Trichloroethylene Contamination in Fractured Bedrock Aquifer in Wonju, South Korea

S.-Y. Yu, 1 G.-T. Chae, 2 K.-H. Jeon, 3 J.-S. Jeong, 3 J.-G. Park 3

² Department of Earth and Environmental Sciences, Korea University, Seoul 136-701, South Korea

Received: 5 July 2005/Accepted: 9 December 2005

Groundwater contamination by trichloroethylene (TCE) is one of the most urgent environmental problems, because TCE is a strong carcinogenic substance (US EPA 2004) and it causes vomiting and abdominal pain when people are exposed to it above 5 μ g/L (US EPA 2003). In addition to its toxicity, TCE is highly mobile in the subsurface and may penetrate the fracture network (Slough et al. 1999; Parker et al. 2004), since it is denser and less viscous than water. If a large quantity of TCE has been released into subsurface, TCE continues to move vertically downward due to gravity until it is confined by aquitard. In case of fractured bedrock aquifer, however, the movement of TCE is not simply predicted. When TCE invades a fractured medium, it will preferentially enter larger fractures and will be distributed both horizontally and vertically according to the size, orientation and the degree of fracture connectivity (Parker et al. 2004). Furthermore, residual TCE in fractures can be a long-term contamination source, slowly dissolving into groundwater (Rivett et al. 2001).

High level of TCE concentration (1.276 mg/L) was detected in a 200 m deep well in Wonju industrial area (Figure 1) in 1995. The concentration exceeded the Korean standard levels, 0.03 mg/L for domestic purpose and 0.06 mg/L for industrial purpose. The promptly following survey found severe groundwater contamination with TCE of wells in a food company, which is within the Wonju industrial area and had used amounts of groundwater (about 1,000 ton/day) for making paper boxes. However, it was not reported that the food company had used TCE. The two contaminated wells were abandoned immediately in 1995 and the other 7 wells also were closed due to high levels of TCE concentration between 1999 and 2002 (Yang 2003). However, TCE contamination in this area has been still issued with source zones unidentified. The difficulty in locating source zones is derived from the fact that the depth of wells where TCE is detected is over 100 m where water comes from the bedrock aquifer.

The objectives of this study are to determine volume and extent of contamination with TCE and to delineate TCE contaminant source zones in the industrial area. In addition, this study aims to suggest the considering factors for advanced research on TCE contamination and remediation. We performed geologic,

Department of Earth Sciences, University of Waterloo, 200 University Avenue West, Waterloo, Ontario, Canada N2L 3G1

³ Environmental Site Assessment and Remediation Team, Environmental Management Corporation, Environmental Research Complex, Kyungseo-Dong, Seo-gu, Incheon 404-170, South Korea

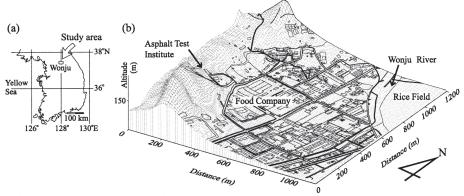


Figure 1. (a) The location of Wonju and (b) topography of Wonju industrial area.

hydrogeologic, and hydrogeochemical study in order to attain the objectives. The project is still ongoing to the next step of groundwater remediation, based on the results of this study, which informs of the serious status of TCE contamination in bedrock aquifer.

MATERIALS AND METHODS

The study area is located in the northern central part of South Korea (Figure 1a) and is a small basin surrounded by small mountains (< 200 m a.s.l.; see Figure 1b) and Wonju River. The climate of the study area is humid and hot in summer, and dry and cold in winter. Mean annual precipitation is about 1,300 mm, of which 60 % occurs during summer (June to September). Mean monthly air temperature ranges from -0.6 °C in January to 25.7 °C in August. The study area, about 0.65km², has been used for industrial activities almost for 30 years. Currently there are about 28 work places in this area, including food company, taxi compound, asphalt and concrete manufacturer, chemical or electrical & electronic factory, machinery factory, laundry, leather industry, and so on. Some work places are intermittently using groundwater for various purposes.

A geological logging survey was performed along two lines crossing the most industrialized area (Figure 2a) in order to get a geological profile. In addition, around the potential contamination source zones such as chemical or electrical & electronic factory, machinery factory, laundry, and leather industry, 112 soil samples were collected at three different depths of 34 locations. We ignored both the first 1m stratum just below the surface due to the volatility of TCE and the stratum just above the water table due to the low solubility of TCE. Collection of soil samples was done with Geoprobe® or Air percussion (DPT type), dependent on the geologic situation. Soil samples were analyzed for TCE using gas chromatography and flame ionization detector (GC/FID) after soxhlet extraction (EPA method 3540C).

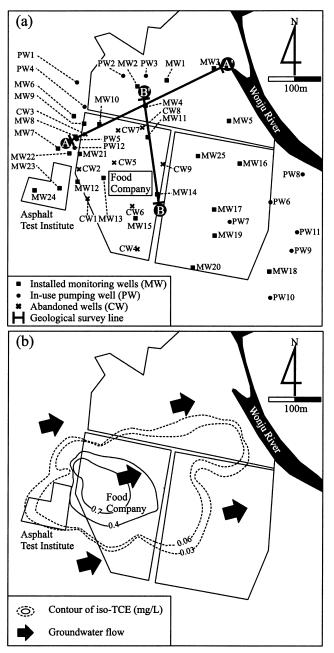


Figure 2. (a) Locations of groundwater sampling locations. (b) The distribution of TCE concentrations in Wonju industrial area.

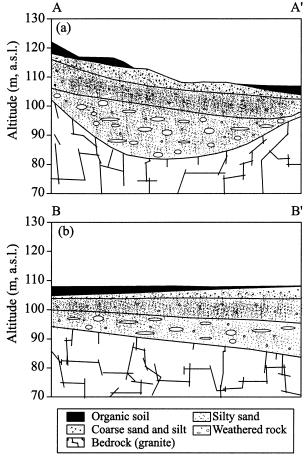


Figure 3. Geological characteristics in profile (a) AA' and (b) BB'.

Groundwater samples for chemical analysis were collected at 25 monitoring wells installed for this study and 12 in-use pumping wells within the industrial area (Figure 2a). All groundwater samples were collected more than twice, including sampling in July and August of 2003, to observe the temporal variation as well as the spatial variation. In addition, groundwater samples at different depths in the same well were collected to delineate water contamination related to the flow characteristics in the bedrock aquifer. The monitoring wells were installed in the alluvium aquifer with screen depth to about $10 \sim 30$ m below the surface (ASTM 1998), whereas the in-use pumping wells have been exploiting waters from the bedrock aquifer with the depth up to 100 m. These in-use pumping wells were cased by concrete to the boundary between alluvium and bedrock, and were not cased below the top of bedrock. Groundwater samples from installed monitoring wells were collected using a conventional bailer, while those from in-use pumping wells were sampled at the tap when the water

temperature was steady after long-term pump operation. Groundwater samples were analyzed for TCE using gas chromatography and flame ionization detector (GC/FID). Careful quality control (QC) was achieved by using field QC samples, and the analyses of laboratory duplicates showed the RSD (Relative Standard Deviation) values of <10%.

RESULTS AND DISCUSSION

The geology of the study area mainly consists of the fractured Jurassic granite which is overlaid by weathered rock. Quaternary alluvium and soil layers cover the weathered rock. The geologic profiles are shown on Figure 3. The thickness of NE dipping alluvium is 10 m consistent along the AA' profile, but thickness of weathered rock is varied from < 1 m to 15 m and thickened in the center of profile. On the other hand, the alluvium and weathered rock are dipping and thickening up to 10 meter respectively, to north in BB' profile. The organic rich layer is observed both in AA' and BB' profiles. In addition, some sets of vertical fractures are observed in logging data. These fractures were also reported when the pumping wells $200 \sim 300$ m deep were installed in the food company. According to the geological description of the Wonju area adjacent to this study area, a large number of fractures with random orientations are observed at depths from 4 to 34 m in granite, and are rather uniformly distributed (Lee and Lee 2000). The lower part of the granite below the fractured zone serves as a lower confining bed for the deeper aquifer.

Groundwater flows from the western mountain to the eastern river in alluvial aquifer (Figure 2b). Although the groundwater flow in the bedrock aquifer depends on the direction and aperture of the fractures, the regional groundwater flow is expected to be similar to that in alluvium. Lee and Lee (2000) reported the hydraulic parameters of Wonju area adjacent to this study area. The groundwater velocities which was measured by tracer tests were $1.02 \cdot 10^{-3}$ m/min in alluvium and $1.05 \cdot 10^{-2}$ m/min in fractures. The hydraulic conductivities were $1.63 \cdot 10^{-3}$ m/min in alluvium and $1.84 \cdot 10^{-3}$ m/min in fractures. In summary, the groundwater in this area mainly flows from west to east and the contamination source might be located in the up flow region of contaminated area, the food company. In addition, groundwater in the bedrock aquifer can flow through the fractures and therefore TCE may be able to reach the bedrock aquifer.

The concentration of TCE above 0.01 mg/L is summarized in Table 1. The result is mean of two or more samples in a location because there is little temporal variation of the water quality, which is found by analyzing major cations and anions to identify water types, and TCE concentrations during the study period. The results show the severe groundwater contamination with TCE. The maximum concentration is 1,524 mg/L at the in-use pumping well located near the food company. High levels of TCE are also detected at installed monitoring wells (up to 1.183mg/L) in the food company. It indicates that groundwater contamination with TCE is severe both in alluvium and bedrock aquifer. Moreover, in-use pumping wells and abandoned wells due to high concentrations

Table 1. TCE concentrations in the Wonju industrial area.

| Sample | Date | Depth | TEC | Sample | Date | Depth | TEC |
|----------------------------|--------|-------|--------|-----------------|--------|-------|--------|
| no. | | (m) | (mg/L) | no. | | (m) | (mg/L) |
| Installed monitoring wells | | | | | | | |
| MW5 | Aug-03 | 3 | 0.217 | MW13 | Aug-03 | 6 | 1.113 |
| | Aug-03 | 6 | 0.075 | | Aug-03 | 11 | 1.183 |
| | Jul-03 | 6 | 0.184 | | Jul-03 | 11 | 0.680 |
| MW7 | Aug-03 | 6 | 0.014 | MW14 | Aug-03 | 5 | 0.505 |
| | Aug-03 | 11 | 0.087 | | Aug-03 | 10 | 0.381 |
| | Jul-03 | 11 | 0.068 | | Jul-03 | 10 | 0.123 |
| MW8 | Aug-03 | 3 | 0.176 | MW21 | Aug-03 | 3 | 0.802 |
| | Aug-03 | 6 | 0.186 | | Aug-03 | 6 | 0.609 |
| | Aug-03 | 9 | 0.486 | | Aug-03 | 9 | 0.669 |
| | Aug-03 | 12 | 0.352 | | Aug-03 | 12 | 0.574 |
| | Jul-03 | 12 | 0.539 | | Jul-03 | 12 | 0.769 |
| MW9 | Jul-03 | 10 | 0.046 | MW23 | Aug-03 | 1 | 0.001 |
| | Aug-03 | 10 | 0.027 | | Aug-03 | 18 | 0.176 |
| MW11 | Jul-03 | 15 | 0.007 | | Jul-03 | 18 | 0.136 |
| | Aug-03 | 15 | 0.198 | MW24 | Aug-03 | 1 | 0.059 |
| MW12 | Jul-03 | 8 | 0.632 | | Aug-03 | 19 | 0.063 |
| | Aug-03 | 8 | 0.441 | | Jul-03 | 19 | 0.054 |
| In-use pumping wells | | | | Abandoned wells | | | |
| PW4 | Jul-03 | 25 | 0.016 | CW1 | Sep-95 | 200 | 1.276 |
| | Aug-03 | 25 | 0.049 | CW2 | Sep-95 | 300 | 1.159 |
| PW5 | Jul-03 | 100 | 0.296 | CW5 | Feb-99 | 100 | 0.065 |
| | Aug-03 | 100 | 0.293 | CW6 | Mar-99 | 100 | 0.116 |
| PW6 | Jul-03 | 50 | 1.524 | CW8 | Nov-01 | 100 | 0.346 |
| | Aug-03 | 50 | 1.160 | CW9 | Jan-02 | 100 | 0.134 |

of TCE in the food company are deep over 100 m (Table 1), which means that TCE has already moved to the deep fractured aquifer along natural or artificial apertures. The depth profile of TCE concentration shows the evidence that TCE concentration tends to increase with depth except MW5, 14, and 21 wells. The concentrations of TCE in MW5, 14, and 21 wells are 0.217, 0.505, and 0.802 mg/L within 5 m from surface, respectively, and the thickness of alluvium around these wells is thin. Thus it is thought that TCE still remains in the interface between alluvium and weathered rock and/or bedrock. TCE is not detected in soil samples except one sample collected in the Asphalt Test Institute, which shows 30 mg/kg of TCE. TCE is reported to be volatile, but can be infiltrated into soil when amounts of TCE leak. Thus, the remaining TCE in the soil sample indicates that amounts of TCE wastes were seeped on the surface in this area.

The extent of groundwater contamination is interpolated by using Kriging method (Figure 2b) under the assumption that groundwater is in the same aquifer. The result shows that the area of contaminated groundwater is about 300,000 m², based on the Korean standard for domestic purpose, 0.03 mg/L. The volume of contaminated plume in the alluvial aquifer is estimated to be about 1,000,000 m³. This estimation does not consider the contamination in the bedrock aquifer and the depth of alluvium is assumed to be constantly 12 m. When high concentration of TCE detected in the deep bedrock aquifer is considered, the problem becomes more serious. It is estimated that a great deal of TCE remains in the fractures. In general, the total contaminant mass is expected to be much larger than the dissolved contaminant plume, because the TCE is hardly dissolved to groundwater. In other words, if a DNAPL (Dense non-aqueous phase liquid) such as TCE is found dissolved in groundwater from an well in amounts of only 1% of the aqueous solubility, there is a substantial probability that DNAPL form is present in the subsurface (Fetter 1999). In summary, the Asphalt Test Institute is presumed as the source of TCE contamination, when considering the topography, hydrogeology, and history of TCE usage in the institute as well as soil contamination. The Asphalt Test Institute is located on western high mountainous area (Figure 1b) and regional groundwater flows from west to east. In addition, the food company near the Asphalt Test Institute pumped amounts of groundwater, which might result in drawdown of the water level and introduction of infiltrated TCE into bedrock. The Asphalt Test Institute has tested the quality of asphalt in pavement samples from roads since 1988 according to the KSF2354. Korean Standards Association. Based on the method, the test for a sample requires over 600 milliliters of pure TCE solvent. The Asphalt Test Institute has used 500 liter of TCE annually and the used TCE had been dumped on the surface in the institute until 1997. Not until 1999 has it been collected in drums and disposed by an expert disposal company. Until the study was finished, there had been no infiltration-protection facilities within the institute, and pure TCE and used TCE wastes had been stored in drums and placed in the back yard without any treatment.

In this study, the plume of contaminant was detected and the status of TCE contamination was quantified. Moreover, the pollution source was estimated for responsibility of remediation. However, the remediation is expected to be more complicated, because the TCE has already reached bedrock aquifer and the extent of contamination in the shallow alluvium is wide. Furthermore, TCE can be diffused to rock matrix when it flows through fractures. According to Slough et al. (1999) and Parker et al. (2004), the TCE can flow through fractures of aquitard and the amount of flow depends on the aperture fractures. Lee and Lee (2000) reported the result of time series analysis of changes of hydraulic head in the area adjacent to this study area. They concluded that the granite bedrock in this area was hydraulically connected to the surface and showed fast response of hydraulic head to the rainfall. It means that fractures in bedrock aquifer play a crucial role in the TCE transport in this area, and therefore the remediation will be challenging. On the other hand, the redox state and/or biological activity in the groundwater system is not elucidated in this study, although TCE in the

groundwater can be attenuated and changed to daughter compounds by microbes in reducing condition (Davis et al. 2002; Lenczewski et al. 2003). Thus, the remedial activity must consider the redox and biology of the aquifer, and additional study is still performing for these purposes. This study would be used as good an example for assessment of TCE contamination and location of source zones in bedrock aquifer.

Acknowledgments. We thank Wonju City government for providing the financial support and the information and documents about the study area. In addition, the authors gratefully acknowledge the co-workers in OIKOS Co. Ltd. and BEC Co. Ltd. for their field and lab work.

REFERENCES

- ASTM (American Society for Testing and Materials) (1998) ASTM Standards related to the phase II environmental site assessment process. ASTM, West Conshohocken, PA
- Davis JW, Odom JM, Deweerd KA, Stahl DA, Fishbain SS, West RJ, Klecka GN, DeCarolis JG (2002) Natural attenuation of chlorinated solvents at Area 6, Dover Air Force Base: characterization of microbial community structure. J Contam Hydrol 57: 41-59
- Fetter CW (1999) Contaminant hydrogeology, 2nd edn. Printice Hall, Englewood Cliffs, NJ
- Lee JY, Lee KK (2000) Use of hydrologic time series data for identification of recharge mechanism in a fractured bedrock aquifer system. J Hydrol 229: 190-201
- Lenczewski M, Jardine P, McKay L, Layton A (2003) Natural attenuation of trichloroethylene in fractured shale bedrock. J Contam Hydrol 64: 151-168
- Parker BL, Cherry JA, Chapmam SW (2004) Field study of TCE diffusion profiles below DNAPL to assess aguitard integrity. J Contam Hydrol 74: 197-230
- Rivett MO, Feenstra S, Cherry JA (2001) A controlled field experiment on groundwater contamination by a multicomponent DNAPL: creation of the emplaced-source and overview of dissolved plume development. J Contam Hydrol 49: 111-149
- Slough KJ, Sudicky EA, Forsyth PA (1999) Numerical simulation of multiphase flow and phase partitioning in discretely fractured geologic media. J Contam Hydrol 40: 107-136
- U.S.EPA (Environmental Protection Agency) (2003) Technical factsheet on: trichloroethylene. U.S.EPA, Washington DC (obtained from the internet site, http://www.epa.gov/OGWDW/dwh/t-voc/trichlor.html)
- US EPA (Environmental Protection Agency) (2004) Symposium on new scientific research related to the health effects of trichloroethylene. US EPA, Washington DC
- Yang JU (2003) Study on the present status of soil contamination and the development of management strategies in Wonju, Kangwon Province. Kangwon Regional Environmental Technology Development Center, Kangwon, Republic of Korea