

## NATURAL ATTENUATION EVALUATION AND MODELING OF GASOLINE IMPACTED GROUNDWATER

K. Brown, L. Tyner, B. Sibbett, D. Daftary, T. Perina  
IT Corporation  
312 Director's Drive  
Knoxville, TN 37923

Denise Caron, Vandenberg AFB, CA

### ABSTRACT

Natural attenuation was evaluated as a containment option for a gasoline-impacted aquifer located at the Vandenberg, AFB (VAFB) Base Exchange Service Station (BXSS). The site, which was found to have a complex geological and hydro geological profile, was impacted through releases from a leaking underground storage tank (UST). Elements of the site evaluation included records search, placement of approximately 40 Geoprobe points and 7 monitoring wells, slug testing of 18 wells, groundwater and soil sampling and analysis, development of a site conceptual model, and completion of fate and transport modeling.

### INTRODUCTION

IT Corporation, contracted through the Air Force Center for Environmental Excellence, completed the evaluation of natural attenuation as a containment option at the VAFB BXSS. The VAFB BXSS was established in 1967 to provide motor vehicle fuel to residents. The BXSS currently consists of the main office building with three gasoline dispensing islands, six automobile service bays, and a four-bay car wash building. It is immediately bordered by trees to the west and south and grassy open fields to the east and north.

In 1967, four 10,000-gallon, single-walled underground fuel tanks, a 250-gallon single walled underground waste oil storage tank, and associated piping were installed at the BXSS. In 1985, two of the four 10,000-gallon USTs were replaced with two 10,000-gallon double-walled fiberglass tanks. In 1991, the two remaining 1967 USTs, along with the associated piping and the underground waste oil storage tank, were replaced with 10,000-gallon USTs.

Site contaminants of concern include benzene, toluene, ethyl benzene, and xylenes (BTEX), total petroleum hydrocarbons (TPH), and methyl tertiary butyl ether (MTBE). The majority of contamination at the site is centralized around the old pump island. Highly contaminated soil in this area extended from 4 to 12 feet bgs. Although no free product was present at the site, the impacted soil appeared to be the source of the groundwater contamination. Outside of the old pump island, soil concentrations dropped off to non detect. Groundwater concentrations of BTEX, TPH, and MTBE increased in and around the old pump island (Figures 1 and 2). Based on the biodegradability of BTEX and TPH, the lack of BTEX and MTBE migration, and the absence of human or ecological receptors in the area, natural attenuation was deemed a feasible alternative for site remediation.

Natural attenuation is most accurately viewed as an effective, natural plume containment process, whereby the intrinsic capacity of the impacted and downgradient aquifer to assimilate contaminants exceeds the contaminant migration rate. As a result, most plumes undergoing natural attenuation achieve a steady-state or stability within a moderate period of time following the release. Some of the advantages of natural attenuation include the fact that it is nonintrusive, less costly than conventional methods and that the most mobile and toxic fuel compounds are generally the most susceptible to biodegradation. The primary limitations of natural attenuation include the fact that it is affected by changes in local hydro geologic conditions, potential future releases, and aquifer heterogeneity and that time frames for completion may be relatively long.

In order to pursue natural attenuation or any technology as a remedy, evidence must be generated documenting the potential and effectiveness of the process. The objectives of the natural attenuation evaluation were to collect evidence to verify or eliminate the potential of natural attenuation as a remedy at the BXSS.

### MATERIALS AND METHODS

Forty Geoprobe points were installed during the site investigation. The Geoprobe method drives a 2-inch-diameter sampler mounted on the end of 1-inch-diameter drive rods into the soil, pushing the soil aside until the desired sample depth is reached. During this process soil and groundwater sampling may be collected. Ten soil samples were collected during the direct-push investigation and analyzed by EPA Methods 6010, 8015, 8260, and 9045 for iron, TPH, VOCs, and pH, respectively. Additional analysis for ammonia as nitrogen, total phosphate, microbial

enumerations, and soil moisture was also conducted. Thirty-five groundwater samples were analyzed by an on-site, mobile laboratory for BTEX and MTBE by modified EPA Method 8020.

Geoprobe data were used to guide the placement of seven additional groundwater monitoring wells around the BXSS. The wells were installed to a depth of 20 feet with a hollow-stem auger in a 10-inch-diameter boring. The wells were completed with 4-inch-diameter polyvinyl chloride casing and 15 feet of screen. Conductivity and natural gamma logs were run in 14 monitoring wells (7 existing and 7 newly installed) and 1 soil boring to characterize the subsurface and provide another method for correlating beds between the new and existing wells.

Site monitoring wells were sampled and analyzed by a fixed-facility using EPA Methods 8260, 8015, for VOC and TPH, as well as several general water chemistry analyses. During groundwater sampling, an electronic water-level indicator was used to measure depth to groundwater and depth to the bottom in each monitoring well. Wells were purged and sampled with a 2-inch "readiflow-2" Grundfos pump at a rate of 1 L/min. Field parameters, such as pH, specific conductivity, turbidity, and dissolved oxygen, were measured with a Horiba U-10 water-quality checker. Turbidity was measured with the HACH 2100P turbidity meter. Redox potential was measured with an Orion 290A pH concentration meter.  $H_2S$  was measured with a qualitative  $H_2S$  kit, and ferrous iron (Fe II) was measured with the HACH 2000 Spectrophotometer.

Following sampling and analysis, slug testing was conducted on 18 wells to characterize the aquifer. A 2.36-inch-diameter, 5.1-foot-long slug constructed of a flush-threaded, 5-foot-long section of stainless-steel pipe with steel caps at both ends was used for the slug tests performed on 4-inch-diameter wells. A 1-inch-diameter, 5.2-foot-long slug constructed of a 5-foot-long section of steel pipe with steel cap at both ends was used for the slug tests performed in 2-inch-diameter wells.

Prior to the slug test, depth to static groundwater was measured using an electrical water level indicator. Changes in water level were digitally recorded during the test using 10-pound-per-square-inch pressure transducers, eight channel Hermit 2000, and LTM 3000 data loggers. The drawdown data were recorded in feet, with a specified reference point of zero feet. Before the tests were started, the pressure transducer constants and test numbers were verified by reviewing the input parameters in the data loggers.

Following the collection of all field data, modeling exercises were initiated. A finite-difference groundwater flow program MODFLOW was selected for the flow portion of the model. MT3D was selected for the transport portion of the model; this code offers a choice of different numerical solution schemes for the transport and can be directly linked to MODFLOW. A graphical processor MODIME for MODFLOW and MT3D was used for model input and output. The degradation of a solute in MT3D is simulated using a first order decay; both dissolved and sorbed phase can be degraded. Only the dissolved phase was allowed to degrade in the presented model. MT3D was selected because of the model's ability to link with USGS MODFLOW, simulate time-varying constant concentration at the source, and input/output portability.

## RESULTS

Geologically, the BXSS sits on an uplifted late Pleistocene marine terrace covered with well-sorted, fine-grained sand and clay beds deposited in a shallow marine or lagoon setting. The sands are very well sorted with rounded and polished quartz grains. A fine-grained to silty sand is present from the surface to a depth of 19 to 28 feet. An upper clay bed 2 to 4 feet thick occurs within the sand, between depths of 12 and 16 feet. The bed consists of silty clay and clayey sand, and is highly deformed with high-angle to vertical beds or blocks of sand within the clay. The clay bed may have been deformed by large animal bioturbation, grazing animals sinking into soft sediments, or some other mechanism of soft sediment deformation. The apparent variable thickness of the upper clay bed may be due to its deformed or irregular nature.

A deep clay bed, approximately 4 to 5 feet thick, is present at a depth of 19 feet under the east side of the site, dipping to a depth of 28 feet northwest of the BXSS. The deep clay grades from a fat clay to a clayey silt and clayey sand from top to bottom. The clay bed is continuous under the site and dips to the northwest.

A perched saturated zone is present from approximately 9 feet below the surface to the deep clay bed. Both the piezometric surface and the underlying clay slope to the northwest. Sand and gravel beds below the deep clay bed are unsaturated, and a deep saturated zone was not found to a depth of 60 feet below the site. A deeper perched groundwater was not found above the clayey silt bed at 38 feet depth, which suggests that little water is migrating through the deep vadose zone. The clay bed at a depth of 15 feet is not expected to be a barrier to groundwater movement

because of the disturbed nature of the bed. The deep clay bed forms an impermeable bottom of the shallow saturated zone and prevents vertical migration of contaminants.

The shallow saturated zone water table was found to be unconfined. The saturated thickness of the shallow zone ranges from approximately 10 feet to 21 feet. Groundwater flow direction is approximately to the north with an average hydraulic conductivity of 0.52 ft/day. Flow into the aquifer beneath the site occurs predominantly from the south and west. Groundwater is also likely recharged from a car wash at the site. The evapotranspiration of Eucalyptus trees along California Avenue appears to have a significant impact on the groundwater flow budget. A groundwater flow model of the site was completed using MODFLOW and a fit within 0.66 foot of the observed water levels was achieved.

Once the site groundwater flow model was established, groundwater data were collected and evaluated to determine the occurrence of biological activity at the site and the loss of contaminants of concern. Biological activity at the site has created a reducing environment in the plume source area (i.e., in or near the old pump island). This area is dominated by anaerobic metabolic pathways such as iron and manganese respiration, sulfate reduction, and methanogenesis. The plume fringe has a high capacity for aerobic metabolism with increased concentrations of nitrate/nitrite and a positive redox. Overall, the biocapacity of the aquifer to assimilate the release exceeds the sum BTEX detected during the September 1996 sampling event.

A first order decay rate for BTEX removal was calculated following correction of the BTEX concentrations for loss of a recalcitrant tracer (1,3,5-trimethylbenzene). Corrected concentrations indicated that within the plume core, 99 percent of the benzene concentrations were removed by biological reduction rather than physical attenuation. Based on these corrected concentrations, a first order decay rate for BTEX was estimated. A decay of  $0.12 \text{ yr}^{-1}$  BTEX removal was calculated. Based on the potential biological reduction of the tracer under field conditions, this rate is considered overly conservative.

Once the plumes were delineated, concentrations determined, and the groundwater flow model calibrated, MT3D was used to simulate contaminant fate and transport. The sum of BTEX components was used to represent the contaminant concentrations in the fate and transport model (MT3D). The results of groundwater sampling were used to represent the current distribution of concentrations. The sum of current maximum concentrations of BTEX components was assumed to represent the current source concentration.

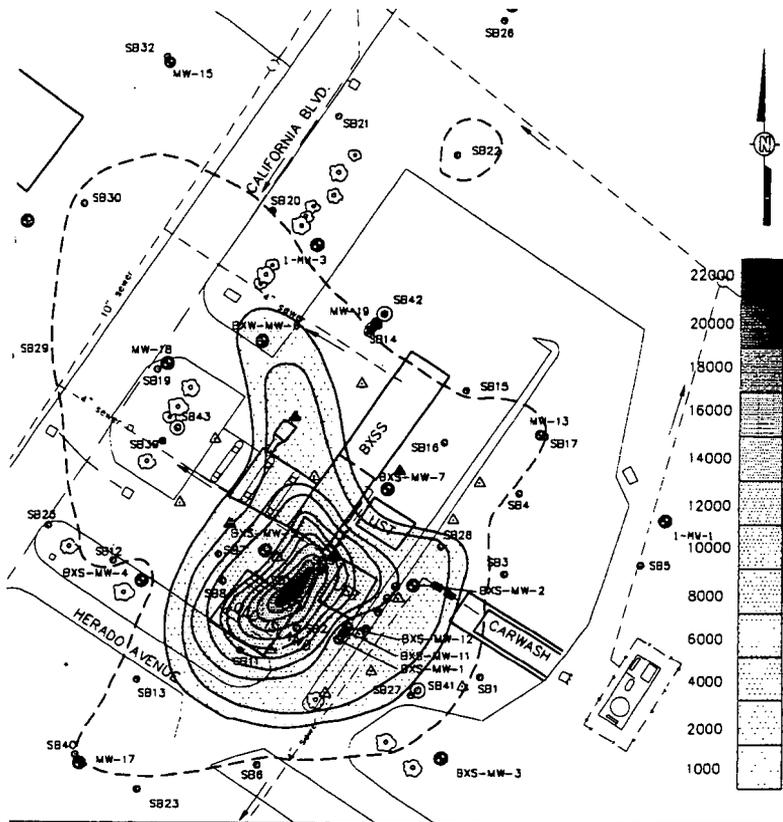
It was assumed that groundwater was first impacted in 1970. The source concentration at the time of release was assumed to be 20 times higher than the current source concentration and was assumed to exponentially decrease over time. A combined aerobic/anaerobic biodegradation rate was used to predict loss due to biological activity. The model results indicate the model is in agreement with the high concentrations in the center of the plume, while concentrations higher than observed were calculated at the plume edges (a conservative result). This may be explained by a faster, aerobic degradation of the actual contaminants at the plume edges. The BTEX attenuation time to achieve 1 part per billion was estimated at less than 100 years.

An exponentially decreasing source concentration was also used to determine the fate and transport of MTBE; the rate of decrease was the same as the rate estimated for the BTEX source. No biological degradation of MTBE was assumed in the model. The MTBE concentrations persisted at the site, with the maximum concentrations occurring in the vicinity of well 1-MW-3. The concentration buildup in this area may be explained by groundwater uptake by the trees. Additional sampling rounds will facilitate the calibration of the fate and transport models.

Although contaminants may persist at the site for an extended period of time, no migration of the MTBE or BTEX plume was identified or predicted. The risk to human health and the environment is also negligible. No drinking water sources are present within 3 miles upgradient or downgradient of the site. And all near-site groundwater production wells are screened from 200 to 400 feet deep. Based on fate and transport modeling, the plume will never reach these wells.

#### CONCLUSION

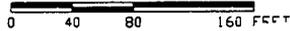
Based on the documented occurrence of biological contaminant reduction, lack of contaminant migration, and the absence of risk that the impacted groundwater poses, natural attenuation should be considered as a means of site remediation and potential closure.



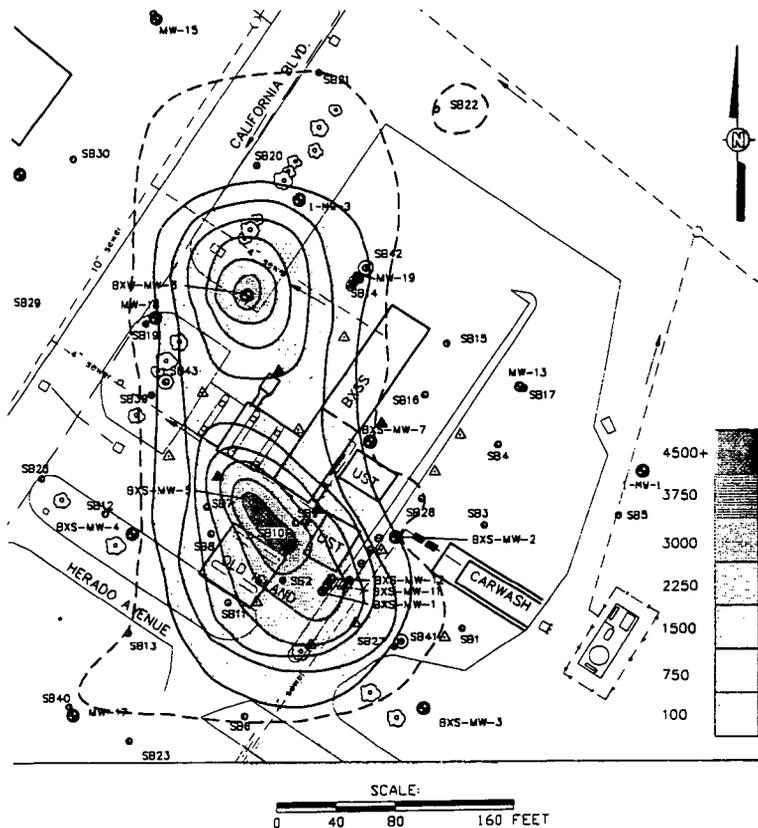
**EXPLANATION**

- ⊙ GROUNDWATER MONITORING WELL  
MW-13
- DIRECT-PUSH SOIL BORING  
SB8
- ⊙ AUGER SOIL BORING  
SB41
- BENZENE CONCENTRATIONS IN ug/L
- - - ND - NON-DETECT

**SCALE:**



**FIGURE 1**  
**BENZENE GROUNDWATER**  
**CONCENTRATION CONTOURS**  
**SEPTEMBER 1996**  
**BASE EXCHANGE SERVICE STATION**  
 PREPARED FOR  
**U.S. AIR FORCE**  
**VANDEMBERG AIR FORCE BASE**  
**CALIFORNIA**



**EXPLANATION**

- ⊙ GROUNDWATER MONITORING WELL  
MW-13
- DIRECT-PUSH SOIL BORING  
SB8
- ⊙ AUGER SOIL BORING  
SB41
- MTBE CONCENTRATIONS IN ug/L
- - - ND - NON-DETECT

**FIGURE 2**

**MTBE GROUNDWATER  
CONCENTRATION CONTOURS  
SEPTEMBER 1998  
BASE EXCHANGE SERVICE STATION**

PREPARED FOR  
**U.S. AIR FORCE  
VANDENBERG AIR FORCE BASE  
CALIFORNIA**