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Treatment Train for Site Remediation at a Petrochemicals-Contaminated Site Within a Petroleum Refinery

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Groundwater contamination is a widespread environmental problem. Accidental releases of petroleum products from underground storage tanks (USTs) are one of the major causes of groundwater contamination. Current attention is focused on human and environmental safety concerning the release of hydrocarbons to the environment. Petroleum hydrocarbons contain benzene, toluene, ethylbenzene, and xylene isomers (BTEX), which are hazardous substances regulated by many nations. In addition to BTEX, other petrochemicals such as naphthalene, 1,3,5-trimethylbenzene (1,3,5-TMB), and 1,2,4-trimethylbenzene (1,2,4-TMB) are also toxic to humans (TPHCWG 1999). In Taiwan, there are approximately 2,300 gas stations, more than 8,000 USTs and many petroleum industrial parks (hundreds of tank farms or terminals) in a small island (36,000km^2). Most of these utilities are located nearby the residential area. The Taiwan government began to enforce the "Soil and Groundwater Remediation Act" in February 2001. Thus, the Taiwanese industries are challenged by the introduction of this government regulation of soil and groundwater remediation. To clean up the contaminated soils and groundwater, efficient and cost-effective remediation technologies are therefore required. It is well known that petroleum is composed of a mixture of hundreds of chemical compounds. These products are typically multi-component organic mixtures containing non-aqueous phase liquids (NAPL). Mobile LNAPL (light NAPL) floating above the water-saturated zone moves vertically as the groundwater elevation fluctuates. Some NAPL held in different pore spaces under dissimilar tension as a result of capillary forces (in the capillary fringe or aquifer) are not easy to migrate to extraction wells and boreholes, and may be a major source for continuing contamination of groundwater. Using conventional techniques for cleaning up contaminants in the subsurface are not technically true cleanup technologies, but rather transfer techniques. In general, these technologies are not entirely effective in removing the pollutants in a reasonable time frame. Intrinsic remediation of BTEX compounds at various petroleum-contaminated aquifers have been reported by numerous authors (Cunningham et al. 2001; Kfan and Husain 2003). Recently, the concept of treatment train (TT) has drawn significant attention due to its high applicability and effectiveness on contaminated site remediation. TT indicates the reduction

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or removal of the toxicity, mobility, or volume of the contaminated materials through thermal, chemical, biological, physical or assembly of any of these implied units (EPA 2001). The TT concept acknowledges the strengths and weaknesses of various remediation strategies and couples promising technologies to overcome limitations. The technical approach requires a thorough consideration of the hydrogeologic and geochemical characteristics of the site and in-depth understanding of the distributions of the contaminants to select some remediation techniques, in series and/or parallel, to reach maximum contaminant removal. The conceptual model has been presented in the mid-1990s (Newell et al. 1995), but few detailed field studies had been performed to evaluate its effectiveness.

The objectives of this study were given as follows: (1) to perform a site assessment to delineate the distribution of petroleum hydrocarbon in the subsurface at the studied site, (2) to develop a TT for site remediation, and (3) to operate the TT and evaluate the performance of this treatment system.

MATERIALS AND METHODS

Two USTs were installed as a part of waste oil storage tank farm within a petroleum refinery in southern Taiwan in late 1980s. In May 1998, a significant amount of various petroleum hydrocarbons (e.g., BTEX, TMB, naphthalene) were detected in the groundwater samples collected around the USTs. To effectively remove the free product on the groundwater and remediate the contaminated groundwater while the petroleum refinery was still in operation, a site-specific TT system was developed for the site. Figure 1 presents the site plan showing the locations of the TT installed and the monitoring system, and the flow direction of groundwater. Site soils consisted of yellowish-brown sandy silt loam and gray clayey sand loam with brown and dark reddish-brown mottles. The soils were moderately alkaline and well drained. The boring log data showed that the surfacial aquifer sediments were relatively uniform sand to silty sand. Depth to the seasonal high water table was approximately 2.8m to 3.6m below ground surface (BGS), and the groundwater flow direction was southwest. The hydraulic gradient in this aquifer was approximately between $3x10^{-3}$ and $5x10^{-4}$. The determined site hydraulic conductivity, percent organic matter, and porosity were approximately 0.025 cm/sec, 1.01%, and 0.372, respectively. The aquifer transmissivity ranged from 3.32x103 m^2/day to 5.03x103 m^2/day and the soil bulk density was approximately 1.66 g/cm^3. Thus, the calculated groundwater seepage velocity, and faction organic carbon was 0.197 m/day and $5.74x10^{-3}$, respectively.

During the processes of site characterization and field-scale remediation, 22 monitoring wells (including three multi-level wells), 10 soil gas monitoring probes, one reference well, and three recovery wells were constructed (see Figure 1). More than 300 soil gas, groundwater, and soil samples were collected and

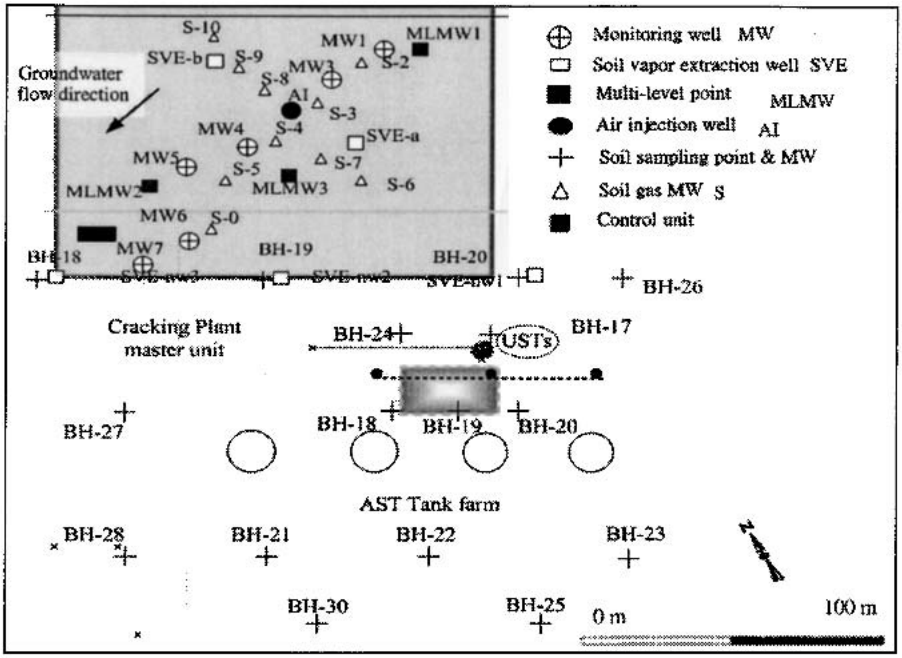

Figure 1. A general layout of the investigated site.

analyzed during the monitoring period. In this study, the anions of the concern were determined by ion chromatography (IC, Dionex, DX-100). Metal ions (Ca, Mg, Co, Fe, Mn, and Na) were analyzed using flame atomic absorption spectrometry. Purge and trap with gas chromatography/photo-ionization detector (P&T-GC/PID), GC flame-ionization detector (GC/FID), portable micro-gas chromatography/thermal conductivity detector (μ-GC/TCD), and solid phase micro-extraction (SPME) in combination with gas chromatography-mass spectrometry (SPME/GC/MS) were applied for organic compounds analysis.

The in-situ soil gas monitoring system (Varian 979C automated portable leak detector and Varian digital flow-meter) was used to detect the distribution of helium gas (the tracer) and the magnitude of gas flow. The collected fumes were stored in SUMMA® passivated stainless steel canisters for further analysis by GC/MS or GC/FID. SPME in combination with GC/MS was used to identify the species in groundwater/soil and to monitor the transport and fate of organic pollutants. In a pervious work (Yang and Wu 2000), this technique has been developed and proved to be suitable for the determination of volatile and semi-volatile compounds ranging from μg/kg to mg/kg levels. The quality control and system performance were modified according to American Society for Testing and Materials (ASTM) D5769-98 (ASTM 1998) and U.S. EPA SW-846 8260B (EPA 2000). The detection limits for naphthalene and benzene were 10 μg/kg and 80 μg/kg, respectively. The μ-GC/TCD was used to analyze the permanent gases (e.g., N_2, O_2, CH_4, and CO_2) in the field.

Based on the results from a preliminary study (data not shown), the vertical engineered barrier (VEB) was constructed by cement-based slurry wall [70m (L) × 1.3m (W) × 4.5m (D)]. Three recovery wells of hydraulic type (labeled as OW70, OW70-1, and OW70-2) were installed at the upgradient locations of the barrier (see Figure 1). Hydraulic containment by a slurry barrier was constructed next to the location where free product was found. Since the local water table varied from 2.8m to 3.6m BGS, the constructed VEB was 4.5m in depth. This would be able to effectively contain the free product for the subsequent removal. The dissolved contaminants would then be transported to the opposite side of the barrier via the devious route beneath the barrier. The subsequent remedial actions such as in situ volatilization and biodegradation were taken downgradient of the barrier for the removal of dissolved organic contaminants. The air sparging system employed included an air compressor, flow meters, pressure gauges, and injection wells. The soil vapor extraction system was directed to a vacuum blower, an air/water separator, and a vapor treatment installed approximately 2.5m BGS. The vapor extracted from the system was directed to a vacuum blower, an air/water separator, and a vapor treatment system.

A tracer test was performed to delineate the radius of influence (ROI) of the air injection wells. In this study, He (helium gas) was used as the tracer and was analyzed by Varian 979C portable leak detector [sensitivity (method detection limit, MDL): 2×10^{-10} atm-cc/sec; working range: 10^{-3} to 10^{-10} atm-cc/sec]. The in situ soil gas monitoring system (Tedlar® bags and flow meter) was used to detect the distribution of He tracer, the species of permanent gas and the magnitude of gas flow. The direct push technology was adopted for collections of soil gas, soil samples, and groundwater samples. Ten vadose vapor extraction probes and eight groundwater monitoring wells were also installed for long-term vapor gas and groundwater sampling and monitoring, respectively.

RESULTS AND DISCUSSION

The present field-scale study was the first well-studied application of TT (VEB/air sparging) at a petroleum facility in Taiwan. The effectiveness of each treatment process was dependent on site characteristics, contaminant species, and operation. The TT system has been operated for three years since its installation in 1998 due to the leakage of USTs. Figure 2 shows the cumulative quantity of free product since the operation of the TT system. It was found that a significant decrease of daily mass of the collected free product was observed as time elapsed. Approximately 1,600L of free product was removed from the subsurface by the extraction and containment system in the 3-year operation period. It was also noticed that the recovered quantity of the free product increased significantly after

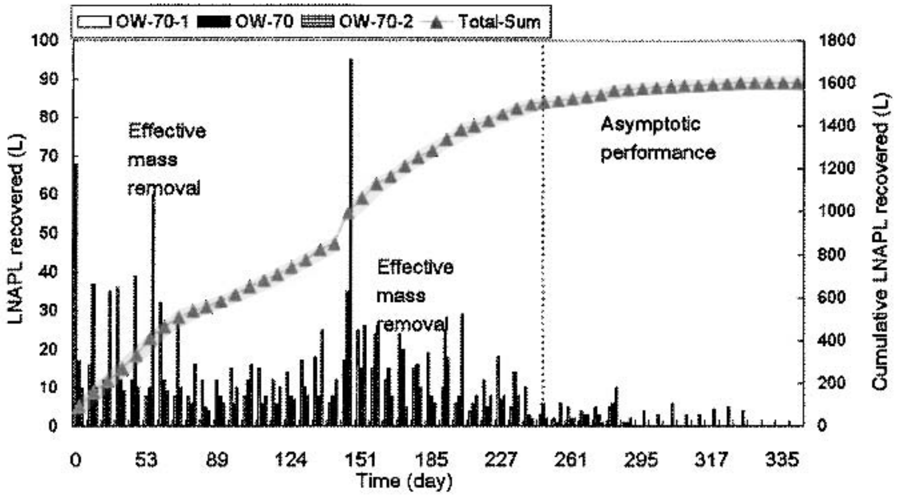

Figure 2. Trend of LNAPL recovery for three pumping wells.

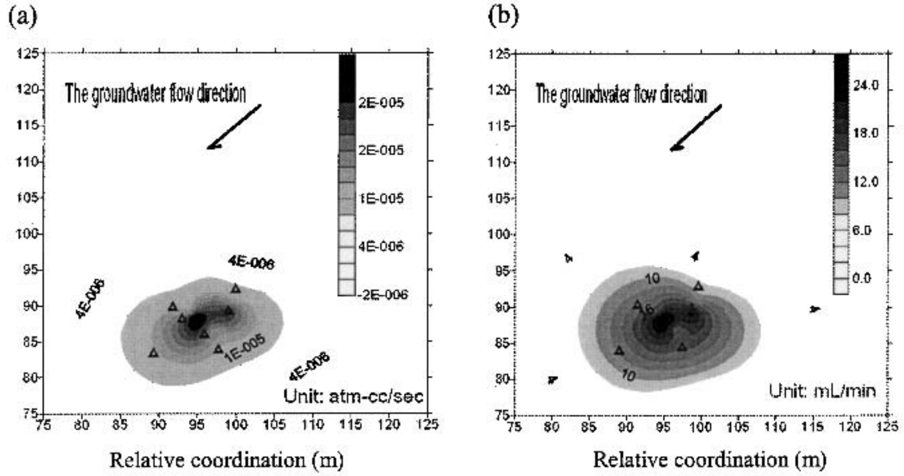

Figure 3. Results of tracer test showing the magnitude of (a) He response (atm-cc/sec) and (b) flow rate (mL/min).

each heavy storm event. Moreover, the VEB system could effectively contain the free product for the subsequent extraction during both dry and wet seasons.

Figure 3 shows the result of tracer tests. It was found that the responses of He (tracer gas) provided an unequivocal indication of the pathway. Figure 3(a) demonstrates the He response contour obtained at 30 minutes after the startup of the test. Figure 3(b) shows the shape of flow distribution determined by the

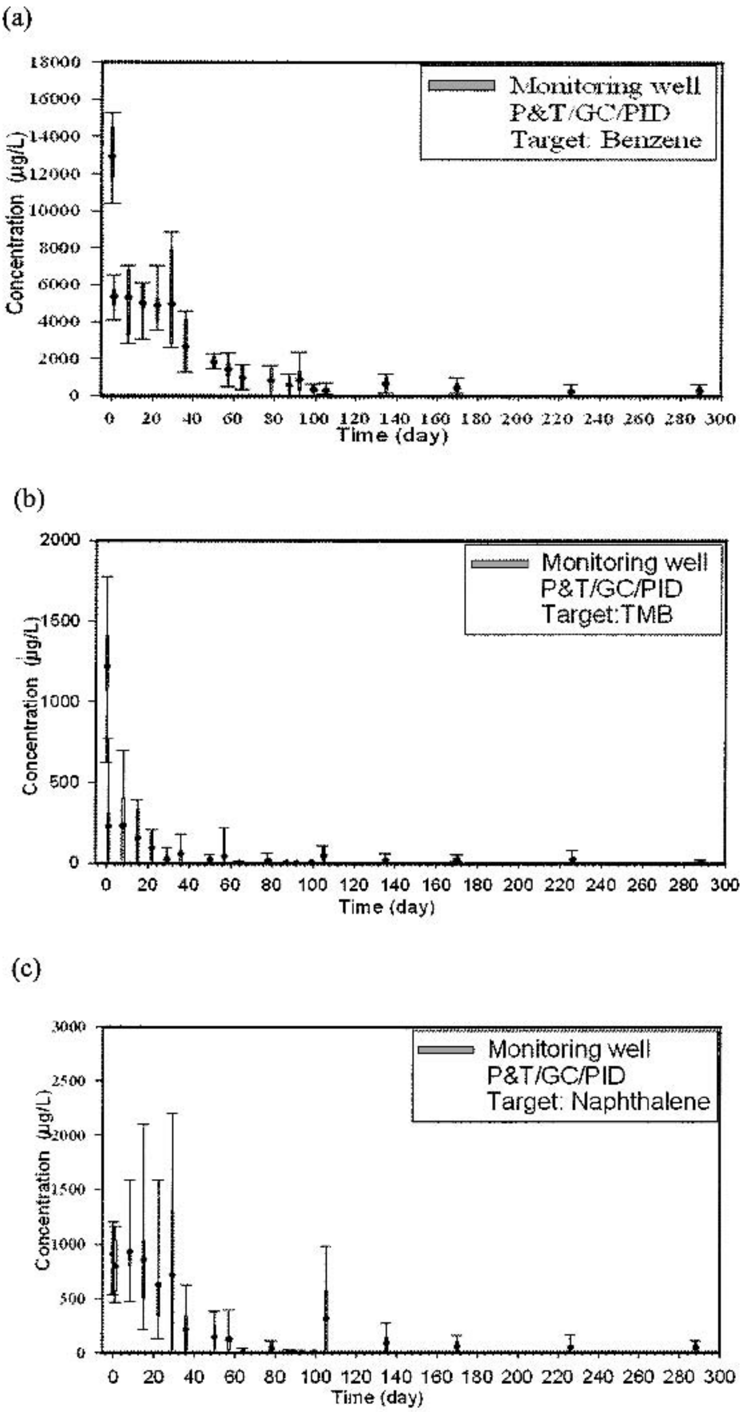

Figure 4. Concentration variations of benzene, TMB, and naphthalene versus time.

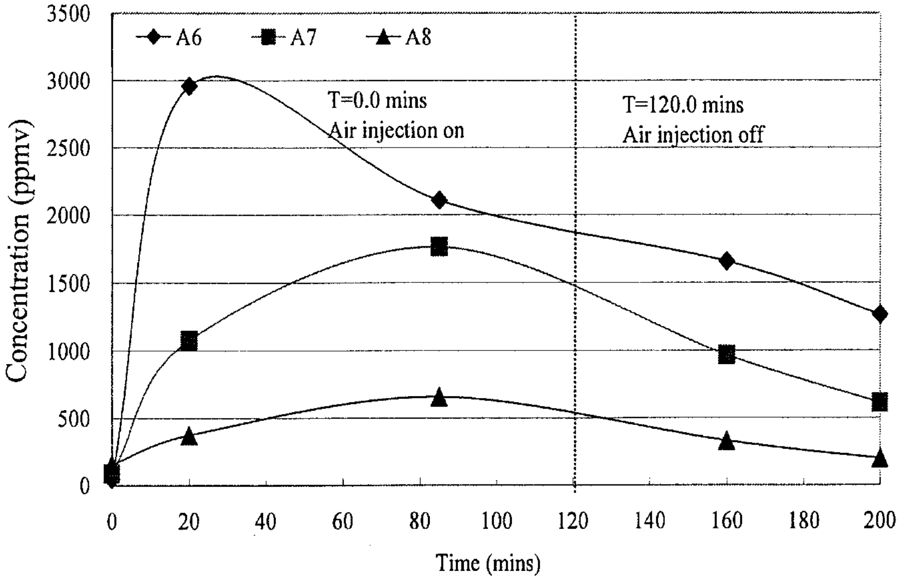

Figure 5. Concentrations of extracted organic constituents after the start of air sparging.

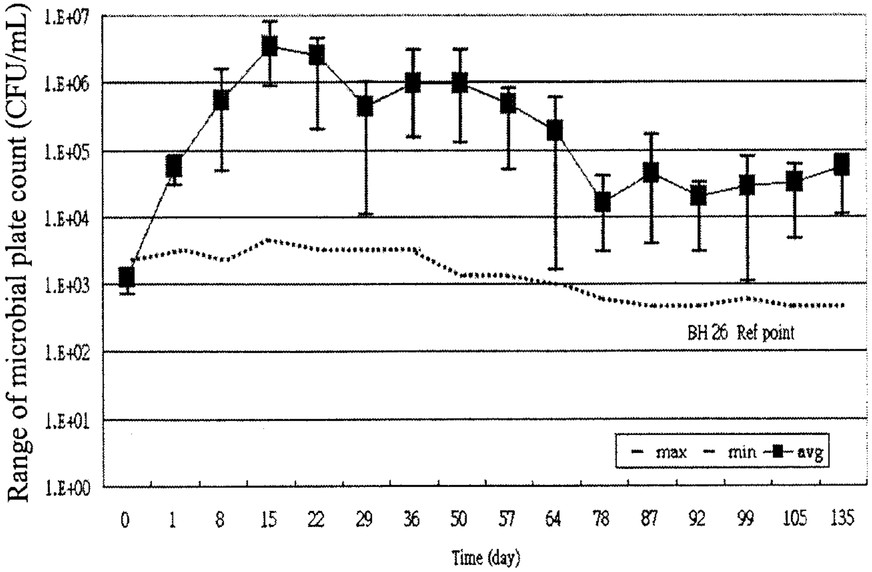

Figure 6. Variations of microbial population versus time.

flow meter on the top of monitoring tube 2m BGS. Based on the field results, the estimated volume of influence was approximately 6,000 m^3 with the dimension of 30m (L) × 25m (W) × 8m (D). The diameter of influence due to air sparging was approximately 20m. The distribution of He gas in the tracer test reveals that the influence zone of the air sparging system could effectively cover the plume, which needed to be remediated. Results have indicated that the tracer test could be applied for the evaluation of effectiveness of the air sparging system.

Figure 4 presents the concentration variations versus time for various contaminants. Figure 4(a) shows a typical trend of concentration variation for BTEX. In general, test results have illustrated that significant decreases of BTEX, TMB, and naphthalene concentrations with time were observed. This reveals that the air sparging system could effectively remove the contaminants in groundwater through volatilization and biodegradation processes. Air injection also resulted in the increased extraction of organic constituents from the extraction wells. Figure 5 illustrates the change of the extracted concentrations versus time. The concentrations of extracted compounds were found to significantly increase with the application of air injection. The trend of contaminant removal at the downgradient edge of the dissolved hydrocarbon plume indicates the occurrence of natural (intrinsic) bioremediation. Figure 6 demonstrates the variations of microbial population versus time. Results have shown that the microbial population ranged from 1.2×10^3 to 8.0×10^6 (CFU/mL) in the groundwater samples. This indicates that an increase of microbial population in the subsurface due to the application of air injection process. The increased bacteria would also play an important role in contaminant biodegradation. The dissolved oxygen (DO) concentrations in groundwater were less than 1.1 mg/L before the air injection activity. Higher DO levels (3.60 ± 1.12 mg/L) in groundwater inside the treatment zone were observed during the air injection process.

In summary, this field-scale site remediation study has provided a streamlined process and guidelines for future remediation work at the petroleum-hydrocarbon contaminated site in Taiwan. The three-year field investigation results have indicated that the constructed TT system is capable of containing the free product and remediating the dissolved petroleum-hydrocarbon plume. The effectiveness of the TT system was verified by the following field results: (1) the increased cumulative amount of collected free product and decreased daily free product recovery, (2) the decreased contaminant concentrations in groundwater samples collected from the downgradient monitoring wells of the barrier, (3) the increased microbial population and O_2 concentrations around the air sparging system, (4) the increased O_2 concentrations and decreased CO_2 concentrations in the vadose zone inside the treatment area, and (5) the decreased NO_3^- concentrations in groundwater. Results obtained from this study have also indicated that the TT system can be applied at an active site without the interruption of the facility's normal operation. Given that it is often not possible to clean up a contaminated site with a single technology, remediation must focus on the development and application of a site-specific TT system. Based on the findings from this study, a sound TT system is believed to be a more efficient and cost-effective measure for site remediation.

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