Impact of Natural Attenuation and Phytoremediation on MTBE and Fuel

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Abstract: Groundwater contamination including MTBE and BTEX resulted from leaking fuel storage tanks at the Base Exchange Service Station at Vandenberg AFB, California. Groundwater was impacted at 9 to 28 feet bgs. A 1996 investigation defined the groundwater plume with concentrations of MTBE and benzene ranging up to 15,600 and 31,000 ppb, respectively. The impacted shallow aquifer is vertically contained by a clay bed (fat clay) dipping from 19 ft bgs to a depth of 28 ft bgs toward the northwest controlling groundwater flow direction. The perched groundwater system is hydraulically recharged by a car wash operation and landscaping irrigation system. Although soil excavation was completed during UST removal for the majority of impacted soil, a small volume (estimated 7,800 cubic yards) remained in place, resulting in a continual source of impact to the groundwater. Groundwater balance and flow were highly impacted by existing mature eucalyptus trees surrounding the station. To confirm this impact, a field investigation was completed.

Transpired gas sampling was carried out on a total of six trees: three trees within, or close to, the impacted area (boundary of the plume) and three trees outside the impacted area. Glass containers approximately 35 centimeters long and 9 centimeters wide were placed over a secondary limb as large as was practical for the vessel. The bottom of the vessel was sealed gently around the limb, and air was forced through the two side ports. Air was drawn from the vessel with an adjustable air pump at approximately 50 milliliters per minute for 10 hours. As the air exited the vessel, it was filtered through a carbotrap tube to collect organic carbon compounds. All samples were analyzed for BTEX, MTBE, tert-butyl alcohol (TBA), methyl acetate, acetone 2-propanol, methanol and tert-butyl formate (Oregon Graduate Institute). Ambient air samples were collected utilizing the same techniques described above.

Composite core samples were obtained using an 18-inch Haglof Increment Borer (Forestry Suppliers, Inc., Jackson, Mississippi) at approximately 4.5 feet above ground level from areas cleared of outer bark. Two cores were obtained from each tree, from approximately opposite sides of the tree. The tree corer was placed on the trunk surface and turned clockwise until the bit penetrated the surface of the trunk to a depth of approximately 10 inches at which point the extractor was inserted into the corer and a sample was removed. Approximately 7 inches of core material was removed from each boring. A minimum of 30 grams of material was collected and homogenized into a single sample. The samples were analyzed for the same parameters listed above. The hole of the coring was treated with tree wound dressing and sealed with a non-toxic wood putty/sealant. This procedure did not harm the overall welfare of the tree. Tree root material was obtained using a 2-inch hand-auger approximately 5 feet from the trunk of the tree at a depth of 4 to 5 feet. Tree roots were immediately rinsed with deionized water to remove entrained soil and placed in sample bottles, sealed, labeled, and placed on ice for shipment. Root material was also obtained from within a monitoring well by the use of a stainless steel 2-inch hand-auger. The hand-auger was lowered into the well, then twisted and pulled upward against the sides of the well casing. The auger bit cut through the root material,

which was then trapped between the bit and the side of the casing. Root material obtained was then rinsed with deionized water and containerized. Samples were analyzed for the same parameters listed above.

To measure soil gases, vapor probes were pneumatically driven to within 2 feet of the water table at five points throughout the site using a 1-inch outside diameter steel pipe fitted with a hardened drop-off steel tip (Macho System, KVA, Moshpee, MA). Soil gas samples were analyzed for oxygen, methane, and carbon dioxide using an in-line probe and meter (Landtech Model GA-90 Air Analyzer).

Samples of leaves were collected from trees within and outside of the impacted area. Samples were collected by stripping numerous secondary branches from within the canopy and placing the leaf material within an 8-ounce jar, sealed, and placed on ice for shipment. Canopy density was derived mathematically through the use of a ceptometer to determine leaf area indices and correlated with subsequent published leaf area indices to correlate transpired gas data to overall transpiration.

The presence of the primary daughter product, TBA, was documented in samples from different groundwater wells at the site as well as in tree samples. TBA concentrations far exceeded any source material where both TBA and MTBE were present, the percent TBA relative to MTBE ranged from 8 to 46 percent.

MTBE and TBA were also found in nearly all of the biomass samples collected. Only three samples were found to be below the detection limit. Those samples were the core and root samples from a presumably impacted tree and the core sample from a presumably unimpacted. However, there was no apparent correlation between groundwater concentrations and biomass concentrations.

All of the biomass samples contained detectable concentrations of BTEX, with a range between 0.532 µg/g and 16.9 µg/g. The highest concentrations in biomass samples correspond to their proximal location to the plume. Overall, there seems to be a trend of higher concentrations in trees that have come into contact with the plume.

The model of a plant leaf presented within the PlantX model (Dr. Stefan, University of Osnabruck, Germany) was felt to provide an acceptable representation of the dynamics of contaminant transpiration; accordingly, the basic equations of the leaf module of the PlantX model were extracted, and manually utilized to examine the transpiration process. The total mass of the contaminants dissolved in groundwater was calculated by kriging the measured data (using the ordinary kriging algorithm in SURFER; Golden Software, 1994). The amount of dissolved BTEX and MTBE was shown to be decreasing over time. Linear trends fitted to the data indicate decreases of 13 lbs/year and 2 lbs/year for BTEX and MTBE, respectively. Plant uptake of BTEX and MTBE was estimated at 17.78 and 19.80 lbs/year. It is important to consider that the trees are removing contamination from the vadose zone as well as from groundwater (the majority of tree roots are above the water table and most of the ground surface near the trees is irrigated daily); therefore, the uptake by trees and decrease in groundwater combined likely represent the overall removal of contamination at the site.

Results showed that MTBE is biodegraded in the subsurface. The sampling and analytical work using tree samples provided evidence that trees are capable of taking up gasoline-related hydrocarbons. The extension of this information made a significant impact on model predictions for contaminant fate. The results of the phytoremediation investigation indicate that the natural attenuation remedial timing estimate of 79 years, for MTBE was an extremely conservative value. Results of this investigation indicate that this value may be reduced to 13 years once the source is removed.