Chemical Fingerprinting

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CHEMICAL fingerprinting is a simple yet powerful technique. It is ideal for differentiating among multiple sources of similar contaminants in groundwater. When combined with traditional hydrogeologic evaluations and numerical fate and transport modeling, it limits the level of effort required to investigate and remediate groundwater contamination. It also assists the allocation of investigation and remediation costs among many potential contributors to a mixed contaminant plume. And, chemical fingerprinting is cost effective.

Chemical fingerprinting involves comparing individual contaminant concentrations and their relationships to one another. The chemical data, including groundwater chemistry from many points in a plume, soil and/or groundwater chemistry from the presumed primary source, and comparable data from other sources, undergo 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 shows 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 to understanding the complex contaminant chemistry, and offers avenues to backtrack to find individual source areas.

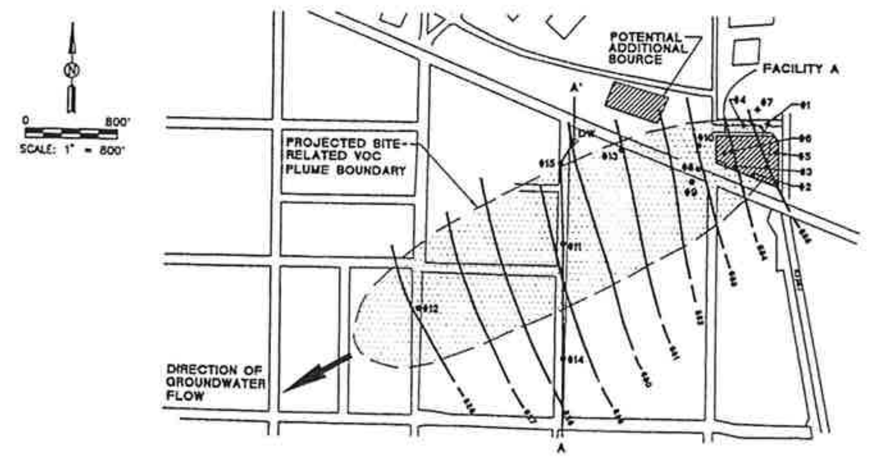

***Figure 1.* Fingerprinting a groundwater contaminant plume at a Superfund site.**

Using Fingerprinting

At a Superfund site in California, where the groundwater contaminant plume is about 1 mile long and 1/4 mile wide and the hydraulic gradient is relatively shallow, the groundwater travels at a rate of about 1.5 feet per day, according to calculations, and the source was originally presumed to be Facility A on the eastern edge of the site (see Figure 1).

Although some upgradient contamination clearly exists, groundwater monitoring wells immediately downgradient of the facility show that volatile organic compound (VOC) concentrations are two orders of magnitude above those entering the facility from upgradient. Contaminants in groundwater below and immediately downgradient from the facility are enriched in trichloroethylene (TCE); 1,1-dichloroethene (1,1-DCE); and cis-1,2,DCE.

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. To limit the scope of the investigation and any subsequent remediation, we decided to determine with precision the nature of the facility's contribution to groundwater contamination.

For these reasons, chemical fingerprinting and traditional hydrogeologic analyses were used to define the limits of the plume affected by the site. To determine the presence of VOCs in the groundwater downgradient from Facility A, we plotted PCE and TCE on subsurface cross sections of the investigation area. Both were contoured across the center of the VOC plume. A cross section of the same area was then constructed on Stiff diagrams for all the depth-specific sampling points in each of the borings (Figure 2). These two independent investigative methods were then evaluated; they permitted us to understand the extent of VOC migration and to predict potential sources.

The investigation confirmed that a distinct change in the fingerprint occurs 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. This is also characteristic of VOCs found in downgradient on-site monitoring wells. By contrast, groundwater from boring No. 15 (Figure 2) is enriched in PCE and contains no cis-1,2-DCE. TCE concentrations increase from non-detectable 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.

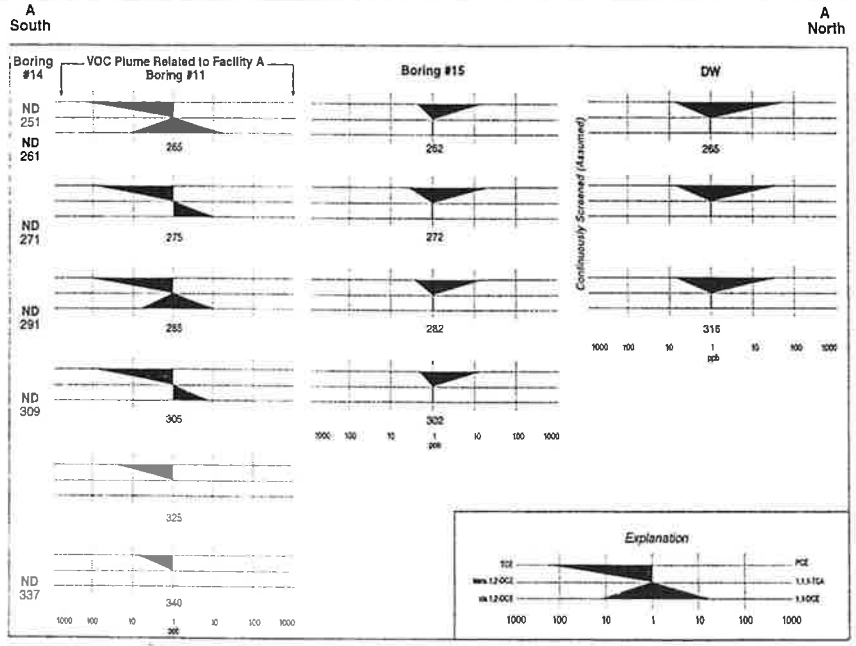

Figure 2. Stiff diagrams of depth-specific sampling points.

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.

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, south of the domestic well, and along the northern boundary of site-affected VOCs, shows a markedly different chemical pattern, one 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 indicates further that at least one outside source of VOCs is affecting groundwater along the northern boundary of the site-affected groundwater. Also, a potential unrelated source, controlled by another party, has been located upgradient of the No. 15 location and is being investigated.

Conclusion

Still, even though the downgradient 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 technique have been limited to only the groundwater affected by the site.

Not only does chemical fingerprinting help limit the level of effort needed to investigate and remediate groundwater contamination, it also helps differentiate among multiple sources of similar contaminants and assists in the negotiation of cleanup cost allocation. TME

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