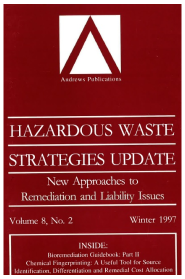
Hazardous Waste Strategies Update
New Approaches to Remediation and Liability Issues
Volume 8, No.2 Winter 1997
pgs. 38-49



Andrews Publications

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STRATEGIES UPDATE
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Identification, Differentiation and Remedial Cost Allocation

CHEMICAL FINGERPRINTING: A USEFUL TOOL FOR SOURCE IDENTIFICATION, DIFFERENTIATION AND REMEDIAL COST ALLOCATION

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Background

Many cases of groundwater contamination involve multiple contributing sources of similar contaminants. This may be the result of similar industrial or commercial operations that are located adjacent to one another or successive occupants of the same site. Older, well-developed industrial or agricultural areas are also often characterized by diffuse background contamination not readily attributable to a known source. All these factors complicate a company's attempt to identify, delineate and differentiate a portion of a plume that may have resulted from their operations. Plume differentiation is crucial in limiting, liability for cleanup as well as any potential liability for third-party claims in property damage, toxic tort or CERCLA contribution actions.

The challenge is not only to develop a logical and technically defensible source differentiation, but to be able to communicate the results convincingly to a judge, jury or arbitrator. The complexity of most fate and transport studies and groundwater models, though necessary to accurately simulate complex hydrogeologic conditions, is often confusing and difficult for a non-technical decision-maker to evaluate. Since a substantial legal and financial impact often accompanies the decisions of judges and juries in environmental cases, a tool that helps to demystify these complex issues would be very useful.

Chemical fingerprinting is a readily understandable tool in differentiating between multiple sources of similar contaminants in groundwater. When combined with traditional techniques, such as hydrogeologic evaluations and numerical fate and transport modeling, chemical fingerprinting is a cost-effective method that helps reduce the time and cost involved in investigation and remediation. It can be used effectively in establishing appropriate allocation of investigation and remediation costs or third-party liability between multiple potential contributors to a mixed contaminant plume.

Simply defined, chemical fingerprinting, is the comparison of individual contaminant concentrations and their relationship to each other to develop a unique chemical signature, or "fingerprint," for a groundwater contamination plume. First, chemical data from multiple points within a plume and from potential suspected sources are collected and validated. The data undergoes a statistical analysis and the results are presented visually. Based on the chemistry of the plume, the primary contaminants are identified and may be plotted on a variety of diagrams that give a visual representation of the parameters and their respective concentrations. These diagrams may depict absolute or average concentration values or the relative percent of each contaminant compared to the total mass of all contaminants. The resulting visual representation, or "fingerprint," provides the basis for an understanding of complex contaminant chemistry and the ability to relate the results to the fingerprint from individual potential source areas. The choice of an appropriate graphical technique to display the chemical signature (Stiff diagrams, pie charts, multivariate plots, phase diagrams) is governed by the available data and the target audience.

Case Study Number I

At a Superfund site in California, the groundwater contaminant plume is approximately 1.5 miles long and 0.3 miles wide and in the alluvial deposits of the Chino Basin. Although the hydraulic gradient is relatively shallow, aquifer testing reveals that groundwater velocity is approximately 1.5 feet per day. The source of the contamination was originally presumed to be Facility A shown on Figure 1. The identification of a source is complicated due to the existence of (background) upgradient contamination and multiple potential sources in the area. However, groundwater monitoring wells immediately down-gradient of Facility A show that volatile organic compound (VOC) concentrations are two orders of magnitude above upgradient background VOC concentrations. Groundwater beneath and immediately downgradient from the facility is contaminated with trichloroethylene (TCE); 1,1-dichloroethene (1,1-DCE); and cis-1,2-dichloroethene (cis-1,2-DCE). The objective of this investigation was to understand the nature of the facility's contribution to regional groundwater contamination in order to limit the scope of the plume delineation investigation and any subsequent remediation to only the facility's contribution. To complicate matters, several other significant potential sources of similar contaminants are located upgradient and cross-gradient from the facility. Groundwater in the area is contaminated with a variety of VOCs, some of which were not found or ever used at Facility A. For this reason, chemical fingerprinting was used in conjunction with traditional hydrogeologic analyses and modeling to define the boundaries and limits of the contaminant plume affected by the site.

To determine if the VOCs in the groundwater downgradient from Facility A could be traced to more than one source, an analysis was conducted that integrated

conventional hydrogeological investigation methods with chemical fingerprinting. Results of selected chemical analyses were plotted on subsurface cross-sections of the investigation area. Figures 2a and 2b show tetrachloroethene (PCE) and TCE concentrations contoured in a north-south cross section of the observed mixed VOC plume. The same cross-section was constructed to show Stiff diagrams (fingerprints) for all the depth-specific sampling points at each boring location along the cross section line (Figure 3). These two independent data representation methods were evaluated to provide an understanding of VOC migration in groundwater and predict potential sources.

The result of this analysis indicates that a distinct change in the fingerprint occurs from south to north across the central axis of the plume. The VOC pattern of groundwater from the Facility A source and borings and monitoring wells in the interior of the plume on Facility A and directly downgradient from Facility A (B-3, B-4, B-5, B-6) is dominated by TCE and cis-1,2-DCE. By contrast, groundwater from B-15 is enriched in PCE and contains no cis-1,2-DCE (Figures 2 and 3). VOC concentrations increase from the southern boundary (B- 14), where no VOCs are detected, to as much as 190 micrograms per liter (µg/L) of the midline of the site-affected plume (B-11), and then decrease to 3.4 µg/L or less, at B-15 to the north and away from the longitudinal axis of the affected area and just south of the domestic well (DW). Two distinct and partially mixed zones of VOCs in groundwater exist, one centered hydraulically downgradient from the site and enriched in TCE and cis-1,2-DCE, and one derived from an as yet unidentified off-site source, enriched in PCE, that occurs along the northern boundary of the observed plume attributed to Facility A (Figures 2 and 3).

An analysis of chemical fingerprints represented on Stiff diagrams (Figure 3) corroborates the hypothesis presented above. Graphical representation of analyses of groundwater samples taken from and directly downgradient from the site consistently show a distinct and similar chemical pattern. This pattern exhibits TCE enrichment, minor presence of cis-1,2-DCE, and little or no PCE. Groundwater from the monitoring well located across the street and south of the domestic well and along the northern boundary of site-affected VOCs exhibits a markedly different chemical pattern enriched in PCE that contains no cis-1,2DCE and little or no TCE. Water sampled from the domestic well exhibits this same pattern of PCE enrichment and TCE depletion. This further indicates that at least one outside source of VOCs is affecting groundwater alone, the northern plume boundary downgradient from Facility A.

A potential unrelated source controlled by another party has been located upgradient of the B-15 location (Facility B) and remains to be investigated (Figure 1). While the extent of the plume continues to be defined and remediation alternatives continue to be examined, regulators have accepted the results of this analysis. Thus, already, the investigation and, ultimately, the remediation have been successfully limited to only the groundwater affected by Facility A.

Case Study Number 2

At another Superfund site, investigations performed over the past 15 years have defined a five-mile long chlorinated solvent plume in saturated alluvial sediments. A suite of VOCs with TCE as the principal parameter and the metal chromium characterize this plume. Other VOCs detected consistently in the area include 1,1,1-trichloroethane (TCA); 1,1-dichloroethene (1,1-DCE); cis-1,2-DCE; and chloroform (CF). The principal source of the groundwater contamination was originally identified as an industrial facility (labeled A) south of the upgradient margin of the plume. The direction of groundwater flow is toward the northwest (Figure 4).

Numerous other potential sources that may have contributed to the plume were identified east of the main axis of the plume in Area B. Initial contaminant transport modeling showed that the plume could be explained solely from documents and sources within Area A or that contributions from Area B could be made to account for some of the northern portion of the plume. More recent detailed site investigations of subsurface geological, hydrological and geochemical conditions near the potential secondary source area have revealed the existence of a clay layer (up to 40-feet thick) below Area B. Although the low permeability hydraulic properties of the clay appear to isolate contaminants that have reached the top of the saturated clay layer, effectively preventing them from passing vertically into the underlying regional aquifer, a westward component of flow above the clay toward the main plume was defined. The potential for a contribution from the secondary potential source (Area B) was possible as the clay thins and pinches out to the west near the main axis of the plume in the regional aquifer. Recent site investigations also provided sufficient new information to allow a comparison of the chemical fingerprint of the main plume in the regional aquifer with that of the shallow water-bearing zone associated beneath the potential secondary source (Area B) to evaluate whether or not the sources in Area B may have contributed to the plume observed in the regional aquifer.

The shallow water-bearing, zone above the clay beneath Area B is characterized by a plume that also has TCE as its prime constituent and includes PCE; 1,1-DCE; carbon tetrachloride (CT); CF; methylene chloride (MC1); benzene; and chromium. This combination of substances yields a chemical fingerprint that can be represented graphically using Stiff diagrams (Figure 5). To enable a representative comparison with the plume chemistry in the regional aquifer, a subset of five VOCs (TCE, 1,1-DCE, cis-1,2-DCE, CF and MC1) and chromium was selected. More than 100 well sampling locations throughout both investigation areas make it difficult to sensibly depict the results of multiple individual fingerprints on a single, large-scale regional map. Therefore, a valid, representative statistical comparison was made by sorting the wells according to their hydrogeologic locations relative to the regional plume, then averaging the results for samples within each of the resultant areas for presentation (Figures 5 and 6). The hydrogeologic subdivisions comprise regional aquifer wells north of Area B, regional aquifer wells south of Area B near primary source Area A, shallow groundwater in potential secondary source Area B, and deep

(regional aquifer) wells beneath the clay layer in potential secondary source Area B (Figure 6).

The Stiff diagrams for the hydrogeologic subdivisions representative of the regional aquifer and shallow zone are distinctive and clearly indicate that the fingerprint of chemical contaminants in the regional aquifer are virtually identical for the portions of the plume north and south of Area B and beneath the clay layer in Area B. The slight differences are explained by decreasing concentrations with increasing distance along the longitudinal axis of the plume. Geochemical processes, such as retardation, dilution, dispersion, and biodegradation, tend to reduce the concentrations of individual substances with increasing distance from the source. Notable is the distinct similarity of the result for wells in the regional aquifer beneath the clay layer at the potential secondary source Area B and the main plume in the regional aquifer. Maps of the regional plume have generally interpreted this potential secondary source to lie near the eastern edge of the main plume. In contrast to the chemical fingerprint of the shallow water-bearing zone in the upper part of the clay layer, the groundwater beneath the clay exhibits a pattern similar to that of the regional plume with some depletion in chromium. Using, this method, it can be demonstrated that the suite of contaminants present in the shallow zone has had little or no effect on the regional aquifer beneath the clay layer, and that deep contamination under Area B originated from sources in Area A. Accordingly, it appears significantly more likely that the northern portion of the regional plume and the contamination in the zone beneath the clay in the potential secondary source Area B can be accounted for by downgradient migration from the primary source Area A to the south, rather than to any contribution from Area B.

One possible criticism of the chemical fingerprint analysis of a large plume like this one is its inability to take account of geochemical transformations that occur naturally in the subsurface environment over time and, in the dynamic medium of groundwater, could appear as spatial variations in chemical fingerprints. Examples of such transformations are the degradation of carbon tetrachloride into chloroform or that of TCA into 1,1-DCE. In the above case, this possibility was considered and accounted for by excluding the precursor substances from the Stiff diagrams.

Moderate spatial differences in the concentrations of the breakdown products of VOCs were also accounted for when the data from widely separated wells within the same subdivisions were averaged. In fact, the appearance of a highly distinctive and unique chemical fingerprint for the shallow water-bearing zone could have been enhanced if the substances 1,2-DCP or benzene (not detected in the regional aquifer) had been included. As it was, these were recognized to be chemically somewhat dissimilar from the majority of other halocarbon substances present in both sites and dropped from the fingerprint plots so as not to impose any bias to the outcome.

In summary, chemical fingerprint analysis, in conjunction with accepted fate and transport studies, is an extremely useful tool in differentiating contributions to groundwater contamination in areas where multiple potential sources with similar

chemical constituents exist. Equally significant, this method is readily understood by and easily presented to non-technical decision-makers in complex environmental litigation. This forensic geochemistry approach, along with traditional hydrogeologic, biodegradation and retardation analyses, can be very useful in the complex process of liability cost allocation at sites with multiple sources.

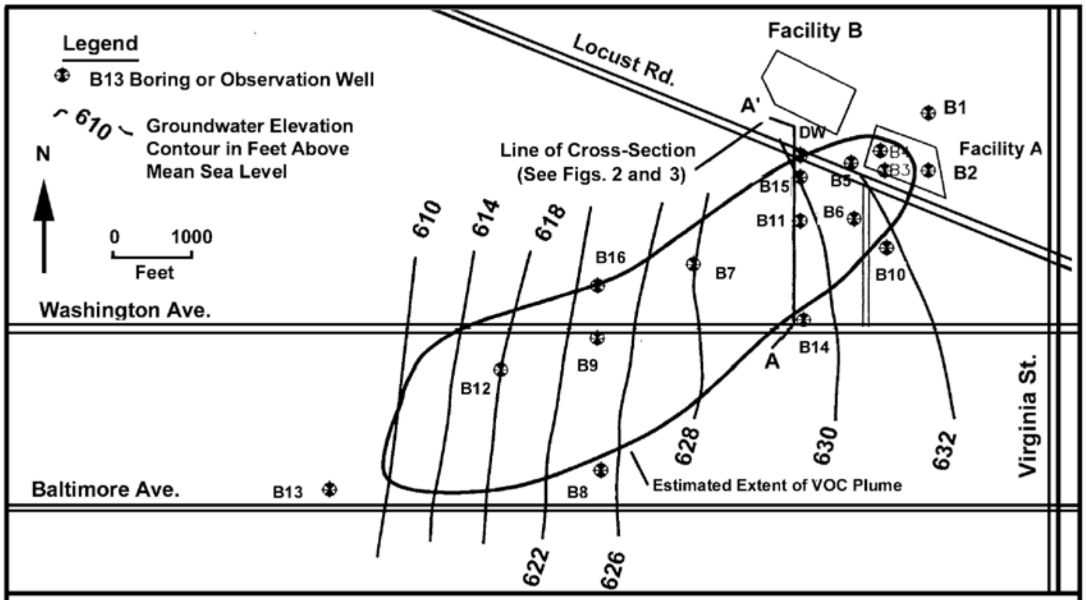


Figure 1: Groundwater Contamination Plume At California Superfund Site

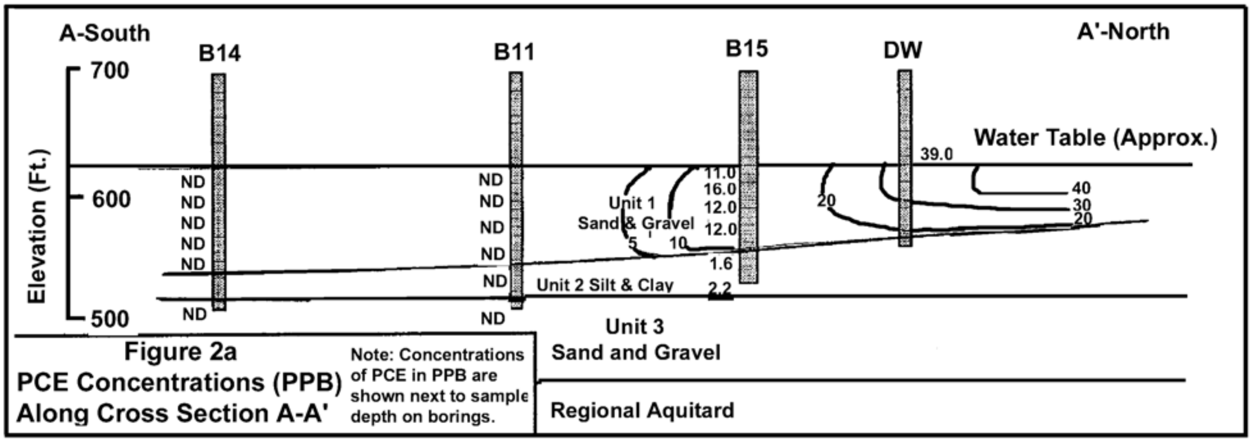
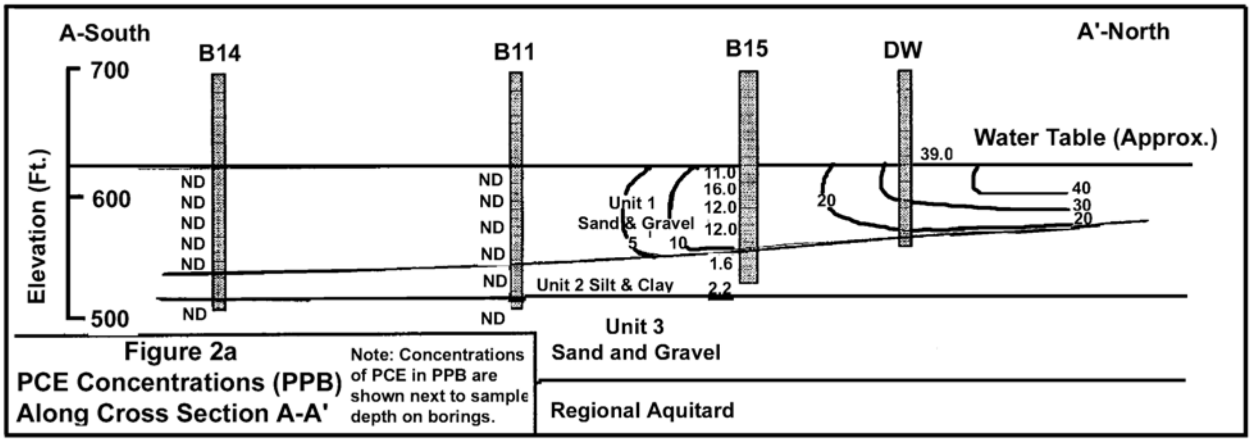


Figure 2a
PCE Concentrations (PPB)
Along Cross Section A-A'

Note: Concentrations of PCE in PPB are shown next to sample depth on borings.



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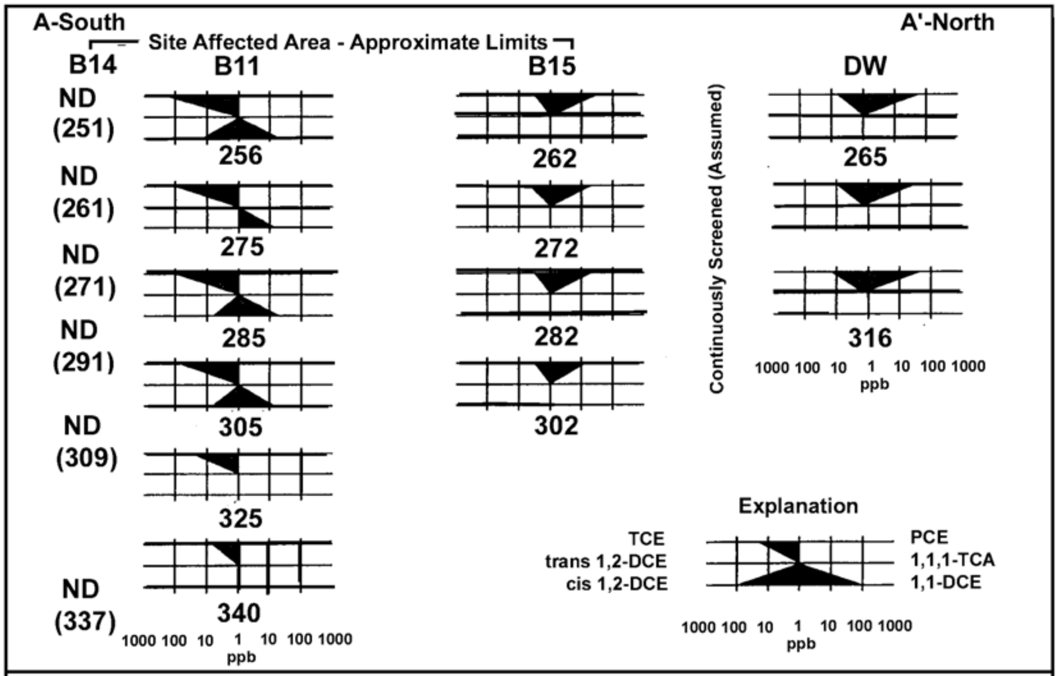


Figure 3: Stiff Diagrams of Depth-Specific Sampling Points Along Cross-Section A-A'

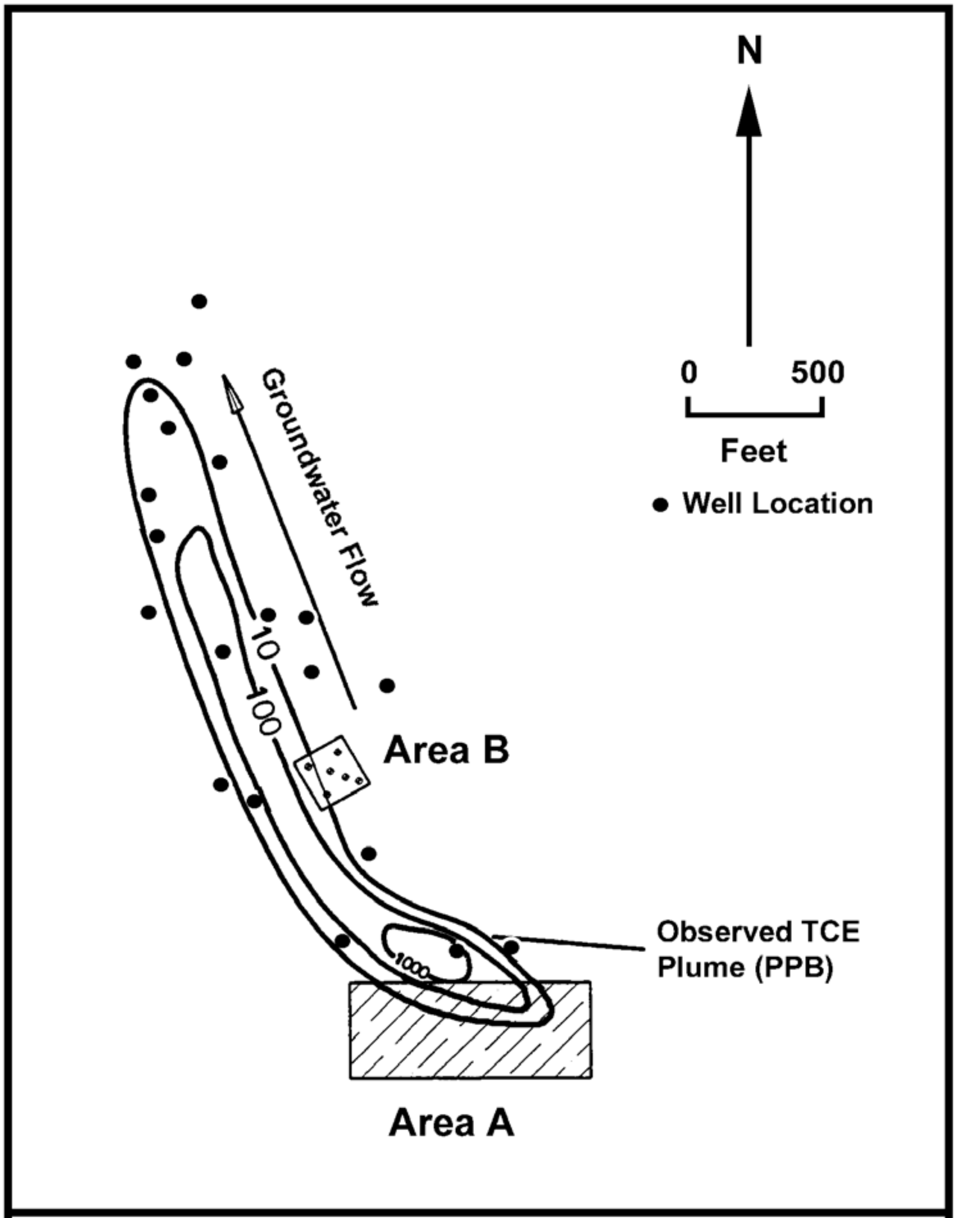
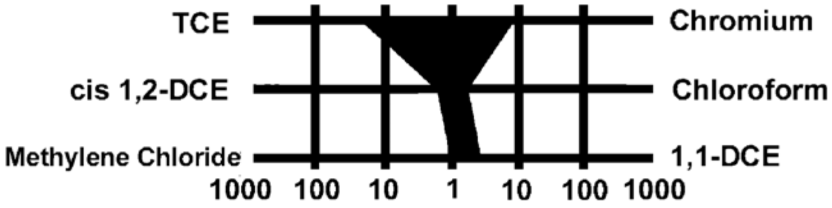
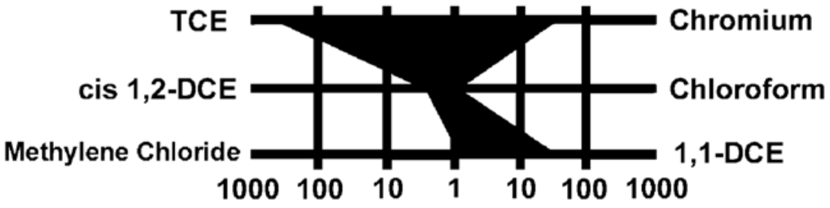


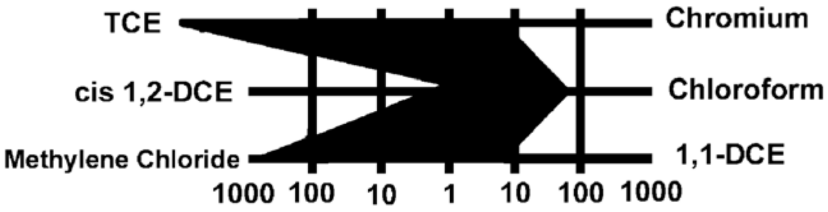
Figure 4: Case Study #2 Site Showing Monitor Well Locations & Two Potential Source Areas



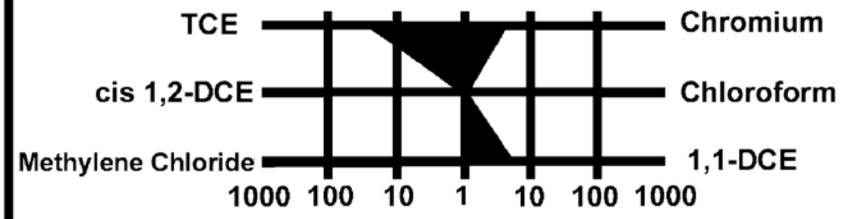
5a: Wells North of Area B



5b: Wells South of Area B



5c: Shallow Wells in Area B



5d: Deep Wells in Area B

All analyses in PPB

Figure 5: Stiff Diagrams Developed from Average VOC Concentrations in all Monitor Wells in each Hydrogeologic Subdivision

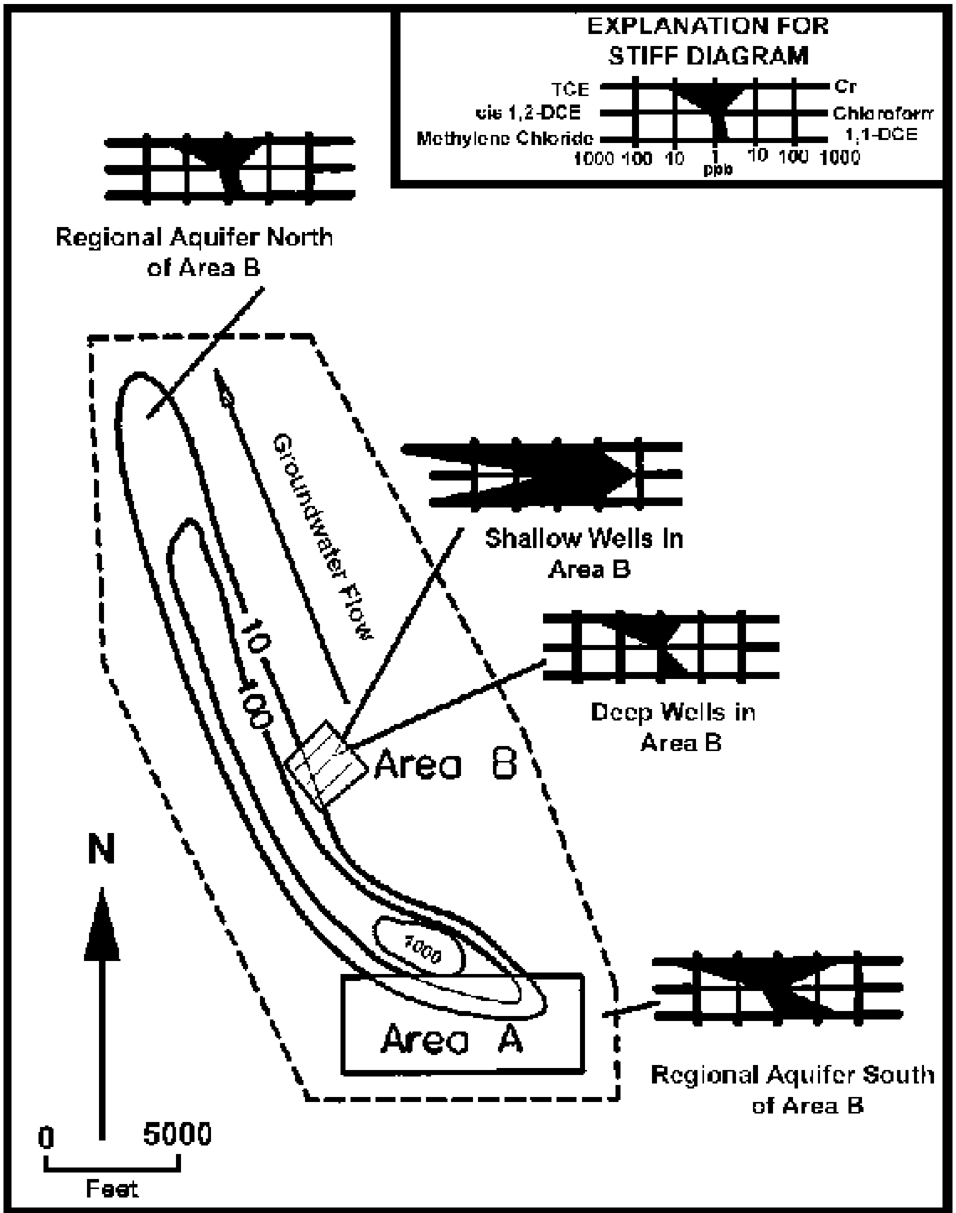


Figure 6: Chemical Fingerprints for Hydrogeologic Subdivisions

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