Technical Approaches for Assessment of Ground Water Contamination with TCE in an Industrial Area

Kweonho Jeon, Soonyoung Yu, Jangsik Jeong, Yanglae Son
Environmental Management Corporation
Environmental Research Complex, Kyungseo-Dong, Seo-gu, Incheon, Korea
Tel 032-560-2244
Fax 032-560-2293
Email attest@emc.or.kr

ABSTRACT

Despite its usability, TCE has been managed as a hazardous material due to the toxicity and many contamination cases were surveyed in some developed countries. U.S.EPA(Kram et al., 2001) suggested DNAPL characterization methods and approaches based on survey experiences at several sites. However, Korea has not the least assessment of contamination and trial of remediation, although there are a lot of doubtable areas where ground water would be contaminated with TCE. In this study, we try to assess the volume and extent of ground water contamination with TCE and delineate the contamination source zones in an industrial area. Ground water in this area flows through fractures and the contaminant TCE has the properties of high volatility, high density and low partitioning to soil material. Thus, we applied a variety of technical approaches to identify the contamination status; documentary, hydrogeochemical, hydrogeological and geological surveys. In addition, additional survey was performed based on the interim findings, which showed that ground water contamination was limited to the relatively small area with high concentrations to the deep place. The contamination source zone is estimated to be the asphalt test institute where a great deal of TCE has been used to analyze the amount of asphalt soluble in TCE since 1984. Based on the contamination characterization and a myriad of documents about ground water remediation, appropriate site remediation management options will be recommended later. This study is now under way and this paper was focused on describing the technical approaches used to achieve the goals of this study.

Key word : Technical approaches, assessment of ground water contamination, TCE, DNAPL, bedrock aquifer, remediation

1. INTRODUCTION

Dense Nonaqueous Phase Liquids(DNAPLs) are related to a wide variety of industrial activities, including almost all facilities where degreasing, metal stripper, chemical manufacturing, or other activities involving chlorinated solvents were performed. However, since the adverse health effects of chlorinated solvents were reported, these materials have been controlled as hazardous and the use has been limited. In case of TCE, U.S.EPA(2003) has found it to potentially cause vomiting and abdominal pain from acute exposures at levels above the Maximum Contaminant Lever(MCL), 5μ g/L. TCE has also the potential to cause liver damage from life time exposure at levels above the MCL. In addition, there is some evidence that TCE may have the potential to cause cancer from a lifetime exposure at levels above the MCL(U.S.EPA, 2003).

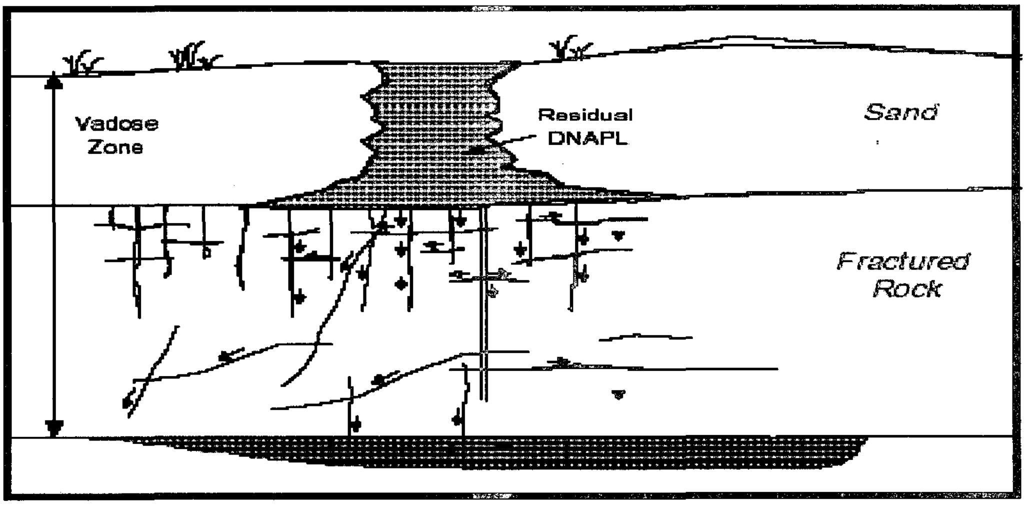

Figure 1. DNAPL spilled into fractured rock systems may follow a complex distribution of the preferential pathways(Huling et al., 1991).

In Korea, TCE was included in the hazardous material list in 1997, although the TCE standard for ground water was stipulated in 1993 when the Ground Water Act was established. Considering that TCE has been used since the 1970's and the waste of used TCE was unattendedly disposed before 1997, contamination with TCE may be widely spreaded around the industrial sites.

If a large quantity of DNAPL have been released, the DNAPL continues to move vertically downward due to gravity until it is confined because the DNAPL has high density, 1.465 at 20℃(U.S.EPA, 2003). Besides, common chlorinated solvents have a greater relative mobility to water because they are denser and less viscous than water. For single phase flow, TCE is 2.31 times more mobile than water(Fetter, 1999). Moreover, if the DNAPL has invades a fractured medium, it will preferentially enter the larger fractures. In the case of a vertical fracture with uneven aperture, the DNAPL will enter the fracture where the width is greatest and migrate downward as a "finger" following the wide spot in the fracture and avoiding the fracture where it is narrow. The DNAPL will be distributed both horizontally and vertically according to the size, orientation and degree of fracture connectivity. Therefore, confirming the DNAPL transport in the fractured bedrock aquifer is very challenging[Figure 1].

DNAPLs, particularly if comprised of chlorinated solvents, usually present a much more formidable remediation challenge than other contaminants for three reasons: (1) chlorinated solvents do not biodegrade very rapidly and persist for long periods of time in the subsurface, (2) the great density of DNAPLs causes the contaminated zone to spread much deeper, (3) chlorinated solvents have physical properties that allow movement through very small fractures and downward penetration to great distance(Fetter, 1999). In addition, The residual DNAPL forms a source that can slowly partition into both the vapor phase and the aqueous phase of the water infiltrating through the vadose zone and continue to contaminate the subsurface environment. Residual DNAPLs in an undissolved state represent an environmental challenge with global implications[Figure 2].

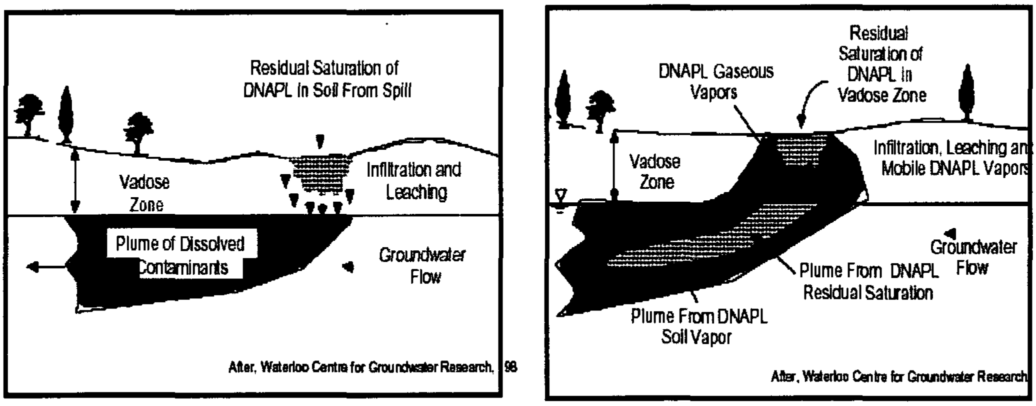

Figure 2. DNAPL may be present in the subsurface in various physical states or what is referred to as phases(Huling et al., 1991) and can be the long-term contamination source.

This study area has all the difficulties mentioned above. In other words, this area is contaminated with TCE to the depth of over 100m, where ground water flows along the fractures. We had to approach the area with as many kinds of technical methods as possible in given cost and time.

In Korea, there are many places where ground water contamination with TCE is doubtable. In particular, most industrial areas have been reported to be severely contaminated, but any in-depth survey has never been done because of the arguments between parties, loose policies, a lot of cost, etc. Therefore, this study will be the cornerstone in surveying the ground water contaminated with TCE.

The objectives of this study are to determine the volume and extent contaminated with TCE in the industrial area and delineate DNAPL contaminant source zones, with implementing various characterization approaches. In addition, the best appropriate site remediation management options will be recommended based on the identification of DNAPL source zones, which is critical to ultimately achieve site remediation and aquifer restoration. This study is now under way with the first site visit on April, 2003 and this paper described the technical approaches used for attaining the goals[Figure 3].

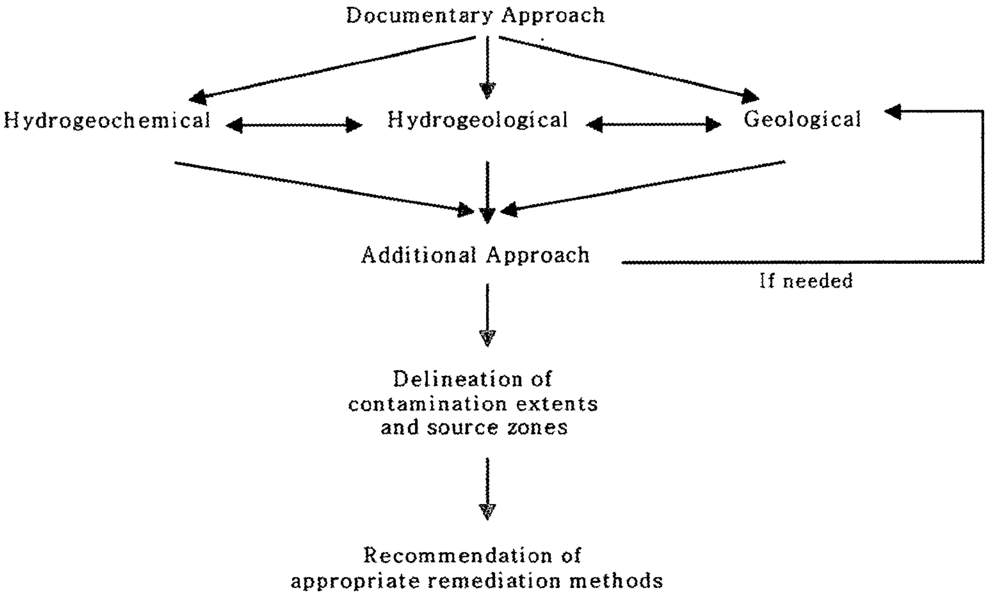

Figure 3. These technical approaches may the best way to get near the goals of this study in given cost and time conditions

2. SITE CHARACTERIZATION

2.1. Site History

This area, about 650,000m2, has been used for industrial activities almost for 30 years since the rice field clearing. Presently, there are about 28 work places in the industrial area, including food company, taxi compound, asphalt & concrete manufacturer, chemical or electrical and electronic business, machinery activities, laundry, leather industry, etc. Some work places are intermittently using the ground water for a variety of purposes.

After Ground Water Act was enacted in 1993, the first ground water quality surveys were performed in 1994-1995 within the industrial area. The results showed the severe ground water contamination with TCE in one food company. The concentrations were 1,207μ g/L and 992μ g/L above the standard levels, 30μ g/L for domestic purpose and 60μ g/L for industrial purpose. The city government promptly started the survey for identifying the source zones. The survey included grasping of TCE use status, collection and analysis of hazardous materials in use, waste water analysis, and water quality surveys of pumping wells around the food company. However, there was no evidence of using TCE and TCE was not detected in any samples. The second analysis confirmed the high concentrations of TCE in 2 pumping wells of the food company, which closed the wells with other 2 wells immediately. In conclusion, the survey failed to delineate the contamination source zones.

2.2. Current Issues

Ground water contamination with TCE within the industrial area has been raised continually and the source zones leave unidentified. In 1999-2002, the 5 remaining wells in the food company were closed because TCE above the standard was detected.

Currently, there are several problems that we can not ignore any more. First of all, although TCE concentrations above several decades of times the standard are detected in pumping wells used for domestic water, the facts are covered up and the adverse health effects on inhabitants are worried. The depth of the pumping wells where TCE is detected is over 100m, which means the contamination has been spreaded into the very deep distance. There is a probability of presence of residual DNAPLs in the fractures. However, there is no evidence of using TCE around the wells and TCE use data before 1997, when TCE was included in the hazardous material list in Korea, is not available. In addition, the land use changed often and all histories of change are not remained. Thus, the identification of source zones would be not easy.

This study is for identifying the volume and extent of ground water contaminated with TCE and delineating the source zones under the given cost and time conditions, and ultimately unraveling these problems.

3. METHOD

3.1. Documentary Approach

3.1.1. Environmental Fate of TCE

Relatively high vapor pressure(57.8mmHg at 20℃) and low adsorption coefficient to a number of soil types(Log Koc=2 for many soil types) indicates ready transport through soil and low potential for adsorption to sediments. Four to six percent of environmental concentrations of TCE adsorbed to two silty clay loams(Koc=87 and 150), no adsorption to Ca-saturated montmorillonite and 17% adsorption to Al-saturated montmorillinate were observed(U.S.EPA, 2003).

The high Henry's Law Constant(0.01 atm-m3/mole) indicates rapid evaporation from water. Half-lives of evaporation have been reported to be on the order of several minutes to hours, depending upon the turbulence. Field studies also support rapid evaporation from water(U.S.EPA, 2003).

TCE is not hydrolyzed by water under normal conditions. It does not adsorb light of less than 290nm and therefore should not directly photodegrade. However, slow(half-life-10.7 months) photooxidation in water has been noted(U.S.EPA, 2003).

3.1.2. Work Status in the Industrial Area

According to the site visits and a variety of documentaries, the industrial area is totally 650,000m2 and there are about 28 work places. Some work places are reported have used TCE, but do not use any more. Some companies intermittently use ground water for a variety of purpose. In particular, the food company had used amounts of ground water until the last 5 wells were closed. Besides, the asphalt test institute, which was out of the first study plan but selected as doubtful source zone based on the interim findings, has used TCE of 500L annually since 1984. The used TCE is said to have been dumped on the surface before 1997 and not until

1999-2000 has it been collected in the drums and disposed by the expert disposal company. However, we can not confirm the fact yet.

3.2. Hydrogeochemical Approach

3.2.1. Soil Sampling and Analysis

TCE infiltrated into the subsurface environment probably from the surface source. In order to delineate the surface source zone, soil samples were collected[Figure 4]. At 30 sites, 3 samples with a different depth for each site were collected. Depth interval was 1m, considering the mobility of TCE in soil. Locating source zones with a 1m sampling frequency can have a low probability of success. As the sampling frequence is increased, the probability of detection increases, but the cost also increases significantly. Therefore, we ignored the first 1m area just below the surface because of the volatility and just above the water table due to the solubility. Sampling locations were determined by soil experts, considering the probability of contamination source zones. Additional sampling was also done at 4 sites based on the interim findings. Samples were analyzed for TCE, PCE and BTEX in accordance with Korean Soil Contamination Analysis Method.

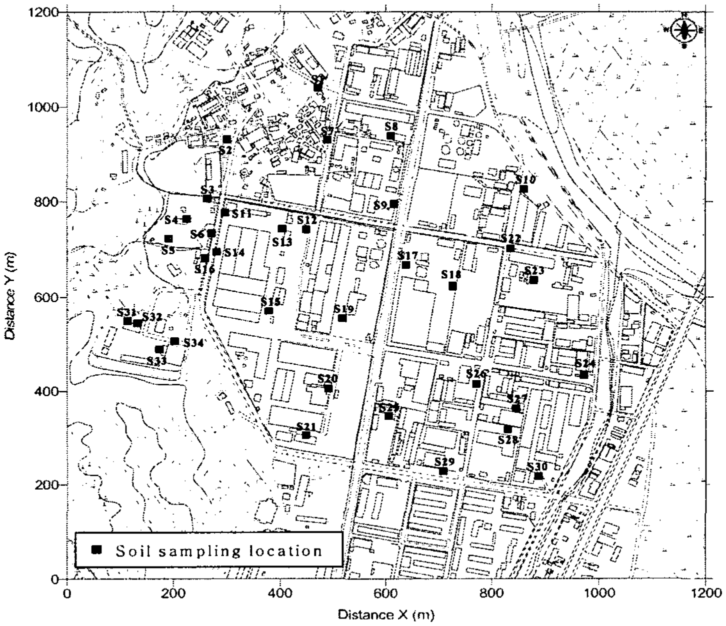

Figure 4. Soil samples were collected and analyzed to pursue the surface source zones.

3.2.2. Ground Water

3.2.2.1. Observation Wells

In-use pumping wells within the industrial area were used as observation wells[Figure 5]. Well depth and even linear intervals between wells were considered to confirm the current situation of contamination with TCE.

3.2.2.2. Installation of Monitoring Wells

The existing pumping wells can not cover the entire survey area. 23 monitoring wells were installed[Figure 5]. First, we constructed the stable borehole with the air percussion drilling equipment and set the well screen and riser to the predetermined level. Then temporary casing was withdrawn with care to minimize lifting the riser. Gravel, sand, and dry bentonite were filled back in the order named, and the grout backfill was placed above the bentonite. Finally the internal cap was fitted on top of the riser and the protective cover with locking cap was set.

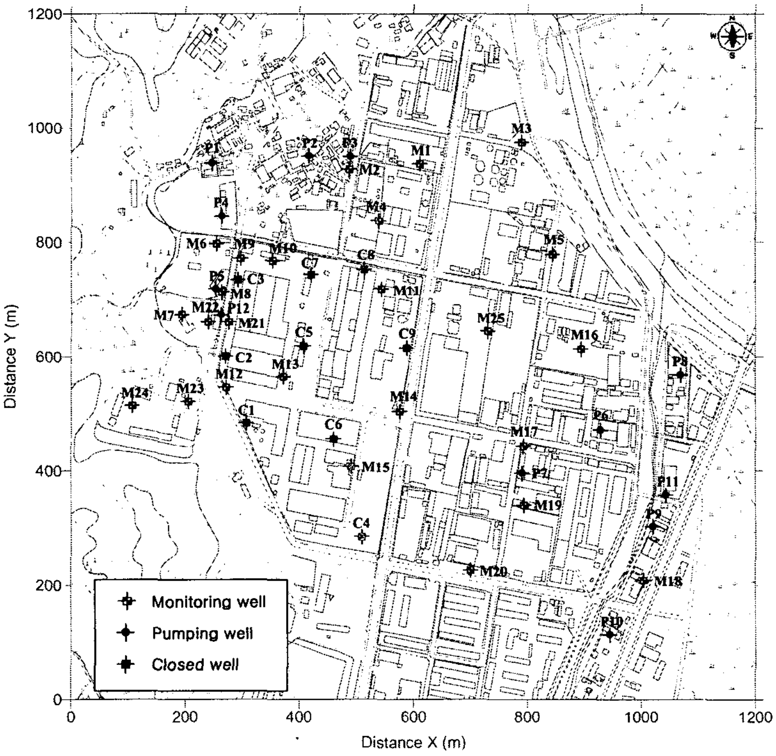

Figure 5. Monitoring wells were installed and used for this study as well as pumping wells. Locations of 9 closed wells in the food company were also marked.

Target depth was 10-30m and monitoring wells were screened to the boring bottom from the water table to collect the water at the very bottom. The diameter of screen was 2 inches to allow for the introduction and withdrawal of sampling or field test devices and the slot size was determined relative to the grain size of the monitored stratum and gradation of filter pack material.

Well development was perform to remove the finer grained materials from the well screen and filter pack that may otherwise interfere with water quality analyses, to restore the ground water properties disturbed during the drilling process and to improve the hydraulic characteristics of the filter pack and hydraulic communication between the well and the hydrologic unit adjacent to the well screen(ASTM, 1998). Pumping and mechanical bailing methods were used together related to the physical characteristics of hydrologic units.

3.2.2.3. Sampling and Analysis

The first ground water samples from monitoring wells were collected at least 7 days after well development using the conventional bailer. Based on the properties of TCE, samples were collected at the very bottom of the well. Water samples at the different depth in the same well were also collected to delineate water type and water contamination related to the flow characteristics in the bedrock aquifer. Waters from observation wells were sampled at the tap after long-term pump operation. All samples were analyzed for TCE, PCE, BTEX, cations(Ca, Mg, Na, K) and anions(Cl, NO3, SO4, HCO3) in accordance with Korean Water Quality Contamination Analysis Method. All samples were collected more than twice to observe the temporal variation as well as spatial variation.

Sampling DNAPL failed because we was not able to know the very bottom of the aquifer. As the documentaries and the geologic survey show, this area has bedrock aquifer flowing along fractures and it is almost impossible to know the very bottom of the aquifer. However, we can guess the presence of the DNAPL from the dissolved TCE concentration. In many cases, the total contaminant mass in the DNAPL phase is much larger than the total mass of even a large dissolved contaminant plume. A guidance document from the U.S.EPA suggests that if a chemical that can occur as a DNAPL is found dissolved in ground water from monitoring wells in amounts of only 1% of the aqueous solubility, there is a substantial probability that DNAPL form is present in the subsurface - so called one precent rule(Fetter, 1999).

3.3. Hydrogeological Approach

3.3.1. Ground Water Level

The contaminant transport depends on the ground water flow as well as other reactions. The source zones can be estimated by observing the well pattern distribution, noting the localized ground water flow patterns, and backtracking upgradient against the direction of ground water flow. Therefore, measuring the water level and confirming the water level distribution are important, although it is the bedrock aquifer. The water level was measured more than twice for each monitoring well by the Water Level Meter.

3.3.2. Time Series Data

Time series data of the water level gives us useful information about patterns of temporal variation of hydrologic process and impulse response characteristics of aquifer systems. We analyzed the response time of aquifer to rainfall, using the time series data of the water level measured by Levelogger, which measured the water level every 6 hours for 30 days at 4 wells.

3.3.3. Permeability Test

Aquifers transmit water from recharge areas to discharge areas and the factors controlling ground water movement can be expressed in the form of an equation by Henry Darcy(1856), where the hydraulic conductivity depends on the size and arrangement of openings and dynamic characteristics of the fluid. The hydraulic conductivity can be used in referring to the water-transmitting characteristic of material in quantitative terms.

To measure hydraulic conductivity of the aquifer, slug tests were performed. The slug test is a method to determine *in situ* hydraulic conductivity values in a single piezometer. This test is initiated by causing an instantaneous change in the water level in a piezometer through a sudden introduction of a known volume of water. The recovery of the water level with time is then observed. There are 2 methods of interpreting the water versus time data; method of Hvorslev(1951) for a point piesometer and Cooper et al.(1967) for a confined aquifer(Freeze, 1979).

3.3.4. Tracer Test

The spreading of contamination through subsurface materials is enhanced by dispersion, which can be calculted by dispersivity measured through some tests. Although longitudinal dispersivity can be measured in the laboratory by passing a nonactive tracer through cylindrical samples collected from boreholes or excavation, we meausred it in the field because dispersivities under field conditions are larger than those indicated by tests on borehole samples probably due to the effects of heterogeneities on the macroscopic flow field.

There is little agreement on the types of field dispersivity tests or methods that are most appropriate(Freeze, 1979). We performed the single-well withdrawal-injection test. In this test, a nonreactive tracer, KBr, was introduced into the ground water system and the tracer was pumped in for a set time period followed by pumping from the well and monitoring the concentration levels. The dispersivity of the formation near the well screen was computed from the concentration response data.

3.3.5. Field Soil Permeability

The permeability of the unsaturated soil has the different value from that of saturated aquifer. Hydraulic properties of unsaturated soil was measured by a tension infiltrometer. Water held under tension infiltrates into a dry soil through a highly permeable nylon membrane. The time dependent infiltration rate recorded manually was used to calculate saturated hydraulic conductivities of the unsaturated soil.

3.3.6. Adsorption Coefficient

Reactive contaminants transported by ground water are distributed between the solution phase and other phases. Simply we focused on the liquid and solid phases. The reaction between the contaminant and the geologic materials may cause a portion of the contaminant to be incorporated into a solid form on the materials as a result of adsorption. DNAPLs' adsorption to aquifer solids tend to make the pollution linger or sometimes apparently disappear, only to return later. Therefore DANPLs can be the long-term contamination source.

The partitioning can be determined by laboratory experiments in which the contaminant in solution is allowed to react under controlled conditions with samples of the geologic materials acquired from the field. Batch experiments in the laboratory was performed. Batch test has the advantage of being relatively quick and inexpensive to conduct and is a standard method for establishing adsorption isotherms of some contaminants, In the test, the contaminated solution and the geologic material in a disaggregated state are brought into contact in a reaction vessel. After a period of time, the degree of partitioning of the contaminant between the solution and the geological materials was determined.

3.4. Geological Approach

Ground water flow and contaminant transport depend on the geological characteristics as well as fluid characteristics. In particular, geological survey is much more important to explain DNAPLs transport in bedrock aquifer. Since DNAPLs are denser than water, their movement can not be governed by the direction of ground water flow as is generally the case for other ground water.

Geological survey was performed at 5 sites to define the geological characteristics of the aquifer and confirm the presence of the fractures. These data were used for the characterization of the aquifer with the logging data acquired during installing of monitoring wells. We drew the lithologic profile of the aquifer and confirmed the presence of the vertical fractures.

3.5. Additional Survey Approach

All conditions considered, this survey can not be completed by only a plan. We designed to change the plan and add the survey sites based on the interim findings. As occasion demanded, we collected more soil and ground water samples and installed monitoring wells additionally.

3.6. Computer Simulation

Computer simulations based on measured hydrogeological properties can be used to generate flownets or particle tracking simulations. Flownets and particle tracking simulations may then be used to elucidate the most probable location of DNAPL source zone(Kram et al., 2001). Using Visual MODFLOW v.3.1. we assess the ground water flow, estimate the contamination process of the past, and predict the probability of the natural attenuation after source removal.

4. INTERIM FINDINGS

Sampling locations were selected based on the site visits and documentary surveys and soil and ground water samples were analyzed for TCE. The interim analysis results showed the severe ground water contamination with TCE. The area of these contaminated ground waters was limited to the area near the food company and contaminated depth was very deep.

Distribution of the ground water level was confirmed and other hydraulic property tests are almost being finished. These data can be used to delineate the source zones with the hydrogeochemical data. Modeling assessment is also under way.

A scenario based on the interim findings is as follows : In the past, the food company pumped an amount of ground water. The cone of depression would be made at the subsurface of the food company. At the similar time, much TCE was used for asphalt chemical test. The test institute is located at the northwest of the food company and has the higher altitude. TCE waste was disposed at the surface without any treatments and would transport along the connected fractures or boreholes made during drilling pumping wells. This institute was out of the first study area and such cases are very common. The history of this institute is being surveyed and additional survey is under way to confirm the source zones.

5. DISCUSSION AND CONCLUSIONS

This study used many of the methods and approaches to detect the contamination status and delineate contaminant source zones in given cost and time conditions. Documentary, hydrogeochemical, hydrogeological, and geological approaches were performed and each technical approach consisted of several methods. As occasion demanded, additional survey was done. Methods described in this paper are clearly not valid for all cases and the level of resolution and detail required for site assessment and remedial design are not generally achievable using these techniques. However, these approaches can serves as confirmation efforts, provided a specific DNAPL source location is suspected based on more rigorous alternatives such as those described in this paper. Because each method has specific advantages and disadvantages, several methods were complementary in an overall site assessment plan, each serving a particular niche.

In this study, the contaminated areas were far from the areas where TCE uses were reported and ground waters were contaminated to the deep places. Therefore, it was not easy to delineate the source zones. Besides, although the presence of the vertical fractures was confirmed, it is almost impossible to locate the all fractures and complete patterns. Based on the interim findings derived from several approaches, we narrowed down the contamination area and got near the probable source zones. These approaches are not the right solution, but can be the best solution for the confirmation of contamination and the delineating of source zones. This "hybrid" approach for assessing the site comprising fractured bedrock aquifer is expected to give the satisfactory results. This study is now under way and we will determine the extent and volume of the contaminated ground water and delineate the source zones based on the final results. In addition, contamination process in the past and the probability of natural attenuation after source removal will be assessed with computer simulation. Finally, we will recommend the appropriate remediation methods.

In Korea there are many contaminated sites where ground water is probably contaminated with DNAPLs, but unattended without any survey, although more concern has been centered in these sites. This study can be the cornerstone of the survey. It will be up to the project managers to determine which approach is most appropriate for their specific site conditions and concerns. In general, cost(Kram et al., 2002) and time will most likely be the determining factors for approach selection. However, several approach limitations should weigh heavily in the ultimate selection of the most appropriate site management strategy. For the human health and the protection of ground water resources from the source zones, such surveys should be encouraged.

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