

## HYDROCARBON AND MTBE REMOVAL RATES DURING NATURAL ATTENUATION APPLICATION

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**ABSTRACT:** Removal rates of hydrocarbons and methyl tertiary butyl ether (MTBE) from the non-aqueous phase liquid (NAPL) residual source floating over the water table were estimated with site characterization data at the petroleum contamination site in the US Coast Guard (USCG) air-base. Site characterization activities included soil and groundwater sampling, total petroleum hydrocarbon (TPH) and components analysis in soil samples, analysis of hydrocarbons and electron acceptors in groundwater, and hydraulic conductivity. Total quantities of hydrocarbons and MTBE in subsurface were estimated from soil sampling data. Dissolution rates of hydrocarbon components from the residual NAPL source into groundwater were estimated with a vertical diffusion model. Estimation of hydrocarbon and MTBE removal from the residual source in soil matrices was verified with mass balance check. Mass balance check allowed the quantitative evaluation of the fate and transport of contaminants from the sources to the sensitive receptors. The conceptual model and quantification of removal rates provided an estimation of application period of natural attenuation at the site as the plume management strategy.

### INTRODUCTION

Transport processes of hydrocarbon contaminants from light non-aqueous phase liquid (LNAPL) such as floating gasoline on the water table include evaporation in gaseous phase, dissolution from the NAPL source into groundwater flowing underneath, dispersive and advective movement, and abiotic and biotic transformations. Ground-water plume management with natural attenuation uses such processes as adsorption/desorption, evaporation, dissolution, dilution, and intrinsic biodegradation to control the plume from reaching the sensitive risk acceptors. In addition to the physical and chemical attenuation processes, sufficient evidence of the contaminant destruction through biotic and abiotic degradations before reaching receptors should be demonstrated to support the implementation of the natural attenuation (Severn, et al., 1997). Implementation of natural attenuation as a plume management strategy should require site characterization in detail to provide the evidences of sufficient biodegradation capacity, retention time for degradation, and fast reaction rates with which the plume control within the control boundary is possible (Cho, et al, 1997).

At the US Coast Guard (USCG) Support Center in Elizabeth City, NC, soil and groundwater contamination have been found in the area between the upgradient old fuel farm and the Pasquotank river. After removal of floating product in the recovery wells, the USCG decided to implement natural attenuation as the plume management strategy. The USCG Civil Engineering Unit (CEU) and US EPA, Robert S. Kerr Environmental Research Center (RSKERC) started detailed site characterization and analyses to assess the hydrocarbon plume at the site. A couple of rounds of soil and ground-water sampling were conducted at the site and TPH and mass of target hydrocarbons and MTBE were estimated from soil and ground-water data. Derived conceptual models were used in the analysis of hydrocarbon loading and transport from the hydrocarbon source to sensitive receptors. Mass loading rates from NAPL source to groundwater were verified with comparing to the outflux along groundwater flow at the source zone boundary for mass balance analysis. Prediction based upon

loading rate and initial assessment of hydrocarbon mass in the source zone allowed to obtain the time scale of the plume management with natural attenuation. Data obtained from the site characterization activities, conceptual models used for the analysis of data, and anticipated results from the data and analysis are presented.

## **SAMPLING AND ANALYSIS**

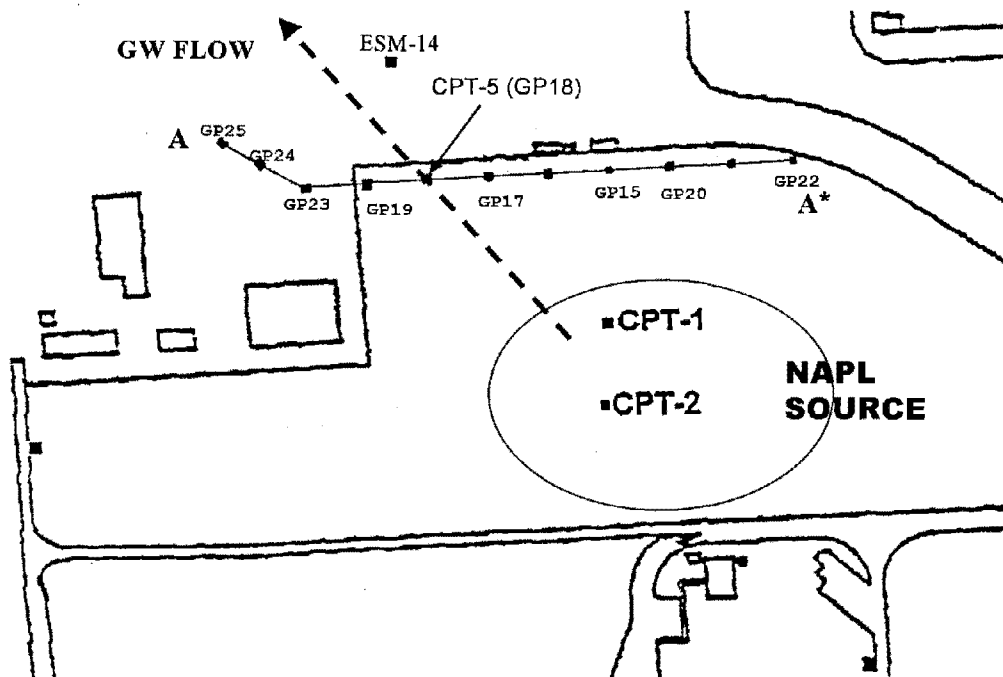
In August, 1996, discrete soil sampling with a small drilling rig was conducted in the source zone in which the original fuel tanks were located and at locations in the downgradient area. The soil type at the site was flood-plain sand and the depth to the groundwater was about 2.7 meter. Soil samples were collected in duplicate. Total 280 samples from nine locations were collected and analyzed. Samples were analyzed with a gas chromatography with flame ionization detector (GC/FID) for quantification of TPH and MTBE, benzene, toluene, ethyl benzene, o-, m-, p-xylene isomers (BTEX) and 1,2,3-, 1,2,4-, 1,3,5-trimethylbenzene isomers (TMBs). Groundwater sampling and hydraulic conductivity measurement in a discrete interval were conducted at the site with a Geoprobe™ direct push system. The first round of ground-water sampling in August, 1996 was conducted at several locations in the source zone and in the downgradient area along the groundwater pathway (Figure 1) just after soil sampling. After hydraulic conductivity measurements, water samples were collected. Ground-water samples were also collected from existing monitoring wells. Ground-water samples were analyzed with a gas chromatography with mass spectrometer detector (GC/MS) for BTEX, MTBE, TBA, TMBs, and naphthalenes.

The second round of ground-water sampling was conducted in September, 1997 along the edge of NAPL boundary (transect A-A\* in Figure 1) to check the mass balance. The sampling and analysis methods were the same as the first round sampling.

## **RESULTS AND DISCUSSION**

**Hydrocarbon Distribution in Soil.** Residual TPH remained over the wide area around the former fuel-storage tanks. The high levels of TPH were found at cpt-1 which was the center of the old fuel farm and at cpt-2 which was about 15 m upgradient from cpt-1. The majority of the residual hydrocarbon was located in the narrow interval of 1.5 to 3.5 meters below the ground surface. This shallow, thin zone is suspected to serve as the long term contamination source to the groundwater. TPH was estimated to be  $3.0 \times 10^5$  kg in the source area. Total mass of benzene in subsurface was approximately 570 kg and MTBE was about 50 kg. Other components are listed in the table 1.

**Hydrocarbon Dissolution into Groundwater in NAPL Source Zone.** Both benzene and MTBE were detected at depths below the bottom of the interval with residual NAPL at 300 cm. Benzene and MTBE had their highest concentrations in groundwater at a depth of 300 cm. Their concentrations decreased with depth into the subsurface to a depth of 500 cm, where increasing hydraulic conductivity allowed lateral transport of the contaminants. Steep concentration gradients of benzene and MTBE between the bottom of the residual NAPL and the top of the highly conductive zone suggest that vertical diffusion/dispersion along the concentration gradient is the major transport process of these contaminants from their source to the deeper, conductive part of the aquifer. Transport processes of chemicals from the NAPL source into the ground-water flow region are conceptualized as the equilibrium dissolution from NAPL source into water in soil pores, the downward diffusion/dispersion due to concentration gradients, and the convective transport with the major groundwater flow. The flux of a dissolved component, diffusing from the concentration



**FIGURE 1. Site Map around the Old Fuel Farm Area, USCG Supply Center, Elizabeth City, North Carolina**

**Table 1. NAPL Source Distribution and Amount**

TPH	3.0 x 10 <sup>5</sup> kg	TMBs	5230 kg
Benzene	570 kg	Naphthalene, MNs	2070 kg
BTEX	5340 kg	MTBE	50 kg

maximum at the NAPL layer contacting groundwater down to the area with higher hydraulic conductivity could be estimated with the vertical dispersion and convective transport equations obtained by Hunt et al (1988), Johnson and Pankow (1992), and Charbeneau et al(1995). Average flux of benzene over the NAPL source zone was estimated to be 1.9 g/m<sup>2</sup>/year. MTBE dissolved into groundwater at 1.3 mg/m<sup>2</sup>/year. With the size of the NAPL zone, (50 m long and 70 m wide), 3500 m<sup>2</sup>, hence, total loading of benzene into the groundwater over the region was estimated to be 6.7 kg benzene per year. It was 4.6 kg per year for MTBE. Since total mass of benzene in subsurface was estimated to be about 570 kg and MTBE mass was over 50 kg, it would take more than 85 years for benzene and 11 years to completely deplete MTBE from the NAPL source with constant removal rates through the entire period of natural attenuation.

**Mass Balance Check.** The second round of groundwater sampling was conducted to verify the mass balance. Total mass of target compounds out of the NAPL source zone through the boundary to the downgradient could be estimated by integrating the flux over the cross-section (A-A\* in figure 1). Total amount of benzene moving out from the source boundary was 2.7 kg/year which is lower than the estimated loading of 6.7 kg/year from the NAPL source. Total amount of dissolved hydrocarbon components including BTEX, TMBs, naphthalene, and 1-, and 2-methyl naphthalene (MNs) moving out from the source boundary was estimated to be 3.9 kg/year. The amount of MTBE flowing out of the boundary was estimated to be 4.1 kg/year which is slightly lower than the loading rate estimation of 4.6 kg/year (Table 2). Tertiary Butyl Alcohol (TBA) which appeared to be the product of MTBE degradation was moving out of the source zone at 1.2 kg/year.

**Table 2. Mass Balance of Major Target Compounds**

Component	Total Mass in Source (kg)	Loading Rates (kg/year)	Outflux (kg/year)	Comments
Benzene	570	6.7	2.7	85 yrs for removal*
BTEX+TMB+ MNs	13640	Not Available	3.9	
MTBE	50	4.6	4.1	11 yrs for removal*
TBA	0	0	1.2	

\*Time estimates for total removal were based upon the loading rates and mass in source.

## SUMMARY

Site characterization analyses at the petroleum contamination site were presented. The purpose of those activities were to provide sufficient data required for implementation of natural attenuation as the plume management. Soil sampling, vertical profiling of groundwater contaminations, and hydraulic conductivities were conducted. Resulting data were analyzed to define the fate and transport of hydrocarbon from the source zone to downgradient. A mass balance approach was adapted to verify the processes. The equilibrium dissolution of hydrocarbon components from NAPL source into the groundwater, diffusive transport due to the vertical concentration gradient, and convective transport along the groundwater flow were conceptualized to estimate the loading and transport rates of MTBE and hydrocarbon components from the source zone to the sensitive receptor downgradient.

A time scale of decades was required for complete depletion of benzene and MTBE from the residual NAPL source. Due to slow removal from the NAPL source through dissolution and dispersive process, it may take extended period of time for total removal of target contaminants from the site with natural attenuation processes and intrinsic biodegradation.

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#### **REFERENCES**

- Charbeneau, R.J., J. W. Weaver, B.K. Lien, 1995, "The Hydrocarbon Spill Screening Model (HSSM), Volume 2: Theoretical Background and Source Codes," EPA/600/-94/039b, US EPA, ORD, Washington, DC.
- Cho, J.S., J.T. Wilson, J.W. Weaver, 1997. "Criteria on Selection of Intrinsic Bioremediation for Petroleum Hydrocarbon Plumes," In Proceedings of the Fourth International In-Situ and On-Site Bioremediation Symposium, New Orleans, LA.
- Hunt, J.R., Sullivan, C.R., Udell, K.S., 1988. "Nonaqueous Phase Liquid Transport and Cleanup, 1. Analysis of Mechanisms," Water Resources Research, 24(8), p1247.
- Johnson, R.L. and Pankow, J.F., 1991. "Dissolution of Dense Chlorinated Solvents in Groundwater, 2. Source Functions for Pools of Solvents," Environmental Science and Technology, 26(5), p896.
- Severn, S., R. Axelrod, C. Stein, L.M. Stolte, A. Short, 1997. "Natural Attenuation as an Effective Solvent Plume Management Strategy," In Proceedings of the Fourth International In-Situ and On-site Bioremediation Symposium, New Orleans, LA.

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