

# The Health Risk Assessment of CCl<sub>4</sub> in groundwater of a Certain Chemical Plant

Di Liu, Benhua Liu, Hao Zhan

School of resource and Environment, University of JiNan , Ji Nan 250022, China

e-mail address: tech-liubh@sohu.com (Benhua Liu)

**Abstract.** Based on the evaluation method for health risks of contaminated sites recommended by USEPA, in combination with the Chinese habit of drinking boiled water, the author conducted a pollution analysis and health risk assessment of groundwater near the downstream of a chemical plant. The analysis showed that the groundwater had been polluted by CCl<sub>4</sub>, with the highest up to 1732.5 times of the national standard (china) and that the most serious polluted area continued to extend to the downstream with an area of 147174m<sup>2</sup>. Health risk assessment shows that groundwater in contaminated areas is no longer suitable for drinking, and the maximum risk of carcinogenesis is more than 15.1 times of the acceptable level. In addition the main exposure way of carcinogenic risk and non-carcinogenic risk is the drinking absorption. The risk of drinking absorption is about 150 times the risk of skin absorption.

## 1. Introduction

CCl<sub>4</sub> belongs to non-aqueous organic matter and can be present for a long time in groundwater, which is mainly harmful to the central nervous system, liver and kidney of the drinker. In addition, CCl<sub>4</sub> was judged as a carcinogen by the International Cancer Research Center (IARC). In recent years, the groundwater pollution caused by accidents has attracted the attention of society. The spatial distribution of pollutants, the analysis of migration and health risk assessment are important contents of risk management <sup>[1]</sup>.

In 2014, the sewage from a chemical plant was not discharged into the sewage treatment plant, but flowing directly into the ground through a well. Although government departments took urgent measures to reduce pollution, CCl<sub>4</sub> of groundwater was still exceeded. In this paper, the pollution degree, spatial distribution, and health risk of CCl<sub>4</sub> were evaluated, which could provide reference for the next step of groundwater restoration.

## 2. Summary of study areas and pollution analysis

### 2.1. Summary of study areas

In 2016, The survey area is located in the downstream of the chemical plant, with an area of about 3.22 km<sup>2</sup>. There were about 10,000 residents in three villages around the chemical plant, whose mainly sources of domestic water are groundwater. Groundwater flows from the northeast to the southwest, whose depth is 3-5 meters. The variation of the four seasons is obvious, with an average annual rainfall of 790.69 mm (1960-2013). Most of the rainfall is in the period from June to August, reaching 65.5% of the annual precipitation.

As the groundwater flows from the northeast to the southwest, the sampling points are mainly distributed in the downstream area of the chemical plant, a total of 25 (Figure 1).



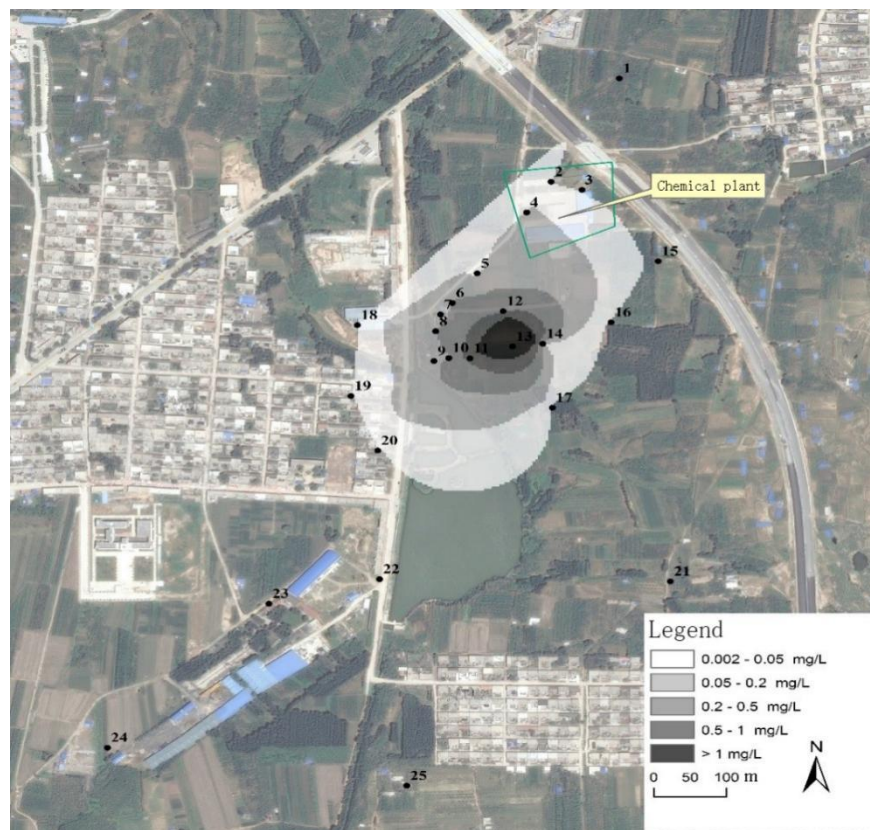


Figure 1. The location of the wells in the study area

### 2.2. pollution analysis

In the 25 wells, 11 wells were detected and the rest were not detected (table1). According to Chinese "groundwater quality standards" (GB/T14848-93), the results indicated that 11 wells exceeded the standard value of 0.002 mg/L, the over standard rate was 37.93%, and the maximum super standard multiple was 1732.5. In ArcGIS, the natural interpolation method was used to make the  $\text{CCl}_4$  spatial concentration pollution map (Figure1). As can be seen from the figure, groundwater had been polluted by  $\text{CCl}_4$ , and that the most serious polluted area continued to extend to the downstream with an area of  $147174\text{m}^2$ .

Table1.  $\text{CCl}_4$  detection value (( $\mu\text{g/L}$ ), quality level, super standard multiple

Well number	4	5	6	7	8	9	10	11	12	13	14
Detection value	61.7	38.4	221.8	138.3	201.2	103.7	170	614.6	354.9	3465	50.2
quality level	V	V	V	V	V	V	V	V	V	V	V
Super III multiple	30.9	19.2	110.9	6.9	100.6	51.9	85.0	307.3	177.5	1732.5	25.1

## 3. Health risk assessment

### 3.1. Carcinogenic toxicity

$\text{CCl}_4$  is a carcinogenic toxic and hazardous substances, which has a buildup effect in the mammalian body and has a damaging effect on the liver of fish and frogs. When the content of  $\text{CCl}_4$  exceeds the standard value in the human body, it can stimulate the human eye, respiratory tract, damage the human liver and kidney, make people collapse, syncope in severe cases, and even make people die due to respiratory failure [2].

### 3.2. Exposure analysis a calculation

The pollutants in groundwater generally entered the body through direct drinking and skin contact, both of which can reach 90% of the total [3]. In combination with local residents' living habits, there are two main ways of exposure of local residents. way1: drinking contaminated groundwater and absorbed by the oral; way2: contacting contaminated groundwater and absorbed by the skin. In addition, the amount of CCl<sub>4</sub> respiration is ignored because the amount of respiration is small and the concentration in the air is too low to be measured.

Due to the volatility of CCl<sub>4</sub>, most of the CCl<sub>4</sub> will evaporate during the heating process, which reduces the concentration of CCl<sub>4</sub> to a great extent. At the same time, the results of the health risk assessment are more sensitive to the change of the concentration. Therefore, the calculation method of CCl<sub>4</sub> adopts the formula which was put forward by Whelan and Droppo [4]. In addition, in combination with the Chinese habit of drinking boiled water, the formula to add a TF (residual ratio of pollutants after evaporation). The residual ratio of CCl<sub>4</sub> is 0.1, Reference Han Bing's research [5].

Way1: drinking contaminated groundwater and absorbed by the oral

$$CDI_{\text{Drinking absorption}} = \frac{\rho \times TF \times U \times EF \times ED}{BW \times AT}$$

Way2: contacting contaminated groundwater and absorbed by the skin

$$CDI_{\text{skin contact}} = \frac{I \times A_{sd} \times EF \times FE \times ED}{BW \times AT \times f}$$

$$I = 2 \times 10^{-3} \times k \times TF \times \rho \times \sqrt{\frac{6 \times \tau \times TE}{\pi}}$$

Most of the evaluation parameters in the above formula refer to the recommended value of USERA . The rest of the parameters related to living habits are estimated value based on local habits rather than accurate statistics. (See Table 2 )

Table 2. Evaluate the parameter name, unit, symbol, and value

Symbol	Unit and name	Value
$\rho$	Concentration of contaminants in water / ( $\text{mg} \cdot \text{L}^{-1}$ )	Measured
$EF$	Exposure frequency / ( $\text{d} \cdot \text{a}^{-1}$ )	365
$BW$	Body weight /kg	60
$U$	Daily drinking water / ( $\text{L} \cdot \text{d}^{-1}$ )	2
$ED$	Exposure cycle (carcinogenic) / $\text{a}^{-1}$	70
$ED$	Exposure cycle (non-carcinogenic) / $\text{a}^{-1}$	30
$AT$	Average exposure time (carcinogenic) /d	25550
$AT$	Average exposure time (non-carcinogenic) /d	10950
$A_{sd}$	Body surface area / $\text{cm}^2$	16600
$FE$	Bath frequency / (times $\cdot$ d-1)	0.5
$\tau$	Delay time/h	0.76
$TE$	Bath time/h	0.3
$k$	Skin Adsorption Parameters/ ( $\text{cm} \cdot \text{h}^{-1}$ )	0.001
$\pi$	Pi / dimensionless	3.14
$f$	intestinal adsorption ratio / dimensionless	1
$I$	The amount of adsorbent per unit area of the bath per unit ( $\text{mg} \cdot \text{cm}^{-2} \cdot \text{times}^{-1}$ )	Calculated
$RfD$	Non-carcinogenic reference dose/( $\text{mg} \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$ )	0.0007
$SF$	Carcinogenic slope factor/( $\text{mg}^{-1} \cdot \text{kg} \cdot \text{d}$ )	0.13

### 3.3. Risk calculation

The carcinogen not only has carcinogenic effects, but also has non-carcinogenic effects, so carcinogenic and non-carcinogenic risk of CCl<sub>4</sub> should be calculated [6].

#### (1) Non-carcinogenic risk

It is generally believed that organisms have a dose threshold for non-carcinogenic substances, which have a negative effect, When it more than dose threshold, the non-carcinogenic risk is usually expressed by the risk index ( $HI$ ). the formula:  $HI=CDI/RfD$ . The total non-carcinogenic risk of a single substance is equal to the sum of the non-carcinogenic risks of each way. For non-carcinogenic risk, the risk value of 1 is an acceptable upper limit, if greater than 1, it causes harm to the human body; if less than 1, the non-carcinogenic risk is acceptable.

#### (2) carcinogenic risk

It is generally believed that carcinogenic substances have no dose threshold on the organism and will pose a hazard to the organism if it is present in a trace amount. Calculated as follows:

Low dose exposure: Risk = CDI×SF

High dose exposure: Risk=1-exp (-CDI×SF) (if the low dose calculation value> 0.01, then for this formula).

The total carcinogenicity risk of a single substance is equal to the sum of the carcinogenic risks of each way. For carcinogenic risk, the USEPA evaluation guideline states that the risk value is acceptable in the range of  $10^{-6}$ - $10^{-4}$ , more than  $10^{-4}$  is unacceptable and can cause harm to the human body.

RfD and SF in the above formula are the recommended value of the USEPA (table2). The calculated values of non-carcinogenic risk and carcinogenic risk are shown in Table 3.

Table 3. CCl<sub>4</sub> risk of carcinogenesis and non-carcinogenic

Well number	Carcinogenic risk			Non-carcinogenic risk		
	Way1	Way2	Total risk	Way1	Way2	Total risk
4	2.67E-05	1.46E-07	2.69E-05	0.2938	0.0016	0.2954
5	1.66E-05	9.07E-08	1.67E-05	0.1829	0.0010	0.1839
6	9.61E-05	5.24E-07	9.66E-05	1.0562	0.0058	1.0619
7	1.54E-04	8.38E-07	1.55E-04	1.6900	0.0092	1.6992
8	8.72E-05	4.75E-07	8.77E-05	0.9581	0.0052	0.9633
9	4.49E-05	2.45E-07	4.52E-05	0.4938	0.0027	0.4965
10	7.37E-05	4.01E-07	7.41E-05	0.8095	0.0044	0.8139
11	2.66E-04	1.45E-06	2.68E-04	2.9267	0.0159	2.9426
12	6.00E-05	3.27E-07	6.03E-05	0.6586	0.0036	0.6622
13	1.50E-03	8.18E-06	1.51E-03	16.5000	0.0899	16.5899
14	2.18E-05	1.19E-07	2.19E-05	0.2390	0.0013	0.2404

### 3.4. Evaluation

In the detected 11 wells, there are three wells (11, 12,13) of groundwater carcinogenic risk exceeds the maximum acceptable level of  $10^{-4}$ . The maximum cancer risk value was 1.51E-03 in the No. 13 well, which is 15.1 times the maximum acceptable level, which means that 15 out of every 10,000 people suffer from cancer due to groundwater. At the risk of non-carcinogenic, four wells (6, 11, 12, 13) exceeded the maximum acceptable level of 1, accounting for 36.36% of the detected wells. The non-carcinogenic risk is also reached at maximum in the No. 13 well, more than 16.59 times. In the unacceptable wells (6, 11, 12, 13) of risk value, the ratio of carcinogenic and non-carcinogenic risks in both pathways was plotted (figure 2). As shown in the figure, the risk of drinking is about 150 times the risk of skin contact, reaching more than 99% of the total risk. So CCl<sub>4</sub> mainly through the way 1 (drinking absorption) into the body.

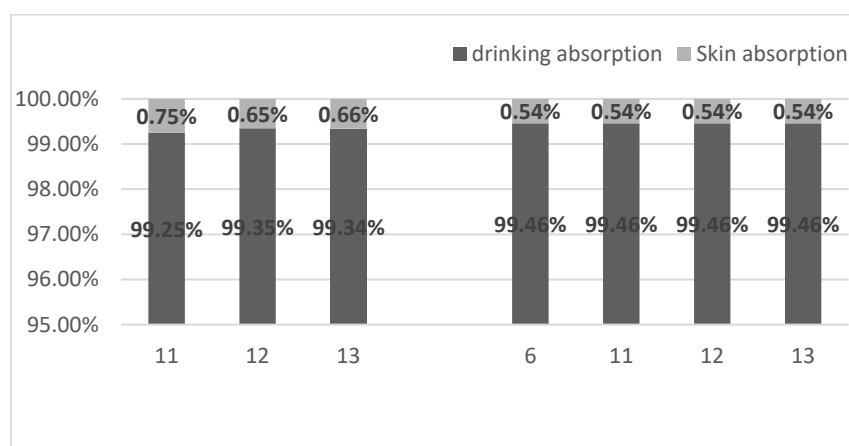


Figure 2. Risk ratio chart of two ways

#### 4. Conclusions and recommendations

(1) The area contaminated with carbon tetrachloride is located mainly in the downstream area of the chemical plant with an area of about 147 174m<sup>2</sup>. In the 11 detected wells, most of the drinking carcinogenic risk reached or approached the maximum limit of  $10^{-4}$ , so the contaminated area of groundwater is not suitable for drinking. Because the risk of carcinogenic and non-carcinogenic of skin contact are within acceptable limits, local residents can still contact groundwater of contaminated areas, such as bathing ,irrigation and so on. Due to the volatility of CCl<sub>4</sub>, it is recommended to use boiled water as much as possible to reduce its risk.

(2) Considering the risk of downstream residents, the relevant departments should help the local residents gradually use tap water instead of groundwater. In addition, some of the parameters used in the evaluation are estimates rather than accurate statistics, which may make the risk inaccurate. As the CCl<sub>4</sub> in the air is not easy to determine, the impact of CCl<sub>4</sub> in the air on the human body is ignored, so that the total risk value is low.

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