Investigation and Remediation

Diving Plumes and Vertical Migration at Petroleum Hydrocarbon Release Sites

by James W. Weaver and John T. Wilson

etroleum hydrocarbons are mostly less dense than water. So they should float or at least hang around the water table, right? Not so fast. There are some fairly common situations where we would expect a plume of petroleum hydrocarbons to move vertically into the aquifer—as a result of water table drawdown associated with pumping from water supply wells, smearing of contaminants due to water table fluctuation and site investigation activities, and movement of water through preferential flow paths in heterogeneous environments. But even in the absence of any of these circumstances, a plume may still move downward, or "dive," into an aquifer.

This diving situation occurs when groundwater recharge enters the top of a shallow water table aquifer. Once in the aquifer, this water begins to move in the direction of groundwater flow. Because the recharge water is entering the aquifer from above, it can push contaminant plumes downward. The amount that a plume "dives" depends on the amount of recharge water entering the system and the relative contribution this additional water makes to flow in the aquifer.

We expect that such diving plume scenarios may occur in the wetter parts of the country, but even in dry climates, recharge-driven diving can occur because of irrigation, leaking water or sewer pipes, or recharge from ephemeral surface water features. In either case, plume diving depends on the localized pattern of recharge, the flow rate in the aquifer, and the distribution of contaminants—as shown in the following East Patchogue, New York, example.

East Patchogue, New York

A gasoline release at an East Patchogue, New York, UST facility

created large BTEX and MTBE plumes. The plumes were detected because a private water supply well, located 4,000 feet downgradient from the source, was in their path. The well screen was about 50 feet below the water table, where much of the MTBE mass was located.

The site investigation started at this point and went upgradient to identify the source.

Because of the importance of the aquifer for drinking water supply, New York undertook an extensive investigation of the site, including vertical characterization of the plumes. Multilevel samplers with 6inch screens at 5-foot intervals were used. A resulting vertical section through the plume showed that BTEX and MTBE tended to dive into the aquifer with distance from the source. (See Figure 1.) It was further noted that a significant amount of diving occurred as the BTEX plumes passed under a gravel pit. By studying the well logs and performing a detailed hydraulic characterization of the aquifer with a borehole flowmeter, investi-

gators ruled out vertical migration controlled by stratigraphy, because the hydraulic conductivities varied by less than a factor of 2 over the aquifer. This left recharge as the most likely explanation for the plume diving. The model described in the sidebar on page 14 was used to simulate the site and provided additional evidence that recharge was the cause of the diving.

This Patchogue example sheds light not only on how recharge pushes the plume downward, but also on what happens when water discharges from aquifers. Where water comes up at discharge points, so will the contaminants—along streams, rivers, lakes, or the ocean.



A vertical cross section through the MTBE, benzene, and total xylene plumes at East Patchogue, New York. The gasoline source is located at the right-hand edge of the sections, and flow is to the left. Each of the plumes dives into the aquifer with transport in the aquifer.

The ocean is the expected destination of the MTBE plume at East Patchogue, where the groundwater flow system discharges into Great South Bay, adjacent to the southern shore of Long Island. The groundwater and contaminants move upward as they approach the discharge point at the bottom of the bay.

Consequences of Missing the Dive

What about the consequences of a diving plume, or more to the point, the consequences of *missing* a diving plume? We averaged the East Patchogue data set to show how the plume would appear if sampled only from long-screened wells. The data were averaged over the top 10 feet of the aquifer to simulate 20-foot well screens—10 feet in and 10 feet out of the aquifer.

The graphs in Figure 2 show two sets of concentrations plotted along the length of the plumes. The first data set (circles) shows the maximum concentrations from the multilevel samplers. This set represents the maximum concentration measured in each sampler, regardless of depth, at each location along the plume. It is intended to be a reference to show the extent of contamination on the xy plot.

The second concentrations (diamonds) are the values for the simulated 10-foot screens. For these, the MTBE concentrations all fall below New York State's threshold of 10 μ g/L. With only these data we would have concluded that there was no MTBE plume at this site. The maximum concentrations, however, indicate a significant MTBE plume in the downgradient portion of the aquifer.

The simulated long-screened data show that the benzene plume appears to be shortened to about onethird its actual length. This effect occurs because plume diving pushes the benzene plume out of the bottom of the sampling network. Along the way, the concentrations appear to decrease, because clean and contaminated water mix in the well. This mixing results in diluted samples and lower concentrations.

Interestingly, the long-screened data also show that the total xylenes and benzene plumes appear to be the same length. Here, because of sorp-



tion, the total xylenes did not travel far enough in the aquifer to drop out of the monitoring network, and there was no apparent shortening of the plume. Nevertheless, these two contaminant distributions hint at a sampling problem. Our expectation is that there should be separation of benzene and total xylenes caused by sorption. In this case, the expected chromatographic separation has been negated by the monitoring network.

Rethinking Our Assumptions

Are plumes longer than we think they are? The short answer is yes! The reason we think that they are shorter is that most LUST site monitoring well networks do not adequately delineate contaminant plumes in three dimensions.

"Conventional" monitoring wells are primarily designed to monitor for the presence of free product floating on the water table. To accomplish this task, conventional wells are constructed with relatively long screens that bisect the water table. This approach is meant to allow for seasonal fluctuations in water table elevation in the hope that the screen will extend below the lowest lowwater elevation and just above the highest high-water elevation.

Also, many monitoring networks consist of relatively few wells, most of which are located on the LUST site property. We've seen that such networks are not well suited for determining the true extent of a plume, nor can they provide accurate information about the vertical distribution of either contaminants or hydraulic conductivity. The lack of such data is a critical limitation for performing a quantitative risk assessment.

Groundwater samples drawn from these conventional wells represent composite samples. Because they mix waters of varying true concentrations, they are diluted and give a falsely low impression of the severity of contamination.

So how do we interpret concentrations of contaminants that are below state or federal action levels? Here, an old dictum applies: The absence of evidence is not evidence of absence.

It may be that, sometimes, low concentrations are just that. But we need assurance that the wells have been located such that they actually

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sample the plume. When we sample from the wrong place, as our Patchogue example shows, we may well think that concentrations are lower than they actually are. As a consequence, we incorrectly believe that plumes are shorter than they are actually, even to the point of apparent nonexistent.

With the prevalence of biodegradation of BTEX (and some emerging news concerning MTBE biodegradation), we may be too quick to attribute short plumes to natural attenuation, rather than to the true cause—a sampling error.

An Approach to Assessing Plume Diving

Is there a universal prescription for a practical assessment of plume diving and vertical migration? We're afraid not. The site assessment process involves putting together the pieces of the puzzle to delineate the extent of contamination. One part of that puzzle is a determination of the vertical contaminant distribution. Because of the potentially detrimental consequences of missing a diving plume, the site investigation should be designed to ensure that a diving plume doesn't extend out of the range of the bottom of the monitoring network. Site-specific factors, such as geology, hydrology, land use, and site geochemistry, provide the evidence for plume diving. The following factors should be evaluated in planning a site investigation:

■ Geology and the Sampling Network

What land form contains the plume? Is it a flood plain, delta, or coastal plain? Do drilling logs indicate that there are discrete zones that yield plentiful water and other zones that do not?

Core logs give information needed to define the stratigraphy, including the geologic units, their consistency, and their orientation. Has a cone penetrometer or borehole flowmeter test been performed? Have the monitoring wells been tested to determine hydraulic conductivity? Have they been tested to determine whether they are screened in intervals known to yield water? What are the properties of the aquifer

The OnSite Plume Diving Calculator

alibrated numerical groundwater flow models, such as MOD-FLOW, can be used to show how much recharge-driven diving might occur in an aquifer. Inasmuch as these models are not applied at most LUST sites, we'd like to suggest that you try some simpler alternatives.

From our experience at the East Patchogue site, a simple simulation model was developed to estimate the prospects for recharge-driven plume diving. The model is a part of EPA's on-line tools for site assessment called OnSite. Use of the tools requires only a standard browser and Internet access. The tools are available at http://www.epa.gov/athens/software/training/WebCourse/part-two/onsite.

The plume diving model allows an aquifer to be split into segments, each with its own hydraulic conductivity, recharge rate, and length. The upgradient and downgradient heads are specified in the aquifer, as is a starting point that represents the source and a well location. Given these specified aquifer parameters, an estimate is given for how deep the top of the plume goes below the water table at the specified well location.

The software has been used on several Long Island sites and found to match the observed plumes. The model, however, is based on a simple one-dimensional conceptualization, and it won't be appropriate for all sites. It does, however, give an idea of the prospects for recharge-driven plume diving.

As the site investigation moves away from the source, the model can be used to predict plume diving. Sampling of the aquifer can then show if the predictions were correct. More to the point, sampling can show if the plume is diving, and the model results give a guide for determining the vertical extent of contamination. ■

with regard to depth, thickness, and hydraulic conductivity? Does the well network characterize the aquifer in two or three dimensions?

Clearly, vertical delineation of a contaminant plume requires threedimensional characterization, which may include the use of permanently installed multilevel wells or temporary push points. Because of the expense of installing and sampling from multilevel wells, temporary push points can be used to reduce the cost of vertical delineation.

Using this push technique, locations can be sampled without installing permanent wells when the vertical location of the plume is not known. Permanent monitoring wells can be installed after the plume has been located. Determining the horizontal extent of contamination may not necessarily be a simple task. Push technologies can be of great benefit here as well.

Answers to the questions posed above help define the stratigraphy, which serves as the geologic control on the contaminant distribution. In many flood plains, for example, the surface material is primarily heavy silts and clays that have been deposited during historical flood events. Beneath these surface silts and clays are sand and gravel deposits associated with previous meanders of the river. The water table is frequently in the surface silt and clay. So the materials with a capacity to carry groundwater (sand and gravel) and transport a plume occur at the bottom of the sequence of deposited sediment.

The Elizabeth City, North Carolina, "Old Fuel Farm Site" illustrates the effects of recharge, stratigraphy, and sampling. It is described in a report, *Natural Attenuation of MTBE in the Subsurface Under Methanogenic Conditions*, available from EPA at <u>http://www.epa.gov/ada/pubs/</u> <u>reports.html.</u>

■ Hydrology and Land Use

From a topographic map, what do elevations of areas such streams and lakes indicate about the groundwater flow system? How much annual rainfall occurs? What recharge estimates have been developed for the area or are commonly used? What are the land use patterns? For example, the flow system at East Patchogue is determined by the regional flow on Long Island, where water generally flows from the center of the island in the north to the Great South Bay in the south. An average of 44 inches of rain falls each year, and the United States Geological Survey (USGS) estimates that the average recharge is about half of the rainfall.

The UST facility property is paved and adjacent to a highway. Downgradient, the land uses include light commercial, playing fields, a gravel pit, and medium-density residential areas. Each of these land uses influences the pattern of recharge, from very low recharge where the surface is paved to very high recharge in the gravel pit.

From this information, we could have suspected that the contaminants were likely to travel toward the bay. If the plumes moved away from the service station property and out from under the paved area, there would be a good chance for diving behavior, particularly if the plumes reached the gravel pit—as indeed they did.

At other sites, unlined drainage ditches, leaking water mains and sewer pipes, irrigation, and the flow pattern in the aquifer can determine the vertical distribution of contaminants.

Thus, where recharge is likely to be the plume diving instigator, the amount of water that infiltrates the area above the plume, and the amount that this recharge contributes to flow in the aquifer, determines where and how much diving will take place.

■ Geochemistry

Simple geochemical tests can be used to spot a plume that is diving because of clean water recharge. In general, uncontaminated recharge water at the top of an aquifer will have oxygen concentrations that exceed 1 mg/L, iron concentrations that are less than 0.5 mg/L, and methane concentrations that are less than 0.1 mg/L. Groundwater that has been contaminated with petroleum hydrocarbons will generally contain oxygen concentrations that are less than 0.5 mg/L and may contain concentrations of iron and methane that are greater than 1 mg/L. If the groundwater is sampled with a bailer, the sample is usually contaminated with atmospheric oxygen during sampling, and the rule of thumb for oxygen should not be applied.

In general, clean recharge water will have low dissolved organic carbon (DOC), usually less than 1.0 to 2.0 mg/L. The plume will usually have elevated DOC, often exceeding 10 mg/L.

Putting the Pieces Together

The stratigraphy of an area provides the first indication that plume diving should be considered. Are the contaminants contained in dipping strata? If so, off-site migration is likely to be controlled by the stratigraphy. Dipping or not, the plume direction will be dictated by the flow that water takes through the geologic structure.

The groundwater flow rate and an estimate of the petroleum release date provide clues about travel time to various downgradient locations. If the rate is low enough, the plume may never reach that gravel pit or unlined ditch that is waiting to drag it to the depths of the aquifer.

So, before taking the site investigation off-site, can an estimate of plume diving be made? In simple aquifers, the OnSite plume diving calculator can be used to estimate diving at a specific location. (See sidebar on page 14.) Subsequent sampling with a direct push probe can provide confirmation (or not) of the location of the plume, both vertical and horizontal, before a commitment to permanent monitoring wells is made.

From our work on sites with diving plumes, it's clear that the prospects for plume diving need to be factored into site investigations. This information can be used to determine whether diving is likely to occur in the downgradient plume. If diving is a possibility, then the sampling design must be such that plumes are fully characterized through the design of the monitoring network.

By the way, plume diving is not a new concept. It was evident in data collected from the first Borden Aquifer dispersion experiment conducted in the 1980s (MacKay et al., 1986, A natural gradient experiment on solute transport in a sand aquifer, Water Resources Research, 22(13) 2017–2029). It was also observed in data from the extensive USGS Cape Cod field study (LeBlanc et al., 1991, Large-scale natural gradient tracer test in sand and gravel, Cape Cod, Massachusetts, Water Resources Research 27(5), 895–910). ■

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What Our Field Survey Shows

DIVING PLUMES

In NEIWPCC's MTBE survey, when asked if they investigate MTBE plumes differently from BTEX plumes because of the potential for diving plumes, 4 states answered "yes" and 15 answered "sometimes." When asked if they require three-dimensional characterization of MTBE plumes, 14 of the 19 states that answered "yes" to the previous question answered that they do "occasionally," 3 answered "most of the time," and 1 said "always." Delaware indicated that the answer depended on the project officer whether it was "occasionally" or "most of the time." Montana commented that if a vertical gradient is apparent, nested wells will be required to verify whether a diving plume exists.

When asked if they are taking any extra steps to make sure MTBE is not migrating beyond standard monitoring parameters, 19 states answered "yes." When asked what kinds of steps, most said that they are using multilevel wells, nested wells, deeper wells, and/or more wells located farther downgradient from the source.