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Transport of Carbon Tetrachloride in a Karst Aquifer in a Northern City, China

Baoping Han^{1,2}, Xueqiang Zhu², Zongping Pei² and Xikun Liu³
¹Xuzhou Institute of Technology,
²China University of Mining and Technology,
³Management Department of Urban Water Resource of Xuzhou,
China

1. Introduction

Carbon tetrachloride (CCl₄) has been used as a grain fumigant, pesticide, solvent for oils and fats, metal degreaser, fire extinguisher and flame retardant, and in the production of paint, ink, plastics, semi-conductors and petrol additives (Agency for Toxic Substances and Disease Registry (ATSDR), 1994). Its properties are shown in Table 1. CCl₄ is classified by the International Agency for Research on Cancer (IARC) and the US Environmental Protection Agency as a Group B2 carcinogen and also listed on the CERCLA Priority List of Hazardous Substances maintained by the Agency for Toxic Substances and Disease Registry (ATSDR, 2008). CCl₄ is a common contaminant in soil and groundwater. CCl₄ is found in approximately 20% of the US Superfund National Priority List sites (Ferguson & Pietari, 2000). But, there are limited published case studies of CCl₄ contamination in karst aquifer. Karst aquifers are distinguished by an abundance of large subsurface openings and are therefore especially vulnerable to chlorinated-solvent contamination (CCl₄, TCE, PCE). The release of chlorinated solvents into karst aquifers presents a difficult challenge to environmental scientists, managers, and regulators. The importance of karst aquifers to

Molecular weight	153.8 g/mol
Density(25 °C)	1.594 g/mL
Vapor pressure at 20 °C	12.2 kPa
Boiling point at 101.3kPa	76.72 °C
Melting point at 101.3kPa	22.92 °C
Critical pressure	4.6 Mpa
Critical temperature	283.2 °C
Solubility in water at 25 °C	785 mg/L
Henry’s law constant at 24.8 °C	2.3×10 ⁻² atm m ³ /mol
Heat of evaporation	194.7 kJ/kg
LogK _{ow}	2.64
LogK _{oc}	2.04

Table 1. Physical properties of carbon tetrachloride (Fouw, 1999)

water supply and their vulnerability to contamination by chlorinated solvents are reasons to seek improved understanding of how chlorinated solvents behave in karst aquifers (Wolfe et al., 1997). This chapter discusses CCl_4 transport and fate in a karst aquifer in a northern city of China based on *years of continuous monitoring* of CCl_4 concentrations.

2. Site characterization

2.1 Site location and pollution source

Karst aquifer investigated is located in the Northern China Plain. Karst aquifers provided averagely $25.8 \times 10^4 \text{ m}^3/\text{d}$ to urban public water supplies from 1981 to 2008 (Liu, 2010). As illustrated in the Fig.1, the karst water is in a relatively confined groundwater system unit and its east and west boundaries are coal seam water-resisting layers and the south and north are groundwater watershed. The karst groundwater system is composed several *relatively independent aquifers*. The CCl_4 pollution occurs in the southern Qiligou water-bearing basin.

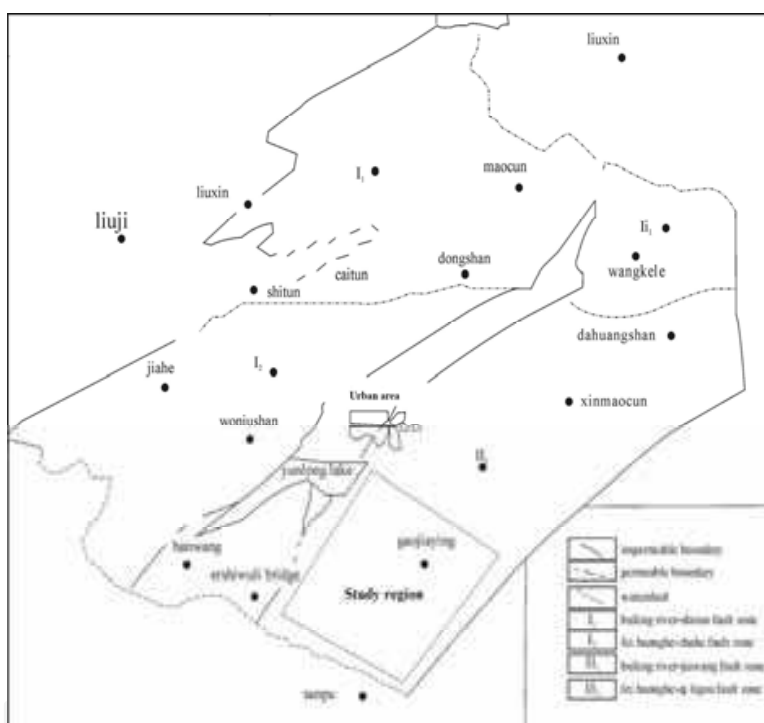


Fig. 1. *Hydro-geological zonation of the karst groundwater system in the city*

According to monitoring data obtained in November, 2000, it has been contaminated with CCl_4 in Qiligou water-bearing basin. The pollution source is a pesticide plant which produced a pesticide that used CCl_4 as a solvent and it has used more than 42 tons of CCl_4 in the past ten years. This plant is located at hill slope in southwestern recharge area of the karst aquifer (Fig. 2). However, emergency measures were taken in 2001, including closing the pesticide plant and intensive pumping from heavily polluted wells. Until May 2001, carbon tetrachloride was found in 53 wells (contaminated area is about 17.3 km^2). The highest CCl_4 concentration in karst water was over $3900 \mu\text{g}/\text{L}$ in a water supply well approximately 465m away from the pesticide plant. The concentration in Chinese standards for drinking water quality is lower than $2\mu\text{g}/\text{L}$ (GB5749-2006) (China's Ministry of Health, 2006). Since then, the contaminated wells have not been used for drinking water. While, some lightly contaminated wells have been pumping for *agricultural and industrial production*.



Fig. 2. View of the pesticide plant and its wastewater drainage

2.2 Geological and hydro-geological settings

As shown in the Fig.3, the contaminated site is a NE synclinal basin with area of approximately 200 km². Its southeastern and northwestern boundaries are two NE mountain chains composed of Cambrian and Ordovician limestone with elevations from 100 m to 248 m above the sea level. Quaternary deposits in the central lowlying area of the basin are composed of alluvium, proluvium, sand, sandyclay and subclay. The thickness of Quaternary is from 5 to 30 m, and the elevation varies from 30m to 40m above the sea level.

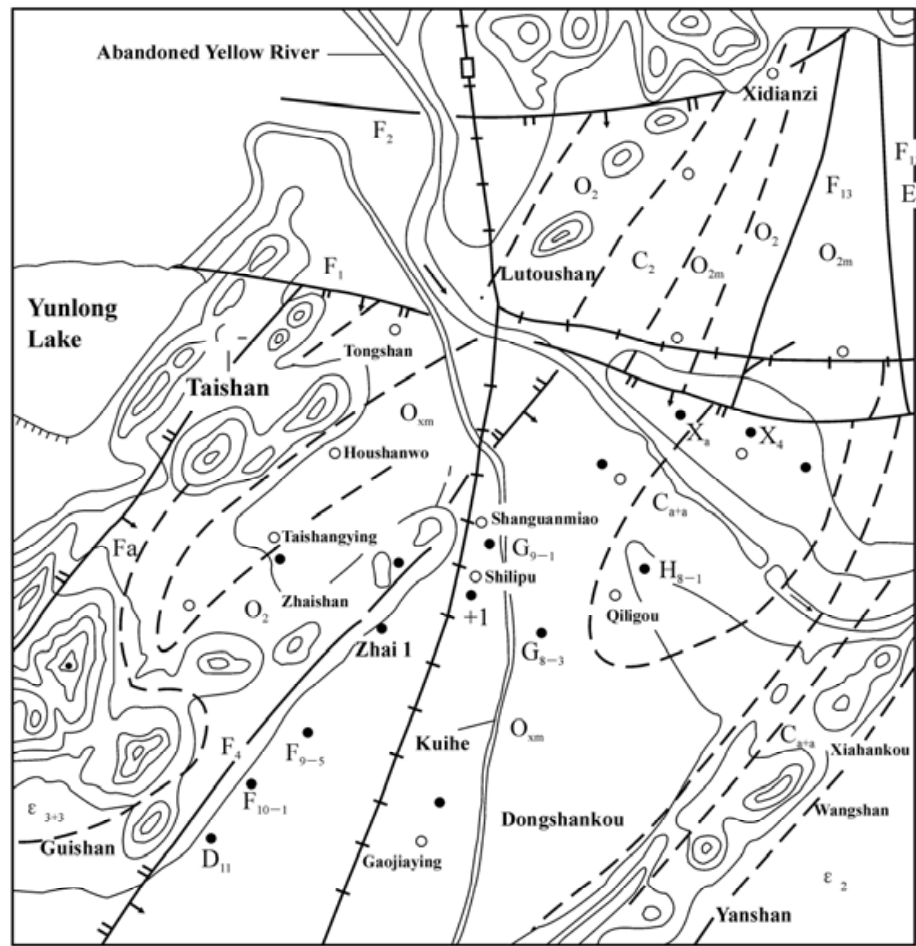


Fig. 3. Bedrock geologic map of Qiligou water-bearing basin

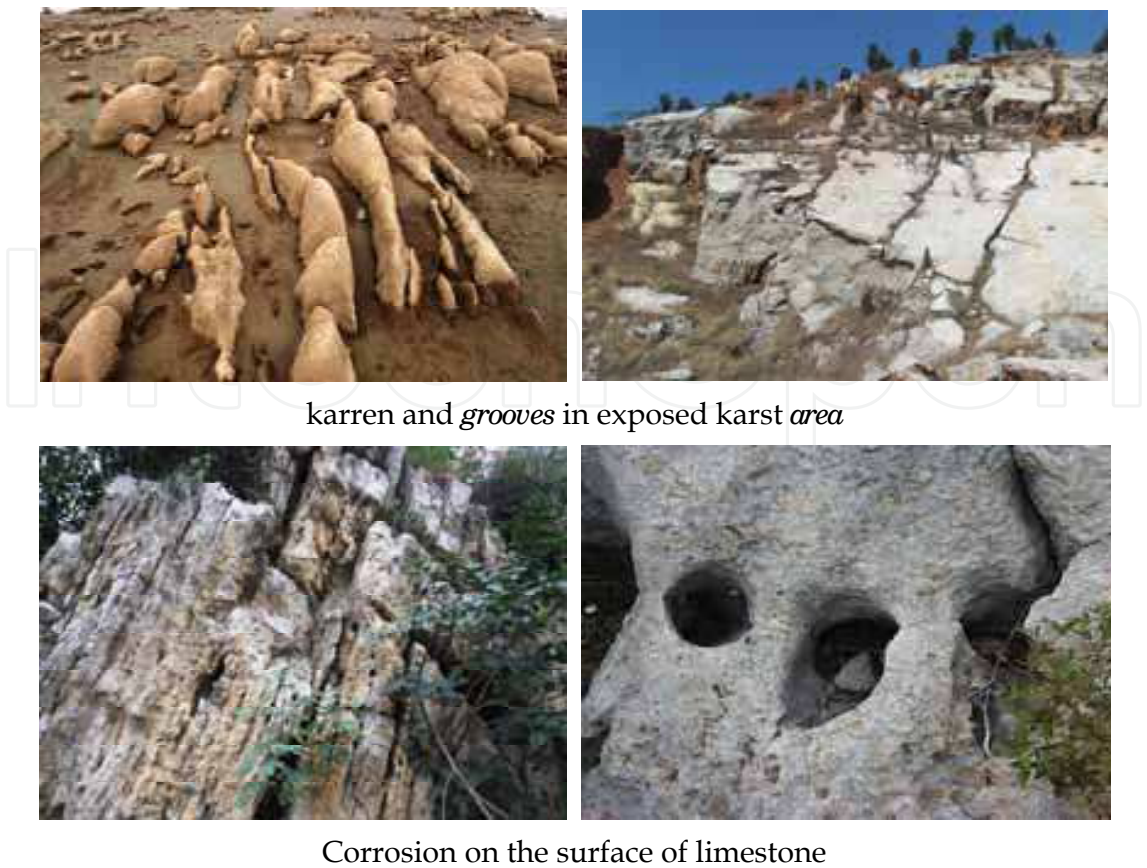


Fig. 4. Surface karst formation in the site

Limestone cropped out along hills contains abundant karst landforms such as caves, blind valleys and sinkholes, which provide pathways for the rapid transport of contaminants into the aquifer. Fig.4 presents the surface karst landform in the studied region. Fig.5 demonstrates the *degree of development* of *karst* in the *subsurface*. Karst caves and fissures are the major structure of water storage. Especially, the honeycomb-like dissolved solution pores are quite well-developed.



Fig. 5. Corrosion of rock core samples

According to borehole data, there are four well developed underground karst or paleokarst zones and they are regarded as the horizontal runoff layers in the karst aquifer (Fig. 6). Of them, the third karst zone with a depth from 90 m to 150 m is the most important runoff layer of karst groundwater. Karst groundwater is recharged mainly from precipitation (about 835mm per year). Rain water seeps into karst aquifer from sinkholes, fissures in outcrop areas or in covered karst area. It first infiltrates into Quaternary phreatic aquifer in lowlying basin area, then infiltrates into underlying karst aquifer from recharge skylight. In middle sub-area, there is a layer of igneous rock and the karst aquifer can be divided into upper water-bearing zone and lower zone because of igneous rock watertight.

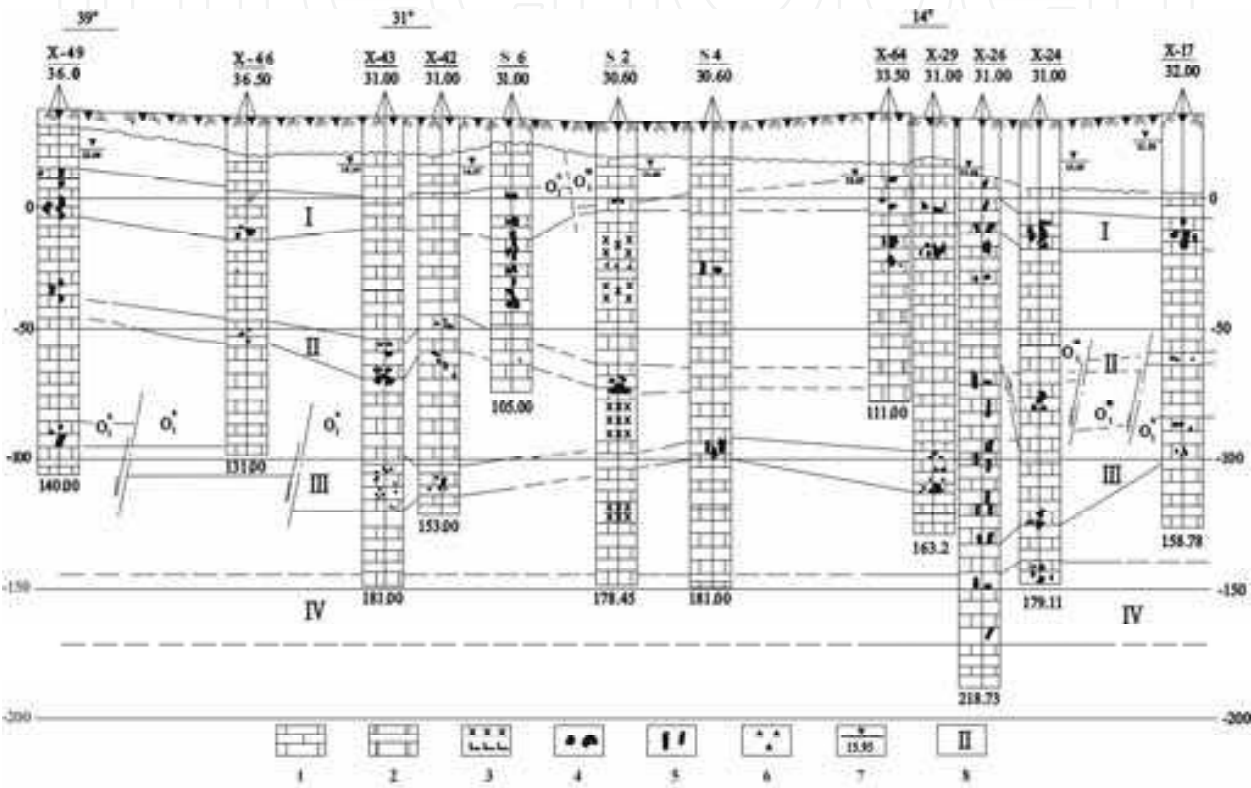


Fig. 6. Vertical zonation of karst development along the groundwater flow path in the site (1. limestone; 2. dolomite; 3. igneous rock; 4. cave; 5. karst fissure;6. fault fracture zone; 7 water table; 8 karst zone)

The variation in groundwater level from 2000 to 2008 is presented in Fig.7. Although the range of groundwater fluctuation in different wells is different, the trend is similar. It suggests there is a good hydraulic connection within the aquifer system, which makes the aquifer more vulnerable to contamination. Many years of groundwater level observations indicate that there is very little change in the karst groundwater flow field. In conclusion, karst water-bearing medium in the site is distinguished as extreme anisotropic and heterogeneous. Hence it can be classified as the combination of fissure network and runoff zones type, which has unified hydraulic field. Tracer results indicates that the karst conduits are well developed along the syncline basin axis and the velocity of groundwater is fast in the runoff zone, which can attain 3027.8m/h when the water source in the mining conditions (Pei, 2007). Therefore the convection is predominant in mass transport of the pollutants in the aquifer. Hence the pollutant in the subsurface can move faster and further with the groundwater flow.

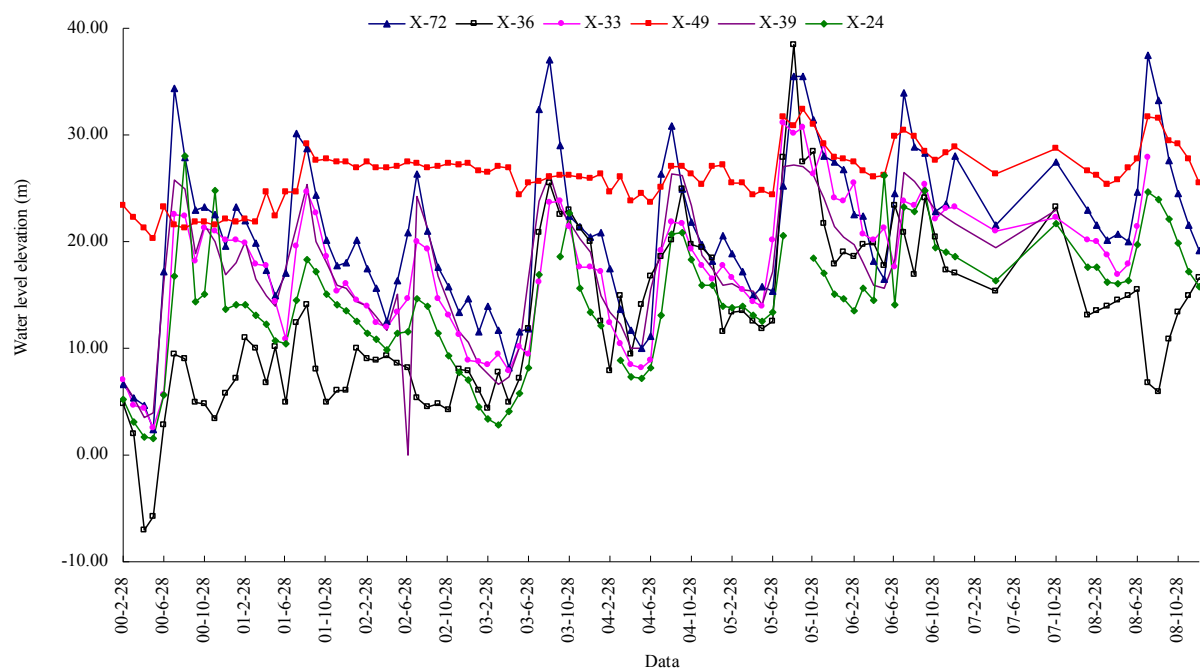


Fig. 7. Variation in piezometric levels in the research region

3. Pollution pathway analysis

3.1 Leakage test

The pesticide plant is located in the hill slope of bedrock. When CCl_4 was first found in November 2000, the drainage ditch running off wastewater was not built. The effluent with high concentrations of CCl_4 could directly leak into the karst aquifer (Fig.8). Under the intervention of provincial environment protection department, the plant built ditch in partial section (Fig.9). Leakage research was conducted to investigate the CCl_4 pollution pathways. Spot S1 to S6 were arranged along drainage ditch for leak off tests (Fig.9). During the flood period of 2001, two tests were performed and the results indicated that the discharged water leakage rate reached approximately 22% and leakage mainly happened in the bare limestone section, namely, effluent with high concentration CCl_4 can flow directly into karst aquifer (Table 2).



Fig. 8. Bare limestone along the wastewater ditch of the pesticide plant

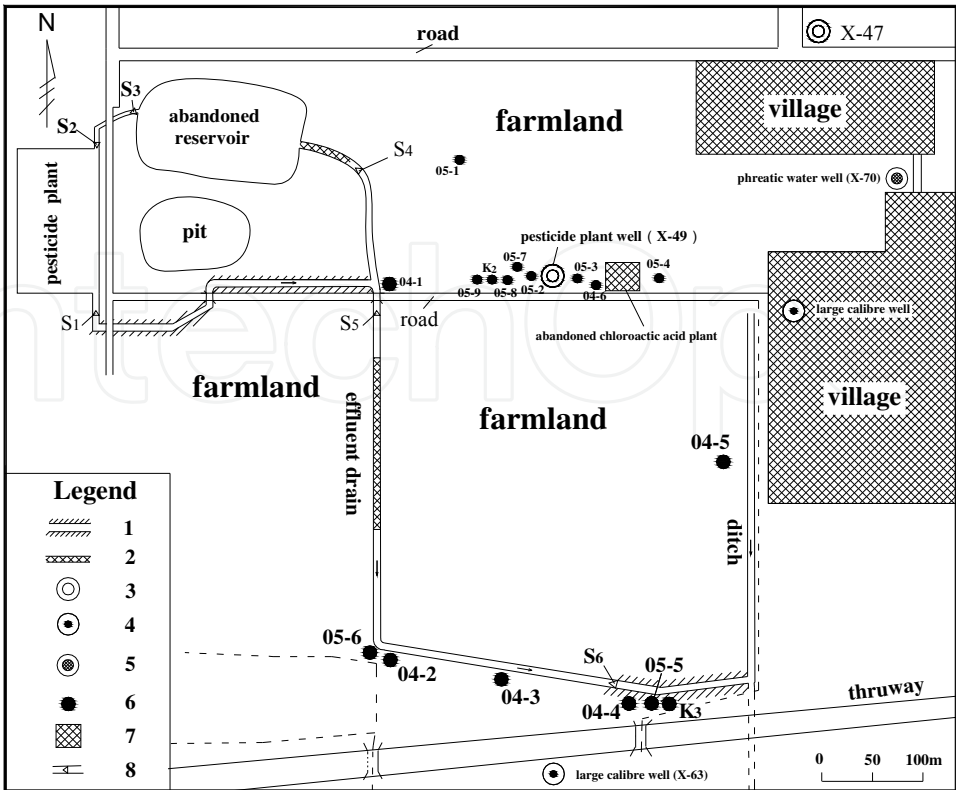


Fig. 9. Boreholes and leakage observation spots location in pollution source sub-area (1, lined ditch; 2, bared limestone; 3, karst groundwater well; 4, large calibre well; 5, phreatic water well; 6, borehole; 7, village; 8, leakage observation spot.)

Observation spot	Distance (m)	Discharge (m³/h)		Leakage rate (%)	
		2001.7.22	2001.8.31	2001.7.22	2001.8.31
S1	1148.0	45.82	45.34	22.10	21.34
S6		35.66	35.66		

Table 2. Results of the leak off tests

3.2 Soil pollution investigation

In order to investigate the feature of effluent leakage into karst aquifer, 17 soil sampling boreholes numbered K2 and K3(2001), 04-1 to 04-6(2004) and 05-1 to 05-9(2005) were drilled with auto-driller (Model: DPP100-3B) and a total 206 soil samples were collected(for locations see Fig. 9). The quaternary deposits are 2.4-10.2m thick. CCl₄ and chloroform were detected in the soil (soil samples of K2 and K3 were analyzed only for CCl₄). CCl₄ was found in the drilling soil along the drainage ditch and nearby the west part of well X-49, and the highest concentration reached 47.1µg/kg (Table 3). The CCl₄ content of soil in the boreholes nearby well X-49, (e.g. 04-6, 05-2, 05-7 and 05-8) are much higher and their highest content is 34.0µg/kg, 42.2µg/kg, 33.5µg/kg and 47.1µg/kg respectively. In general, CCl₄ was found in the soil at depths than 3 meter, and the content increased with the increase of the soil depth. CCl₄ was not detected or was relatively low in the topsoil. Chloroform, the daughter product of CCl₄, was also detected, of which was in the range of 2.6 to 26.5µg/kg. For borehole 04-2, 04-3 and 04-3, the chloroform distribution was larger than that for CCl₄.

Samples with the highest content chloroform were collected from clay-limestone interlayer (depth at 6.5 to 6.7m), intensive weathered igneous rock layer (depth at 9.0 to 9.2m) and fissured clay layer (depth 7.8-8.0m) respectively.

Borehole number	Borehole depth (m)	CCl ₄			Chloroform		
		Detected depth (m)	Content (g/kg)	Depth of maximum content (m)	Detected depth (m)	Content (g/kg)	Depth of maximum content (m)
K2	9.1	0.8-8.7	1.3-2.9	4.6-4.8	NT	NT	NT
K3	6.0	0.8-5.3	1.1-7.7	6.5-7.0	NT	NT	NT
04-2	7.0	1.5-1.7, 6.5-7.0	0.9-2.8	6.5-6.7	5.0-6.7	9.5-19.8	6.5-6.7
04-3	10.5	4.0-6.7	0.7-1.1	5.5-5.7	2.5-10.2	5.3-11.7	9.0-9.2
04-4	9.2	5.0-8.7	0.7-1.1	8.5-8.7	7.8-8.0	15.8	7.8-8.0
04-6	5.0	0.5-4.7	0.7-34.0	4.0-4.2	ND	ND	ND
05-1	8.1	ND	ND	ND	0.5-8.1	5.3-9.2	5.0-5.2
05-2	4.7	2.5-4.7	3.3-42.2	4.0-4.2	0.2-4.7	2.7-26.5	4.0-4.2
05-3	5.7	ND	ND	ND	1.2-5.7	2.7-7.3	1.0-1.4
05-4	6.7	5.5-6.2	1.0-1.8	5.5-5.7	1.0-5.7	2.6-8.0	3.5-3.7
05-6	6.2	ND	ND	ND	0.2-6.2	6.9-11.3	2.5-2.7
05-7	5.7	2.7-4.9	7.6-33.5	4.2-4.4	ND	ND	ND
05-8	5.4	3.2-5.4	1.8-47.1	5.2-5.4	ND	ND	ND

ND- Not detected, NT-Not test.

Table 3. CCl₄ and chloroform contents in the soils

3.3 Pollution pathways

There are three pollution pathways of karst groundwater. Specifically: Wastewater directly entering the karst aquifer in the pesticide plant area (Fig.10); Flowing into the aquifer through bare section of limestone in drainage ditch; and Leaking under ditch by soil (Fig11).

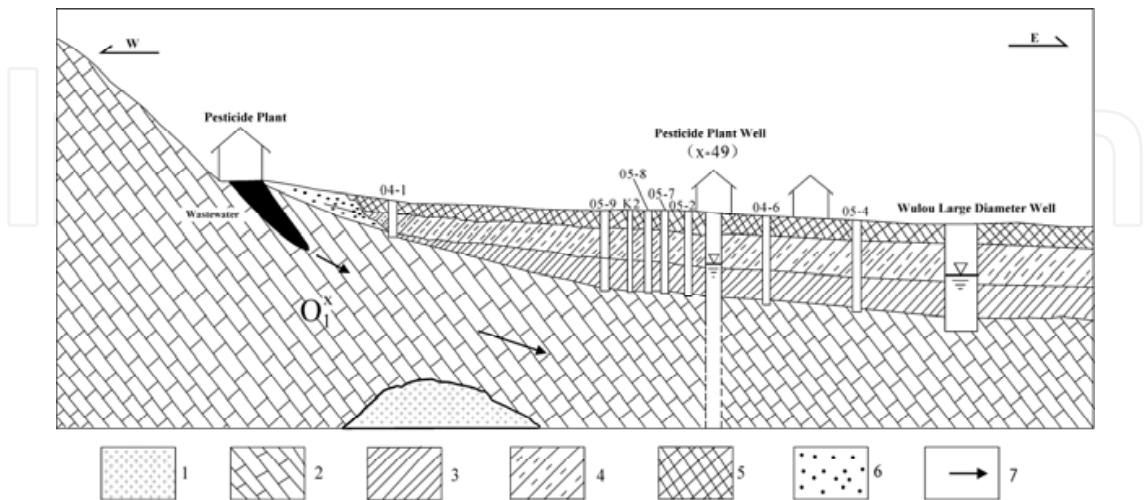


Fig. 10. Generalized pollution pathway of direct seepage into the karst aquifer within the pesticide plant (1. Intrusive igneous rock; 2. limestone; 3. clay; 4. silty clay; 5. cultivated soil; 6. sand; 7. Movement direction of CCl₄)



Fig. 11. Wastewater with CCl₄ seeping *through* the soil *into* the karst aquifer

4. Spatial distribution of CCl₄ in the karst aquifer

4.1 Plane distribution of the CCl₄ plume

The size and shape of the CCl₄ plume in the aquifer was confirmed by multiple samples from multiple water supply wells. In porous media aquifer or unconsolidated aquifer, the plume concentration decreases with the distance from the pollution source. But the plume distribution in the studied site was quite different. Karst conduits develop along preferential pathways between areas of groundwater recharge and discharge. CCl₄ in groundwater was recharged from the southern pollution source and transported into northern supply wells forming a long belt-like plume. Based on CCl₄ concentration data, the contaminated area can be divided into three sub-areas: southern pollution source sub-area, northern sub-area of artificial discharge center and transition sub-area or middle sub-area. The CCl₄ plume in the karst aquifer was "dumbbell" shaped, with high contamination located in the southern and northern sub-area and relatively light concentrations in the middle transitional sub-area, as shown in Fig. 12.

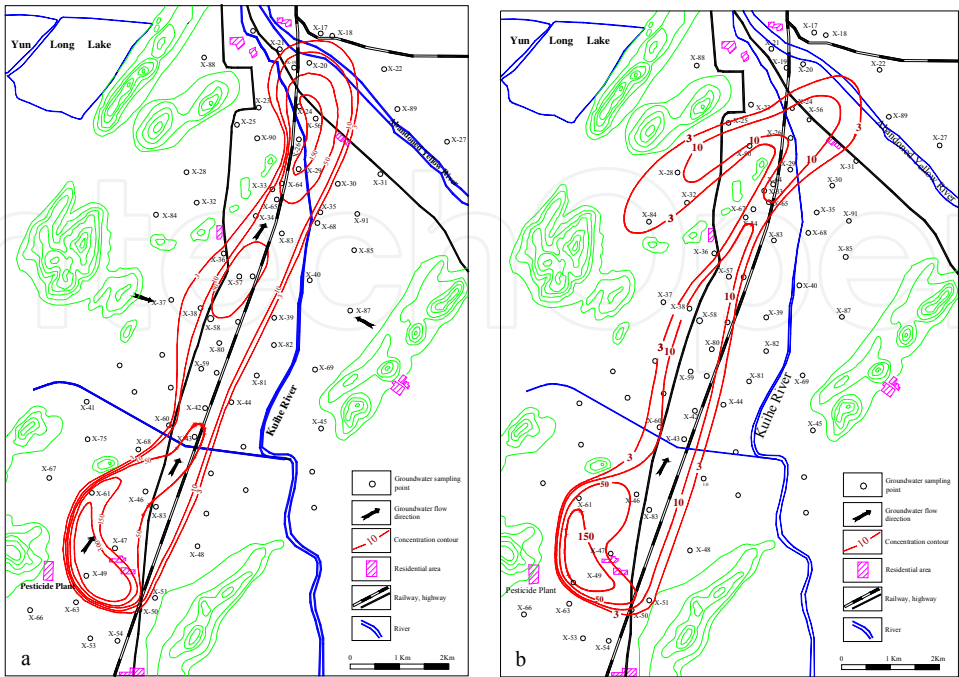


Fig. 12. CCl₄ plume distribution in the karst aquifer (a. 2001-4-18; b. 2008-4-30)

Because of the obstruction of higher-level water in the southern and western parts of the pollution source, polluted water could transport to northern sub-area along well-developed karst conduits. Transition sub-area has formed an obvious depression cone by artificial withdrawal and the water level was about 5.00 m lower than of the southern sub-area. Karst fissures and caves are most well developed in both horizontal and vertical direction in the northern sub-area. Water development experience in past fifty years has revealed this zone is the most water-yielding section and also the most intensive pumping area in the water-bearing basin. Consequently, northern sub-area is the centre of the depression cone and the CCl₄ is accumulated in this area. In the middle sub-area, there is a layer of diabase igneous rock aquifuge at a depth from 100 m to 150 m, which separates the aquifer into two individual layers without hydraulic connection. Because the depth of most wells in the middle sub-area is less than 150 m, CCl₄ concentration of the wells in this sub-area is relative lower.

4.2 Vertical distribution of CCl₄ in the karst aquifer

The high density and low viscosity of CCl₄ cause it to migrate downward until they encounter openings too small to enter. The influence of well depth on the CCl₄ concentration in wells was studied. CCl₄ concentration in Qiligou wells and Sanguanmiao wells increased with the increase of the well depth (Fig. 13). The transport of CCl₄ in the groundwater is controlled primarily with gravity under similar hydro-geological conditions. Therefore, with deeper the wells, there is higher CCl₄ concentration of groundwater is.

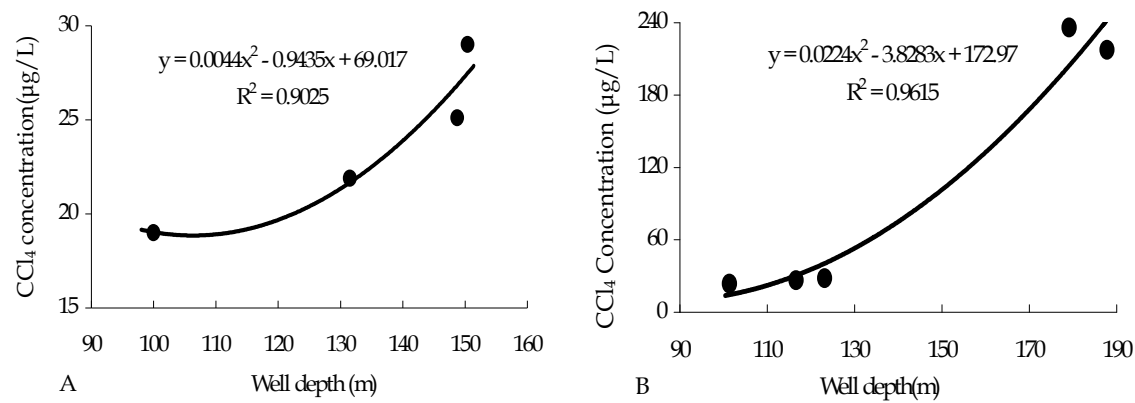


Fig. 13. Relationship between CCl₄ concentration and the well depth (A: Sanguanmiao wells; B: Qiligou wells)

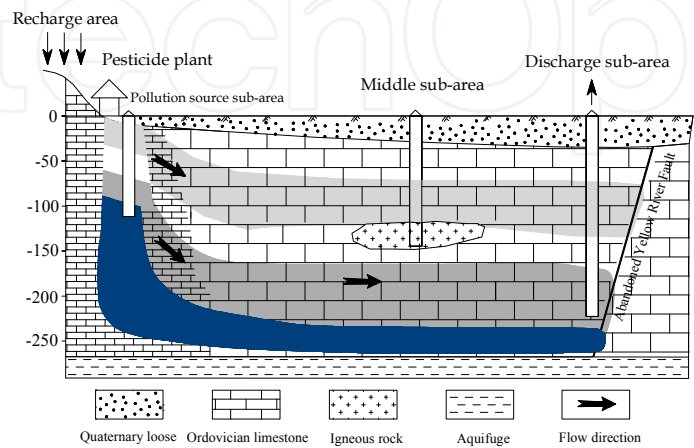


Fig. 14. Conceptual model for CCl₄ transport in the karst aquifer (Han et al., 2004)

According to geologic, hydro-geologic setting and monitoring data of CCl₄ concentration in the past years, transport of CCl₄ in the complex karst aquifer can be generalized as shown in Fig. 14.

5. Temporal change in CCl₄ plume in the karst aquifer

5.1 Temporal change in CCl₄ concentration in the aquifer

The changes in CCl₄ concentration in typical wells are presented in Table 4 and Fig.15. However, there is a general downward trend in concentration, CCl₄ concentration in most of the wells increased in 2010. This may be due to the decrease in groundwater exploitation.

Well		2001		2004		2005		2006		2007		2008		2009		2010	
X-49	25% quantile	n=16	1279.4	n=20	369.6	n=52	90.1	n=29	500.0	n=27	201.3	n=19	146.6	n=12	70.1	n=49	222.3
	50% quantile		1722.6		1662.6		104.6		815.0		264.5		218.3		119.6		272.5
	90% quantile		2584.3		2911.9		681.4		1313.6		620.5		587.9		193.8		627.6
X-61	25% quantile	n=12	181.5	n=20	248.0	n=54	61.8	n=32	17.7	n=27	9.1	n=25	13.0	n=12	20.3	n=55	65.1
	50% quantile		907.7		325.2		96.0		52.2		19.0		21.6		30.4		108.5
	90% quantile		2241.5		609.0		212.7		168.1		163.7		104.0		122.4		152.0
X-47	25% quantile	n=14	59.6	n=20	8.9	n=52	21.6	n=28	18.5	n=27	25.5	n=23	25.0	n=11	8.8	n=49	11.8
	50% quantile		69.0		29.3		68.5		53.4		74.5		48.5		18.4		15.3
	90% quantile		134.8		162.8		216.6		136.6		107.2		116.9		27.7		39.0
X-83	25% quantile					n=53	6.3	n=32	17.8	n=25	14.5	25	16.2	n=12	10.4	n=53	15.5
	50% quantile						25.1		27.3		45.4		24.6		11.3		18.9
	90% quantile						204.0		115.8		78.8		75.7		21.4		29.2
X-59	25% quantile			n=21	14.6	n=56	13.2	n=30	8.8	n=27	10.9	n=25	7.5	n=12	4.9	n=53	20.8
	50% quantile				24.2		23.1		14.0		14.2		11.3		6.5		23.6
	90% quantile				44.6		58.8		39.2		39.5		16.9		19.2		27.7
X-64	25% quantile			n=21	30.0	n=40	22.4	n=29	16.0	n=25	14.4	n=25	11.9	n=12	8.2	n=24	29.8
	50% quantile				40.2		31.0		23.6		16.2		14.4		8.7		33.1
	90% quantile				115.0		67.5		81.2		31.1		28.2		17.4		37.2
X-56	25% quantile			n=20	92.0	n=56	24.5	n=32	13.6	n=27	11.9	n=25	10.9	n=12	8.7	n=48	33.6
	50% quantile				115.8		43.2		23.8		18.1		13.5		9.9		37.8
	90% quantile				196.4		89.1		67.8		27.8		30.0		16.9		45.2

“n” is the number of the samples

Table 4. Summarizes of changes in the average CCl₄ concentrations with time (µg/L)

The Fig. 15 shows that: (1) the CCl₄ concentration in karst auifer has obvious seasonal variation. In general, CCl₄ concentration of groundwater during the drought period from February to June is relative lower and during the rainy period from August to October is much higher. (2) CCl₄ changes rapidly with time, which is notably different from the

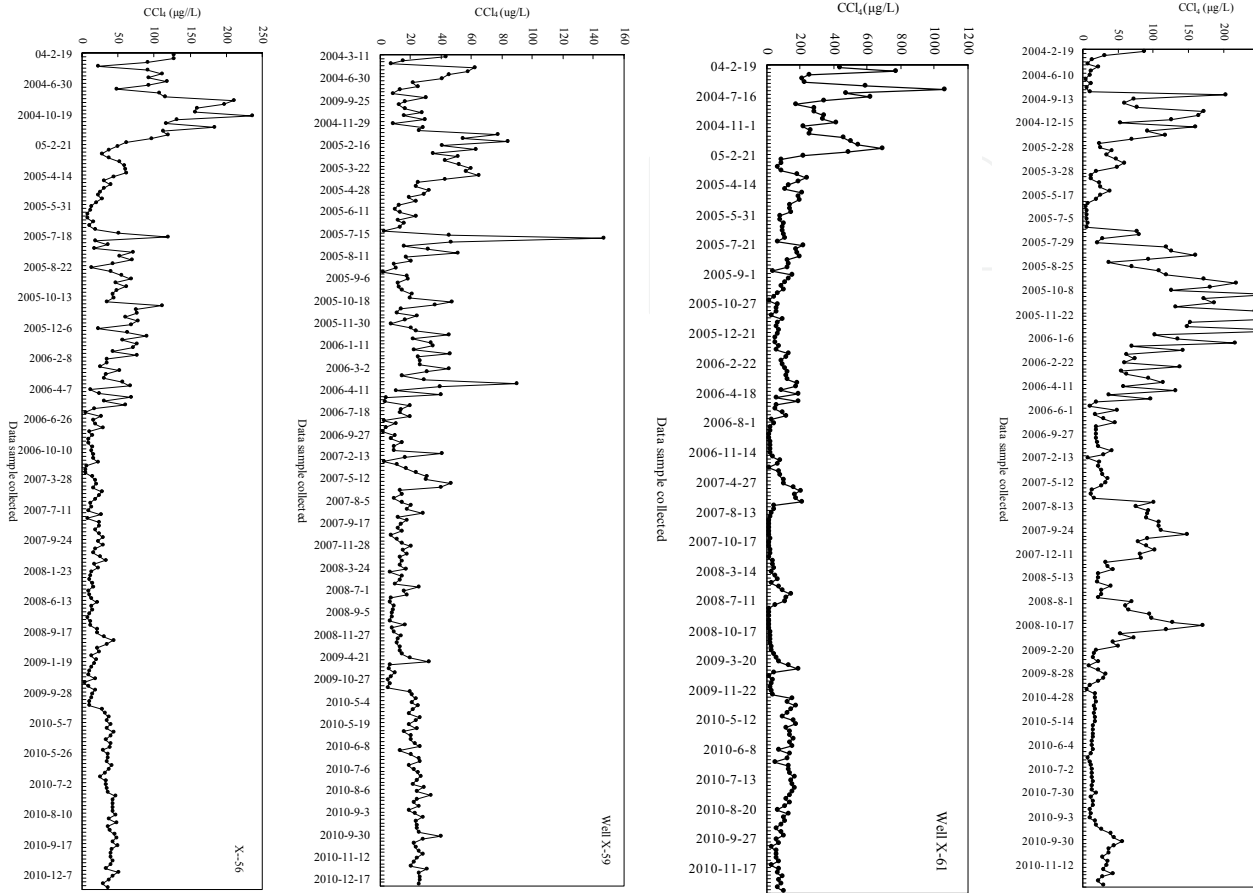


Fig. 15. The variation of CCl_4 over time in typical supply wells

common porous media aquifer. This may be due to the facts that: (1) The groundwater velocity in the aquifer is much higher than that in the porous media, which can reach 131.9m/h-3027.0 m/h. As a result, the advective flow dominates the movement of pollutant; (2) Local groundwater flow regime changed frequently. It was one of the important water supply source with over 80 wells owned by different departments for different purposes. Pump stopping and starting at different wells caused change in local flow field and subsequently cause change in CCl₄ concentration; and (3) CCl₄ transport channel is complex.

5.2 Mann-Kendall trend tests

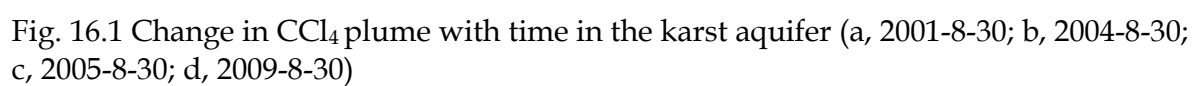
The non-parametric Mann-Kendall test was used to detect monotonic (increasing or decreasing) trends in time-series of CCl₄ concentrations for the eight typical wells during the period 2004-2010. The Mann-Kendall test is widely used in environmental science for the detection of trends in time-series data. A 5% significance level was used to indicate statistically significant trends in the current study. The Mann-Kendall trend statistics (Z) indicates significant decreasing ($Z < -1.96$, $p < 0.05$) and increasing ($Z > 1.96$, $p < 0.05$) trends. Table 5 presents that there are a highly significant decreasing trend in CCl₄ in the karst aquifer and the decreasing trend in pollution source sub-area and the north sub-area area are more significant.

Well	Time	Z	Trend
X-49	2004.02-2010.09	-4.35532	Decreasing, Significant
X-62	2004.02-2010.09	-5.72119	Decreasing, Significant
X-47	2004.02-2010.09	-4.74661	Decreasing, Significant
X-83	2005.02-2010.09	-2.35838	Decreasing, Significant
X-43	2004.02-2008.12	-3.38838	Decreasing, Significant
X-59	2004.02-2010.09	-2.80019	Decreasing, Significant
X-74	2004.02-2010.08	-4.67132	Decreasing, Significant
X-56	2004.02-2010.09	-5.11015	Decreasing, Significant

Table 5. The Mann-Kendall trend statistic (Z, $p < 0.05$) in CCl₄ concentration in typical wells

5.3 Temporal change in CCl₄ plume distribution

The Fig. 16 gives the change in CCl₄ plume over time. In almost ten years, there was very little change in the distribution of CCl₄ in the range of 3-10µg/L or 10-50 µg/L. There was a major reduction in the volume of groundwater containing concentrations between 50 and 300µg/L. The plume extended westward and eastward in northern sub-area to in the flood period every year. It should be noticed that the plume expanded eastward. Based on observed trends in the development of a plume, plumes can be grouped as four categories: expanding, stable, shrinking and exhausted (Rice at al., 1995). In this study, the length of pollution plume of CCl₄ in the water-bearing aquifer was found to be stable while concentration is shrinking, which indicates that the plume decreased faster in concentration than in length. Dynamic groundwater flow field is one of the most important factors controlling the CCl₄ plume (Han et al., 2006). CCl₄ plume in the aquifer is similar with the groundwater flow field, which is shown in Fig. 17. CCl₄ diffusion was confined by higher water level around the plume (Zhu et al., 2008). The scope of seriously polluted wells was similar with the center of cone of depression. CCl₄ concentration in the center of the local cone of depression was higher than that in the wells outside of the center.



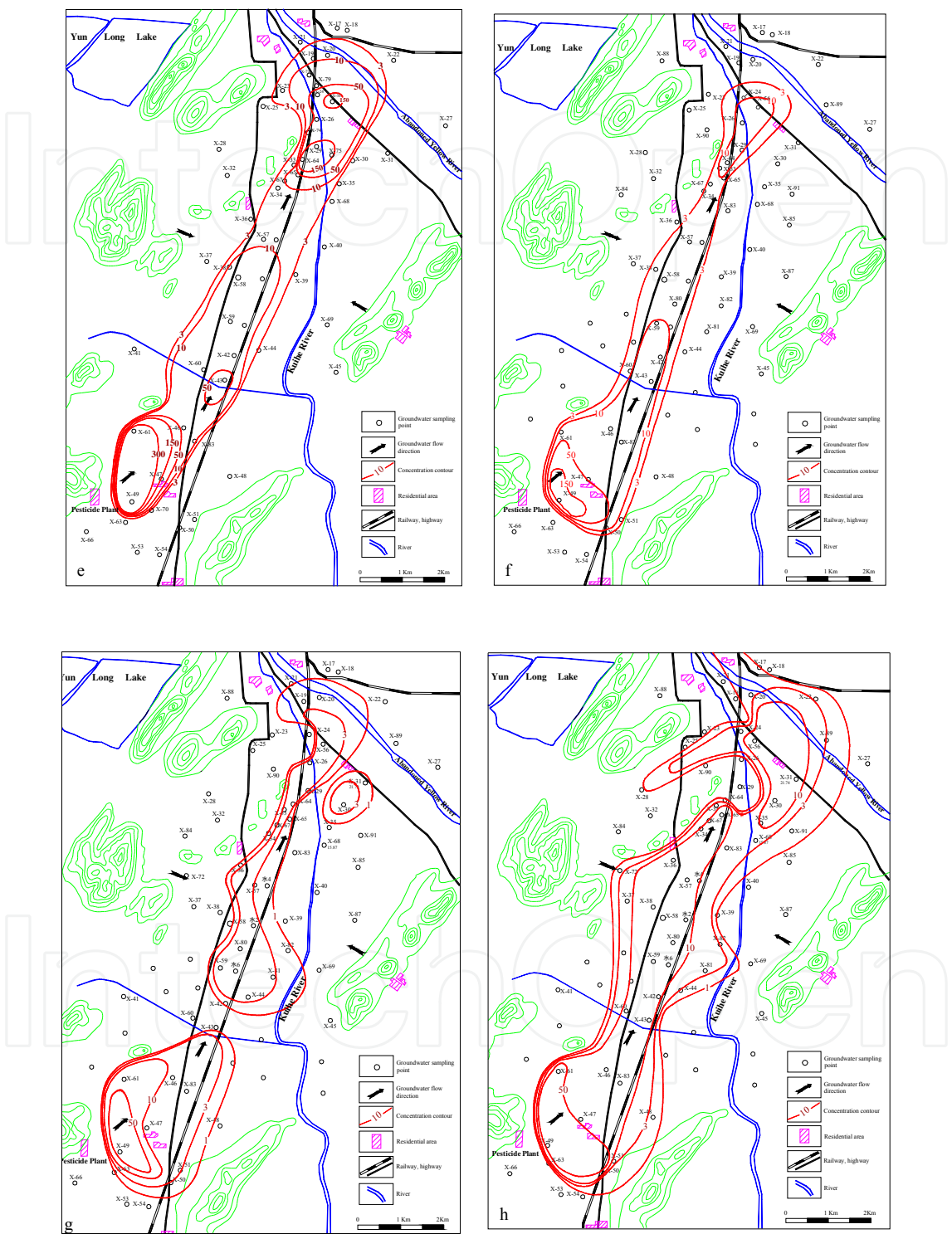


Fig. 16.2 Change in CCl₄ plume with time in the karst aquifer (e, 2004-12-30; f, 2008-12-30; g, 2009-12-30; h, 2010-12-30)

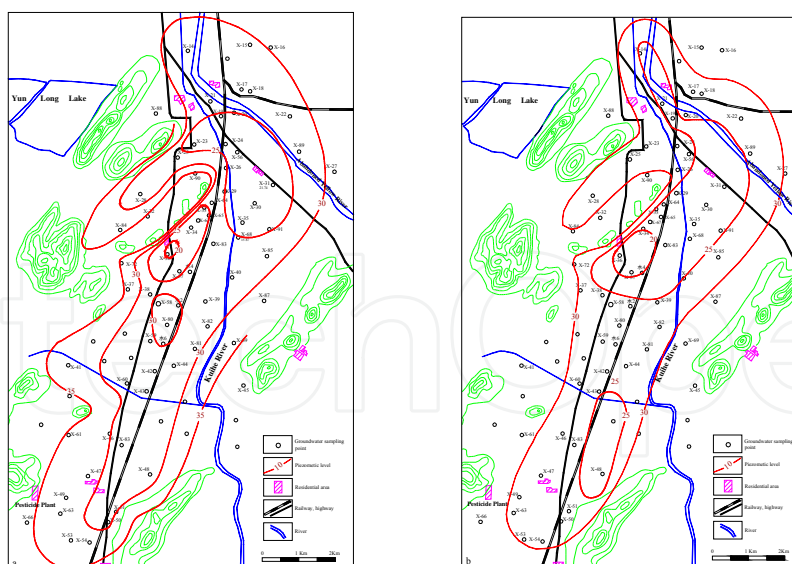


Fig. 17. Contours of the karst aquifer piezometric level (a, 2009-8-30; b, 2009-12-30)

5.4 Factor analysis of CCl_4 attenuation in the Karst aquifer

Concentration of CCl_4 decreased in the karst aquifer because of the influence of CCl_4 fate (volatilization, dilution, adsorption, chemical reaction, biological degradation) and it's difficult to describe CCl_4 attenuation in karst aquifer because of shortage of parameters. The main factors are as follows:

1. Free-phase CCl_4 existence in observation well

Most organics exist as the NAPLs which are the long-term sources of dissolved-phase organics in the aquifer. The EPA found the NAPL was the main-factor that affects the rate of pumping and it's important to determine its existence in the reservation well. Highly-concentration dissolved-organics are barely measured due to the low solubility of NAPL and dilution of reservation well. EPA presents an indirect way to measure the NAPL (1% principle): NAPL will exist if the concentration of chemical materials that related with NAPL was exceeded pure-phase or 1% of valid solubility. The pure-phase CCl_4 solubility is 785 mg/L at 25°C. The CCl_4 has been measured in groundwater at about 3909.9 $\mu\text{g/L}$, which is approximately 0.5 percent of its solubility, suggesting that there is no evidence to determine the CCl_4 NAPL existence.

2. Passive extraction

Passive extraction is the main factor decreasing the concentration of CCl_4 due to the fact that research area was the water supply source in the city with extraction of $2000 \times 10^4 \text{ m}^3/\text{a}$. The groundwater exploitation has decreased dramatically since 2001, however, there are several irrigation wells and industrial wells situated within the contaminated area still in use. It is estimated that the discharge of CCl_4 for 2001, 2004, 2005 and 2008 were 5.42, 1.27, 0.26 and 0.14 tons respectively according to the groundwater exploitation volume and the average CCl_4 concentration (Pei, 2009).

3. Dilution

Convection is one of the most important processes leading to dissolved-phase of contaminants transport in saturation area and concentration decrease. The trace experiment illustrates that convection is the dominant rather than dispersion during CCl_4 transport because of the high flow rate of karst water. Funnel-shape water levels were generated during pumping and the concentration of CCl_4 in reservation wells changed due to the water flow from the aquifer around the well.

4. Volatilization

Contaminants distribution in liquid-gas phase is governed by Henry's law. The trend between liquid phase and gas phase is determined by the Henry's constant. Volatile organics in groundwater could volatilize into atmosphere via soil. The volatilization should be considered if Henry's constant $> 1 \times 10^{-5}$ atm m³/mol and molecular weight < 200 g/mol. Thus the volatilization is dominant in the CCl₄ decrease according to Henry's constant of CCl₄ (2.76×10^{-2} atm m³/mol) and molecular weight (153.82). It is estimated that CCl₄ volatilization for 2004, 2005 and 2008 were 5.38, 9.06 and 4.44 kg respectively (Pei, 2009).

5. Adsorption

Organic matters and clays are the most important factors which contribute to adsorption in aquifer and organic matters are dominant. The adsorption equilibrium of CCl₄ is associated with concentration of organics and K_{OC}. Silva (Silva et al., 2000) indicated that pore filling was main factor in solute distribution. The aquifer in Qiligou has the characteristics of high runoff, intense flash and less pore fillings, due to the high burial depth, long-term exploration and large production, which is shown in Fig.5. Therefore, adsorption has less influence on decrease of CCl₄.

6. Biological degradation

The CCl₄ was transformed into chloroform by biological degradation in the soil. It was manifested by the fact that CCl₄ and chloroform both existed in the soil samples around the pesticide plant and only CCl₄ was founded in the pore water (Zhu et al., 2006). Chloroform was not detected in the wastewater discharged from the pesticide and the karst groundwater. This suggests that the CCl₄ bio-degradation for its attenuation in the karst aquifer can be ignored.

6. Conclusions

In this chapter, the spatial distribution and temporal evolution of CCl₄ in the karst aquifer of a northern city in China were studied through groundwater and soil sampling and testing, groundwater level observation, analysis of water-bearing media, hydrodynamic conditions and artificial exploitation.

1. The water-bearing media is characterized as the multi-system of karstific apertures, fissures and caves. By the control of lithological and geological structure, the karst is extremely heterogeneous.
2. The CCl₄ plume in the karst aquifer was "dumbbell" shaped, with high contamination located in the southern and northern sub-area and relatively light concentrations in the middle transitional sub-area.
3. The concentration of CCl₄ in the aquifer is changed rapidly with time, which is different from the common porous medium aquifer because of the high groundwater velocity in the aquifer and migration channel, complex local flow field and good hydraulic connection. CCl₄ concentration was generally decreasing over time.
4. The length of pollution plume of CCl₄ in the water-bearing aquifer is stable while concentration is shrinking. The attenuation of CCl₄ in the water-bearing aquifer is controlled by passive pumping, volatilization, convection dilution and biodegradation.

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Pesticides in the Modern World - Risks and Benefits

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Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
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Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

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