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PART X: Site Assessment

Chapter 25

DYE TRACER STUDY—TRIED AND TRUE METHOD YIELDS SURPRISING RESULTS

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ABSTRACT

The use of tracer dyes is a technically valid and cost-effective method for characterizing contaminant fluxes and hydraulic properties in complex hydrogeologic systems. Dye tracing methods were successfully employed at a site in New Jersey to evaluate the effectiveness of the groundwater containment system and to update the conceptual site model (CSM). The data has driven a reevaluation of the groundwater containment system and CSM, including a review of interim alternative technologies to increase efficiency while a new approach capping the remedial action timeframe at 15 years is tested and implemented.

Uncertainty with regard to the persistence of constituents in downgradient monitoring wells and the influence of long-term pumping from the interconnected overburden and basalt bedrock aquifers led to the evaluation of methods that would both address multiple hypotheses on contaminant flux and update the CSM. The property contains several distinct features that add to its complexity, including a former surface impoundment underlain by alluvial sediments and fractured bedrock, and the immediate presence of water bodies.

The fluorescent dyes fluorescein, eosine, and rhodamine WT were selected for the Dye Tracer Study (DTS) and individually injected at three locations following

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baseline sampling. The injection locations considered the presence of source material (former surface impoundment), hydraulic properties of the aquifers (pumping induced gradients, travel times, heads from adjacent water bodies), and parent/daughter compound concentration relationships. The DTS was conducted over 14 months and involved the collection of grab and composite samples from monitoring and extraction well networks, and along an adjacent brook.

A single dye, fluorescein, was identified over the course of the DTS. The fluorescein was injected in the former surface impoundment and travelled south at an approximate rate of ten feet/day. The DTS illuminated flow pathways that were unexpected in terms of speed of groundwater migration and extent laterally and vertically.

Keywords: dye tracing, groundwater tracer, fluorescein, eosine, rhodamine WT, contaminant flux, groundwater flow, site assessment, site characterization.

1. INTRODUCTION

Tracer dyes have been used to aid understanding of complex systems for at least the last century, with applications ranging from characterizing human disease vectors to anthropomorphic contributions to environmental degradation (USGS, 1986). Tracer dyes are used to understand receptor pathways related to an identified condition. The following discussion focuses on the use of tracers at an environmental remediation project where contaminant flux was poorly understood, including uncertainty with regard to groundwater containment and the applicability of the working conceptual site model (CSM).

Dye tracer methods were employed to test three hypotheses on groundwater flow and contaminant migration mechanisms. The data revealed flow pathways that proved the least anticipated hypothesis, which is now the basis for the revised CSM.

2. PROJECT BACKGROUND

Soil and groundwater contamination was identified at a former organic pigments manufacturing plant located in northern New Jersey in the mid-1980s. The contamination consists of chlorinated ethenes and benzenes, primarily tetrachloroethylene (PCE) and 1,2-dichlorobenzene (IT Corporation, 1990). Lime neutralization sludge was disposed in surface impoundments located in the northern half of the property (North Yard) prior to 1940 (earliest records available) and continuing through the mid-1970s. Manufacturing was located in the southern half of the property (South Yard).

Remedial investigations revealed contamination in soil and groundwater. The remedial action construction consisted of demolishing the manufacturing plant, capping the North Yard and South Yard, and startup of a groundwater and soil vapor extraction and treatment system. Prior to activation of the groundwater extraction and treatment system (GETS), volatile organic compounds (VOC) exhibited concentrations exceeding the New Jersey Department of Environmental Protection (NJDEP) Ground Water Quality Standards (GWQS) at overburden compliance wells located to the east across a brook. Since GETS startup, VOC concentrations in the overburden compliance wells have been reduced by three orders of magnitude. However, several compounds continue to exhibit concentrations above GWQS despite extraction system upgrade programs. Consequently, it remained unclear as to whether VOC migrated to compliance wells from the west beneath the brook (working CSM) or via an upward gradient from the underlying bedrock (remedial investigation finding). A third hypothesis proposed contaminant migration from the North Yard along the shallow fractured basalt bedrock.

As a result of the extraction system upgrade outcomes and the competing hypotheses on groundwater flow and contaminant migration mechanisms, GETS effectiveness remained uncertain. Dye tracing was considered the most efficient method for characterizing groundwater flow and contaminant migration to compliance wells (OUL, 2002). A Dye Tracer Study Work Plan was therefore developed and implemented in October 2005 and the field phase completed in December 2006. Two additional rounds of dye tracer data have since been collected: November 2007 and January 2009.

3. PHYSICAL AND GEOLOGIC SETTING

The property is situated in the valley formed by the First Watchung and Second Watchung mountain ranges (NJGS, 2003). Property topography ranges from approximately 206 feet above mean sea level (msl) to 170 feet above msl, with the topographic gradient toward the southeast. The topographic high is the North Yard and the topographic low is a brook channel at the southeastern corner of the South Yard. Storm water infiltration is limited by an impermeable liner incorporated into the cap across the property and is instead conveyed to the brook.

The brook, which drains a watershed between the crests of the two mountain ranges, runs into the northern limit of a man-made pond (dammed). The pond is situated adjacent to the north border of the North Yard. The brook then exits the southern side of the pond via a dam spillway and enters the property at the northeastern corner, adjacent to the North Yard. The elevation of the brook transitions from approximately 179 feet msl at the northeastern corner of the

property to approximately 175 feet msl at a second spillway located approximately 900 feet south of the dam. The brook elevation drops approximately four feet at the spillway and exits the property near the southeastern corner of the South Yard at an approximate elevation of 170 feet msl.

The head in the pond likely drives water as seepage into the local sediments at and surrounding the dam and, where the brook leaves the pond, the heads are still held artificially higher. The pond potentially forces a southerly gradient locally. In addition, being situated in the valley between the two Watchung Mountains increases the potential that higher-velocity depositional environments existed during glacial episodes. Therefore, glacio-fluvial deposits are likely to exist in the native sediments (NJGS, 2003). Where glacial or post-glacial streams were running, coarse sediments would have been deposited. These features, called “paleo-channels”, now buried by subsequent sedimentation and artificial fill, would create a significant permeability contrast with typical till sediments and could act as important conduits for overburden groundwater flow.

Bedrock across the property consists of two distinctly different formations: Metamorphosed sedimentary rock (of the Triassic Newark Basin), including shale and sandstone layering, and Jurassic Age basalts of igneous origin that were intruded into and flowed over the shale and sandstone (Geraghty & Miller, Inc., 1993). Erosion and folding/faulting of the rock formations produced the current subsurface conditions, along with surface weathering and erosion. Basalt bedrock outcrops in and along the brook at the northeastern section of the property. The basalt outcropping transitions to a gravelly stream bed as the brook flows from the North Yard to the South Yard. This transition is complete in the vicinity of the concrete spillway and indicates that glacial-alluvial sediments may extend under and across the brook.

The basalt is encountered at varying depths across the property, but tends to be present at shallower depths in the northern and eastern portions and ranges from approximately 25 feet to 45 feet below ground surface (bgs). The bedrock surface generally slopes to the southwest, with minor undulations. The shallow basalt is in contact with alluvial sediments, and was observed to have a highly weathered zone—boring logs indicate the presence of significant vertical joints or fractures (IT Corporation, 1990). The exposed shallow basalt at the northeast corner of the property exhibits a high degree of weathering and fractures. The deeper basalt unit was shown via boring logs to have generally lesser amounts of fracturing and thus appears to have lower (or significantly lower) permeability than the shallow basalt (Geraghty & Miller, Inc., 1993). Significant decreases in head measured during drilling and in ongoing water level monitoring indicate that this layer acts generally as a confining unit. Primary porosity in the Watchung

Basalt is negligible. Secondary porosity is provided by joints. This is exemplified by the presence of a lineament located along the western portion of the property. The lineament has revealed a bedrock fault or fracture system that is under the direct influence of the deep bedrock groundwater extraction system as evidenced by pumping induced hydraulic gradients in South Yard wells.

Groundwater is approximately 20 feet deep in the overburden aquifer and shallower in the immediate vicinity of the brook. Depth to groundwater in the fractured bedrock is generally similar. Depth to water in the deep bedrock beneath the South Yard is much deeper, ranging from more than 75 feet to almost 200 feet. The lower water levels in the deep bedrock are attributed to the long-term remedial pumping. The vertical gradient between the overburden and the shallow fractured bedrock groundwater is typically downward and low, indicating a strong hydraulic connection. The vertical gradient between the shallow and deep bedrock groundwater is high, indicating a weak hydraulic connection.

The North Yard was constructed over time as a series of surface impoundments and contains an estimated 94,000 cubic yards of lime neutralization sludge, including some with pigments and residues (IT Corporation, 1990). The sludge has a relatively low permeability and is in direct hydraulic connection with native sediments (alluvium) and weathered/fractured basalt. Remediation features in the North Yard include four overburden and shallow bedrock groundwater extraction wells on the eastern perimeter, west of the brook, 40 dual-phase vapor extraction (DPVE) wells installed in the former surface impoundment, and two deep bedrock groundwater extraction wells.

The South Yard includes a former equalization basin and its predecessor, an unlined process lagoon, as well as thick, reworked sediments and fill, and the slabs/foundations of former manufacturing buildings. Based on boring logs, artificial fill and/or constructed features comprise almost all of the shallow subsurface materials above bedrock in the South Yard. Remediation features in the South Yard include six overburden and shallow bedrock groundwater extraction wells on the eastern perimeter, west of the brook, and a network of 20 soil vapor extraction (SVE) wells installed in the vicinity of the former lagoon.

4. DYE TRACER STUDY METHODS

The Dye Tracer Study (DTS) was designed to test hypotheses on groundwater flow and contaminant transport mechanisms from three sections of the property: North Yard, South Yard, and the topographic and hydraulic high point at the western edge of the property. The objectives of the DTS were to evaluate groundwater flow conditions and contaminant flux within and between the

alluvium and the shallow fractured bedrock, identify discharge zones and estimate travel times, and evaluate the degree of mixing.

4.1 Tracer Dye

Three tracer dyes were employed for the DTS: fluorescein, eosine, and rhodamine WT. The tracers are of a class of fluorescing compounds known collectively as xanthenes dyes (i.e., derived from xanthene). Xanthene dyes are water soluble, stable (i.e., not easily affected by geochemical changes), readily disperse (i.e., not adsorbed by formation materials), and are not known to cause toxicological impacts. They are strongly fluorescent, making detection possible even under highly dispersive conditions. For these reasons, xanthene dyes are considered conservative tracers in a groundwater environment (Flury and Wai, 2003).

Fluorescein and eosine were procured as a powder containing approximately 75 percent dye equivalent and 25 percent diluent. Diluent (typically starch) in dye mixtures is a standardizing material used by manufacturers to ensure that different batches of dye have the same fluorescence intensity. Diluents may also improve the mixing performance of the dye. The fluorescein was received in six, 22-liter carboys, while the eosine was received in three, 22-liter carboys. Each carboy was filled with four pounds of powdered dye. To each carboy, four gallons of municipal water were gradually added to thoroughly dissolve the dye. Fluorescein was introduced to the North Yard lime sludge/alluvial sediments at six randomly selected DPVE wells. Eosine was introduced via an overburden monitoring well (hydraulic high point) located along the western border of the property.

Rhodamine WT (water tracing) was received pre-mixed in four, 1-quart Nalgene bottles (20 percent dye equivalent and 80 percent water). Nothing additional was required for this dye in terms of preparatory work. Rhodamine WT was introduced via an SVE well located in the western portion of the South Yard.

4.2 Background Data

The DTS design considered the potential for interference (analytical peaks in or near acceptable wavelength ranges) by naturally fluorescing substances or similar manmade dyes that may be associated with former production (OUL, 2002). To investigate potential sources of fluorescence interference in groundwater and surface water, two rounds of background sampling were conducted. Background concentrations of a compound with a fluorescence wavelength similar to that of fluorescein (approximately 515 nanometers [nm]) were identified in wells and brook monitoring stations. Neither eosine or rhodamine, nor substances which

fluoresce at or near the wavelengths of these dyes, were detected above analytical method detection limits.

A second unknown fluorescing substance was identified during background sampling. Wavelength peaks of this substance were in the 483 nm range. This compound was labeled the 483 dye and was identified in several monitoring stations that exhibited background concentrations of the compound fluorescing at 515 nm. However, while background concentrations of the 515 nm substance were exhibited widely across the property, the 483 dye was limited to locations in the vicinity of the former unlined process lagoon and the northern section of the North Yard. Final deposition in the North Yard occurred in the northern section and reportedly consisted of materials excavated from the unlined process lagoon. The identification of the 483 dye at the two distinct locations suggests that it may have been associated with former production, whereas the 515 nm background substance is either from naturally occurring processes or is an artifact of historic production, which has had a longer period to disperse. Sampling of upgradient groundwater to determine true background quality was not performed due to a lack of monitoring wells (NJDEP, 2005).

4.3 Field Methods

The dyes were introduced on November 1, 2005. The injection wells were tested with potable water prior to dye introduction to measure the rate of intake. Due to the sensitivity of the analytical method and the high potential for false positives from cross-contamination, care was taken in the transport and handling of the dyes during introduction. Each dye was transferred to its respective injection point in dedicated poly-sheeting. Dedicated funnels were used at each injection point to introduce the dyes. All disposables used during dye introduction at a given injection point were disposed afterwards and replaced with new disposables prior to commencing dye introduction at the next well. A dilute solution of bleach was available to neutralize spilled dye. No injection location was subsequently used for monitoring.

Prior to introducing a dye, water was added through a funnel to wet the well casing/riser pipe. This helped to prevent dye loss to the inside surface of the well casings. The entire volume of the dye was introduced as a single slug. Each well was flushed with ten gallons of municipal water at a rate equivalent to the observed intake.

Monitoring of dye transport through the aquifer system was accomplished by setting carbon composite samplers at each station for a period of one week. Grab samples of water were also collected to provide dye concentrations at a known point in time. The one week period was maintained throughout the DTS to ensure

consistency in the analytical data. After one week, the carbon samplers were collected from their respective stations along with the water grab samples. Groundwater levels were measured prior to sample collection. To prevent cross-contamination, new latex gloves were used at each sample station. All samples were shielded from sunlight during collection to prevent the dyes from degrading. Carbon composite samplers were bagged separately from the water vials. All samples were documented/tracked using chain of custody procedures (NJDEP, 2005) and shipped on ice directly to Ozark Underground Laboratories (OUL).

The carbon samplers were supplied by OUL and constructed of a fiberglass mesh (1.3 millimeters [mm] to 1.5 mm). Each sampler was pre-filled with a standardized 4.25 grams of Barnebey and Sutcliffe Type AC Activated Carbon and heat sealed. In preparation for deployment, each carbon sampler was triple-soaked in distilled water for ten minutes per soak.

The first round of carbon samplers were deployed on October 31, 2005, one day prior to dye introduction to ensure that any rapid movement through the aquifer system would be identified. During the first six weeks after dye introduction, carbon samplers were set and retrieved on a weekly basis. After the initial six rounds of weekly sampling, carbon samplers were set biweekly until August 22, 2006. The carbon samplers were set once per month thereafter, beginning in September 2006, until field phase termination on December 19, 2006.

4.4 Analytical Methods

The carbon composite samplers were washed at OUL (Aley, 2003) with dye-free, unchlorinated water to remove sediment and organic matter. After washing, the packets were shaken to remove excess water, and the carbon emptied into new disposable plastic beakers. The dyes were then eluted from the carbon with a solution of five percent aqua ammonia (29 percent ammonia) and 95 percent isopropyl alcohol (70 percent alcohol, 30 percent water), and enough potassium hydroxide flakes to supersaturate the solution. The potassium hydroxide was added until a supersaturated layer was visible at the bottom of the container. The supersaturated layer was not used for the elution. Fifteen milliliters of the solution were poured over the washed charcoal, the beaker capped, and the sample allowed to stand for one hour. The liquid was subsequently decanted into a new disposable beaker.

Three milliliters of elutant were extracted using a disposable polyethylene pipette and transferred to a disposable polystyrene cuvette specifically designed for fluorometric analysis. The cuvette was then placed in the spectrofluorophotometer for analysis. The spectrofluorophotometer performs a

synchronous scan of the sample and generates a plot. Emission fluorescence is depicted on the plot. The fluorescence peak represents the concentration of a given dye in parts per billion (ppb), which is calculated by separating fluorescence peaks due to dyes from background fluorescence and then calculating the area of the peak. The area is proportional to the area obtained from a standardized solution. The wavelength emitted indicates which type of dye is present.

Water grab samples were normally tested without pre-treatment, unless extremely turbid. In instances where samples were turbid, the laboratory let the solids settle from the sample, centrifuged the sample, or diluted the sample.

Ozark Underground Laboratory has established normal emission fluorescence wavelength ranges for the dyes used. A range is equivalent to mean values plus and minus two standard deviations. Detection limits for the dyes were determined by OUL based on the concentration necessary to produce emission fluorescence peaks where the signal to noise ratio is three. For OUL to deem a concentration a positive dye recovery, the following conditions must be met:

In the elutant and the water, there must be at least one fluorescence peak at the station between the minimum and maximum wavelength peak for a given dye.

A positive dye detection in elutant must be at least three times the detection limit and at least ten times the concentration detected in a given background sample. The peak must resemble the typical shape exhibited by the dye.

For a peak to be deemed a positive recovery of dye in water (grab sample), there must be a corresponding positive recovery of dye in the elutant (composite sample) from the same station. The concentration must be at least three times the detection limit.

5. RESULTS AND DISCUSSION

Fluorescein was the only tracer dye to exhibit concentrations during the DTS. Eosine exhibited low concentrations at one downgradient location during post-DTS sampling. The groundwater flow and contaminant flux pathways that are now established by way of the DTS findings have driven significant revisions to the CSM.

5.1 Groundwater Flow and Discharge

Fluorescein was injected into North Yard DPVE wells, which are constructed through the alluvial sediments to the top of the shallow fractured bedrock surface. Fluorescein was subsequently detected in a majority of the monitoring points,

exhibited a wide range of travel times and concentrations, and followed a north to south transect across the property. The relative concentrations of fluorescein observed during the DTS and VOC observed during quarterly groundwater sampling mirror each other at all monitoring points. The fluorescein travel time correlated with the presence and relative concentrations of VOC daughter products at a given monitoring well. Only extraction wells were available for sample collection from the overburden and shallow fractured bedrock. Therefore, dye travel times and relative concentrations are influenced by placement of the screened interval, formation characteristics, and extraction rates.

Fluorescein was positively identified in an overburden extraction well located at the southeast corner of the North Yard during week 4 and peaked during week 18 (February 28, 2006). Fluorescein was positively identified in an overburden extraction well located at the northeast corner of the South Yard during week 16 (February 14, 2006). The approximate distance between these two points is 355 feet. Fluorescein was also positively identified in overburden and shallow bedrock extraction wells along the eastern edge of the South Yard during week 16. These points form a north to south transect (South Yard transect) from the North Yard, with the shallow bedrock extraction well situated the furthest, approximately 725 feet, from the closest fluorescein injection point.

Fluorescein velocities were calculated by dividing the distance between the closest North Yard injection point and a given monitoring point by the time elapsed between injection and the first positive dye concentration at that given monitoring point. This equated to a velocity of approximately 6.1 feet per day (ft/d) for fluorescein to reach the southeast corner of the North Yard. Velocities between the closest North Yard injection point and the extraction wells along the South Yard transect ranged from 4.3 ft/d to 6.9 ft/d (shallow bedrock). The velocities drop by a factor of roughly two if calculated based on when the maximum concentration is observed and by a factor of roughly three when the mid-point of the decreasing concentration is used for the calculation. The change in velocity at a given monitoring point was a function of the trend, which in turn is a function of well location, formation in which the well is screened, extraction rate, and tracer dye dispersion.

The fluorescein trend lines, which reflect relative concentrations, travel time, and dispersion, can be related to VOC concentration data. For example, each well along the South Yard transect exhibits high concentrations of parent (PCE) and daughter compounds (trichloroethylene, cis-1,2-dichloroethylene, vinyl chloride) in groundwater samples. Conversely, an overburden extraction well located at the southern edge of the South Yard, which exhibited low concentrations of fluorescein late in the DTS (week 36, July 3, 2006), but high concentrations of 483 dye, also exhibits high concentrations of daughter products in groundwater

samples (parent compounds are typically not observed). The location of this well may represent a low velocity overburden plume, which is undergoing biodegradation and may or may not be isolated from shallow bedrock.

The data collected from two bedrock monitoring wells located at the northeast and southeast corners of the South Yard demonstrate the preferential flow in the shallow fractured bedrock. These wells are situated at the northern and southern extent of the South Yard transect. Each of these wells is installed below the shallow fractured zone of the basalt. The bedrock well located at the northeast corner of the South Yard did not exhibit positive detections of fluorescein until late in the DTS (week 34, June 19, 2006). The highest fluorescein concentration was exhibited in samples collected at the end of the DTS (December 19, 2006). The well is situated in a portion of the property from which past groundwater elevation data has demonstrated a strong downward vertical gradient between the overburden and shallow basalt zones and the deep basalt as a function of the extraction system. The bedrock well located at the southeast corner did not exhibit fluorescein during the DTS. Instead, the well consistently exhibited concentrations of the 483 dye and the 515 nm background substance. These data indicate that groundwater flow and contaminant migration occurs through the shallow fractured basalt, while the deeper competent basalt has low primary and secondary permeability.

Variability of flow and location were key drivers for whether the brook acted as a discharge or recharge boundary for groundwater. Data indicate that the section of the brook lying above the spillway acts as a recharge boundary except in periods of very low flow. This observation is verified by the fact that VOC are generally not observed during monitoring events in samples collected from the brook and the compliance well situated above the spillway. During low flow conditions, combined with the change in hydraulic head on the downstream side of the spillway, the southern reach of the brook is a groundwater discharge zone. This is verified by surface water and compliance well analytical data which intermittently exhibit low VOC concentrations. Fluorescein was detected in the compliance well located below the spillway late in the DTS.

5.2 Contaminant Flux

Sampling results from the remedial investigations and subsequent monitoring has demonstrated that contaminated groundwater persists in portions of the bedrock. The North Yard continues to emanate significant contaminant fluxes to the groundwater extraction system. While groundwater concentrations have dropped from initial operations, contaminant fluxes measured at the extraction points have been relatively steady over the past several years. Based on the dye-tracer testing and the observed pattern of highest concentrations in the shallow groundwater

flow system, the contact zone between the overburden and upper basalt appears to be of the highest transmissivity and fastest groundwater flow zone. The breakthrough of fluorescein to the South Yard transect indicates that the prevailing velocity could be as high as 10 ft/d and the estimated horizontal hydraulic conductivity could be on the order of 100 ft/d.

A significant finding during the DTS was the presence of the 483 dye. The 483 dye is considered a marker for historic contaminant migration since it has been identified only at locations that represent longer periods of contaminant flux than for the DTS injected tracers. The presence of 483 dye in extraction wells along the South Yard transect is a strong indicator of contaminant migration in the shallow fractured bedrock from the North Yard. With several exceptions, the shallow bedrock extraction well on the South Yard transect exhibited the highest concentrations of the 483 dye over the course of the DTS. While the presence and higher concentrations of the 483 dye in the shallow bedrock extraction well may be due to its proximity to the former unlined process lagoon, its presence in all extraction wells along the South Yard transect is a strong indication of a North Yard flux.

5.3 Extended Period Dye Tracer Data

Two additional rounds of dye tracer data were collected: November 2007 and January 2009. The January 2009 round had the advantage of incorporating wells installed during a groundwater remedial investigation conducted between November and December 2008.

The fluorescein concentration exhibited in a new shallow bedrock well installed in the central portion of the South Yard was high compared with other wells sampled in January 2009. The 483 dye was also present at a relatively high concentration, indicating a long-term flux from the North Yard. The contaminant concentrations in this well are the highest of any well on the property. This is consistent with preferential flow in the uppermost portion of the fractured basalt where the well was constructed.

Fluorescein was detected at higher concentrations in new shallow bedrock compliance wells installed to the east of the brook than in the corresponding overburden wells. Similarly, contaminant concentrations across the brook are higher in the shallow bedrock wells than in the overburden wells. Since GETS startup, contaminant concentrations in the overburden wells east of the brook have decreased by up to three orders of magnitude. There are no baseline analytical data available for the shallow bedrock groundwater east of the brook. It is important to note that, as with the fluorescein concentrations, contaminant concentrations in the wells to the east of the brook are several orders of magnitude

below concentrations in the extraction wells and the monitoring wells located to the west in the South Yard. Therefore, though the primary groundwater flow direction in the shallow fractured bedrock is south, parallel to the brook, based on dye and contaminant trends across the brook, preferential flow in the bedrock is the likely mechanism for contaminant migration east of the brook.

Based on hydraulic head data and observations during pumping, the bedrock monitoring well located at the southwest corner of the South Yard is hydraulically connected to a deep bedrock extraction well in the North Yard. The bedrock monitoring well exhibited increasing fluorescein concentrations, nearly tripling between November 2007 and January 2009. This indicates that fluorescein is reaching deeper bedrock strata over time. The two North Yard deep bedrock extraction wells also exhibited increasing fluorescein trends, indicating further downward migration over time.

The presence of low fluorescein, and for the first time eosine, concentrations in a shallow bedrock monitoring well located near the western border of the South Yard during the January 2009 sampling event is considered a model for groundwater flow and contaminant flux at the property. Neither dye was detected in the overburden well of the well pair. The well pair is located south of the North Yard and the eosine injection point. As with the low concentrations in the shallow bedrock wells to the east of the brook, the fluorescein and eosine at this well represents preferential migration from the North Yard, albeit at very low concentrations. Contaminant concentrations are correspondingly low. The migration of eosine (injected in the overburden at the western edge of the property) demonstrates the interconnection between the overburden and shallow bedrock and the preferential flow in the fractured zone. Eosine has moved vertically under the influence of the prevailing hydraulic head from the overburden to the shallow fractured bedrock and migrated to the south.

6. CONCLUSIONS

Dye tracer methods identified and correlated source area contaminant flux, groundwater concentrations, groundwater discharge locations, and travel times as related to the presence of parent compounds and daughter products. Based on the results of the tracer sampling, the established CSM has been revised. The revised CSM now recognizes the contaminant flux from the North Yard and its southerly migration with the predominant hydraulic gradient.

Summarily, the North Yard contaminant flux migrates along the contact zone between the alluvial sediments and the underlying shallow fractured basalt. This contact is not impervious but slightly leaky, as fluorescein eventually did migrate

into the competent basalt under stressed (pumping) conditions. While the presence of a South Yard source area cannot be discounted, the tracer data indicate that once in the South Yard, the contaminant flux migrates vertically through primary fractures under the influence of the deep bedrock groundwater extraction system.

Dye tracer methods were selected over more traditional means, such as monitoring wells/piezometers, due to the complexity of the aquifer system. Dye tracer methods allowed the testing of three hypotheses, essentially eliminating the need to conduct three separate, albeit interrelated, remedial investigations. The DTS yielded valuable data on groundwater flow and contaminant migration at a low cost when compared to traditional means. Compounding the value was the fact that the least anticipated hypothesis is now the basis for the revised CSM.

7. NEXT STEPS

Modification of the North Yard DPVE well containment system will be required to control contaminant flux to the alluvial sediments/shallow fractured bedrock interface. Control of the South Yard contaminant flux vertically to the deep bedrock must also be considered. The first step in this process was the completion of a State of the Art Technology Evaluation and Economic Analysis Report, which identified alternatives for North Yard source control and outlined a pre-design investigation work plan.

8. REFERENCES

- Aley, Thomas. 2003. Procedures and Criteria: Analysis of Fluorescein, Eosine, Rhodamine WT, Sulforhodamine B, and Pyranine Dyes in Water and Charcoal Samplers. Ozark Underground Laboratory. August 22, 2003.
- Flury, M. and N. N. Wai. 2003. Dyes as Tracers for Vadose Zone Hydrology. *Rev. Geophys.* 41(1), 1002, doi: 10.1029/2001RG000109.
- Geraghty & Miller, Inc. 1993. Results of the Phase II Deep Bedrock Remedial Investigation. March 1993.
- IT Corporation. 1990. Phase One Remedial Investigation Report. August 1990.
- NJDEP (New Jersey Department of Environmental Protection). 2005. Field Sampling Procedures Manual.
- NJGS (New Jersey Geological Survey). 2003. Surficial Geology of the Paterson Quadrangle; Passaic, Bergen, and Essex Counties, New Jersey. Open File Map 54.
- OUL (Ozark Underground Laboratory). 2002. Groundwater Tracing Handbook.
- USGS (United States Geological Survey). 1986. Fluorometric Procedures for Dye Tracing, Chapter A12, Techniques of Water-Resources Investigations of the United States Geological Survey. Revised 1986.