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# Historical Case Analysis of Chlorinated Volatile Organic Compound Plumes

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## March 8, 1999

1 Technion-Israel Institute of Technology
2 Savannah River Technology Center
3 Lawrence Berkeley National Laboratory
4 San Francisco Bay Regional Water Quality Control Board
5 U.S. Department of Energy
6 U.S. Air Force Center for Environmental Excellence
7 Private Consultant
8 University of Waterloo
9 Oregon Department of Environmental Quality
10 University of California, Berkeley
11 U.S. Naval Facilities Engineering Command
12 California State Water Resources Control Board

# Environmental Protection Department

**Environmental Restoration Division**

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# Preface

There are several national initiatives that continue to re-evaluate chlorinated volatile organic compound (CVOC) cleanup processes. These include efforts by the United States Environmental Protection Agency (US EPA) to reconsider the manner in which CVOC toxicity factors are developed; efforts by many investigators to evaluate the mechanisms and impacts of natural attenuation at individual sites; and efforts by the Department of Energy (DOE), the Department of Defense (DOD), and the US EPA to evaluate the use of enhanced natural attenuation during CVOC cleanup and to demonstrate new remediation technologies. Missing from these initiatives is a cross-cutting evaluation of the large amounts of CVOC historical case data that are available.

This document describes the findings and conclusions resulting from a study of nationwide historical case data gathered from sites with groundwater contaminated by CVOCs. The purpose of this initiative (the "Initiative") is to use a statistical perspective and data from multiple sites to evaluate the hydrogeologic, biogeochemical, and physiochemical factors affecting the extent and growth behavior of CVOC plumes in groundwater. This evaluation is important because of the significant role that plume behavior plays in the management of human health, environmental decision making, and resource risk evaluation.

The CVOC Initiative is a cooperative partnership between a variety of organizations and agencies involved in the cleanup of CVOC plumes. The Environmental Council of States, Interstate Technology and Regulatory Cooperation (ITRC) working group serves as a link to state regulatory bodies. The US EPA, DOE, US Navy, US Air Force, industry, and ITRC member states have provided CVOC historical case data in support of this Initiative.

The data management, statistical analysis, and modeling efforts conducted within the framework of the Initiative were performed by a team of scientists and environmental professionals from Lawrence Livermore National Laboratory (LLNL), Lawrence Berkeley National Laboratory (LBNL), and Savannah River Technology Center (SRTC). On behalf of DOE, LLNL has served as the overall Initiative Coordinator. Throughout the project, ITRC member states have been regarded as the appropriate entities to consider the development of any recommendations that would be warranted on the basis of the scientific evaluation of the historical case data, as presented here.

As part of this Initiative, two groups were formed: a Working Task Force (WTF) and a Peer Review Panel (PeerRP). The WTF focused on the technical issues of historical CVOC case data collection and analysis as well as preparing draft findings and conclusions based on the data analysis. The PeerRP was called upon to review key deliverables, raise technical issues, and review and comment on draft findings, conclusions, and recommendations. The members of the WTF are:

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# Executive Summary

## Overview of the Study

Knowledge about 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. By analyzing populations of plumes, likely CVOC plume behavior scenarios can be better understood.

The present study represents an attempt to understand the factors affecting the behavior of CVOC plumes in groundwater from a broad, statistically oriented perspective. One of the key issues in using historical case data is the often-unknown quality of the data, and yet these data are typically used as the basis for site cleanup decision making. Thus, a key goal of this study is to evaluate a large population of historical CVOC case data and evaluate which aspects of CVOC plume behavior and CVOC risk management can be supported by historical case data. 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 characteristics can be identified, albeit on a statistical basis. As such, the general findings of this study are not necessarily applicable to any individual site. However, managers of specific sites will benefit from the analysis and its conclusions, as their understanding of plume behavior is enhanced through an examination of data from many sites. It is believed that focusing on the major factors influencing plume behavior will increase the efficiency of planning site investigation and cleanup operations.

Specifically, the following general questions involving the applicability of historical case data to CVOC risk management are addressed:

1. Can historical case data be used to predict CVOC plume behavior?
2. What are key uncertainties associated with evaluating CVOC plume behavior using historical case data and what other types of data are needed?
3. How may CVOC historical case analysis be used in CVOC cleanup decision-making?

A number of more specific questions of interest to researchers and managers of CVOC cleanup regarding the factors that are related to CVOC plume behavior are also addressed by this study. These questions include:

4. How often is a dense non-aqueous phase liquid (DNAPL) inferred to be present at sites within the CVOC historical data set and what is the relationship of inferred DNAPL presence to the plume length at a given site?
5. How often are transformation processes encountered in CVOC plumes in the data set and what are the relationships between the indications of transformations and plume length?
6. Do daughter product plumes behave differently compared to parent CVOC plumes?

7. What is the relationship of fuel hydrocarbon co-contamination to CVOC plume behavior?

## Methodology

The primary analysis approach during this study was 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 using correlation analyses and population inference tests. To conduct the study, procedures for data collection and analysis included the following specific tasks:

1. Candidate sites were screened using a site checklist. Sites were accepted for inclusion in the study if: (a) data were available from at least six monitoring wells over a three-year monitoring period prior to remediation, (b) site plumes did not significantly daylight, (c) site 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 and was accepted in the study, CVOC historical monitoring data were obtained electronically, and hydrogeologic data were extracted from site reports.
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, a representative mean site value was quantified by utilizing the geometric mean of values reported for individual monitoring wells through pumping tests or slug tests. 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, plume length and plume length growth rate, were estimated for all individual CVOCs at each site in the study. Plume lengths were estimated using an algorithm that used CVOC concentration data to systematically quantify the distance from the location of the reported maximum CVOC concentration in a plume to a distal 10-ppb, 100-ppb, or 1000-ppb contour. Relative plume growth rates were estimated on an individual CVOC basis using time-series analysis of plume data from individual sites.
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.
5. Probabilistic plume modeling was employed to provide a mathematical conceptual framework 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 to the statistical reasoning used during the analyses of the CVOC field data. Agreements between the two approaches provided validation of the study findings.

The study involved the collection and analysis of data from 65 sites representing a variety of hydrogeologic settings and release scenarios (e.g., large industrial facilities, dry cleaners, and landfills). Data collection involved a variety of federal and state agencies and included participation from the U.S. Department of Defense, the Department of Energy, and private industry. Plumes were defined per CVOC per site, yielding a total of 247 plumes delineated by the 10-ppb contour and subsets of 134 plumes and 58 plumes delineated by the 100- and 1000-ppb contours, respectively. A total of 16 different CVOCs were included in the study.

## Findings

An evaluation of the CVOC historical case data collected to date found the following general characteristics:

- The contaminant chemistry was generally found to be the most complete of the data types reviewed. Data on hydraulic conductivity and organic carbon content of soils and groundwater were less systematically collected and/or reported. Theoretically, these parameters should be key to understanding the fate and transport of subsurface contaminants.
- As an aggregate population, CVOC plume lengths are approximately lognormally distributed, although with some deviations. In particular, the frequency of small plume lengths appears to be under-represented in this data set based on a lognormal probability distribution model.
- Among the sites in this study, the longest CVOC plume lengths from each site are also lognormally distributed. Among these plumes, the median CVOC plume length was approximately 1600 ft, and 90% of the CVOC plumes in this study were less than approximately 6300 ft in length.
- There are no statistically significant differences between CVOC species with regard to their log-transformed 10-ppb plume lengths, including likely transformation daughter products such as *cis*-1,2-DCE and vinyl chloride.

Correlation analysis and population inference tests revealed a number of trends in the field data. These include:

- Plume lengths are positively correlated with maximum historical CVOC concentrations and mean groundwater velocity at each site.
- Based on the observed maximum historical concentrations, approximately 40% of the TCE plumes may be associated with DNAPL based on a 1% solubility limit rule-of-thumb, and approximately 10% of the TCE plumes may be associated with a DNAPL based on a 10% rule-of-thumb. Based on these solubility limit rules-of-thumb, the presence of DNAPL is suggested in a majority of cases where a 1000-ppb TCE plume can be defined.
- The effects of reductive dehalogenation on the plume length are measurable, but only when the influences of source area mass (maximum groundwater concentration) and groundwater velocity are factored out. Plume lengths adjusted for these variables are shorter when there is strong evidence of reductive dehalogenation. These results suggest

that the role of transformation processes in influencing CVOC plume lengths is relatively subtle. There is also evidence that plumes at sites exhibiting strong reductive dehalogenation show less plume growth than those from other sites.

- Large daughter product plumes do not commonly extend a large distance downgradient of the parent product plumes.
- The statistical association between fuel hydrocarbons, elevated bicarbonate alkalinity, and the presence of vinyl chloride plumes provides circumstantial evidence that fuel hydrocarbon co-contamination may be an important factor in the reductive dehalogenation of CVOC plumes in the historical case analysis data set. Elevated manganese concentrations at sites with vinyl chloride plumes is consistent with the presence of an anaerobic environment at these sites.
- Variability in maximum concentration between sites is positively correlated with literature derived CVOC-specific organic carbon partitioning coefficients. In addition, some positive correlation may exist between the Henry's Law constant and variability in maximum concentration between sites. Furthermore, there is a possible correlation between plume length and the Henry's constant once factors such as source strength and groundwater velocity are factored out. Although these relationships are statistically significant and are consistent with idealized conceptualizations of plume behavior, these results must be viewed as preliminary in nature. Further studies must be conducted to independently confirm these observations.

Monte Carlo simulation, using an analytical plume model and inferred probability distributions of hydrogeologic variables, was used to generate populations of synthetic plumes. Application of the same analytical approaches used for the field data to the synthetic plume data, yielded similar results in terms of plume length relationships.

## Conclusions

This study provides the first statistical analysis of data from a relatively large population of CVOC plumes. From this analysis, the following conclusions result:

- This study demonstrates that broad trends in relationships between plume behavior and key site variables can be determined through the statistical analyses of historical field data from a large number of sites. This finding is important because it 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 completely obscured, and (2) useful average values for site variables such as hydraulic conductivity and groundwater velocity can be quantified in most situations.
- This study also shows that statistical methods, such as general linear models and comparison of probability distributions of plume length indices[1], are useful to quantify expected relationships between plume length and site and CVOC variables within a population of CVOC plumes. In addition, they provide population statistics that may be used to bound the uncertainty inherent in expected plume behaviors.

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1 Plume length index is defined as the plume length divided by the groundwater velocity and by the maximum groundwater concentration of the contaminant.

- This study provides quantitative confirmations that plume behaviors can be grouped and that these groupings are based on expected hydrogeologic processes.
- One of the major features of this study is that its analyses and conclusions are based primarily on actual field observations, i.e., data from actual CVOC plume historical cases. At present, there is no evidence that the historical case data can be used predictively outside the range of data reviewed. The strength of the conclusions arising from statistical analyses of the CVOC data are dependent upon data set characteristics, particularly the representativeness and the quality of the data. It must be noted that the plume length distributions, relative plume growth rates, 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. As more data are added to the CVOC historical data set, representativeness will be enhanced.
- Based on the rules-of-thumb as indicators of free-phase CVOCs, the results of this study suggest that the DNAPL may be influencing plume behavior to a certain extent, although, not in the case of daughter product species, e.g., *cis*-1,2-DCE, vinyl chloride, and possibly 1,1-DCA and 1,1-DCE in some cases. It must be emphasized that these inferences are based entirely on very general rules-of-thumb that have been established in the contaminant hydrology literature. In reality, there is no direct way of ascertaining whether or not DNAPLs are present at the sites given the data provided for this study. However, the relationships between plume length and reported maximum concentration are likely to reflect the overall strength of the source term, which may in turn be influenced by the presence or absence of DNAPL as well as the capacity for any residual DNAPL to be actively leached into groundwater.
- An important conclusion of this study is that the presence of a vinyl chloride plume indicates that reductive dehalogenation may be playing a role in reducing the extent of CVOC plumes at approximately one-third of the sites examined. In contrast, the presence of a *cis*-1,2-DCE plume in the absence of a vinyl chloride plume appears to indicate reductive dehalogenation rates that are insufficient to effectively reduce the extent of CVOC plumes at a site. Little evidence was found in the data to suggest that plume lengths and plume growth rates are substantially affected by reductive dehalogenation in these circumstances.
- Another important conclusion is that CVOC transformation rates through dehalogenation exert less impact on plume length than source strength and groundwater velocity. Thus, plumes with weaker source strength and slower groundwater velocities may be better candidates for the application of natural attenuation remedies.
- The statistical results of the CVOC historical case analysis suggest that the association between fuel hydrocarbons and reductive dehalogenation may be widespread. 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.

## Discussion and Recommendations for Future Work

It is clear that variability is a fundamental characteristic of CVOC sites and that conclusions stemming from the current study are general and should not be strictly applicable at any specific site. Although the emphasis in this study is on examining correlations between plume length and hydrogeologic variables, it is apparent that there is enormous variability in both plume length and maximum concentration.

Continued data collection is recommended because a more comprehensive data set would shed light on some of the questions not answered completely in this present study. These questions include:

- Are there significant differences in plume behavior across different geographic hydrogeologic regimes (e.g., as specified in Heath, 1984)?
- Is there a dependence of plume behavior on climatic factors such as mean annual rainfall, evapotranspiration rate, or vegetative cover at the site?
- What is the quantification of statistical relationships between site natural organic carbon content and (1) retardation of plume length or normalized plume length and (2) reductive dehalogenation? With regard to reductive dehalogenation in particular, a comparison of the roles of natural organic carbon and anthropogenic carbon sources (e.g., fuel hydrocarbons) would be of significant interest.
- Are there differences in the relationships of plume behavior to site variables, particularly the classes of plumes specifically excluded from this study, e.g., plumes that daylight. The use of exclusion criteria may systematically under-represent very short and very long plumes in the data set.

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

1. A more detailed analysis of retardation phenomena contingent upon availability of soil organic carbon data.
2. Geostatistical analyses of plume spatial moments to include dispersion (in three dimensions) as a variable.
3. Development of a significantly expanded data set (i.e., hundreds of sites) which 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:

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.

The results of this historical case analyses may be used by a site manager to develop initial site conceptual models and help focus characterization resources on data that will be most useful in confirming or denying conceptual model hypotheses. In addition, the study provides information on the types of data that are not currently being collected that should be collected in the future, e.g., organic carbon analysis.