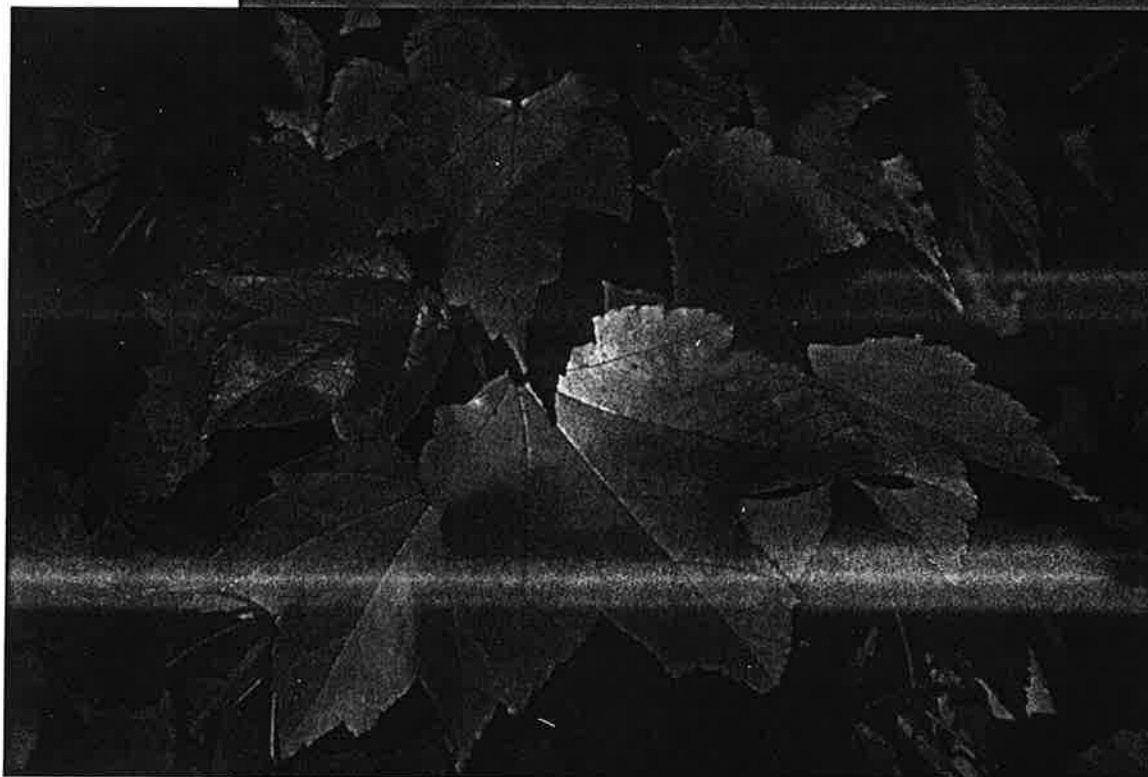


INSIGHTS

Fall 1996

A Quarterly Publication



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Chemical Fingerprinting:

NARROWING DOWN THE LIST OF CONTAMINANT SOURCES

A simple yet powerful technique, chemical fingerprinting is ideal for differentiating between multiple sources of similar contaminants in groundwater. When combined with traditional hydrogeologic evaluations and numerical fate and transport modeling, chemical fingerprinting is a cost-effective method that not only reduces the level of effort for groundwater contamination investigation and remediation, but also assists in the negotiation of appropriate allocation of investigation and remediation costs between multiple potential contributors to a mixed contaminant plume.

How Chemical Fingerprinting Operates

During chemical fingerprinting, groundwater chemistry from multiple points within a plume, soil and/or groundwater chemistry from the presumed primary source, and comparable data from other sources undergo a statistical treatment. From this analysis, a visual representation of the contaminant chemistry in the groundwater — a “fingerprint” — is created by identifying and plotting the primary contaminants on Stiff diagrams, multivariate plots, bar charts, and phase diagrams. This fingerprint illustrates the parameters and their respective concentrations, and may depict absolute or average concentration values or the relative percent of each contaminant compared to the total mass of all contaminants. The resulting fingerprint also provides the basis for an understanding of complex contaminant chemistry and the ability to back track to find individual source areas.

Case Study: California Superfund Site

At a Superfund site in California, the groundwater contaminant plume is approximately one mile long and a quarter mile wide. Although the hydraulic gradient is relatively shallow, groundwater has been calculated to travel at an approximate rate of 1.5 feet per day. The source of the contamination was originally presumed to be the facility on the western edge of the site; labeled as Facility A on the site map. Although some upgradient contamination (background) clearly exists, groundwater monitoring wells immediately downgradient of

the facility show that volatile organic compound (VOC) concentrations are two orders of magnitude above VOC concentrations entering the facility from upgradient. Contaminants in groundwater below and immediately downgradient from the facility are enriched in trichloroethene (TCE); 1,1-dichloroethene (1,1-DCE); and cis-1,2-DCE. To limit the scope of the investigation and any subsequent remediation to only the facility's contribution, the nature of the facility's contribution to groundwater contamination had to be determined.

To complicate matters, there are several potential sources of similar contaminants upgradient and cross-gradient from the facility. Contaminants in the plume downgradient from the site are enriched in TCE and tetrachloroethene (PCE) and depleted in cis-1,2-DCE and 1,1-DCE. For this reason, chemical fingerprinting was used in conjunction with traditional hydrogeologic analyses to define the limits of the plume affected by the site.

To determine if the VOCs found in the groundwater downgradient from the facility could be traced to more than one source, an analysis was conducted that integrated conventional methods with chemical fingerprinting. PCE and TCE were plotted on subsurface cross-sections of the investigation area. A cross-section of the same area was then constructed that shows Stiff diagrams for all the depth-specific sampling points in each of the borings. These two independent investigative methods were evaluated to provide an understanding of VOC migration in groundwater and predict potential sources.

The investigation found that a distinct change in the fingerprint occurs from south to north across the approximate center of the plume. The VOC pattern of groundwater from the borings and monitoring wells in the interior of the plume and downgradient from the site is dominated by TCE and cis-1,2-DCE, which is also characteristic of VOCs found in downgradient on-site monitoring wells. By contrast, groundwater from boring No. 15 is enriched in PCE and contains no cis-1,2-DCE. TCE concentrations increase from non-detect at the southern boundary (boring No. 14), to as much as 190 micrograms per liter (ug/L) at the

midline of the site-affected plume, and then decrease to 3.4 ug/L or less, at boring No. 15 to the north and away from the interior of the affected area and just south of the domestic well. 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 along the northern boundary of the site-affected groundwater.

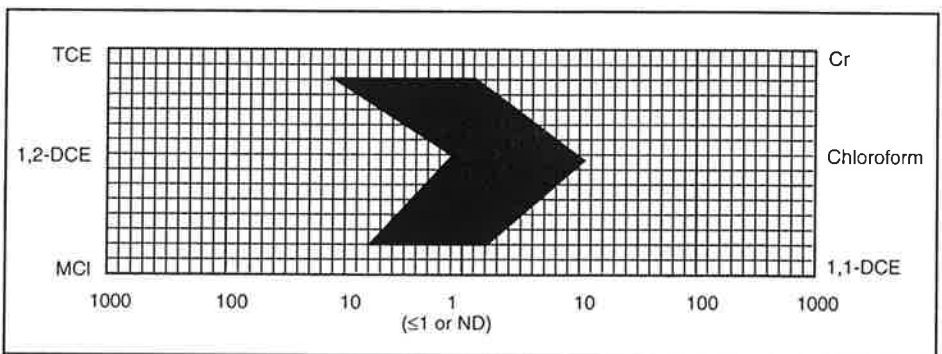
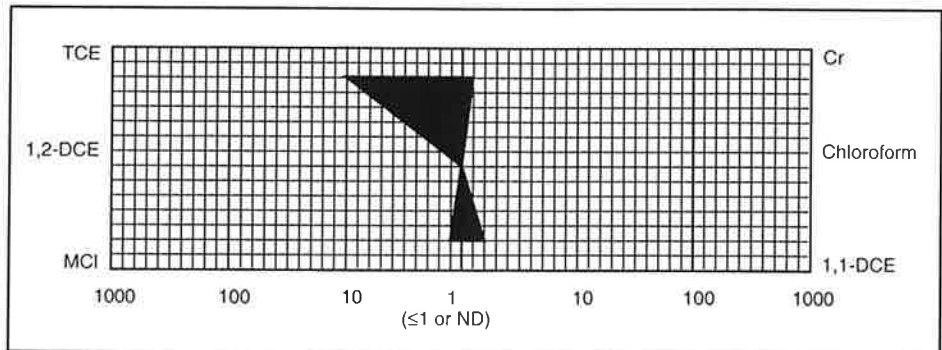
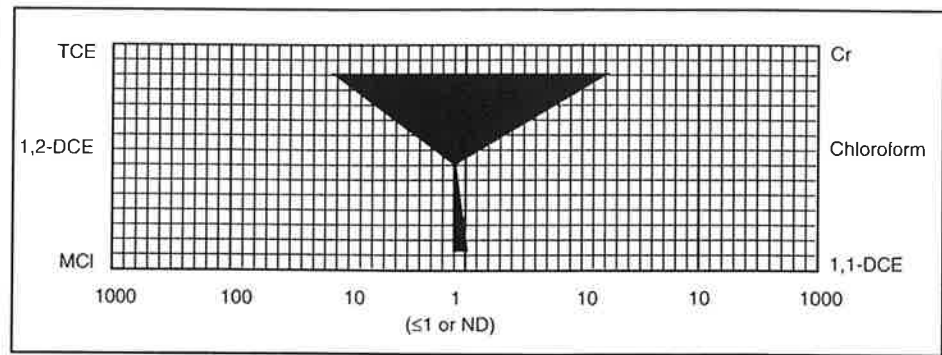
Interpreting Stiff Diagrams

Stiff diagrams 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 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-1,2-DCE 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 along the northern boundary of the site-affected groundwater.

A potential unrelated source controlled by another party has been located upgradient of the No. 15 location and is being investigated. While the downgradient extent of the plume continues to be defined and remedial alternatives examined, regulators have accepted the results of this analysis, and the investigation, and ultimately the remediation, has been limited to only the groundwater affected by the site.

There are many benefits of chemical fingerprinting. Not only does it help limit the level of effort for the investigation and remediation of groundwater contamination, chemical fingerprinting also helps differentiate between multiple sources of similar contaminants and assists in the negotiation of cleanup cost allocation.

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Above:
Sample Stiff diagrams.

Below:
The site map for a Superfund site in California.

