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Evaluating Chlorinated Hydrocarbon Plume Behavior Using Historical Case Population Analyses

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Abstract

A nationwide survey of chlorinated volatile organic compound (CVOC) plumes was conducted across a spectrum of sites from diverse hydrogeologic environments and contaminant release scenarios. The goal was to evaluate significant trends in the data that relate plume behavior to site variables (e.g., source strength, mean groundwater velocity, reductive dehalogenation regime) through correlation and population analyses. Data from 65 sites (government facilities, dry cleaners, landfills) were analyzed, yielding 247 individual CVOC plumes by compound. Data analyses revealed several trends, notably correlations between plume length and maximum observed concentration (presumably reflecting the source term) and mean groundwater velocities. Reductive dehalogenation, indicated by daughter products and groundwater geochemistry, appears to exert a relatively subtle effect on plume length, apparent only after the contributions of source strength and groundwater velocity are factored out. CVOC properties (K_{oc}, Henry's constant) exert significant effects on variability in maximum observed concentrations between sites but hold little influence on plume length. Probabilistic plume modeling, entailing Monte Carlo simulation of an analytical solution for average plume behavior with parameter distributions derived from site data, was used to produce a synthetic plume set for comparison with field data. Modeling results exhibited good agreement with field data in terms of parameter sensitivity.

Key words: Case history analyses, chlorinated hydrocarbons, contaminant transport, natural attenuation, plume length.

1.0 Introduction

An understanding of the general patterns in behavior of chlorinated volatile organic compound (CVOC) plumes, their transformation daughter product plumes, and relationships between plume behavior and site variables is essential to managers and decision-makers engaged in CVOC plume investigation and remediation. In principle, the behavior of a contaminant plume in an aquifer is affected by a number of variables, including the release history of the contaminant, the hydraulic properties of the porous medium, partitioning properties of the contaminant, and the local biogeochemical regime. Studies conducted at individual sites typically reveal combinations of physical and biogeochemical variables that, in turn, produce a plume that has its own particular morphological variables (e.g., length, rate of growth). However, field data are often sparse, so a detailed understanding of plume behavior at a given site is more the exception than the rule. Nevertheless, the same flow, transport, and transformation mechanisms influence essentially all CVOC plumes, although at a magnitude that may vary greatly from site to site. Thus, it is reasonable to expect that by analyzing site specific field data from a relatively large number of CVOC releases, the relationships between CVOC plumes and site variables can be identified and quantified on a statistical basis.

In this study, we attempt to understand the factors affecting the behavior of CVOC plumes in groundwater from a broad, statistically oriented perspective. Several previous studies have attempted to compare CVOC plume behavior using a limited number of sites, focusing primarily on the effectiveness of the groundwater pump-and-treat techniques. Doty and Travis (1991) evaluated 16 sites, the U.S. EPA evaluated 19 sites (Keely, 1989; US EPA, 1989) and 24 sites (US EPA, 1992), the National Research Council (1994) evaluated 72 sites, and Bartow and Davenport (1995) evaluated 37 sites. However, none of these previous studies had attempted to evaluate the effects of site variables on plume size under natural conditions, the principal concern of this study. Our goal was to assimilate chemical and hydrogeologic data from a variety of sites representing different release scenarios and environmental settings, quantify mean site variables, and compare plume behavior with site variables under natural conditions. This strategy entails a key hypothesis: that site-specific features (e.g., preferential flow pathways, atypical release history, pumping effects) do not affect plume behavior to the point that correlations with macro-averaged variables (e.g., mean site groundwater velocity) cannot be ascertained. Ultimately, the value in quantifying such relationships lies in (1) comparing the relative effects site variables have on plume behavior, and (2) providing a standard reference frame, via an integrated statistical model, against which individual plumes may be compared, facilitating the identification of anomalies (e.g., plumes that appear excessively short or long for their environmental setting in comparison to other plumes). Both assessments would aid site investigators in terms of prioritizing characterization efforts and in developing or refining conceptual models of plume behavior.

2.0 Data Set and Methods of Analysis

The overall approach employed in this study was to use correlation analyses and population inference tests to identify and quantify trends and relationships in the data between plume characteristics (e.g., plume length) and site hydrogeologic, biogeochemical, and CVOC physiochemical variables. Procedures for data collection and analysis included a number of specific tasks:

1. Candidate sites, solicited by state regulatory agency contacts, were screened for suitability based on a set of criteria. Sites were accepted for inclusion in the study if:
    (a) Data were available from at least six monitoring wells over a three-quarter monitoring period prior to remediation, and
    (b) Plumes were not truncated by surface water bodies, and
    (c) Plumes were not significantly affected by pumping in nearby wells, and
    (d) Interpretation of plume length was not complicated by multiple CVOC sources.

Once a site passed the screening process and was accepted in the study, CVOC historical monitoring data were obtained electronically and hydrogeologic data were extracted from site reports. For the phase of the study reported in this paper, data were collected from a total of 65 sites, representing U.S. Department of Energy and Department of Defense Facilities, landfills, dry cleaners, and commercial industrial sites. A total of 18 states were represented by sites in the data set (Table 1).

2. Mean values were estimated for site hydrogeological variables, such as groundwater velocity. Different variables required different approaches to quantify mean site values. For example, in the case of hydraulic conductivity (used to calculate groundwater velocity via Darcy's law), a representative mean site value was quantified by utilizing the geometric mean of pumping test and slug test values reported for individual monitoring wells. Reductive dehalogenation potential was treated as a categorical variable, defined by the presence of certain reductive dehalogenation daughter products and supported by an analysis of trends in groundwater geochemistry.

3. The key plume characteristics, such as plume length, were estimated for all individual CVOCs at each site in the study. Plume lengths were estimated with an algorithm that employed CVOC concentration data to systematically quantify the distance from the location of the reported maximum CVOC concentration in a plume (presumably reflecting the source area location) to the most distal 10 part-per-billion (ppb) contour line. Plume lengths for subsets of these plumes were also delineated for the 100-ppb and 1000-ppb contour lines when concentrations permitted.

4. Statistical analyses were performed to identify relationships between plume length and site hydrogeological variables, the physiochemical properties of individual CVOCs, and the identified biogeochemical transformation categories. Statistical tests included analysis of correlation, comparison of population means, and the development of a general linear statistical model using analysis of covariance (ANCOVA).

5. Because the results of the statistical analyses are empirical in nature, probabilistic plume modeling was employed to provide a mathematical conceptual framework with which to relate observed correlations to fate and transport mechanisms. The mathematical modeling provided an

inferential line of reasoning that was used as a basis of comparison for statistical analyses of the CVOC field data.

A total of 247 individual CVOC plumes were identified and analyzed from the 65 sites included in the study. These plumes represented 16 individual CVOCs, including both the original contaminants and their transformation daughter products (Table 2). Plume length summary statistics are given in Table 3.

3.0 Analyses of Field Data

3.1 Source Strength

A 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 dense non-aqueous phase liquid (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 1. Although a great deal of scatter is present in these relationships, statistically significant trends exist. 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 Dooher, 1998).

3.2 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 values 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 available 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 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 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 more representative global average of site conditions than small plumes which may attenuate as a result of insufficient mass or highly localized reductive dehalogenation. 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 implied minimum and maximum groundwater velocities. 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.

3.3 Reductive Dehalogenation and Plume Length: Initial Analyses

3.3.1 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, as discussed below.

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, 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).
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 – 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 4. The hydrocarbon and bicarbonate alkalinity indicators, exhibiting statistically significant differences between the reductive dehalogenation categories, suggest that fuel hydrocarbon oxidation is a common process at sites characterized by strong evidence of reductive dehalogenation. Manganese and chloride concentrations, while exhibiting differences in median values that are consistent with reductive dehalogenation, do not differ in a statistically significant manner among the site categories. Thus, taken as a whole, the lumped statistical comparison of geochemical indicators from the data provides partial validation of the categorization scheme based on the presence of presumed daughter products.

3.3.2 Raw and Adjusted Plume Lengths. 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 4 (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:

$$PLI = \frac{L}{C_{\max} v} \tag{1}$$

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 5. Plume length indices from sites in the Strong RD category (i.e., vinyl chloride plume present) appear to be significantly smaller than those of the other two categories. 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 several possible 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 concentration or plume length 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). A 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 probably not well instrumented, 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 also 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. Finally, the geographic bias associated with data predominantly from the states of California and Oregon may also induce some effect.

3.3.3 General Linear Model/ANCOVA. The plume length index is a concept that has not been previously suggested in the literature; therefore, the results were validated by other more traditional multivariate statistical methods. Statistical analysis by means of a general linear model (GLM) (Searle, 1987) was performed to test the hypothesis that CVOC plume lengths are no different among three groups of plumes: those with no evidence, weak evidence, or strong evidence of reductive dehalogenation. In addition to the main effect in the statistical model, reductive dehalogenation, two other continuously measured variables, maximum concentration and mean velocity, were included. These two concomitant plume measurements covaried with the plume length and are thus called covariates. This form of the general linear model is more commonly known as an Analysis of Covariance (ANCOVA) (Steele and Torrie, 1980). The ANCOVA model revealed that, after accounting for the correlation of plume length with maximum concentration and mean groundwater velocity, plume lengths from sites with strong evidence of reductive dehalogenation are significantly shorter than plumes from the other two groups (by roughly a factor of two). The same conclusion was reached when the variables were analyzed by an equivalent nonparametric test (Conover, 1980), as well as when the analyses were statistically bias-corrected (Gilbert, 1987) by removing the indicator daughter plumes (cis-1,2-DCE and vinyl chloride).

4.0 Other Effects: 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 were chosen from a survey of published values:

Standen (1964)
Hine and Mookerjee (1975)
Dilling (1977)
Chiou et al. (1979)
U.S. EPA (1980)
Mackay and Shiu (1981)
Horvath (1982)
Lyman et al. (1982)
Roberts and Dandliker (1983)
Verschueren (1983)
Hunter-Smith et al. (1984)
Jury et al. (1984)
Lincoff and Gossett (1984)
Nicholson et al. (1984)
Abdul et al. (1987)
Gossett (1987)
Warner et al. (1987)
Chin et al. (1988)
Pankow and Rosen (1988)
Schwille (1988)
Valsaraj (1988)
Mercer et al. (1990)
CRC Handbook (1992)
Broholm and Feenstra (1995)
Pankow et al. (1996)

4.1 Organic Carbon Partitioning

Differences in the organic carbon partitioning coefficient among various CVOCs may yield trends in multi-site concentration data that can be identified even in the absence of total organic carbon (TOC) data from individual sites. For example, at sites with little TOC, 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 (e.g., release volume, solubility) are equivalent. However, at sites characterized by high TOC, a CVOC with a high K_{oc} would be expected to adsorb strongly onto the organic-rich material, so that its measurable aqueous-phase concentrations would be significantly lower than those of a CVOC with a low K_{oc}. Given these simple scenarios 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 exhibit more variability in concentration than those with lower K_{oc} values.

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 variation was defined by the standard deviation of the logarithm of maximum concentration, divided by the average of the log 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 variation in maximum concentration is shown on Figure 6. A significant positive correlation exists between the coefficient of variation 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. 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}.

4.2 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. For example, for 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 two CVOCs with different Henry's constants, K_h, would be expected to be similar if other variables such as release volume and K_{oc} were equivalent. In the contrasting case of plumes in an unconfined aquifer, more of an opportunity would exist for the more volatile CVOC to escape into the gaseous phase, reducing the observed aqueous concentrations in comparison to those of the less-volatile CVOC. 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 variation of maximum concentration, as defined previously, is shown on Figure 7. 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.

A weak inverse relationship is also suggested between the mean of the log plume length indices and log K_h, ($r = -0.48$) (Figure 8). 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. It is possible that such small mass losses may exert an effect on plume length that is detectable statistically, after correcting for the effects of source strength and groundwater velocity. However, this observation is empirical at this point; it must be followed by further analyses to confirm its validity.

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 definitive 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.

4.3 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.

5.0 Probabilistic Plume Modeling

5.1 Overview

The trends observed in the statistical evaluations of the field data, while intuitive, are empirical owing to the nature of the analyses. Reconciliation of these empirical findings with conceptual mathematical models of plume behavior can provide a theoretical basis for interpreting the observations. Given the emphasis of the present study on identifying and quantifying relationships between averaged site hydrogeologic variables and plume variables defined in a broad context, analytical solutions are highly suitable models for a probabilistic approach. They also produce simplified representations of plume behavior that are readily amenable to statistical analyses. In this context, the heterogeneity in the groundwater flow field, which often severely limits the application of analytical solutions, may be addressed through the macrodispersion coefficients.

Domenico (1987) presented a solution for concentration, *C*, as a function of *x*, *y*, and *t*, which also accounts for the effects of dispersion in the vertical direction:

$$C(x,y,t)=\left(\frac{C_0}{8}\right)\exp\left\{\left(\frac{x}{2\alpha_x}\right)\left[1-\left(1+\frac{4R\lambda\alpha_x}{v}\right)^{1/2}\right]\right\}\bullet\operatorname{erfc}\left[\frac{x-\frac{v}{R}t\left(1+4R\lambda\alpha_x/v\right)^{1/2}}{2\left(\alpha_x\frac{v}{R}t\right)^{1/2}}\right] \qquad (2)$$

$$\bullet\left\{\operatorname{erf}\left[\frac{(y+Y/2)}{2(\alpha_y x)^{1/2}}\right]-\operatorname{erf}\left[\frac{(y-Y/2)}{2(\alpha_y x)^{1/2}}\right]\right\}\bullet\left\{\operatorname{erf}\left[\frac{Z}{2(\alpha_z x)^{1/2}}\right]-\operatorname{erf}\left[\frac{-Z}{2(\alpha_z x)^{1/2}}\right]\right\}$$

Here, C_0 refers to a vertical rectangular-source (dimension Y x Z), of solute concentration along the upstream boundary, v the uniform groundwater velocity in the x-direction, α_x, α_y, and α_z the respective longitudinal, transverse, and vertical transverse dispersivities, R the retardation coefficient, and λ the first-order transformation rate. This solution is only valid for a semi-infinite homogeneous aquifer. From. Eq. (2), the plume's length along the x-axis may be estimated by setting $y = 0$ and C equal to some specific contour interval (i.e., $C = 10$ ppb), and solving for x using a suitable numerical approach (in this case a bisection search algorithm).

Application of Monte Carlo simulation techniques to analytical solute transport models can provide valuable insights into factors affecting plume behavior when combined with population studies of existing groundwater plumes. Monte Carlo analyses are routinely used in engineering probability forecasting applications (e.g., Ang and Tang, 1984). Woodbury *et al.* (1995) discussed the use of Monte Carlo analyses in practical ground water engineering applications. The main reason for resorting to a probabilistic analysis of phenomena of transport making use of a mathematical model stems from the lack of sufficient field data on site-specific features of plume behavior. Probabilistic modeling of contaminant transport involves employing user-specified probability distributions of physical and chemical model variables, based on available data, to produce forecasts through multiple Monte Carlo realizations. The Monte Carlo approach allows uncertainties in hydrogeological data (e.g., hydraulic conductivity, hydraulic gradient), nature of the source, and chemical data (e.g., degradation rates) to be translated into uncertainties regarding plume extents and rates of growth. Sensitivity analyses based on comparing uncertainties in input variables to the variance in corresponding forecast results may provide insight into the critical data for quantifying the behavior of plumes.

5.2 Parameter Distributions

For the modeling analysis, synthetic plumes were generated using random combinations of the variables in Eq. (2). Wherever possible, the values of these variables were constrained by probability distributions developed from field data (Table 5). Probability distributions of groundwater velocity were obtained by applying Darcy's law to ranges of K and ∇h values noted at sites included in the study. Similarly, a probability distribution for C_0 could be estimated from the ranges of maximum historical concentrations. In this case, values of C_{max}, representing maximum measured concentrations, were chosen from the overall C_{max} probability distribution observed in the field data set. For each synthetic plume realization, this value was assumed to represent 10% of the actual boundary concentration, C_0, based on the 10% saturation rule-of-thumb for inferring the presence of DNAPL (Feenstra and Cherry, 1988). Thus the geometric mean value of the C_0 probability distribution is a factor of ten higher than the C_{max} distribution, although the standard deviation is identical.

Ranges of other variables (e.g., Y, Z, R, α_x, α_y, t), while not well-constrained by the database, can be assumed within reason using best professional judgment. The retardation coefficient, R, for example, may be calculated from the relationship,

$$R = 1 + \frac{K_{oc}\, f_{oc}\, r_{b}}{f} \tag{3}$$

where K_{oc} is the organic carbon partitioning coefficient, f_{oc} is the fractional organic carbon content, ρ_b the bulk density, and ϕ the porosity. The probability distribution of f_{oc} could not be determined from the site database because of a paucity of data. However, a probability distribution could be postulated from a published distribution of f_{oc} values observed at a number of field sites (Wiedemeier *et al.*, 1997). First-order degradation rates ranging from $\lambda = 0.7$ to $\lambda = 0.07$ year^{-1}, corresponding to half-lives from 1 year to 10 years, were chosen from an informal survey of reported values in the literature. The survey of reductive dehalogenation rates of TCE by Aronson and Howard (1997) recommends half-lives of 1.2 years to 13.2 years as conservative estimates. Half of the synthetic plumes were assigned degradation rates within this range, while the remainder of the plumes were assigned a degradation rate of $\lambda = 0$ as a control set representing stable CVOCs (representing, for example, the Strong-RD and No-RD groups, as discussed earlier).

5.3 Model Results

The output of the Monte Carlo simulations consisted of a distribution of plume lengths, each corresponding to a unique set of random input variables chosen from the defined probability distributions. A total of 2000 realizations were developed. To mimic the nature of the field data analyses as much as possible, only simulated plumes with lengths falling within the range of observed plume lengths (approximately 100 feet to 10,000 feet) were included in the analysis. To simulate the size of the field data set, 100 plumes were drawn at random from the transforming population and the stable population each. Relationships between plume length and C_{max} (assumed equal to 1/10 the C_0 value for each realization) as well as plume length and specified site groundwater velocity, v, are shown for all synthetic plumes on Figures 9 and 10, respectively. The scatter evident in both relationships illustrates the effect of multiple variables on plume length, even under ideal conditions (uniform groundwater velocity field, Fickian-type dispersion, uniform transformation rate, isotropic two-dimensional aquifer, and constant boundary conditions). The relationship between plume length and C_{max} reproduces the scatter observed in the field data fairly well (Figure 1). In contrast, considerably more scatter is evident in the field data with respect to the plume-length-versus-velocity relationship (Figure 3) than in the simulated plume set. The explanation for this difference is likely to stem from the difficulty in defining a mean site groundwater velocity for a real field site, in contrast to the specified (known) uniform velocities characterizing the synthetic plumes.

Synthetic plume length distributions for transforming and stable CVOC plumes are shown on Figure 11 (top). These results are very similar to analysis of the field data; transformations appear to exert little influence on raw plume lengths above the noise in the data caused by other factors. However, the definition of a plume length index for the synthetic plumes in a manner analogous to the measured plume lengths (Eq. [1]) produces a significant separation of the two probability distributions (Figure 11, bottom). This analysis procedure and the results are consistent with those associated with the field data. The findings thus support the conclusion that source strength and groundwater velocity exert a strong enough influence on plume length to be directly discernible. In contrast, transformation rates are slow enough so that plume length effects cannot be easily identified above the noise associated with plume data without normalization procedures.

Rank-based correlation coefficients quantifying the relationships between plume length, the plume length index, and the various model variables are shown in Table 6. The correlation coefficients indicate the importance of groundwater velocity variability and variability in the boundary concentration in influencing plume length relative to other variables. Dividing plume length by v and C_{max} reduces the effects of these two variables, so that the correlations between other variables such as λ and the plume length index improve. This may explain why the plume length index concept is successful at identifying differences between the plumes from the No RD and Strong RD groups; the indexing procedure improves the correlation of plume extent with the rate of transformation.

6.0 Discussion

This study represents an initial attempt to use historical case analysis to understand plume behavior from a population-oriented perspective. As such, the results should be considered preliminary, with perhaps the principle contribution of the effort being a demonstration of the feasibility of the approach. Among the conclusions that may be drawn from the analyses:

- Broad trends in relationships between plume length and site CVOC variables are consistent with expected physical behavior on a multi-plume scale. This demonstrates that (1) specific hydrogeologic conditions and contaminant release scenarios at individual sites are not so unique that expected overall trends in the data are not completely obscured, and (2) useful average values for site variables such as hydraulic conductivity and groundwater velocity can be quantified in many situations.

- With regard to specific findings, CVOC transformation processes appear exert less of an impact on plume length than source strength and groundwater velocity. At sites where reductive dehalogenation is observed, analyses suggest a common association with fuel hydrocarbon co-

contamination. It is important to recognize, however, that the West Coast-bias in the site representation in the data set may influence these results. For example, sites from the eastern U.S., characterized by higher precipitation and therefore a greater preponderance of vegetation, may be characterized by larger quantities of natural organic carbon which would be available to facilitate reductive dehalogenation. In such instances, the influence of fuel hydrocarbon co-contamination may be less pronounced.

- Probabilistic plume simulation, using a highly idealized analytical plume model, quantitatively reproduces elements of the plume behavior dependencies identified in the field data. This finding suggests the possibility of developing more comprehensive probabilistic simulations that could be used to explore source term and dispersion models for CVOC plume sites, once calibrated against historical case data from multiple sites.

The strength of the conclusions arising from the study are, of course, dependent upon data set characteristics, particularly the representativeness and the quality of the data. It must be noted that the plume length distributions and the types of CVOCs involved are reflective of the 65 sites in the project database exclusively. There is no way of ascertaining whether or not these distributions present an unbiased sample of the entire population of CVOC plumes across the U.S. without conducting a much larger survey on a vast scale. With the data set at hand, it is apparent that there is enormous variability in both plume length and maximum concentration. Thus, it must be stressed that the results of this study are most appropriately applied to groups of plumes, whereas application to individual plumes must always be treated with a high degree of caution.

In summary, this study sets a precedent for future historical case analysis studies that might include:

(1) A more detailed analysis of retardation phenomenon and reductive dehalogenation contingent upon availability of soil TOC data.

(2) A geostatistical analyses of plume spatial moments to include dispersion (in three dimensions) as a variable.

(3) The development of a significantly expanded data set (i.e., hundreds of sites) that would allow subsets of site classes to be evaluated separately and then be compared to one another.

The ultimate goal of such follow-on studies should be to develop a comprehensive statistical model for plume behavior. This statistical model could provide the following benefits:

(1) Individual site investigators with a plume reference model against which a given plume may be compared and used to identify anomalous behavior.

(2) Regulatory agencies with an integrated survey of plume behavior under a variety of conditions

(3) Validation for theoretical models and anecdotal studies of plume behavior within a probabilistic conceptual framework.

7.0 Acknowledgements

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory (LLNL) under Contract W-7405-Eng-48. We wish to thank the members of the LLNL's CVOC Initiative Working Task Force for facilitating data collection and participating in discussions of methodology and findings and the many organizations and individuals fostering the contribution of site data for the project, including in particular the U.S. Department of Defense and the Interstate Technology and Regulatory Cooperation Working Group.

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List of Tables

Table 1. Distribution of sites among U.S. states.

State	No. of sites
California	27
Oregon	10
Ohio	4
South Carolina	4
Idaho	3
Washington	3
Nebraska	2
Pennsylvania	2
Arizona	1
Florida	1
Illinois	1
Kansas	1
Kentucky	1
Missouri	1
New Jersey	1
Tennessee	1
Texas	1
Utah	1

Table 2. Chlorinated hydrocarbon (CVOC) plumes included in study.

CVOC	10 ppb Plumes (from 65 sites)	100 ppb Plumes (from 55 sites)	1000 ppb Plumes (from 30 sites)
TCE	55	37	19
PCE	32	20	8
1,1-DCE	29	17	8
Cis-1,2-DCE	29	17	7
1,1,1-TCA	23	16	9
Vinyl chloride	20	10	4
1,1-DCA	18	10	2
Chloroform	8	1	0
Trans-1,2-DCE	8	0	0
Carbon tetrachloride	7	2	1
1,1,2-TCA	6	0	0
1,2-DCA	6	2	0
Chloroethane	2	1	0
Chloromethane	2	0	0
Methylene chloride	1	1	0
1,1,2,2-TCA	1	0	0
TOTAL	247	134	58

Table 3. Probability distributions of *maximum* CVOC plume lengths per site, based on minimum concentration contour definition.

Quantile	10-ppb-Defined Plumes	100-ppb-Defined Plumes	1000-ppb-Defined Plumes
10th	420 ft	250 ft	90 ft
	(128 m)	(76 m)	(27 m)
25th	790 ft	500 ft	230 ft
	(241 m)	(152 m)	(70 m)
50th	1,600 ft	1,100 ft	650 ft
	(488 m)	(335 m)	(198 m)
75th	3,210 ft	2,400 ft	1,830 ft
	(979 m)	(732 m)	(558 m)
90th	6,030 ft	4,840 ft	4,630 ft
	(1,838 m)	(1,476 m)	(1,412 m)

Table 4. Site median concentrations of geochemical indicator compounds from sites representing different reductive dehalogenation groups.

	90th percentiles			
Geochemical Indicator Species	No RD	Weak RD	Strong RD	Student t-test p-values (log-transformed concentrations); No RD vs. Strong RD groups
Cl^- (mg/L)	120	162	310	0.30
Mn^{2+} (μg/L)	130	420	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 5. Transport model parameter probability distributions.

Parameter	Distribution	Basis
Maximum concentration (ppb), C_0	Lognormal. 10th-percentile: 29 90th-percentile: 23,750	Lognormal distribution fit to observations, uniformly multiplied by 10.
Source area width (ft), Y	Uniform. 5-60	Postulated.
Source area depth (ft), Z	Uniform. 5-60	Postulated.
Hydraulic conductivity (ft/day), K	Lognormal. 10th-percentile: 0.19 90th-percentile: 246	Lognormal observations fit to geometric mean values from each site[1].
Hydraulic gradient, ∇h	Lognormal. 10th-percentile: 0.0011 90th-percentile: 0.0614	Lognormal observations fit to reported values from each site
Porosity, ϕ	Normal. 0.25 ± 0.03	Postulated.
Fractional soil organic carbon, f_{oc}	Lognormal. 10th-percentile: 0.01% 90th-percentile: 1%	Postulated.
Transformation half-life (yrs), $t_{1/2}$	Uniform. 1-10	Postulated; based on an informal review of literature values.
Ratio of longitudinal dispersivity, α_x, to plume length	Lognormal. 10th-percentile: 0.033 90th-percentile: 0.33	Postulated; based on the common assumption of the ratio of α_x to plume length ~ 10%.
Ratio of longitudinal dispersivity, α_y, to plume length	Lognormal. 10th-percentile: 0.0033 90th-percentile: 0.033	Postulated; based on the common assumption of the ratio of α_y to α_x ~ 10%.
Ratio of longitudinal dispersivity, α_z, to plume length	Lognormal. 10th-percentile: 1.67×10^{-3} 90th-percentile: 1.67×10^{-2}	Postulated.
Elapsed time since release (yrs), t	Uniform. 10-50	Postulated; informally based on typical reported site use histories.

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[1] Based on reported pumping test or slug test results.

Table 6. Rank correlation coefficients (Spearman's r) between simulated plume length and plume length indices and model variables.

	Rank correlation with respect to L		Rank correlation with respect to PLI	
Variable	r	p	r	p
Groundwater velocity, v	0.73	1.3×10^{-17}	–	–
Maximum concentration, C_{max}	0.32	0.001	–	–
Retardation coefficient, R	-0.20	0.05	-0.32	0.001
Ratio of vertical dispersivity to plume length, α_z:L	-0.20	0.05	0.06	0.57
First-order degradation coefficient, λ	-0.12	0.22	-0.21	0.03
Ratio of longitudinal dispersivity to plume length, α_x:L	0.06	0.54	0.15	0.14
Transverse extent of source area, Y	-0.04	0.73	0.25	0.01
Vertical extent of source area, Z	-0.04	0.70	0.18	0.08
Ratio of transverse dispersivity to plume length, α_y:L	-0.01	0.94	-0.16	0.12
Elapsed time since source term initiation, t	0.00	0.97	-0.01	0.89

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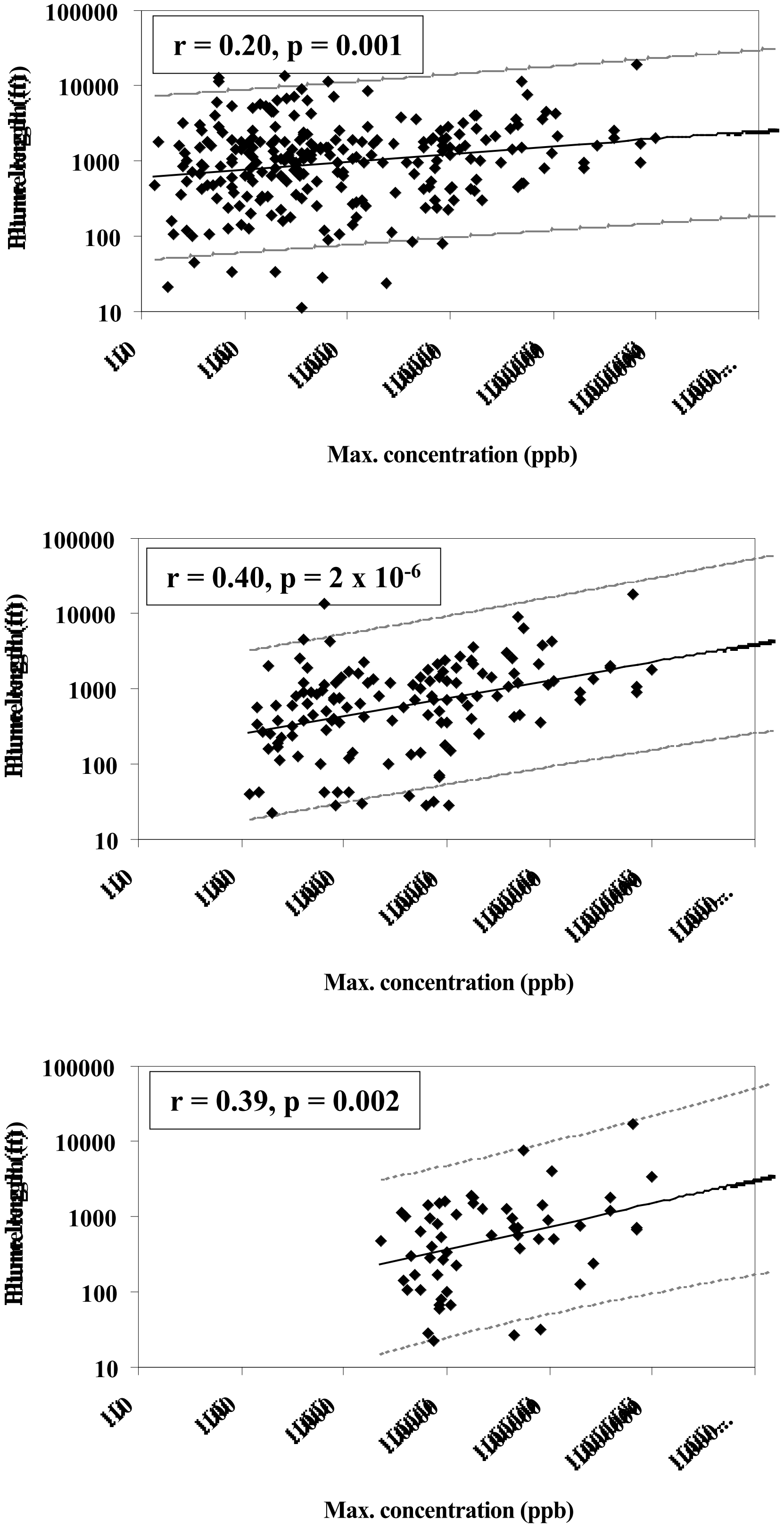


Figure 1. Correlation between log plume length and log maximum historical concentration (per CVOC) for 10-ppb-defined plumes (top), 100-ppb-defined plumes (middle), and 1000-ppb-defined plumes (bottom). The correlation coefficient, *r*, is based on linear regression of the log-transformed values, the null hypothesis probability (i.e., the likelihood that the slope does not differ significantly from zero) is indicated by the *p*-value. Dashed lines denote the 95% prediction confidence band.

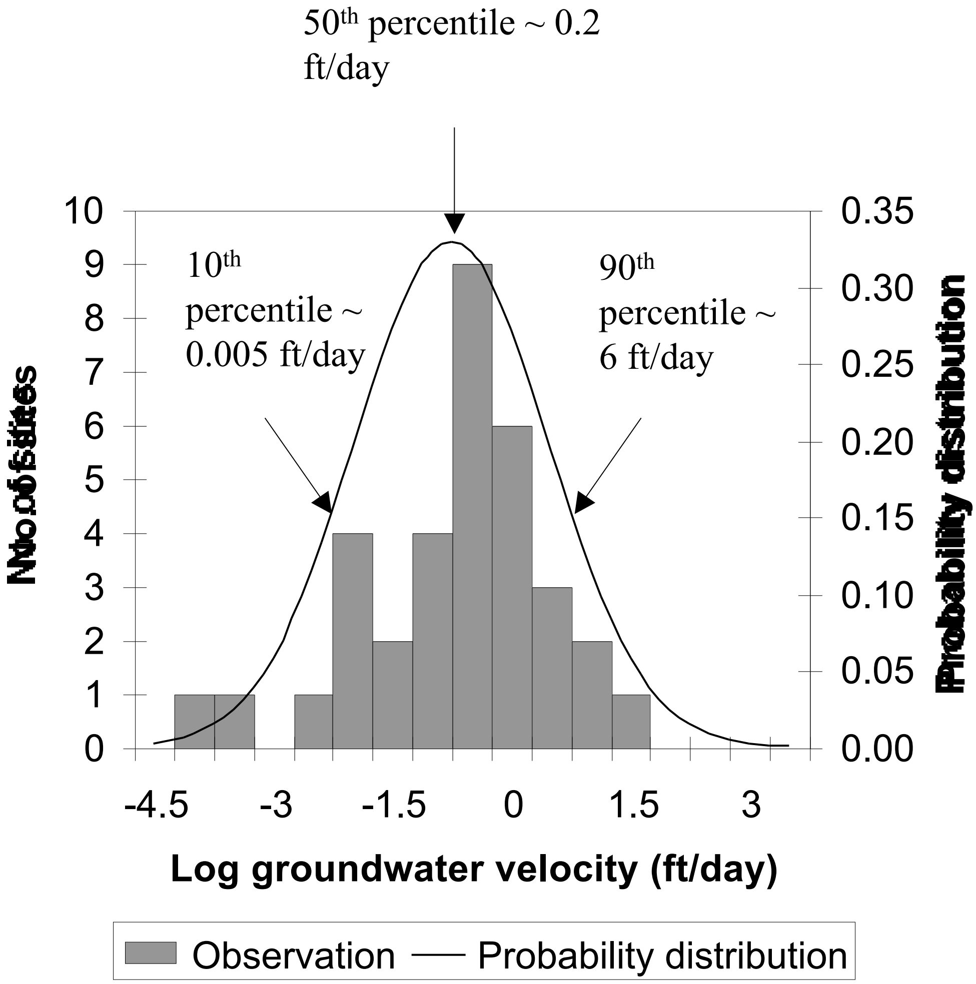


Figure 2. Histogram and best-fit lognormal probability distribution of groundwater velocities from the 34 sites that provided hydraulic conductivity and gradient estimates.

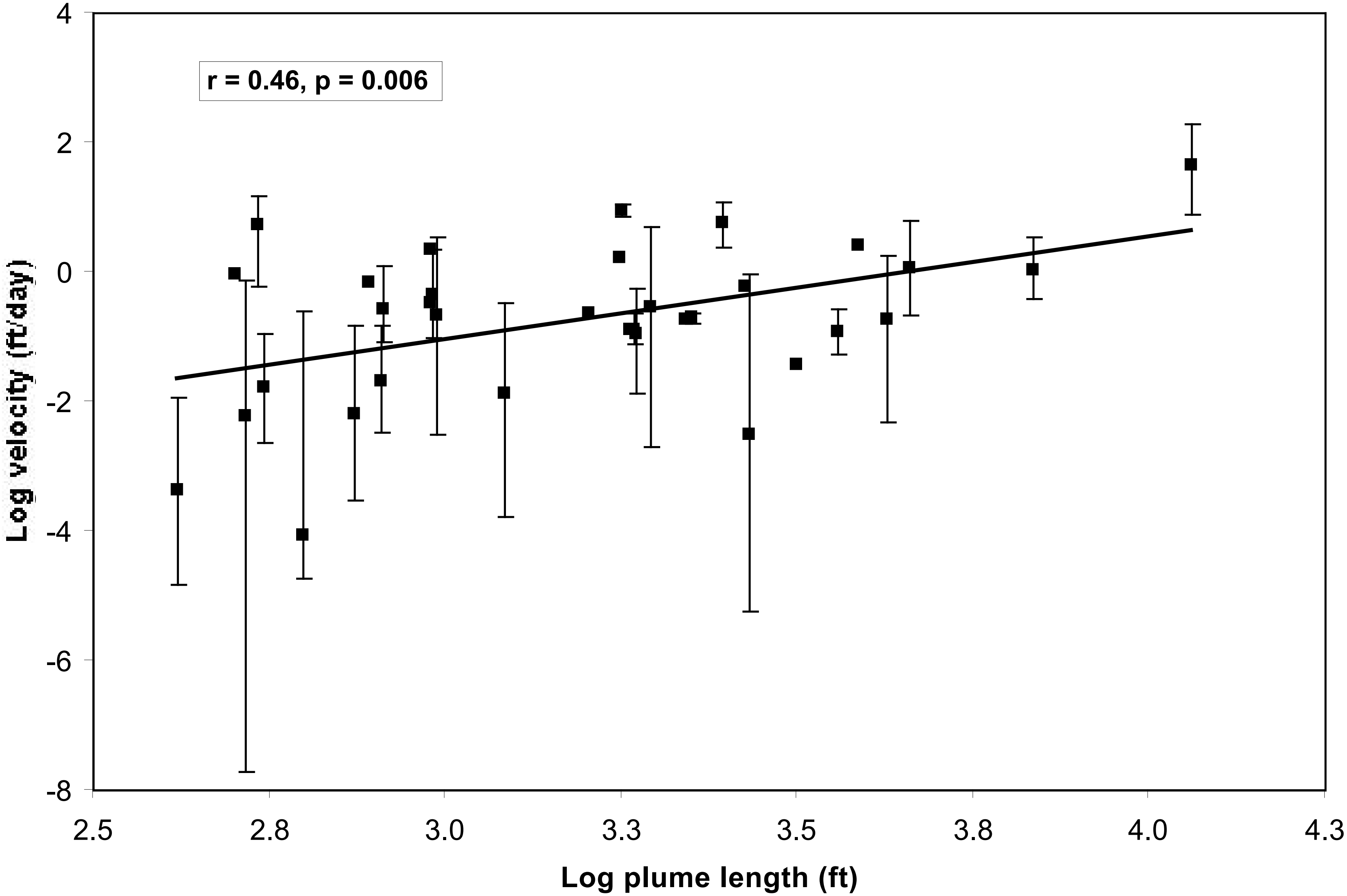


Figure 3. **Relationship between log maximum plume length per site and mean log site groundwater velocity (square symbols), with uncertainty bars showing ranges of velocity calculated from site-specific minimum and maximum hydraulic conductivity values. The independent variable, log groundwater velocity,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

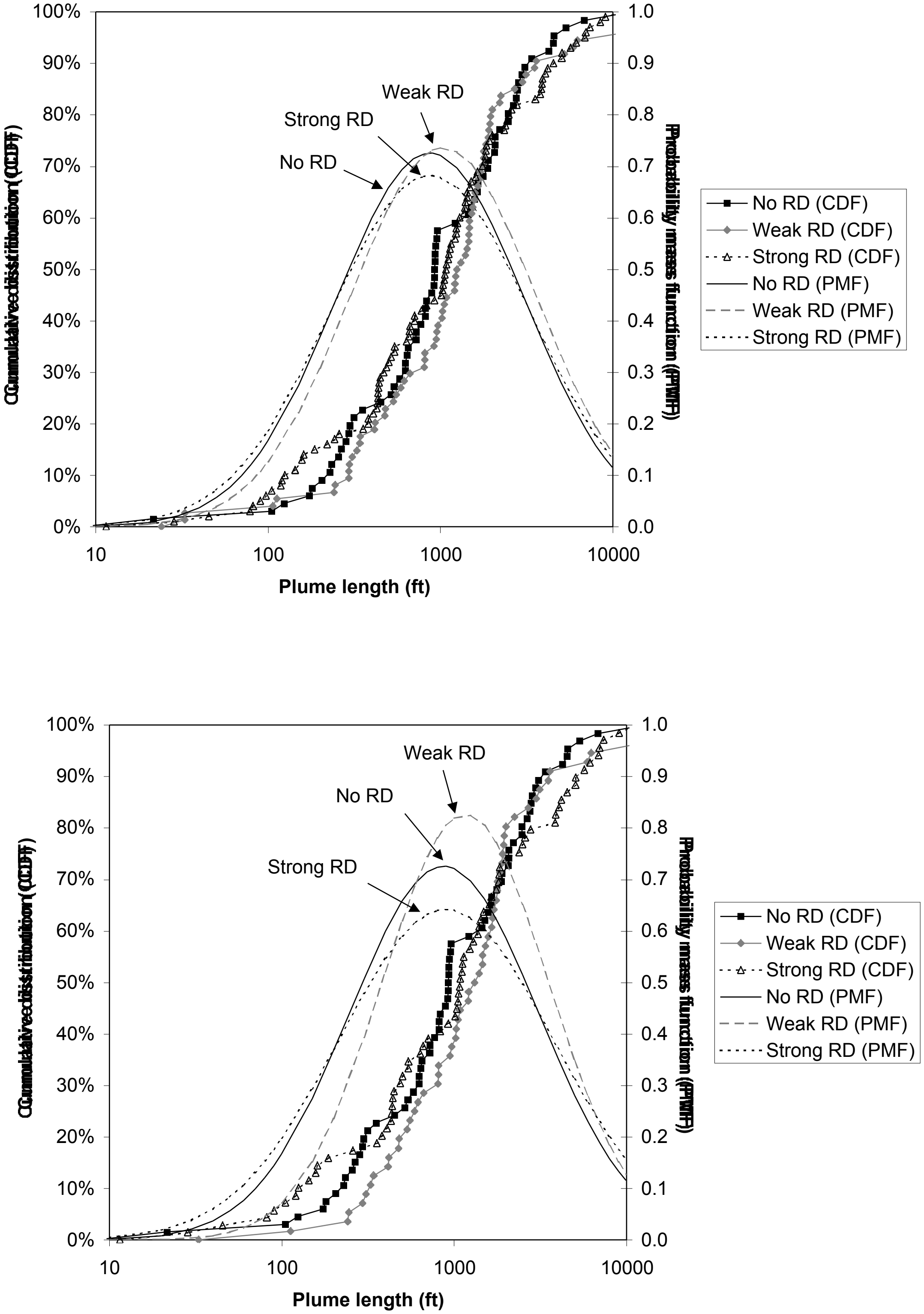


Figure 4. Cumulative distributions of plumes lengths from sites exhibiting no evidence of reductive dehalogenation, weak evidence, and strong evidence, all CVOCs from each site (top) and CVOCs exclusive of cis-1,2-DCE and vinyl chloride daughter products (bottom). Frequency distributions determined by a best-fit lognormal distribution model are indicated on the second y-axis.

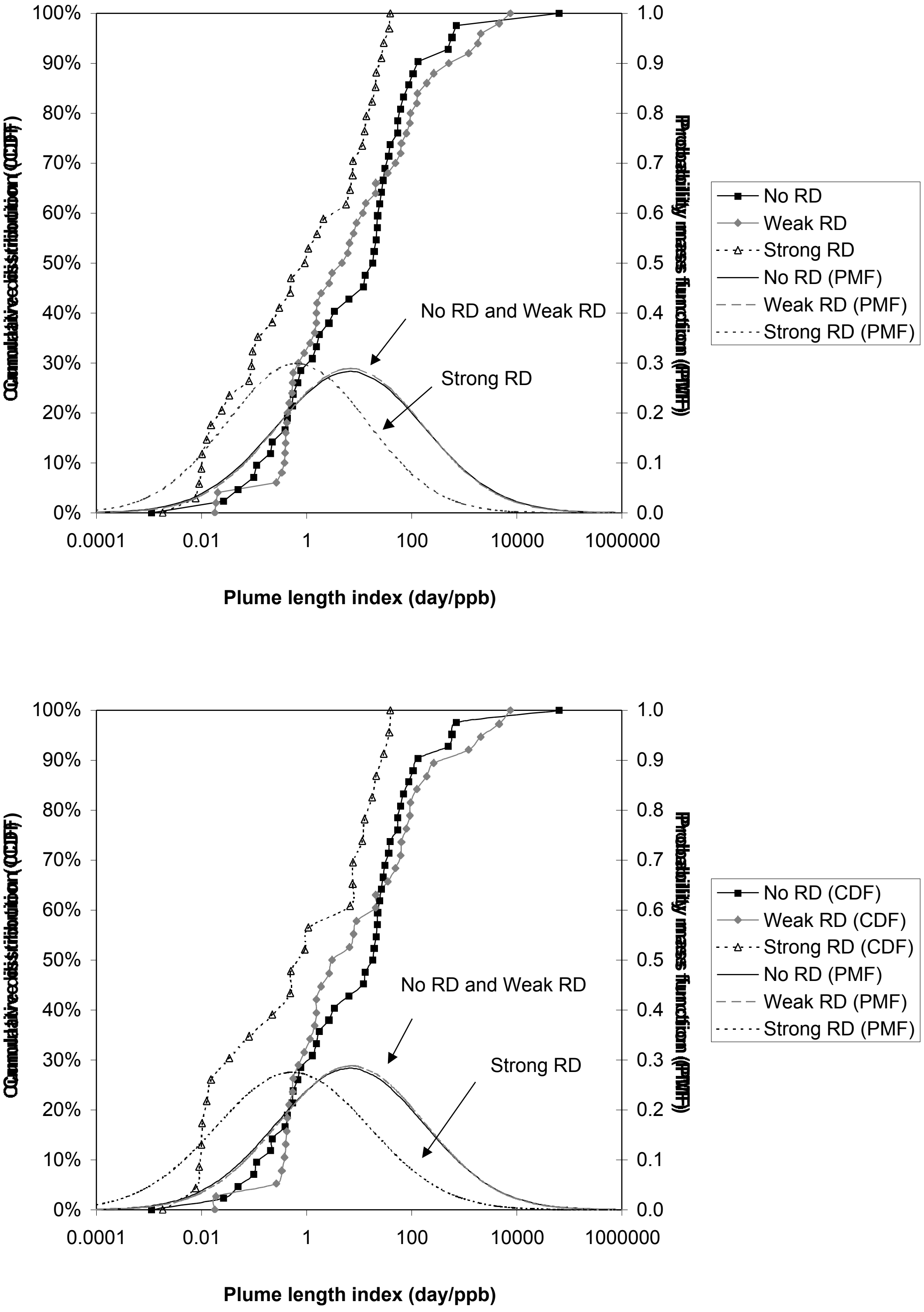


Figure 5. Cumulative distributions of plumes length indices from sites exhibiting no evidence of reductive dehalogenation, weak evidence, and strong evidence, all CVOCs from each site (top) and CVOCs exclusive of cis-1,2-DCE and vinyl chloride daughter products (bottom). Frequency distributions determined by a best-fit lognormal distribution model are indicated on the second y-axis.

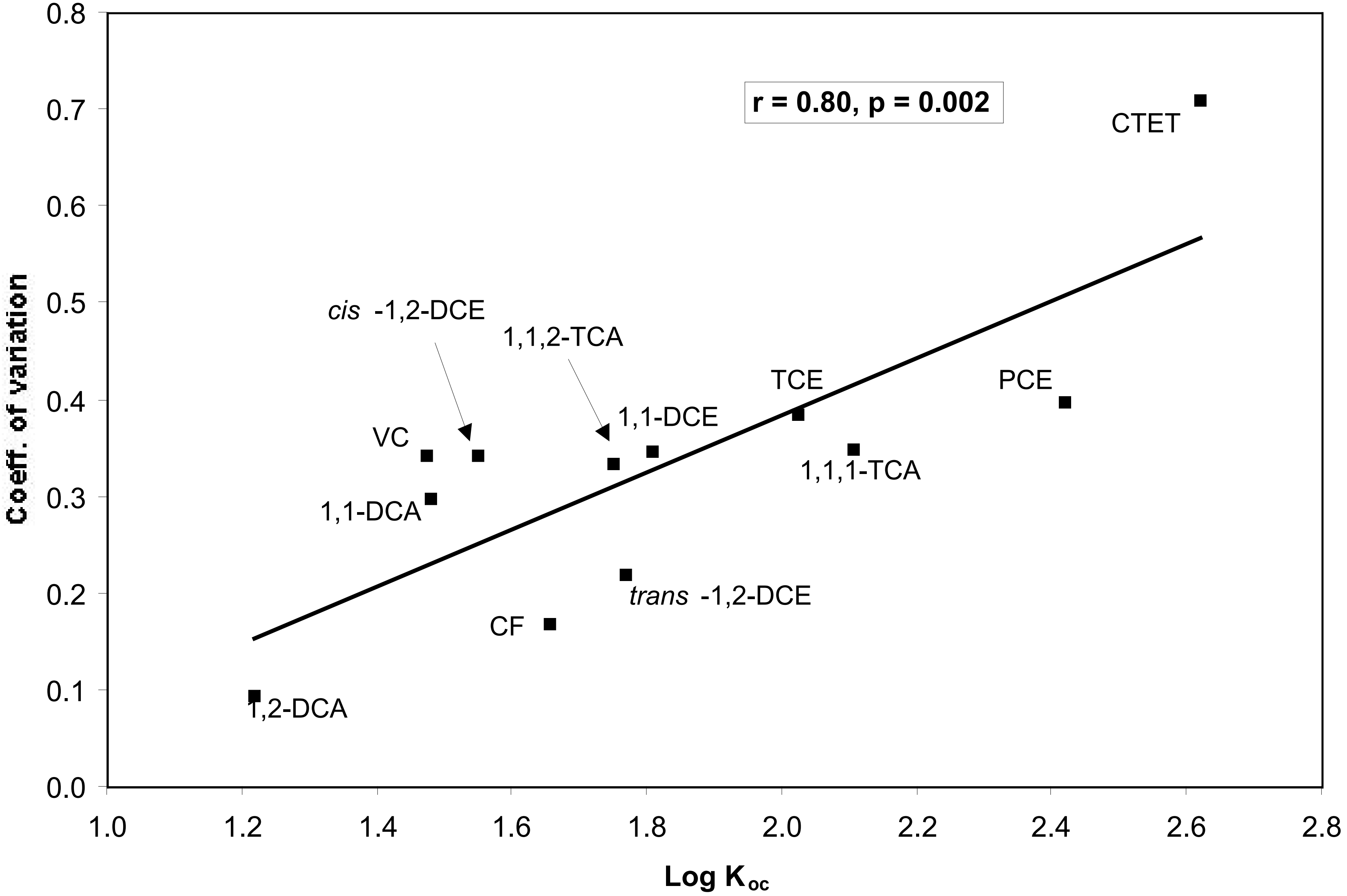


Figure 6. Relationship between the coefficient of variation in maximum historical concentration between sites and the organic carbon partitioning coefficient for CVOCs represented by six or more plumes.

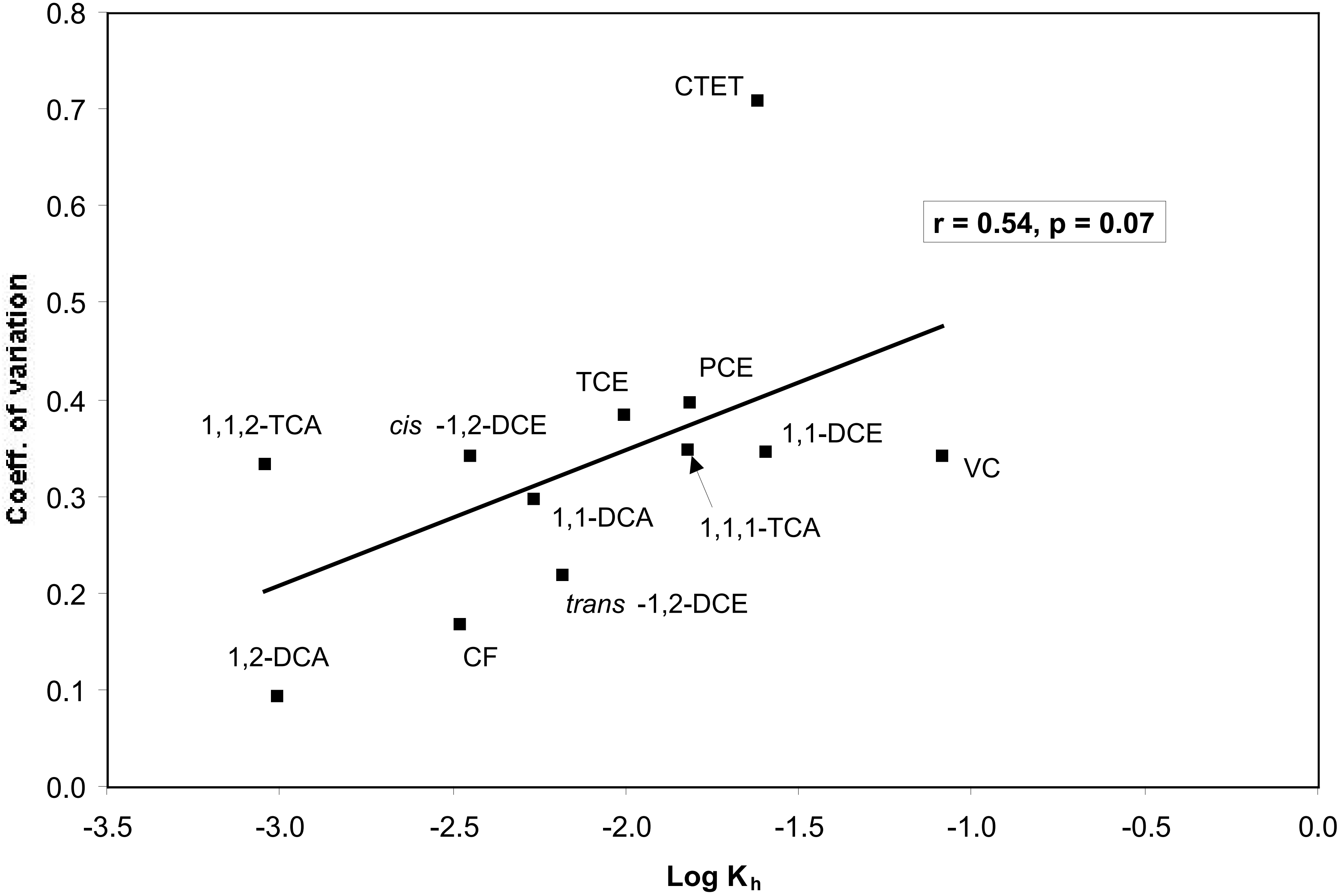


Figure 7. Relationship between the coefficient of variation in maximum historical concentration between sites and the Henry's constant for CVOCs represented by six or more plumes.

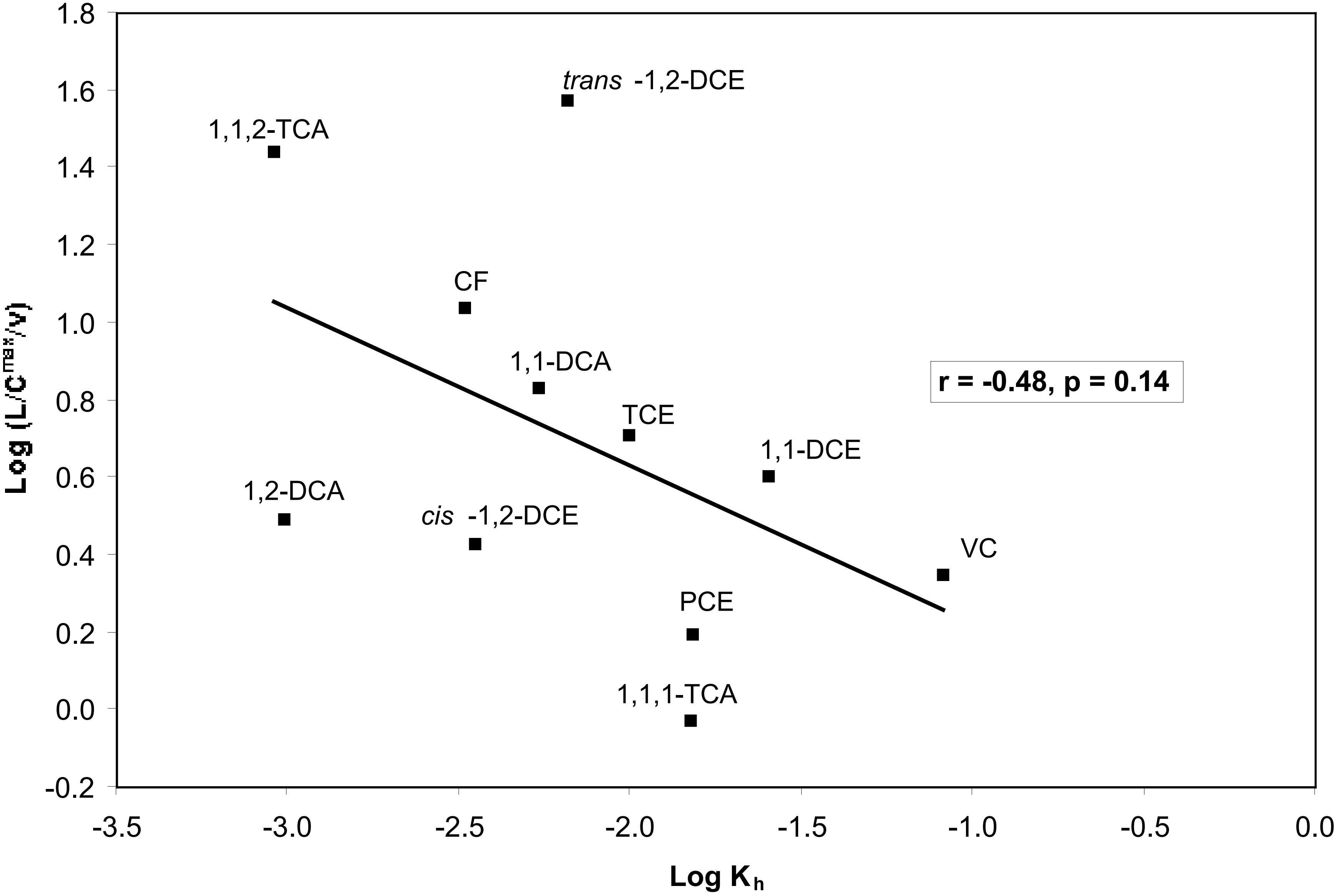


Figure 8. Relationship between the mean of the log plume length indices and the Henry's constant for CVOCs represented by three or more plumes.

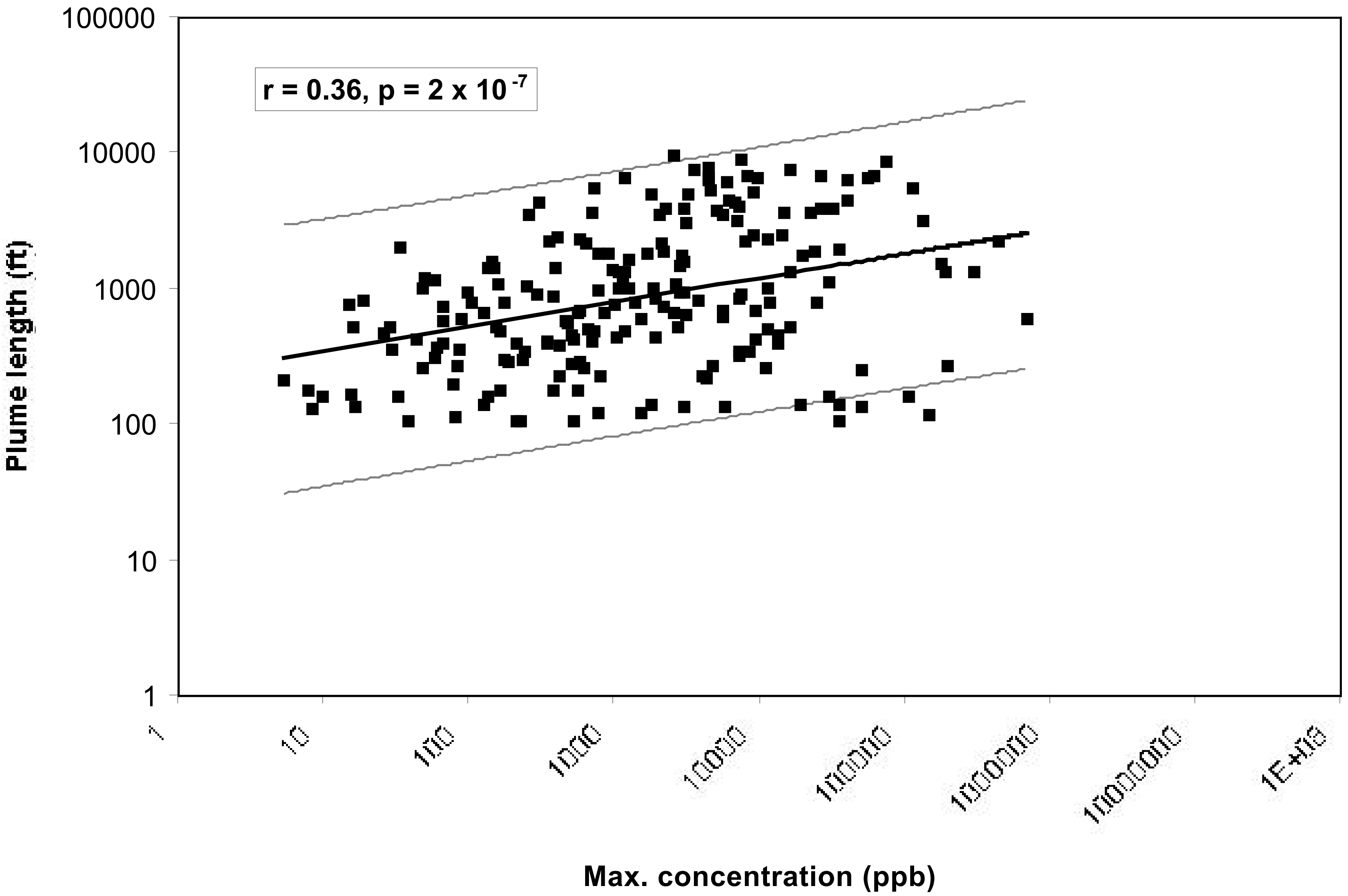


Figure 9. Relationship between log plume length and log C_{max} for the synthetic 10-ppb plume population. Dashed lines denote the 95% prediction confidence band.

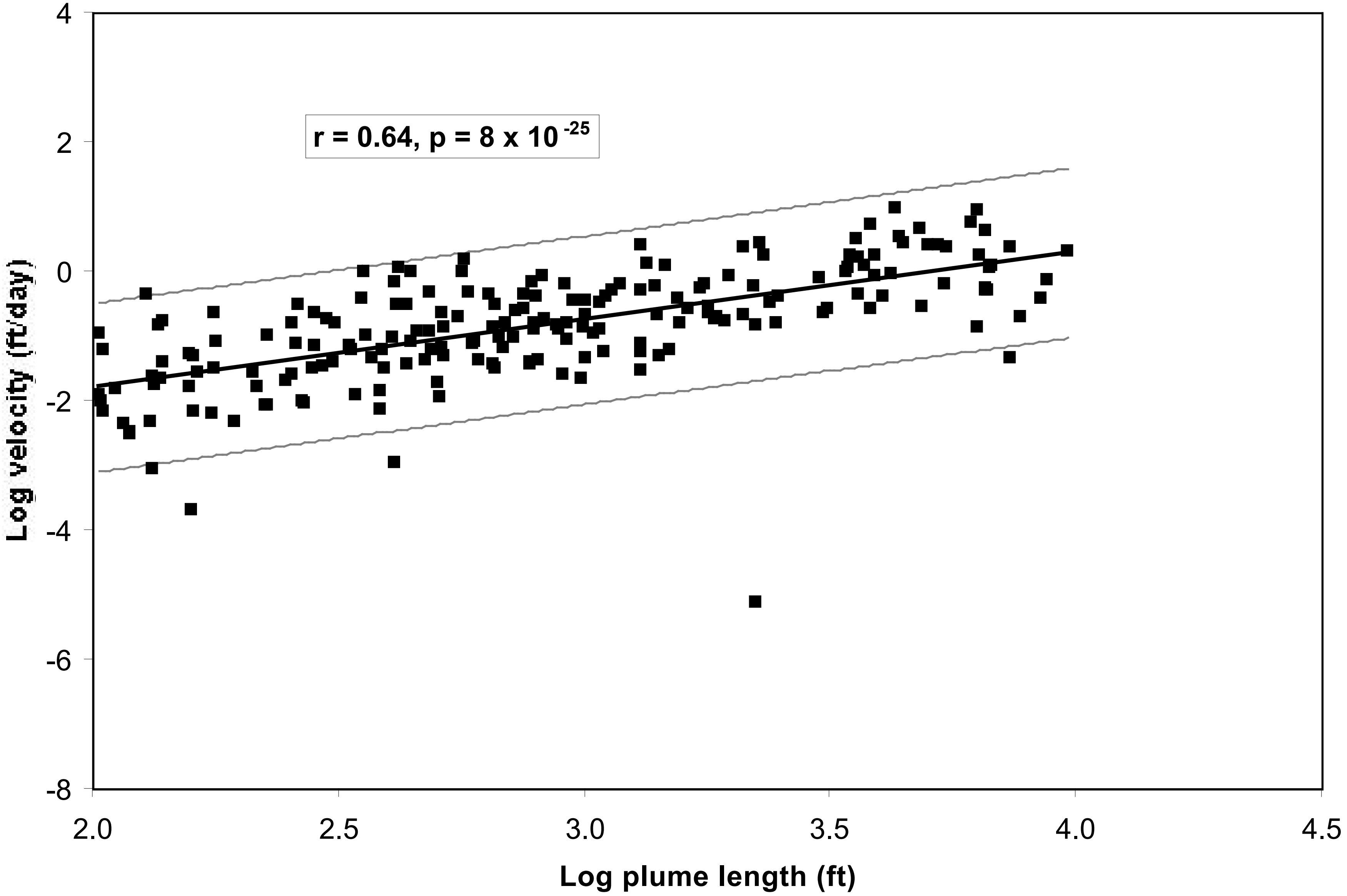
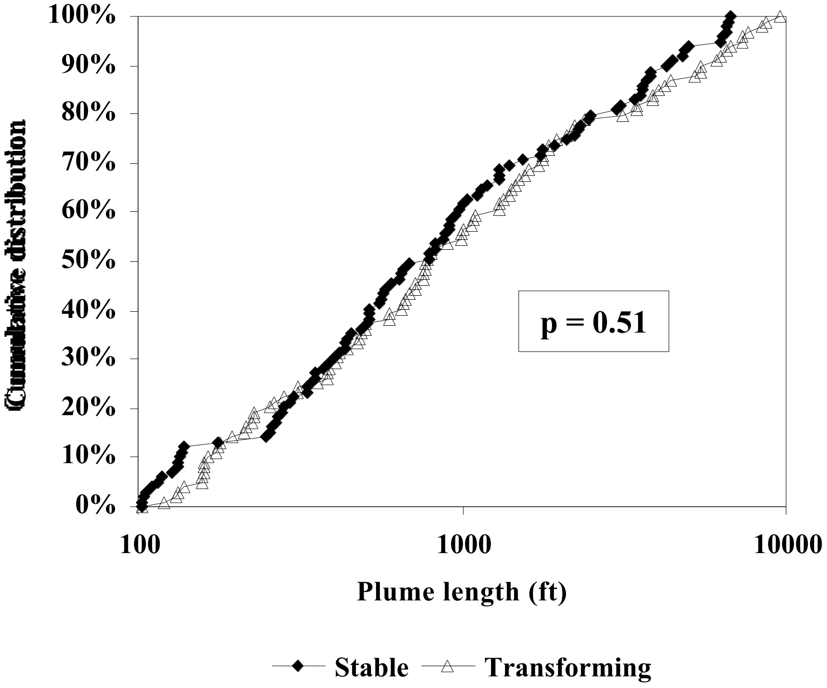


Figure 10. Relationship between log plume length and log specified *v* from the synthetic plume. The independent variable, log *v*, is plotted on the y-axis to maintain consistency with Figure 3. Dashed lines denote the 95% prediction confidence band.



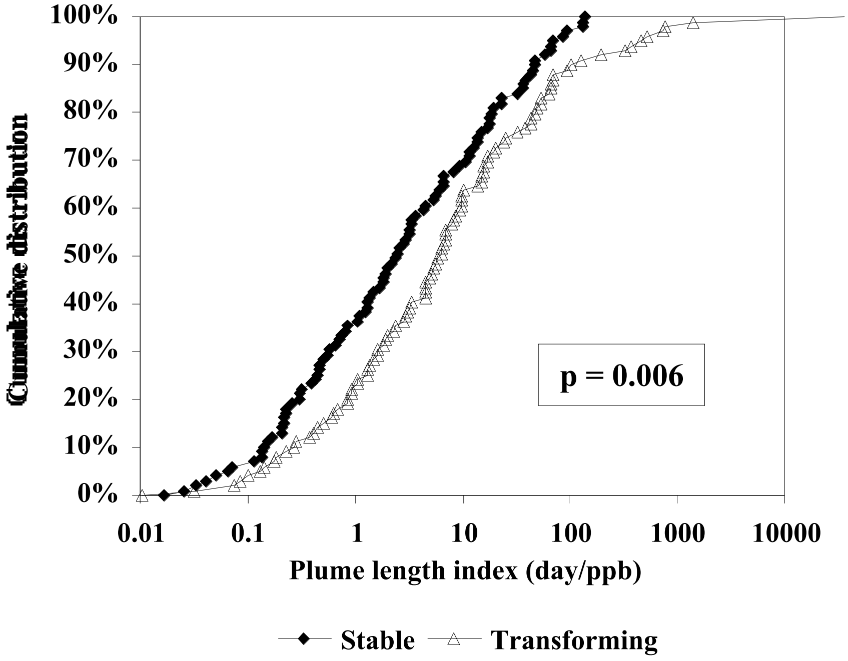


Figure 11. Cumulative distributions of plume lengths for synthetic stable and transforming plumes (top), and distributions of plume length indices (bottom). P-values refer to the null hypothesis probability (i.e. the probability that the two data sets have equal geometric means).