characterized by a pore water velocity four times as large, but with a maximum concentration 1/200th as large. The shortest plume (D) corresponds to the second smallest pore water velocity and a maximum historical concentration between 1,000 and 10,000 ppb. In general, plumes from sites with the shortest elapsed operational history are among the shortest, with two noticeable exceptions, (E) and (F). In summary, some plumes are consistent with simple hydrologic reasoning, while others may be influenced by either heterogeneity within the site that is poorly represented in the averaged data or other variables. Note that five (out of seven) of the TCE plumes with maximum concentrations greater than 100,000 ppb do not appear on this figure because mean hydraulic gradient values, used in the calculation of the pore water velocity, were not available for those sites. This lack of hydrogeological data provides an example of the difficulty of analyzing the present data set in which not all site data are available at each site. Such limitations inherent in the data point to the need for caution in the application of statistical analyses to this data set.

In general, while the variability in age would be expected to exert some effect on plume length distributions, this effect is probably relatively minor in comparison with those of other variables. For example, a difference in plume age of only a factor of 2 or 3 is very small in comparison to variability in mean groundwater velocity, which varies over orders-of-magnitude

(Fig. A-2). Thus, the latter factor is likely to exert a much larger influence on plume length variability than the former.

In addition to the mean rate of advection at a site, macrodispersion resulting from a heterogeneous flow field, matrix diffusion, and other effects would also be expected to impact plume length as defined in the context of this study. However, because plume dispersion is a mathematical concept which averages the effects of a number of processes occurring on small spatial scales relative to the overall size of the plume, there are no measurable variables available from field sites with which to perform correlation analyses. Hence, plume macrodispersion was not considered in these analyses.

A-2. Transformation Processes and Plume Length

A-2.1. Reductive Dehalogenation

A-2.1.1. Site Categorization

The primary mechanism responsible for the breakdown of CVOC compounds in certain groundwater biogeochemical settings is reductive dehalogenation (Bouwer et al., 1981; Vogel et al., 1987; Freedman and Gosset, 1989; Lee et al., 1995; Semprini et al., 1995; Butler and Barker, 1996; McCarty, 1996). This process, the sequential replacement of chlorine atoms with hydrogen atoms on the CVOC molecule, involves electron transfer and is microbiologically mediated. Because the reaction is a chemical reduction, reductive dehalogenation is generally observed only in anaerobic environments. Ideally, for purposes of this study, mean CVOC biotransformation rates would be quantified as continuous variables at sites where reductive dehalogenation is occurring. Statistical analyses of potential relationships between the mean biotransformation rate and plume length could then be conducted. However, given the limited spatial and temporal data available from many of the sites in the study, the systematic quantification of biotransformation rates at most of the sites was not feasible. Therefore, reductive dehalogenation was treated as a categorical variable.

Assignment of a reductive dehalogenation category to plumes at a given site was based primarily upon the presence of likely daughter products, such as *cis*-1,2-DCE or vinyl chloride derived from partial dechlorination of TCE or PCE. To evaluate reductive dehalogenation in this study, sites were categorized according to the presence or absence of these two potential daughter products. Specifically, sites with chloroethene plumes were assumed to:

1. Exhibit no reductive dehalogenation if *cis*-1,2-DCE and vinyl chloride plumes were both absent (No RD sites),
2. Exhibit some reductive dehalogenation activity if a *cis*-1,2-DCE plume was present, but a vinyl chloride plume was absent (Weak RD sites), or
3. Exhibit the highest degree of reductive dehalogenation activity if a vinyl chloride plume was present (Strong RD sites).

This classification scheme is based on the assumption that stronger reducing conditions are required to produce vinyl chloride than *cis*-1,2-DCE (Vogel et al., 1987). In all, 23 sites fell in the first category (no reductive dehalogenation), 18 in the second category (weak reductive

dehalogenation), and 20 in the third category (strong reductive dehalogenation). Three sites could not be characterized because chloroethenes were absent altogether, while an additional site could not be characterized because the detection limits for potential daughter product compounds were too high to allow the presence or absence of daughter plumes to be ascertained.

Possible geochemical indicators of reductive dehalogenation provide an independent means for testing the integrity of the categorization scheme. Concentration distributions of four key geochemical indicators (e.g., chloride ion, manganese, total xylenes, and bicarbonate alkalinity) were compared among the sites assigned to the three reductive dehalogenation categories. Ideally, elevated chloride concentrations would be expected in association with reductive dehalogenation, while elevated fuel hydrocarbon concentrations (as xylenes) and elevated bicarbonate would indicate the presence of a carbon source to fuel the reductive dehalogenation process. Manganese is reflective of the groundwater oxidative-reductive chemistry; elevated concentrations would indicate an anaerobic environment favorable for reductive dehalogenation whereas low concentrations would be indicative of an unfavorable aerobic environment. At each site where one or more of these concentrations of these geochemical indicators were provided, the 90th percentile value was noted for the indicator(s). The median values among the 90th percentile concentrations for each indicator for each reductive dehalogenation category are given in Table A-2. Taken as a whole, the geochemical indicators are consistent with expectation in terms of the potential for reductive dehalogenation. For example, in comparing the strong reductive dehalogenation sites to the other two categories, it appears that fuel hydrocarbon oxidation to bicarbonate alkalinity is a common phenomenon, producing an anaerobic environment (hence elevated manganese) resulting in dechlorination of the CVOCs (hence elevated chloride). Nevertheless, these findings must be treated with caution as the null hypothesis *p*-values suggest some uncertainty in these patterns, particularly for chloride and manganese.

A-2.1.2. Reductive Dehalogenation and Plume Length

The most straightforward analysis of the effects of reductive dehalogenation on CVOC plume length is to compare plume length distributions of all CVOC plumes from each reductive dehalogenation site category. Cumulative plume length distributions and idealized frequency distributions (based on a lognormal distribution best-fit to the data) for the three categories are shown on Figure A-6 (both with and without the *cis*-1,2-DCE and vinyl chloride daughter products). The close overlap of the distributions among the categories suggests that the influence of reductive dehalogenation processes on plume length is rather subtle in comparison to other variables that may exert more significant influences.

Given the observed patterns in the data set, identification and quantification of reductive dehalogenation effects requires factoring out the effects of demonstrably significant variables, namely the source strength and the groundwater velocity. One means for accomplishing this is to define a *plume length index* (PLI) that adjusts plume length based on a presumed linear dependence on maximum concentration and groundwater velocity:

$$PLI = \frac{L}{C_{\max} v} \quad (\text{Eq. A-1})$$

where L refers to the observed plume length, C_{max} the maximum observed historical concentration for the particular CVOC, and v the mean site groundwater velocity. Short plume lengths relative to high C_{max} and v may reflect attenuation processes such as reductive dehalogenation.

Cumulative distributions of plume length indices and best-fit lognormal frequency distributions for CVOC plumes from each reductive dehalogenation category are shown on Figure A-7. Plume length indices from sites in the Strong RD category (i.e., vinyl chloride plume present) exhibit significantly smaller values than those from the other groups. For example, the null hypothesis p -value given by the application of the student's t -test to logarithms of the data indicate $p = 0.98$ for the raw plume lengths alone (i.e., plume length distributions are similar) for the No RD and Strong RD groups, whereas $p = 0.002$ for these groups using the PLI (i.e., plume length index distributions are distinct). These patterns exist regardless of whether or not the daughter product species (*cis*-1,2-DCE and vinyl chloride) are excluded from the analyses. Thus, the plume length index concept demonstrates differences in plume behavior between sites featuring vinyl chloride plumes and those that do not, whereas such differences are not readily apparent upon first inspection of plume lengths alone.

There are at least two explanations as to why the effect of reductive dehalogenation on plume length is not immediately apparent in the raw plume length data but is identifiable in the plume length indices. One is simply that noisy data preclude the ready identification of subtle trends, and that the indexing scheme removes enough of the noise element so that such trends may become apparent. This possibility is explored in this study using a probabilistic plume modeling approach (see discussion below). The second possibility is that the overlap of raw plume length distributions reflects biases in the data collection and reporting process. For example, plumes undergoing strong reductive dehalogenation at sites with low groundwater velocities and small source terms would tend to be relatively short, hence not well characterized, and thus may have been excluded from the data collection effort. Conversely, non-transforming plumes emanating from high concentration source areas at high groundwater velocity sites would tend to be quite large and hence subject to pump-and-treat remediation efforts early in the site investigation history (and therefore excluded from the study). The net result is that selectively "long" plumes undergoing reductive dehalogenation may be grouped with selectively "short" plumes from non-reductive dehalogenation sites in the data set, systematically obscuring the effects of reductive dehalogenation on plume length. Nevertheless, the range of plume lengths encountered is of the foremost interest to stakeholders, so this possible bias does not necessarily detract from the validity of the study.

The plume length index is a new concept that has not been previously suggested in the literature. Hence, for validation, the results must be buttressed by independent multivariate statistical methods. To address this need, an examination of the relationships between plume length, maximum historical concentration, groundwater velocity, and reductive dehalogenation category was conducted using analysis of covariance (ANCOVA) along with a general linear model (GLM). The findings of these analyses are entirely consistent with those suggested by the plume length indices; plume length is affected by reductive dehalogenation (Strong RD data set) once the effects of source strength and groundwater velocity are accounted for. This appears to be true regardless of whether or not *cis*-1,2-DCE and vinyl chloride plumes are considered in the analyses. The ANCOVA and GLM analyses are presented in Appendix C.

A-2.1.3. Daughter Product Plumes

Given that reductive dehalogenation occurs, in principle, in a sequential manner, daughter product plumes will develop in association with the parent plume. If the daughter product species are not readily transformed into subsequent degradation products, these daughter product CVOCs could eventually accumulate downgradient of the parent product plume, despite the attenuation of the original contaminant compound. Given the metrics used in this study, this would complicate the task of defining the plume length associated with a given CVOC release. In the case of vinyl chloride, a daughter product of reductive dehalogenation of PCE or TCE, this extension beyond the parent plume would pose an additional problem because of the relatively high apparent toxicity of vinyl chloride in comparison to either PCE or TCE. However, if daughter product CVOCs such as vinyl chloride were readily attenuated, the daughter plumes would be largely encompassed within the original parent product plume, and risk-management characterization and constraints on the parent plume would also address the daughter products as well.

Statistical evidence collected in this study suggests that large daughter product plumes in comparison to the parent product plumes are not the norm but rather the exception. There are three lines of evidence to support this finding:

1. Among all of the CVOCs represented by more than six 10-ppb-defined plumes in the data set, analysis of variance (ANOVA) suggests that there is no statistically significant difference among logarithms of plume lengths by CVOC.
2. At sites with co-existing parent and daughter product CVOCs (among TCE, *cis*-1,2-DCE, and vinyl chloride), the parent CVOC plume length is indicated as being longer than corresponding daughter plume length(s) in 73% of the cases (37 out of 51 cases).
3. The locations at which maximum historical concentrations of parent and daughter product CVOCs are measured are typically separated from one another by distances on the order of 10% to 25% of the longest plume length at the given site. In other words, the source areas of daughter plumes are not greatly offset from parent plumes in most instances.

To gain further insight into the spatial relationships between parent and daughter product CVOC plumes, TCE and vinyl chloride plumes (as defined by the 10-ppb contour) were compared at the 17 sites where both coexisted. The mean direction that each CVOC plume at was headed at each site was estimated by quantifying the angle formed by the sentry well (the well farthest from the presumed source area with a concentration greater than 10 ppb), the well exhibiting the maximum historical concentration, and due east. Presumably, both parent and daughter plumes should be sub-parallel to one another; departures from this would indicate poorly characterized, ill-defined plumes or spatially variable biogeochemical processes yielding daughter product plumes of irregular shape. The resulting distribution in the differences between the directions of TCE and vinyl chloride plumes among the 17 sites are shown on Figure A-8. The distribution is clearly bimodal, with one group exhibiting sub-parallel plumes (generally less than 20° apart), with the other group featuring approximately anti-parallel plumes (near 180° apart).

Among the 11 sites in the sub-parallel group, the respective measurement locations of the maximum historical concentrations of TCE and vinyl chloride differ from one another by a

distance equivalent to about 15% (median value) of the maximum plume length (TCE or vinyl chloride). In other words, within this group of sites, the areas of maximum concentration of the parent and daughter plumes are roughly co-located. At the same time, TCE plume lengths are, as a group, longer than the respective vinyl chloride plumes in this set of sites, with the median ratio of TCE-to-vinyl chloride plume length approximately 1.6. Only 3 of the 11 sites featured a vinyl chloride plume length that appeared longer than that of the corresponding TCE plume (by 7%, 12%, and 23%, respectively).

The second set of sites consisted of six examples where the parent and daughter plumes appeared to the plume length algorithm to be oriented in approximately opposite directions. This was generally the result of the maximum historical concentration of vinyl chloride being observed a significant distance downgradient of the maximum concentration location of the TCE plume. Indeed, the median separation distance between the TCE and vinyl chloride maximum concentration locations was approximately 55% of the maximum plume length at each site. A number of possible explanations exist for this phenomenon, including: (1) high analytical detection limits for vinyl chloride in the presence of high concentrations of TCE, (2) chance artifacts of the monitoring well network spatial configuration and sampling history, (3) a detached daughter product plume reflective of very slow rates of reductive dehalogenation, or (4) spatial heterogeneity in the biogeochemical environment. Regardless of the cause(s), it is not appropriate to compare plume lengths directly in these cases because the parent and daughter plumes may not overlap. Instead, a combined TCE-vinyl chloride plume definition, derived by adding the concentrations of the two CVOCs in each groundwater sample, is a more direct reflection of the impact of CVOCs to groundwater at these sites. Application of the plume algorithm to the combined data sets from these six sites suggests that the TCE plumes, and not the vinyl chloride daughter product plumes, are the principal factors in determining the combined CVOC plume length. Combined TCE-vinyl chloride plume lengths clearly exceed those of the individual TCE plumes at only two of the six sites (by 10% and 38%, respectively).

A-2.1.4. Time Series Analysis

Relative rates of plume growth were assessed for 141 of the 247 10-ppb-defined plumes using rank correlation (i.e., linear regression of the ranks of the plume length as the dependent variable and rank of the monitoring year as the independent variable). The qualification of plume length trends as increasing or decreasing, with student *t*-test *p*-values as a means of quantifying significance, are shown in Tables A-3(a) and (b) for plumes from the Strong RD group and those that are not, respectively. Regardless of the confidence level, the two populations of plumes do appear to differ from one another according to this analysis in that the plumes from the Strong RD group exhibit a diminished tendency toward increases in plume length than those plumes from the No RD and Weak RD groups. Previous historical case analyses of fuel hydrocarbon plumes (Rice et al., 1995, Mace et al., 1997) indicated that only a small minority of hydrocarbon plumes (on the order of 10%) were experiencing discernable plume growth, presumably as a result of the limiting effects of biotransformation processes. Thus, the differences in apparent CVOC plume growth rates provides an independent line of evidence to support the conclusion that reductive dehalogenation influences plume length behavior at sites where vinyl chloride plumes are present.

A-2.2. Abiotic Transformation of 1,1,1-TCA

1,1,1-TCA is unique among the commonly encountered CVOC contaminants found in groundwater in its abiotic transformation, yielding acetic acid and 1,1-DCE as daughter products through separate pathways (Vogel and McCarty, 1987a, b; Haag and Mill, 1988; Jeffers et al., 1989; McCarty, 1996). These reactions do not rely on microbial mediation and are independent of the local groundwater geochemistry in terms of the biogeochemical redox regime. The associated pseudo-first-order half-life of 1,1,1-TCA is on the order of one to two years, depending primarily on temperature. As such, 1,1,1-TCA should serve as a marker compound for the effects of transformation processes on plume length. Cumulative probability distributions (along with best-fit lognormal frequency distributions) for 1,1,1-TCA plume lengths, compared with those of all other CVOCs, are shown on Figure A-9 (top). The median values of both groups of plume length are very similar, indicating that transformation of 1,1,1-TCA is not exerting a major effect on plume length compared to other factors (although the 1,1,1-TCA plume lengths do exhibit a tighter clustering about the mean than the other CVOCs). When plume lengths are transformed into plume length indices via Eq A-1, the plume length indices of 1,1,1-TCA appear shorter than those of the other CVOCs (Fig. A-9, bottom). The *p*-value associated with the null hypothesis for the two plume index populations (i.e., the probability that the two means are the same) is 0.14 by the student's *t*-test applied to the logarithms, suggesting a good possibility that the apparent difference is significant. However the population size of the 1,1,1-TCA plume length indices is rather small so this conclusion must be considered tentative. Nevertheless, the results are similar to those obtained from analyses of the reductive dehalogenation site categories, so similar explanations may apply to the 1,1,1-TCA data as well.

A-3. Partitioning Phenomena

Partitioning relationships pertain to the distribution of CVOC mass between the aqueous, DNAPL, and gaseous phases and present another class of variables that may influence CVOC plume behavior. The effects of these partitioning relationships on CVOC plume behavior can be assessed through statistical analyses of the relationships between plume variables and partitioning coefficients. Specifically, partitioning relationships include the solubility of the CVOC in water, the vapor pressure of the CVOC DNAPL in contact with the gas phase, the distribution of mass between the aqueous and gaseous phases (Henry's Law partitioning), and adsorption of the CVOC from the aqueous phase onto the solid matrix. In this case, the properties of the individual CVOCs (i.e., solubility, vapor pressure, Henry's constant, organic carbon partitioning coefficient) are the independent variables rather than the site hydrogeologic variables. Representative values of these partitioning coefficients for the CVOCs evaluated in this study are given in Table A-4.

A-3.1. Organic Carbon Partitioning

Consider the two hypothetical release scenarios illustrated on Figure A-10. In Scenario 1, little or no organic carbon is present in the sediments at the site, so two CVOCs with very different organic carbon partitioning coefficients, K_{oc} , would tend to exhibit similar concentration distributions following release, assuming that all other factors (release volume, solubility) are equivalent. In Scenario 2, however, CVOC A would be expected to adsorb strongly onto the organic-rich material, so that the measurable aqueous-phase concentrations of CVOC A would

be significantly lower than those of CVOC B. Given this simple model and assuming a wide range of organic carbon content values across a number of sites, the more hydrophobic CVOCs (those with relatively high K_{oc} values) would be expected to show more variability in concentration than those with lower K_{oc} values.

Statistical analyses of inter-site maximum concentration variability among the CVOCs is consistent with this hypothesis. The maximum historical concentrations of individual CVOCs across multiple sites appear lognormally distributed. Given this, a coefficient of variability was defined by the standard deviation of the logarithm of maximum concentration, divided by the geometric mean of the maximum concentrations for each CVOC where at least six or more plumes exist in the data set. The relationship between the median literature-derived log K_{oc} and the observed coefficient of variability in maximum concentration is shown on Figure A-11. A significant positive correlation exists between the coefficient of variability of maximum concentration and log K_{oc} , for twelve CVOCs. If representative fractional organic carbon content (f_{oc}) data were available from a sufficient number of sites, this possible relationship could be further assessed.

Beyond this correlation, relationships between K_{oc} and other plume variables could not be readily identified. For example, the relationship between the geometric mean plume length index and log K_{oc} is weak or absent; with correlation coefficients (r) ranging from -0.22 to -0.49 , depending on the minimum number of plumes used to define geometric mean plume length index per CVOC. Additional analyses involving estimates of plume growth rates may identify relationships between the change in plume length as a function of time and the K_{oc} .

A-3.2. Henry's Law Partitioning

Ideally, partitioning of CVOCs between the gas phase and the aqueous phase might be expected to exert effects on concentration variability similar to those suggested by the K_{oc} analyses. Consider, for example, the two hypothetical release scenarios shown on Figure A-12. In Scenario 1 (plumes in a confined aquifer) little opportunity exists for the exchange of mass from the dissolved phase into the gaseous phase in the vadose zone. Under such conditions, concentration distributions of both CVOC A and B would be expected to be similar if other variables such as release volume and K_{oc} were equivalent. In the case of plumes in an unconfined aquifer (Scenario 2), more of an opportunity would exist for the more volatile CVOC A to escape into the gaseous phase, reducing the observed aqueous concentrations in comparison to those of CVOC B. An alternative possibility would be that differences in precipitation between sites would influence the opportunity for exchange of mass across the capillary fringe. In any event, a variety of hydrogeologic or hydrologic conditions may exist across a number of sites to enhance or suppress the exchange of CVOCs between the gaseous and aqueous phases. As a result, compounds characterized by higher Henry's constants might exhibit greater variability in maximum concentration between sites than those with a low Henry's constant. The relationship between the median literature-derived log K_h and the observed coefficient of variability of maximum concentration, as defined previously, is shown on Figure A-13. A positive correlation appears to exist between the coefficient of variability and log K_h , ($r = 0.54$) for the twelve CVOCs represented by six or more plumes.

Both this analysis and the previous assessment of log K_{oc} suggest that a portion the inter-site variability in maximum concentration for a given CVOC is related to both the Henry's constant

and the organic carbon partitioning coefficient. This suggests that a multivariate model may explain more of this variability than either coefficient alone. A three-dimensional scatter plot depicting such a model is shown on Figure A-14. The multivariate correlation coefficient associated with a best-fit plane to these data is approximately $r = 0.83$.

A weak inverse relationship is also suggested between the mean of the log plume length indices and $\log K_h$, ($r = -0.48$) (Fig. A-15). Plume length indices can only be defined for a subset of the total plume population, as mean groundwater velocities were not available from all the sites. Thus, the eleven CVOCs included in this analysis were each represented by a minimum of three plume length indices. This relationship could conceivably reflect small losses of CVOC mass into the vadose zone from thin plumes near the water table in unconfined aquifers. After correcting for the effects of source strength and groundwater velocity, it is possible that such small mass losses may exert an effect on plume length that is detectable statistically. However, this observation is empirical at this point; it must be followed by further analyses to confirm whether or not it is a real effect.

On this last point, it is important to recognize that all of these observations regarding partitioning relationships represent statistical trends in the data that are consistent with plausible physical explanations. This does not necessarily constitute a definite proof that the explanations are indeed correct. For example, both of the Henry's Law relationships could also be explained by systematic preferential losses of the more volatile CVOCs during sample collection and handling at sites and analytical laboratories involved. Hence, these results should be regarded as tentative in nature and should be subject to further testing as additional data become available.

A-3.3. Solubility and Vapor Pressure

Relationships between plume behavior and K_{oc} or K_h involve CVOCs that are dissolved in the aqueous phase. In contrast, CVOC solubility and vapor pressure partitioning relationships pertain directly to the presence of DNAPL, either in contact with the aqueous phase or the gaseous phase. Because data collection and analyses efforts associated with the present study have focused exclusively on the aqueous phase, the effects of DNAPL solubility and vapor pressure could only be assessed indirectly, i.e., as effects on CVOC mass in the aqueous phase.

No apparent relationships were identified between plume variables (geometric mean maximum concentration, coefficient of variability of maximum concentration, geometric mean plume length) and either solubility or vapor pressure based on median values noted in the literature for common CVOCs. Furthermore, the exclusion of likely daughter product CVOCs (i.e., *cis*-1,2-DCE and vinyl chloride), which would not be present as DNAPL, from the analysis did not exert any notable effect.

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Table A-1. Fraction of plumes possibly associated with DNAPL for CVOCs represented by more than 10 plumes.

CVOC	Total no. of 10-ppb-defined plumes	Fraction of plumes with conc.> 1% solubility	Fraction of plumes with conc.> 10% solubility
TCE	55	36% (20 plumes)	11% (6 plumes)
PCE	32	38% (12 plumes)	13% (4 plumes)
1,1-DCE	29	10% (3 plumes)	0%
<i>Cis</i> -1,2-DCE	29	7% (2 plumes)	3% (1 plume)
1,1,1-TCA	23	26% (6 plumes)	4% (1 plume)
Vinyl chloride	20	0%	0%
1,1-DCA	18	0%	0%

Table A-2. Site median concentrations of geochemical indicator compounds from sites representing different reductive dehalogenation groups.

Geochemical indicator species	90 th quantiles			Student t-test p-values; No RD vs. Strong RD groups
	No RD	Weak RD	Strong RD	
Cl ⁻ (mg/L)	120	162	310	0.30
Mn ²⁺ (μg/L)	130	430	1340	0.34
Total xylenes (μg/L)	6.3	8.9	74.1	0.20
Bicarbonate alkalinity (mg/L)	260	356	552	0.009

Table A-3(a). Temporal trends in plume length for CVOC plumes from the Strong RD group characterized by monitoring data from three or more years.

<i>p</i> -value	Decreasing length	Increasing length	No significant trend
0.01	9% (4 plumes)	4% (2 plumes)	87% (41 plumes)
0.05	11% (5 plumes)	13% (6 plumes)	77% (36 plumes)
0.1	13% (6 plumes)	15% (7 plumes)	72% (34 plumes)
0.2	21% (10 plumes)	19% (9 plumes)	60% (28 plumes)
0.3	21% (10 plumes)	26% (12 plumes)	53% (25 plumes)
0.5	23% (11 plumes)	28% (13 plumes)	49% (23 plumes)

Table A-3(b). Temporal trends in plume length for CVOC plumes from the No RD and Weak RD groups characterized by monitoring data from three or more years.

<i>p</i> -value	Decreasing length	Increasing length	No significant trend
0.01	9% (8 plumes)	14% (13 plumes)	78% (73 plumes)
0.05	10% (9 plumes)	21% (20 plumes)	69% (65 plumes)
0.1	12% (11 plumes)	27% (25 plumes)	62% (58 plumes)
0.2	14% (13 plumes)	34% (32 plumes)	52% (49 plumes)
0.3	17% (16 plumes)	38% (36 plumes)	45% (42 plumes)
0.5	19% (18 plumes)	44% (41 plumes)	37% (35 plumes)

Table A-4. Literature values of partitioning coefficients for CVOCs in data set.

CVOC	K_{oc} (ml/g)	K_h (atm m ³ /mol)	Solubility (mg/L)	Vapor pressure (mm Hg)
1,1-DCA	30.2 (Schwille, 1988)	4.3 x 10 ⁻³ (Mercer et al., 1990)	5500 (Verschueren, 1983)	180 (Verschueren, 1983)
		5.5 x 10 ⁻³ (Warner et al., 1987)		182 (Mercer et al., 1990)
		5.7 x 10 ⁻³ (Hine and Mookerjee, 1975)		
1,1-DCE	64.6 (Schwille, 1988)	1.5 x 10 ⁻² (Warner et al., 1987)	2250 (Mercer et al., 1990)	591 (Verschueren, 1983)
		2.1 x 10 ⁻² (Schwille, 1988)		600 (Mercer et al., 1990)
		3.0 x 10 ⁻² (CRC Handbook, 1992)		
		3.4 x 10 ⁻² (Mercer et al., 1990)		
1,1,1-TCA	104 (Chiou et al., 1979) 151 (Schwille, 1988)	1.3 x 10 ⁻² (Schwille, 1988)	720 (Mackay and Shiu, 1981)	100 (Verschueren, 1983)
		1.3 x 10 ⁻² (Hunter-Smith et al., 1984)	1250 (Broholm and Feenstra, 1995)	123 (Mercer et al., 1990)
		1.4 x 10 ⁻² (Mercer et al., 1990)	1495 (Horvath, 1982)	
		1.5 x 10 ⁻² (Roberts and Dandliker, 1983)	1500 (Mercer et al., 1990)	
		1.6 x 10 ⁻² (Hine and Mookerjee, 1975)	4400 (Verschueren, 1983)	
		1.7 x 10 ⁻² (Lincoff and Gossett, 1984)		
		1.8 x 10 ⁻² (Lyman et al., 1982)		
1,1,2-TCA	56.2 (Schwille, 1988)	1.2 x 10 ⁻³ (Mercer et al., 1990)	4500 (Verschueren, 1983)	19 (Verschueren, 1983)
		7.4 x 10 ⁻⁴ (Pankow and Rosen, 1988)		30 (Mercer et al., 1990)
		9.1 x 10 ⁻⁴ (Hine and Mookerjee, 1975)		
1,2-DCA	14.1 (Schwille, 1988) 19 (Chiou et al., 1979)	9.1 x 10 ⁻⁴ (Schwille, 1988)	8520 (Mercer et al., 1990)	61 (Mercer et al., 1990)
		9.8 x 10 ⁻⁴ (Mercer et al., 1990)	8690 (Pankow et al., 1996)	64 (Verschueren, 1983)
		1.1 x 10 ⁻³ (Warner et al., 1987)		
CA	17 (Mercer et al., 1990) 26.9 (Chiou et al., 1979)	8.5 x 10 ⁻³ (Hine and Mookerjee, 1975)	5740 (Mercer et al., 1990)	1000 (Mercer et al., 1990)
		9.3 x 10 ⁻² (Pankow and Rosen, 1988)		
		1.1 x 10 ⁻² (Gossett, 1987)		
		1.5 x 10 ⁻² (U.S. EPA, 1980)		

Table A-4. (Continued)

CVOC	K_{oc} (ml/g)	K_h (atm m ³ /mol)	Solubility (mg/L)	Vapor pressure (mm Hg)
CF	43.7 (Schwille, 1988)	2.9 x 10 ⁻³ (Mercer et al., 1990)	7920 (Horvath, 1982)	151 (Mercer et al., 1990)
	47 (Mercer et al., 1990)	2.9 x 10 ⁻³ (Jury et al., 1984)	7925 (Mackay and Shiu, 1981)	160 (Verschueren, 1983)
		3.2 x 10 ⁻³ (Valsaraj, 1988)	8000 (Verschueren, 1983)	
		3.2 x 10 ⁻³ (Dilling, 1977)	8200 (Mercer et al., 1990)	
		3.4 x 10 ⁻³ (Warner et al., 1987)	8700 (Broholm and Feenstra, 1995)	
		3.9 x 10 ⁻³ (Nicholson et al., 1984)		
		4.3 x 10 ⁻³ (Lincoff and Gossett, 1984)		
		5.3 x 10 ⁻³ (Roberts and Dandliker, 1983)		
CM	25.1 (Chiou et al., 1979)	6.6 x 10 ⁻³ (Pankow and Rosen, 1988)	4000 (Verschueren, 1983)	3800 (Verschueren, 1983)
	35 (Mercer et al., 1990)	8.8 x 10 ⁻³ (Gossett, 1987)	6500 (Mercer et al., 1990)	4310 (Mercer et al., 1990)
		1.0 x 10 ⁻² (Hine and Mookerjee, 1975)	7400 (Lyman et al., 1982)	
		4.4 x 10 ⁻² (Mercer et al., 1990)		
CTET	224 (Abdul et al., 1987)	2.3 x 10 ⁻² (Jury et al., 1984)	757 (Mercer et al., 1990)	90 (Verschueren, 1983)
	417 (Chin et al., 1988)	2.4 x 10 ⁻² (Mercer et al., 1990)	780 (Broholm and Feenstra, 1995)	
	437 (Schwille, 1988)	2.4 x 10 ⁻² (Robert and Dandliker, 1983)	785 (Pankow et al., 1996)	
		2.4 x 10 ⁻² (Hunter-Smith et al., 1984)	793 (Horvath, 1982)	
		3.0 x 10 ⁻² (Warner et al., 1987)	1000 (Mackay and Shiu, 1981)	
PCE	210 (Chiou et al., 1979)	2.9 x 10 ⁻³ (Warner et al., 1987)	150 (Verschueren, 1983)	14 (Verschueren, 1983)
	263 (Abdul et a., 1987)	1.3 x 10 ⁻² (Schwille, 1988)	200 (Pankow et al., 1996)	17.8 (Mercer et al., 1990)
	363 (Schwille, 1988)	1.5 x 10 ⁻² (Pankow and Rosen, 1988)		20 (Standen, 1964)
		1.8 x 10 ⁻² (Lincoff and Gossett, 1984)		
		2.6 x 10 ⁻² (Mercer et al., 1990)		

Table A-4. (Continued)

CVOC	K_{oc} (ml/g)	K_h (atm m ³ /mol)	Solubility (mg/L)	Vapor pressure (mm Hg)
TCE	64.6 (Abdul et al., 1987) 106 (Garbarini and Lion, 1986) 126 (Schwille, 1988)	9.1 x 10 ⁻³ (Pankow and Rosen, 1988)	1050 (Mackay and Shiu, 1981)	58 (Mercer et al., 1990)
		9.1 x 10 ⁻³ (Mercer et al., 1990)	1100 (Horvath, 1982)	60 (Verschueren, 1983)
		9.9 x 10 ⁻³ (Roberts and Dandliker, 1983)	1100 (Verschueren, 1983)	
		1.0 x 10 ⁻² (Lincoff and Gossett, 1984)	1400 (Broholm and Feenstra, 1995)	
		1.2 x 10 ⁻² (U.S. EPA, 1980)		
VC	2.5 (Karickhoff et al., 1979) 57 (Mercer et al., 1990)	1.1 x 10 ⁻² (CRC Handbook, 1992)	1100 (Verschueren, 1983)	2660 (Mercer et al., 1990)
		2.2 x 10 ⁻² (Pankow and Rosen, 1988)	2670 (Mercer et al., 1990)	
		5.6 x 10 ⁻² (Hine and Mookerjee, 1975)		
		8.2 x 10 ⁻² (Mercer et al., 1990)		
		1.2 (Dilling, 1977)		
		2.4 (Jury et al., 1984)		
<i>Cis</i> -1,2-DCE	22.9 (Kenaga, 1980) 47.9 (Schwille, 1988)	1.3 x 10 ⁻³ (Pankow and Rosen, 1988)	800 (Verschueren, 1983)	200 (Verschueren, 1983)
		3.6 x 10 ⁻³ (U.S. EPA, 1980)	3500 (Mercer et al., 1990)	208 (Mercer et al., 1990)
		7.6 x 10 ⁻³ (Mercer et al., 1990)		
<i>Trans</i> -1,2-DCE	58.9 (Schwille, 1988)	5.3 x 10 ⁻³ (U.S. EPA, 1980)	600 (Verschueren, 1983)	324 (Mercer et al., 1990)
		6.6 x 10 ⁻³ (Mercer et al., 1990)	6300 (Mercer et al., 1990)	
		7.2 x 10 ⁻³ (Pankow and Rosen, 1988)		
MeCl	8.7 (Schwille, 1988)	2.0 x 10 ⁻³ (Mercer et al., 1990)	20,000 (Verschueren, 1983)	349 (Verschueren, 1983)
		2.9 x 10 ⁻³ (Lincoff and Gossett, 1984)		362 (Mercer et al., 1990)
1,1,2,2-TCA	46 (Chiou et al., 1979) 117 (Schwille, 1988)	3.8 x 10 ⁻⁴ (Mercer et al., 1990)	2900 (Verschueren, 1983)	5 (Verschueren, 1983)
		3.8 x 10 ⁻⁴ (Pankow and Rosen, 1988)		
		4.6 x 10 ⁻⁴ (Hine and Mookerjee, 1975)		

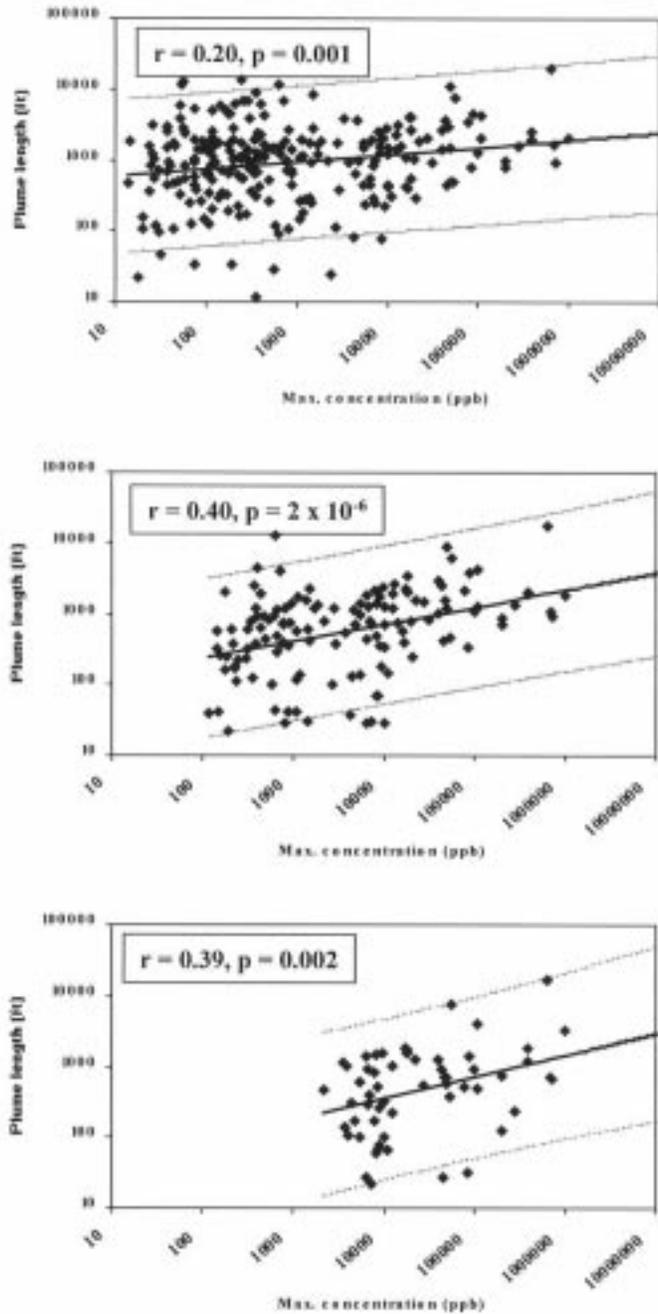


Figure A-1. Correlation between log plume length and log maximum historical concentration (per CVOC) for 10-ppb-defined plumes (top), 100-ppb-defined plumes (middle), and 1000-ppb-defined plumes (bottom). Null hypothesis probabilities are indicated by p -values. Dashed lines denote the 95% prediction confidence band.

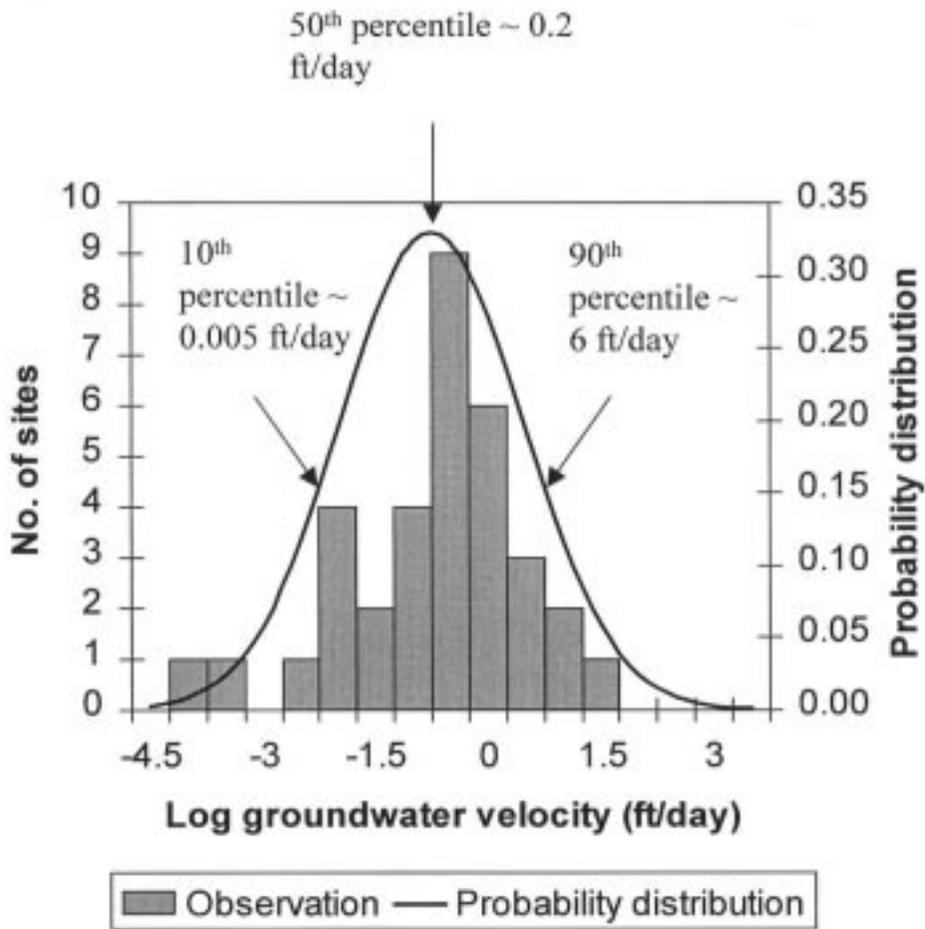


Figure A-2. Histogram and best-fit lognormal probability distribution of groundwater velocities from the 34 sites that provided hydraulic conductivity and gradient estimates.

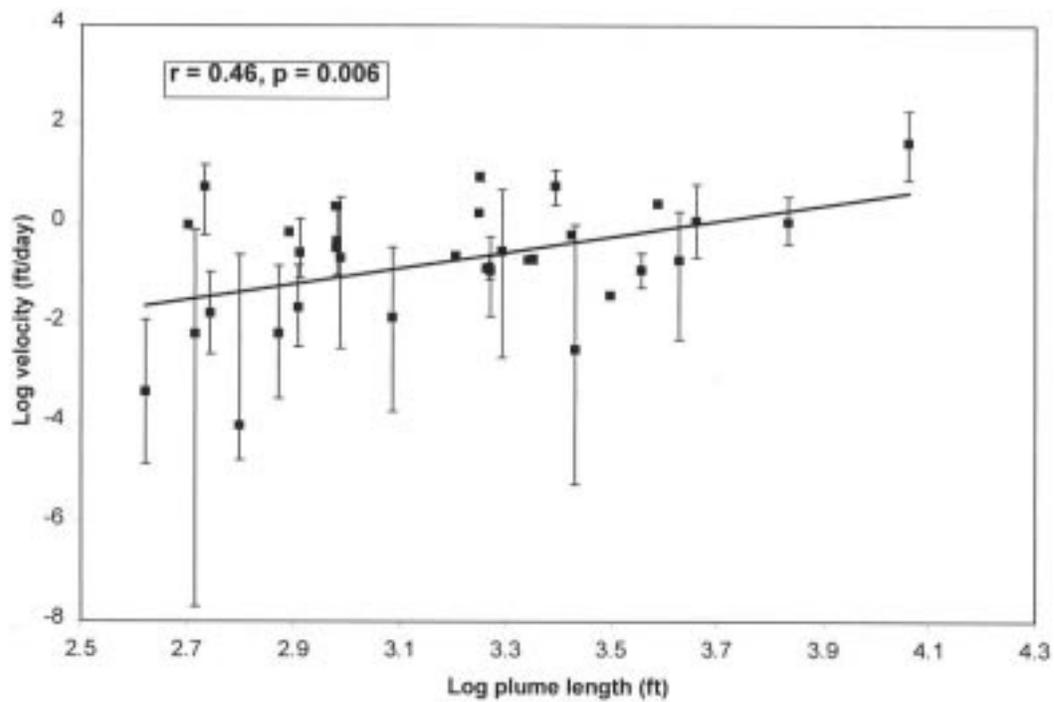


Figure A-3. Relationship between log maximum plume length per site and mean log site groundwater velocity (square symbols), with uncertainty bars showing ranges of velocity calculated from site-specific minimum and maximum hydraulic conductivity values. The independent variable, log groundwater velocity, is plotted on the y-axis to facilitate inspection of the uncertainty bars.

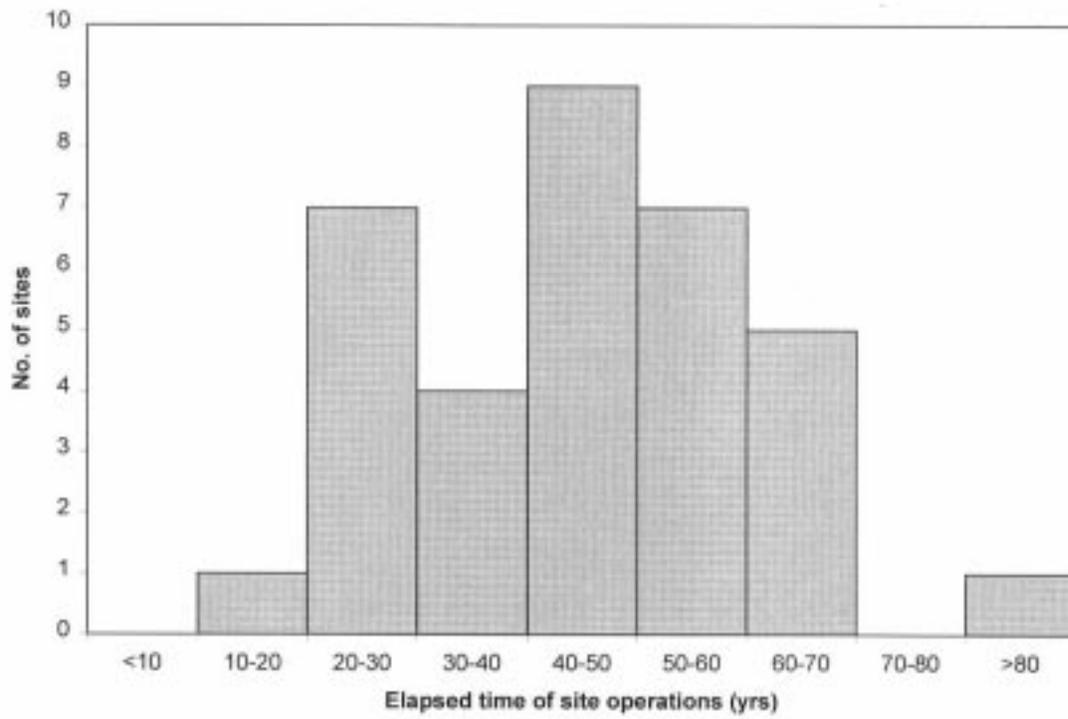


Figure A-4. Distribution of plume ages from sites in the data set reporting operational history, inferred from elapsed time of site operations.

Color of symbol represents range of maximum historical TCE concentration.
Black: > 100,000 ppb. Dark gray: between 10,000 and 100,000 ppb.
Light gray: between 1,000 and 10,000 ppb. White: < 1,000 ppb.

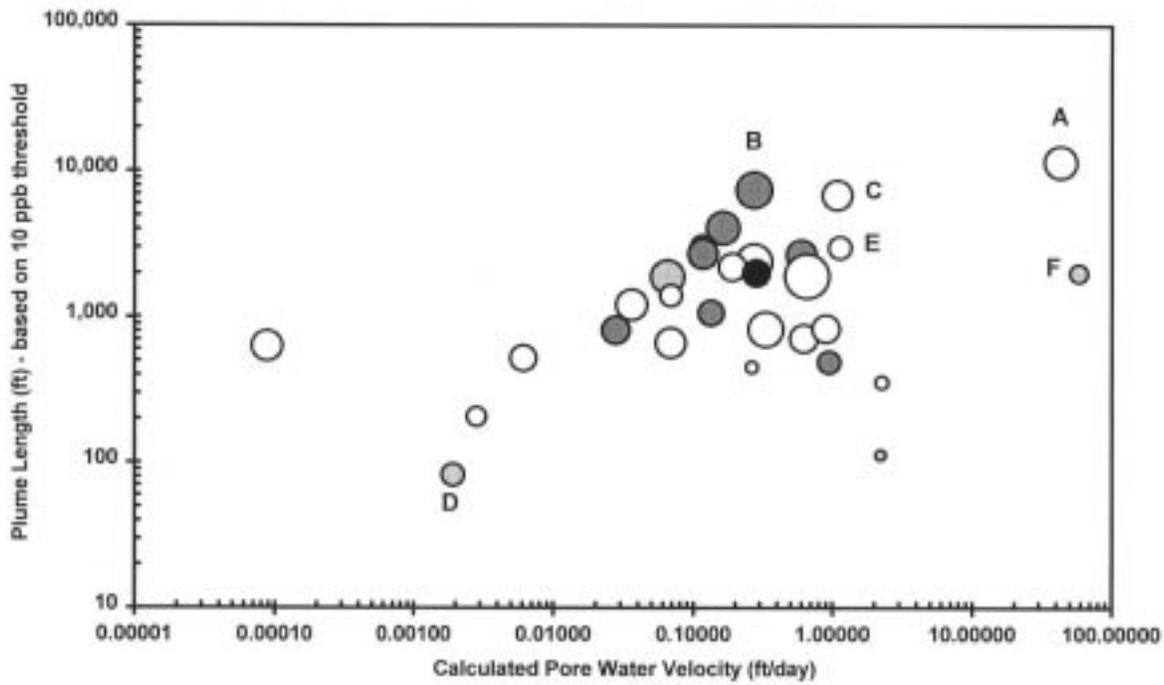


Figure A-5. Distribution of TCE plumes with respect to calculated plume length and calculated pore water velocity. The circle size represents the estimated age of the plume, and the shading of the disk represents the range of maximum concentration as indicated. See text for explanation of labeled points.

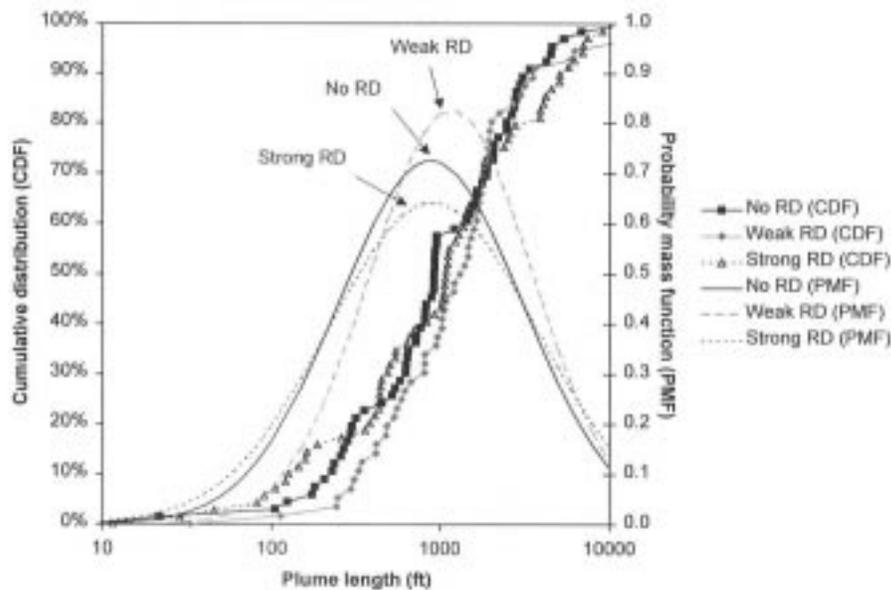
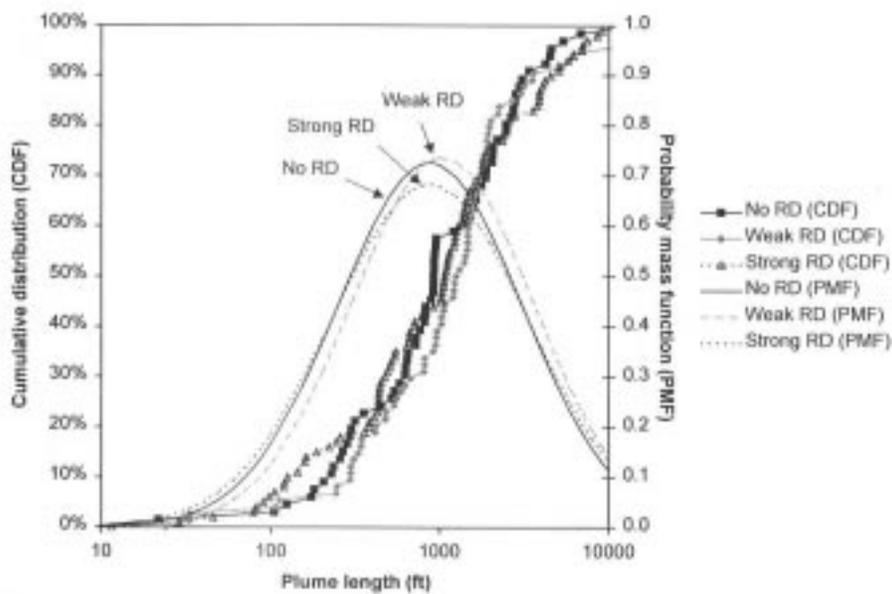


Figure A-6. Cumulative distributions of plumes lengths from sites exhibiting no evidence of reductive dehalogenation, weak evidence, and strong evidence, all CVOCs from each site (top) and CVOCs exclusive of *cis*-1,2-DCE and vinyl chloride daughter products (bottom). Frequency distributions determined by a best fit lognormal distribution model are indicated on the second y-axis.

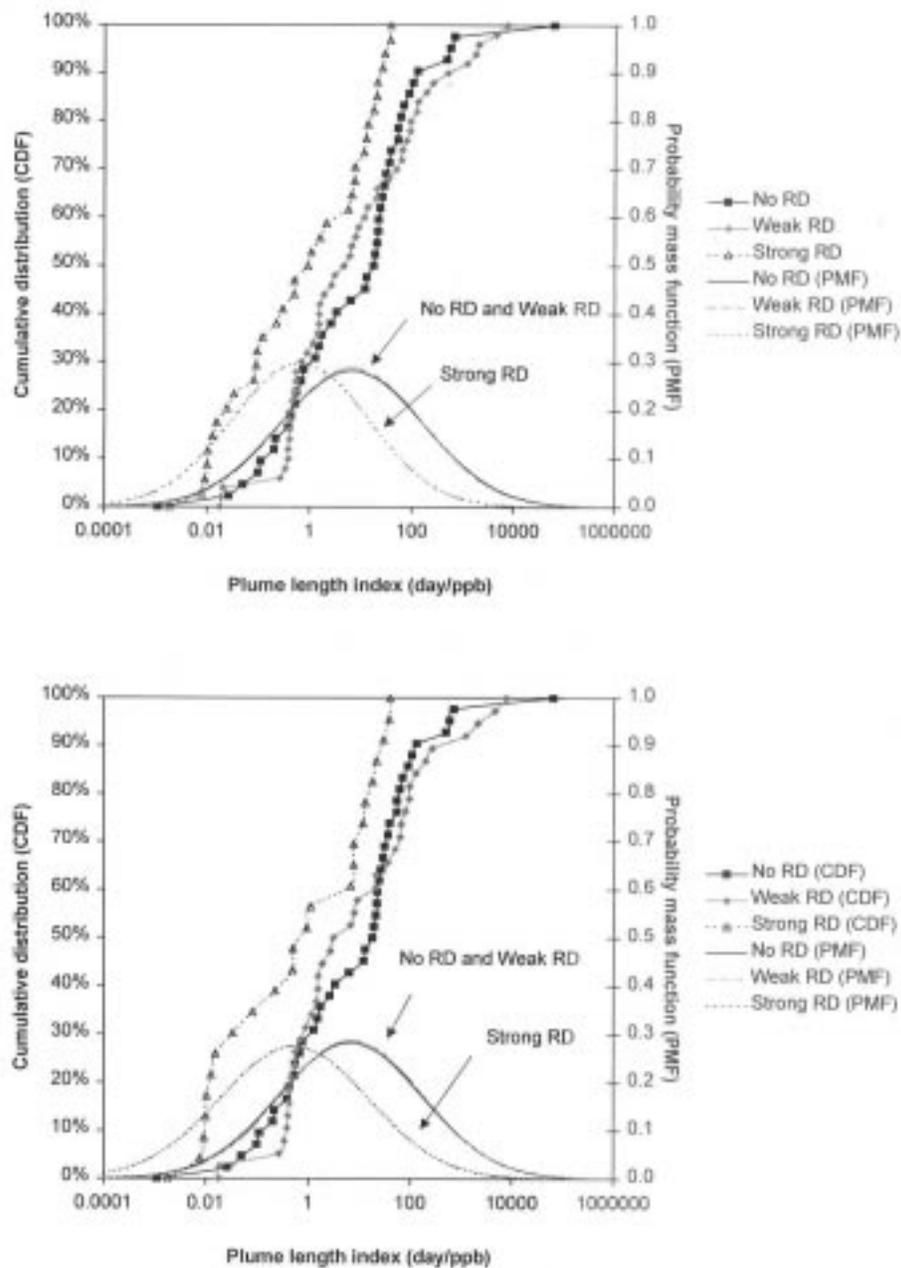


Figure A-7. Cumulative distributions of plumes length indices from sites exhibiting no evidence of reductive dehalogenation, weak evidence, and strong evidence, all CVOCs from each site (top) and CVOCs exclusive of *cis*-1,2-DCE and vinyl chloride daughter products (bottom). Frequency distributions determined by a best fit lognormal distribution model are indicated on the second y-axis.

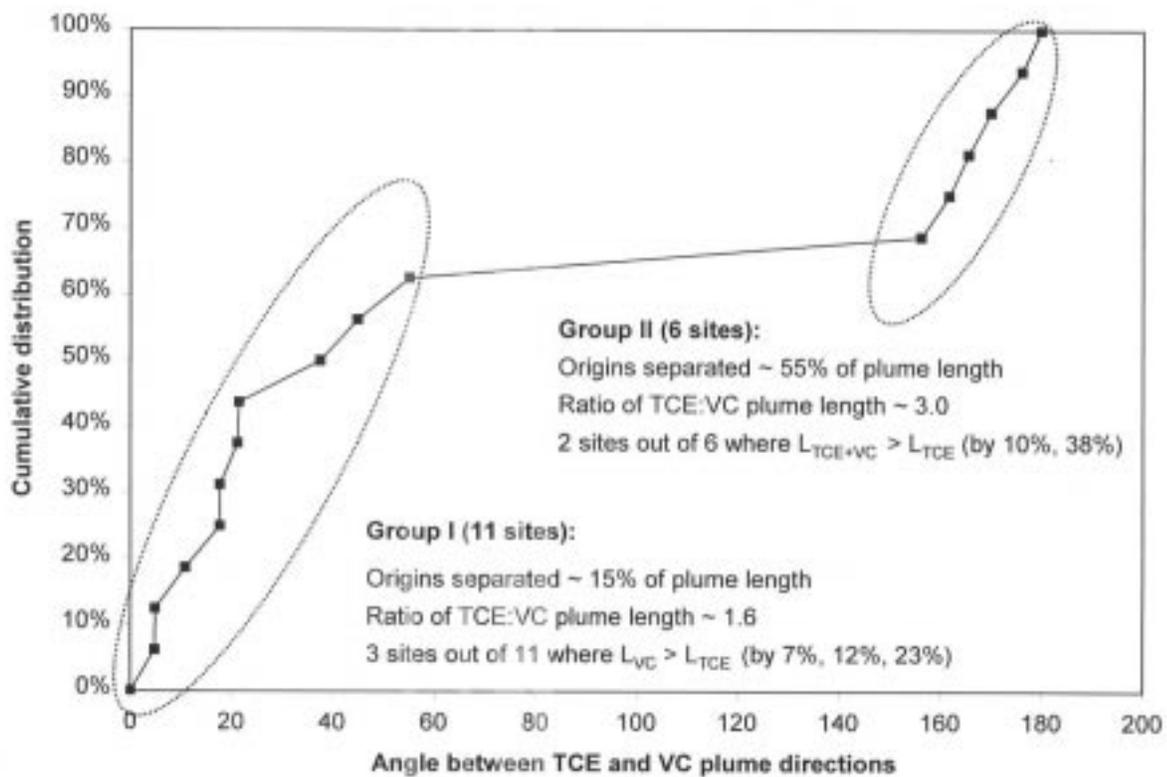


Figure A-8. Cumulative distribution of angles between TCE and vinyl chloride plume directions as interpreted by the plume algorithm

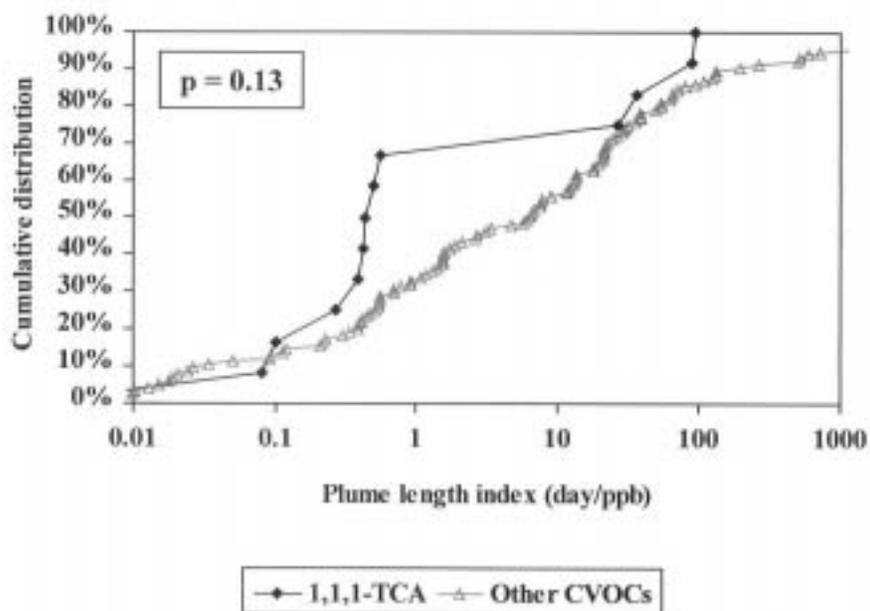
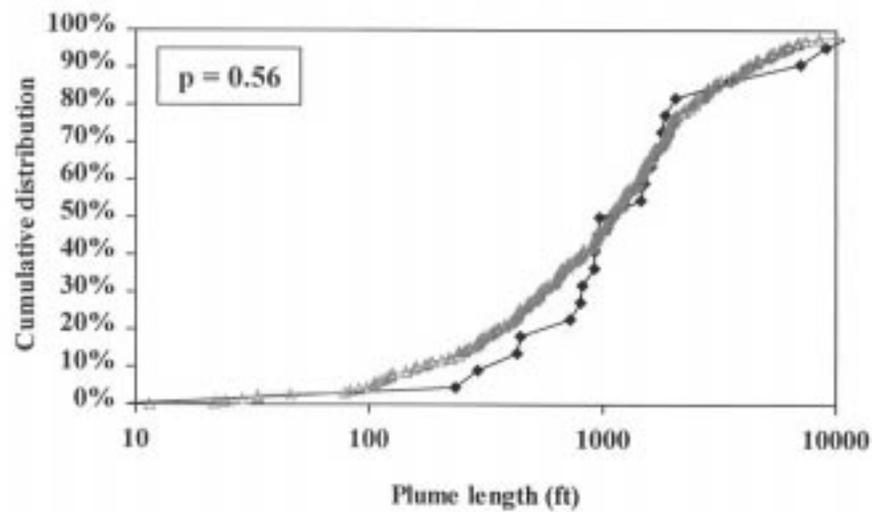
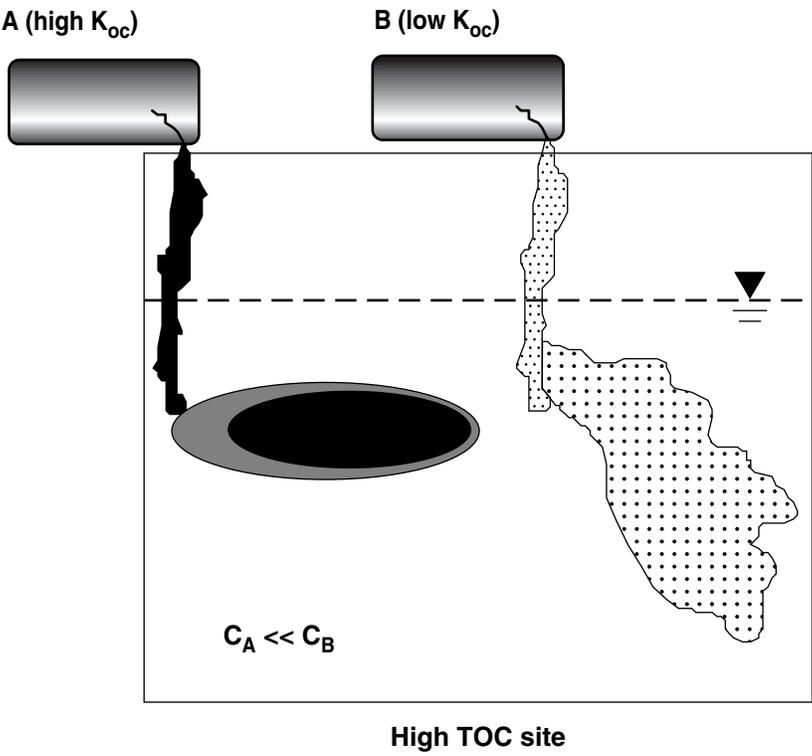
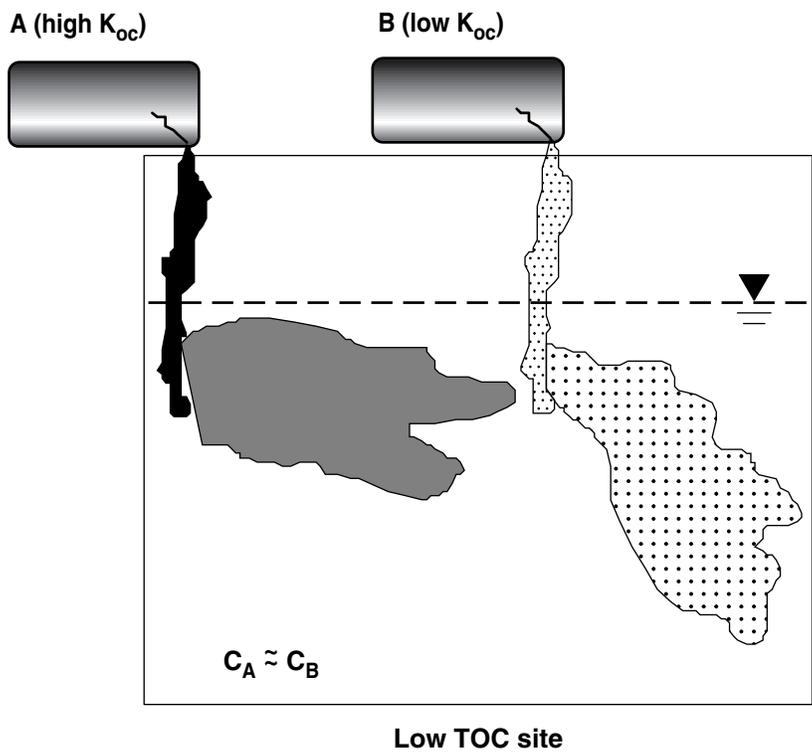


Figure A-9. Cumulative distributions of 1,1,1-TCA plume lengths and those of other CVOCs (top), and distributions of plume length indices (bottom).



ERD-LSR-99-0042

Figure A-10. Idealized release scenarios for CVOCs with low and high organic carbon partitioning coefficients, low organic carbon environment (top) and, high organic carbon environment (bottom).

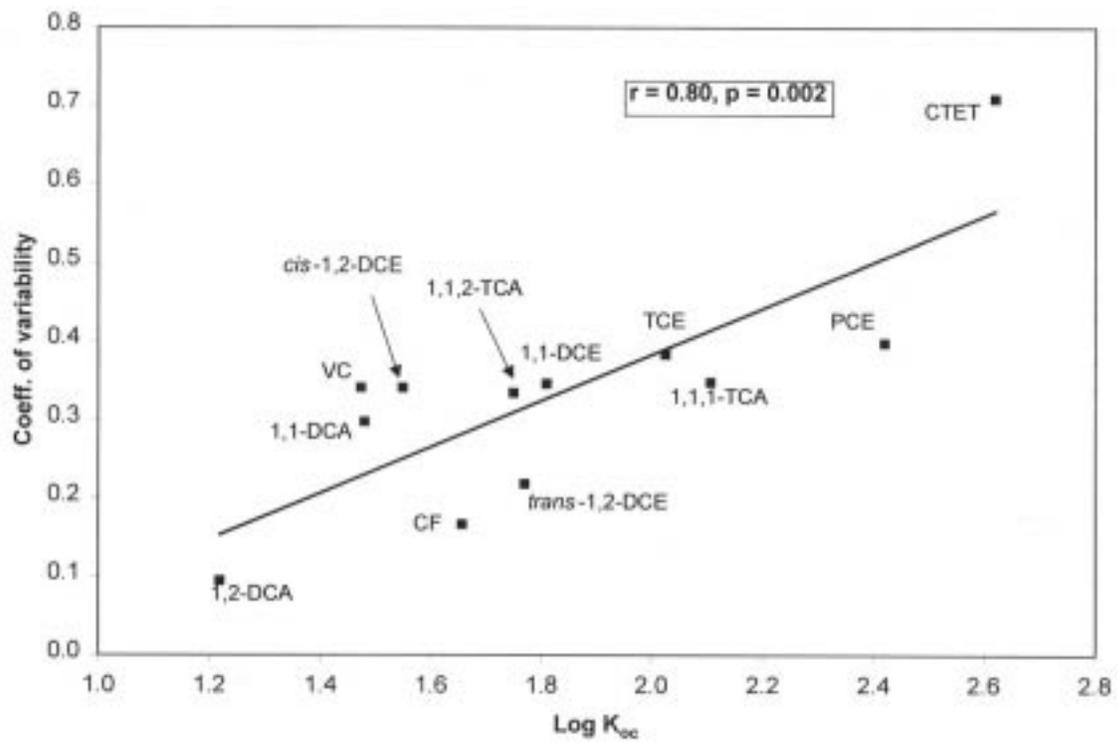
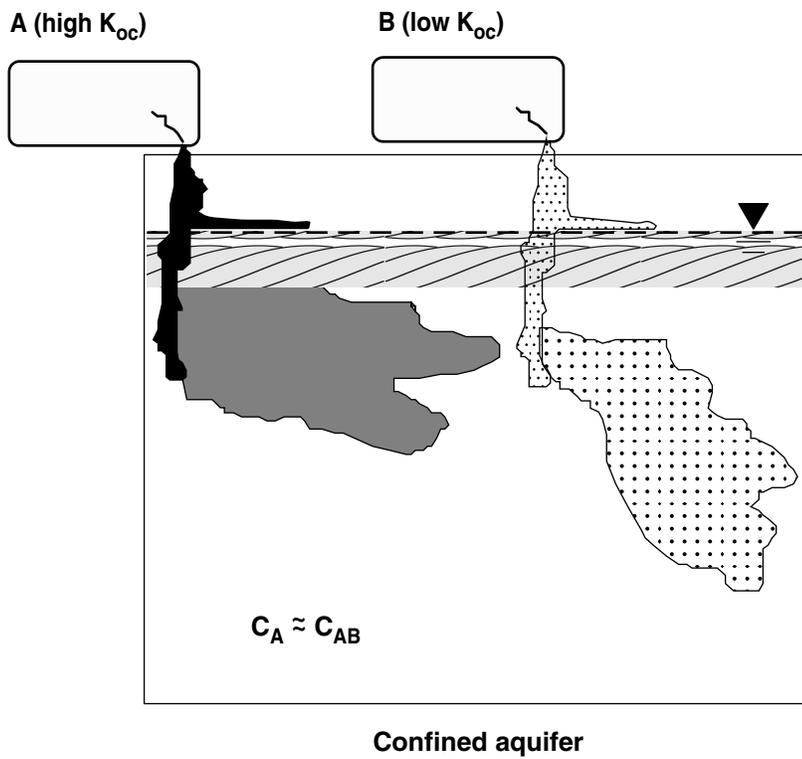
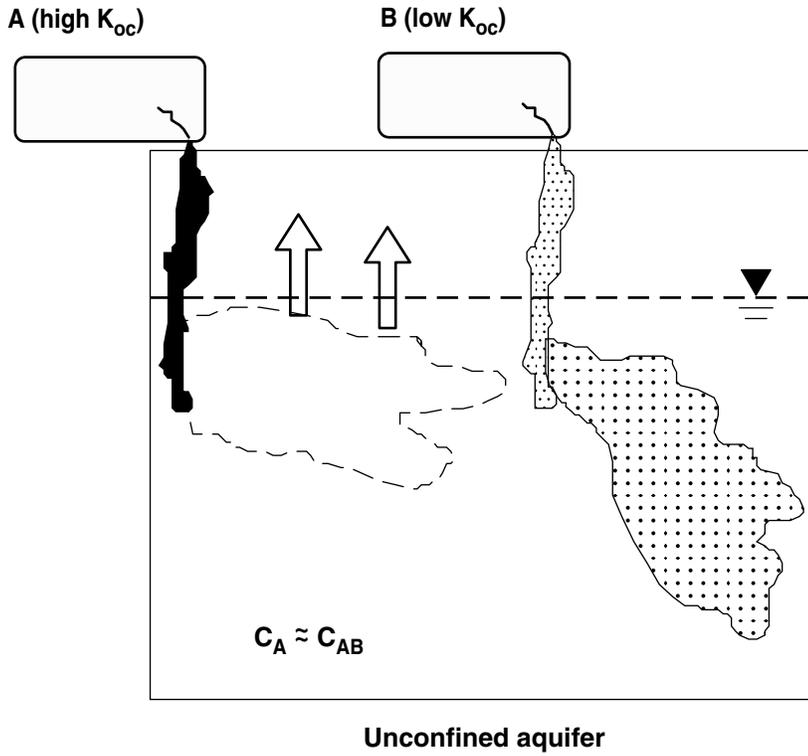


Figure A-11. Relationship between the coefficient of variability in maximum historical concentration between sites and the organic carbon partitioning coefficient for CVOCs represented by six or more plumes.



ERD-LSR-99-0053

Figure A-12. Idealized release scenarios for CVOCs with low and high Henry's constants, confined aquifer (top) and unconfined aquifer (bottom).

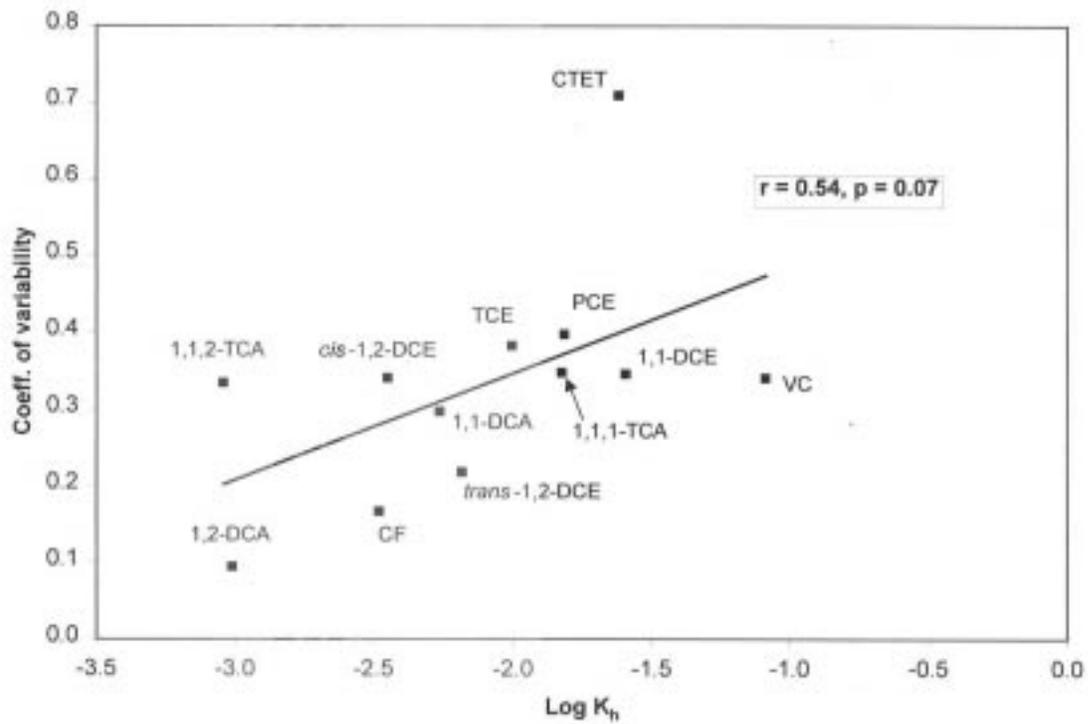


Figure A-13. Relationship between the coefficient of variability in maximum historical concentration between sites and the Henry's constant for CVOCs represented by six or more plumes.

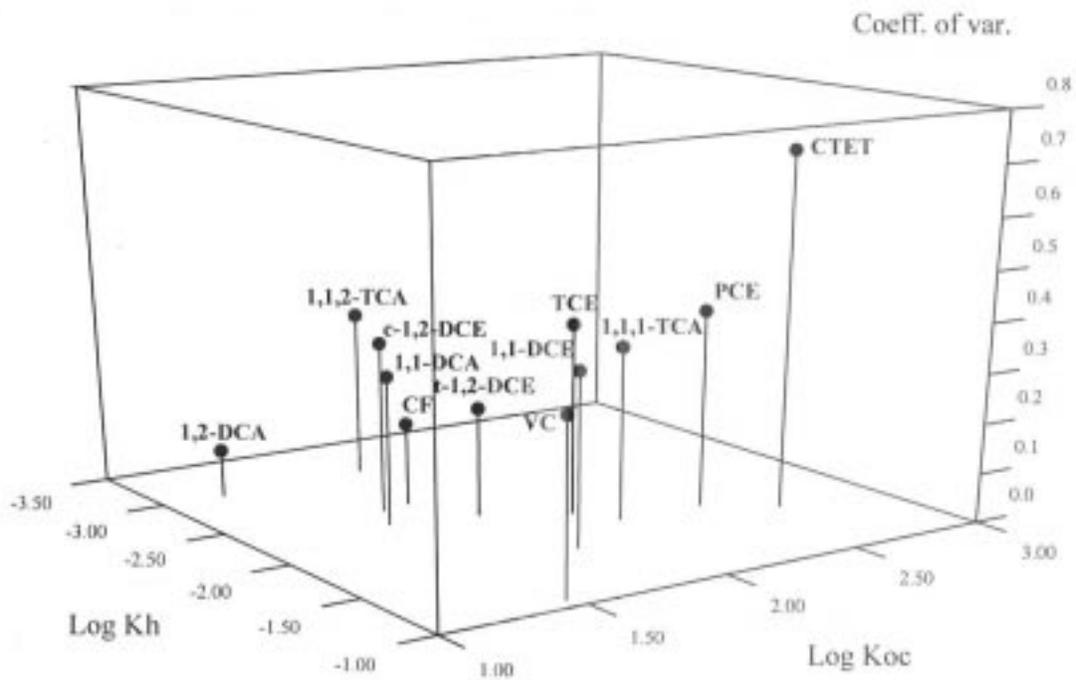


Figure A-14. A three-dimensional scatter plot showing the relationship between coefficient of variability in maximum historical concentration between sites and the organic carbon partitioning coefficient and the Henry's constant for CVOCs represented by six or more plumes.

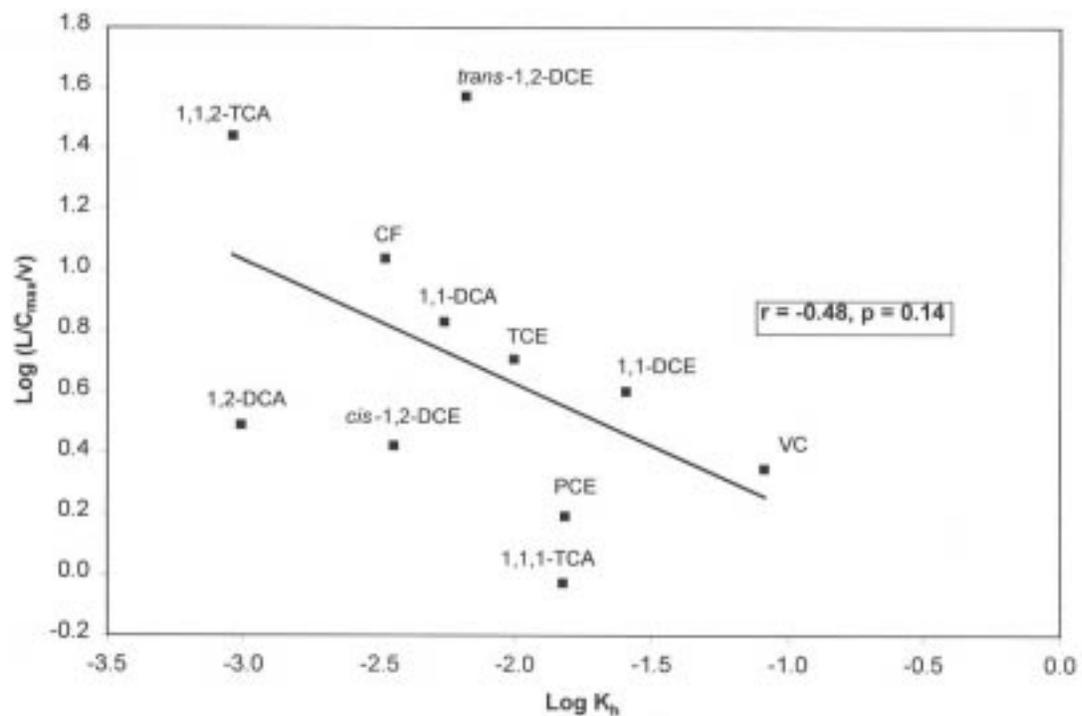


Figure A-15. Relationship between the mean of the log plume length indices and the Henry's constant for CVOCs represented by three or more plumes.