



저작자표시-동일조건변경허락 2.0 대한민국

이용자는 아래의 조건을 따르는 경우에 한하여 자유롭게

- 이 저작물을 복제, 배포, 전송, 전시, 공연 및 방송할 수 있습니다.
- 이차적 저작물을 작성할 수 있습니다.
- 이 저작물을 영리 목적으로 이용할 수 있습니다.

다음과 같은 조건을 따라야 합니다:



저작자표시. 귀하는 원저작자를 표시하여야 합니다.



동일조건변경허락. 귀하가 이 저작물을 개작, 변형 또는 가공했을 경우에는, 이 저작물과 동일한 이용허락조건하에서만 배포할 수 있습니다.

- 귀하는, 이 저작물의 재이용이나 배포의 경우, 이 저작물에 적용된 이용허락조건을 명확하게 나타내어야 합니다.
- 저작권자로부터 별도의 허가를 받으면 이러한 조건들은 적용되지 않습니다.

저작권법에 따른 이용자의 권리는 위의 내용에 의하여 영향을 받지 않습니다.

이것은 [이용허락규약\(Legal Code\)](#)을 이해하기 쉽게 요약한 것입니다.

[Disclaimer](#)

이학석사학위논문

**A gas monitoring approach to estimate the residual TCE location
in the unsaturated zone of Woosan Industrial Complex (WIC)**

원주 우산공단지역 불포화대내 잔류 TCE 의 위치예측을 위한 가스
모니터링 접근법

2013 년 8 월

서울대학교 대학원

지구환경과학부

고윤언

Koh, Youn Eun

School of Earth and Environmental Sciences

Graduate School

Seoul National University

**A gas monitoring approach to estimate the residual TCE location
in the unsaturated zone of Woosan Industrial Complex (WIC)**

원주 우산공단지역 불포화대내 잔류 TCE 의 위치예측을 위한

가스 모니터링 접근법

지도교수 이 강 근

이 논문을 이학석사 학위논문으로 제출함

2013 년 8 월

서울대학교 대학원

지구환경과학부

고윤언

고윤언의 이학석사 학위 논문을 인준함

2013 년 8 월

위원장 김 준 모 
부위원장 이 강 근 
위원 김 규 범 

**A gas monitoring approach to estimate the residual TCE location
in the unsaturated zone of Woosan Industrial Complex (WIC)**

Koh, Youn Eun

**A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENT FOR THE DEGREE OF MASTER OF SCIENCE
IN EARTH AND ENVIRONMENTAL SCIENCE**

August, 2013

School of Earth and Environmental Sciences

Graduate School

Seoul National University

ABSTRACT

An area accommodating various industrial facilities has fairly high probability of groundwater contamination with multiple chlorinated solvents such as trichloroethene (TCE), carbon tetrachloride (CT), and chloroform (CF). Source tracing of chlorinated solvents in the unsaturated zone is an essential procedure for the management and remediation of contaminated area. From the previous study on seasonal variations in hydrological stresses and spatial variations in geologic conditions on a TCE plume, the existence of residual DNAPLs at or above the water table has indicated. Since TCE is one of the frequently detected VOCs (Volatile Organic Compounds) in groundwater, residual TCE can be detected by gas monitoring. Therefore, monitoring of temporal and spatial variations in the gas phase TCE contaminant at an industrial complex in Wonju, Korea, were used to find the residual TCE locations. In each field test, TCE gas samples were collected at 4 different depths above the water table from the well, KDPW-2, with/without a packer and were analyzed using SPME (Solid Phase MicroExtraction) fiber and Gas Chromatography (GC). The results showed that the highest TCE concentration appeared near at 12 m depths in each test and the range of TCE concentration decreased as the sampling period went from May to November. With these concentration data, the radius of influence (ROI) was calculated and applied on the real scale map of WIC. Therefore, this gas monitoring approach could be used as a method to find the approximate location of residual DNAPLs in the unsaturated zone. Moreover, it will be helpful for the efficient remediation of groundwater by giving the idea of the source's location.

Key words: Residual DNAPLs, Trichloroethene (TCE), Gas monitoring, Radius of Influence (ROI)

TABLE OF CONTENTS

ABSTRACT	i
TABLE OF CONTENTS	ii
LIST OF FIGURES	iv
LIST OF TABLES	vi
1. INTRODUCTION	1
1.1 Background	1
1.2 Objectives	3
2. STUDY AREA	4
2.1 Site Description and History	4
2.2 Hydrogeological Characterization	6
2.3 Monitoring Wells	8
3. MATERIALS AND METHODS	11
3.1 Materials	11
3.2 Methods	17
3.2.1 Gas Sampling	20
3.2.2 Analysis of TCE Concentration	24
3.2.3 Calculation of Radius of Influence (ROI)	25

4. RESULTS AND DISCUSSION	30
4.1 TCE Gas Concentration	30
4.2 Radius of Influence (ROI)	42
5. SUMMARY AND CONCLUSION	46
6. REFERENCES	48

LIST OF FIGURES

Figure 2-1. Map of Woosan Industrial Complex (WIC)	5
Figure 2-2. Map of all monitoring wells and the study well, KDPW-2.....	9
Figure 2-3. The drill log of KDPW-2	10
Figure 3-1. Different types of the caps in (a) case -1 and (b) case -2.....	13
Figure 3-2. Experiment settings (a) A packer (b) an air pump and an air sampler	14
Figure 3-3. The depth-discrete valve in (a) a scheme and in (b) the experiment.....	15
Figure 3-4. A process of SPME Fiber.....	16
Figure 3-5. Total experiment scheme.....	19
Figure 3-6. N ₂ injection process.....	22
Figure 3-7. Field test process.....	23
Figure 3-8. A scheme of a leaky confined aquifer.....	26
Figure 3-9. A matched curve of a distance-drawdown of test no. 1 and type curve for Hantush-Jacob leaky confined aquifer.	28
Figure 3-10. Eight pressure drawdown graphs of each test (a) test no.1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 7, (h) 8	29
Figure 4-1. Case-1 Results (a) Packer (b) No Packer.....	31
Figure 4-2. 1 st result of Case-2 (No Packer)	35
Figure 4-3. 2 nd result of Case-2 (Packer)	37
Figure 4-4. 3 rd result of Case-2 (No Packer)	39
Figure 4-5. 4 th result of Case-2 (No Packer)	41

Figure 4-6. Radius of Influence at the experiment site45

LIST OF TABLES

Table 2-1. Values of TCE Concentration and water table at KDPW-2	7
Table 3-1. Summary of sampling events	18
Table 3-2. Information of pressure drawdown test and values from graph matching	27
Table 4-1. Values in radius of influence (ROI) calculation	43
Table 4-2. Values of the leakage factor and transmissivity from pressure-drawdown test....	44

1. Introduction

1.1 Background

As the awareness of groundwater contamination due to its harmfulness to human health has grown globally, the Korea Ministry of Environment (KMOE) began monitoring groundwater wells. In fact, dense non-aqueous phase liquids (DNAPLs) such as trichloroethene (TCE), carbon tetrachloride (CT), and chloroform (CF) are highly toxic, which can arouse cancers to human with small amount (Maull et al., 1997). The importance of monitoring DNAPLs contaminants is acknowledged not only because of their impacts on human health, but also of Korea's unique geological characteristic such as having aquifers closely to the ground. This geological condition increases the possibility of TCE contamination even on the fracture zone of the aquifer (Yu et al., 2006).

Especially in the cities and the industrial complexes, TCE and PCE are known to be the major sources of groundwater contamination due to industrial facilities' heavy usage of chemical substances (Mercer et al., 1993). However, it is difficult to find DNAPLs sources in non-aqueous phase (NAPL) due to the sources' tendencies to move downward. Once those DNAPLs sources reach the groundwater table, they spread in every direction and become possible contaminants in aqueous phase. Moreover, it is suggested that residual DNAPL in the vadose zone also could be the hidden source of groundwater contamination (LaPlante, 2002). Therefore, there would be no fundamental cleanup for groundwater without finding DNAPLs contaminants' location in the vadose zone before start of remediation designing.

The Wonju Industrial Complex (WIC), the study site, is one of the highly contaminated regions with TCE. Over the past few years, many studies have been conducted on source identification and on finding the effective remediation techniques regarding DNAPLs contaminants in this area (EMC, 2003; Yang et al., 2003; Yu et al., 2006; KMOE,

2009, 2010, 2011; Baek et al., 2010; Yang et al., 2011). With all these results, it was suggested that residual TCE in the unsaturated zone plays an important role as a contamination source in groundwater at WIC. However, those previous experiments were limited to horizontal distribution of contaminants in the soil level and required artificial changes on natural environment. In fact, the previous attempts to monitor contaminant distribution at the various depths were failed due to the lack of information about the wells (KMOE, 2011).

It is still known as technically hard tasks to determine the free phase DNAPL existence and to run a satisfactory remediation of chlorinated solvents (Siegrist et al., 2006; Baek et al., 2010). As one solution, the direct soil coring could be applied to prove the existence of residual TCE and to trace it, but it cannot be relied fully due to the physical characteristic of DNAPLs and the site's hydrogeological heterogeneity (KMOE, 2010). However, those residual TCE sources can be detected in gas phase due to their characterization as volatile organic compounds (VOCs). If a residual DNAPL source is in the unsaturated zone around the well, TCE concentration in gas phase will be higher than the concentration in only water existing well. In fact, a new vapor-phase-based approach for groundwater monitoring has done in the laboratory in 2009 and then applied on the field investigation in 2011 (Adamson et al., 2009, 2011). They proved that this convenient method of detecting VOCs could accurately determine the VOC concentration in the associated groundwater at or below maximum contaminant levels. Therefore, this gas sampling approach could detect VOCs from the residual DNAPL source and estimate the location of the source at WIC in more handy way.

1.2 Objectives

The main purpose of this study is applying a method of gas sampling to prove the existence and to estimate the location of residual TCE in the unsaturated zone at WIC in Wonju, Korea. The detailed objectives are followings:

- 1) To conduct initial experiments on gas sampling method at highly TCE-contaminated location to prove the existence of residual DNAPL
- 2) To estimate the location of residual DNAPL by sampling gas from the different depths
- 3) To calculate the radius of influence (ROI) as a parameter for optimizing SVE (Soil Vapor Extraction) tests

2. Study Area

2.1 Site Description and History

The study site for this research, the Woosan Industrial Complex (WIC) covers 0.70 km² of Wonju, Korea and the west side of the complex meets Wonju stream, which flows from southeast to northeast. WIC, which became the complex in 1970s, includes one large company and approximately 23 small companies. About 91% of the ground is paved, so only the remained 9% can have groundwater recharge (KMOE, 2011).

According to the previous researches, the known main source area of DNAPLs is the Road Administrative Office (RAO) of Gangwon Province (Yang et al., 2003). RAO is located approximately 135 m above the average sea level (m, a.s.l.) and 17m higher than it of WIC. Since the main source area is located at higher a.s.l., the effect of TCE, carbon tetrachloride, and chloroform is significant to groundwater contamination of WIC (Figure 2-1).

It is known that there was an asphalt quality test, which might have used many unknown solvents, at RAO in 1980s for 16 years. Since 1995, the year when the DNAPL contaminants such as TCE and CT were detected for the first time, the concentration of TCE has reported by many research institutes. The low-thermal desorption method was applied by Gangwon Province in 2004 to get rid of contaminated ground at RAO (Yang et al, 2011). However, getting rid of the DNAPLs contaminants at soil's top part cannot be the fundamental way to remediate groundwater.

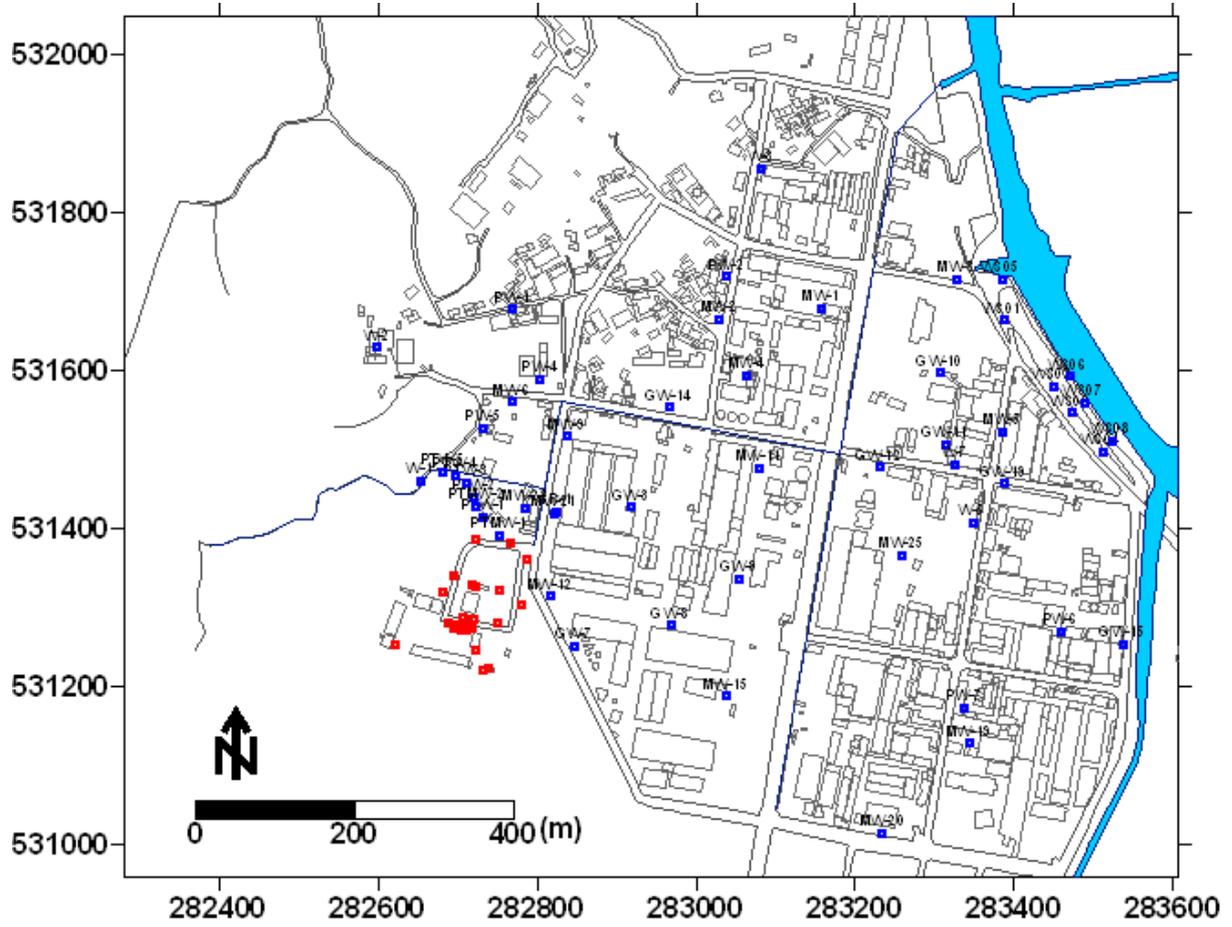


Figure 2-1 Map of Woosan Industrial Complex (WIC).

2.2 Hydrogeological Characterization

According to Korea Institute of Geoscience and Mineral Resources (KIGAM), the subsurface of WIC is consisted of an unconsolidated soil layer, weathered rocks, and a Jurassic biotite granite bottom zone. The thickness of the unconsolidated layer is about 5 to 29 m. Due to its highest hydraulic conductivity, unconsolidated layer is the main path of groundwater and various DNAPLs contaminants.

The flow path of groundwater at RAO is from southwest to northeast and meets Wonju stream, whereas it at WIC is from west to east. The groundwater table level showed a different trend at different locations. The water table fluctuated within a range of 4.64 m in the well near the source area such as KDPW-4. Meanwhile, it fluctuated within a range of 1.4m in the well, MW-3, located in the industrial complex.

According to Wonju's weather report on rainfall, the average yearly rainfall was 1,517 mm from 2007 to 2011. During this period, the highest monthly rainfall was 550 mm in September, 2011 and the lowest was 6.5 mm in January, 2006. Also, 74% of the average yearly rainfall at WIC was happened heavily in June, July, August, and September (Yang et al, 2011). Both trends of heavy rain in summer and relatively small amount of rain in winter showed that the rainfall has impacts on contaminant transport.

A research using the diffusion samplers showed that the highest contaminant's concentration at WIC was 11.57 mg/L, which exceeded the maximum standard level as 0.03 mg/L for TCE and PCE in drinking water set by the Korea Ministry of Environment (Lee, 2011). This contaminant, mainly known as TCE, was at the water table at the monitoring well (KMOE, 2011). From here, it was assumed that there might be residual TCE in the unsaturated zone due to the increase in TCE concentration as water table rises.

Table 2-1. Values of TCE Concentration and water table at KDPW-2

Well ID	Date	Water level (m, a.s.l)	TCE concentration (mg/L)
	2010.11	125.80	3.41
	2011.02	123.20	3.81
	2011.05	121.90	2.56
	2011.08	127.10	3.11
KDPW-2	2011.11	124.10	2.71
	2012.02	122.80	3.11
	2012.05	122.30	3.62
	2012.08	123.20	2.01
	2012.11	124.20	2.27

2.3 Monitoring Wells

There were 51 monitoring wells in 2009 for conducting various researches on groundwater. Then, 60 more wells were added in addition to the previously located 11 wells of industrial and living usage in November, 2010 for the monitoring groundwater-quality purpose. After 6 more monitoring wells were added for the same purpose in 2011, 10 more wells were also added for the DNAPLs monitoring, the hydraulic fracturing test, and the tracer test, respectively (KMOE, 2011). Therefore, there are 96 monitoring wells at WIC as of December, 2011. Among them the monitoring well KDPW-2, located in the Road Administrative Office (RAO) of Gangwon Province, was used in this experiment (Figure 2-2). Since the well KDWP-2 was screened entirely from 4.5 m, the gas monitoring near water table of average 13 m could be conducted (Figure 2-3).

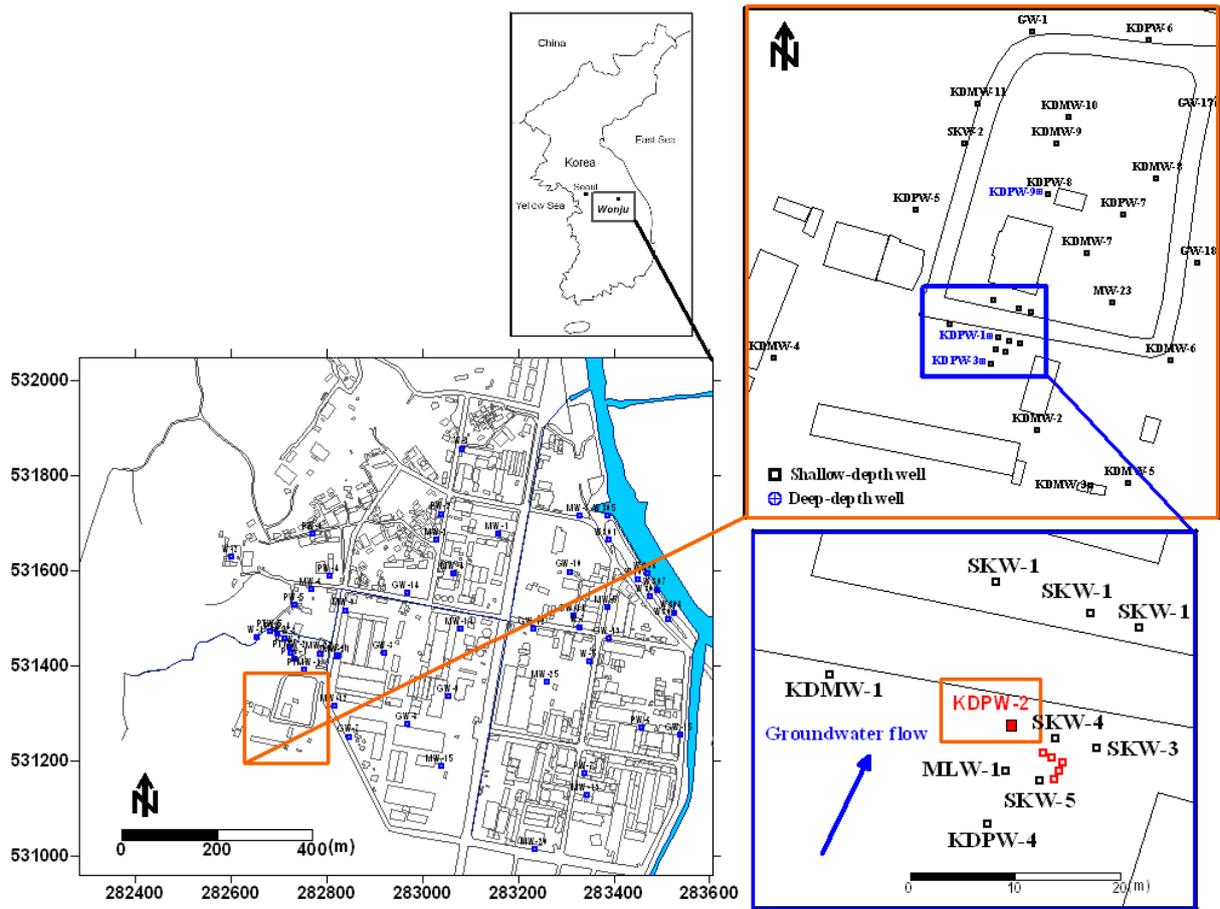


Figure 2-2. Map of all monitoring wells and the study well, KDPW-2.

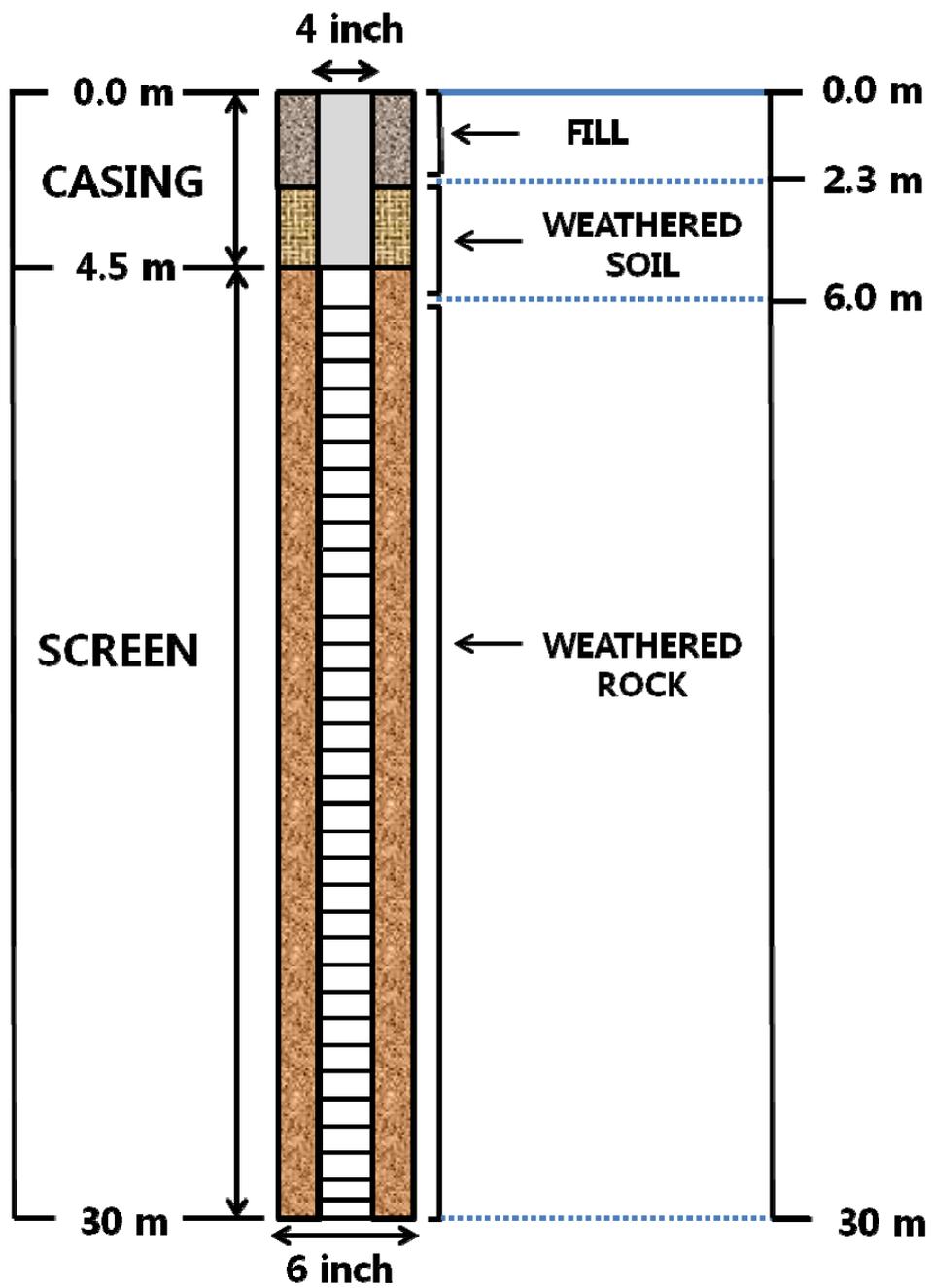


Figure 2-3. The drill log of KDPW-2.

3. Materials and Methods

3.1 Materials

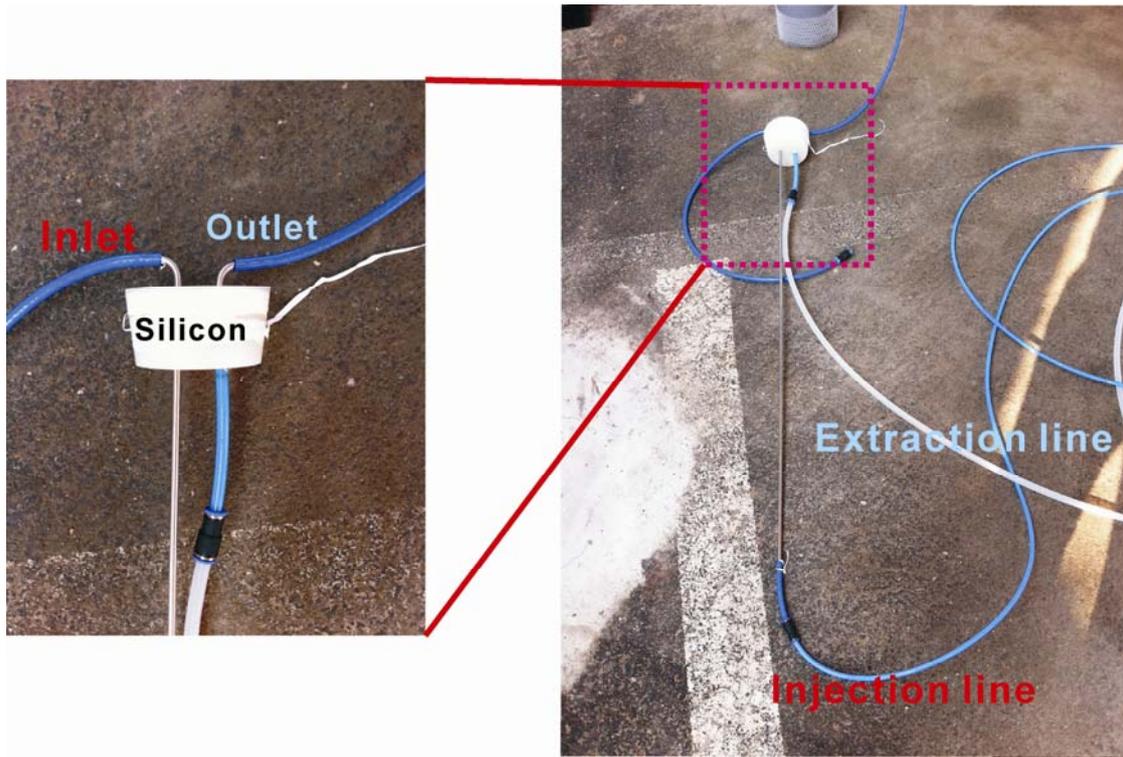
To capture gas samples from the wells, a lung sampler, two air pumps, 1L Tedlar bags (gas bags), N₂ gas, a single packer for the case-1 experiment, two different types of specially designed caps for case-1 and case-2 experiments, and a depth-discrete valve for the case-2 experiment were used. Once the gas samples were collected, a Solid Phase MicroExtraction (SPME) fiber (MW 75 μ m) and the Gas Chromatography (GC) were used for analysis in the laboratory. Meanwhile, N₂ gas was used for purging gas in the well for cleaning up inside the well, because it has relatively same molecular weight as air.

The specially designed cap for the 1st case was made of silicon body and two 0.64 cm stainless tubes. The top part of the body, which has the wider diameter compare to the bottom part, matched with the diameter of the well to be investigated. Meanwhile, the silicon body had a little bit of inclination to fit in the well tightly. For the two stainless tubes, they were bent at the top and straight at the bottom part due to the depth of well case above the ground surface. The two stainless tubes had different lengths; the longer one was an inlet tube and the other one was an outlet. The reason for the stainless tubes having different length was to collect gas from bottom to upper area of the wells. The lengths of the blue-polyethylene tubes were based on the water table level of the wells at each field investigation. The cap for the 2nd case was same as described above except that it had four stainless tubes (Figure 3-1).

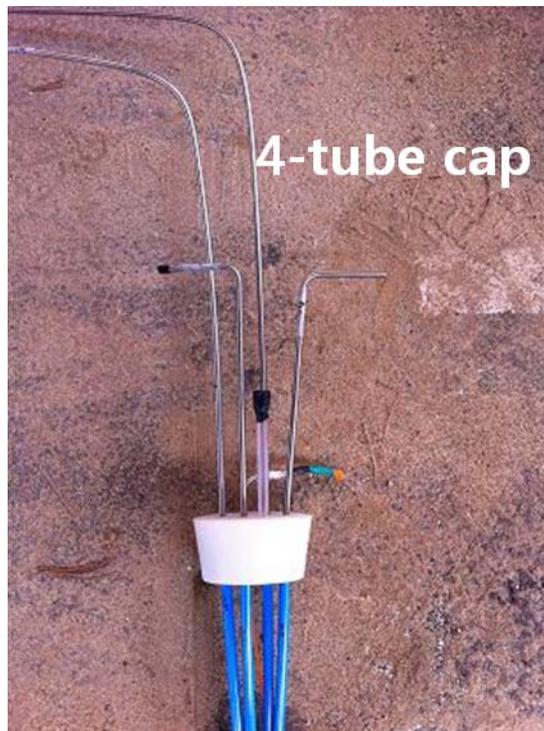
Only in case-1 test, a single packer was placed about 1 m above the water table for blocking volatile organic compounds of groundwater in the well. Once gas in the well was ready to capture, a lung sampler and 1L Tedlar bags were used (Figure 3-2). The Tedlar bag, also commonly called as the gas bag, had a valve to close and lock the sample in the bag for up to two weeks long. Each gas bag was connected with the outlet tube and then placed in the

lung sampler. Once the lung sampler was on, the inside of the lung sampler became the vacuum condition and pulled gas from the well into the gas bag. Also, the lung sampler was automatically turned off when the gas bag was fully filled with gas sample. However, a depth-discrete valve was used for the 2nd case experiment; it consisted of two valves, connected to the air sampler and the air pump, for each depth in total of 8 valves. This valve enabled gas sampling at different depth simultaneously in the 2nd case experiment (Figure 3-3).

For analyzing gas samples, Shimadzu gas chromatography (GC) – 17A, located at the Sejeong campus of Korea University was used. The advantage of using GC as opposed to liquid chromatography (LC) is that GC provides four to five orders of magnitude greater sensitivity than LC. Meanwhile, a SPME fiber was used to transfer gas from the gas bag to the injector of GC. For using GC as an analytical technique, the headspace method, a technique where the vapors in the gas above, and in equilibrium with a solid or liquid is sampled, as opposed to sampling, solely, the solid or the liquid themselves, is mostly well-known. However, the headspace method requiring extraction procedures and equipments were replaced with a SPME fiber method in this experiment. The principle of SPME fiber is that once the fiber was in contact with the sample, the compounds in the sample will move and adsorbed to the fiber (Figure 3-4). Then, the compounds will be desorbed inside of GC due to high temperature of GC injector and analyzed. The advantage of using SPME fiber is that the fast and simple extraction is possible without any specific solvents needed. Also, the samples can be in either phase of liquid or gas. Therefore, a SPME fiber and GC were used for gas analysis in this experiment.



(a) A description of a 2-tube cap's each part

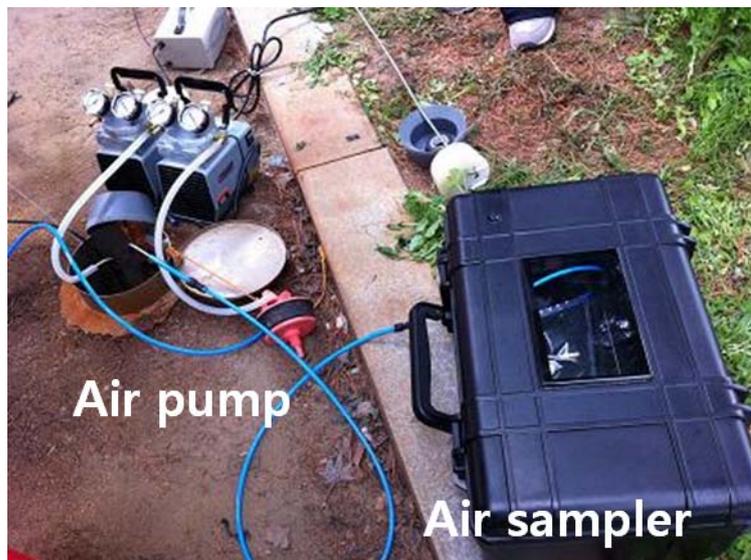


(b) A cap for case-2 with 4 tubes

Figure 3-1. Different types of the caps in (a) case -1 and (b) case -2.

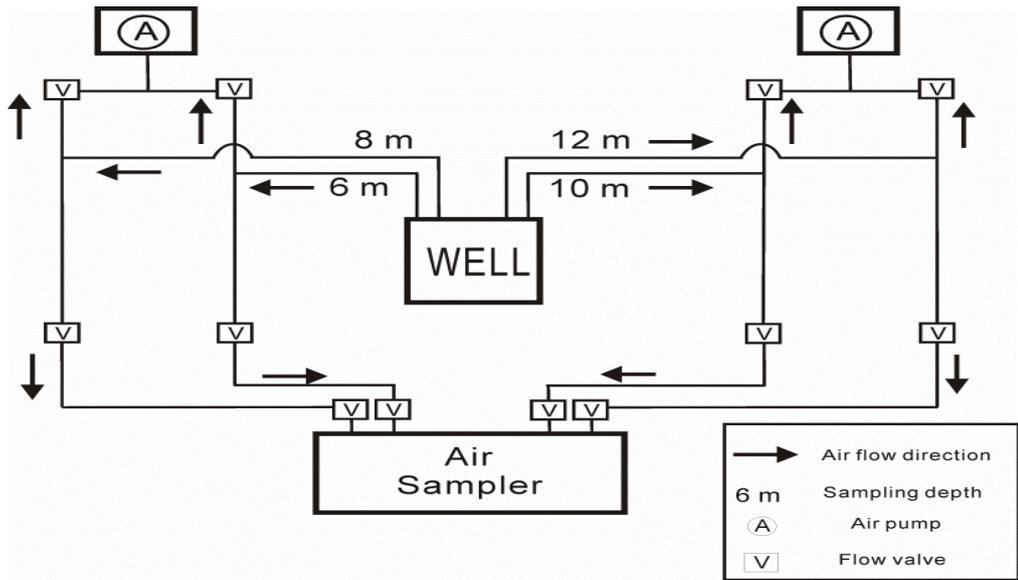


(a) A packer



(b) An air pump and an air sampler

Figure 3-2. Experiment settings (a) a packer (b) an air pump and an air sampler.



(a) A scheme for depth-discrete valve



(b) A gas sampling valve in the experiment

Figure 3-3. The depth-discrete valve in (a) a scheme and in (b) the experiment.

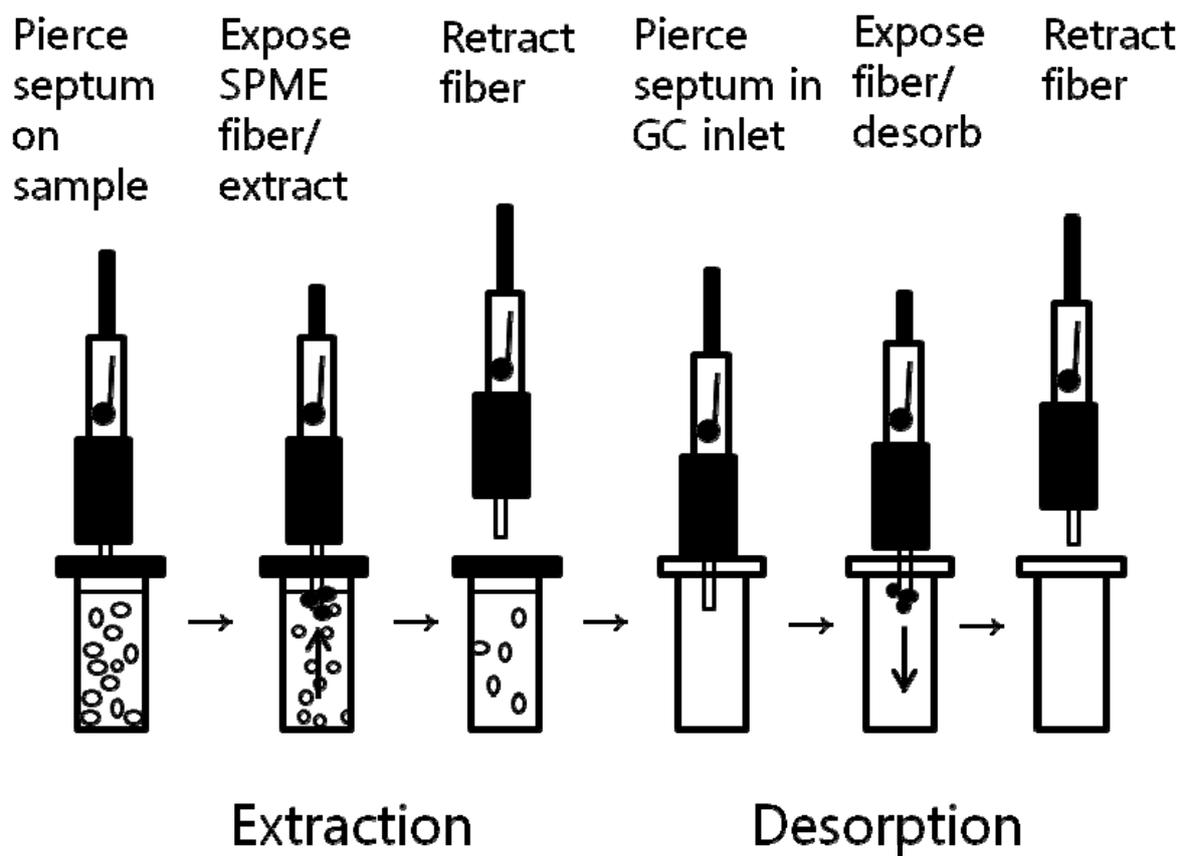


Figure 3-4. A process of SPME Fiber (Modified from Ormsby, 2005).

3.2 Methods

Since this experiment is to find the residual TCE area in the unsaturated zone, the well was chosen based on its locations and the previous researches on TCE concentration and the rainfall effect. In addition, several pilot tests were conducted at several different wells to find out the most effective setup and the well for the experiment. After all, the well named KDPW-2 was chosen for this experiment based on its high TCE concentration, 3.8 mg/L at its highest, and water table depth (Table 3-1).

This whole experiment consists of two parts: (1) field test (gas sampling) (2) lab test (analysis on TCE concentration) (Figure 3-5). Then, the field test is differentiated into case-1 and case-2 based on the experimental settings and the purpose; the case -1 experiment is to see the existence of dissolved TCE gas in water by placing a packer above groundwater in the well and the case-2 experiment is to find out the location of residual TCE contaminants by sampling gas in depth-discrete way. Overall, two different experiments were to find the location of residual DNAPLs.

Table 3-1. Summary of sampling events

Parameter	
Number of wells	1
Well ID	KDPW-2
Number of sampling events	6
Case-1	May 1 st – packer
at 6, 10 m depth	May, 7 th – no packer
Date	----- May 21 st – no packer
Case-2	May 29 th - packer
at 6, 8, 10, 12 m depth	September 4 th – no packer
	November 5 th – no packer

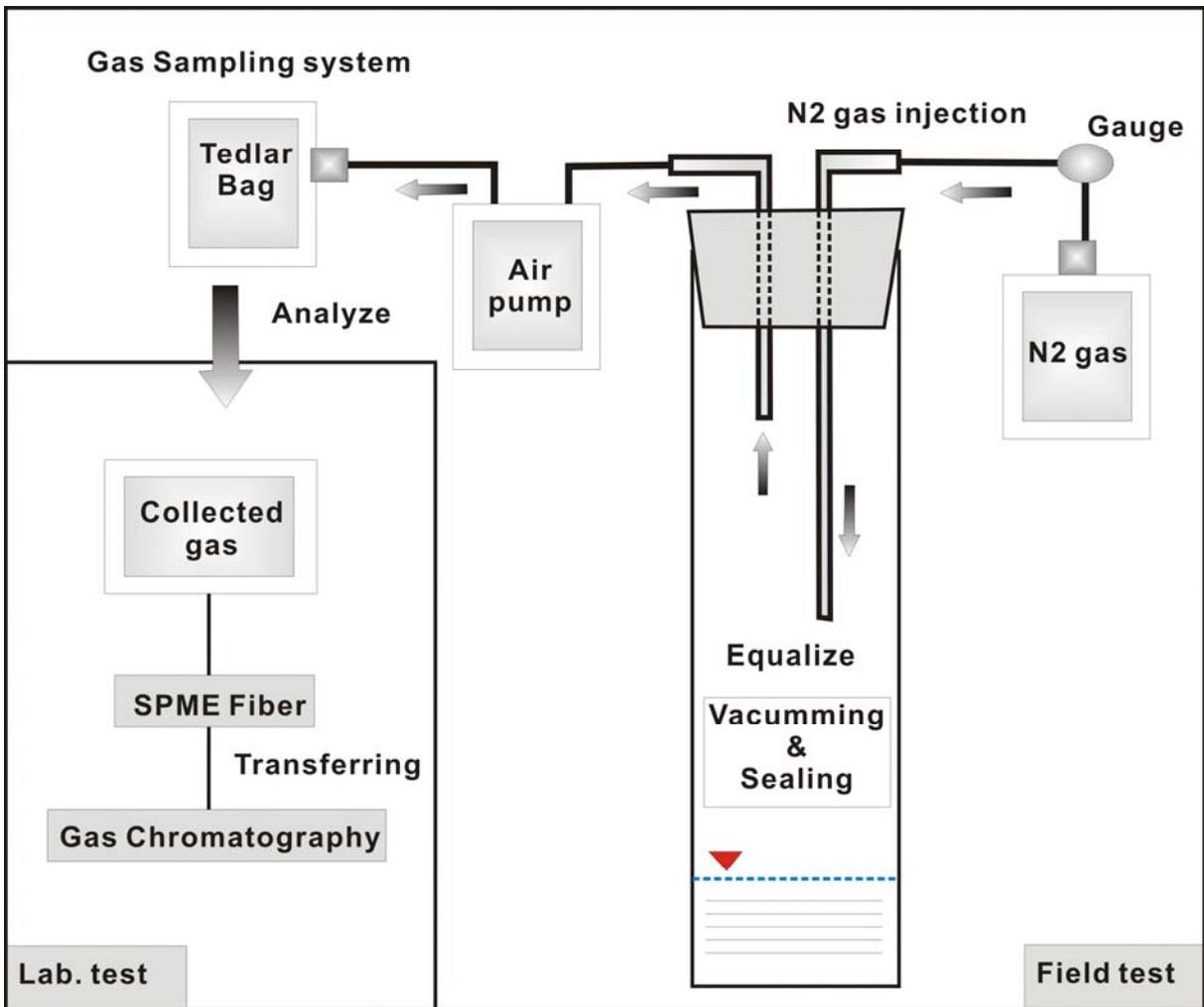


Figure 3-5. Total experiment scheme.

3.2.1 Gas Sampling

The procedure commonly carried by each experiment is following; first, the depth of water table was measure to determine where the injection and extraction tubes to be placed inside. Then, the well was closed with the custom made cap and tightly sealed with the Teflon film around the cap. The purging process using N₂ gas was done for two purposes; (1) excluding the possible contact between gas in the well and the outside air (2) flushing out existing gas in the well. The amount of N₂ gas to be injected was calculated based on the volume of headspace using following equation:

$$\text{headspace volume} = \pi * r^2 * h \quad (\text{Eq.4-1})$$

Where r is the radius of the well and h is the height from the top of the well to the water table.

Once the volume was calculated, it was converted to the amount of gas. For example, 9.45 L of N₂ gas was flushed for a minute in the well KDPW-2 having 0.095 m³ as a headspace volume (Figure 3.6). While N₂ gas was injected, the outlet tube of the cap remained open. After a minute, both inlet and outlet tubes were tightly closed with Teflon film and the tape for a certain period of time. While waiting, a 1 L gas bag was placed in the lung sampler. After a certain time has passed, only the outlet tube of the cap was opened and connected to the inlet of the lung sampler right away. Then, the lung sampler was on to transfer gas from the well to the gas bag. Once the bag was full of gas, the lung sampler was automatically off. The same procedure has done repeatedly with time variation (Figure 3-7). While the experiment was going on for a few days, two air pumps, connected to the inlet and outlet tube, were remained on with average rate of 50 L/min.

Case-1

The experiments of case-1 were conducted each on the 1st and the 7th of May with the

same procedure except whether packer was used or not. As the water table was at 12 m depth, the two inlet tubes were placed at 6 and 10 m inside the well. The difference between two experiments is that on May 1st, the packer was placed about 50 cm above the water table whereas there was no packer during the gas sampling on May 7th. Each experiment has the same sampling time-lap and was conducted for a day.

Case-2

The three experiments of case-2 were conducted each on 21st of May, 4th of September, and 5th of November with the same procedure carried as in case-1 experiments except there was no packer used at all. Based on the Case-1 tests and the depth of water table, the lengths of the tubes were originally chosen as 6 m, 8 m, 10 m, and 12 m. However, the tube at 12 m was shortened by 1 m for the 2nd and 3rd test due to rain during each experiment. For this case, each experiment was conducted for more than a day; about two days for the 1st and the 2nd test, and about three days for the last test on 5th of November. Also, the time-lap for these three experiments was same for each other.

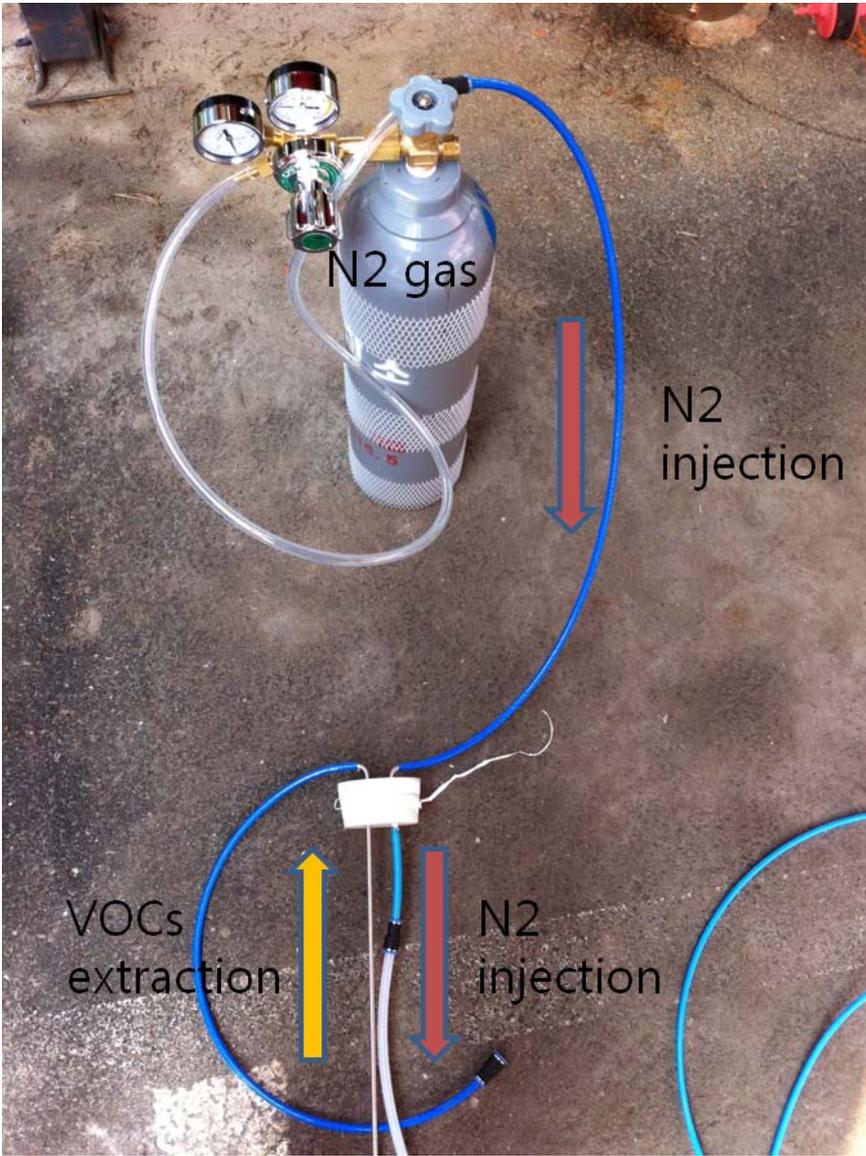
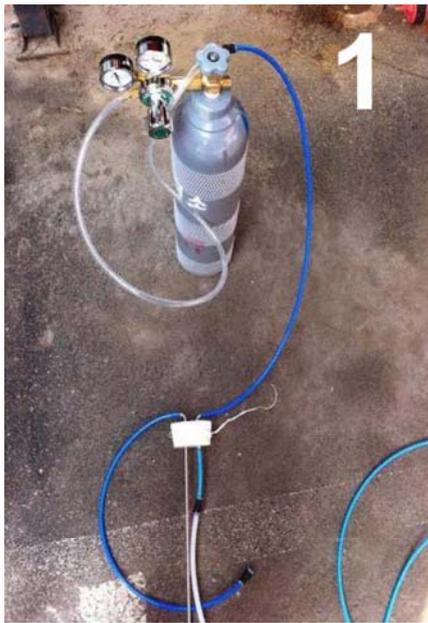


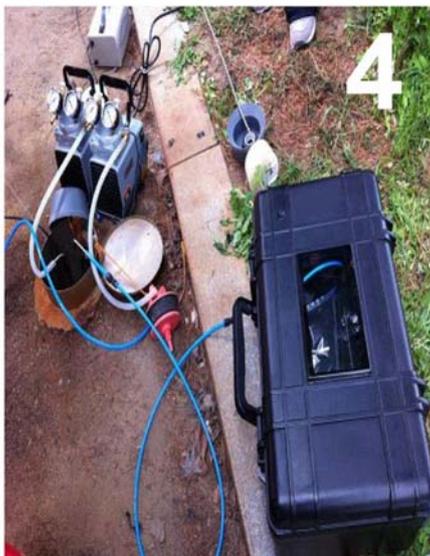
Figure 3-6. N₂ injection process.



N₂ gas Purging



Valve Setting



Gas Sampling



Packing

Figure 3-7. Field test process.

3.2.2 Analysis of TCE Concentration

The lab test, the 2nd part of the whole experiment, is analyzing gas samples using the SPME fiber and the gas chromatography (GC). First, the SPME fiber was injected to the gas bag through the septum on the gas bag. Then, the fiber was out from the fiber support so that the compounds can be absorbed onto the fiber. After 7 minutes, the fiber was placed back in the fiber support and the SPME fiber was out from the gas bag. Once GC was ready to run, the SPME fiber was placed on the injector of the GC for about 80 seconds. As absorbed compounds on SPME fiber was desorbed inside the GC, the analysis went on. After GC run has done, the area of peak values were recorded and analyzed by the calibration curve, obtained by the experiment with known TCE concentration. The coefficient of determination, represented as R^2 , of the calibration curve was 0.9959, which meant the coefficient of standard curve would predict the future outcomes well.

3.2.3 Calculation of Radius of Influence (ROI)

Based on recharge drawdown of air from the atmosphere, the Hantush-Jacob equation for leaky confined aquifer was used to calculate the radius of influence (ROI), determined as “the distance at which a sufficient level of vacuum will be present to induce airflow” (Suthersan, 1997) (Figure 3-8). It has been defined differently as 0.1 in. H₂O, 1.0 in. H₂O, or 10% of the applied vacuum of the extraction well. However, the ROI in this experiment was defined as 1.0 inch (0.0254 m) of H₂O (Eq. 3-2).

$$\Delta P = \frac{Q_v \mu}{4 \pi b k_a} W\left(u, \frac{r}{B}\right) \quad (\text{Eq. 3-2})$$

Where ΔP is pressure-drawdown difference in m, Q_v is flow rate in m, μ is gas viscosity in kg/m s, r is distance from center of well in m, B is a leakage factor, b is thickness of unsaturated zone in m, k_a is air permeability m², $W(u, r/B)$ is the leaky well function. Then, the function $W(u, r/B)$ was read from the values of the Leaky Confined Aquifer Function to obtain the r , the radius of influence (Batu, 1998).

Before applying to the equation, a graph of $W(u)$ vs. $1/u$ and a distance-drawdown data in log-log scale were matched to get a leakage factor, B and transmissivity, T , in m²/sec. Since there was no pressure drawdown experiments were conducted at KDPW-2, the data obtained from BH wells, 4.2 m apart from KDPW-2, was used for the distance-drawdown graph (Figure 3-9). Total of eight pressure-drawdown tests were conducted at this area and the average values of B and T were used to get the value of r/B (Table 3-2). Once the value of r/B was determined from the table of Hantush-Jacob leaky confined aquifer, it was multiplied to the leakage factor to calculate the ROI (Batu, 1998).

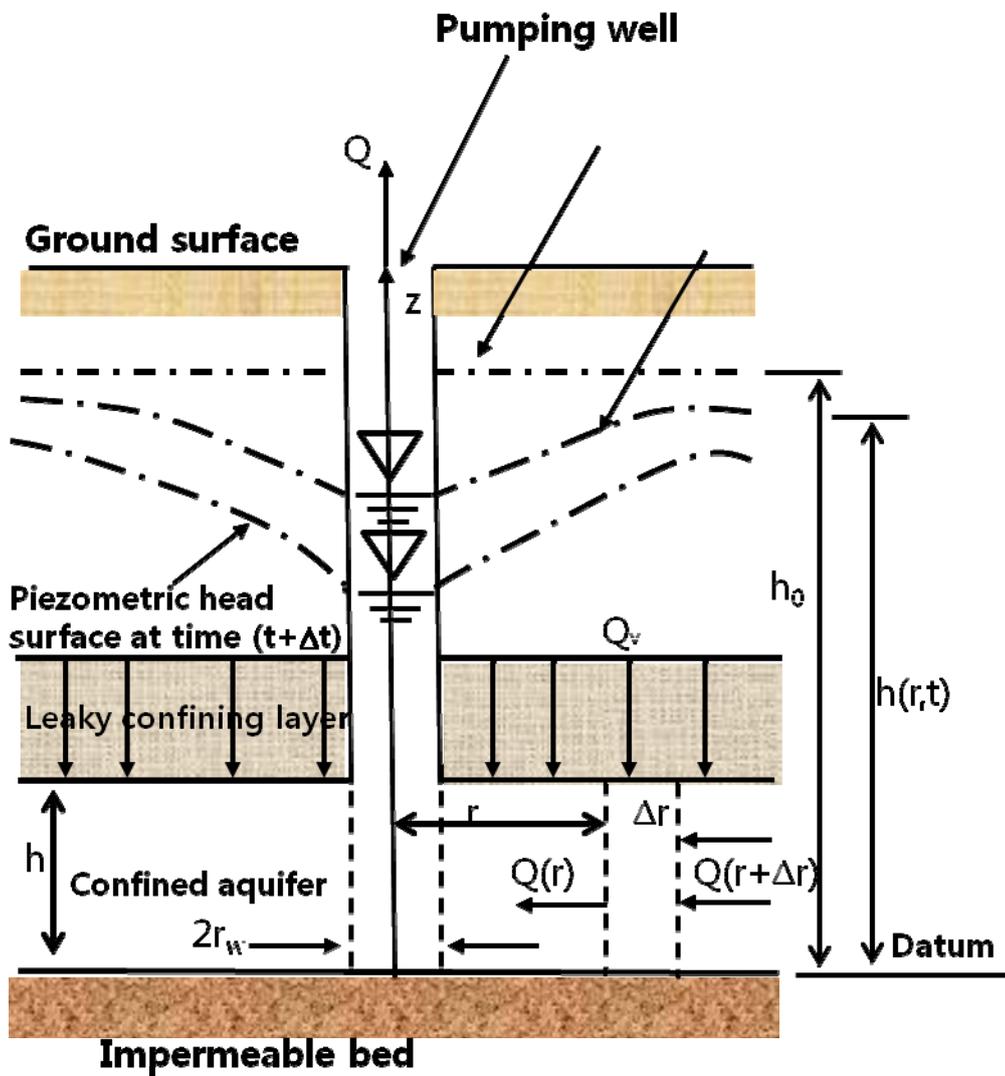


Figure 3-8. A scheme of a leaky confined aquifer (Modified from Batu, 1998).

Table 3-2. Information of pressure drawdown test and values from graph matching

Test No.	Monitoring Well ID	Extraction Well ID	Distance, r (m)	Leakage factor, B	Drawdown, S (m)	Time, t (sec)	W (r, r/B)	r/B
1	BH-1	BH-2	1	0.67	70	130	0.4	9
2	BH-1	BH-4	1	1.25	30	50	1.0	7
3	BH-2	BH-1	1	0.67	70	130	0.4	9
4	BH-2	BH-3	1	1.00	110	100	0.9	9
5	BH-3	BH-2	1	0.67	70	130	0.4	9
6	BH-4	BH-1	1	1.25	30	50	1.0	7
7	BH-4	BH-5	1	0.67	70	130	0.4	9
8	BH-5	BH-4	1	1.25	30	50	1.0	7

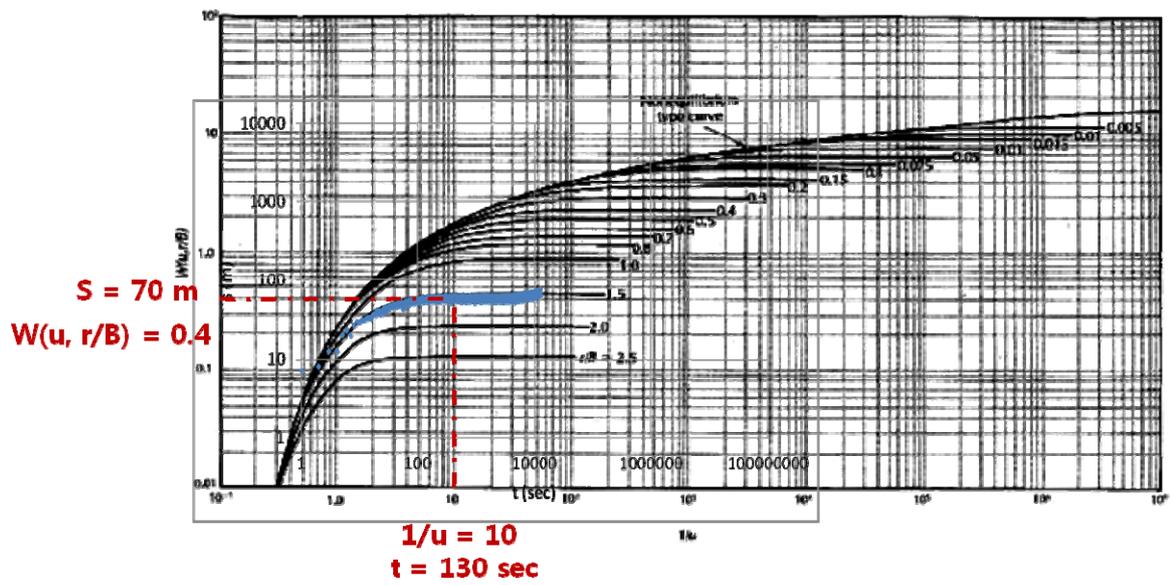


Figure 3-9. A matched curve of a distance-drawdown graph of test no. 1 and type curve for Hantush-Jacob leaky confined aquifer.

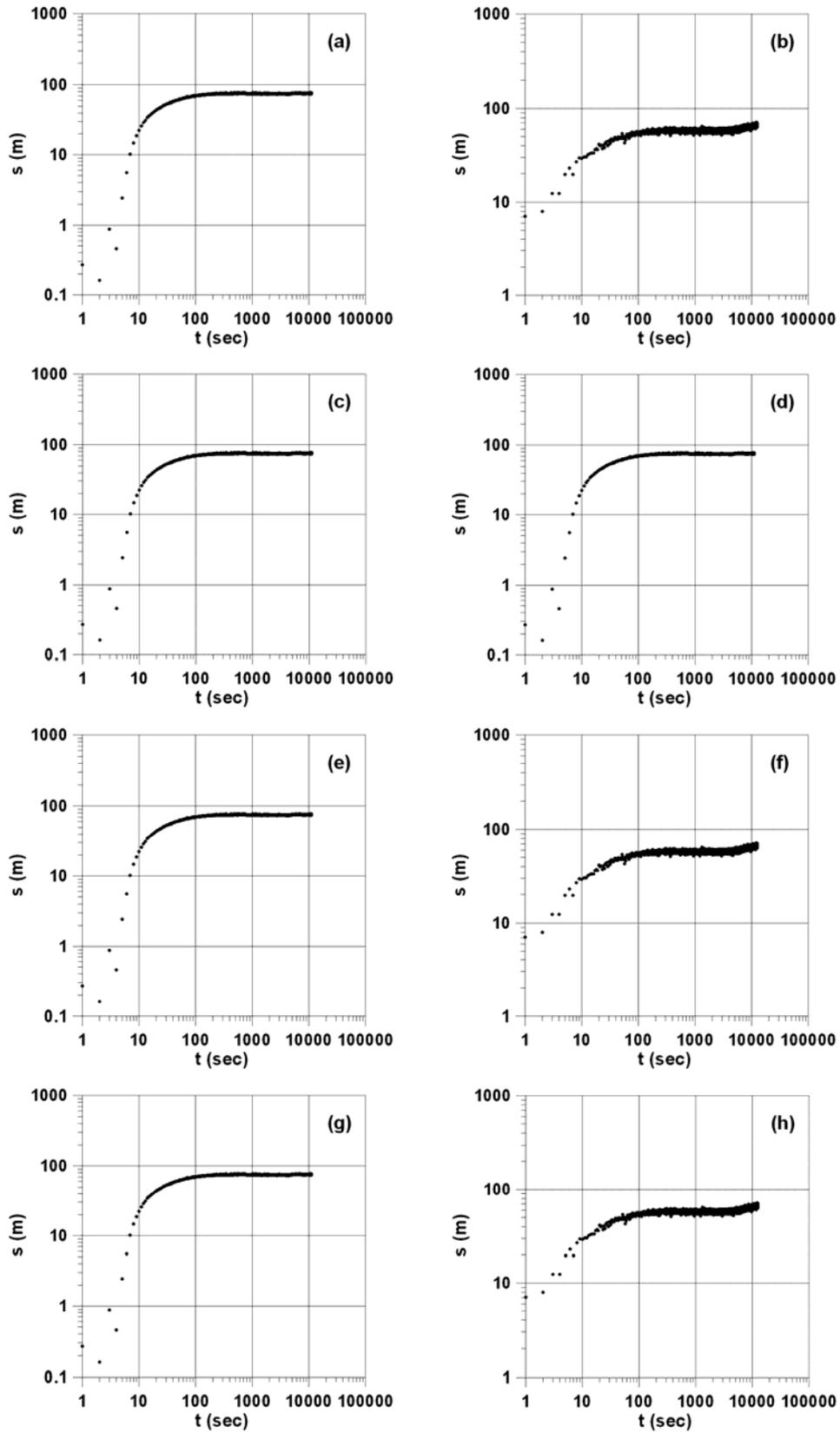


Figure 3-10. Eight pressure drawdown graphs of each test (a) test no.1, (b) 2, (c) 3, (d) 4, (e)

5, (f) 6, (g) 7, (h) 8.

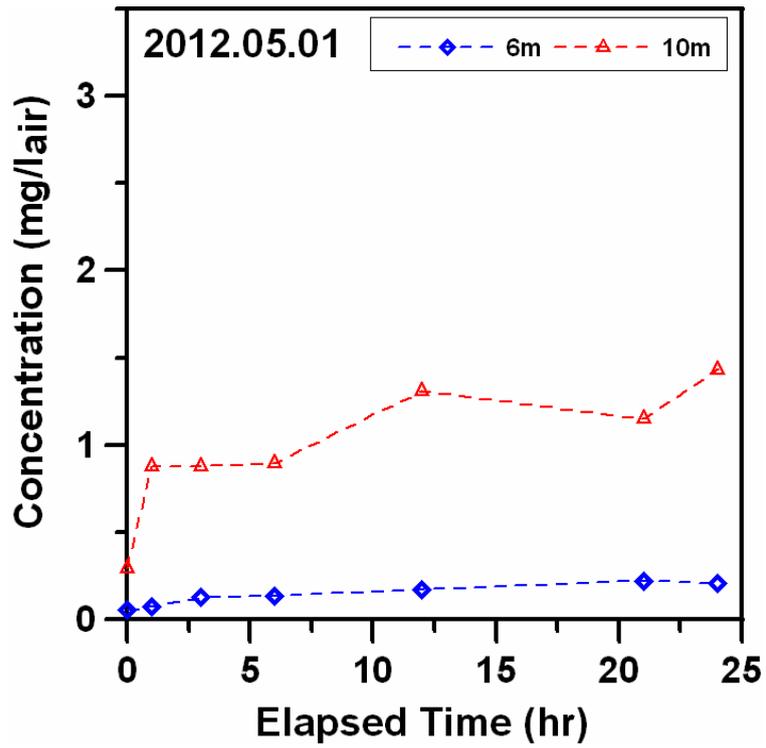
4. Results and Discussion

4.1 TCE Gas Concentration

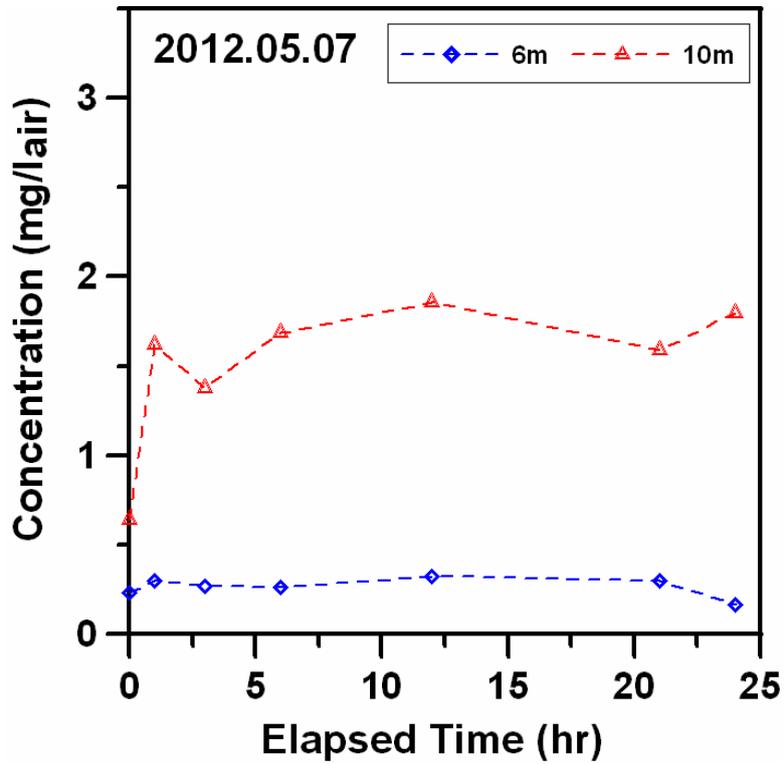
In this experiment, the gas monitoring method was examined in two cases at the monitoring well KDPW-2, which has shown the highest TCE concentration in water samples. The first case was to verify practicality of the gas sampling method at this site and to compare TCE gas concentration with the packer blocking vaporized TCE gas from water. Also, the second case was to estimate the location of residual DNAPL sources in the unsaturated zone by monitoring at different depths. The results for previously conducted experiments as pilot tests were not included in this paper, since the data was to show the probability of this experiment. Therefore, only the results for the case-1 and case-2 were mentioned below.

Case-1

The conditions such as atmosphere temperature, the injection tubes' depth, types of equipments, and pumping rates, were same in the experiments conducted on May, 1st and 7th. The results showed that the TCE concentration distributions in the same condition were different in the usage of packer. It was observed that there was a higher TCE concentration values at 10 m depth than it at 6 m. Moreover, irrelevant to the depths, there was a higher TCE concentration values when there was no packer above the water table than packer was placed. Especially, there was a significant concentration difference at 10 m whether the existence of packer. The other notification was that at 10 m depth, there was a big increase from the initial concentration after the purging whereas no such happening at 6 m (Figure 4-1).



(a) Packer



(b) No Packer

Figure 4-1. Case-1 Results (a) packer (b) no packer.

From these results, two assumptions could be made: the existence of residual TCE gas and the influence of initial purging on the movement of VOCs. The packer effectively blocked vaporized VOCs from groundwater, so it made possible to collect vaporized TCE gas only from the unsaturated zone. This was shown by the difference in TCE gas distribution based on existence of the packer. The maximum TCE concentration at 10 m with the packer was 1.43 mg/L_{air}, where as it without the packer was 1.86 mg/L_{air}. In other words, sampled TCE gas with packer was from the residual DNAPL sources of outside the well. This meant the existence of residual TCE gas in the unsaturated zone. Also, it could be estimated that the residual DNAPL sources were located near the sampling depth at 10 m rather than 6 m. This assumption could be proved by the higher TCE concentration at 10 m than it at 6 m.

The other assumption made by initial purging was shown by the relatively high initial TCE concentration jump between the 1st and 2nd sampling values. The concentration value at elapsed time 0 meant the initial TCE gas concentration before start the experiment and the next value meant the TCE gas concentration after N₂ purging. In the experiment on May, 1st, the concentration jumped from 0.56 mg/L_{air} to 0.87 mg/L_{air} and on May, 7th, it jumped from 0.68 mg/L_{air} to 1.61 mg/L_{air}. Since the injected N₂ gas broke the equilibrium among other gases in the unsaturated zone, the molecular velocities of the residual DNAPL source would increase due to the pressure. Therefore, the more TCE gas was captured right after the N₂ injection.

Overall, the results of case-1 showed that there are the residual DANPL sources in the unsaturated zone, especially around 10 m depth down from the ground. Also, the higher concentration with packer proved that the packer well blocked the vaporized TCE gas from groundwater. Furthermore, it could be concluded that interference between vaporized TCE from groundwater and from the residual DNAPL sources were minimized by using the packer.

Therefore, the packer should be used for source identification using gas sampling method.

However, this suggestion on the sources' locations was based on the results of case-1, limited to a short period of sampling time as of 24 hours. Therefore, this suggestion was examined more closely in case-2 to estimate the location of sources more accurately in longer sampling periods at the four depths.

Case-2

Even though the rough location of residual DNAPL source was suggested as near 10 m from the case-1, it was not cleared whether the source is in the zone above 10 m up to 6 m or below 10 m until the water table. Therefore, two more sampling points were added, 8 m and 12 m, to examine the location of residual DNAPL more closely in case-2. Also, the total sampling period was extended up to 72 hours since the case-1 data was limited to interpret further due to the short period of sampling time. Total of four experiments were done in case-2 settings where three experiments without packer were those on May, 21st, September, 4th, and November, 5th.

The 1st experiment conducted on May, 21st showed the similar TCE concentration pattern, jump after initial N₂ purging, as it of case-1. Moreover, the higher concentration was observed as the deeper sampling depth. At the time when 5 hours after the initial purging, the highest concentration was observed at 12 m, and 10 m, 8 m, 6 m as the lowest of all. From this result, it was suggested that the residual DNAPL sources are located at between 10 m and 12 m, which means that the residual sources are near the water table. This well supported the observations made in the previous studies about having the highest concentration at the water level and the increase in TCE concentration as the water table increases due to rainfall (Yang et al., 2012).

The new notification in this experiment was that there was a big concentration jump at all 4 points after 42 hours of sampling unlike case-1, which had no such incident due to short sampling period (Figure 4-2). This incident was examined closely in the 2nd experiment with packer.

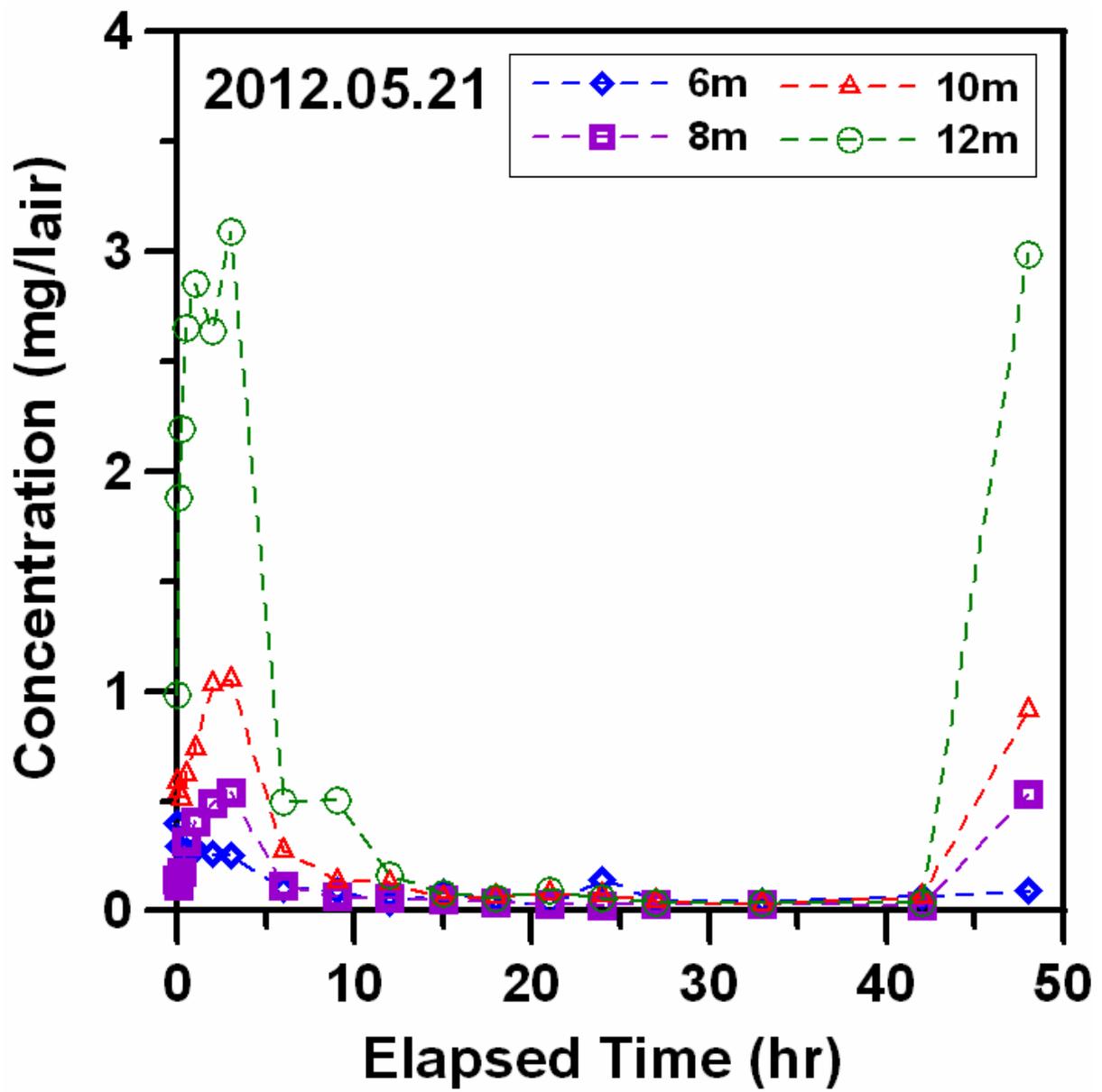


Figure 4-2. 1st result of Case-2 (No Packer).

The 2nd experiment with the same condition except that the packer was placed above the water table was done on May, 29th. The data showed the similar pattern of concentration jump after initial N₂ purging, order of concentration values, and big concentration jump at all 4 points after 42 hours of sampling. Since there was packer, the highest TCE concentration of the 2nd experiment was 2.27 mg/L_{air}, lower than it of the 1st experiment having 3.09 mg/L_{air}. This result well matched with it of case-1, which showed the existence of residual DNAPL sources in the unsaturated zone.

Moreover, the results showed the great increase in TCE concentration after 42 hours of sampling period in both 1st and 2nd experiments in case-2. This was assumed due to the different pore sizes near the well in the unsaturated zone. It suggested that the pore size of nearer zone is bigger than it of far zone in the unsaturated zone. If the pore size is bigger, then it would be easier for free phase DNAPL source to be captured in short period of time. In the other words, it would take more time for free phase DNAPL source in the small pores to be captured. Since the rate of air pump remained same, the time related to capturing time could be based on the pore size. Therefore, such concentration pattern suggested that the nearer zone of the well has of pores with the bigger size compare to pores in the far zone.

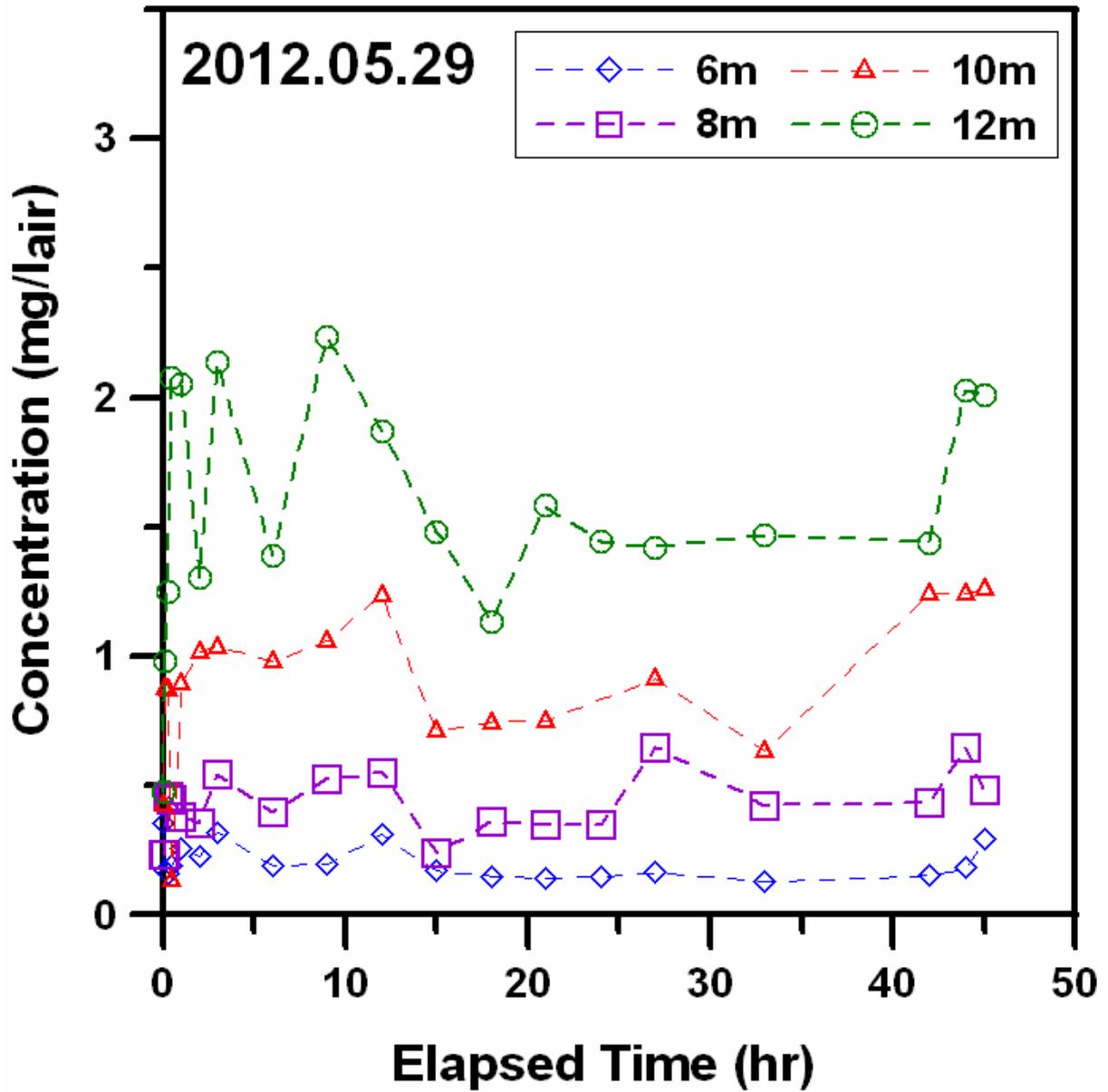


Figure 4-3. 2nd result of Case-2 (Packer).

The 3rd experiment with the same experiment settings as the 1st one was conducted on September, 4th to see the different distribution patterns in the middle of the sampling period of former two experiments. The only difference in experiment – conditions was the weather; there was rain on September, 4th unlike no rain on May, 21st. Because of rain, the water table was raised from 13.8 m in the 1st experiment to 11.6 m. In the previous study on TCE concentration of water, it was increased due to increasing water table by rain (Yang et al., 2012). However, it was expected to be no influence of rain on TCE gas concentration since the residual DNAPL source itself has not gone by rainfall.

In 3rd experiment, the tendency to increase after 42 hours was similar to it of previous experiments. This meant that sampled gas in 3rd experiment was also captured from the nearer residual DNAPL source first, and then was captured from the further source.

However, there was a drop in TCE gas concentration after the initial sampling unlike the increases shown in former two experiments. It could be explained by the time interval between the 1st and the 2nd sampling time. In former two experiments, the time interval between the initial and the next sample was 15 minutes, whereas 1 hour in the 3rd experiment. This suggested that the effect of N₂ purging on VOCs movement, as shown in the result of case-1, happens in the beginning for short period of time, but no impact as time goes. This is due to the properties of gas molecules being in equilibrium as time goes.

Another notification from this data was that the total concentration range was kept in maximum of 1 mg/L_{air}, lower than the 1st experiment of 3.09 mg/L_{air} and the 2nd experiment of 2.27 mg/L_{air} (Figure 4-4). This incident, the decrease in total concentration range, was examined closely in the 4th, the last experiment of this study.

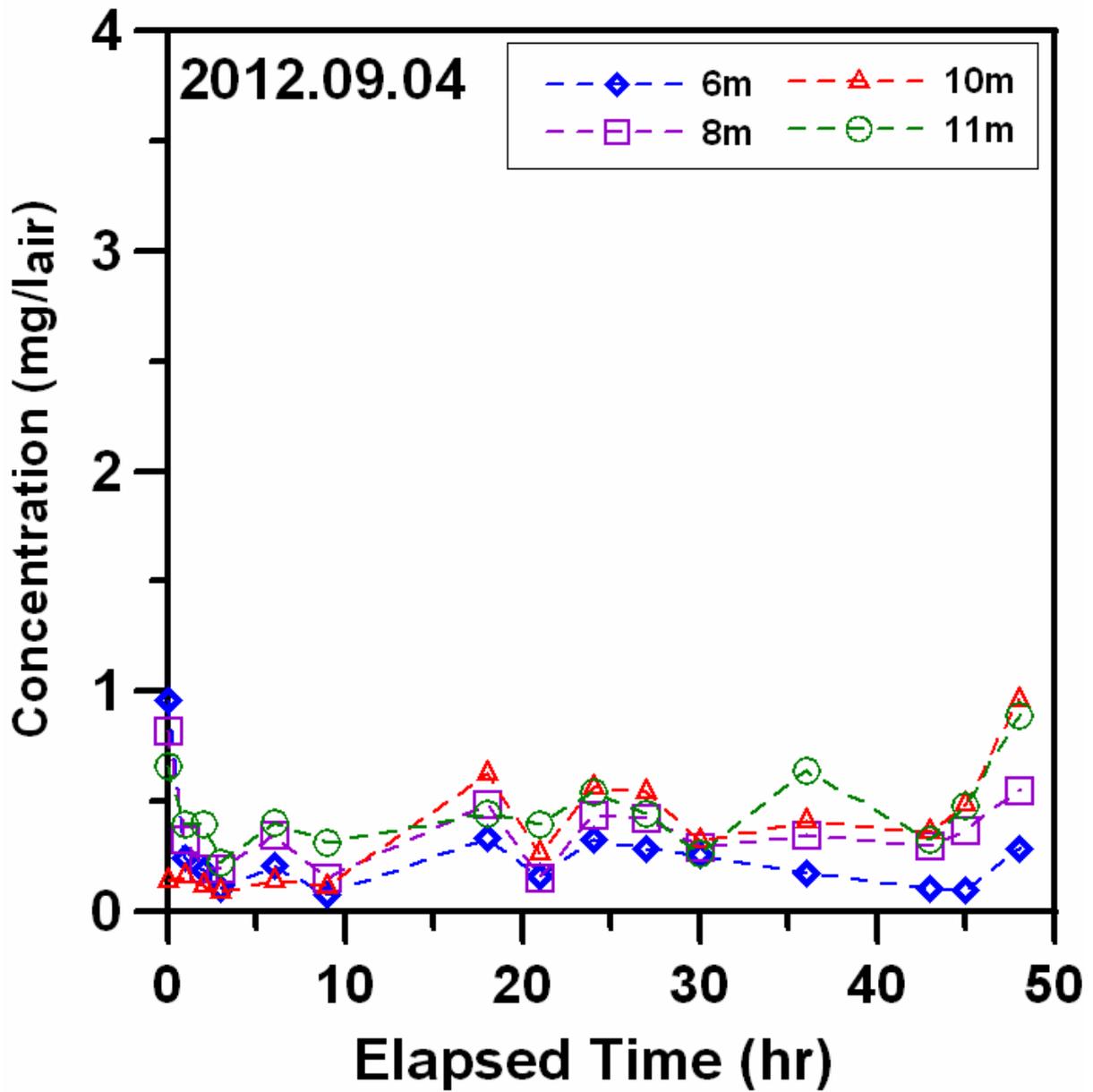


Figure 4-4. 3rd result of Case-2 (No Packer).

The 4th experiment was conducted on November, 5th in the same setting of the 3rd experiment except that the sampling period was 72 hours instead of 48 hours. The 4th experiment was to evaluate the two previously mentioned incidents, the decrease in total concentration-range and the different concentration-pattern in the middle of the sampling time. This data also showed the concentration drop in the beginning similar to the previous result, since the time-gap of 1st and 2nd sampling period were similar to the time-gap of 3rd experiment. Also, there was a decrease in total concentration-range such as maximum of 1 mg/L_{air}, similar to the total concentration-range of the 3rd experiment. These incidents on September and November tests suggested the possibility of fundamental concentration-decrease of the residual DNAPL sources due to repeatedly done gas sampling. Overall, the results of case-2 well proved the existence of the residual DNAPL source in the unsaturated zone by gas sampling. Moreover, the results suggested the estimated vertical location of the residual DNAPL source. However, they could not give an idea of the horizontal location of the residual DNAPL source.

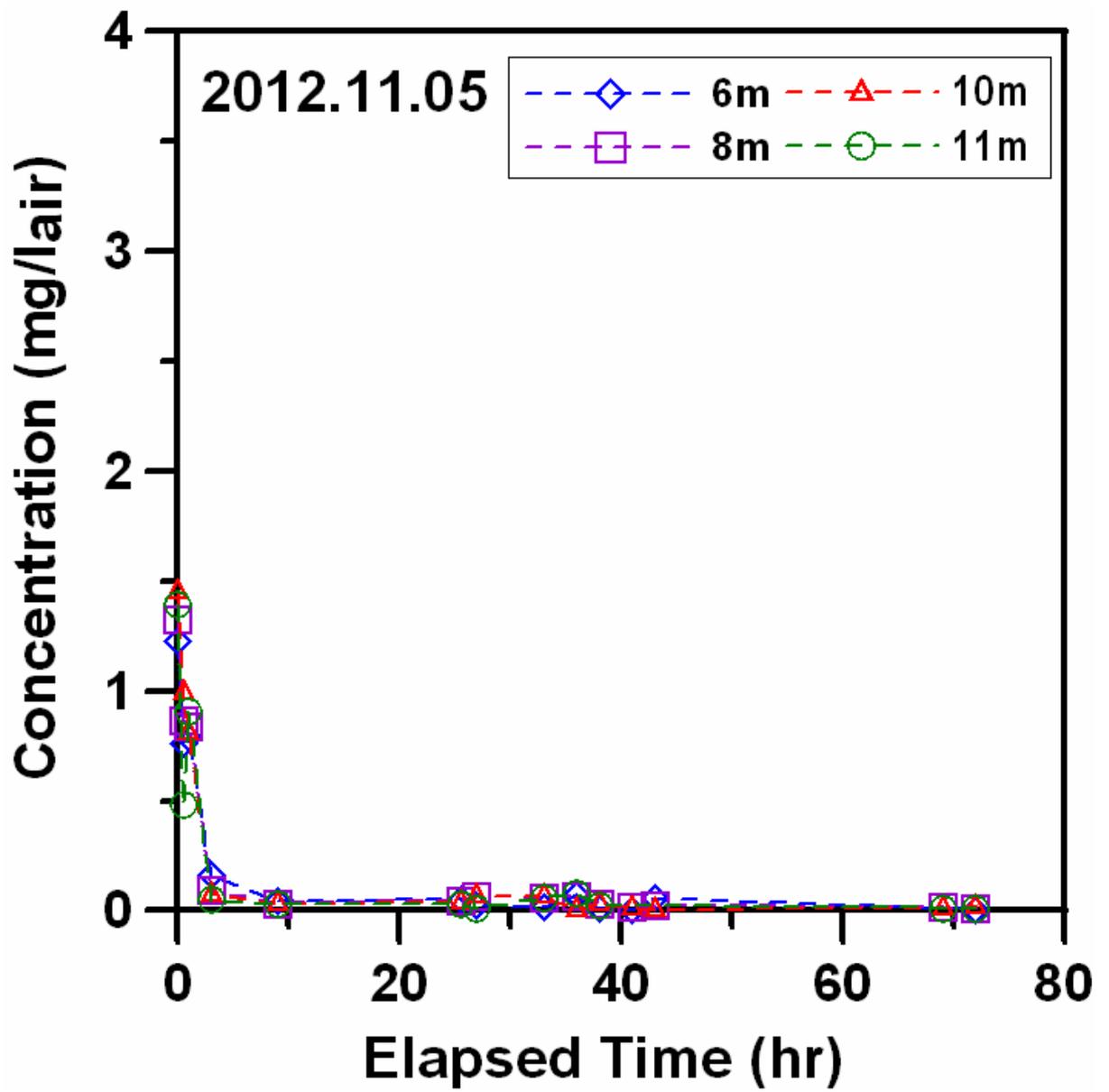


Figure 4-5. 4th result of Case-2 (No Packer).

4.2 Radius of Influence (ROI)

The radius of influence was calculated to estimate the horizontal location of residual DNAPL source by using Hantush's equation for air (Table 4-1). Since this experiment used gas phase TCE, it was converted in the form of head difference in air by adapting Bernoulli's equation. Also, the average values of the leakage factor, B and transmissivity, T were calculated (Table 4-2). With these values, the radius of influence (ROI) was calculated as 7.4 m. Because the well SKW-4 was 7.2 m apart from KDPW-2, the result meant that the sampled gas for this experiment was not solely captured in the unsaturated zone of KDPW-2 (Figure 4-6). With this calculated radius, the horizontal location of residual DNAPL source was estimate and suggested that the smaller pumping rate should be used in order to capture gas only from KDPW-2. Furthermore, this calculated radius of influence could be used for optimizing parameters for a site-specific SVE (Soil Vapor Extraction) method for remediation by giving the initial information of the contaminant sources' locations.

Table 4-1. Values in radius of influence (ROI) calculation

Parameter	Value	Unit
Flow rate, Q_v	7.50×10^{-4}	m^3/sec
Thickness, b	9.00	m
Viscosity, μ_{air} at $20^\circ C$	1.98×10^{-5}	kg/m·sec
Density, ρ_{air} at $20^\circ C$	1.20	kg/m ³
Gravity Constant, g	9.81	m/sec ²

Table 4-2. Values of the leakage factor and transmissivity from pressure-drawdown tests

Test No.	Leakage Factor, B	Transmissivity, T (m²/sec)
1	0.67	3.64 x 10 ⁻⁷
2	1.25	2.09 x 10 ⁻⁶
3	0.67	3.64 x 10 ⁻⁷
4	1.00	4.45 x 10 ⁻⁷
5	0.67	3.64 x 10 ⁻⁷
6	1.25	2.09 x 10 ⁻⁶
7	0.67	3.64 x 10 ⁻⁷
8	1.25	2.09 x 10 ⁻⁶
Average	0.93	1.02 x 10⁻⁶

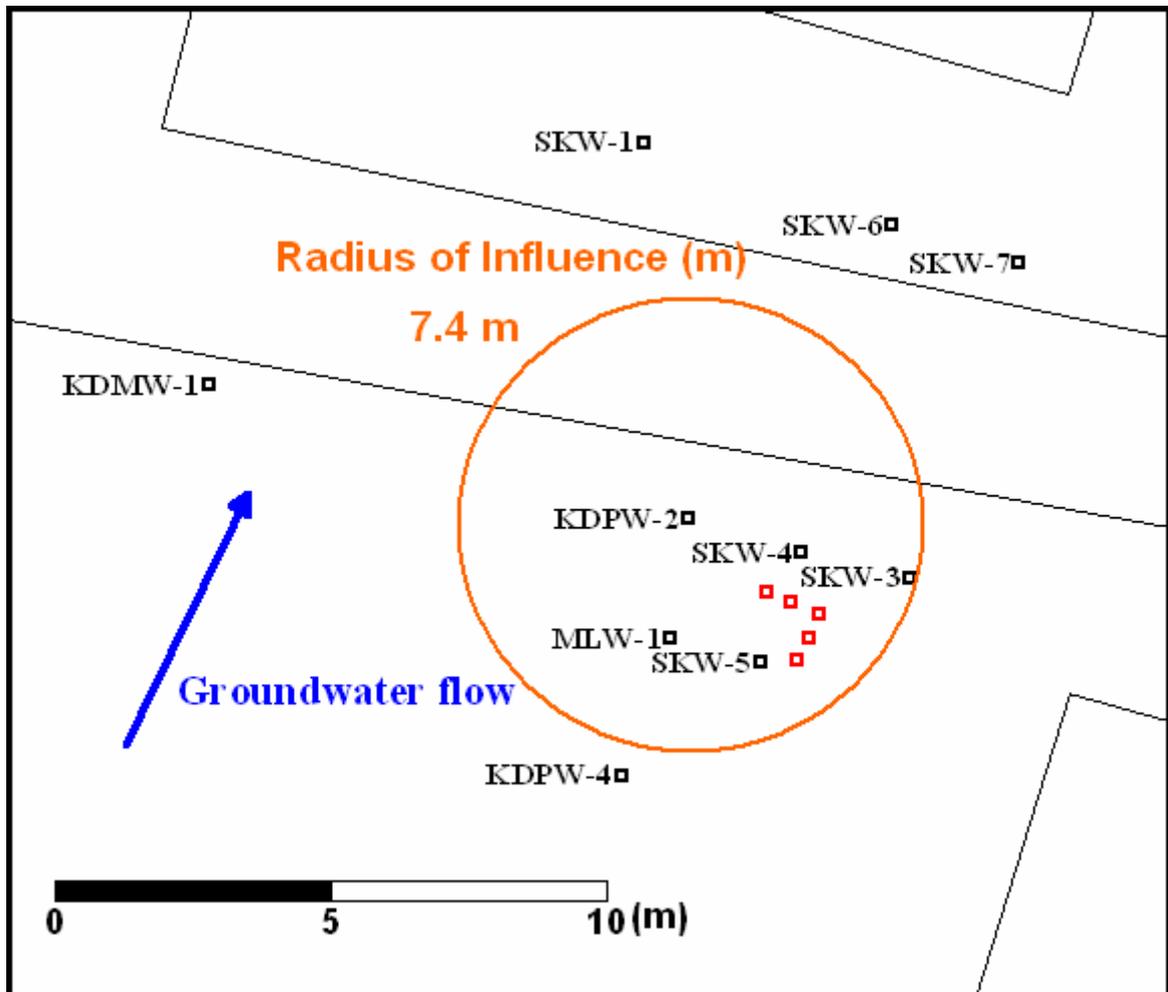


Figure 4-6. Radius of Influence at the experiment site.

5. Summary and Conclusion

For the effective and precise site remediation, it is necessary to spot the locations of contamination sources. Especially, finding the residual DNAPL sources in the unsaturated zone is a key factor since they tend to move downward in the pores and make the complete clean-up of the site hard. In fact, the residual DNAPL source's characteristic as volatile organic compounds could be used to detect the source in the unsaturated zone. Therefore, the experiment to estimate the location of residual contamination sources at Wonju was conducted by sampling gas of residual DNAPL sources. It was done at the monitoring well, KDPW-2, located in the main contamination area.

In case-1 experiment, a packer for blocking vaporized gas from groundwater in the well was used to prove the existence of the residual DNAPL sources. The result of higher TCE gas concentration in the experiment without packer than in the experiment with packer proved that there is the residual DNAPL source around the well in the unsaturated zone. Moreover, the fact that the higher concentration at 10 m depth than at 6 m depth suggested the possible location of the residual source as near 10 m rather than 6 m.

In case-2 experiments, two more depths were added to test the assumption made from the result of case-1. Total of four experiments were conducted in almost same experiment-conditions with a few variations such as the usage of packer, sampling period, and weather. Based on these experiments, these three major results were obtained: the estimated location of the residual DNAPL source in the vertical direction, the possibility of different pore sizes in the unsaturated zone, and the concentration decrease of the actual source due to repeated gas sampling. Firstly, the highest TCE gas concentration in all four experiments appeared at 12 m sampling depth, which suggested that the residual DNAPL source is located at between 10 m and 12 m or near 12 m. Then, the pattern showing the

concentration jump after 42 hours of sampling suggested the possibility of different pore sizes in the unsaturated zone around the well. It jumped from 0.034 mg/L_{air} to 2.99 mg/L_{air} at 12 m in the 1st experiment, from 1.44 mg/L_{air} to 2.03 mg/L_{air} in the 2nd, from 0.33 mg/L_{air} to 0.89 mg/L_{air} in the 3rd, and from 0.01 mg/L_{air} to 0.04 mg/L_{air} in the 4th experiment. Since it took longer time for the gas molecules in the smaller pore size, the concentration jump proved that the pore size near by the well is bigger than the pore size far away from the well. Finally, the pattern of the decrease in total concentration range suggested that the concentration of actual residual source has dropped due to the repeated sampling experiments. The maximum TCE gas concentrations of three experiments with no packer are 3.09, 0.96, and 1.45 mg/L_{air} on May 21st, September 4th, and November 5th, respectively. In addition, the radius of influence was calculated to see the capturing zone of this experiment. The radius was 5.8 m and notified that the captured samples in this experiment were also from the other well, SKW-3.

Based on these field results and calculation, it was assumed that the residual DNAPL sources are in between 10 m and 12 m depth. Also, it showed that the total concentration has decreased as the residual DNAPL sources of nearer location of having radius of 7.4 m have decreased due to the repeated experiments. Overall, this gas sampling method suggested a way to estimate the location of residual DNAPL sources in vertical direction by depth-discrete experiments and in horizontal direction by calculated radius of influence. Therefore, this method will be useful for the sites where the locations of underground sources are unknown to be remediated.

6. Reference

- Adamson D.T., McHugh T.E., Rysz M.W., Landazuri R., Newell C.J., 2009. Laboratory validation study of new vapor-phase-based approach for groundwater monitoring. *Remediation* 20, no.1: 87-106.
- Adamson D.T., McHugh T.E., Rysz M.W., Landazuri R., Newell C.J., 2011. Field investigation of vapor-phase-based groundwater monitoring. *Ground Water Monitoring & Remediation* 32, no. 1: 59-72.
- Aeschbach-Hertig W., Peeters F., Beyerle U., Kipfer R., 1999. Interpretation of dissolved atmospheric noble gases in natural waters. *Water Resources Research*, 35, 2779-2792.
- Baek W., Lee J.Y., 2010. Source apportionment of trichloroethylene in groundwater of the industrial complex in Wonju, Korea: a 15-year distribute and perspective. *Water Environment Journal*, 25, 336–344.
- Chai X., Falabella J.B., Teja A.S., 2005. A relative headspace method for Henry’s constants of volatile organic compounds. *Fluid Phase Equilibria*, 231, 239-245.
- Clement T.P., Kim Y.C., Gautam T.R., Lee K.K., 2004. Experimental and numerical investigation of DNAPL dissolution processes in a laboratory aquifer model. *Ground Water Monitoring & Remediation*, 24, 88–96.
- Cohen, R.M., Mercer, J.W., 1993. DNAPL site evaluation. In: Smoly, C.K. *Library of cataloging-in-publication data*.
- Gangwon Province. Detailed investigation and Basic Remediation Design for Contaminant Soil and Groundwater in Woosan Industrial Complex, Wonju City, Gangwon Province, Korea, 2005.
- Graber E.R., Laor Y., Ronen D., 2008. Aquifer contamination by chlorinated–VOCs: the case of an urban metropolis megasite overlying the Coastal Plain aquifer in Israel. *Hydrogeology Journal*, 16, 1615–1623.
- Jo Y.J., Lee J.Y., Yi M.J., Kim H.S., Lee K.K., 2010. Soil contamination with TCE in an

industrial complex: contamination levels and implication for groundwater contamination. *Geoscience Journal*, 14, 313–320.

Jochmann M.A., Blessing M., Haderlein S.B., Schmidt T.C., 2006. A new approach to determine method detection limits for compound-specific isotope analysis of volatile organic compounds. *Rapid Communication in Mass Spectrometry*, 20, 3639–3648.

Jochmann M.A., Yuan X., Schmidt T.C., 2007. Determination of volatile organic hydrocarbons in water samples by solid-phase dynamic extraction. *Anal Bioanal Chem*, 387, 2163-2174.

KMOE (Korea Ministry of Environment), 2009, 2010, and 2011. Annual report of DNAPL-contaminated site characterization and its contamination evaluation and transport prediction techniques. GAIA Project.

Lara-Gonzalo A., Sanchez-Uria J.E., Segovia-Garcia E., Sanz-Medel A., 2008. Critical comparison of automated purge and trap and solid-phase microextraction for routine determination of volatile organic compounds in drinking waters by GC-MS. *Talanta*, 74, 1455-1462.

LaPlante L, P.E., 2002. Innovative strategy to locate VOC sources deep in the subsurface. *Remediation of Chlorinated and Recalcitrant Compounds*.

Lee, H. G., 2011. Characteristic of TCE contaminant in groundwater of an Industrial complex, Wonju, Korea. *Seoul National University, Thesis for an M.S. Degree*.

Luciano A., Viotti P., Papini M.P., 2010. Laboratory investigation of DNAPL migration in porous media. *Journal of Hazardous Materials*, 176, 1006–1017.

Maul, E.A., Cogliano, V.J., Scot, C.S., Barton, H.A., Fisher, J.W., Greenber, M., Rhomberg, L., Sorgen, S.P., 1997. Trichloroethylene health risk assessment: A new and improved process. *Drug and Chemical Toxicology*, 20, 426-442.

Nilsson T., Pelusio F., Montanarella L., Larsen B., Facchetti S., Madsen J.O., 1995. An evaluation of solid-phase microextraction for analysis of volatile organic compounds in drinking water. *Journal of High Resolution Chromatography*, 18, 617-624.

Nobre M.M.M., Nobre R.C.M., 2004. Soil vapor extraction of chlorinated solvents at an industrial site in Brazil. *Journal of Hazardous Materials*, 110, 119-127.

Ormsby M., 2005. Analysis of laminated documents using solid-phase-microextraction. *Journal of the American Institute for Conservation*, 44, 13-26.

Siegrist R.L., Lowe K.S., Crimi M.L., Urynowicz M.A., 2006. Quantifying PCE and TCE in DNAPL source zones: effects of sampling methods used for intact cores at varied contaminant levels and media temperatures. *Ground Water Monitoring Remediation*, 26, 114-124.

Suthersa, S. S., 1997. Remediation engineering: design concepts. *CRC Press, Inc.*

Tolgyessy P., Hrivnak J., 2006. Analysis of volatiles in water using headspace solid-phase microcolumn extraction. *Journal of Chromatography A*, 1127, 295-297.

Urmann K., Gonzales-Gil G., Schroth M.H., Hofer M., Zeyer J., 2005. New field method: gas push-pull test for the In-situ quantification of microbial activities in the vadose zone. *Environmental Science & Technology*, 39, 304-310.

Wonju City and Environmental Management Corporation (EMC). Detailed investigation report on contaminated soil and groundwater in the Woosan Industrial Complex and Joongang-dong area in Wonju City, Wonju City, Korea, 2003.

Yang E.E., Kim H.G., Kim D.J. Final research report on investigation of potential soil contaminated area and its management plan in Wonju City. Gangwon Regional Environmental Technology Development Center (KETeC), Korea, 2003.

Yang J.H., Lee K.K., Clement T.P., 2011. Impact of seasonal variations in hydrological stresses and spatial variations in geologic conditions on a TCE plume at an industrial complex in Wonju, Korea. *Hydrological Processes*, DOI: 10.1002/hyp.8236.

Yu S.Y., Chae G.T., Jeon K.H., Jeong J.S., Park J.G., 2006. Trichloroethylene contamination in fractured bedrock aquifer in Wonju, South Korea. *Bulletin of Environmental Contamination and Toxicology*, 76, 341-348.

국문 초록

산업단지 내 지하수는 트리클로로에틸렌 (trichloroethene), 사염화탄소 (carbon tetrachloroethene), 클로로폼 (chloroform) 와 같은 여러 종류의 유기용제로 오염될 가능성이 높고 불포화대내 이러한 복합 오염물의 위치 추적은 효과적인 정화에 필수적이다. 기존의 트리클로로에틸렌 (TCE) 주 오염원에서 수행된 계절적 강우에 의한 지하수 함양 그리고 이에 따른 지하수위 변동에 따른 복합 오염물들의 농도 분석을 통해 지하수 수위 주변의 잔류 DNAPL의 존재 가능성을 보여줬다. 이러한 TCE는 지하수 내 가장 흔히 발견되는 휘발성물질 (volatile organic compounds) 이기 때문에 만약 불포화대내 잔류 TCE가 존재한다면 가스상태로 존재 할 수 있다. 이미 외국에서는 DNAPL의 가스모니터링 (gas monitoring)이 활발히 연구 중이며 이 방법이 장기적인 수질분석 (water monitoring) 보다 비용절감 효과가 있다고 한다. 따라서, 원주 우산공단지역 내 잔류 TCE의 위치를 예측하기 위한 가스 상태의 TCE 오염물의 시간적, 공간적 분석이 이뤄졌다. 각 필드 실험에서는 실험 조건에 따라 2개의 경우로 나뉘어 주 오염원 내 위치한 관정, KDPW-2에서 TCE가스 샘플링 (sampling)이 수행되었다. 첫 번째 경우는 팩커 (packer)의 유무에 따른 가스TCE의 농도를 보기 위함 이었고 두 번째는 4개의 심도별 실험을 통해 잔류DNAPL의 대략적인 수직적 위치를 밝히기 위함 이었다. 이러한 포집된 샘플들은 SPME (Solid Phase MicroExtraction) fiber와 가스크로마토그래피 (gas chromatography)를 통해 분석되었다. 이 결과를 통해 잔류 TCE가 수위 주변인 12 m에 위치함과, 그 후 계산한 영향반경 (radius of influence)를 통해 대략적인 수평적인 위치도 예측하였다. 본 연구를 통해 이러한 DNAPL의 휘발성 성질을 이용한 가스샘플링 (gas sampling)이 불포화대내 잔류 DNAPL의 수직적, 수평적인 공간분포도를 제시할 수 있을 것으로 판단된다.

주요어: 트리클로로에틸렌 (trichloroethene), 가스모니터링 (gas monitoring), 잔류 DNAPL, 영향반경 (radius of influence)

감사의 글

이 논문이 완성되기까지 도움과 격려를 주신 모든 분들께 깊은 감사의 인사를 드리고자 합니다. 먼저, 너무나도 부족한 제게 공부할 수 있는 기회와 열정을 주시고, 제 연구에 무한한 애정과 관심, 그리고 조언을 해주신 이강근 교수님께 감사드립니다. 그리고 논문 심사를 맡아주시고 아낌없는 조언을 해주신 김준모 교수님과 김규범 교수님께도 진심으로 감사드립니다.

더운 날 원주필드에서 실험하면서 같이 고생하고 실험결과를 함께 고민해주신 연구실 선, 후배님들 너무 고맙고 수고하셨습니다. 또, 연구 외에 연구실 생활에 잘 적응할 수 있도록 도와주신 연구실 식구들께도 정말 감사드립니다. 모두의 도움으로 무사히 연구를 마치고 즐거운 학교 생활을 할 수 있었습니다.

마지막으로 항상 저의 든든한 후원자이자 친구로써 아낌없는 사랑과 조언을 주신 부모님과 동생 그리고 항상 마음속으로 기도와 응원해주신 가족분들께 깊이 감사드립니다. 항상 조금씩 더 발전해 나가는 겸손한 사람이 되고자 노력하겠습니다.