HISTORICAL CASE ANALYSIS OF CHLORINATED VOLATILE ORGANIC COMPOUND PLUMES

PEER REVIEW PANEL REPORT

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Dear Sirs:

We are members of the Peer Review Panel formed as part of the *Initiative to Improve VOC Cleanup Process by Using Historical Case Analysis*. Our role has been to "review key deliverables, raise technical issues, and review and comment on draft findings and conclusions, and any recommendations." As such we reviewed plans for the analysis, reports of progress, draft copies of the final report, and now the final report titled, *Historical Case Analysis of Chlorinated Volatile Organic Compound Plumes* dated March 8, 1999. We prepared written comments and suggestions to the Working Task Force for this initiative on April 7, 1997; June 3, 1997; September 29, 1997; October 15, 1998; and January 11, 1999. This is our final report and is prepared for members of the Interstate Technology and Regulatory Cooperation to convey our overall evaluation of this major effort.

The Working Task Force gathered data from 65 contaminated sites for this study, 57% of which are located in California and Oregon. These sites contained 247 co-mingled parent and daughter plumes representing 16 different chlorinated methane, ethane, and ethene contaminants. The dominant contaminants are the chlorinated solvents, trichloroethene (TCE), tetrachloroethene (PCE), 1,1,1-trichloroethane (TCA), and their degradation products. This large data set is being made available to others in an electronic format that should be most useful for further study and evaluation.

Three different methods of analysis of the data set were used, a statistical comparison between plume lengths and individual hydrogeological variables, a correlation analysis between plume lengths and multiple hydrogeological variables, and a plume modeling effort that mathematically generated a set of plumes that could be compared in a similar fashion to the collected data sets. The use of three independent approaches to data analysis proved most useful to illustrate consistency in results obtained by different methods, providing greater confidence in the conclusions reached.

An important conclusion is that no statistical difference in plume length could be found when only partial transformation of PCE and TCE to the intermediate *cis*-1,2-dichloroethene (*cis*-1,2-DCE) was present. However, reduced plume lengths could be detected statistically when more complete transformation at a site was evidenced by the presence of the more dehalogenated daughter product, vinyl chloride. Such a reduction was indicated directly in the correlation analysis, but required some normalization of the influence of contaminant concentration and plume velocity when using individual hydrogeological variables. For this normalization, a plume length index was developed that equals the plume length divided by the groundwater velocity and the maximum groundwater concentration of the contaminant. Thus, three variables were drawn into one. A further significant conclusion from this analysis is "...that the role of transformation processes in influencing CVOC plume lengths is relatively subtle."

Interest is high in the potential for natural attenuation of chlorinated volatile organic compounds to control plume length. The data set collected is arguably limited and gathered largely from only one segment of the United States, and thus may not be representative for the country as a whole. However, with as much as two-thirds of the CVOC plumes, data were insufficient to tell whether or not with time plume lengths were increasing, decreasing, or staying the same. This represents a significant deficiency in the data obtained. Biological reductive dehalogenation would be expected to destroy CVOCs in the plume, and make the plume shorter than it would be in the absence of reductive dehalogenation. However, only one-third of the PCE and TCE plumes showed strong evidence of reductive dehalogenation and of these only 11 to 15 percent provided strong statistical evidence of plume shrinkage with time. The percentage of plumes showing strong statistical evidence of plume shrinkage with time is about the same for plumes with and for those without strong evidence of transformation. Why some plumes appear to be shrinking both with and without strong evidence of transformation is not known. This may be due to processes occurring at individual sites other than transformation in the groundwater plume.

While evidence is provided in this study that plumes are shorter for contaminants that show strong evidence of transformation, neither the degree to which they are shortened nor the variability in this shortening is clearly indicated. Additionally, such shortening is accompanied by the formation of vinyl chloride, a compound that is a known human carcinogen and of more concern than the PCE and TCE from which it is derived. Additionally, the study indicated that about one-third of the vinyl chloride plumes had maximum concentrations significantly down gradient from the TCE plumes from which

they originated, and about one-third of these had combined TCE/vinyl chloride plume lengths that were longer than the TCE plume length alone. The number of plumes involved in this analysis is too small to derive good conclusions. While natural attenuation may be significant in reducing some CVOC plume lengths and in some such cases may provide an acceptable remediation alternative, the percentage of cases where this may apply is not clear from this analysis.

The conclusion that dehalogenation exerts less impact on plume length than source strength and groundwater velocity is an important one. This indicates that site hydrogeological characteristics are highly significant factors affecting the movement and fate of CVOCs. Thus, generalizations about CVOC plume lengths may not be highly relevant at an individual site. Even when strong evidence of reductive dehalogenation is in evidence, site specific characterization is still needed to understand plume movement and contaminant fate.

Another conclusion reached is that the plume length index is "...useful to quantify expected relationships between plume length and site and CVOC variables within a population of CVOC plumes." While use of the plume length index allowed a differentiation between lengths of plumes with strong evidence of transformation and those without, a good scientific basis for this index is not provided. In order for such an index to gain wide acceptance, a more rigorous derivation and evaluation of this tool is necessary so that its applicability and limitations when and if applied to individual sites can be better understood.

The report recommends continued data collection. If this is felt warranted by the ITRC, then we suggest that future data collection efforts be more directed to pick a selection of plumes that will help to answer key questions of interest, rather than collecting data from a group of plumes at random. This CVOC study has shown that the hydrogeological and chemical variables between sites greatly complicates the drawing of statistically valid conclusions with large random data sets. For example, with this data set a statistically valid shortening of TCA plumes could not be obtained, even though it is well known that TCA transforms chemically and such shortening should be occurring. If such phenomena were of interest, then efforts to collect several TCA and daughter product plumes in particular would allow one to draw firmer conclusions about TCA plumes. Use of this approach of course requires that key questions of interest be defined carefully before the data collection begins.

We appreciate very much the cooperation and assistance provided to us by the Working Task Force. They were very willing to share their thoughts and progress, and were open to our comments and suggestions. We had many good discussions and interchanges. We hope that our comments will be useful to the ITRC in their discussions and decisions about CVOC plumes and the possible need for further studies.

Sincerely yours,

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