Locating plume sources of multiple chlorinated contaminants in groundwater by analyzing seasonal hydrological responses in an industrial complex, Wonju, Korea

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ABSTRACT: An area accommodating various industrial facilities has fairly high probability of groundwater contamination with multiple chlorinated solvents. Source identification of multiple chlorinated solvents is an essential procedure for the management and remediation of contaminated groundwater. Hydrogeologic investigations and periodic collection of groundwater chemical data in an industrial complex in Wonju, Korea were used for the source identification of multiple chlorinated solvents. In this study, an example is presented highlighting the potential impact of seasonal rainfall events as the key factor for discriminating between contaminant sources. This method was effective in identifying and allocating sources of small contaminant plumes masked by a major contaminant plume. The apparent main sources of high concentration multiple chlorinated contaminants such as trichloroethene, carbon tetrachloride, and chloroform were located in the uppermost area of the study site. By using the proposed method, additional contaminant source locations were identified. This result demonstrates that source allocation is effective by using simply concentration data under the influence of temporal groundwater recharge. When this method is incorporated with compound-specific stable isotope analysis based on the chemical evolution of the chlorinated contaminants, the source identification results can be more decisive in a complex study area with multiple overlapping plumes.

Key words: trichloroethene (TCE), carbon tetrachloride (CT), chloroform, seasonal impact analysis, contamination source identification

1. INTRODUCTION

An industrial complex accommodates different types of facilities, and some of them use chlorinated solvents for several purposes. In Korea, tetrachloroethene (PCE), trichloroethene (TCE), carbon tetrachloride (CT), and chloroform, collectively called dense non-aqueous phase liquids (DNA-PLs), have been the most frequently detected organic contaminants in groundwater. The Korea Ministry of Environment (KMOE) reports that the detection ratio of PCE and TCE within industrial and urban areas ranges up to approximately 19% of the samples analyzed, due to the widespread use of degreasing and cleaning agents in industrial and commercial applications (KMOE, 2010). The occurrence, health risk and remediation of such hazardous chlorinated contaminants in groundwater are key topics of recent researches (Clement et al., 2000; Clement et al., 2002; Chapman et al., 2007; Rolle et al., 2008; Abe et al., 2009; Baek and Lee, 2011; Clement, 2011). Particularly at sites of industrial complexes and storage facilities, these chlorinated contaminants show complicated contamination patterns as a consequence of complex hydrogeologic characteristics, and they provide persistent sources of contamination for a long period (Clement et al., 2004; Glaser et al., 2005; Squillace and Moran, 2007; Blessing et al., 2009).

The occurrence of multiple sources of chlorinated contaminants in groundwater may be assessed by various techniques such as chemical fingerprinting, historical archives, and compound-specific isotope analysis (CSIA) (Mansuy et al., 1997; Atmadja and Bagtzoglou, 2001; Alimi et al., 2003; Hunkeler et al., 2004; Jochmann et al., 2006; Chartrand et al., 2007). Each method has its limitations and cannot provide complete information.

Chemical fingerprinting of contaminant concentrations combined with a mathematical approach such as geostatistics, inverse modeling, or regression can be useful in discerning multiple sources under simple geometrical and groundwater flow conditions. However, if the concerned area is overwhelmed by the main toxic plume with high contaminant concentrations originated from an upgradient area, the sourcing of origins can be obscure (Duffy and Brandes, 2001; Basu et al., 2008; Blessing et al., 2009). A historical approach to the identification of chlorinated contaminants generally may provide inaccurate results. Because of the limitations of the two approaches, CSIA has been recently applied for the identification and allocation of chlorinated contaminants in groundwater (Okuda et al., 2002; Slater, 2003; Walker et al., 2005; Abe et al., 2009). The chlorinated solvents may exhibit different stable isotopic signatures for different products (Benson et al., 2006). Many field studies showed that if the biodegradation of chlorinated contaminants is weak, and with sufficient field data, the source identification of chlo-

rinated contaminants can be successfully made using stable isotopic signatures with an accuracy of more than 1‰ $\delta^{13}C$ (Slater, 2003; Hunkeler et al., 2004; Glaser et al., 2005). However, the CSIA method may also give ambiguous results if a small plume originating from the contaminant with the same production source is overlapped by, or mixed with, a main plume with high concentrations as in the case of this study.

Therefore, the other method is needed to complement the CSIA for better source identification, especially when many sources of several chlorinated contaminants coexist in a site with overlapping plumes. Yang et al. (2012) demonstrated that the concentrations of TCE dissolved in groundwater showed temporal fluctuations according to groundwater recharge events from rainfalls and this phenomenon could be used for DNAPL source identification.

The purpose of this study is to propose a method to identify the sources of chlorinated contaminants in groundwater by analyzing the influences of seasonal rainfall events on the concentrations of contaminants in groundwater. This method of locating contaminant plume sources based on the seasonal impact analysis will be especially effective when there are multiple contaminant plumes with low concentrations that are overlapped with a main contaminant plume.

2. MATERIALS AND FIELD SAMPLING METHODS

2.1. Site Description and History

The study area in the Woosan Industrial Complex (WIC) is located in Wonju City, approximately 120 km from Seoul, Korea (Fig. 1). The study site occupies about 0.70 km² and most of the surface area is covered by buildings, roads, and factories. About 9% (0.06 km²) of the study area is unpaved and thus rainwater infiltration can occur over the limited area. The industrial complex was constructed in 1970 and is surrounded by low relief hills (Figs. 1 and 2).

The Road Maintenance Office (RMO) of Gangwon Province located uphill of the WIC surrounded by forest and grassland area is generally known as the main source of the multiple chlorinated contaminants, while other small sources exist in the downgradient area of the main source location (EMC, 2003; Yang et al., 2003; Gangwon province, 2005; Yu et al., 2006; Jo et al., 2010; Baek and Lee, 2011; Yang et al., 2011). There are no exact records on the use of the solvents. According to personal communications with the workers of the RMO laboratory, various solvents for the asphalt quality test were used for 16 years prior to 1997. The exact names and dumped quantities of solvents are unknown. The TCE and CT detected in the groundwater of the study site are known to be the main spilled contaminants in the WIC area. Chloroform detected in groundwater at the site had been considered, without any supporting evidence, as a by-product that was formed by biodegradation of carbon tetrachloride.

2.2. Hydrogeologic Conditions

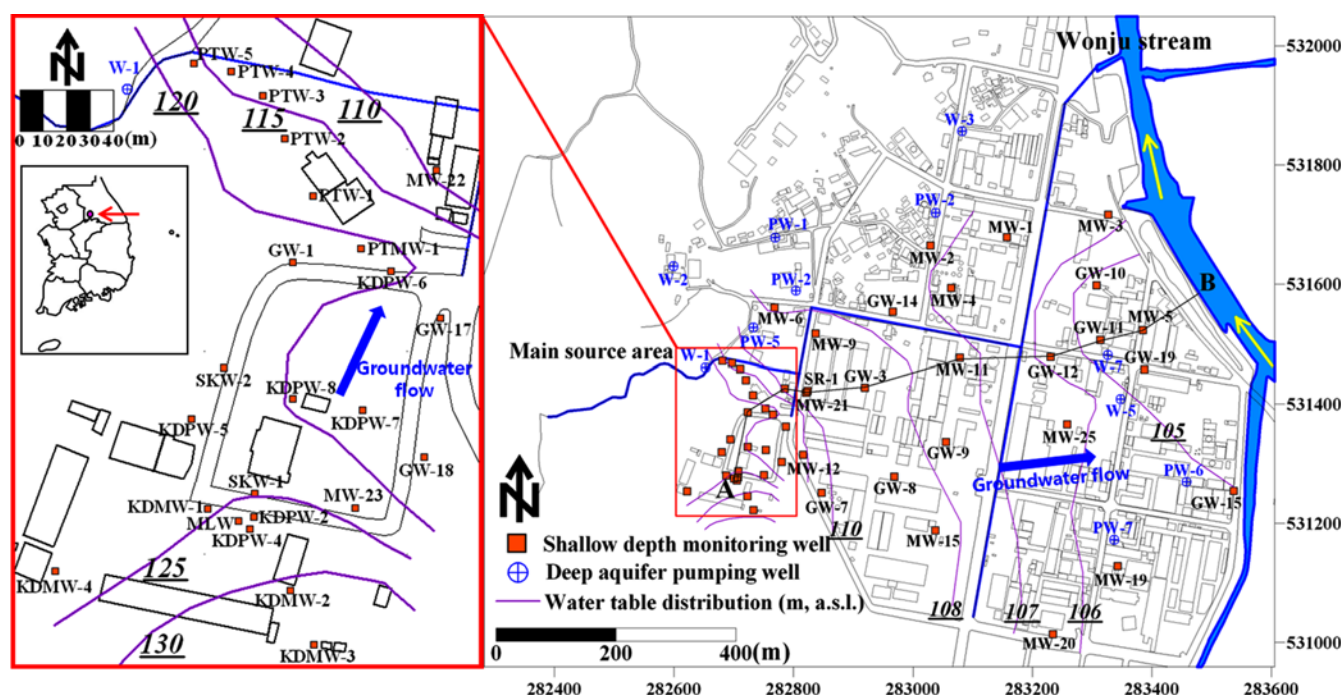Annual average rainfall in the area was 1,413 mm (for the past five years) and approximately 70% of the annual rain-

Fig. 1. The study area showing the monitoring wells and the distribution of water levels (m, a.s.l.) with the groundwater flow direction measured in August 2010.
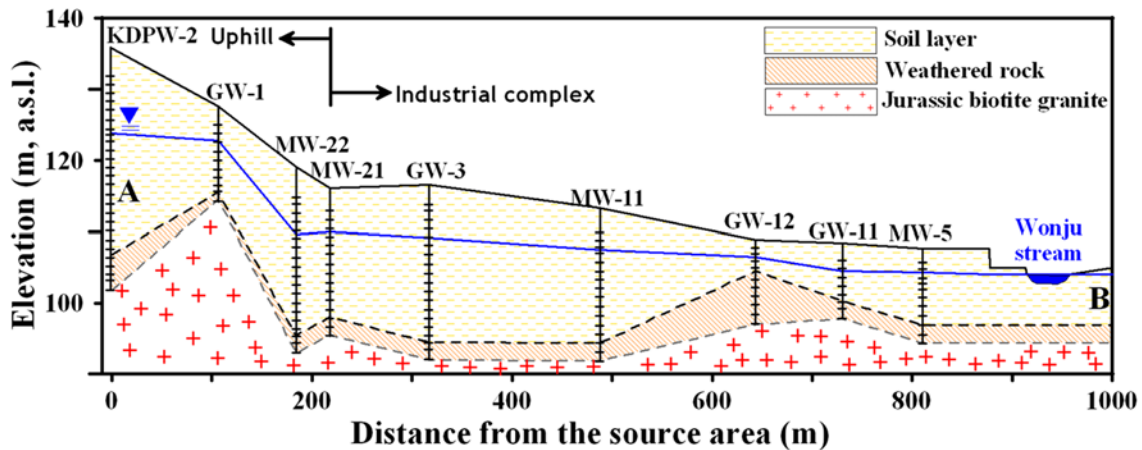
Fig. 2. Hydrogeologic section A-B showing the well intervals with water table location measured in August 2010.

fall is concentrated in the June–September period. The observed direction of groundwater flow is from southwest to northeast in the upgradient area and from west to east in the downgradient area (Fig. 1). The hydraulic gradients measured near the main contamination source area near the RMO and at the downgradient areas in WIC during the rainy season were 0.025 and 0.008, respectively, while in the dry season the hydraulic gradients were 0.014 and 0.006, respectively, implying different surface conditions resulting in a big difference of the groundwater recharge potential. The main RMO spillage area of multiple chlorinated contaminants is surrounded by a forest and grassland area possessing high groundwater recharge potential. The recharge potential in this area is approximately twice as large as that
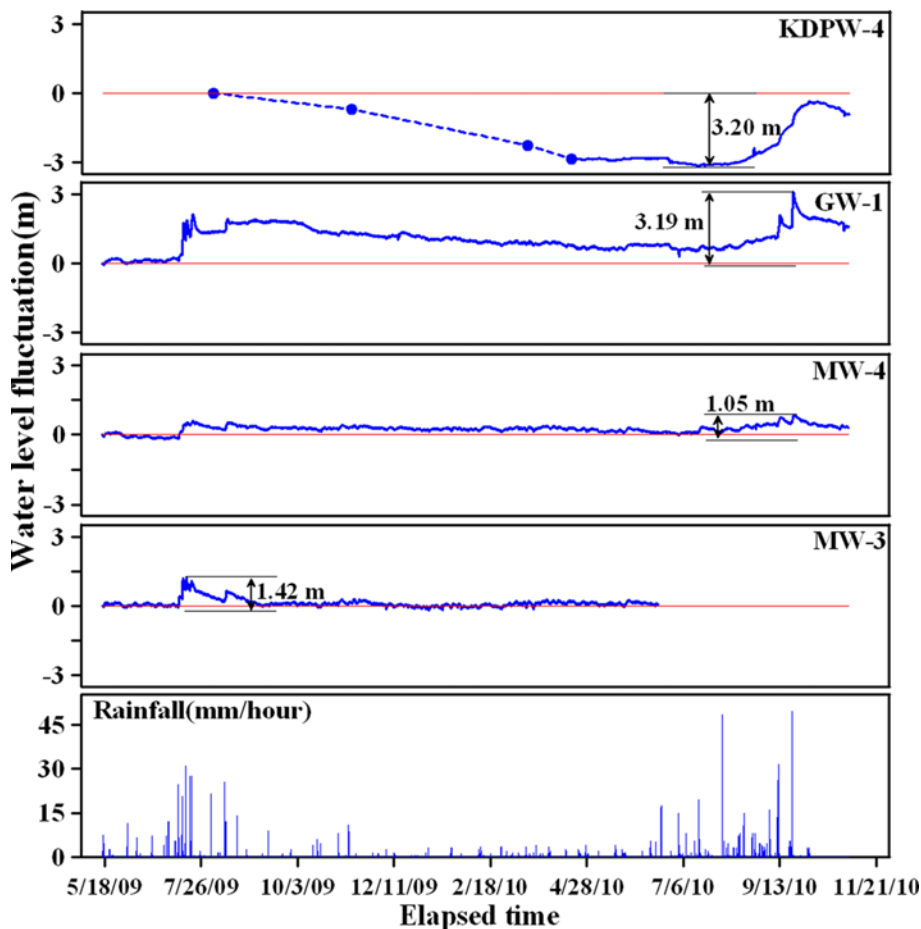

Fig. 3. Water level fluctuations and rainfalls in the study area. The initial water level at KDPW-4 measured in August 2009 was 126.59 (m, a.s.l.). A GW-1, MW-4, and MW-3 measured in May 2009 the water levels were 122.20, 106.73, and 103.14 (m, a.s.l.), respectively.

of downgradient WIC area. The vertical fluctuation ranges of the water table during the period of August 2009–October 2010 at the RMO and at the WIC are 3.20 m and 1.05 m, respectively. Therefore, the effects of rainfall events on groundwater recharge and water table fluctuations clearly reflect the different surface conditions (Fig. 3).

2.3. Groundwater Sampling and Water Quality Analysis

Six rounds of groundwater sampling surveys were performed during the period of May 2009–August 2010. For the analyses of contaminant concentrations and water quality, at least three well volumes were purged using a low-rate submersible pump attached to a polyethylene hose, and the hose was repeatedly changed at each sampling point to avoid cross-contamination. All groundwater samples were immediately collected in a closed flow-through cell. The samples collected for analyzing multiple chlorinated contaminants and their daughter products were directly sampled from the continuous water stream in 40 ml amber glass vials with Teflon-lined septa and no headspace. All samples were stored at 4 °C prior to laboratory analysis, and at least 10% of the samples were duplicated. All samples were transferred to the laboratory within a day, about 1 km distant from the sampling area. The concentrations of the multiple chlorinated contaminants were analyzed with a gas chromatography mass spectrometry method using a Saturn 2100T, VARIAN GC/MS.

2.4. Automatic Water Table Monitoring and Depth-Discrete Contaminant Concentrations

Water level fluctuations at four selected wells were observed at one-hour intervals using an automatic level logger CTD-diver, VANESSEN and level logger, SOLINST. All hydraulic heads were transformed to the heights above the average sea level (m, a.s.l.) and were used to analyze the seasonal impact of rainfall events on the identification of multiple chlorinated contaminants.

For the samples of depth-discrete groundwater at various depths in KDPW-2 well and a multilevel well (MLW), diffusion samplers were used in November 2009, May 2010, and August 2010. The diffusion sampler consists of a semi-permeable sample chamber filled with deionized water, drawstring, and drawstring hanger (Ehlke et al., 2004; Harter and Talozi, 2004; ITRC, 2005). The multiple chlorinated contaminants in the groundwater permeated into the sample chambers at each depth until the multiple contaminant concentration gradient equilibrated between the groundwater and the semi-permeable sample chambers. The sample chambers were withdrawn after every three weeks and the solutions inside the chambers were directly collected into 40 ml amber glass vials with Teflon-lined septa and no headspace for laboratory analysis.

3. RESULTS AND DISCUSSION

3.1. Historical Approach and Chemical Fingerprinting

Historical surveys were conducted for site-specific information on the contamination. Information was obtained from the laboratory staff at the RMO (Gangwon Province, 2005). Based on the historical surveys and the spatial distribution pattern of the DNAPL contaminants, it was concluded that the RMO was the main source of TCE and CT contamination in the study area. Extensive soil sampling analyses and the contaminant plume distributions also showed that another possible TCE source existed near the GW-19 monitoring well (Gangwon Province, 2005; Baek and Lee, 2011). However, based on the historical surveys, more potential sources of the chlorinated contaminants were present, causing the groundwater contamination (Yang et al., 2003).

The chemical fingerprinting of the TCE contamination was performed in August 2009 and indicated that a possible TCE source existed at or near GW-10 well location (Fig. 4a). However, another chemical fingerprinting showed that apparent TCE sources could not be successfully identified in the dry season while it was possible for the March 2010 data. Such difference suggests that it is difficult to identify the sources when a small TCE plume in the downgradient area was temporally overlapped by a large plume from the main source in the upgradient area (Fig. 4b). Furthermore, in August 2010, possible TCE sources were obscured by seasonal migration of the TCE contaminant plumes by rainfall events in the summer 2010 with smaller precipitation than in summer 2009 (Fig. 4c). Herewith, the distribution of TCE plumes in August 2010 resulted from a relatively small source of TCE contamination at the upgradient of the main TCE source (i.e., RMO).

The source of CT contamination revealed by chemical fingerprinting showed that one main source was also located upgradient of the RMO (Fig. 4d). The size of CT contaminant plume was relatively small and was restricted to the western half of the study area (Figs. 4e, f). Details on the identification of multiple chlorinated contaminants are discussed below.

3.2. Depth-Discrete Contaminant Concentrations

The depth-discrete concentrations of contaminants were examined periodically using the diffusion sampler at the KDPW-2 well and the MLW monitoring well which are 5 m apart from each other. The concentrations of chlorinated contaminants varied distinctly with depth (Fig. 5). In general, high concentrations of contaminants occurred at the top of each well and then abruptly decreased with depth. This tendency was obvious for TCE. This implies that the residual or free phase of contaminants preferentially exists near the water table and acts as a continuous source of aque-
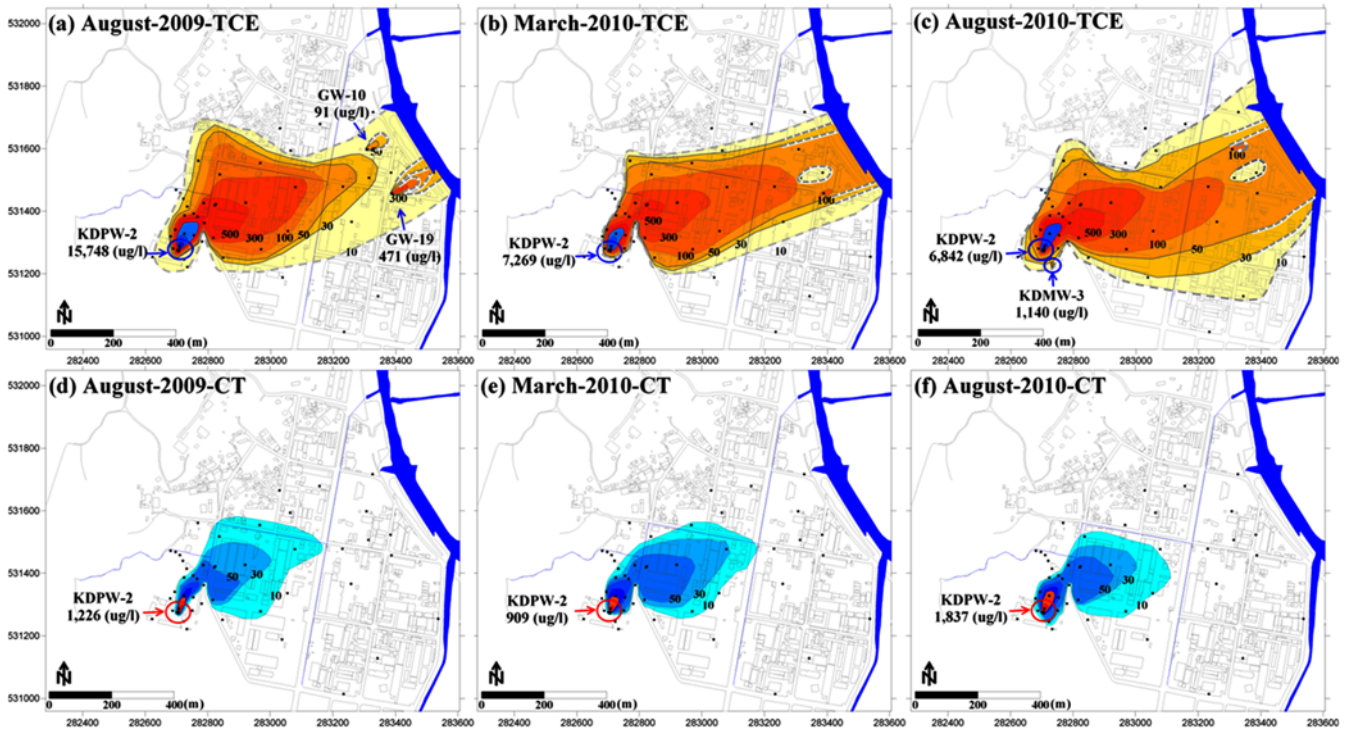
Fig. 4. Distribution of the TCE and CT plumes in August 2010, showing the sources identified by conventional methods, such as the historical approach and chemical fingerprinting.
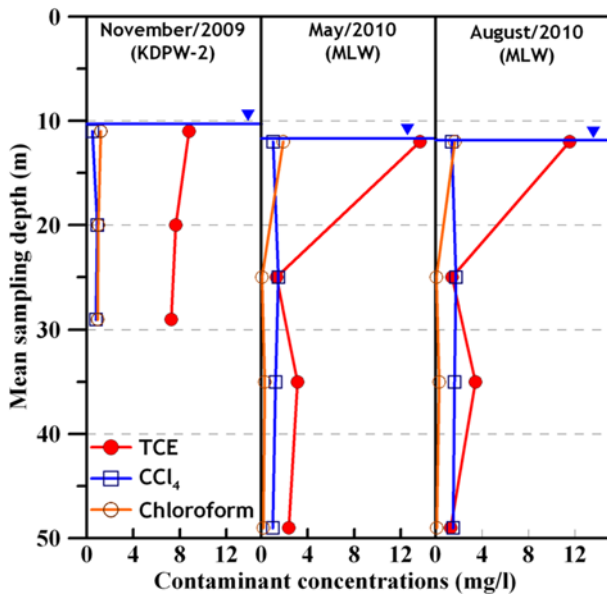

Fig. 5. Depth-discrete TCE, CT, and chloroform concentrations in groundwater obtained by the diffusion sampler at KDPW-2 in 2009 and in the MLW in 2010.

ous phase contaminants toward the downgradient region.

3.3. Seasonal Impact Analysis for Source Identification and Allocation

In the study area, the main contaminant plume and its

source can be easily identified from the aqueous phase concentration data together with the contamination history information. However, small plumes from the other small contamination sources were very hard to be discernible when the main plume masks them. Therefore, in this study, the seasonal impact of rainfall events was analyzed for source allocation by examining the correlation between the chlorinated contaminant concentrations (C/C_0) and the fluctuation of hydraulic head (Δh). The contaminant concentrations and hydraulic heads at each sampling point were compared with each reference value indicating a base concentration (C_0) and hydraulic head (h_0) for each well. For a comparative purpose, the measurements at March 16, 2010 were used as reference contaminant concentrations (C_0) and hydraulic head (h_0) for each well. Data on the concentration and head for any sampling event could have been used as the references C_0 and h_0 since relative changes of the concentrations and hydraulic head change are meaningful.

The distributions of the relative concentration ratio (C/C_0) versus head deviation (Δh) are shown in Figure 6. The sampling points showing positive correlations possibly represent the source(s) of contamination where the contaminants exist mainly as a residual phase. The correlation trends observed at potential source points are shown in Figure 7 and are summarized in detail in Table 1. The potential source points are marked with (+) signs in Figures 6 and 7. The possible but rather ambiguous sources of contamination are marked with (Δ) signs in the figures. However, it is note-
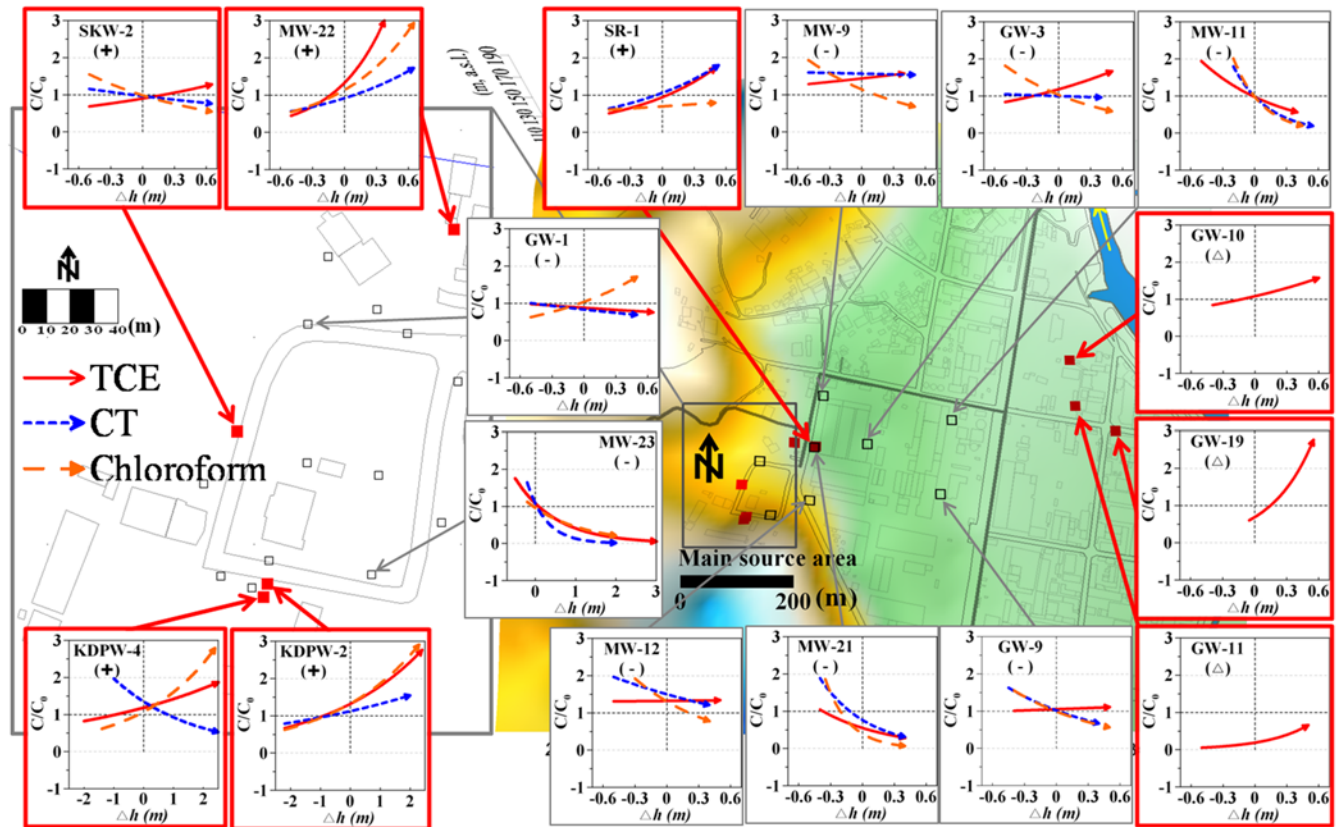
Fig. 6. The results of the seasonal impact analysis showing the positive or negative relationship for each well.

worthy that the source points show positive correlations for some specific components but also show negative correlations for other components. This may imply that several chlorinated contaminants exist and each source point in the study area has different histories in the use of chlorinated compounds.

3.3.1. Source-A

Source-A covering the sampling points of KDPW-2, KDPW-4, and SKW-1 in the territory of RMO (see Fig. 1) forms the main source of TCE and CT. Based on the historical information and chemical fingerprinting, the KDPW-2 well in the unconfined aquifer showed the highest concentrations of TCE and CT, 15,748 μg/l and 1,226 μg/l, respectively, in August 2009 (Fig. 4). The general shape and distribution of TCE and CT plumes in the study area undoubtedly showed that the Source-A forms the main source of DNAPL contamination in the study area. The seasonal changes of groundwater recharge and the accompanying fluctuation of the concentrations of contaminants were examined in the Source-A area (Fig. 7a). The concentrations of TCE, CT and chloroform at KDPW-2 strongly correlated ($R^2 = 0.69$, 0.70, and 0.77) with a hydraulic head increase caused by rainfall events.

At the monitoring well KDPW-4, the concentrations of

TCE and chloroform also showed a positive correlation ($R^2 = 0.55$ and 0.93) with a hydraulic head increase. However, CT showed a negative correlation. These data imply that observed increase of the concentrations of aqueous TCE and chloroform is possibly the result of the increased dissolution of residual DNAPL phase during the rise of water table. The simple dilution effect caused by the inflow of rain cannot explain the observations. At SKW-1, only the CT concentrations were correlated ($R^2 = 0.81$) with the water table rise. This may indicate that only CT occurs as a residual phase near the groundwater table at the well.

In the study area, TCE and CT are the main contaminants, while chloroform was previously considered as a by-product of biodegraded CT. However, geochemical data indicated that aerobic conditions are prevailing in groundwater and the analysis of degradation products of TCE showed the very weak dechlorination processes (Fig. 7a). Therefore, the strong correlation ($R^2 = 0.93$) of the chloroform concentration with the water table rise, which is comparable with those for TCE and CT, may indicate that the chloroform is not a by-product of biodegraded CT but one of the inherent main chlorinated contaminants in this study area, because its concentration should decrease by dilution during rainfall periods if chloroform was a by-product of CT.
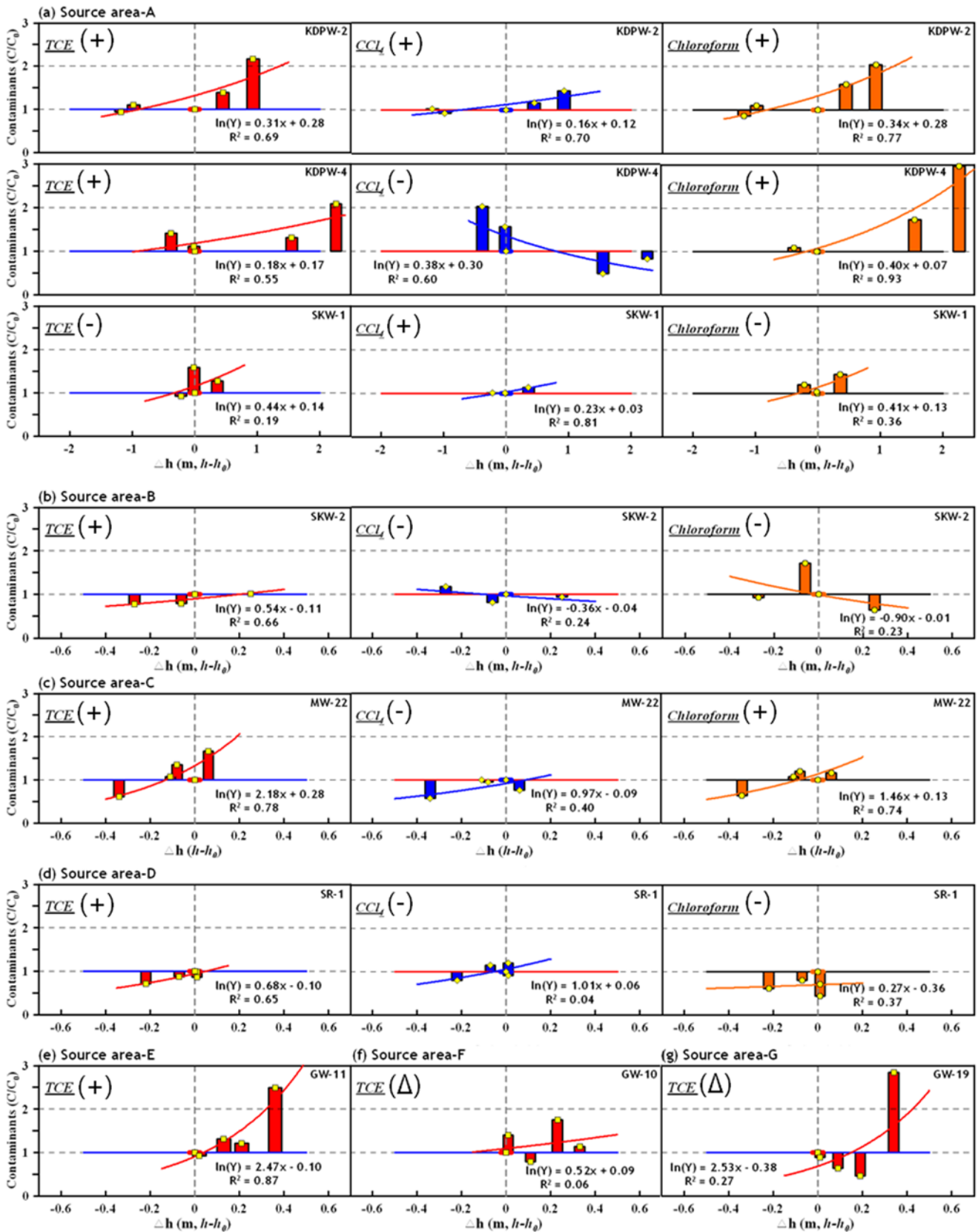
Fig. 7. Results of seasonal impact analyses showing the relationship between the multiple contaminant concentrations and the water level rise in the source area.

Table 1. The results of the seasonal impact analyses

Area	Well number	Depth (m)	Annual Δh^a (m)	TCE $(C/C_0)/\Delta h$	CT $(C/C_0)/\Delta h$	Chloroform $(C/C_0)/\Delta h$	Residual DNAPLs
	KDPW-2	29.20	2.11	$(+)^b/R^{2d} = 0.69$	$(+)/R^2 = 0.70$	$(+)/R^2 = 0.77$	TCE, CT, Chloroform
Source-A	KDPW-4	28.05	2.64	$(+)/R^2 = 0.55$	$(-)^c/R^2 = 0.60$	$(+)/R^2 = 0.93$	TCE, Chloroform
	SKW-1	30.00	0.58	$(-)/R^2 = 0.19$	$(+)/R^2 = 0.81$	$(-)/R^2 = 0.36$	CT
Source-B	SKW-2	30.00	0.52	$(+)/R^2 = 0.66$	$(-)/R^2 = 0.24$	$(-)/R^2 = 0.23$	TCE
Source-C	MW-22	23.60	0.40	$(+)/R^2 = 0.78$	$(-)/R^2 = 0.40$	$(+)/R^2 = 0.74$	TCE, Chloroform
Source-D	SR-1	11.85	0.23	$(+)/R^2 = 0.65$	$(-)/R^2 = 0.04$	$(-)/R^2 = 0.37$	TCE
Source-E	GW-11	8.55	0.36	$(+)/R^2 = 0.87$	$(-)$	$(-)$	TCE
Source-F	GW-10	13.97	0.33	Unclear (Δ)	$(-)$	$(-)$	TCE
Source-G	GW-19	12.04	0.34	Unclear (Δ)	$(-)$	$(-)$	TCE
Source-H	KDMW-3	30.58			Upgradient of the Source-A		

^{a}Annual Δh: Maximum hydraulic head change from August 2009 to August 2010.
^{b}(+): Positive relationship.
^{c}(−): Negative or no relationship.
$^d R^2$: Determination coefficient.

3.3.2. Source-B

The areas located at the downgradient of the main source area (i.e., Source-A) were also contaminated by the main plume. However, the existence of other possible contaminant sources could not be easily distinguished because of the masking effect by a large-sized main plume. This downgradient area is designated as the Source-B and is located around the well SKW-2 which is 74 m away from the Source-A. For the identification of possible small sources of chlorinated contaminants, the seasonal impact analysis was applied (Fig. 7b). In this spot, the TCE concentration was strongly correlated ($R^2 = 0.66$) with the water level rise, while the other contaminants such as CT and chloroform were negatively correlated ($R^2 = 0.24$ and 0.23). This observation may indicate that TCE exists mainly as a residual phase near the well, forming another small source of TCE contamination in the study area.

3.3.3. Source-C

The Source-C is 167 m distant from the Source-A and were also largely affected by the Source-A because contaminant plume in this area were always completely masked by the main plume from the Source-A. According to the local residents of the study area, the Source-C spot near the well MW-22 had been used as a leather factory and now used as a laundry shop. The results of seasonal impact analyses in this spot showed that the concentrations of TCE and chloroform were strongly correlated ($R^2 = 0.78$ and 0.74) with the water level rise while CT showed the irregular concentration change (Fig. 7c). This means that the existence of another small source of TCE and chloroform is highly probable around this spot and they may exist as residual phases.

3.3.4. Source-D

The Source-D is located in the middle of the study area

and had been used as a leather factory like the Source-C according to personal communications with residents. Now this spot is used as a food processing factory. The SR-1 monitoring well located at the Source-D is approximately 40 m from the MW-22 monitoring well (Source-C). The TCE concentrations were positively correlated ($R^2 = 0.65$) with the water level rise while the other contaminants varied irregularly (Fig. 7d). These data indicate that another small source of dissolvable TCE (i.e., residual phase) is potentially occur in this source area, which acts as one of the continuous sources of a TCE plume in the downgradient area.

3.3.5. Source-E

The Source-E near the well GW-11 is located in the eastern part of the study area and has been used as a garage for large trucks. Based on chemical fingerprinting, the distributions of TCE in the Source-E were irregularly masked by upgradient TCE sources. The TCE concentrations in this spot were detected with a range of 13–70 µg/l during the investigation period, while the CT and chloroform were below the detection limits (1 µg/l). Although low-level TCE concentrations were detected and were strongly affected by rainwater recharge in this spot, higher concentrations of *cis*-DCE, when compared with the concentrations at the other sampling points, were detected in the range of 100–672 mg/l. This suggests the probable existence of another TCE source and the dechlorination of TCE in this spot. The seasonal impact analyses supported the result of chemical fingerprint approach. The TCE concentration in this source area was positively correlated ($R^2 = 0.87$) with the water level rise while the *cis*-DCE did not show the distinct correlation. Therefore, these phenomena indicate the existence of another small source of TCE near the well GW-11 (Fig. 7e).

3.3.6. Source-F, -G, and -H

The Source-F (GW-10) is located adjacent to the Source-E (GW-11) and is 78 m from the GW-11 monitoring well. This spot was previously considered as another possible TCE source based on the examination of seasonal distribution of the TCE plume. Using the seasonal impact analysis, however, the TCE concentrations fluctuated irregularly with no positive correlation between the TCE concentration and the water level rise (Fig. 7f). Therefore, we suggest that a TCE source is located in the upgradient area with some distance apart from the Source-F point.

The Source-G (GW-19) is located 98 m southeast of the Source-E (GW-11) and was discerned by a historical approach and chemical fingerprinting. In the seasonal impact analysis, however, the Source-G (GW-19) also showed irregular fluctuations of TCE with the water level rise (Fig. 7g). Thus the source of TCE is located slightly distant from the monitoring point.

Based on the chemical fingerprinting, the Source-H (KDMW-3) is another spot of small TCE plume. Because the Source-H is located upgradient of the main source spot (i.e., Source-A), the TCE plume from the Source-H could not be overshadowed by the main plume.

4. SUMMARY AND CONCLUSIONS

A conceptual idea of identifying sources of chlorinated contaminants by observing concentration changes before and after rainfall recharge was examined at an industrial complex near Wonju, Korea. Based on careful examinations of the potential impacts of seasonal rainfall events on the water level change and associated fluctuations of the concentrations of several contaminants, we could identify small contamination sources that were masked by a major contaminant plume. This study showed that the contaminant sources and their source locations can be successfully identified with the combined use of seasonal impact analysis, historical approach, and chemical fingerprinting (Fig. 8). In such source area, the concentrations of contaminants were positively correlated with a hydraulic head increase by rainfall episodes. Our field study also showed how effectively the conventional method using the concentration data can be used for source identification when used together with the analysis of seasonal changes of the concentrations derived from rainfall recharge. In the case of unidentifiable small contaminant plumes arising from multiple sources that are masked by a major plume from a main source, sea-
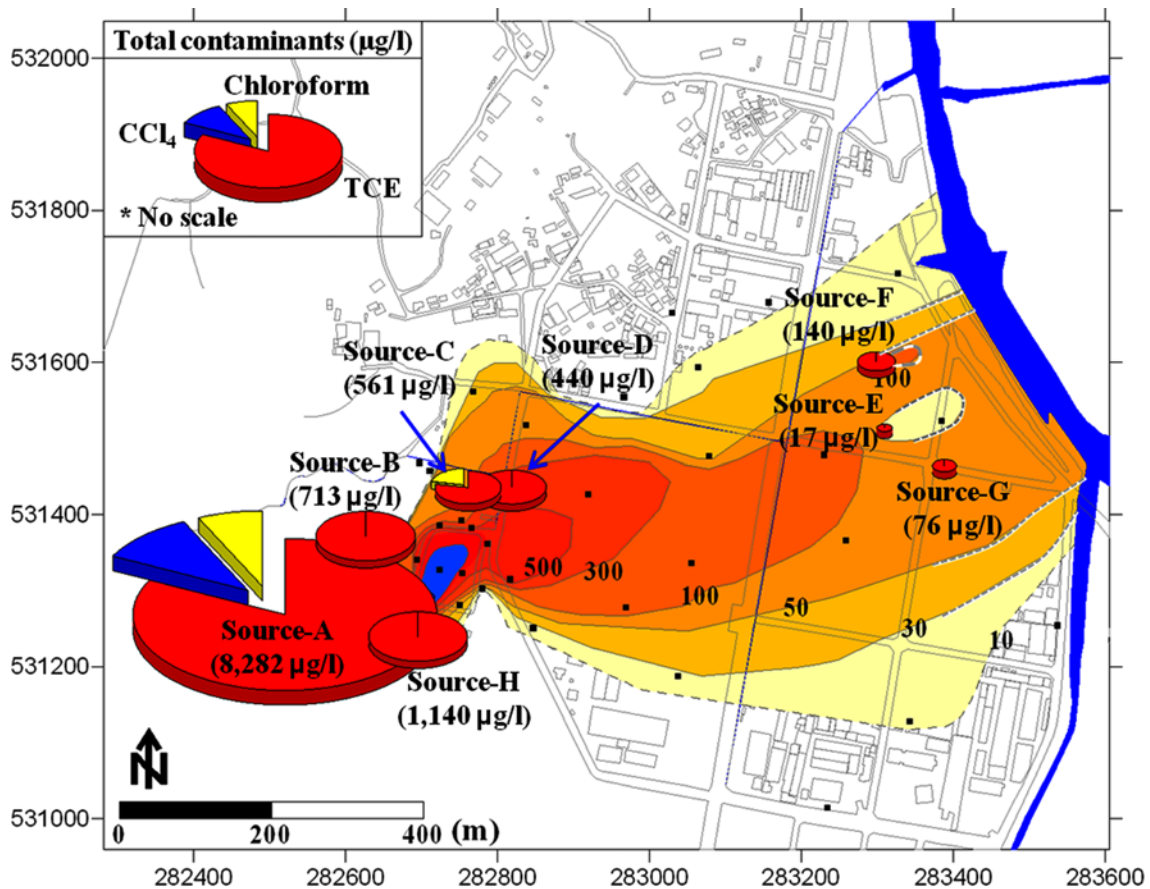

Fig. 8. Identification of multiple chlorinated contaminant sources using seasonal impact analysis with the TCE plume distribution in August 2010.

sonal impact analysis can provide reliable information on the presence of minor plume-producing sources.

The sites of the contaminant source with the residual phases of DNAPLs can be considered to exist at or adjacent to the well showing the positive correlation. The source locality is not necessarily the same with the sites of chemical spill or release.

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