ESTIMATING AND REFINING THE BOUNDARIES OF A DNAPL ZONE WITH SUCCESSIVE INVESTIGATIONS AT A SUPERFUND SITE

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ABSTRACT
Assessment of DNAPL presence and delineation of DNAPL source zones in both overburden and bedrock is subject to uncertainty because of the tortuous and heterogeneous manner in which DNAPL is distributed in naturally occurring heterogeneous deposits. This uncertainty can be addressed by delineating both a 'probable/confirmed' DNAPL source zone, and a 'potential' DNAPL source zone. Because DNAPL can migrate in hydraulically upgradient and cross-gradient directions, it is important to consider structural controls and historical pumping activities when citing monitoring wells. It is best to use multiple lines of converging evidence when assessing DNAPL presence and delineating the source zone, rather than a single line of evidence. Appropriate lines of evidence include site use and history, visual observation, soil boring programs, assessment of groundwater concentrations (with respect to magnitude, spatial trends, and temporal trends), the presence of alcohols in groundwater, soil concentrations above a calculated threshold, and anomalous plume configurations.

1. INTRODUCTION

Soil and groundwater contamination by dense, non-aqueous phase liquids (DNAPLs) such as chlorinated solvents, PCB oils, creosote, and coal tar is a common occurrence throughout industrialized areas of North America and other parts of the world. These liquids are denser than water, vary widely with respect to viscosity, are typically volatile, and are only sparingly soluble in water. Upon release to the subsurface, DNAPLs will come to rest as both disconnected blobs and ganglia of organic liquid referred to as residual, and in continuous distributions referred to as pools. The volume of the subsurface containing residual and pooled DNAPL is referred to as the DNAPL source zone. As groundwater flows through the source zone, aqueous phase plumes develop. Because of the low aqueous solubility of most DNAPL compounds, the lifespan of DNAPL in the source zone is expected to be on the order of hundreds of years for most DNAPL types and most geological settings.

Chlorinated solvent and PCB DNAPL usage in North America increased rapidly during the 1950s and 1960s as a result of increases in industrialization and population. This rise in usage, coincident with a general lack of understanding of the environmental impact of these compounds, was associated with an increased frequency of release to the subsurface. Of the thousands of DNAPL sites that are known to exist in North America today, the vast majority are the result of releases to the subsurface that occurred during the 1950s through to the 1970s. Most of these sites were not discovered until the 1980s when industry and research institutions started to gain an understanding of DNAPL occurrence and behaviour in the subsurface.

Prior to selection and implementation of remedial measures at hazardous waste sites exhibiting soil and groundwater contamination by organic compounds, an assessment of DNAPL presence is typically carried out. If the assessment concludes that DNAPL is present at the site, the DNAPL source zone is delineated. DNAPL assessment and delineation strategies have evolved since their introduction in the late 1980s. The objective of this paper is to illustrate the evolution of DNAPL assessment and delineation techniques at a well characterized U.S. Superfund site where environmental investigations have been ongoing since the late 1980s.

2. SITE HISTORY

The subject site is located in the northeastern United States and was used as a solvent recycling facility from approximately 1955 until the facility's closure in 1991. During this period spent solvents were received from customers and distilled to remove impurities. It is estimated that the facility handled approximately three to five million gallons of liquid wastes and 100,000 pounds of solid wastes annually. The liquid wastes processed at the facility included unrecoverable or spent solvent-based fuels, spent chlorinated solvents, and waste oils generated from fuel-blending operations. Waste liquids generated onsite included still-bottom sludge, contact and non-contact steam from the distillation process, non-contact cooling water from the fuel-blending operations, water generated from an onsite groundwater recovery system, boiler blow down generated from boiler steam condensate, and stormwater runoff.

Figure 1 illustrates the general site configuration. From 1957 to approximately 1967, the non-recoverable portion of distilled solvents was discharged from the distillation columns into unlined lagoons in the Operations Area. The lagoons sometimes were filled beyond their capacity with solvent sludge and overflowed to the ditch along the west side of the B&M Railroad tracks. The secondary lagoon was reportedly used for skimming of free oils for use in a fuel blending program. In 1967, sludge disposal in the lagoons was discontinued, the sludge was excavated and the lagoons were filled. After the closure of the lagoons, wastes including still-bottom sludge and flammable liquids were incinerated in an open onsite pit or were disposed of offsite. The open pit incinerator burned approximately 1,000 gallons of solvent sludge per day between 1966 and 1974, when it was decommissioned. By about 1976, most of the solvent sludges were incorporated into a fuel blending program. In 1989 and 1990, site paving and control measures were installed in accordance with a Resource Conservation and Recovery Act (RCRA) Corrective Measures Plan. The site was placed on the National Priorities List (NPL) in 1983, and ceased operations in 1991.

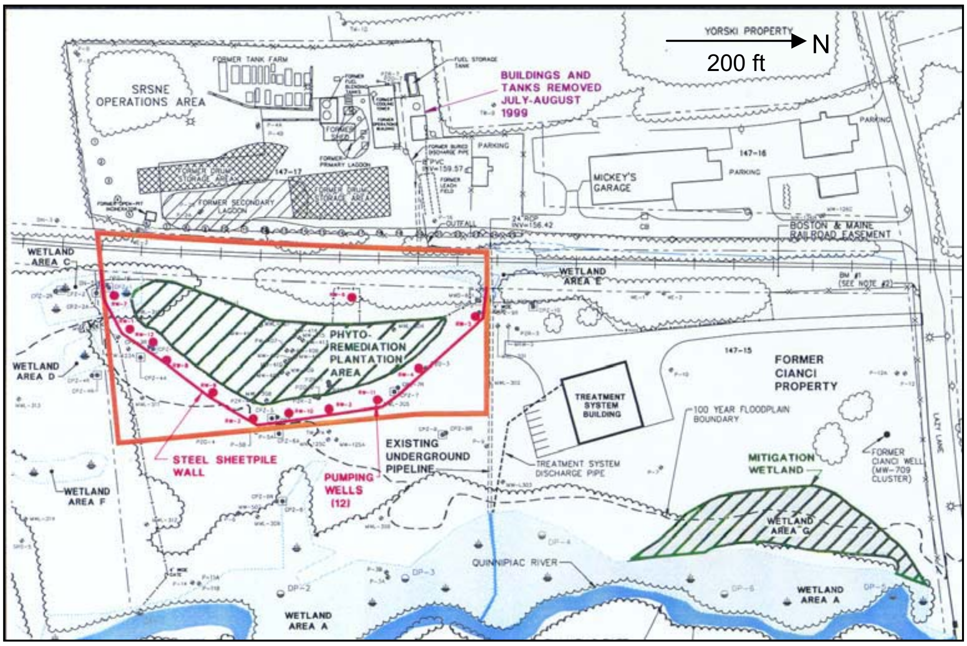

Figure 1. General site configuration

3. HYDROGEOLOGY

The overburden geology beneath the site consists of two main unconsolidated layers. The shallow, upper outwash layer extends from ground surface to approximately 10 to 25 feet below grade and consists of reddish-brown silty sand and gravel deposits, interbedded with discontinuous layers of silt and relatively well sorted sand and gravel. The lower layer consists of glacial till, a generally unstratified unit consisting of reddish-brown clay, silt, sand, gravel, cobbles, and boulders, but also including isolated, discontinuous sandy seams. Fill materials are present above the outwash in isolated areas where grading operations have reworked the upper few feet of soil and filled low areas. In the area south of the site the entire overburden grades to a coarser overall grain size, and resembles classic stratified drift throughout the overburden thickness. The deeper portion of the overburden south and southeast of the site generally lacks fines, and is described as "gravelly drift." In the immediate vicinity of the site, hydraulic conductivity varies over five orders of magnitude with a geometric mean of 6.4E-04 cm/s.

The depth to bedrock (sandstone) varies throughout the study area from approximately 15 to 40 feet below grade at the Operations Area, to approximately 25 to 45 feet below grade east of the Operations Area and approximately 80 to 100 feet below grade south of the site. The bedrock surface dips toward the east in the vicinity of the site. Core samples and drilling observations at the site indicate that the upper 5 feet of bedrock is severely weathered and partially decomposed. The bedrock in the depth interval between five and 30 feet below the top of bedrock is more competent than the weathered bedrock, but is still highly fractured and permeable. At depths of 30 feet or more below the top of bedrock, the rock is characterized by relatively few fractures and may exhibit slightly lower hydraulic conductivity. The deep bedrock can transmit groundwater flow, however, and is the primary zone tapped by private water supply wells north and east of the site. The results of hydraulic testing of bedrock wells, core logging, and analysis of rock core indicate an average fracture spacing of 1.42 m, an average fracture aperture of 96 microns, an average bedding plane fracture dip of 22 degrees to the east-southeast, an average matrix porosity of 7.7%, and an average matrix fraction organic carbon content of 0.36%.

Essentially all overburden and bedrock groundwater within the monitored geologic zones ultimately discharges to the river located east of the site. The overburden and bedrock units are recharged primarily via precipitation, although groundwater underflow also occurs from the north within the saturated zone in the vicinity of the river. Where the till layer is relatively thick, it may limit the rate of groundwater flow between the two aquifers. In areas where till is anomalously thin or absent ("till windows"), or lacks fine-grained material, more groundwater flow may occur between the overburden and bedrock aquifers.

The subject site has undergone approximately 15 separate environmental investigations since 1978. This has resulted in approximately 275 monitoring wells over the 50 acre study area. Various numerical models have been developed to simulate groundwater flow and solute transport at the site. The DNAPL source zone is currently hydraulically contained in both bedrock and overburden by groundwater pumping systems with on-site treatment.

4. NAPL PROPERTIES

NAPLs have been visually observed and recovered from approximately 7 locations on site, including both overburden and bedrock. The DNAPL density varies between 1.07 g/cc and 1.23 g/cc. The DNAPL viscosity ranges from 0.99 cS to 5.59 cS. The DNAPL-water interfacial tension ranges from 3.1 dynes/cm to 9.0 dynes/cm. LNAPL has also been observed, but in insufficient quantities for physical characterization. The NAPLs are composed of a wide range of organic compounds, primarily chlorinated solvents such as trichloroethylene (TCE) and tetrachloroethylene (PCE), aromatics such as toluene, and ketones. An evaluation of Raoult's Law was conducted by comparing calculated effective solubilities (based on measured component composition of the NAPL) to measured effective solubilities (based on analysis of a water sample in equilibrium with the NAPL). The evaluation is depicted in Figure 2, and indicates that Raoult's Law is a reasonable means of calculating effective solubilities at this site.

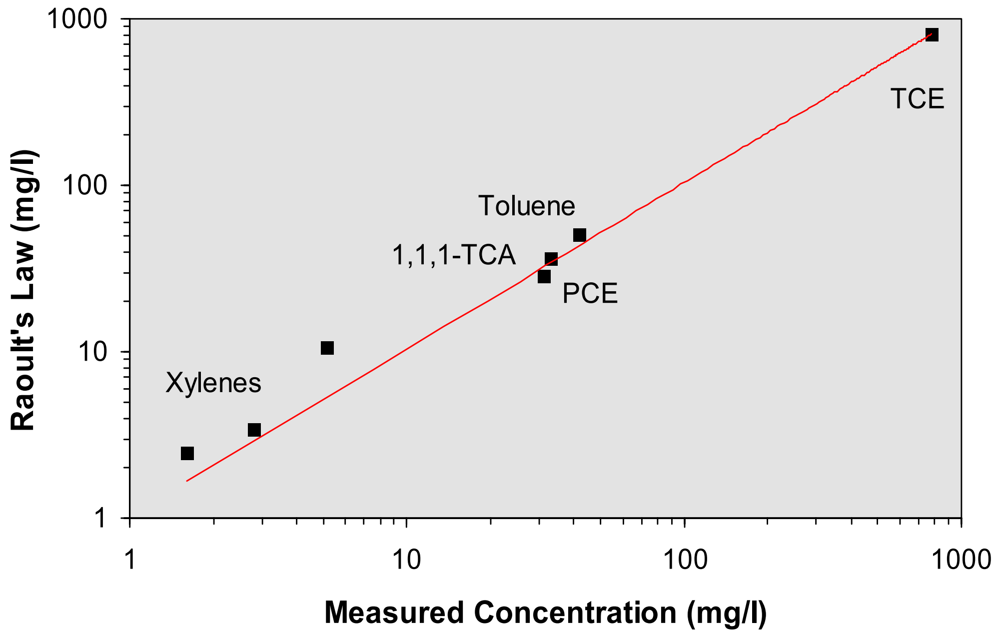

Figure 2. Comparison of calculated and measured effective solubilities

5. DNAPL SOURCE ZONE DELINEATIONS

5.1 First Delineation of DNAPL Source Zone

Figure 3 presents a plot total VOC concentrations in overburden groundwater based on 1992 sample results. DNAPL had not yet been visually observed at the site and site investigators had not concluded that DNAPL was present. At that point in time DNAPL assessment and delineation strategies were in their infancy, and USEPA had not yet published any guidance or technical documents on the subject. The refereed literature did not contain any articles on the issue of DNAPL assessment and delineation. In practice, however, a rule-of-thumb had been adopted by some investigators suggesting that both site use and history combined with aqueous phase constituents detected at 1% of effective solubility may indicate upstream DNAPL presence (this rule-of-thumb is documented in professional short-course notes from 1990 onwards). Given the fact that TCE (solubility = 1100 mg/l) was a major component of overburden VOC composition, it would have been plausible for site investigators to conclude that DNAPL was present at the site given known site disposal practices and the fact that overburden total

VOC concentrations were in excess of 650 mg/l. With respect to delineation, it would have been reasonable at the time for site investigators to conclude that DNAPL may be present within the 10,000 ppb total VOC contour, as depicted by shading in Figure 3. It should be noted that monitoring well P-101B, located east of the river in Figure 3, exhibited a total VOC concentration of 466 mg/l. Using a threshold of 400,000 ppb total VOCs would therefore have extended the inferred DNAPL zone eastward approximately the same distance as a 10,000 ppb total VOC threshold.

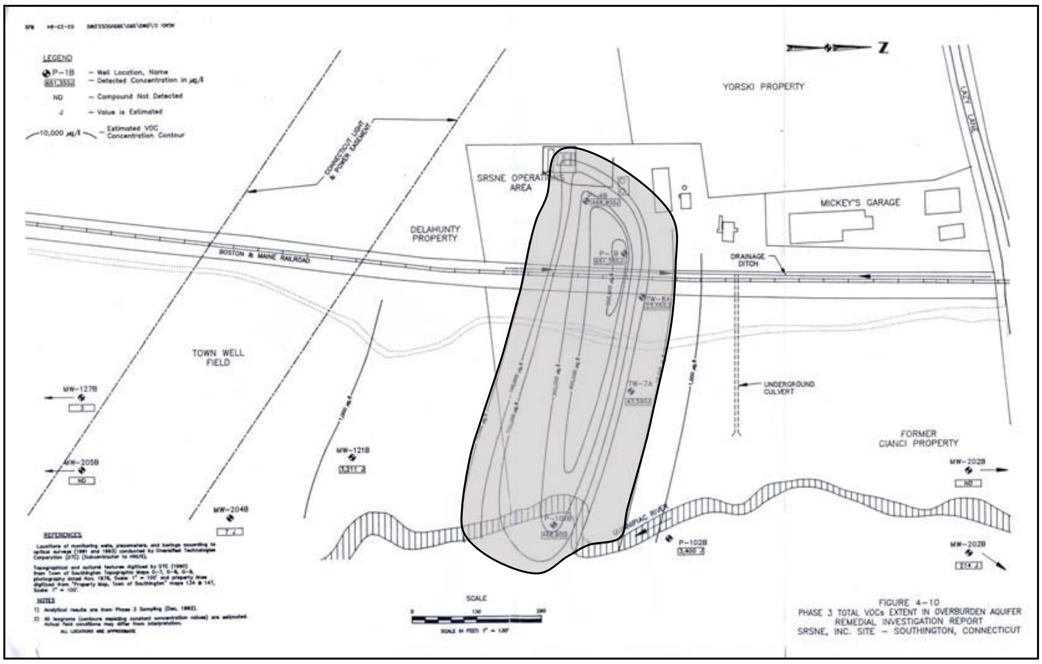

Figure 3. Total VOC concentrations in overburden groundwater based on 1992 data. The shaded area encompasses total VOC concentrations in excess of 10,000 ppb.

Figure 4 presents a plot of total VOC concentrations in bedrock groundwater based on 1992 sample results. As with overburden, DNAPL had not yet been visually observed in bedrock. Although the professional community was aware that DNAPLs could enter bedrock (e.g., Kueper and McWhorter, 1991), the issue of assessment and delineation was not as mature as that for overburden deposits. Using a 10,000 ppb total VOC threshold, the DNAPL source zone in bedrock would be as depicted by shading in Figure 4. In this case, the southward extent of the inferred DNAPL zone would be based on only 1 monitoring well. At this point in time, it was inconclusive whether or not DNAPL was present in bedrock.

5.2 Second Delineation of DNAPL Source Zone

Figure 5 presents a plot of total VOC concentrations in overburden groundwater based on 1995 sample results. As of this sampling round, DNAPL had only been observed in an apparent trace quantity in one overburden monitoring well. Given the high total VOC concentrations (> 500 ppm) and site use and history, investigators had concluded that DNAPL was likely present in overburden. With respect to delineation, it was concluded that the 10,000 ppb total VOC contour (shaded in Figure 5) represented a reasonable estimate of the area within which DNAPL may be present. USEPA had published its first guidance document on the issue of DNAPL assessment (USEPA, 1992), which stated that DNAPL may be present upgradient of a monitoring well if aqueous phase concentrations exceeded 1% effective solubility. The 1992 document also presented other lines of evidence indicating DNAPL presence such as site use/site history, soil concentrations exceeding a calculated threshold, and anomalous plume locations. The shaded area in Figure 5 encompasses monitoring locations where soil concentrations exceed the calculated threshold, and groundwater concentrations exceed 10,000 ppb. Comparison of Figure 5 to Figure 3 shows that the addition of monitoring locations resulted in a wider inferred DNAPL source zone in the vicinity of the Operations Area, but that the 1995 inferred source zone does not extend to the river as a result of the reduced concentrations observed in the vicinity of monitoring well P-101B.

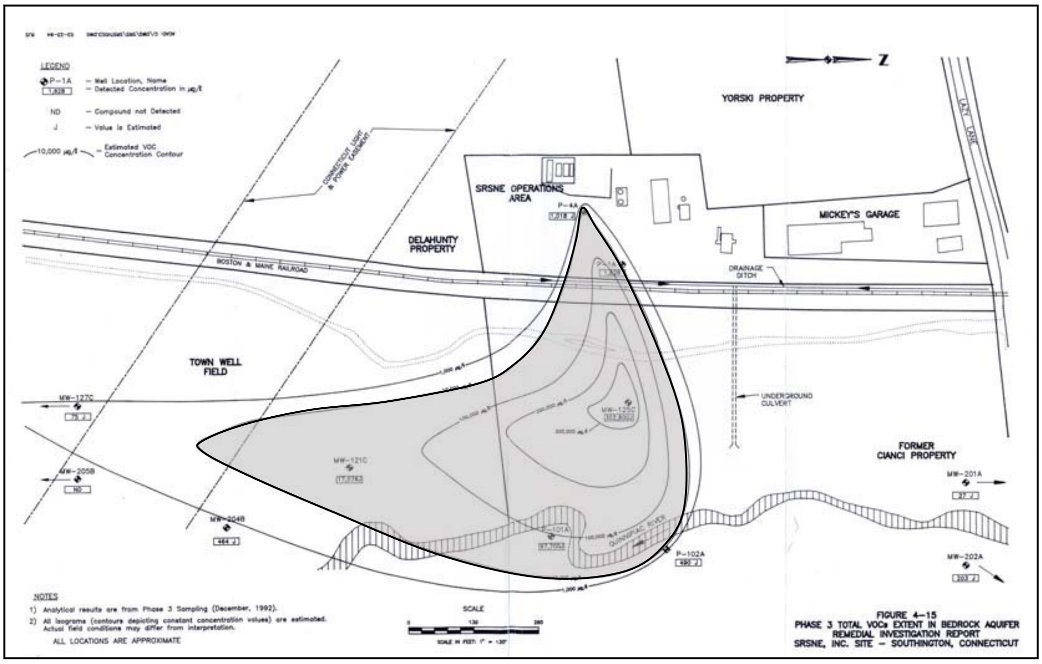

Figure 4. Total VOC concentrations in bedrock groundwater based on 1992 data. The shaded area encompasses concentrations in excess of 10,000 ppb.

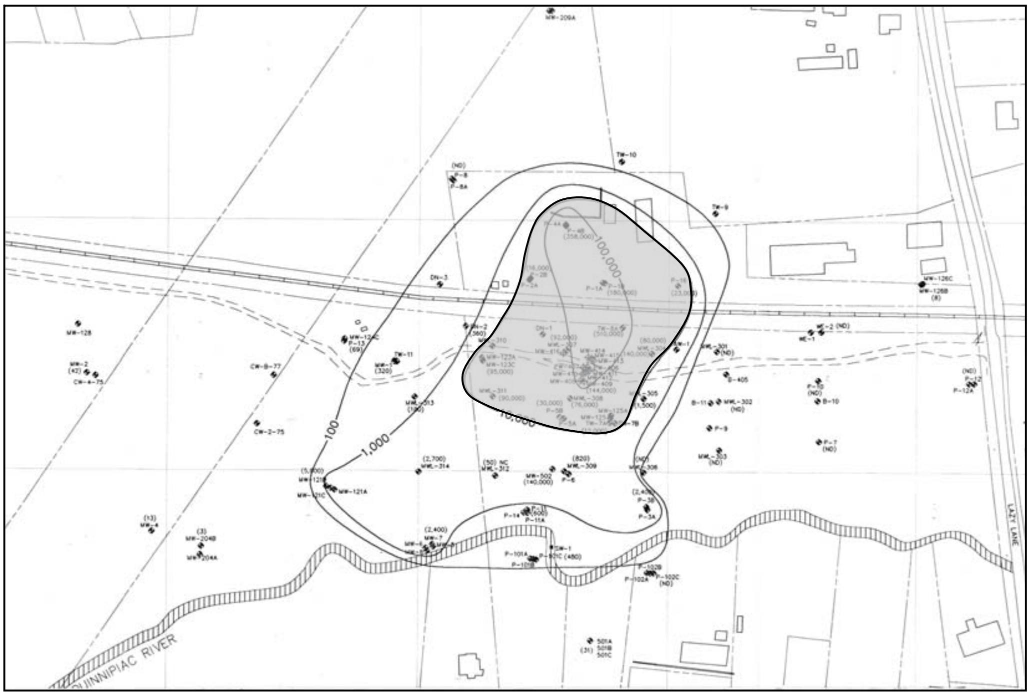

Figure 5. Total VOC concentrations in overburden groundwater based on 1995 data. The shaded area encompasses concentrations exceeding 10,000 ppb.

Figure 6 presents a plot of total VOC concentrations in bedrock groundwater based on 1995 sample results. The shaded area represents the inferred DNAPL zone at the time, based on total VOC concentrations in excess of 10,000 ppb. DNAPL had still not yet been visually observed in bedrock, but investigators had concluded that DNAPL was likely present in bedrock (on the basis of site use/site history, and high total VOC concentrations). Comparison of Figure 6 to Figure 4 shows that the inferred DNAPL zone is smaller in 1995 compared to 1992. It is clear that using groundwater concentrations to infer DNAPL presence is associated with uncertainty because of temporal fluctuations in VOC levels and changes in spatial distribution of data as additional wells are installed. It is also of interest to note that the bedrock DNAPL source zone depicted in Figure 6 is displaced to the east relative to the one shown in Figure 4. It was concluded at this time that the high concentrations observed in bedrock west of the railway tracks in 1992 (Figure 4) may have been the result of vertical mobilization occurring during drilling, and that a likely pathway for DNAPL entry into bedrock in the vicinity of the Operations Area was a line of interceptor wells located immediately west of the railway tracks.

5.3 Third Delineation of DNAPL Source Zone

Figure 7 presents a plan view of the 1996 delineated DNAPL source zone in overburden based on 1995 and 1996 data. At this point in time site investigators had recognized that delineation of DNAPL source zones can be subject to considerable uncertainty because of the tortuous and sinuous nature of DNAPL distributions in the subsurface. The 1996 delineation presents the concept of both a ‘probable/confirmed’ DNAPL source zone, and a larger ‘potential’ DNAPL source zone. The probable/confirmed DNAPL source zone encompasses the area within which there are stronger and more numerous lines of evidence to support DNAPL presence. For the depiction illustrated in Figure 7, the probable/confirmed DNAPL source zone corresponds to the area within which (i) visual observations of DNAPL have occurred (approximately 7 locations), (ii) groundwater concentrations exceed 10% effective solubility, (iii) significant alcohol concentrations have persisted with time (i.e., many alcohols partition preferentially into NAPLs), (iv) soil concentrations exceed a calculated NAPL threshold, (v) historical DNAPL disposal areas occur, and (vi) anomalous plume configurations occur. The potential DNAPL source zone encompasses the area within which (i) groundwater concentrations exceed 1% effective solubility, and (ii) anomalous plume locations occur.

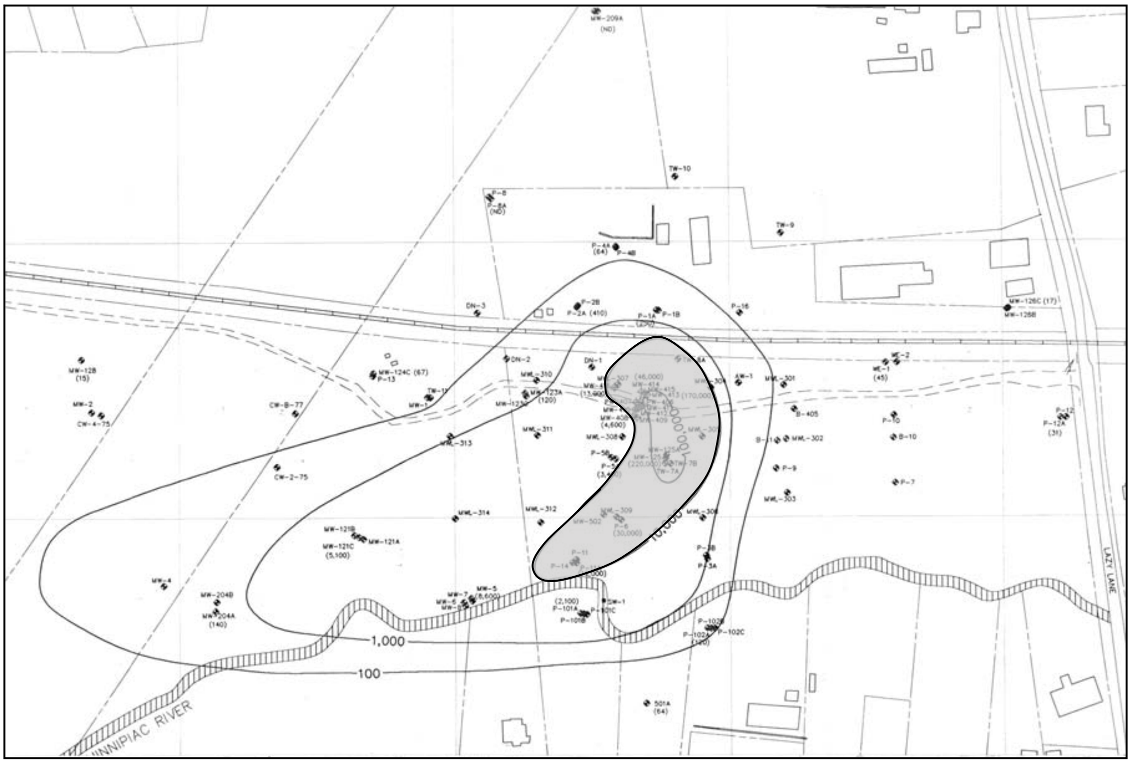

Figure 6. Total VOC concentrations in bedrock groundwater based on 1995 data. The shaded area encompasses concentrations in excess of 10,000 ppb

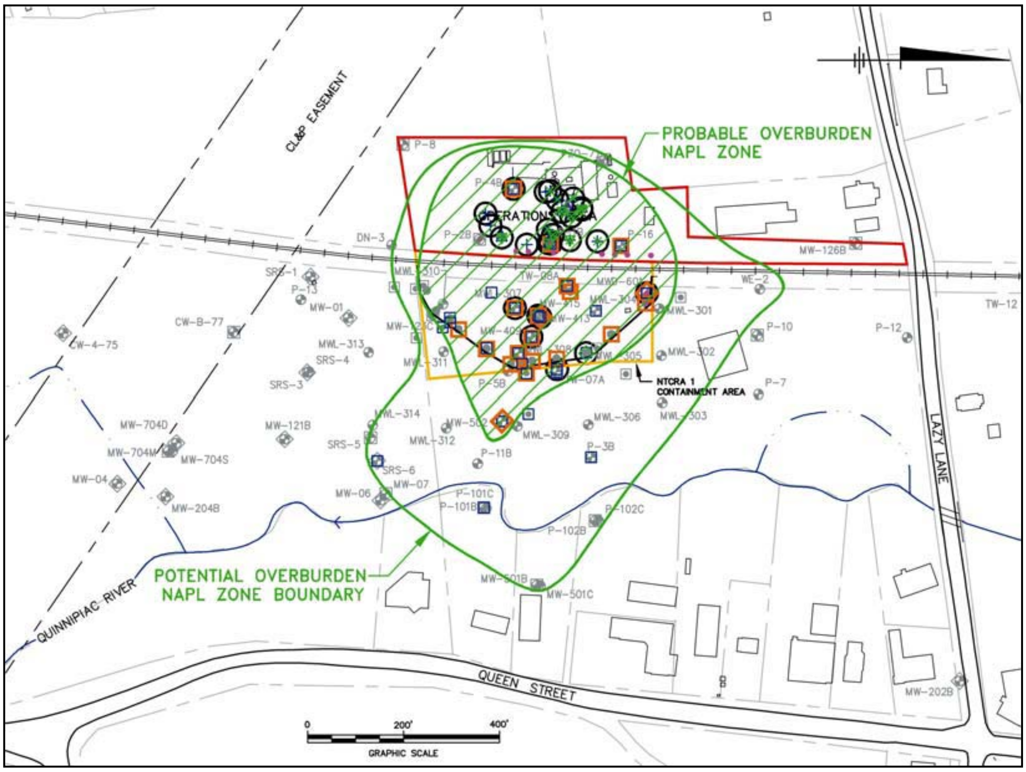

Figure 7. Probable/confirmed and Potential NAPL source zones in overburden based on 1995 and 1996 data

Figure 8 presents a plan view of the 1996 delineated DNAPL source zone in bedrock based on 1995 and 1996 data. As with overburden, both a ‘probable/confirmed’ DNAPL source zone and a ‘potential’ DNAPL source zone were delineated to reflect uncertainty. The most significant feature of the 1996 delineation compared to earlier delineations is the extension of the source zone northward to Lazy Lane. The persistent and anomalous VOC concentrations in that vicinity suggest that historical operation of a water supply well immediately south of Lazy Lane mobilized DNAPL northward along bedding plane fractures. This interpretation is supported by the fact that (i) DNAPL was visually observed in bedrock at bedrock well MW-705DR, (ii) bedrock bedding plane fractures that intersect the supply well ‘daylight’ at the top of rock in the Operations Area (i.e., accounting for strike and dip), and (iii) hydraulic gradients can easily mobilize pooled DNAPL in bedrock fractures. It is of interest to note that the visual observation of DNAPL in bedrock well MW-705DR is completely outside of the total VOC plume mapped on the basis of both the 1992 and 1995 data sets.

5.4 2003 Overburden Boring Program

An overburden boring program was completed in November of 2003 to further refine the estimate of the overburden DNAPL source zone. The boring program involved the use of a push sampling device (PowerProbe) to collect continuous overburden cores from ground surface to the top of bedrock. Each core was screened for VOC presence using a PID monitoring device, visually inspected, and subjected to a hydrophobic dye test where DNAPL was suspected or visually observed. The results of the boring program confirmed that DNAPL is present in overburden within the probable/confirmed DNAPL Source zone. The positive DNAPL identifications during the boring program occurred west of the railway tracks, directly beneath known DNAPL entry points. This supports the use of high groundwater concentrations (also present in this area), high soil concentrations (also present in this area), and site use and history in assessing DNAPL presence. The lack of observed DNAPL east of the railway tracks during the boring program is attributed to a sparser distribution of DNAPL in that area. It should be noted that although DNAPL was visually encountered east of the railway tracks on two separate occasions prior to 2003 (i.e., free product recovery in RW-5 and MWD-601), it was not observed in the vicinity of those locations during the recent boring program. This suggests that a boring program is subject to considerable uncertainty given the tortuous and sinuous distribution of DNAPLs in naturally occurring heterogeneous deposits, and that secondary lines of evidence should also be used to assess DNAPL presence and spatial extent.

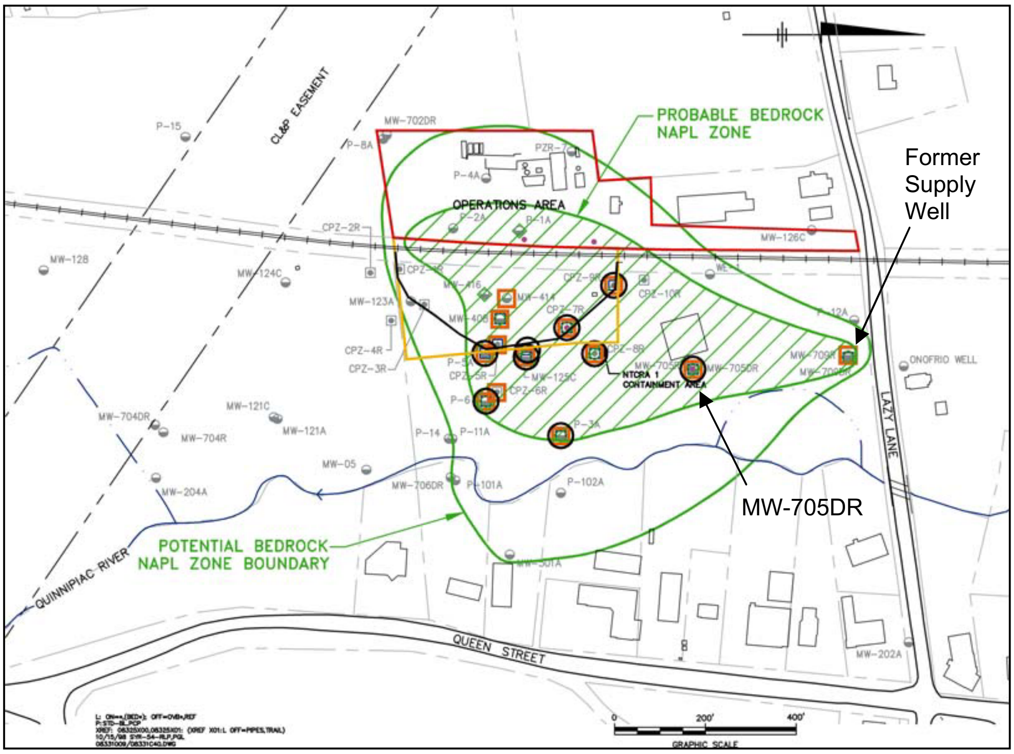

Figure 8. Probable/confirmed and Potential DNAPL source zones in bedrock based on 1995 and 1996 data

6. LESSONS LEARNED

The large number of environmental investigations that have been conducted at this site provide a valuable historical perspective on DNAPL assessment and delineation activities suitable for use at hazardous waste sites. The most important 'lessons learned' can be summarized as follows:

1) Exact delineation of the DNAPL source zone is not possible because of the tortuous manner in which DNAPL distributes itself in the subsurface.
2) The use of both 'probable/confirmed' and 'potential' DNAPL source zones is a practical means of reflecting uncertainty in delineation.
3) DNAPL can migrate hydraulically upgradient, downgradient, and cross-gradient, implying that site investigation programs need to carefully consider not only groundwater flow directions, but structural controls and historical pumping activities when citing monitoring wells. A sufficient number of sample points must be present in the upgradient and cross-gradient directions.
4) No single line of evidence is sufficient to delineate a DNAPL source zone. Converging lines of evidence provide the highest degree of confidence; these should include visual observations, boring programs, assessment of groundwater concentrations (spatial variability and temporal trends), assessment of soil concentrations, consideration of alcohols in groundwater, site use/site history, and assessment of anomalous plume locations.
5) The lateral and upgradient extents of the DNAPL source zone may be the easiest to delineate; greater uncertainty will exist in the downgradient direction because of the complicating effects of dispersion, biodegradation, well placement, and well bore dilution.

7. REFERENCES

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