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Health Risk Assessment of Groundwater Pollution—A Case Study of Typical City in North China Plain

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ABSTRACT: This article presents an application of assessing human health risk in typical city of North China plain. Combined with water quality and multi-element analysis, Pb, Cd, Cr^{6+}, Mn, NO_3^-, F^-, and As in groundwater samples were chosen to be used for human health risk assessment of drinking water pathway and dermal contact pathway, and results show a good effect. Results indicate that (1) poor water quality is caused by salinity and hardness overstandard; (2) in noncarcinogenic risk, samples that do not pose noncarcinogenic risk only account for 28.46%; in carcinogenic risk, samples that do not pose carcinogenic risk account for 73.08%; (3) the noncarcinogenic risk in the study area decreased in the following order: NO_3^->Mn>As>F^->Cr^{6+}>Cd>Pb and the carcinogenic risk of the study area decreased in the following order: As>Cd=NO_3^-=Mn=F^-=Cr^{6+}=Cd=Pb=0, because the slop factors were not available for the other pollutants, except for As; and (4) in terms of whole study area, the main contribute order of drinking water pathway and dermal contact pathway in human body is drinking water pathway>dermal contact pathway.

KEY WORDS: groundwater, water composition, assessment system, inorganic pollutant, human health.

INTRODUCTION

Groundwater is widely used for ideal water supply in North China plain. Generally speaking, groundwater cannot be polluted easily because it is buried under the ground. Therefore, groundwater pollution has the characteristics of difficult to find and control. Once contaminated, it must pay cost for treatment and remediation (Morgenstern et al., 2000).

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However, in recent years, with the rapid development of the society and the accelerated development of industrialization, urbanization, and agricultural modernization, impacts of human activities have caused groundwater pollution to a great degree (Chenini et al., 2008; Mohammed et al., 2008; Zhu and Yang, 2008; White et al., 2003; de Vries·Ian Simmers, 2002). Pollutants can be dispersed and accumulated in humans by consumption of water. Human health risk assessment has been used to determine if exposure to a chemical, at any dose, could cause an increase in the incidence of adverse effects to human health (Li et al., 2008). As a result, people are concerned more about the relationship between human health and groundwater pollution than pollution itself, so health risk assessment is particularly important.

For those purposes, guidelines for assessment of groundwater pollution have been published. In recent years, risk assessment procedures used for determining the need for remediation or redevelopment actions at contaminated sites have become especially well developed and documented (U.S. EPA, 1989). Health risk assessment steps were defined as four steps specifically by the U.S. National Academy of Sciences (NAS) in 1983, which consisted of four stages: (1) hazard identification, (2) toxicity (dose-response) assessment, (3) exposure assessment, and (4) risk characterization, had been widely recognized in academic fields and "Cancer Guide" was published in 2005 (http//:www.cfpub.epa.gov/ncea/raf/recordisplay.cfm; U.S. EPA, 1992). In the current work, the study of environmental risk assessment had been carried out in the United Kingdom, the Netherlands, Italy, Canada, Australia, New Zealand, Japan, and Chinese Taipei. Several real health risk assessment system had been built for its own country combined with the assessment method of the United States (LSW, 2003; CCME, 2001; Cushman et al., 2001; NEPC, 1999; Krishnan et al., 1997).

At present, most studies in China have focused on the health risk of drinking water pathway, and there is little research considering both drinking water pathway and dermal contact pathway, which is mainly the introduction and application research results of abroad (Dong et al., 2008; Han et al., 2006; Qiu and Wang, 2003; Pi et al., 2001; Hu, 2000; Tian, 1999; Zeng et al., 1998; Yang, 1996). It does not have a complete human health risk assessment approach as well as evaluation index system of pollutants itself in China, especially in human health risk assessment of groundwater pollution. Appropriate management of water-bearing basins is critical for country development. Health risk assessments of large-scale areas are urgently needed (Li et al., 2010).

The current health risk assessment system in China has three problems: (1) the evaluation model is too influx; (2) the evaluation exposure route is singleness, especially in human health risk assessment; and (3) the evaluation content has no innovations. To achieve more reliable risk analysis for decision-making, this article reports a case study of an integrated risk analysis to estimate the human health risk in the study area.

STUDY AREA

The study area is one of the most and oldest developed regions in North China plain. Heavy industrial development and fast urbanization have resulted in significant water pollution. It has limited water supply, and the deterioration of water quality has hastened the shortage of water resources, especially for groundwater. Therefore, great attention should be paid to the impacts on human health caused by groundwater pollution.

The study area is located in the northeast of North China plain, and its ground elevation is mostly 10 to 50 m, and surface gradient is about 0.6‰. It belongs to warm and humid-semi-humid climate zone with four different seasons. During many years, mean annual temperature is 12.5 ℃, mean annual rainfall stands at 500 to 750 mm, and mean annual evaporation is 1 775 mm. The precipitation infiltration coefficient is about 0.3, and the groundwater runoff modulus is about 10 to 150 000 $m^3 \cdot a^{-1} \cdot km^{-2}$. The aquifer, which mainly consists of fine sand and the medium sand, is a multilayer structure and the single-layer thickness ranges from 4 to 14 m. Groundwater is mainly Quaternary pore water and karst water. Total area of catchments is 1 150 km^2, which contains exposed karst area of 38 km^2 and hidden surface karst area of 1 112 km^2.

DATA AND METHODOLOGY

Sample Collection and Results of Testing

In 2009, 130 groundwater samples were collected, and the distribution of the samplings is shown in Fig. 1. As a result, 7 kinds of contaminants were determined in groundwater samples because their concentrations were completely high and maybe they would do harm to people's health. The purposes of this study were (1) to investigate the contamination levels of these contaminants and (2) to assess the total risk of health effects to humans.

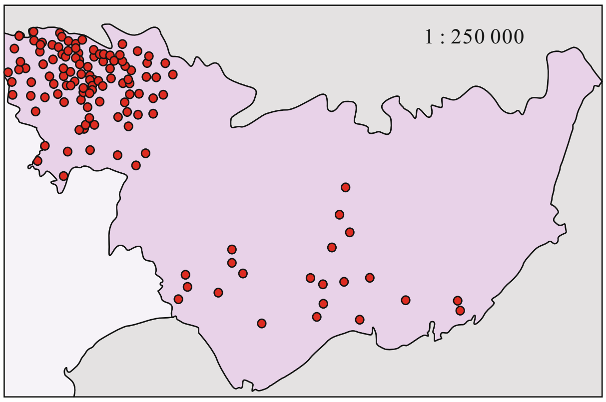

Figure 1. Distribution of samples in study area. Map scale of 1 : 250 000 had been marked (Land and Resources Survey Program of China).

All the collection work was subjected to strict quality-control procedures of "Geological Survey Assessment of Groundwater Pollution Norms". Nitric acid of 1 : 1, Watson's pure water, marked with "standard solution" (preparation of standard solution must be in strict accordance with GB/T601 "Chemical Preparation of Standard Solution Reagent"), freezers, incubators, sampling apparatus and equipment, labels, disposable gloves, and non-phosphorus detergent were prepared before sampling. The calibration and cleaning of instrument were carried out in accordance with instructions. Seven indexes such as temperature, water temperature, pH, conductivity, redox potential, dissolved oxygen, and turbidity should be measured directly on field. Samplers should be washed with detergent apparatus after completing each sampling. At each sampling point, water sample was collected in 500 mL plastic bottles for trace elements analysis with 3 mL nitric acid (1 : 1) added and water sample was collected in 1 L plastic bottles for full analysis without any reagent added. All samples were refrigerated at <4 ℃. All chemical analytical results of this study were performed by quality-control system, which includes reagent blanks and replicate samples. Sampling workers may not smoke and should operate at the downwind.

The materials of sampling well casing and pumping were TFE (PTFE), carbon steel, low carbon steel, galvanized steel, and stainless steel. There must be a valve on the drainage pipe of lift pump, and the distance from valve to well could not be farther than 30 m. If drainage pipe was installed with valve on the branch, and the distance from outfall to branch pipe was farther than 2 m, the PTFE-lined PE hose (polyethylene) would be connected to the branch directly, and a stainless steel tube with about 350 mm length and 5 mm diameter would be connected to the other end of sampling tube (Fig. 2a). If drainage pipe was installed with valve on the branch, but distance from outfall to branch pipe was shorter than 2 m, a section of tube should be installed to extend connect the distance from outfall to sampling tube more than 2 m (Fig. 2b).

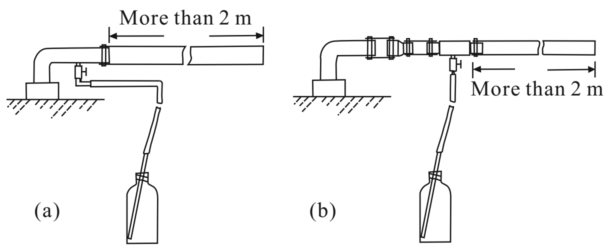

Figure 2. Connection examples for sampling pipes. (a) Connection examples for sampling pipes; (b) connection examples for sampling pipes.

In all test indexes, 27 of inorganic indexes were indispensable: total dissolved solids, total hardness, potassium permanganate index, metasilicate, nitrate, nitrite, ammonium ion, sulfate, carbonate, heavy carbonate, chloride ions, fluoride, iodine ion, sodium, potassium, calcium, magnesium, iron, manganese, lead, zinc, cadmium, hexavalent chromium, mercury, arsenic, selenium, and aluminum; 20 selected index for special area: volatile phenol (in phenol dollars), cyanide, anionic synthetic detergent (water sources indispensable), sulfide (special districts indispensable), total phosphorus, bromine, total chromium, copper, barium, beryllium, molybdenum, nickel, boron, antimony, silver, and thallium.

Samples were tested by Groundwater Mineral Water and Environmental Supervising and Testing Center of the Ministry of Land and Resources and Tianjin Institute of Geology and Mineral Resources, which had already passed the quality of certification and verification by China Geological Survey Bureau. The test instruments and types were atom absorption spectrophotometer Hitachi Z-5000, Hitachi 180-80, and WFX-IE3; ion chromatograph: Dionex ICS-1500 and ICS-2500; and atomic fluorescence spectrometer XGY1012. Advanced equipment and high level of professional workers provided a powerful guarantee of the accurate determination for samples. Seven kinds of typical inorganic contaminants that harmful to human health were selected, and testing results are presented in Table 1, because their concentrations were completely high and maybe they would do harm to people's health.

When compared with the permissible levels set by the People's Republic of China for environmental quality standards for groundwater standard (GB/T 14848-93) (Table 2), the levels of contaminants of most sampling sites attained the second or fourth level. However, groundwater in the southern site attained the fifth level. The salinity of shallow groundwater was comparatively high, so poor water quality was caused by salinity and hardness overstandard (Table 2).

The concentration of NO_3^- in 34% of the sampling sites exceeded the third level (≤20) by 1.2 times and the highest concentration was 226 mg/L; the concentration of Mn exceeded the third level (≤0.1) by 30 times and the highest concentration was 3.00 mg/L; the highest F^- concentration was 2.96 mg/L, which exceeded the target level (≤1.0) by 3 times; and the highest Cr^{6+} concentration was 0.73 mg/L, which exceeded the target level (≤0.05) by 14 times. In addition, the highest concentration for Cd was 7.54 μg/L.

Industrial uses of water may also affect water quality in study area. The survey result demonstrates that wastewater comes from domestic use and mixed sources (including industrial sources and agricultural sources). The industries that produce sewage are mainly distributed in the northern, eastern, northwest urban, and southern suburb of the city. Their discharge includes food production, papermaking, chemical fertilizer, brewage, mineral dressing, and so on. As a result, the concentration levels of those contaminants are completely high.

Overall, the main factors for groundwater pollution in study area is mainly geological, geomorphological, and hydrogeological conditions. This makes contaminants in upper area enter the aquifer through infiltration; thus, the shallow groundwater is polluted seriously.

Exposure Dose Calculation

The *CDI* value indicates the quantity of chemical substance ingested, inhaled, or absorbed through the skin per unit body weight per unit time ($mg \cdot kg^{-1} \cdot d^{-1}$). In accordance with the assessment system, this paper calculated the amount of exposure dose in ingested route and inhaled route (e.g., U.S. EPA, 1989). The parameters in *CDI* formulas are presented in Tables 3 and 4.

The formulas and parameters are as follows.

Drinking water pathway

$$CDI = \frac{\rho_i \times U \times EF \times ED}{BW \times AT} \tag{1}$$

where *CDI* is exposure expressed as mass of a substance contacted per unit body weight per unit time ($mg \cdot kg^{-1} \cdot d^{-1}$); ρ_i is contamination concentration in water (mg/L); and U is ingestion rate per unit time water (L/d).

Dermal contact pathway

$$CDI = \rho_i \times K_i \times S_A \times \frac{EF \times ED \times EV \times CF}{BW \times AT} \tag{2}$$

where *CDI* is exposure expressed as mass of a substance contacted per unit body weight per unit time ($mg \cdot kg^{-1} \cdot d^{-1}$); ρ_i is contamination concentration in water (mg/L); K_i is dermal adsorption parameters (cm/h); S_A is body surface areas (cm^2); EV is bathing frequency (times/d); and CF is unit conversion factors (L/cm^3).

Health Risks Calculation

Risk characterization was considered separately for carcinogenic and noncarcinogenic effects and included a discussion of factors that may result in either an overestimation or an underestimation of the risks

Table 1 The summary of typical contaminants' monitoring concentration in research area

Item number	Pb	Cd (ug/L)	Mn	Cr^{6+}	NO_3^-	F^-	As (mg/L)	Total hardness	Salinity
YM001	<0.01	0.032	254	0.001 6	0.39	0.77	0	447	642
YM002	0	0.048	0.34	0.002 2	174	0.58	0	487	780
YM003	0.01	0.078	0.14	0.002	179	0.63	0	494	832
YM004	0	0.037	<0.010	0.002 6	99	1.14	0	456	572
YM005	0	0.051	0.2	0.004 2	181	0.76	0	443	792
YM006	0	0.052	0.16	0.004 6	101	1.5	0	436	579
YM007	0	0.028	0.14	0.002 4	29	1.12	0	405	518
YM008	0	0.13	1 750	0.000 3	0.98	1.02	0.003	1 190	1 840
YM009	0.011	0.064	5.26	0.000 6	45.9	0.84	0	462	860
YM010	0	0.072	1.9	0.001 7	258	0.81	0	490	1 000
YM011	0.056	0.079	0.62	0.003	80.7	0.58	0	347	534
YM012	0	0.13	1.18	0.002 6	124	0.52	0	514	889
YM013	0	0.14	1.39	0.047	94.9	0.55	0	351	966
YM014	0	0.2	1.64	0.003	650	0.43	0	734	1 440
YM015	0.031	0.068	1.76	0.004 8	60.7	0.5	0	401	746
YM016	0.088	0.16	921	0.003	170	0.48	0	434	793
YM017	0.05	0.06	2.68	0.004 2	78.4	0.57	0	361	494
YM018	0.052	0.22	1 430	0.004 6	98.6	0.58	0	730	1 340
YM019	0.12	0.093	1.92	0.003 2	142	0.55	0	437	758
YM020	0.067	0.097	1.14	0.003 4	145	0.65	0	420	734
YM021	0.051	0.053	1.21	0.005 4	74.6	0.59	0	320	458
YM022	0.11	0.062	0.89	0.002	83.1	0.66	0	424	619
YM023	0.11	0.11	1.36	0.007 4	98.3	0.51	0	514	838
YM024	0.051	0.072	1.24	0.003	98.1	0.54	0	341	416
YM025	0.067	0.098	1.1	0.003	157	0.76	0	419	674
YM026	0.05	0.12	1.77	0.001 6	154	0.72	0	488	770
YM027	0.18	0.076	1.1	0.005 4	81.2	0.42	0	298	402
YM028	0.072	0.1	1.12	0.005 8	31.7	0.52	0	272	406
YM029	0.21	0.054	1.17	0.004 2	17.5	0.52	0	254	380
YM030	0.09	0.058	1.54	0.003 4	0.79	0.47	0	193	296
YM031	0.068	0.1	20.5	0.001 5	0.62	0.45	0	445	520
YM032	0.075	0.1	16.5	0.003 4	5.98	0.4	0	371	468
YM033	0.068	0.037	0.93	0.011	59.3	0.94	0	266	372
YM034	0.051	0.062	1.17	0.014	92.4	0.73	0	286	495
YM035	0.097	0.12	1.13	0.018	92.2	0.75	0	329	506
YM036	0.033	0.082	1.14	0.017	137	1.01	0	333	614
YM037	0.06	0.022	0	0.008 8	48.3	1.5	0	252	415
YM038	0.12	0.006	0.14	0.008 8	46.3	1.56	0	238	396
YM039	0.025	0.021	0	0.011	34	0.91	0	243	540
YM040	0.04	0.033	0.083	0.011	71.6	0.76	0	297	522
YM041	0.019	0.029	0	0.019	42.1	0.81	0	276	474
YM042	0.12	0.039	0.8	0.012	18	0.73	0	427	839
YM043	0.008	0.018	0	0.009 6	35.2	0.68	0	259	606
YM044	0.026	0.011	0	0.007 6	87.8	1.13	0	251	462

Continued

Item number	Pb	Cd (ug/L)	Mn	Cr^{6+}	NO_3^-	F^-	As (mg/L)	total hardness	salinity
YM045	0	0.058	411	0.005 2	168	1.01	0	458	1 240
YM046	0	0.002	79.4	0.01	1.89	0.85	0.006	164	312
YM047	0.006	0.01	2.76	0.006 2	26	2.04	0	340	970
YM048	0	0.005	18	0.004 8	0.83	1.12	0	146	324
YM049	0	0.007	68.3	0.012	28.6	1.17	0	194	508
YM050	0.011	0.015	1.3	0.008	50.6	0.84	0	210	418
YM051	0.067	0.088	2 060	0.014	0.91	1.12	0	570	1 430
YM052	0.09	0.048	192	0.011	1.7	1.55	0	352	802
YM053	0.13	0.019	2.78	0.012	154	1.68	0	316	692
YM054	0.11	0.034	0.92	0.014	103	1.7	0	244	680
YM055	0.068	0.015	0.43	<0.004	67.2	0.8	0.002	318	314
YM056	0.032	0.042	0.55	<0.004	62.7	0.53	0.003	318	298
YM057	0.036	0.13	0.53	<0.004	61	0.52	0.015	929	1 700
YM058	0.12	0.04	0.33	<0.004	119	0.52	0.003	349	406
YM059	0.13	0.037	2.28	<0.004	80.2	0.3	0.002	258	371
YM060	0.1	0.012	0.3	<0.004	45.2	1.01	0.002	214	194
YM061	0.034	0.03	0.16	<0.004	84.9	0.48	0.002	316	294
YM062	0.094	0.055	0.3	<0.004	153	0.47	0.002	494	540
YM063	0.11	7.54	73 600	<0.004	96	0.34	0.001	4 340	4 900
YM064	0.027	0.047	23.1	<0.004	65.6	0.76	0.002	488	639
YM065	0.087	0.016	1.02	<0.004	32.7	0.79	0.006	278	270
YM066	0.036	0.046	7.18	<0.004	206	0.58	0.002	544	782
YM067	0.07	0.077	20.4	<0.004	222	0.56	0.001	758	1 050
YM068	0.056	0.078	0.46	<0.004	207	0.82	0.003	611	960
YM069	0.028	0.032	0.25	<0.004	122	0.58	0.001	420	483
YM070	0.034	0.054	0.61	0.005	219	0.52	0.002	556	810
YM071	0.12	0.058	0.48	<0.004	184	0.52	0.002	464	676
YM072	0.11	0.019	260	<0.004	52.7	0.62	0.007	304	378
YM073	0.11	0.025	92.8	<0.004	1.25	1	0.002	127	88
YM074	0.072	0.018	380	<0.004	1.02	0.52	0.014	183	183
YM075	0.21	<0.01	174	<0.004	1.63	0.58	0.005	115	90
YM076	0.099	0.068	3.77	<0.004	215	0.34	0.005	492	746
YM077	0.11	0.054	2.45	<0.004	168	0.28	0.002	445	640
YM078	0.063	0.033	0.51	<0.004	86.1	0.32	0.004	252	320
YM079	0.063	0.033	0.51	<0.004	79.8	0.44	0.001	266	302
YM080	0.067	0.11	30.6	<0.004	159	0.52	0.001	814	1 110
YM081	0.068	0.031	0.88	0.007	82.2	0.47	0.003	401	520
YM082	0.05	0.051	0.43	<0.004	130	0.48	0.003	353	424
YM083	0.13	0.061	206	<0.004	202	0.27	0.005	627	1 090
YM084	0.18	0.012	107	<0.004	<0.046	0.59	0.006 5	111	68
YM085	0.079	0	67.5	<0.004	<0.046	0.48	0.006	194	257
YM086	0.058	0	109	<0.004	<0.046	0.5	0.13	200	604
YM087	0.07	0.057	384	<0.004	2.73	0.48	0.004	806	2 080
YM088	0.032	0	99.6	<0.004	<0.046	0.59	0.009	198	286
YM089	0.23	0	96.5	<0.004	<0.046	0.58	0.003	195	274

Continued

Item number	Pb	Cd (ug/L)	Mn	Cr^{6+}	NO_3^-	F^-	As (mg/L)	Total hardness	Salinity
YM090	0.018	0.012	2.29	<0.004	44	0.44	0.003	260	394
YM091	0.026	0.057	0.74	<0.004	167	0.54	0.004	504	874
YM092	0.044	0	0.56	<0.004	48.2	0.6	0.003	238	314
YM093	0.036	0.11	3.79	<0.004	258	0.47	0.002	586	1 290
YM094	0.061	0.12	1 610	<0.004	8.31	0.64	0.005	998	1 710
YM095	0.16	0.14	411	<0.004	93.4	0.66	0.007	1 120	1 950
YM096	0.092	0.14	52	<0.004	409	0.93	0.015	952	2 220
YM097	0.058	0.11	2 330	<0.004	0.17	0.62	0.004	792	1 760
YM098	0.028	0.047	177	<0.004	8.97	0.67	0.003	340	608
YM099	0.046	0.027	467	<0.004	0.25	0.58	0.003	405	1 450
YM100	0.073	0.25	3 090	<0.004	<0.046	0.49	0.001	1 390	2 800
YM101	0.003	<0.01	2.049	<0.004	0.74	0.52	<0.01	2 407	1 582
YM102	0.009	<0.01	<0.010	<0.004	135	0.2	<0.01	1 164	588.5
YM103	0.01	<0.01	0.305	<0.004	15.7	0.34	<0.01	1 186	634.4
YM104	0.006	<0.01	1.153	<0.004	22.6	0.44	<0.01	1 337	734.3
YM105	0.009	<0.01	0.273	<0.004	3.1	0.28	<0.01	851.4	551.4
YM106	0.003	<0.01	0.113	<0.004	2	0.76	<0.01	1 552	274.4
YM107	0.008	<0.01	0.247	<0.004	13.2	0.3	<0.01	867.4	492
YM108	0.008	<0.01	0.369	<0.004	12.9	3.5	<0.01	1 201	316.5
YM109	0.002	<0.01	0.105	<0.004	2.9	0.1	<0.01	479	191.4
YM110	0.003	<0.01	0.198	<0.004	2.8	0.22	<0.01	482.8	165.7
YM111	0.004	<0.01	0.218	<0.004	1.5	0.26	<0.01	466.1	202.7
YM112	0.014	<0.01	0.112	<0.004	2.4	0.26	<0.01	499.6	190.4
YM113	0.004	<0.01	0.091	<0.004	3.9	0.48	<0.01	510.1	121.2
YM114	0.004	<0.01	0.063	<0.004	1.7	0.46	<0.01	466.2	101.4
YM115	0.004	<0.01	0.252	<0.004	2.4	0.34	<0.01	559.2	175.6
YM116	0.003	<0.01	0.09	<0.004	2.7	0.36	<0.01	473.6	136
YM117	0.006	<0.01	0.065	<0.004	1.9	0.22	<0.01	484	131
YM118	0.013	<0.01	0.106	<0.004	1.8	0.4	<0.01	450.5	91.48
YM119	0.013	<0.01	0.074	<0.004	3.6	0.34	<0.01	468.9	91.48
YM120	0.017	<0.01	1.141	<0.004	6.72	NA	<0.01	1 366	613.2
YM121	0.007	<0.01	0.032	<0.004	0.96	0.22	<0.01	415.9	89.01
YM122	0.008	<0.01	0.024	<0.004	1.28	0.34	<0.01	460.9	74.17
YM123	0.005	<0.01	0.638	<0.004	510	0.42	<0.01	9 231	1 652
YM124	0.009	<0.01	0.032	<0.004	1.68	0.76	0.01	590.7	19.78
YM125	0.005	<0.01	0.114	<0.004	<0.046	0.74	<0.01	304.6	121.2
YM126	0.01	<0.01	0.374	<0.004	<0.046	2	0.038	501.9	222.5
YM127	0.007	<0.01	0.067	<0.004	239.5	NA	0.016	1 195	593.4
YM128	0.006	<0.01	0.184	<0.004	3.68	0.96	0.046	414.6	226.5
YM129	0.005	<0.01	0.016	<0.004	0.72	1.2	0.045	477.4	39.56
YM130	0.008	<0.01	0.517	<0.004	0.6	0.3	<0.01	1 157	581

"0" means the detectable concentration is zero; "<0.01" means below the detection limit concentration; NA. not available.

Table 2 People's Republic of China for environmental quality standards for groundwater standard (GB/T 14848—93) (mg/L)

Item	Cr^{6+}	Pb	F^-	NO_3^-	Mn	As	Cd	Total hardness (calculated by $CaCO_3$)	Salinity
First level (1)	≤0.005	0.005	≤1.0	≤2.0	≤0.05	≤0.005	≤0.000 1	≤150	≤300
Second level (2)	≤0.01	≤0.01	≤1.0	≤5.0	≤0.05	≤0.01	≤0.001	≤300	≤500
Third level (3)	≤0.05	≤0.05	≤1.0	≤20	≤0.1	≤0.05	≤0.01	≤450	≤500
Forth level (4)	≤0.1	≤0.1	≤2.0	≤30	≤1.0	≤0.05	≤0.01	≤550	≤1 000
Fifth level (5)	>0.1	>0.1	>2.0	>30	>1.0	>0.05	>0.01	>550	>2 000

Table 3 Toxicological characteristics of the main pollutants in study area

Pollutants	Non-carcinogenic reference dose ($mg \cdot kg^{-1} \cdot d^{-1}$)			Carcinogenic slope factors ($mg^{-1} \cdot kg \cdot d$)			Carcinogenic
	Drinking water pathway	Dermal contact pathway	Inhalation pathway	Drinking water pathway	Dermal contact pathway	Inhalation pathway	Classifications
Pb	0.001 4	NA	NA	NA	NA	NA	Non-carcinogenesis
Cd (in water)	0.000 5	0.000 005	NA	NA	NA	6.3	Non-carcinogenesis
Cr^{6+}	0.003	0.000 06	0.000 029	NA	NA	42	Non-carcinogenesis
Mn (in water)	0.046	0.001 84	0.000 014	NA	NA	NA	Non-carcinogenesis
NO_3^-	1.6	0.8	NA	NA	NA	NA	Carcinogenesis
F^-	0.1	NA	NA	NA	NA	NA	Carcinogenesis
As	0.000 3	0.000 123	NA	1.5	3.66	15.1	Carcinogenesis

NA. Not available.

Table 4 The reference parameters of all pollutants (U. S. EPA, 2003)

Parameters	Meaning	Value	Unit
EF	Exposure frequency	365	d/a
ED	Exposure duration	Non-carcinogens is 30 (namely 10 950 d); Carcinogens is 70 (namely 25 550 d)	a
BW	Body weight	70	kg
AT	Average exposure time	Non-carcinogens is 30 (namely 10 950 d); Carcinogens is 70 (namely 25 550 d)	a
U	Ingestion rate	2	L/d
S_A	Body surface areas	16 600	cm^2
EV	Bathing frequency	1	time/d
CF	Unit conversion factor	0.002	L/cm^3
K_i	Dermal adsorption	0.001	cm/h

for study area (Table 3). Potential noncarcinogenic risks for exposure to contaminants of potential concern were evaluated by comparison of the estimated contaminant intakes from each exposure route (oral, dermal) with the reference dose (RfD) to produce the hazard quotient (HQ), defined as follows (U.S. EPA, 1989).

Following the above-mentioned formula, exposure doses were calculated based on associated calculation of the risks, and the formulas are as follows.

Noncarcinogenic Risks

$$HQ=CDI/RfD \quad (3)$$

where *HQ* is hazard quotient (unitless) and *RfD* is reference dose ($mg \cdot kg^{-1} \cdot d^{-1}$). To assess the overall potential for noncarcinogenic effects posed by more than one chemical, the *HQ*s calculated for each chemical are summed and expressed as a *HQ* (U.S. EPA, 1989).

$$HQ=HQ_1+HQ_2+\ldots+HQ_n \quad (4)$$

In cases where the *HQ* does not exceed unity ($HQ<1$), it is assumed that no chronic risks are likely to occur at the site. If the *HQ* were greater than unity as a consequence of summing several *HQ*s, it would be appropriate to segregate to compounds by effect and by mechanism of action and to derive separate *HQ*s for each target organ group (U.S. EPA, 1989).

Carcinogenic Risks

Carcinogenic risks were estimated as the incremental probability of an individual developing cancer over a lifetime as a result of exposure to a potential carcinogen; the following linear dose carcinogenic risk equation was used for each exposure route (e.g., U.S. EPA, 1989).

Low-dose exposure $\quad Risk=CDI \times SF \quad (5)$

High-dose exposure $\quad Risk=1\text{-}\exp(-CDI \times SF) \quad (6)$

where *Risk* is cancer risk and *SF* is cancer slope factor of contaminants $(mg \cdot kg^{-1} \cdot d^{-1})^{-1}$. If the calculated value is higher than 0.01, then take the formula (6) instead. If it has multiple carcinogenic contaminants, cancer risks for each carcinogen and each exposure route are added (assuming additives of effects) and compared with the accepted risk. *Risk* in the range of 10^{-6} to 10^{-4} typically is to be acceptable by the Chinese (U.S. EPA, 1992a, b, 1991). Parameters of chemical and toxicological properties of typical contaminants in study area are shown in Table 3.

ANALYSIS AND DISSCITION

Noncarcinogenic Risks

Figure 3 shows the results of noncarcinogenic risk for the study area. The combined *HQ* value for all contaminants ranged from 0.081 to 99.40 (Fig. 3a), and the highest risk *HQ* was 99.40 at YM063 and the lowest risk *HQ* was 0.081 at YM121. The results indicated that for noncarcinogenic risk there might be 71.54% samples that exceeded the limit level of 1.0 in study area, and only 28.46% did not pose noncarcinogenic risk. The distribution of noncarcinogenic risk index classification and formation of noncarcinogenic risk index classification are shown in Figs. 3b and 3c.

For exposure routes

Figures 3a and 4 present the total noncarcinogenic risk value of all the samples for two exposure routes in study area. As shown in Fig. 4a, drinking water pathway was assumed to be the main exposure route of pollutants to humans in the risk assessment, which is a probabilistic distribution pie of two parts, including drinking water pathway that accounts for 77.01% and dermal contact pathway that accounts for 22.99%. These probability results suggest that drinking water pathway contributes to increasing the noncarcinogenic risk of the residents in study area. It can be initially speculated that it may be associated with characteristics of pollutants themselves.

For pollutants

For each sample, most of the total risk *HQ* did not exceed the permissible level, but after concentration addition of the same contaminant in all 130 samples, the *HQ* becomes relatively high (Figs. 5a–5c).

As shown in Fig. 5a, *HQ* value for all contaminants ranged from 1.334×10^{-1} to 1.951×10^{2}. The main source of risks associated with noncarcinogenic substances was contributed by NO_3^- from oral and dermal exposure. The highest total noncarcinogenic risk was 1.951×10^{2} and the lowest total noncarcinogenic risk was 1.334×10^{-1}. The *HQ* order of the main contaminants decreased in the following order: $As>F^->Cr^{6+}>Cd>Pb$, and their risk values were 1.951×10^{2}, 1.176×10^{2}, 5.005×10^{1}, 2.521×10^{1}, 1.215×10^{1}, 4.102, and 1.334×10^{-1}, respectively.

Figure 5b shows statistical graph of noncarcinogenic risk for dermal contact pathway, and *HQ* value for all contaminants ranged from 0.000 to 6.105×10^{1}. The *HQ* order of the main contaminants decreased in the following order: $Mn>NO_3^->Cr^{6+}>As>Cd>F^-=Pb$, and their risk values were 6.105×10^{1}, 1.551×10^{1}, 8.305, 4.767, 3.330, 0.000, and 0.000, respectively. The results demonstrate that, in dermal contact pathway, Mn posed the highest noncarcinogenic risk value

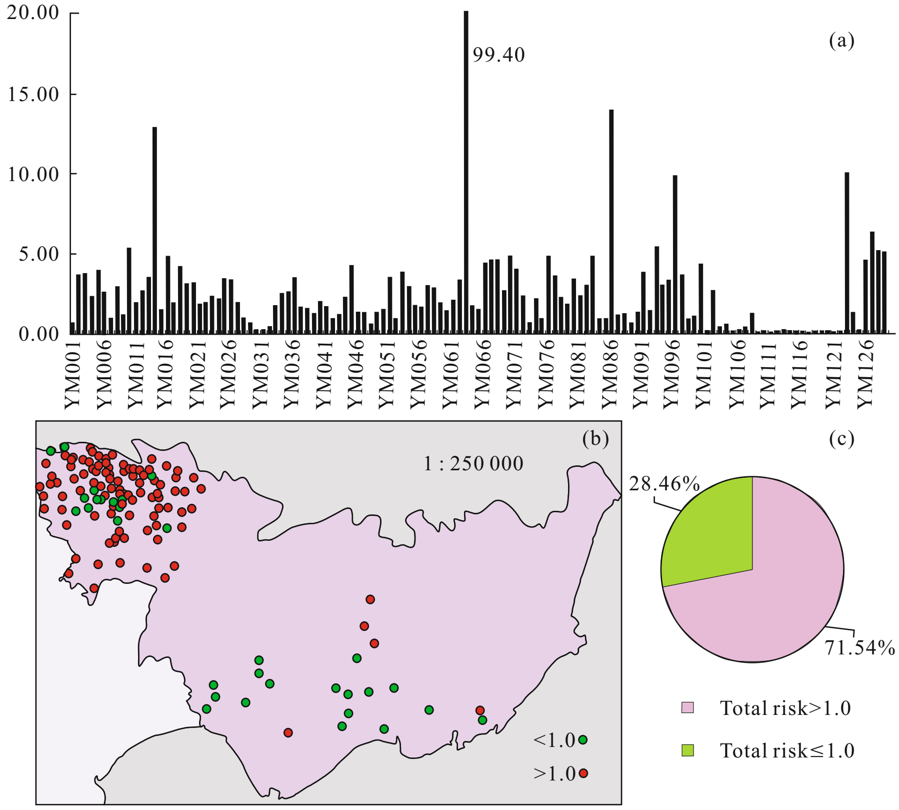

Figure 3. Formation of health risk for all exposure routes in study area. (a) Formation of noncarcinogenic risk for all exposure routes in study area (Map scale of 1 : 250 000 had been marked); (b) distribution of noncarcinogenic risk index classification; (c) formation of noncarcinogenic risk index classification.

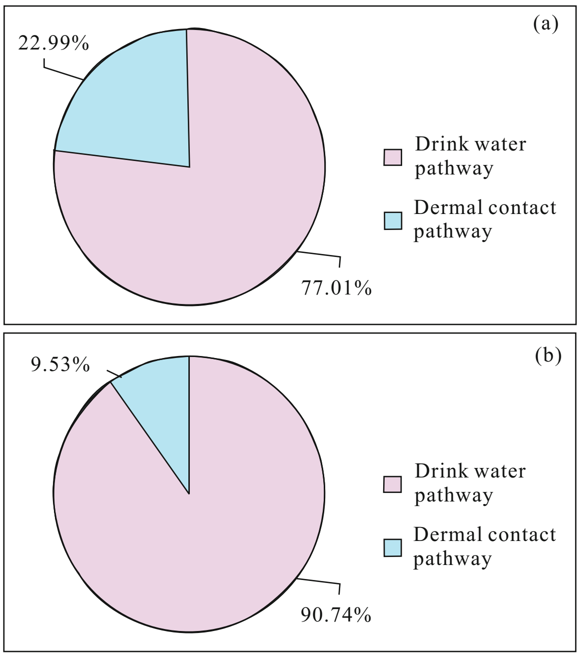

Figure 4. Risk index classification of all samples. (a) Statistical graph of total noncarcinogenic risk for all samples; (b) statistical graph of total carcinogenic risk for all samples.

of 6.105×10^{1}. Therefore, for one thing, great attentions should be paid to Mn; for another, the monitoring for samples should be strengthened and appropriate measures should be taken to remove Mn in water for reducing the harm.

Figure 5c shows statistical graph of noncarcinogenic risk for drinking water pathway, and *HQ* value for all contaminants ranged from 1.334×10^{-1} to 1.796×10^{2}. The *HQ* order of the main contaminants decreased in the following order: NO_3^->Mn>As>F^->Cr^{6+}>Cd>Pb, and their risk values were 1.796×10^{2}, 5.658×10^{1}, 4.529×10^{1}, 2.521×10^{1}, 3.849, 7.715×10^{-1}, and 1.334×10^{-1}, respectively. Therefore, drinking water pathway of NO_3^- in groundwater is considered to pose the greatest risk to human health in this area, and only Cd and Pb did not exceed the permissible noncarcinogenic risk limit level of 1.0.

Carcinogenic Risk

Only oral and dermal potential carcinogenic risks from exposure to the water of As were evaluated because the slope factors for other contaminants were

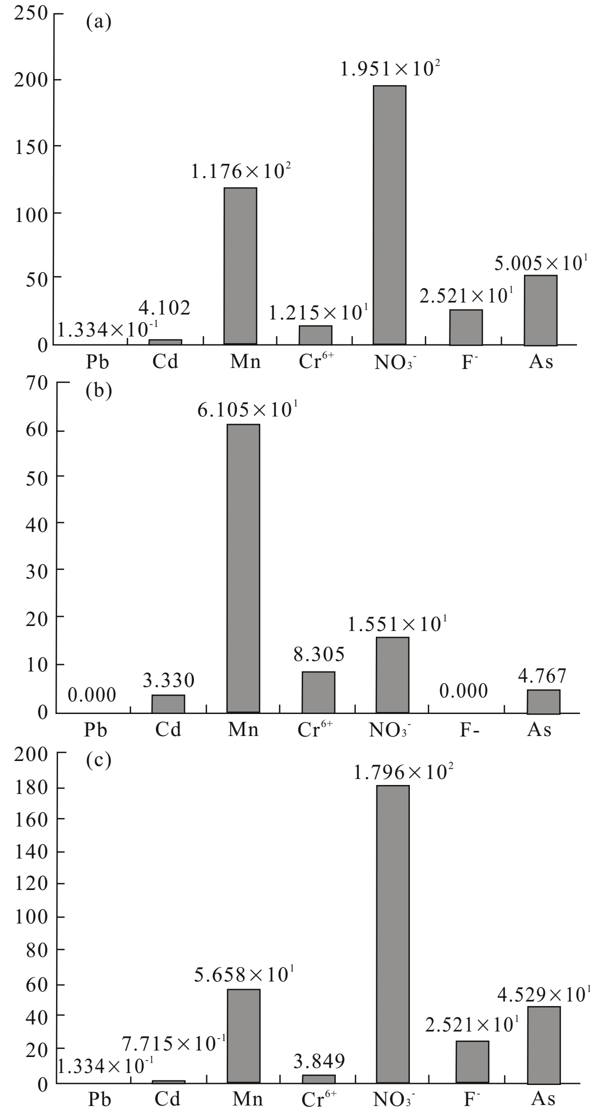

Figure 5. Statistical graphs of the noncarcinogenic risk indexes of all samples. (a) Statistical graph of total noncarcinogenic risk for all contaminants in study area; (b) statistical graph of noncarcinogenic risk for dermal contact pathway; (c) statistical graph of noncarcinogenic risk for drinking water pathway.

not available. The potential carcinogenic risk from oral and dermal risk exposure to As was 0.000 to 6.200×10^{-3} (Fig. 6a). The highest level was at YM086, which was 6.200×10^{-3}. Figures 6b and 6c demonstrate the percentages of carcinogenic risk indexes for all samples, which is a probabilistic formation pie of two parts, including intervals $>10^{-4}$ and $\leq10^{-6}$–10^{-4}, respectively. It shows that, for all samples, samples that do not pose carcinogenic risk account for 73.08% and all the other 26.92% pose carcinogenic risk.

For exposure routes

Figures 4b and 6a present the total carcinogenic risk value of all the samples for three exposure routes in study area. Figure 4b shows that drinking water pathway covers the largest portion of the whole carcinogenic risk distribution, which accounts for 90.47%. The proportion for dermal contact pathway is 9.53%. Therefore, these probability results suggest that drinking water pathway contributes to increasing the carcinogenic risk of the residents in study area. Although these harms are potential chronic, it should be paid attention to.

Figures 6d and 6e show the total carcinogenic risk value of As for dermal contact pathway and drinking water pathway, respectively. For dermal contact pathway (Fig. 6d), the samples' number of risk value was 0, between 10^{-6} and 10^{-4}, and exceeded the limit level of 10^{-6} to 10^{-4} was 77, 49, and 4, respectively. For drinking water pathway (Fig. 6e), the samples' number of risk value was 0, between 10^{-6} and 10^{-4}, and exceeded the limit level of 10^{-6} to 10^{-4} was 77, 18, and 35, respectively.

For pollutants

Only oral and dermal potential carcinogenic risks from exposure to the water of As were evaluated because the slope factors for other contaminants were not available. But these did not mean that all the others did not pose carcinogenic risk. The potential carcinogenic risk from oral and dermal risk exposure to As was 0.000 to 6.200×10^{-3} (Fig. 6a). For all samples, the samples' number of risk value was 0, between 10^{-6}–10^{-4} and exceeded the limit level of 10^{-6}–10^{-4} was 77, 18 and 35, respectively.

CONCLUSIONS

When comparing health risk assessments all over the world, the human health risk assessment system in typical city of North China plain provides a good example for groundwater contaminated site and also provides a practical experience to establish a workable risk assessment system for groundwater pollution.

Through application of health risk assessment system of groundwater pollution in typical city of North China plain, some conclusions have been drawn as follows.

(1) In an overall pattern of investigation and analyzing of study area, seven kind pollutants of Pb, Cd, Cr^{6+}, Mn, NO_3^-, F^-, and As were identified in 130 groundwater samples. The water quality and multi-element analysis

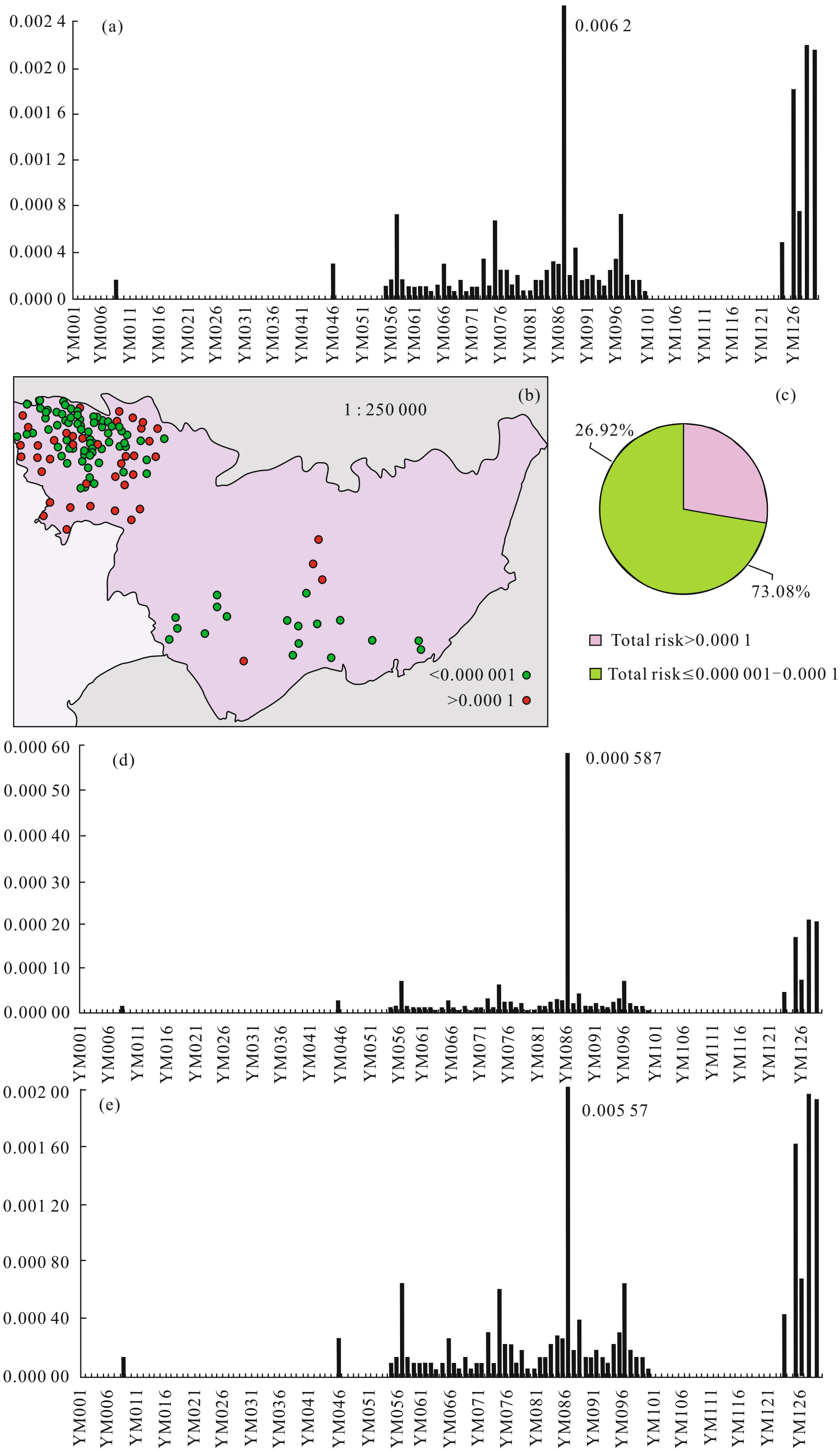

Figure 6. Carcinogenic risk index classification of all samples. (a) Statistical graph of total carcinogenic risk for all samples; (b) distribution of carcinogenic risk index classification; (c) formation of carcinogenic risk index classification; (d) statistical graph of carcinogenic risk of As for dermal contact pathway; (e) statistical graph of carcinogenic risk of As for drinking water pathway.

show that excessive hardness and salinity are main reasons for poor water quality. Health risk assessment results indicated that the study area had been polluted to a certain extent. As a result, there are differences between water composition analysis and health risk assessment.

(2) The level of noncarcinogenic risk for groundwater in the area is relatively high and carcinogenic risk for groundwater in the area is relatively low.

Noncarcinogenic Risk: Samples that do not pose noncarcinogenic risk only account for 28.46%. The noncarcinogenic risk value of >1.0 and ≤1.0 accounts for 71.54% and 28.46%, respectively.

Carcinogenic Risk: Samples that do not pose carcinogenic risk only account for 19.23% and all the rest pose carcinogenic risk. The carcinogenic risk $>10^{-4}$ and $\leq 10^{-6}$–10^{-4} accounts for 26.92% and 73.08%, respectively.

As for samples with higher noncarcinogenic risk index and cancer risk index, it is suggested that the water source be re-searched because they are no longer suitable for drinking. Some components should be treated appropriately according to industrial use. In addition, long-term monitoring and treatment measures should be strengthened for understanding water quality and industrial reuse so that the concentration of pollutants could be reduced as well as the health risks.

(3) The noncarcinogenic risk order of the study area decreased in the following order: $NO_3^->Mn>As>F^->Cr^{6+}>Cd>Pb$ and the carcinogenic risk of the study area decreased in the following order: $As>Cd=NO_3^-=Mn=F^-=Cr^{6+}=Cd=Pb=0$, because the slop factors were not available for the other pollutants.

(4) In terms of the whole study area, in both noncarcinogenic risk and carcinogenic risk, the main contribution order of two exposure routes is drinking water pathway>dermal contact pathway.

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