

The Application of Geochemical Principles to the Investigation of DNAPL Contamination at Manufactured Gas Plant Sites

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INTRODUCTION

One of the most persistent and difficult problems relating to the clean-up of former manufactured gas plant (MGP) sites is the presence of dense nonaqueous phase liquid (DNAPL). DNAPL is encountered as tars and heavy oils and provides a continuing source of groundwater contamination. Before groundwater remedial designs can be finalized, the nature of the DNAPL, including the distribution and hydrogeochemical interactions, must be understood. The U.S. Environmental Protection Agency (EPA), in their 1993 *Guidance for Evaluating the Technical Impracticability of Ground-Water Restoration*¹ has stated that 'DNAPL contamination may have a significant impact on site investigations and the ability to restore contaminated portions of the subsurface'. A recently completed literature review,² with the purpose of identifying geochemical, statistical, and data evaluation methods to be applied to DNAPL sites, is available and serves as the basis of this paper.

NATURE OF DNAPL SOURCES

DNAPL sources at MGP sites are dominated by coal tars which have been released to the environment through the handling and storage of manufactured gas condensate (coal tar). These coal tars vary from site to site in absolute concentrations of volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs). Sixteen PAH compounds are regulated in the United States. The tars have resulted from the different gas generating processes, including coal carbonization, carbureted water gas and oil gas, and from different unit operations within each plant, namely the gas washing, cooling, and condensing sequences. However, there are certain commonalities among different tars. In a recent Electric Power Research Institute (EPRI) study,³ it was determined that the relative amounts of different PAH groups were the same in various tars having similar consistency. Non-pumpable tars had a larger percentage of Group 5 and Group 6 PAHs than more fluid tars. This finding means that, as MGP tar ages or weathers under different environmental processes, the PAH signature will change. Lower molecular weight PAHs will

volatilize and desorb over time and thus be reduced in relation to the high weight compounds. Naphthalene will always predominate the tar mixture, averaging at least 30% of all the PAHs in pure tar mixtures. Another feature of the coal tars is that they are physically either fluid or semisolid when released into the environment. Only the pitch-like tars or those allowed to weather on the ground surface are found in a solid state. MGP tars in the subsurface are slightly denser than water, ranging between 1.06 and 1.2 gm/cc according to EPRI.³

Release of PAHs from coal tar in the subsurface is governed primarily by solubility. Until recently, the common assumption with respect to dissolution of coal tar constituents was that PAH concentrations would be equal to, or less than, the corresponding aqueous solubility of the pure compound. From recent work by EPRI,⁴ it has been theorized and empirically demonstrated that the concentration of a constituent in the aqueous phase in equilibrium with an 'ideal' organic mixture (tar) is proportional to the mole fraction of that constituent in the organic phase. This relationship suggests, for example, that naphthalene, with a pure phase solubility of 32 mg/l, having a mole fraction of 30% in a tar mixture, will result in an aqueous-phase solubility of no more than 10 mg/l. Actually, based on liquid-liquid partitioning data, there is a deviation from the ideal behavior by a factor of two or less. Field measurements at the EPRI Site 24 research station have corroborated the solubility of individual PAH compounds from a tar mixture through very careful well placement and groundwater sampling. Here, within one meter of the tar mixture, naphthalene was measured at 5.4 mg/L and is considered to be at the solubility limit.

PHYSICAL BEHAVIOR

Current efforts to investigate and remediate coal tar are hindered by the inability to characterize the nature and location of the tar source in the subsurface. There is a complex physical and chemical regime that dictates the deposition and migration of DNAPLs. Tars become distributed throughout the subsurface as discrete 'blobs', at a residual saturation or at higher saturations in 'pools', in the capillary fringe or on top

of low permeability media. Although gravitational forces largely dictate the vertical migration, capillary forces also play a role, resulting in the lateral spreading of DNAPL through subsurface systems with even small-scale heterogeneities. When a DNAPL reaches the water table, the organic phase will spread laterally through the capillary fringe until the organic phase has sufficient head to overcome the displacement pressure of the water-filled medium. The displacement pressure controlling DNAPL entry into the saturated zone is a function of the interfacial forces between the organic and aqueous phase, the wetting characteristics of the porous medium, and the geometry of the pores. The Laplace equation can be used to estimate the displacement pressure. For coal tar, the displacement pressures are greater for fine-grain material than for coarse-grain material, as illustrated in Table 1.

As DNAPL migrates through the subsurface, it is trapped as discrete 'blobs' or 'ganglia', due to the interaction among capillary and viscous, buoying, or gravitational forces. At the pore scale, the non-wetting phase will readily enter a large pore body. If a coal tar enters a large pore but does not have the pressure to overcome the capillary force required to exit through a smaller throat, it will become isolated in a phenomenon called 'snap off'.

The amount of DNAPL entrapped within a porous medium is called the residual saturation ($S_{r,n}$). This designation represents the volume of DNAPL per total void volume. Schwille⁵ has determined in the laboratory that residual saturation can range between 10 to 35%. It has been determined at DNAPL research sites that small-scale heterogeneities caused by fine bedding planes can alter vertical migration and force more lateral spreading.

Regarding the rate of dissolution into the aqueous phase from the tar mixture, the specific interfacial area may have the greatest impact. Here, the specific surface area is defined as the surface area per unit volume of porous medium. Hunt *et al.*,⁶ and Powers, *et al.*,⁷ have tested and confirmed the theory that dissolution can decrease by orders of magnitude when the tar source changes from small globules to a single large ganglia without any difference in overall DNAPL mass. The distribution of DNAPL as pools on top of low permeability media results in even lower interfacial mass transfer rates.

As briefly discussed, the migration, distribution, and dissolution of coal tar in the subsurface is highly dependent on the geometry of the porous media.

GRAPHICAL ANALYTICAL METHODS

Standard techniques for characterizing the presence or true nature of distribution of coal tar DNAPL at MGP sites is often inadequate due to limitations and constraints placed on investigatory programs. Also, for many completed investigations, interpretations too often are based on tabulations of soil and groundwater concentrations of VOCs and PAHs. Presence of DNAPL at one time was based on comparing groundwater concentrations of PAHs to pure phase solubility; however, the use of mole fraction solubility for complex mixtures is becoming more widely practised.

Graphical techniques can be used to better depict the chemistry of soil and groundwater data from MGP sites. One of the simplest methods of extracting useful information on MGP DNAPL sites is to plot relative concentrations of specific compounds. An organic chemist would rely only on chromatographs; however, bar charts have been used to illustrate the 'signature' or 'finger print' of various tars and other hydrocarbons. The predominance of naphthalene in certain proportions to other PAHs can be a strong indicator of MGP tar. Relatively higher percentages of BTEX with no naphthalene can be indicative of a petroleum fuel rather than MGP tar.

Trilinear plots are an alternative for plotting data that involve the correlation of three variables. Petroleum geologists use this method to differentiate between different crude oils. Relative proportions of benzene and toluene to naphthalene in a tarry soil sample can be indicative of the state of source weathering. The trilinear plotting of different combinations of BTEX and PAH across a site can provide inferences regarding the type and location of contaminant sources, especially where multiple site uses occurred and more than one source has been identified.

Star (or radar) plots are an effective tool for the analysis of data with more than three variables. These plots use polar coordinates with the number of axes equal to the number of variables. The dependent variable is plotted as a data point on each axis, and the points are connected to form a polygon. The shape of the polygon is the source 'signature'.

The use and configuration of graphical techniques to map out the location and distribution of DNAPL coal tar is limited only by the creativity and imagination of the data interpreter. Three-dimensional techniques of utilizing computer enhancement software are now evolving into a more common analytical tool. The science of chemometrics utilizes graphic and

Table 1.² Estimated depth of DNAPL that will develop above a finer-grained lens prior to DNAPL entry into the lens during infiltration

Soil in lens	Mean grain diameter (pm)	Estimated depth (m)		
		Coal tar	TCE	FOB
Medium sand	0.04	5	0.4	0.2
Fine sand	0.02	10	0.8	0.3
Silt	0.001	200	15.0	6.0
Clay	0.0002	1000	75.0	30.0

statistical methods to evaluate large databases that are applied to MGP sites.

SUMMARY

MGP residuals in the subsurface are distributed according to the nature of the tar source mixture, the dynamics of the aquifers and, most important, according to the pore configuration of the geologic materials. Every site has a different set of circumstances and often the distribution patterns are complex. Some research sites, such as EPRI Site 24, have provided valuable insight into the migration potential of the DNAPL tars. The physical and chemical research on the nature of various tars shows interesting commonalities, while dissolution and adsorption of organic mixtures (tars) are being studied and better understood. Before remediations at MGP sites can be designed, it is the responsibility of the investigators to portray the nature and distribution of the tar source. Graphic techniques for data display can go a long way in making a complex site contamination more understandable to the design engineer.

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