Organic Contamination of Soil and Goundwater in the Piedimont Plain of the Taihang Mountains

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Abstract: The risk of groundwater contamination following the infiltration of waste surface water, is of great interest, particularly in areas experiencing water shortage. In this study, the distribution characteristics of contaminants along the Cihe River, in the piedimont plain of the Taihang Mountains, China, was investigated by measuring the soil and water samples. The main organic contaminants detected in different media include hydrocarbons, chlorinated hydrocarbons, polycyclic aromatic hydrocarbons, and pesticides. The main contaminants found in different media are mostly derived from the river water, which can be seen from the results of waste water from the river and groundwater, from the soil samples from different depth and distance of the profiles along the river. The distribution characteristics showed that there has been a natural attenuation of the contaminants from the river during their transportation through the soils and groundwater. The sorption of organic compounds to soil organic matter is thought to be a main mechanism of natural attenuation.

Keywords: groundwater; organic contamination; natural attenuation; Cihe River; piedmont Plain of Taihang Mountains; North China Plain

1. Introduction

Groundwater contamination has received significant attention worldwide (Datta et al. 1997; Egusa et al. 2005; Zhao et al. 2007), due in part to the hazardous nature of groundwater contamination to both human and environmental health; including organic contaminants and some inorganic compounds such as NH_4^+, NO_2^-, and NO_3, and therefore threaten our potable water resources and natural ecosystems. Recent research over the past two decades has shown the persistant nature of organic contaminants in the groundwater-soil system. The active remediation of contaminated groundwater is often very expensive so that cost-effective alternatives have to be found (Schirmer et al. 2004). In some cases, natural attenuation resulting from processes such as sorption, biodegradation and dispersion may be sufficient to keep the contaminant concentration below the legal standards at a downgradient receptor (Grathwohl et al. 1998). Therefore, in this groundwater contamination investigation, we aim

to assess whether this natural attenuation exists during the transport from the contamination source to groundwater, and to determine to what degree this attenuation is in order to assess the risk of contamination of the groundwater along this river gradient.

The Quaternary aquifer of the North China Plain (NCP) is one of the worlds' largest aquifer systems and supports a vast demand and subsequent exploitation of this groundwater for farming, industry, and drinking water supply (Foster et al. 2004). With the rapid development of economy, there is not only quantitative problem but also water quality issue. The contamination of groundwater caused by wastewater released by human activities has been paid increasingly more attention. To understand the distribution and transport of contaminants from river water to groundwater through the soil is of great importance for the drinking water safety and risk assessment. Similar to the national water-quality assessment program (NAWQA) conducted by USGS (Squillace et al. 2007), a national wide groundwater quality investigation has also been being carried out by China Geological Survey (CGS) in China since 2006. The NCP area is one of the earliest areas to be investigated.

The Cihe River is located in the piedmont plain of the Taihang Mountains, which is a part of NCP. Previous work showed that there were contaminants found in the Cihe River due to the release of wastewater from both industry and sewage (Li et al. 2003). Since there is some adverse effect of organic contaminants (chlorinated compounds (e.g. PCE, TCE, and DCE) and fuel components) (Grandel et al. 2004; Wiedemeier 1999), evidence of natural attenuation from their distribution in various media should be paid more attention in this work.

The objectives of this work are to identify the main organic contaminants in soils and groundwater, to illustrate the distribution characteristics in different media and the possible attenuation mechanisms of major contaminants during their transport from the Cihe River to groundwater.

2. Materials and methods

Within the NCP, samples were taken from shallow groundwater, the Cihe Rive, and soils from designed profiles, (Fig. 1). The dominant inorganic and organic contaminants in the samples were analyzed in qualified laboratories. Based on the field investigation on the types and distribution of contamination sources, hydrological conditions, distribution of existing wells, and hydrogeological conditions in the study area, the sampling sites and profiles were designed.

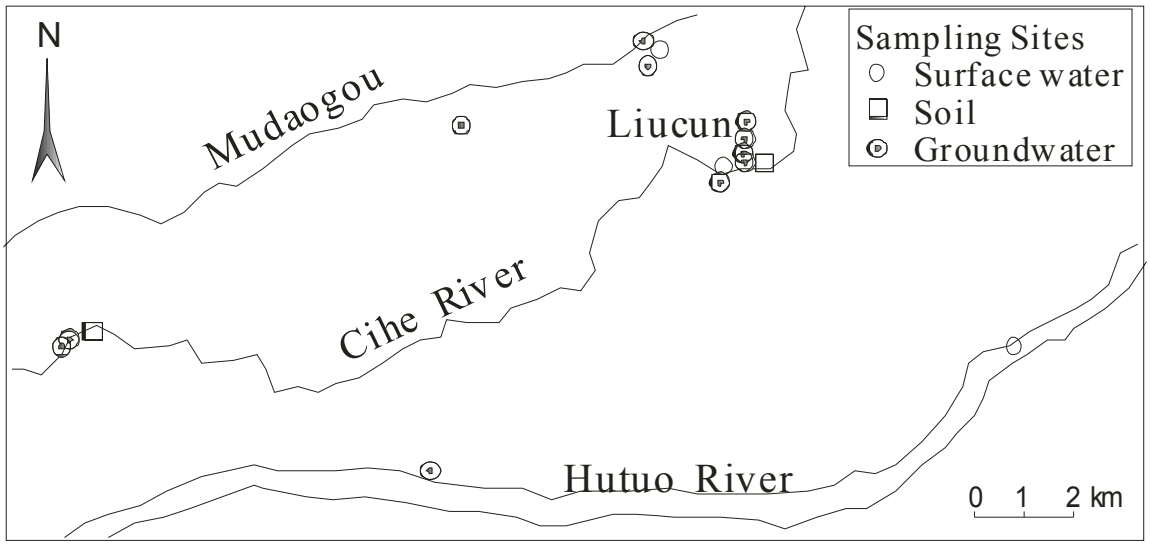

Fig. 1: Distribution of sampling sites in study area, Cihe River, China

Along the profile perpendicular to Cihe River at Liucun, 13 groundwater water samples from the shallow aquifer (dots inside circles shown in Fig. 1) were collected. The distance of the wells from the rivers were 15, 30, 40, 63, 76, 80, 118, 192, 256, 294, 369, and 430 m, respectively. At different distances from the river, four soil profiles at Liucun and one upstream of Cihe were chosen to take the soil samples from different depth (squares Fig. 1). The depth of the soil profiles ranged between 140 cm and 260 cm (Fig. 2).

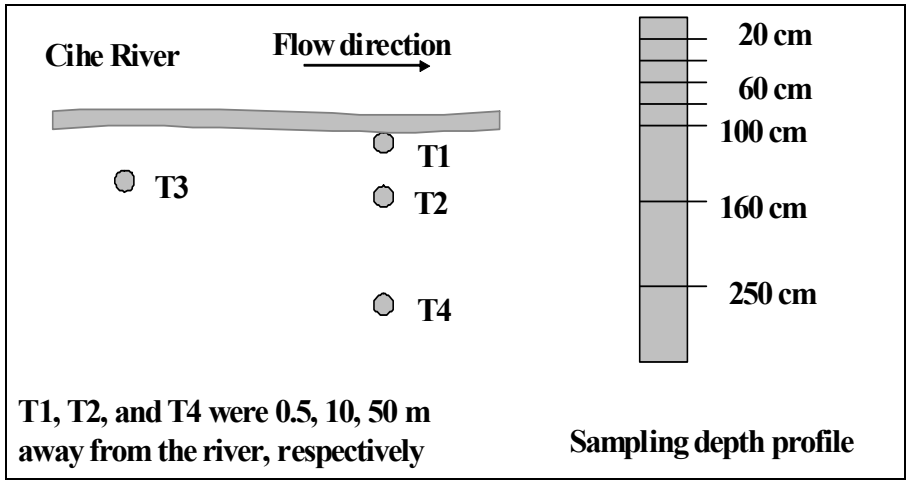

Fig. 2 Design of the soil sampling profile at Lucun site

Five surface water samples were collected from Mudaogou (1 sample), Cihe River (3 samples), and Hutuo River (1 sample) (circles in Fig. 1).

All the water and soil samples were collected and stored according to the terms set out by the guidelines issued by China Geological Survey (CGS). The samples were analyzed by Monitoring Center for Groundwater and Mineral Water of Ministry of Land and Resources, Geological Analytical Center of China University of Geosciences (Beijing), and Geological Analytical Center of Tianjin, which are the laboratories qualified by CGS for water and soil sample analysis.

3. Results and discussion

3.1 Contaminants in river water

The analytical data of river water (mainly wastewater) samples from the different sites indicated that the total dissolved solid (TDS), chemical oxygen demand (COD), sodium (Na^+), chlorine (Cl^-), ammonium (NH_4^+) and nitrogen dioxide (NO_2^-) were the main compounds or indexes controlling the water quality. Arsenic (As), cadmium (Cd) and chromium (Cr) were not detected in the samples.

The main organic compounds include hydrocarbons, chlorinated hydrocarbons, poly-aromatic hydrocarbons (PAHs), and pesticides. Except naphthalene, the concentrations of other PAHs and pesticides were in the magnitude of a few ng/L. Since the quality of surface water changes with time quite significantly, only the compounds with high concentrations and commonly detected are listed in Table 1.

Table 1: Organic compounds detected in surface waters

Compounds	Benzene	Toluene	Dichloromethane	Chloroform
C(ug/L)	1.30~32.10	7.30 ~37.90	14.50 ~ 107.00	64.10 ~ 91.80
Compounds	1,1,2-trichloroethane	Trichloromethane	Naphthalene	
C(ug/L)	6.00~17.70	0 ~98.80	0.45~1.98	

3.2 Contaminants in soils

The key sampling details and properties of the collected samples are listed in Table 2. In the soil profiles at Liucun (see location in Fig. 1 and sampling depth in Fig. 2), the vertical distribution of contaminants at ST1 (0.5 m away from the river) showed that the highest content of contaminants was found at a depth range between 20 and 50 cm. With an increase of distance from the river, the contaminant content in soil significantly decreases in the first 10 m, then no obvious change was observed.

Table 2: Sampling depth and main properties of soil samples

Sample Number	Depth (cm)	PH of soil	CEC(mmol/kg)	foc（%）	Classification
ST1-20	20	8.05	54.40	1.39	Sandy silt
ST1-40	40	7.20	77.55	1.37	Sandy silt
ST1-60	60	7.70	65.97	0.76	Clayey silt
ST1-80	80	7.89	57.10	0.49	Clayey silt
ST1-100	100	8.07	187.11	1.30	Clay
ST1-120	120	7.76	68.29	0.78	Sandy silt
ST1-140	140	7.69	81.02	0.57	Sandy silt
ST2-40	40	7.73	65.20	0.59	Sandy silt
ST2-80	80	7.73	69.06	0.46	Sandy silt
ST2-120	120	7.55	59.03	0.73	Sandy silt
ST2-170	170	7.75	63.27	0.57	Sandy silt
ST2-200	200	7.66	92.98	0.48	Sandy silt
ST2-250	250	7.63	49.38	0.84	Sandy silt
ST4-100	100	7.57	67.13	0.43	Sandy silt
ST4-140	140	7.59	53.24	1.06	Sandy silt
ST4-200	200	7.57	55.56	0.62	Sandy silt
ST4-260	260	7.63	58.64	0.24	Sandy silt

The distribution characteristics of inorganic and organic compounds are quite similar (Figs. 3 and 4). The concentration ranges of the main organic compounds within soils are listed in Table 3.

Table 3: Statistics results of main organic compounds for the soil samples at Liucun

Compounds	Benzene	Toluene	1,2-dichloroethane	Benzo(a)pyrene	Total DDT	4,4'-DDE
C (ug/kg)	0.3 ~ 7.07	0 ~ 4.47	3.53 ~ 24.1	0.52 ~ 46.1	0.15 ~ 28.3	0.15 ~ 24.8

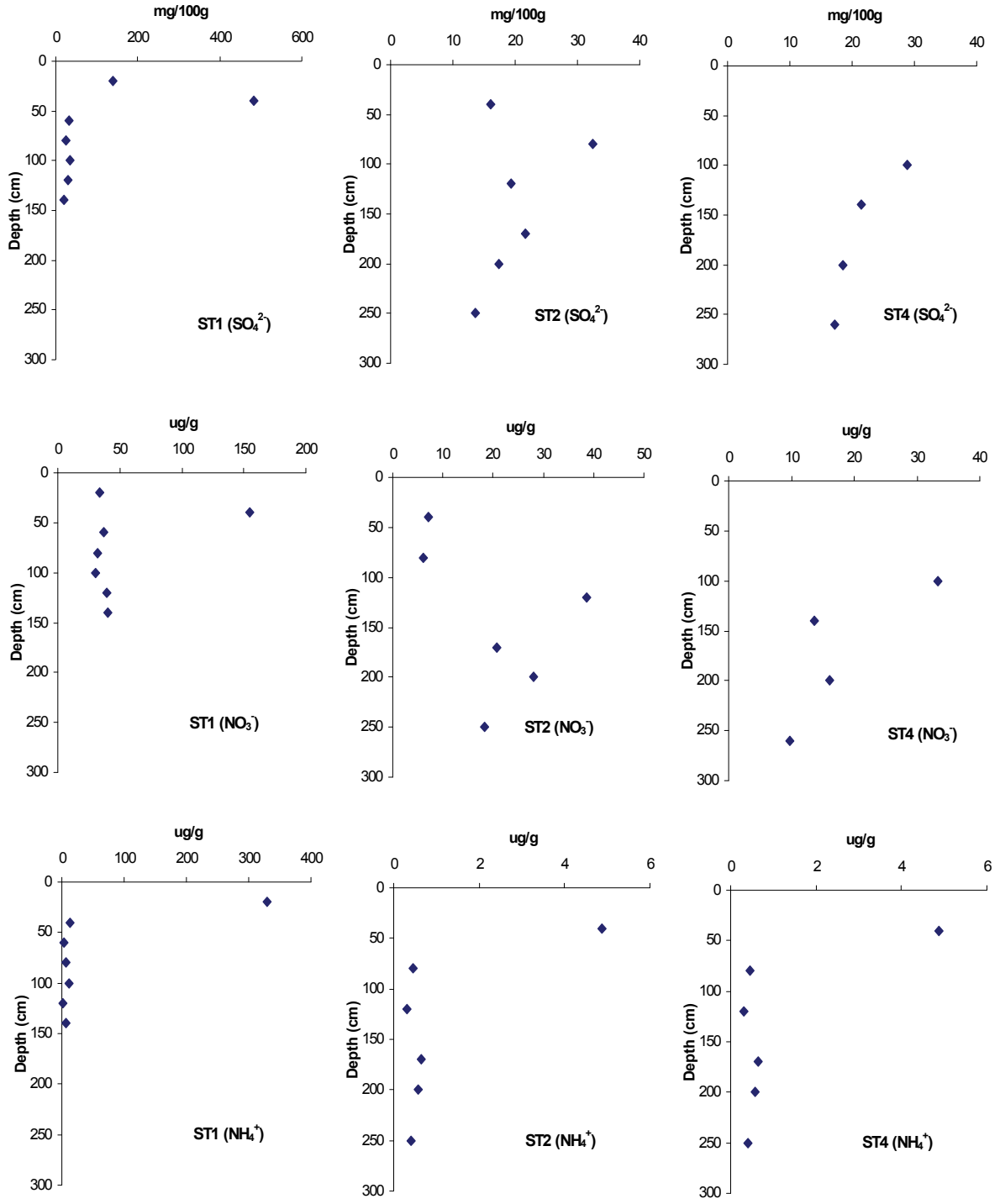

Fig. 3: Distribution characteristics of inorganic compounds in soils at Liucun profiles (the distances of ST1, ST2, and ST4 from the river are 0.5 m, 10 m, and 50 m, respectively).

Fig. 3 displays an abrupt decrease in the contents of inorganic and organic contaminants across the soil profiles that are located at a distance of 10 m from the river. At a distance of 50 m from the river, the vertical soil profile displays a maximum of contaminants at depths from 20 cm to 50 cm.

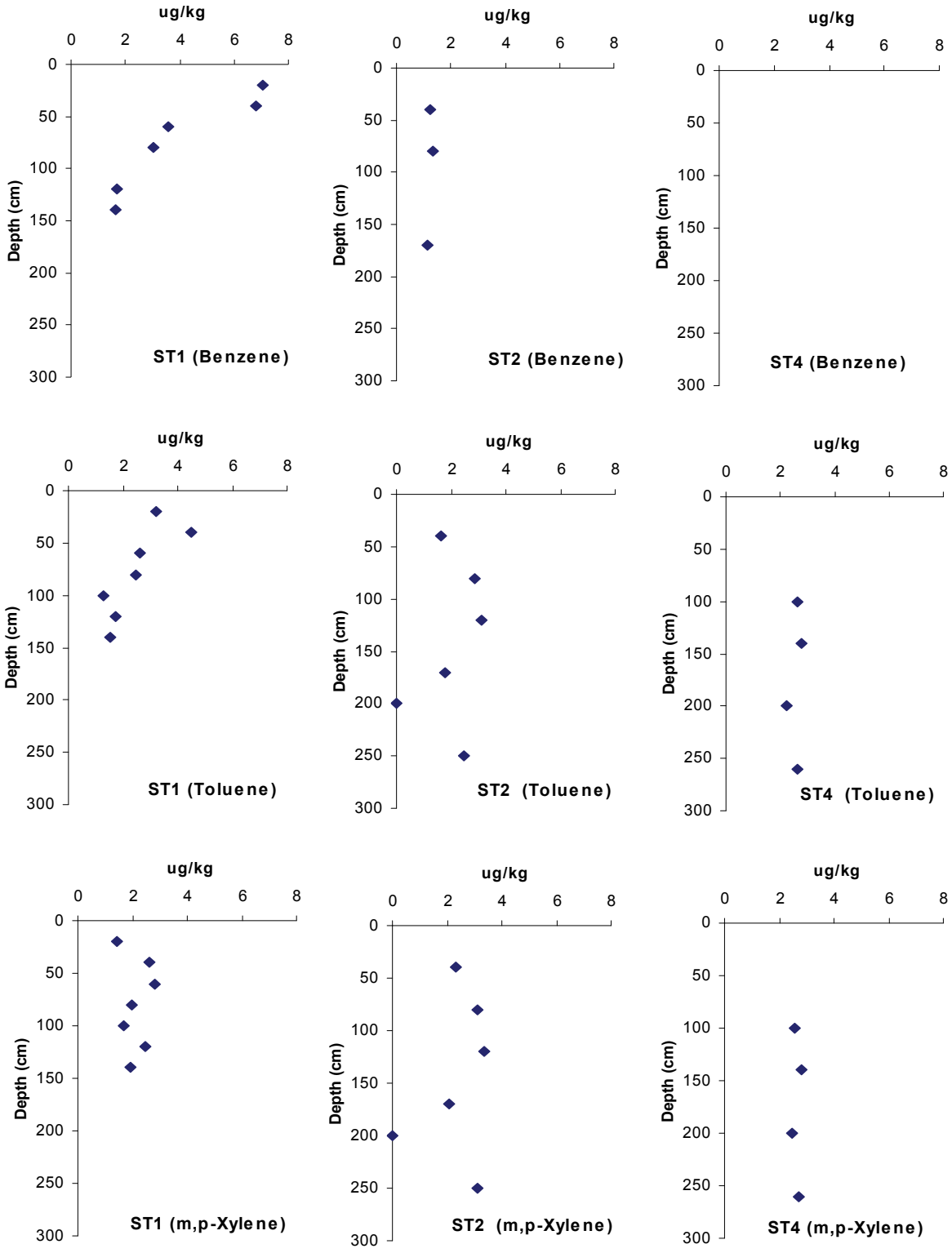

Fig. 4: Distribution characteristics of organic compounds in soils at Liucun profiles (the distances of ST1, ST2, and ST4 from the river are 0.5 m, 10 m, and 50 m, respectively. Benzene was not detected at ST4 profile)

The sampled soils included sandy silt, clayey silt, and clay soils (Table 2), whereby the fine particles (i.e clay) limit or indeed prevent the infiltration of surface water to groundwater. The organic matter in soils also plays an important role in the attenuation of organic contaminants, mainly through sorption. When the soil organic matter (SOM) exceeds 0.1%, the sorption of organic contaminants to SOM is normally thought to be the main sorption mechanism (Schwarzenbach et al. 2002). In the study area, the SOM content of the soil samples ranges from 0.24 to 1.39% (Table 2). It can be found that at ST1 the organic contaminant concentrations are higher at the surface than that in the deeper part of the profile due to the higher content of organic carbon in the soil (Table 2 and Fig. 4). At ST2, above the depth of 170 cm of the profile, the soil organic carbon ranged from 1.15% to 1.36%. This resulted in a narrow concentration range of the investigated organic contaminants. Since the organic contaminants detected are all non-polar compounds, therefore their sorption is mainly affected by SOM (Schwarzenbach et al. 2002), as opposed to soil pH and cation exchange capacity (CEC) (Bi et al. 2006; Bi et al. 2007).

3.3 Contaminants in groundwater

Organic contaminants of the shallow groundwater samples were only detected in a few wells and their concentration can still meet the standards of drinking groundwater. The groundwater quality is mainly dependent on the inorganic compounds, such as TDS. In the profile at Liucun, the concentration of hardness and TDS do not change significantly with the distance from the river.

In groundwater, detection frequency of benzene, PCE, 1,1,2-trichloroethane, total DDT, and p,p'-DDE is 4.5%, and the detection frequency of 1,2-dichloroethane, toluene, and benzo-a-pyrene (B[a]P) is 9.1%. The detected concentration of all the organic contaminants is at least six times lower than the respective standard for drinking water. Therefore, there is no threat from these compounds for human health at the sampling time. However, further monitoring work should be performed in order to get seasonal trends of groundwater quality.

According to the available date, it can be found that the river water does not significantly affect the quality of groundwater. If there is, it is still in the very limit range, for example, less than 10 m from the river. The concentration of contaminants decreased greatly with the distance from the river showed the evidence that there is natural attenuation processes (e.g. sorption to soil organic matter) of contaminant during their transport from surface to groundwater. In previous studies, the geochemical/hydrogeochemical data indicated the natural attenuation of PAH and benzene in groundwater (Bolio and P.A. 1999; Kao et al. 2001), chlorinated volatile organic compounds in a freshwater tidal wetland (Lorah et al. 1999) and in a shallow sand aquifer (Nobre et al. 2004). Therefore, the natural attenuation indicated by the distribution characteristics of contaminants is of significance to assess the risk of contamination of groundwater.

3.4 Correlation of contaminants in different media

The results of the soil, wastewater from the river, and the groundwater from the profiles suggest that the main contaminants found in different media (i.e. soil and water) are highly correlated, reflecting their origin. According to the analyzed data of the water and soil samples, the main organic contaminants detected in surface water, sediment of river, and soils are hydrocarbons, chlorinated hydrocarbons, poly-aromatic hydrocarbons (PAHs), and pesticides. The contaminants in the soils close to the surface water are related to these in sediments, especially BTEX, dichloromethane, and trichloromethane.

4. Conclusions

In this work, the distribution of the main contaminants, which were detected in the water of Cihe River in the piedimont plain of the Taihang Mountains, was studied systematically. The soil

samples from different depths and distance along the river indicated that the contaminants are primarily sourced from the river. Because of the natural attenuation processes (e.g. sorption to soils), the content of contaminants in soils decreases significantly with depth from ground surface and distance from the river.

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