Study on the Regional Hydrological and Hydrochemical Processes Affected by the Human Activities in the North China Plain

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中国華北平原における広域水文・水質特徴
およびそれに関わる人間活動の影響について

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Abstract

The North China Plain (NCP) is one of the most water scarce areas in China. Groundwater is the main water source in the NCP. Water resource problems are mainly manifested in water quantity and water quality degradation, impacting on economic development in the NCP.

In this study, the Xiaohe River basin was chosen to understand the movement of water and to evaluate water quality in the semi-arid area of the NCP. Environmental isotopes, chlorofluorocarbons (CFCs) and hydrochemistry were used to study the influence of surface water on regional groundwater. Based on a mass balance approach with chloride charged by surface water was estimated as 50–60 %. CFC results indicated that the resident time of groundwater that recharged by the river varied from 22.5 to 39.5 years. The vertical flow velocity of groundwater was estimated at about 1.8–3.5 m year^{-1}. Nitrate concentrations in groundwater varied from 9 to 157 mg L^{-1}, and exceeded WHO drinking water standard of 50 mg L^{-1} in most aquifers shallower than 80 m bordering the Xiaohe River. The $\delta^{15}N–NO_3$ data indicates that the major sources of nitrogen in groundwater are human sewage and animal excreta.

To understand the distribution and behavior of phenolic endocrine-disrupting chemicals (EDCs) in surface water and suspended particulate matter (SPM), the Xiaohe River in the NCP was investigated. The river concentrations (means; ng/L) of EDCs varied from 21–83 (54) for octylphenol (OP), from 39–1819 (570) for nonylphenol (NP), and from 49–775 (391) for bisphenol A (BPA). Particulate concentrations (means; ng/L) for OP, NP and BPA were in the range of 12–20 (23), 14–1197 (785), and 18–32 (23), respectively. SPM accounted for 23–

54%, on average, of the total phenolic EDCs pollution in surface water. The averaged particulate OP, NP and BPA proportions were 24, 61 and 11%, respectively, of their total concentration in water columns. A mass balance equation based on chloride was used to evaluate the mixing effect on the behavior of EDCs along the river, showing that mixing process was the predominant factor to determine EDCs concentrations in the Xiaohe River. Based on the combined effect models, potential environmental risks were assessed showing that most surface waters contaminated by EDCs have a medium effect on aquatic organisms in the Xiaohe River basin.

Key words: surface water, groundwater, environmental isotopess, nitrate, CFCs, hydrochemistry, endocrine-disrupting chemicals, NCP

要旨

半乾燥地域である華北平原は中国で最も水資源不足地域の一つであり、農業・産業・都市用水はほとんど地下水に頼っている。その結果、水量不足及び水質悪化問題が深刻化になり、その原因究明が急務である。そこで、本研究は、典型的な Xiaohe 流域を選び、華北平原の水循環・水質変化特徴及びその影響要因を明らかにすることを目的とした。

本研究では、塩化イオン濃度、水素および酸素同位体に基づき、Xiaohe 河地表水による地下水への涵養量貢献は 50-60%であることがわかった。また、フロン類の解析結果から地下水涵養年齢は 22.5 から 39.5 年の間であり、地下水流動鉛直速度が約 1.8-3.5 メートル/年であることが推定された。研究地の水循環特性を明らかにしたうえ、河川水及び地下水中窒素分布を調べた。地下水の硝酸態窒素濃度が 9-157mg L^{-1} であり、特に Xiaohe 河沿いの地域では深度 80 メートルより浅い地下水のほとんどが窒素に関する飲用水基準を超えていた。窒素同位体のデータから生活排水と動物糞尿が地下水中の主な窒素汚染源であることが示唆された。

また、Xiaohe 河地表水及び浮遊物質（SPM）におけるフェノール類内分泌かく乱化学物質（EDCs）の分布や挙動を理解するために、典型的な EDCs であるノニルフェノール(NP)、オクチルフェノール(OP)およびビスフェノール A(BPA)を調査した。その結果、地表水中の NP、OP および BPA 濃度はそれぞれ 39-1819ng L^{-1}、49-775ng L^{-1} および 21-83ng L^{-1} であった。また、SPM 中の NP、OP、BPA 濃度がそ

れぞれ 12-20ng L^{-1}、14-1197ng L^{-1} および 18-32ng L^{-1} の範囲に変化していた。塩化物に基づく質量収支バランスを仮定し、混合過程が河川水の EDCs 濃度変化に影響を与える主要因であることを明らかにした。更に、Xiaohe 河における水生生物に対する EDCs 潜在的な環境リスクを総合評価した。

キーワード：地表水、地下水、安定同位体、硝酸態窒素、フロン類、水質、内分泌かく乱物質、華北平原

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Chapter 1 Introduction

1.1 Hydrologic cycle

The hydrologic cycle is a conceptual model that describes the storage and movement of water between the atmosphere, lithosphere, biosphere, and hydrosphere (Valero et al., 2011) (Figure 1-1). Water on the earth is stored in the following major reservoirs: atmosphere, oceans, lakes, rivers, soils, glaciers, snowfields, and groundwater. Water moves from one reservoir to another by way of processes like evaporation, condensation, precipitation, deposition, runoff, infiltration, sublimation, transpiration, melting, and groundwater flow (Lankao, 2010).

More than 30% of all freshwater is groundwater (Pimentel et al., 2004). Groundwater is the largest accessible fresh water reservoir for human. Especially, in arid or semi-arid regions, groundwater is commonly the most important water resource for domestic, industrial and agricultural uses (Akkad, 1989).

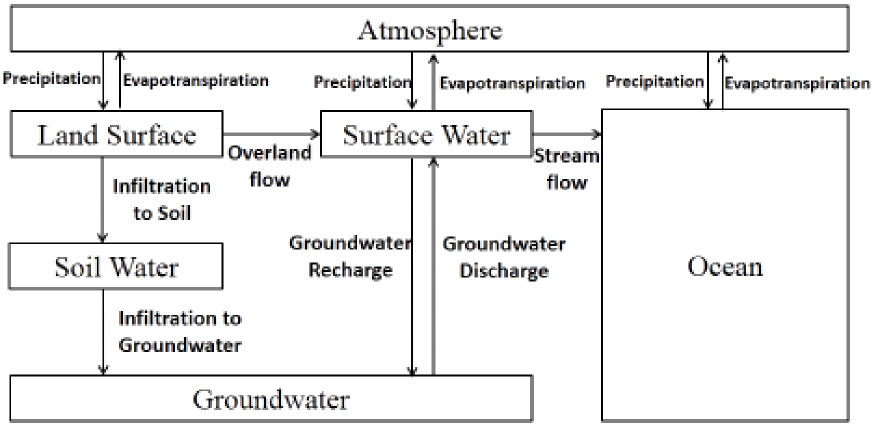


Figure 1-1 Concept map of hydrologic cycle

1.1.1 Water in arid or semi-arid regions

Drylands (arid or semi-arid regions) are expanding and represent approximately 30% of the global land area (Dregne, 1991), and support two billion people, 90% of whom live in developing countries (EMG, 2011). Arid or semi-arid regions are climatic regions that receive precipitation below potential evapotranspiration, extremely or not extremely. A more precise definition is given by the Köppen climate classification that treats steppe climates as intermediates between desert climates and humid climates in ecological characteristics and agricultural potential (Peel et al., 2007).

Surface water resources are usually scarce and greatly undependable in arid and semiarid regions, with the result that groundwater is primary important source of water in these regions. The International Atomic Energy Agency (IAEA) estimates that much of the groundwater being developed in arid and semiarid regions is fossil water and is not sustainable.

In recent years, increasing demands on limited water supplies result in a serious status of groundwater recharge in arid and semiarid regions. Currently, an estimated 1.1 billion population lacks access to sources of clean drinking water (WHO, 2003). Water shortage will become more and more critical in the future as population growth in arid and semiarid regions (Scanlon et al., 2006). Sustainable management of these aquifers to meet the requirements of human and ecosystem needs will require accurate estimates of groundwater recharge.

1.1.2 Recharge of groundwater

Various studies of recharge have been conducted in the past, focussing on arid and semi-arid regions. The purpose of recharge studies has decided to some extent the method used to estimate recharge and the scale of the studies. Recharge estimation for water quality studies focusses on spatial variability in recharge, which is critical for contaminant transport (Scanlon et al., 2006). Environmental tracers including meteoric Cl^-, ^{36}Cl, ^3H, δ^2H, and $\delta^{18}O$ are used to evaluate uncertainties in water flux and age in the Chihuahuan Desert of Texas (Scanlon, 2000). A study investigated the groundwater recharge by leakage of the Tanghe Wastewater Reservoir, which is the largest industrial wastewater channel on the NCP. Large linear wastewater ponds that lack anti-seepage measures can act as river channels that cause the deterioration of groundwater quality (Wang et al., 2014). In summary, information on interactions between surface water and groundwater is critical for developing sustainable groundwater management plans in arid and semi-arid regions.

1.2 Hydrochemistry

Hydrochemistry is the science that explains the chemical composition of natural waters and the laws control the changes in composition as a result of the chemical, physical, and biological processes (Appelo and Postma, 2005). Such as the transport of salts from land to sea (by erosion of rocks and surface runoff) and from sea to land (by evaporation, cloud formation, and precipitation) and the age and origin of groundwater in desert regions and of ice sheets and glaciers.

The hydrochemistry study includes a wide range of chemicals in the water, such as major, minor or trace elements, environmental isotopes chemistry, inorganic and organic pollutants.

1.2.1 Research on the major ions composition of waters

The major ions composition of waters (e.g., Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, SO_4^{2-} and Cl^{-}) reveals the mechanisms that control the chemical composition of waters, such as the nature of weathering, patterns and linkages between evaporation and anthropogenic processes on a basin wide scale (Gibbs, 1970).

Many previous studies have reported the major ions hydrochemistry of many major rivers in the world, e.g. the Amazon (Gibbs, 1970), the Mississippi (Forester, 1986), the Orinoco River (Forester, 1986), the Ganga river (Sarin et al., 1989) and the Danube (Pawellek et al., 2002). For Chinese rivers, most studies have focused on the Changjiang (Yangtze River) (Chen et al., 2002; Edmond et al., 1985), the Huanghe (Yellow River) (Zhang et al., 1995), the Zhujiang (Pearl River) (Chen and He, 1999; Zhang et al., 2009a) and the Huai River (Yang et al., 2012b; Zhang et al., 2011a).

Based on hydrochemical data for numerous rain, river, lake, and ocean samples, the three major natural mechanisms controlling world surface water chemistry can be defined as atmospheric precipitation, rock dominance, and the evaporation-crystallization process (Gibbs, 1970).

Anthropogenic activities can thoroughly change water quality (Meybeck and Helmer, 1989). The major ion chemistry can also be affected by a variety of human activities. Pollution from various sources is an obvious example of direct effects. This has become particularly important in China due to drastically intensified industrial and agricultural activities (Chen, 2010). Indirect effects may include changes in water–rock reactions in soils and aquifers caused by increased concentrations of dissolved oxidants, protons, and major ions.

1.2.2 Environmental isotopes ($\delta^{18}O$, δD) in hydrologic cycle

Environmental isotopes ($\delta^{18}O$, δD) for hydrology have been used since the 1950s and 1960s with the development of nucleus science. The main applications of environmental isotope technology in hydrologic cycle research is to determine compositions and sources of waters and determine recharge process for surface water and groundwater. $\delta^{18}O$ and δD were used to separate rainfall event flow from pre-event flow, because rain water often has a different isotope composition with water already in the catchment (Kendall and Caldwell, 1998). The stable isotope composition of regional groundwaters around Lake Tyrrell, Victoria, Australia indicates that the groundwaters are derived entirely from meteoric water that has undergone some degree of evaporation during recharge (Herczeg et al., 1992). A study used chemical and isotopic tracers to characterize the interactions between ground water and surface water in Mantled Karst (Katz et al., 1997).

1.2.3 Dating the young groundwater with CFCs

Resident time of water in watershed is a key to understand the movement of water and chemicals in watersheds. There are many studies used geochronological methods, isotope methods to identify the history of alluvial fan (Harvey et al., 1999; Ritter et al., 2000; Sweeney and Loope, 2001). In the past decades chlorofluorocarbons (CFCs) has been used to data groundwater. Dissolved CFCs concentrations are converted to equilibrium partial pressures for temperature in recharge water. Partial pressures are then compared to atmospheric data to determine the year that recharge water contacted with air. As a result, the concentrations of CFCs in groundwater were reported to provide information on groundwater residence times and mixing processes for the groundwater up to 50 years old (Plummer and Busenberg, 1999). CFCs have been successfully used to determine groundwater ages and flow paths (Busenberg and Plummer, 2008; Cook and Solomon, 1995; Gooddy et al., 2006; Han et al., 2012; Oster et al., 1996), and to understand and to understand the long-term impacts of anthropogenic activities on quantity and quality of groundwater (MacDonald et al., 2003; Wassenaar et al., 2006). Also, combined use of CFCs dating, chemical, and nitrogen isotope analyses had been used to resolve the history and fate of nitrate contamination in groundwater (Böhlke and Denver, 1995; Cao et al., 2013).

1.2.4 Nitrate contamination and wastewater irrigation

Anthropogenic nitrogen inputs to the Earth's surface has increased greatly during the past two centuries. Increases in nitrogen inputs can lead to highly undesirable changes in ecosystem structure and function (Vitousek et al., 1997a; Vitousek et al., 1997b). Nitrate contamination is a worldwide problem in both surface water and groundwater (McIsaac et al., 2001; Orban et al., 2010; Yang et al., 2004a). Many studies were reported that elevated NO_3^- concentrations in rivers (Beaulieu et al., 2011; Mulholland et al., 2008; Paerl et al., 1998; Panno et al., 2008; Pellerin et al., 2012; Richardson et al., 2004), aquifers (Burns et al., 1998; Jalali, 2005; Plummer et al., 2006) and catchment headwaters (Molenat et al., 2008; Williams et al., 2014). Unfortunately, high concentration of nitrate has a serious threat to drinking water supplies because it may cause methemeoglobinemia in infants and be responsible for increases in stomach cancer in others (Morales-Suarez-Varela et al., 1995; Yang et al., 1998). The World Health Organization (WHO) has set a limit of 10 mg N L-1 for drinking water. The elevated groundwater nitrate concentrations can have detrimental ecological effects and can cause public health problems (Agrawal et al., 1999; Kumazawa, 2002; Li et al., 2008b; Nolan and Hitt, 2006; Weiskel and Howes, 1992; Zhang et al., 1996).

Wastewater has long been used for irrigation in many country around the world. Wastewater had been used to irrigate crops and dispose in the USA since the late 1800s. Wastewater was used to irrigate an area of 1.5×10^6 ha in the 1970s. At the same time, wastewater irrigation also caused a series of ecological problems. Elevated nitrate concentrations were found in the groundwater in the Mezquital Valley, Hidalgo, Mexico.

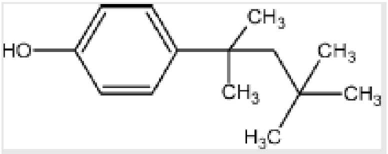
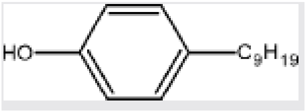
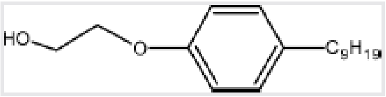
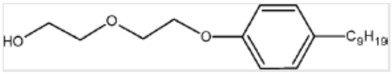
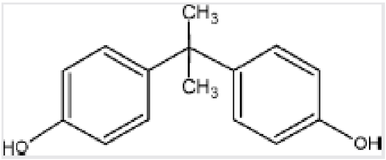
Nitrate concentration in groundwater exceeded drinking water standards and were greater than those in surface water. Due to untreated wastewater has been used for decades to irrigate in this area, wastewater irrigation appears to have a negative impact on groundwater quality (Gallegos et al., 1999).

Due to urbanization processes, scarcity of water resources and insufficient capacity in wastewater treatment, wastewater has become an important water resource in recent years in NCP. Wastewater irrigation was started as early as 1958, and the primary aim at that time was to reuse the nutrients dissolved in wastewaters and thus save on the cost of fertilizer. More recent reuse of such kind of water is due mainly to water shortage (Chen et al., 2006b). Since the 1960s, wastewater has been used for irrigation in the regions around Shijiazhung, like many other big cities in the NCP (Tang et al., 2004). About 80% of the wastewater discharged from cities is industrial wastewater, 80% of wastewater has been used for irrigation without treatment. Surface water and groundwater pollutions have been very serious regarding wastewater irrigation, which is a common practice in the suburbs of principal cities of China, especially in NCP.

1.2.5 Endocrine disrupting compounds

The endocrine-disrupting chemicals (EDCs) can be classified as estrogenic, androgenic, or thyroidal compounds based on its respective adverse effects (Campbell et al., 2006). In the past decades, the environment has been continuously exposed to EDCs released by urban communities and industries. Table 1-1 gave the molecular structures of several widely studied EDCs in environmental science. Some studies have demonstrated the origin, behavior and biodegradation of Nonylphenol (NP), Octylphenol (OP) and Bisphenol A (BPA), named as EDCs, in the environment (Soares et al., 2008; Ying et al., 2002b). The behavior and fate of alkylphenols (APs) and BPA, have been paid serious attention because of their estrogenic activities and ubiquity in the aquatic environment (Sumpter and Johnson, 2005). Recently, these chemicals have already been designated (Kreuzer et al., 2009)as priority hazardous substances in Water Framework Directive of European Union (EU) and they are subject to an environmental risk assessment. However, there is no law or statue in China for restricting the produce and consumption these chemicals (Xu et al., 2006). Therefore, the three EDCs (NP, OP and BPA) would be used as target chemicals in order to study the hydrodynamic behavior of important organic contaminants in the study.

Table 1-1 Molecular structures of EDCs (Xie and Ebinghaus, 2008)

Compound	CAS number	Chemical formula	Chemical structure
Octylphenol (OP)	140-66-9	$C_{14}H_{22}O$	
Nonylphenol (NP)	25154-52-3	$C_{15}H_{24}O$	
Nonylphenol Monoethoxylate	104-35-8	$C_{17}H_{28}O_2$	
Nonylphenol diethoxylate	20427-84-3	$C_{19}H_{32}O_3$	
Bisphenol A (BPA)	80-05-7	$C_{15}H_{16}O_2$	

1.2.5.1 Sources and characteristic of EDCs

Different EDCs have different physical-chemical properties. The present, behavior and fate of them in environment are usually related to those properties. NP and OP are xenobiotic compounds consisting of a phenol ring and a nine or eight carbon chain. For NP, it is a viscous liquid with a light pale color under ambient conditions and it is produced industrially by the alkylation of phenol with nonene under conditions of acidic catalysis. The final technical mixture is composed of more than 22 isomers of 4-substituted monoalkylphenols (Thiele et al., 2004; Wheeler et al., 1997). The main physical and chemistry characteristics of NP, OP and BPA including Henry's law constant, molecular mass, vapour pressure, aqueous solubility, octanol-water partition coefficients are listed in Table 1-2 (Staples et al., 1998; Ying et al., 2003).

Table 1-2 The physical-chemical properties of OP, NP and BPA

Compound	Molecular mass (g mol^{-1})	Vapour pressure (Pa)	Aqueous sobulility (mg L^{-1})	Henry's law constant (Pa m^3 mol^{-1})	Log K_{ow}
OP	206	3.14×10^{-2}	1.26	5.57	4.12
NP	220	3.0×10^{-1}	6.00	11.00	4.48
BPA	228	5.33×10^{-3}	210.00	5.76×10^{-6}	3.32

Alkylphenol ethoxylates (APEs) are APs metabolites and the major constituents of APs found in surface water. APEs are widely used as non-ionic surfactants in industrial, domestic and commercial applications, such as lubricating oil additives, detergents and antistatic agents (Fenet et al., 2003). The annual worldwide APEs production is estimated at approximately 650,000 tons, and 60% of APEs are released into the aquatic environment (Guenther et al., 2002; Jobling et al., 1996). APEs are mainly composed of nonylphenol ethoxylates (NPEs) and octylphenol ethoxylates (OPEs). NPEs account for approximately

80% of the total APE use; OPEs account for most of the remaining 20% of APEs (Ying et al., 2002b). NP and OP are considered to be more toxic than their precursor APE compounds. In China, annual APE production is approximately 50,000 tons, which accounts for 10% of the total global production (Fu et al., 2007).

BPA is an important intermediate that is used primarily to produce polycarbonate plastics, epoxy resins and other plastic materials (Kleĉka et al., 2001; Staples et al., 1998). With the various usages of polycarbonate plastic and epoxy resin in household applications and industrial products including automotive parts, food packaging and adhesives etc, the annual growth demand of BPA was expected at 6-10% (Kang et al., 2007). In China, BPA production and consumption were approximately 32,000 tons and 105,000 tons, respectively, in 2001 (Zeng et al., 2006).

1.2.5.2 Fate, behavior and toxicity of EDCs in aquatic environment

Most EDCs enter the aquatic environment from sewage treatment plant (STP) effluents, which led to a net accumulation in the aquatic ecosystem of urban rivers (Céspedes et al., 2008; Kang et al., 2007; Ying et al., 2002b).

After entering the aquatic environment, the physicochemical properties of NP, OP and BPA play predominant roles in determining their fates in different environmental compartments. Many studies have reported on the occurrence and fate of these chemicals in a variety of environmental media including surface water, groundwater (Cailleaud et al., 2007;

Latorre et al., 2003), sediments (Fu et al., 2007; Khim et al., 1999) and aquatic organisms (Belfroid et al., 2002; Pojana et al., 2007). Recently, some studies have reported that dilution might play an important role in controlling the variation of these chemicals in urban riverine systems (Yi et al., 2011).

1.3 Purpose of the study

Many new hydrological issues associated with disrupted water cycles need to be addressed in response to increasing water demands in arid and semi-arid areas. In this paper, regional hydrological and hydrochemical processes affected by the human activities in the NCP is intensively discussed. Investigating the impact of surface water on groundwater is a key of water problems in NCP. In recent years, the rapid development of urbanization and industrialization in NCP has resulted in elevated concentrations of chloride, nitrate, sulfate, and organic solvents drained to the river through industrial wastewater and domestic sewage, which is seriously affected the water quality in NCP. However, there is limited knowledge of the processes involved. The aim of this study was using a combination of multiple tracers, such as environmental isotopes ratios (δD, $\delta^{18}O$, $\delta^{15}N$) and CFCs, to

(1) identify the effect of river water on regional groundwater, estimate groundwater residence times, and recharge rates;
(2) assess the hydrochemistry and patterns of river water, groundwater and soil;
(3) evaluate the transport and fate of nitrate in aquifer and soil structure in unsaturated zone and

(4) determine the occurrence, distribution and behavior of EDCs in Xiaohe River, and evaluate the combined effect toxicity of EDCs in the aquatic river environment.

Schematic of structure, content, and scientific issues of this paper were shown in Figure 1-2.

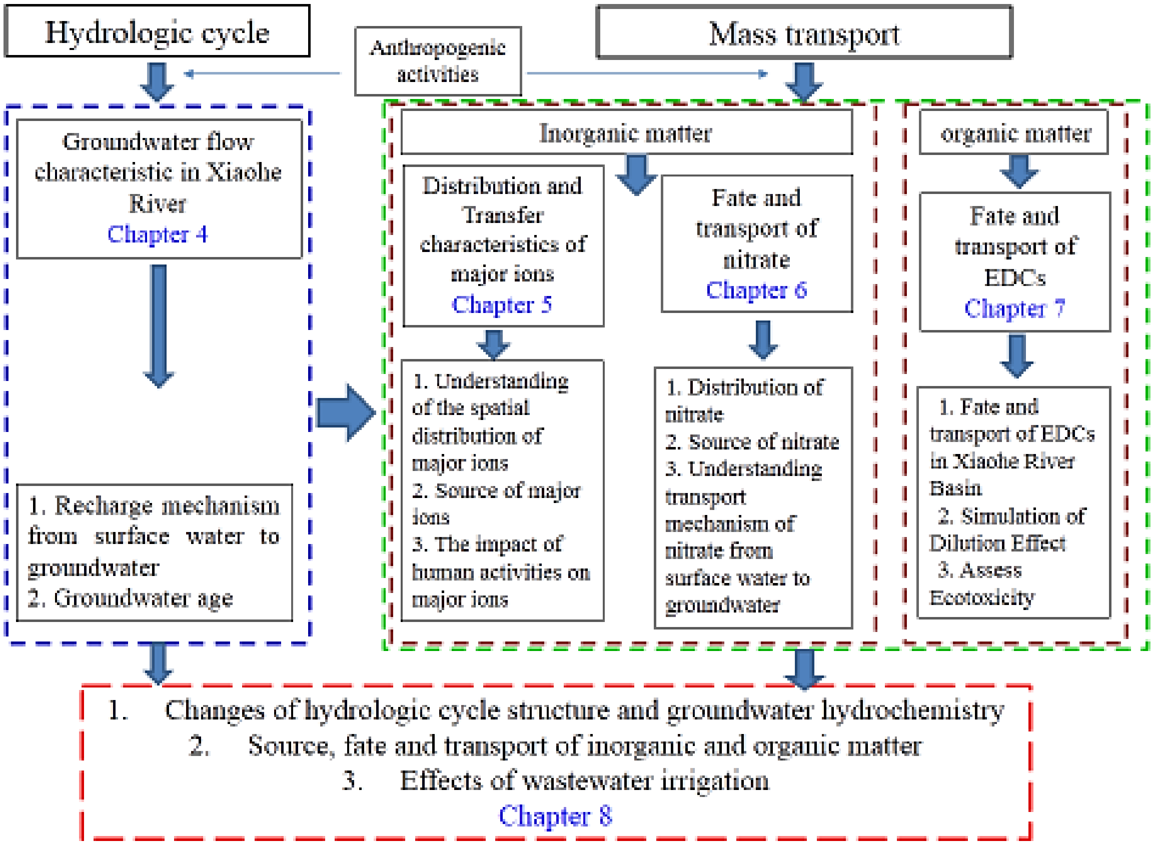


Figure 1-2 Schematic of structure, content, and scientific problems discussed in this study.

Chapter 2 Site descriptions of Study area

2.1 Description of regional condition in the North China Plain (NCP)

2.1.1 General regional condition

The NCP is located in the eastern coastal region of People’s Republic of China and is the largest alluvial plain of eastern Asia. The NCP between 34°46’ − 40°25’ north latitude, and 112°30’ – 129°30’ east longitude (Figure 2-1). The NCP is one of China's most important social, economic, and agricultural regions. It covers Beijing, Tianjin, the whole plain of Hebei Province and the plain north of the Yellow River in Henan Province and Shandong Province, with an area of 139238 km^2. There are 19 cities and 227 counties. The population of the NCP was 213.9 million, 172.5 million of whom lived in agricultural areas and 41.4 million in urban areas estimated in 1998.

The NCP belongs to continental arid and semi-arid climate with the mean annual temperature of 12 °C. The annual precipitation ranges from 500 to 600 mm, most of which are available in the period from June to August. Spatially, it ranges from about 800 mm in the south to 500 mm in the north. The mean potential evaporation ranges from 1100 to 1800 mm. The NCP produces about 1/4 of the China’s total grain yield, mainly winter wheat, summer maize and cotton.

Groundwater is the main water source in the NCP, as one of the most water scarce areas in China, with about 450 m^3 water resources per capita (Kreuzer et al., 2009). The water resource shortage has seriously impacted on economic development in the NCP (Liu and Xia, 2004; Liu et al., 2001). At present, the NCP has 1.8×10^7 ha of cultivated lands, 71 % of which is irrigated. The amounts of irrigation water are more than 70 % of the total water used in NCP. Because the demand for industrial, domestic, and agricultural water is increasing accordingly, water shortage has occurred in many cities and agricultural production areas. In general, surface water is used in areas accessible to rivers or reservoirs, and groundwater in other areas. The average exploitation of groundwater in the NCP was 156.57×108 m^3 per year in 1970s, and up to 211.09×108 m^3 per year till 1980s. The depression cones of shallow and deep groundwater have formed since 1970s, and extended as large as 73000 km^2 in 2005. As a result, over-exploitation of groundwater has caused declining of water table, with serious delegation in both water quantity and quality.

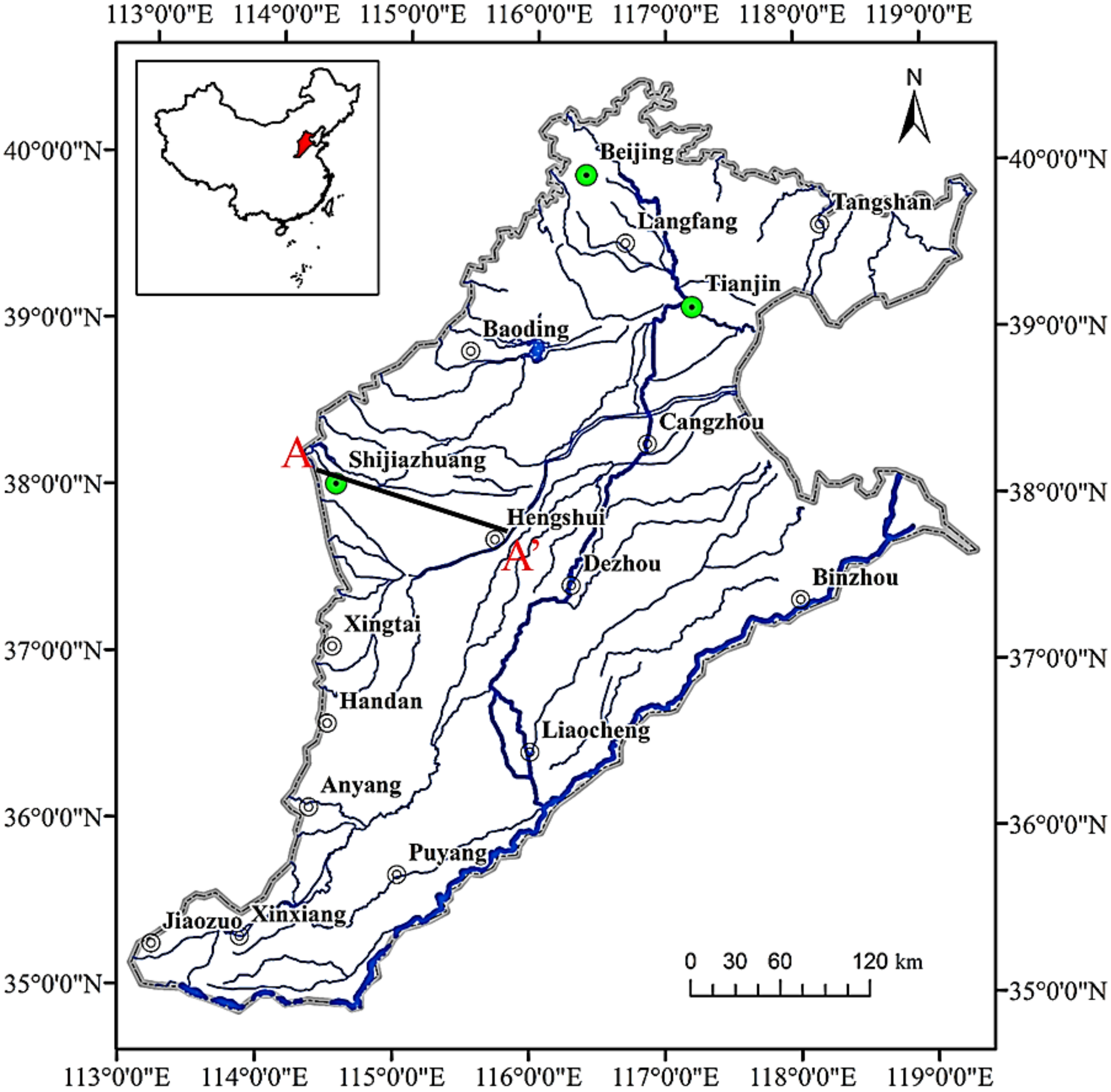


Figure 2-1 Location of North China Plain.

2.1.2 Regional hydrogeological and hydrochemical characteristics

The NCP covers a thick Cenozoic sedimentary basin bordered by the Taihang Mountains to the west, by the Bohai Sea to the east, by the Yanshan Mountain to the north, and by the Yellow River to the south (Figure 2-2). The elevation of NCP decreases from ≥ 100 m above mean sea level in the west to 1-2 m above mean sea level in the east. The NCP geographically can be divided into three parts: (1) the piedmont fluvial plain; (2) the central alluvial flood plain; and (3) the littoral delta plain. This study focuses on the fluvial plain and the central alluvial plain near the city of Shijiazhuang in the NCP.

The bedrock of NCP consists of archean gneiss and Proterozoic carbonate rocks covered by thick tertiary and quaternary deposits. The quaternary deposits are from 150 to 600 m thick and consist of fluvial deposits in the piedmont plain, alluvial and lacustrine deposits in the central plain, and alluvial deposits interbedded with marine deposits in the littoral plain (Chen et al., 2005b).

There are four aquifers in NCP: (1) Holocene (QI), (2) Upper Pleistocene (QII), (3) Middle Pleistocene (QIII), and (4) Lower Pleistocene (QIV).

QI is a phreatic aquifer, ≤ 60 m thick, containing of coarse-grained sand in the piedmont plain to fine-grained sand in the littoral plain. Ground water is fresh in the piedmont plain.

QII is a semi–confined aquifer, 60 m thick, containing of sandy gravel, medium to fine sand. QII is the main water supply stratum for agriculture and industry in the area. In the absence of a stable aquiclude, there is direct exchange between QI and QII.

QIII is a confined aquifer, more than 90 m thick, containing of sandy gravel in the piedmont plain to medium to fine sand in the central and the littoral plains. Compare with QI and QII, ground water is old, with TDS of 0.3 to 0.5 g L^{-1}.

QIV is a deep confined aquifer, 50 to 60 m thick and > 350 m deep, containing of cemented sandy gravel and a thin layer of weathered sand 20 to 40 m thick. TDS in this aquifer are <1000 mg L^{-1}. QIV originates from induced recharge from overlying aquifers. QIII and QIV are the main targets of groundwater exploitation.

According to groundwater exploitation and aquifer distribution, groundwater can be divided into shallow groundwater and deep groundwater. Shallow groundwater mainly occurred in QI and QII, while deep groundwater in QIII and QIV. Hydrochemical and isotopic composition clearly separate younger and older waters, which have a boundary at about 100 m in deep (Chen et al., 2003b; Lu et al., 2008).

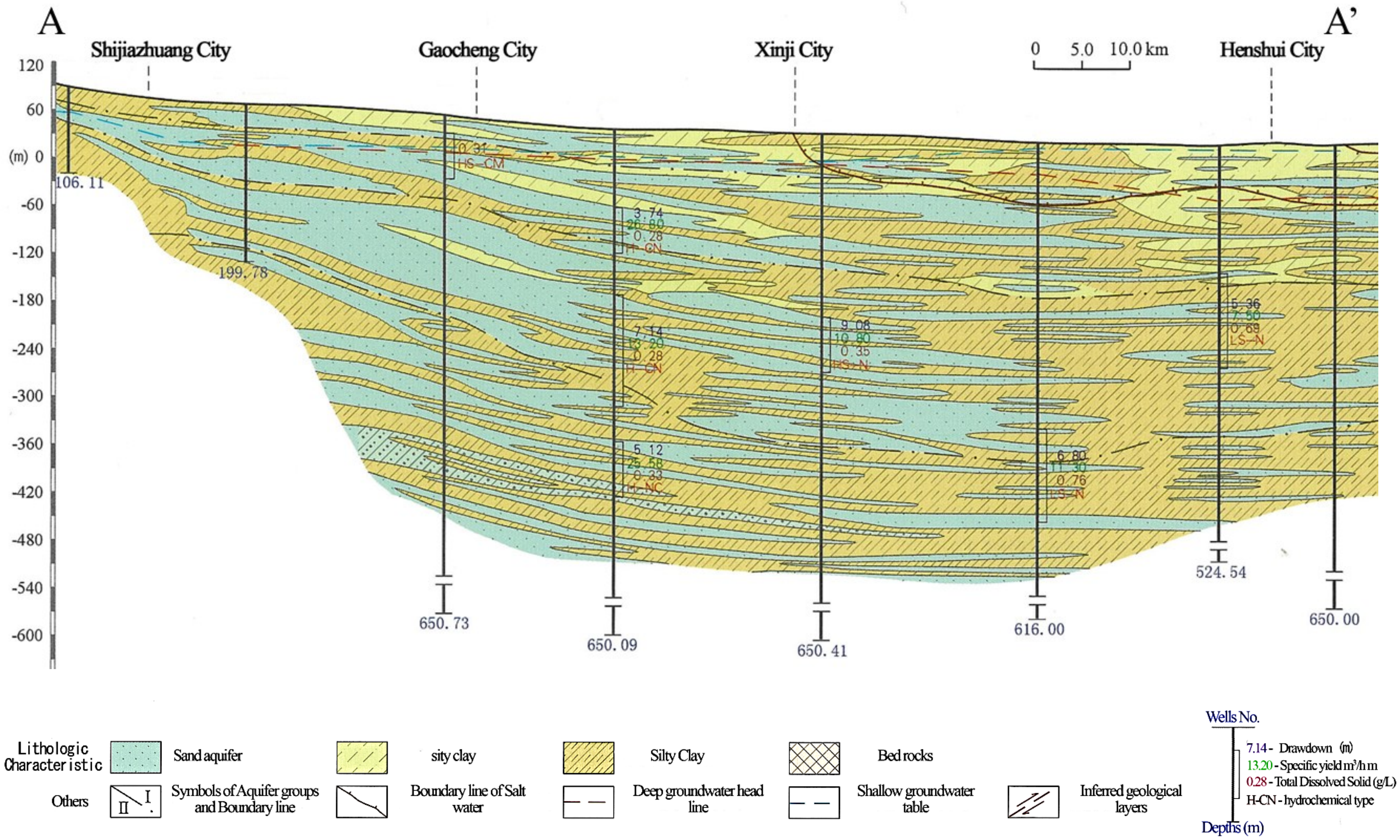


Figure 2-2 Hydrogeological profile of section line from Shijiazhuang City - Henshui City. (According to (Zhang et al., 2009c))

2.2 Description of the Xiaohe River basin

The study area is located on the alluvial plain of the Taihang Mountains near the city of Shijiazhuang in the NCP (Figure 2-3). It has a continental, semi–arid climate with a mean annual temperature of 14 °C, and an annual mean relative humidity of 65 %. Annual precipitation ranges from 335 to 1168 mm, with a mean annual precipitation of 573 mm (based on data for the period 1951–2003). The rainy season, which is characterized by large temporal and spatial variations, occurs from July to September and accounts for 70 % of the annual precipitation avaliable (Yang et al., 2006). Potential evaporation is about with 1928 mm year^{-1} (Li et al., 2008a).

The Xiaohe River is 110 km long, and is one of a few rivers that still flow in the NCP. It originates in the Taihang Mountains, and flows through Shijiazhuang, Lunancheng, Zhaoxian and Ningjin, before entering the Fuyang River. Shijiazhuang, the capital of Hebei province, has developed from a small village to one of the biggest cities in the NCP in the past 70 years. The population of the city is about 2.31 million, and its urban area has expanded to 155 km^2. When the Huangbizhuang Reservoir, one of the biggest reservoirs in the Taihang Mountains, was built in the upstream portion of the Xiaohe River in 1958 to manage the water supply for industry, domestic water in Shijiazhuang and agriculture in the study area.

Both agriculture and the city area of Shijiazhuang. For a conviency in this study, the Xiaohe River has been divided into three parts: upper reach, middle reach (city zone) and lower reach.

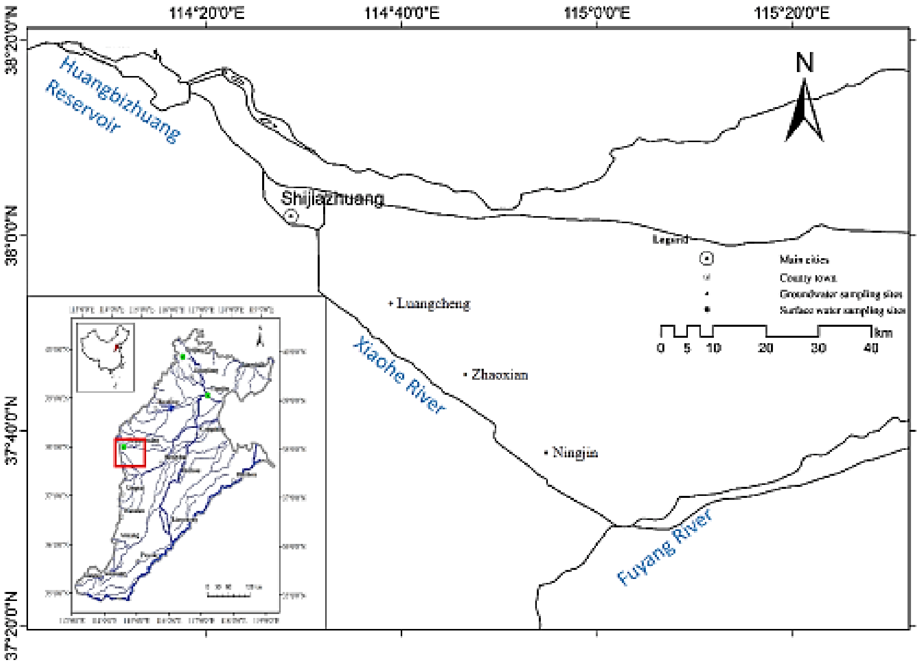


Figure 2-3 Location of the Xiaohe River basin.

2.2.1 Exploitation of groundwater in Xiaohe River basin

Groundwater is the most important water resources in the Xiaohe River basin. Over the past 50 years, groundwater has played an important role in the agricultural and industrial development of the Xiaohe River basin. The changes of groundwater table in the Xiaohe River basin can be divided into four stages.

(1) Before 1964, groundwater were in natural condition with little of over exploitation. Shijiazhuang was a small town with water supply of 3.9×10^5 m^3 per year, mainly for domestic water, and water table was about 3 to 5 meter in depth.

(2) 1964 – 1972, huge amount of groundwater has been pumped up to meet the needs for developing industry, agriculture and urbanization. Water table declined locally with a gradual increase in the groundwater exploitation. Huangbizhuang Reservoir were built in the 1958s, in the Taihang Mountain, and drainage channels were built in study area. Overexploitation has changed the patterns of runoff and recharge, making the drying up of rivers in middle and lower reach. The local depression cones resulted in the change of the natural groundwater flow system.

(3) From 1972 – 1985, the exploitation of groundwater increased dramatically, as a result, the regional water table rapidly declined at the rate of 3m/year in deep aquifers and 0.9m/year in shallow aquifers and the area of depression cones expanded on a large scale.

(4) After 1985, the decline of the groundwater table triggered a series of hydrogeological problems and geological hazards. The water table decreased at the rate of 1.1 m/year from 1986 to 2001, respectively. The depths to the potentiometric surface in the central parts of these cones have declined from 3 m in 1968 to 80 m in 1998. Increasing water demands associated with rapid urban development and expansion of irrigated land have led to overexploitation of groundwater. As a result, excessive use of groundwater in the study area have changed the structure of hydrological cycle so that the river has become the recharge source for groundwater.

2.2.2 Degradation of groundwater quality

Owing to severe water shortages, 80% of irrigation water is urban wastewater for the farmland in the Xiaohe River basin. Untreated wastewater has been used for irrigation in the Xiaohe River basin around Shijiazhung, like many other big cities in the NCP since the 1960s (Tang et al., 2004). The amounts of wastewater used for irrigation depended fundamentally on rainfall during the crop growing seasons. The average amounts of wastewater used for irrigating wheat and maize are estimated as 265 mm $year^{-1}$ and 155 mm $year^{-1}$, respectively. Using waste water for irrigation has caused groundwater pollution problems (Chen et al., 2006b; Li et al., 2008b; Yang et al., 2012a). Wastewater that leaches from the riverbed or infiltrates to farmland is threatening the drinking water source aquifers. As a result, surface water and groundwater quality problems have been very serious.

2.2.3 Particle size distribution and moisture content of soils

Particle size distribution was determined by direct sieving for the sand, the silt and clay fraction. Particle size of the sand, the silt and clay fraction were >0.074mm, 0.074-0.005mm and <0.005mm, respectively. Particle size distribution in wastewater irrigation area and groundwater irrigation area was shown in Figure 2-4. Soil samples were dried to constant weight at 105°C, moisture content,ϴ, was calculated as:

$$\Theta = \frac{m_{wet} - m_{dry}}{m_{wet}} \qquad \text{Equation 2-1}$$

where m_{wet} and m_{dry} are the masses of the sample before and after drying in the oven.

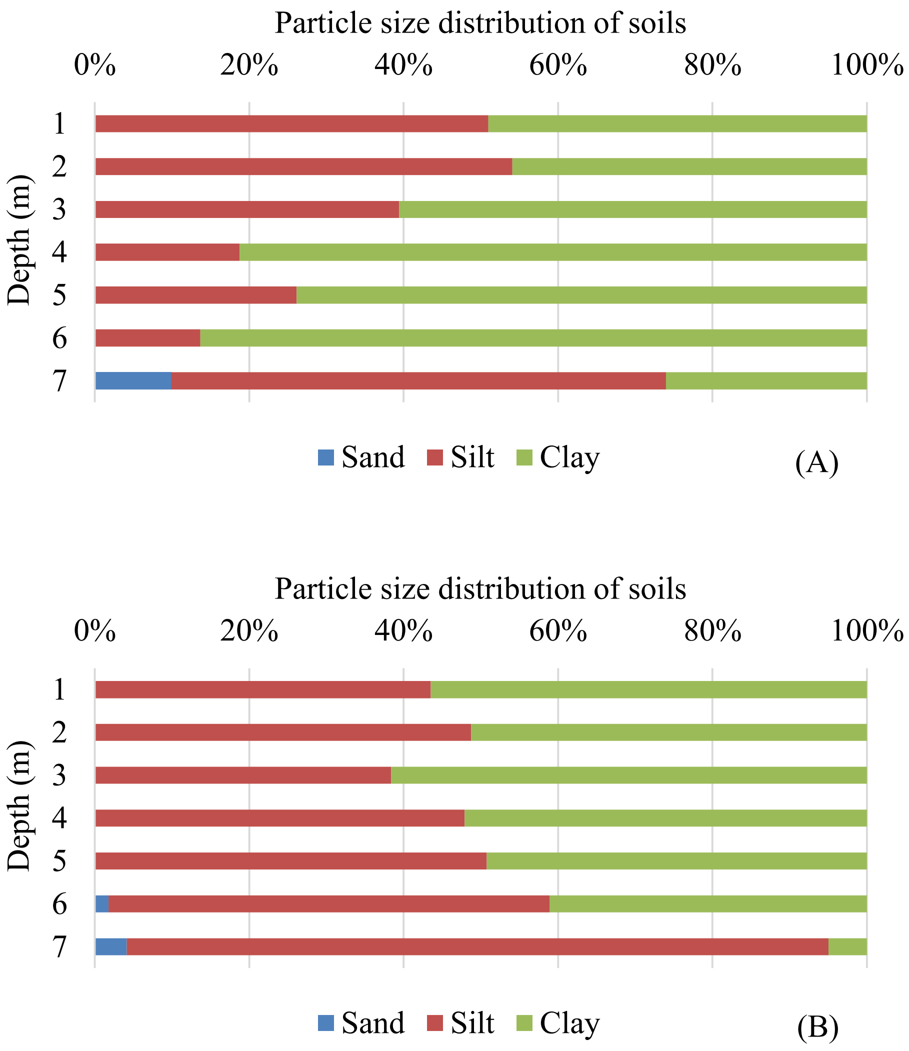


Figure 2-4 Particle size distribution of soils in depth (A) wastewater irrigation area (B) groundwater irrigation area.

Clay fraction was the main component in this study, with increasing depth silt and sand fraction content increased. The nature of the soil were divided into clay type and silty clay type.

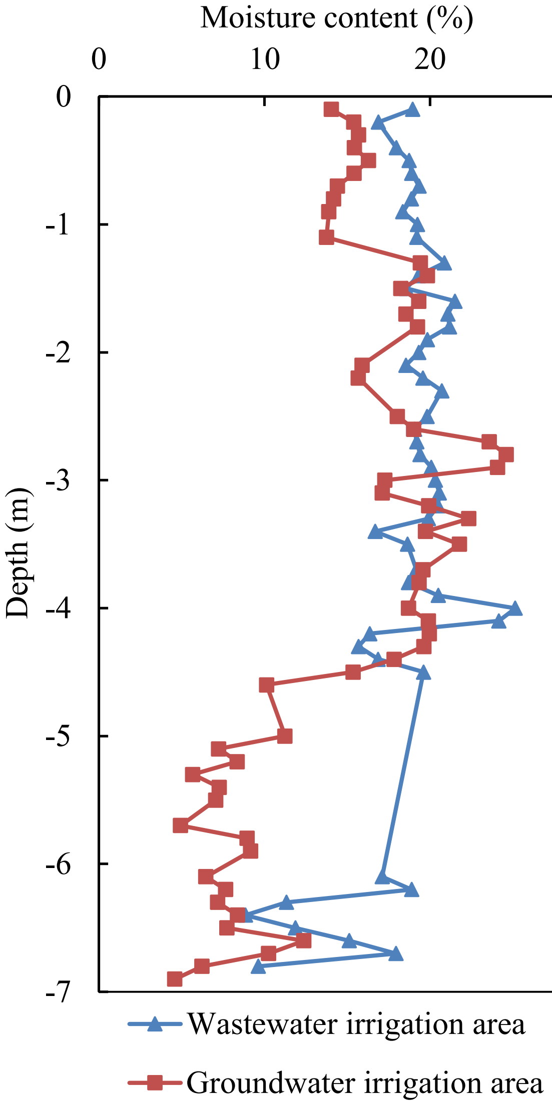


Figure 2-5 Moisture content in depth in wastewater irrigation area and groundwater irrigation area.

Moisture content of soils were between 5% and 25%, with increasing depth moisture content were decreased.

Chapter 3 Methodology

3.1 Field surveys and Sample collection

Field surveys were conducted to collect surface water and groundwater samples in March and October 2010. Surface water samples were collected at 12 sites along the Xiaohe River. A total of 16 groundwater samples were collected, 9 in March and 7 in October. All of the sampled wells were used for domestic, industrial or agricultural purposes, and were purged before sampling. Basic information, such as groundwater usage, well depth, screen position and land use, was acquired from well managers. Electrical conductivity (EC), dissolved oxygen (DO), oxidation-reduction potential (ORP) and pH were measured on-site using portable meters (D-55, D-54, Horiba®, Japan). Measuring precisions of EC, DO and pH were 1 $\mu S \cdot cm^{-1}$, 0.01 mg L^{-1}m, 1 mV and 0.1 pH, respectively. A global positioning system (GPS) was used to locate the sampling points. 200 ml water were collected to analyze major ions and environmental isotope ($\delta^{18}O$ and δD), 1 L water for $\delta^{15}N\text{-}NO_3^-$ in each site and water samples were brought back to a laboratory and stored at 4°C until analysis.

Groundwater samples for CFCs analysis were collected in October 2010. Samples were conserved in the field in a 100 mL brown glass bottle. The brown glass bottles were baked at 450 °C for 3 h to remove contamination and then used for sampling CFCs. For collecting samples for CFCs analysis, the baked brown glass bottle was set into an air-tight stainless container with a copper tube, the sample water was allowed to though the copper tube to the bottom of the glass bottle. In order to avoid the contamination of the atmosphere, when the bottle was filled, sealed the bottle under water with an aluminium–lined cap.

At each site, 2 L of water was collected in a pre-rinsed brown glass bottle and filtered through a 0.45 μm glass fiber filter (GF/F, Millipore®, USA) for extraction of EDCs. Samples were then acidified by 3 M HCl to $pH < 2$ and refrigerated until extraction. In addition, 50 ml of each surface water sample was used to determine the total organic carbon (TOC) by the total organic carbon analyzer (5000A, Shimadzu®, Japan).

3.2 Major ions Sampling collection and analysis

Major ions are very useful to understand spatial and temporal distribution of surface water and groundwater. Each sample was filtered through a 0.2 μm cellulose acetate filter membrane before determining major ion concentrations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-}) with ion chromatography (IC, LC-10AD, Shimadzu®, Japan). The limitation of detection (LOD) is 0.05mg L^{-1} in this study. Concentrations of HCO_3^- were measured by titration using 0.01N H_2SO_4. Results of chemical analyses were accepted only when the charge balance error was within ±5%. Total dissolved solids (TDS) were calculated as the total of all the major ions.

3.3 Environmental isotope: $\delta^{18}O$, δD, $\delta^{15}N$

3.3.1 Analysis method for environmental isotope deuterium (δD) and oxygen ($\delta^{18}O$)

Deuterium (δD) and oxygen ($\delta^{18}O$) isotope ratios were determined with laser spectroscopy (DLT-100; Los Gatos Research Inc.), as described by G. Lis (Lis et al., 2008). The results were reported as the per mil deviation relative to Standard Mean Ocean Water (SMOW) with precisions of ± 2.0 ‰ and ± 0.1 ‰ for δD and $\delta^{18}O$, respectively. A standard was measured once every ten samples as a quality control measure. The isotopic results were given in δ units, defined as

$$\delta^{18}O\ (\delta D) = \frac{R_{sample} - R_{standard}}{R_{standard}} \times 10^3\ ‰, \qquad \text{(Equation 3-1)}$$

where R is the ratio of the heavy isotope to the light isotope ($^{18}O/^{16}O$ or D/H).

3.3.2 Isotope analysis for $\delta^{15}N$–NO_3

The sampling and analytical procedures for $\delta^{15}N$–NO_3 determinations were conducted using the methods suggested by Silva et al. (2000). A column filled with Cl^- anion exchange resin (DOWEX® 1–X8 200–400 mesh, Sigma–Aldrich, USA) was used to extract nitrate. The anion-exchange column used contains 1.5g resin. Before using the column, 10 ml of 3 M HCl solution was dripped through the column to insure that the exchange sites have been fully occupied by chloride ions. It was followed by rinses of 30 mL deionized water (DW) to remove any excess chloride. The last 0.5 mL DW was held in the column to keep the resin beads completely hydrated. The columns were then tightly capped and stored at 4ºC until used.

Water sample was taken and filtered through a 47 µm glass microfiber filters (Whatman®, England) to remove particles that might clog the resin. Filtered water sample was allowed to flow through the column at a rate of 500-1000 ml h^{-1} by adjusting the stopcock on the separatory funnel in laboratory.

The NO_3^- sorbed was stripped from the columns by gravity dripping five 3 mL of 3M HCl through the column. The 15 mL of nitrate-bearing eluant was collected in 50 mL glass beakers. Because HNO_3 is volatile, it must be neutralized before freeze drying. Excess 6.5 g silver oxide (Ag_2O) was used for neutralization of the eluant. A final pH of about 5.5 - 6 was verified by pH test paper. The AgCl precipitate was removed by filtration. Additional DW was used to rinse the sample nitrate through the filter, bringing the sample volumes to about 40 mL each. Then the eluent is dried by freeze-drying, because $AgNO_3$ is light-sensitive, the treatment process above were taken to minimize exposure to light. The dried $AgNO_3$ is then combusted to N_2 in sealed quartz tubes for analysis by integrated elemental analyzer–isotope ratio mass spectrometer system (Integra-CN, PDZ Europa Ltd, UK). A standard was measured once every five samples as a quality control measure. The results were reported as the per mil deviation relative to AIR with analytical precisions of ± 0.2 ‰. It was given in δ units, defined as

$$\delta^{15}N = \frac{R_{sample} - R_{standard}}{R_{standard}} \times 10^3\ ‰, \qquad \text{(Equation 3-2)}$$

where *R* is the ratio of the heavy isotope to the light isotope ($^{15}N/^{14}N$).

3.4 Analysis method for CFCs

To understand how river water influenced groundwater, the age of the groundwater in this study was determined by analyses of CFC–12 and CFC–13, based on the methods of Oster et al. (1996). The CFCs in water samples was collected and purified by a purge and trap extraction system. In the system, the ultra-pure N_2 was used as purging and carrier gas. To avoid contamination and to reduce noise of system background, all devices were made without any plastics. Firstly, the sample was introduced into a stripping chamber, and the CFCs were purged with ultrapure N_2 and quantitatively collected in a trap (35 cm long, 1/8 Steel Use Stainless pipe, filled with Res-sil C and Porapak T) cooled at -40 ^{o}C by a refrigerant mixture of methanol and dry ice. Then the trap should be heated to 95 ^{o}C in the hot water to let the CFCs be injected into the gas chromatography through pre-column and analytical column in sequence by carrier gas. After CFCs entered the analytical column, the pre-column was back flushed to remove all other highly retentive halocarbons. CFCs were analyzed by a gas chromatograph (GC-14B, Shimadzu®, Japan) equipped with an Electron Capture Detector (ECD). After analysis had been completed, the water sample was drained into a pre-weighed beaker and then weighed for the calculation of CFCs concentration which was reported in pmol kg^{-1} of water. The uncertainties for CFCs determinations were approximately 1% for water equilibrated with the current atmosphere.

3.5 Analysis method for EDCs

3.5.1 Chemicals

All solvents used for sampling and analysis including acetone and methanol were HPLC grade. 4-tert-octylphenol (CAS No. 140-66-9), bisphenol A (CAS No. 80-05-7), 4-norm-nonylphenol (CAS No. 104-4-5) and phenanthrene-d10 (CAS No. 1517-22-2) were purchased from Wako Pure Chemical Industries (Japan). 4-nonylphenol (CAS No. 84852-15-3) that corresponded to a mixture of different isomers was obtained from Tokyo Chemical Industry (Japan). All glassware was baked for 4 - 5 h at 450 °C prior to use to remove organic contamination.

3.5.2 Extraction methods from environmental samples

Solid Phase Extraction (SPE) has been employed in analyzing water samples (Isobe et al., 2001; Laganà et al., 2004). In SPE, the sample is percolated through a SPE cartridge which retains the target substances and impurities (Figure 3-1). Then, the cartridge was eluted with solution of different compositions to separate the target substances and impurities. SPE technique offers the unique advantages of high concentration of the final extract, can be used to extract analytes of interest from a wide variety of environmental matrices, including water and soil.

The method to pretreat the water and SPE samples was based on previous reports from our laboratory (Tao et al., 2011; Zhang et al., 2011b; Zhang et al., 2009b). Each aliquot filtrate was spiked with 4-n-nonylphenol as a recovery indicator (100 ng L^{-1}) and extracted by a SPE cartridge (DSC-18 Resin, Supelco®, USA). The cartridge had been previously washed with 5 mL each of methanol and ultrapure water. Each filtered water sample was passed through one cartridge at a flow rate of 20 mL min^{-1}. Then, all of the cartridges were washed with 5 mL of a mixed solution of methanol and ultrapure water (1:19, v/v). The analytes were eluted from the cartridges with 20 mL dichloromethane for 40 min, and then the solution was concentrated to 0.2 mL under a gentle stream of high purity nitrogen. An appropriate volume of the internal standard (phenanthrene–d10) was added to the samples prior to GC – MS analysis.

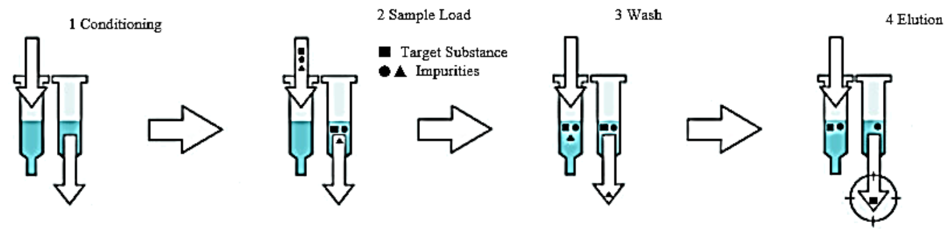


Figure 3-1 The process for SPE extraction.

The filter, which was used to trap the suspended particulate matters (SPM), was ultrasonically extracted with 30 mL methanol three times. Each extract was spiked with 4-n-nonylphenol as a recovery indicator (100 ng L^{-1}). The eluent was filtrated, and the residue on filter was washed with methanol. Subsequently, the filtrate was concentrated to approximately 5 ml by rotary evaporator at 30 ^{o}C. The residual solution was concentrated to 0.5 ml under a gentle stream of high purity nitrogen. An appropriate volume of the internal standard (phenanthrene–d10) was added to each sample and then diluted to a 1 ml volume prior to GC-MS analysis. In this study, considering the volume of the water samples filtered, the volume basis concentrations (i.e., ng L^{-1}) of the EDCs were calculated for particulate EDCs as described by Tao et al. (2011).

3.5.3 Procedure of GC-MS analysis

The concentrations of NP, OP and BPA were analyzed by gas chromatography–mass spectrometry (GC–2010, MS – Parvum2, Shimadzu®, Japan). An Rtx–5MS silica capillary column (30 m, 0.25 mm, 0.25 µm film thickness) was used for separation with helium as the carrier gas at a constant flow rate of 1 mL min^{-1}. GC-MS operating conditions were as follows: ionization potential of 70 eV and electron multiplier voltage of 1100 eV. The GC column oven temperature was programmed as follows: 70 °C hold for 2 min, then increased at 30 °C/min to 180 °C, 2°C/min to 200 °C, 30 °C/min to 310 °C and maintained for 30 min. The injection was set on a splitless mode at 250 °C. The MS interface temperature was maintained at 310 °C and was operated in the full-scan mode from m/z 50–500 for qualitative analysis. These ions (i.e., m/z = 107, 121, 135, 149, 163, 177, 220) were used as characteristic ions to identify NP in the SIM mode. Moreover, in the SIM mode, the characteristic ions for identifying OP were m/z=135, 107, 57 and for BPA, were m/z=213, 119, 228. (Table 3-1).

Table 3-1 Retention time and selection ions of EDCs in GC-MS-SIM mode.

Compounds	Retention time	Selected ion (abundance)	
4-t-OP	8.84	135 (100)	107(12.4)
4-t-NP	9.92	135 (100)	121(49.8)
		149(37.9)	107(72.6)
Phe-d10	11.35	188(100)	94(21.1)
4-n-NP	12.85	107(100)	220(9.7)
BPA	19.5	213(100)	119(29.7)

3.5.4 Quality assurance and quality control (QA/QC)

Linearity of the analytical method was determined with five different concentration working standards, and good linearity was observed ($r^2 \geq 0.99$). The average recoveries of water and particulate materials were 82.3 – 96.5 % and 78.2 – 113 %, respectively. In addition, for every batch of 10 samples, a solvent blank, a procedural blank and a standard mixture were run to assess for contamination. Furthermore, a field quality assurance protocol was performed with the field blanks, which were made from organic-free distilled water and subjected to the same sample processing as the water samples, to determine the potential for contamination. According to these results, there was no blank correction to be performed because of undetected amounts of background EDCs.

Chapter 4 Groundwater flow

4.1 Introduction

The North China Plain (NCP) is the largest alluvial plain in eastern Asia, and is one of China's most important social, economic and agricultural regions (Liu et al., 2001). The increased demands on water for agricultural, industrial and domestic purposes have caused a water crisis in the NCP (Chen, 2010). Water extraction from thousands of pumping wells has caused the water table in the unconfined aquifer to decrease at a rate of approximately 1 m year^{-1}, and the regional groundwater depression cone has expanded by more than 14,000 km^2 (Yang et al., 2004b). It is clear that the regional water cycle in the semi-arid NCP has been severely disrupted, because of long-term human activities. (Liu and Xia, 2004; Sato et al., 2008). Information on recharge is critical for sustainable groundwater management in NCP.

Many dams have been built in the last half-century to regulate the rivers that flow across the NCP (Chen et al., 2012). Runoff and recharge patterns have changed greatly (Zhuang et al., 2011) such that rivers have become the main source of groundwater recharge in the NCP. Worldwide, there is great interest in using hydrochemical and environmental isotopes (δD and $\delta^{18}O$) methods to help understand relationships between surface water and groundwater (Barbecot et al., 2000; Bennetts et al., 2006; Darling et al., 2003; Dor et al., 2011; Lang et al., 2006; Sophocleous, 2002). Song et al. (2011) analyzed environmental isotopess and major hydrochemical components in the Huaisha River basin and the Taihang mountain region to examine the interactions between surface water and groundwater, as well as the hydrochemical characteristics.

The key to understanding the movement of water in the watershed is the residence time. Dating techniques based on transient tracers such as chlorofluorocarbons (CFCs) have been used to indentify groundwater age (Gooddy et al., 2006; Han et al., 2012; Oster et al., 1996). Groundwater recharge rates and residence times can also help us to understand the migration of chemicals in aquifers (Busenberg and Plummer, 2008).

Many new hydrological issues associated with disrupted water cycles need to be addressed in response to increasing water demands in arid and semi-arid areas. However, there is limited knowledge of the processes involved. The aim of this study was to use a combination of multiple tracers, such as environmental isotopes ratios (δD, $\delta^{18}O$) and CFCs, to (1) identify the effect of river water on regional groundwater; and (2) estimate residence time of groundwater.

4.2 Site description

The site description has been presented in Chapter 2. For the sake of discussion in this study, the Xiaohe River has been divided into three parts: upper reach (S1), middle reach (city zone; S2 – S4) and lower reach (S5 – S12; Figure 4-1).

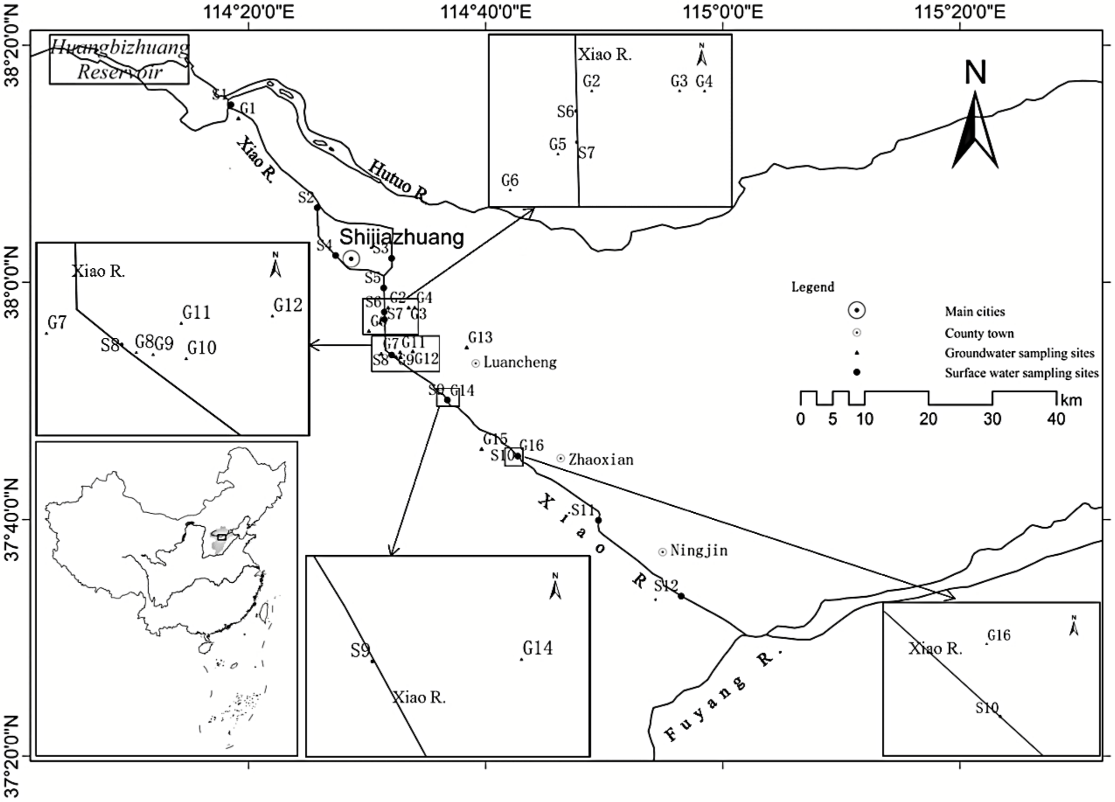


Figure 4-1 Study area and sampling locations.

4.3 Sampling method

The methodology has been presented in Chapter 3.

4.4 Results

4.4.1 δD, δ^{18}O and Cl^- in surface water and groundwater

Cl^- concentration ranged from 52.6 mg L^{-1} to 313.6 mg L^{-1} with a mean of 233.7 mg L^{-1} in surface water, and ranged from 8.9 mg L^{-1} to 178.6 mg L^{-1} with a mean of 95.0 mg L^{-1} in groundwater, respectively (Table 4-1). Cl^- concentration in surface water was significantly higher in groundwater.

The values of δ^{18}O and δD in surface water samples ranged from -8.36 ‰ to -7.23 ‰, with a mean of -7.88 ‰, and from -60.51‰ to -54.13‰ with a mean of -57.91 ‰, respectively (Table 4-1). The composition of δ^{18}O and δD values in groundwater varied from -9.85 ‰ to -7.53 ‰ with a mean value of -8.72 ‰ and from -67.90 ‰ to -54.26 ‰ with a mean value of -62.67 ‰, respectively. The mean values of δ^{18}O and δD in groundwater were lower than that in surface water.

Table 4-1 Cl^- concentration and environmental isotope (δ^{18}O, δD) in autumn.

ID	δ^{18}O	δD	Cl^- (mg L^{-1})
S1	-7.2	-54.1	52.6
S5	-8.1	-60.5	134.6
S6	-7.8	-60.5	274.5
S8	-7.9	-56.7	250.2
S9	-7.7	-56.4	313.6
S10	-8.0	-57.1	276.4
S11	-8.0	-58.0	299.3
S12	-8.4	-60.0	268.3
G1	-7.5	-54.3	47.8
G8	-8.5	-61.7	178.6
G9	-9.3	-64.9	104.2
G10	-9.8	-67.9	8.9
G14	-8.4	-61.6	163.7
G15	-9.1	-66.0	38.2
G16	-8.4	-62.3	123.4

4.4.2 Measured concentrations of CFCs

Concentrations of CFC-12 and CFC-11 in groundwater were analyzed at 7 sites to estimate the residence time of groundwater in the aquifer. Excepting to G10, CFC-11 and CFC-12 were detected from groundwater. Among them G8 has hightest concentrations of CFC-11 (4.436 pmol kg^{-1}) and CFC-12 (14.448 pmol kg^{-1}), respectively (Table 4-2). G10 in depth with 150m has the deepest depth of 7 sites, was not detected the presence of CFC-12 and CFC-11.

Table 4-2 Groundwater well data and measured CFCs concentrations.

ID	Well depth (m)	Distance away from river (km)	Measured CFC–12 (pmol kg^{-1})	Measured CFC–11 (pmol kg^{-1})
G1	112	1.15	0.694	1.647
G8	58	0.005	14.448	4.436
G9	120	0.244	0.328	0.627
G10	150		0	0
G14	60	0.086	0.659	2.114
G15	80	2.492	0.148	0.163
G16	75	0.113	1.184	2.497

4.5 Discussion

4.5.1 Surface water as an agent to recharge groundwater

Since the 1970s, water demand has doubled because of the rapid development of cities and industries, and the expansion of farmlands. The groundwater level was found to decrease afterwards due to excessive exploitation. Figure 4-2 shown a clear trend of the water table decreases at Luancheng Experimental Station (altitude is 50.27 m above sea level). The water table dropped from 10.9m in 1975 to 28.8 in 1999, at an average rate of 0.7 m/year. The water table rose sharply to 2.2 m in 1997, responding to the heavy rainfall and the flooding event of 1996 (Chen et al., 2003a). The overuse of surface water resources and excessive exploitation of groundwater have drastically altered the regional hydrological cycle in the NCP. As a result, water table in the study basin was more than 30 m below the surface, and the Xiaohe River has become an important recharge source for the local groundwater.

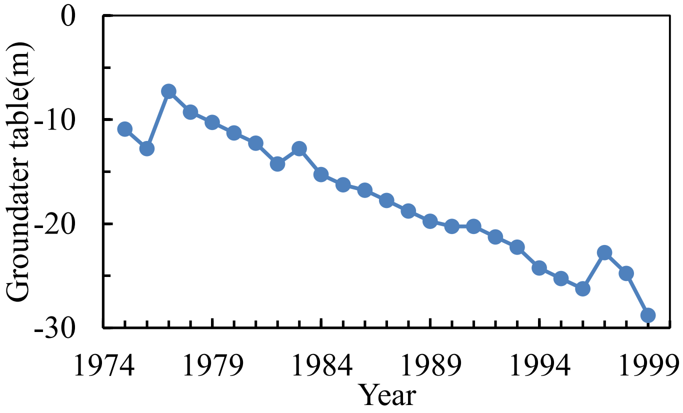


Figure 4-2 Changes in groundwater table at Luancheng Experimental Station from 1974 to 1999 (Chen et al., 2003a).

The trend of chloride in groundwater reflecting infiltration process from surface water to groundwater (Figure 4-3). Cl^- concentration in groundwater decreased rapidly in the Xiaohe River basin, from more than 230 mg L^{-1} to about 50 mg L^{-1} (mean of 133.16 mg L^{-1}), as distance from the river increased. This indicates that regional groundwater in the Xiaohe River basin is strongly influenced by river infiltration, except in certain deep wells such as

G10. G10 is protected by an aquiclude with a low Cl⁻ concentration (8.8 mg L^{-1}), and no significant pollutants were observed at this site.

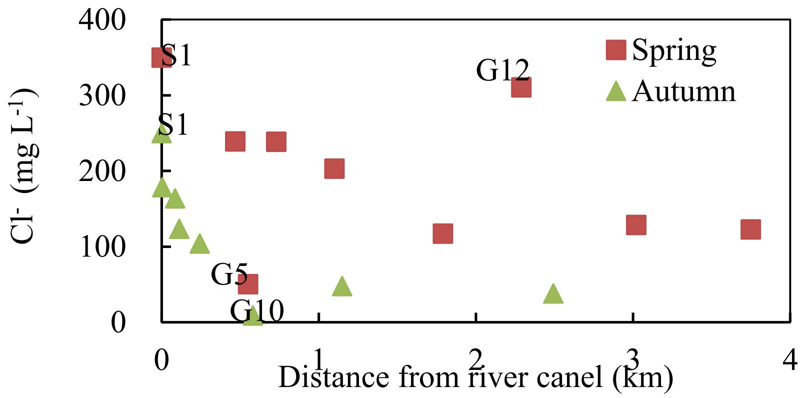


Figure 4-3 Variations in Cl⁻ concentrations in groundwater with distance from the river channel.

Because of the mixing processes of different waters and the variation in the isotopic composition of precipitation, the $\delta^{18}O$ and δD values in groundwater and surface water can be used to identify the interaction between of them (Négrel et al., 2003). The local meteoric water line (LMWL) for Shijiazhuang was determined with the 'Global Network Isotope in Precipitation' data in the period from 1985 to 2003 (WMO/IAEA, Figure 4-4). Both the groundwater and surface water isotopic composition deviated from the LMWL in a direction indicative of fractionation due to strong evaporation.

The heaviest values for $\delta^{18}O$ (–7.2 ‰) and δD (–54.1 ‰) were found at the reservoir site (S1), indicating the increased evaporation relative to other sites. Because of the similar isotope composition to the surface water at S1, groundwater at site G1 is recharged by the reservoir water. The lightest isotopic compositions in groundwater were found at site G10, with values of –9.8 ‰ for δ^{18}O and –67.9 ‰ for δD. Compared with the LMWL, the stable isotopic compositions of δ^{18}O and δD in groundwater in the study area indicate a predominantly meteoric source. Groundwater data was scattered, and was to the right of the meteoric water line. Deep groundwater in NCP receives lateral recharge from the mountains with δ^{18}O values lower than -9 ‰ in the aquifers deeper than 100 – 150 m (Zhang et al., 2000).

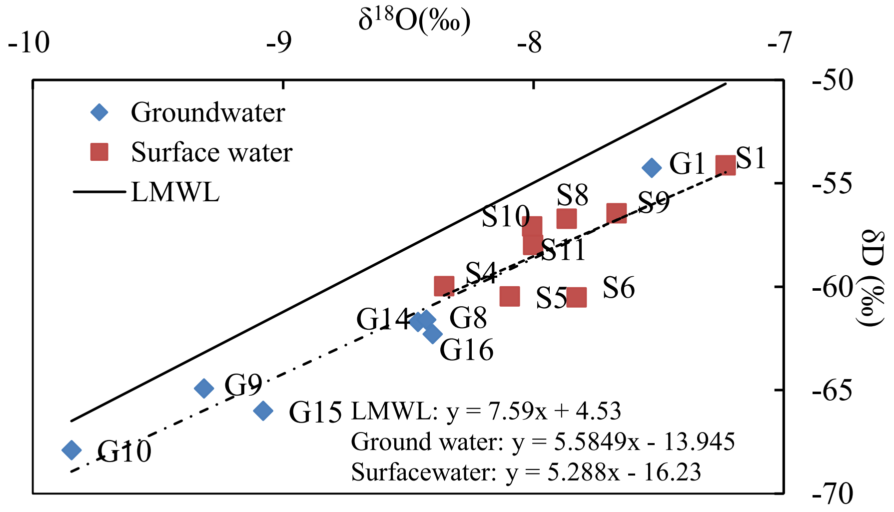


Figure 4-4 Relationship between δ^{18}O and δD in groundwater and surface water of the study region in autumn.

The contribution of the river water to groundwater is a key to assessing the quality and quantity of regional groundwater along the Xiaohe River. Assuming that groundwater is the result of mixing old groundwater and river water, the following equation can be used to assess the contributing fraction (*cf*) of river water to the groundwater in the study area:

$$cf = \frac{C_i - C_{OG}}{C_{Ri} - C_{OG}} \times 100\,\% , \qquad \text{(Equation 4-1)}$$

where C_i, C_{Ri} and C_{OG} are the contents of Cl^-, δD or $\delta^{18}O$ (mg L^{-1} or ‰) for groundwater at site i; the river water at the sampling point nearest to site i; and the old groundwater without influenced of the river. In the NCP, groundwater with $\delta^{18}O$ values lower than –9 ‰ is considered to have formed before 10 ka (Zhang et al., 2000). Because of the lowest $\delta^{18}O$ value of G10 and undetected CFCs, G10 was selected as the old groundwater in this study (Table 4-3).

Accordingly, the average contribution of the Xiaohe River for groundwater were estimated as 50, 47 and 60 %, respectively. It suggests that more than half the volume of local groundwater is recharged by the Xiaohe River in the area on both sides of the river. Therefore, the Xiaohe River is the main source to the regional groundwater.

Table 4-3 Estimated of the contributing fraction (*cf*) of river water to groundwater.

C_i				C_R				*cf* (%)			
ID	Cl^- (mg L^{-1})	δD (‰)	$\delta^{18}O$ (‰)	ID	Cl^- (mg L^{-1})	δD (‰)	$\delta^{18}O$ (‰)	ID	Cl^- (mg L^{-1})	δD (%)	$\delta^{18}O$ (%)
G1	47.83	-54.26	-7.53	S1	52.57	-54.13	-7.23	G1	89	99	89
G8	178.62	-61.70	-8.46	S8	250.18	-56.70	-7.87	G8	70	55	70
G9	104.21	-64.92	-9.32	S8	250.18	-56.70	-7.87	G9	40	27	27
G14	163.66	-61.60	-8.43	S9	313.55	-56.45	-7.67	G14	51	55	65
G15	38.19	-66.01	-9.08	S11	276.39	-57.08	-8.01	G15	11	17	42
G16	123.43	-62.29	-8.40	S10	276.39	-57.08	-8.01	G16	43	52	79

4.5.2 Dating by considering the recharge from the river

Because of the recharge of surface water to groundwater, the mean of contributing fraction (*cf*) estimated from Cl^-, δD or $\delta^{18}O$ was used to calculate the CFCs concentration of young groundwater (Calc.-CFCs) expected to have mixed with older groundwater in the aquifer.

$$Calc.-CFCs \quad = \frac{Anal.-\ CFCs}{cf} \qquad \text{(Equation 4-2)}$$

where Anal.-CFCs is analysis concentrations of CFCs for groundwater samples; *cf* is the contributing fraction of river water to groundwater.

The corresponding apparent recharge year for groundwater are shown in Table 4-4. Results indicate that groundwater at sites G1, G8, G9, G14, G15 and G16 was recharged the period from 1965 to the present. Among them the youngest groundwater was fround at G8, close to the river, while the oldest groundwater at G10. Considering groundwater flow and the sampling location, it was found that apparent recharge year for increases as the distance away from the river. Rohden et al. (2010) employed several environmental tracers (^{3}H – ^{3}He, noble gases, and the environmental isotopes ^{18}O and ^{2}H) to estimate groundwater recharge and residence times in the Shijiazhuang area. They showed that groundwater in the unconfined parts of the piedmont plain contained tritium to depths of about 100 m and exhibited ^{3}H – ^{3}He ages of less than 40 years.

Based on information of well depth and CFCs apparent recharge year, the vertical velocity of groundwater in the study area was estimated at about 1.8–3.5 m year^{-1} which was close to results estimated as 2.5 m year^{-1} by tritium (von Rohden et al., 2010) as well as 2.0-2.5 m year^{-1} by nitrate (Chen et al., 2006b).

Table 4-4 The average contributing fraction of river water to groundwater calculated CFCs values and the apparent recharge year

ID	Average Contributing fraction [a] (%)	Calculated CFC–11 (pmol kg^{-1})	Calculated CFC–12 (pmol kg^{-1})	Apparent recharge year (by CFC–11)	Apparent recharge year (by CFC–12)
G1	92	0.752	1.785	1972	1973
G8	65	C.	C.	New	New
G9	31	1.060	2.024	1974.5	1974
G10	NA	ND	ND	Old	Old
G14	57	1.156	3.710	1975	1983.5
G15	23	0.631	0.698	1970.5	1965
G16	58	2.050	4.324	1984.5	1987

C.: CFCs concentration is greater than possible values in equilibrium with modern air.

NA: not applicable. ND: not detected.

[a] Contributing fractions were calculated by Cl^-, δD or $\delta^{18}O$.

4.6 Conclusions

In this study, chloride, environmental isotopes and CFCs were used to study the characteristics of surface water and groundwater. The main findings are as follows:

1. Due to continuous declining in groundwater levels, surface water has become one of the most important recharge sources to local groundwater in study area.
2. The values of $\delta^{18}O$ and δD in surface water ranged from -8.36 ‰ to -7.23 ‰ and -60.51‰ to -54.13‰. The composition of $\delta^{18}O$ and δD values in groundwater varied from -9.85 ‰

to -7.53 ‰ and -67.90 ‰ to -54.26 ‰, respectively. About 50 – 60 % volume of local groundwater were considered as the recharge from the Xiaohe River.

3. CFCs results indicated that groundwater at sites G1, G8, G9, G14, G15 and G16 was recharged the period from 1965 to the present. CFCs is undetected at G10 is considered as the old groundwater in this study. The vertical flow velocity of groundwater was calculated as about 1.8–3.5 m year^{-1}.

Chapter 5 Characteristics of major ions in surface water, soil and groundwater

5.1 Introduction

The major ions composition of waters (e.g., Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, SO_4^{2-} and Cl^{-}) reveals the mechanisms that control the chemical composition of waters, such as the nature of weathering, patterns and linkages between evaporation and anthropogenic processes on a basin wide scale (Gibbs, 1970; Gorham, 1961). Quantifying the major ions composition of river water also has wide effects, e.g. water type, hydro chemistry characteristics, rainfall rock and weathering processes (Cruz and França, 2006).

Many previous studies have reported the major ions hydrochemistry of many major rivers in the world, e.g. the Amazon (Gibbs, 1970), the Mississippi (Forester, 1986), the Orinoco River (Forester, 1986), the Ganga river (Sarin et al., 1989) and the Danube (Pawellek et al., 2002). For Chinese rivers, most studies have focused on the Changjiang (Yangtze River) (Chen et al., 2002; Edmond et al., 1985), the Huanghe (Yellow River) (Zhang et al., 1995), the Zhujiang (Pearl River) (Chen and He, 1999; Zhang et al., 2009a) and the Huai River (Yang et al., 2012b; Zhang et al., 2011a). However, few studies have focused on the Xiaohe River, an artificial river of the Shijiazhuang City, NCP, China.

Chemical analyses of surface water, groundwater, and soil samples were evaluated as part of an investigation of Xiaohe River basin. The Samples were analyzed for major ions to characterize the hydrochemical composition of waters in different media, to relate these characteristics to hydrogeochemical processes.

In many farmed areas, intensive application of agricultural chemicals and pumped groundwater for irrigation have led to water quality issues. Unsaturated-zone processes, play a major role in these effects but are not well understood.

In this chapter, the Xiaohe River Basin was chosen to determine the variations of hydrochemical characteristics, geochemical processes and impact of human activities in surface water, groundwater and soil.

5.2 Site description

Sampling sites for both surface water groundwater have been presented in Chapter 4.2.

In order to study the vertical distribution of major ions in unsaturated zone.Two soil cores were collected in farmland under different irrigation practices (Figure 5-1). One soil core was collected in the area irrigated by wastewater, the other one in the area irrigated by pumping groundwater. Since the wastewater contained large amounts of nutrients, little chemical fertilizers were applied in wastewater irrigation area. In groundwater irrigation area, large amount of chemical fertilizers were used. The same crops were winter wheat and summer maize were planted in both areas.

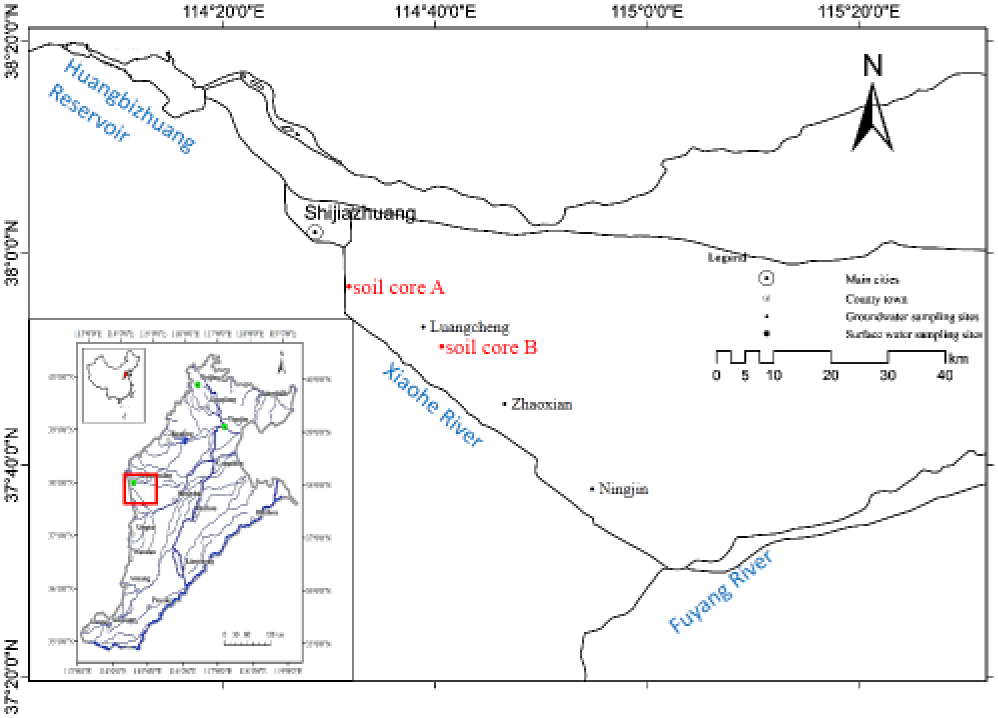


Figure 5-1 Study area and sampling locations of soil cores.

5.3 Methods

5.3.1 Water sample collection

The sample collection for surface and groundwater has been presented in chapter 3.

5.3.2 Undisturbed soil cores sampling and analyses

Soil cores were taken in the way of direct push drill rig (Model 54DT, Geoprobe®, US). Borehole depth was 7.4 and 7.9 m in wastewater irrigation area (A) and groundwater irrigation area (B), respectively. Soil cores were collected for every 1.2 m-interval in plastic sample sleeves, capped, and freezing stored in the field.

Soil samples were taken by cutting soil cores in 5 cm-interval, put in plastic bags and stored in freezing until analysis. Soil samples were oven dried at 105°C for 48 hr to determine soil moisture content. In order to analyze the major ions content in soil, 50 mL of deionized water (DW) was added to 10 g of dried soil. The mixture was placed in a reciprocal shaker at 120 rpm for 6 hr, centrifuged at 3,000 rpm for 20 min, and the supernatant was filtered through a 0.2 μm syringe filter (Minisart®, US). The pH, EC and major ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-}) of infiltrate were measured in the way described in Chapter 3.

5.4 Results

5.4.1 pH, EC, DO and ORP in the Xiaohe River

The water pH value is an important parameter for considering the water geochemical evolution in a river. The pH values of surface water samples collected in the Xiaohe River ranged from 7.5 to 8.8 with a mean value of 8.1 in spring and from 6.7 to 9.7 with a mean value of 7.3 in autumn, respectively. The pH values of surface water in most of the samples were above 7.0 (Figure 5-2). The lowest pH value was found at S6 in autumn, where a large number of urban wastewater discharged to the Xiaohe River.

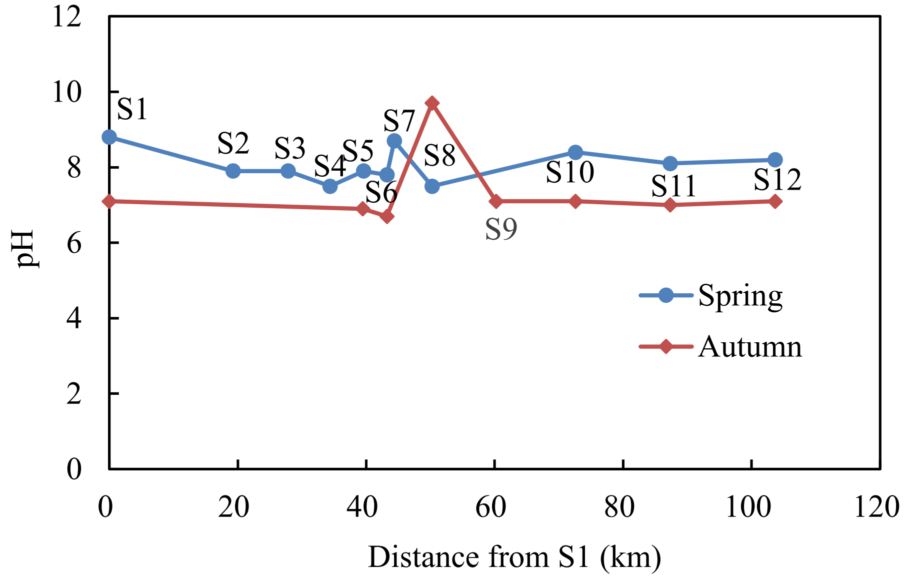


Figure 5-2 Variation of pH in surface water along the Xiaohe River.

The EC values ranged from 241 to 2,690 µS cm^{-1} with a mean value of 1,584 µS cm^{-1} in spring and from 603 to 2,260 with a mean value of 1,832 µS cm^{-1} in autumn, respectively. The lowest value of EC was found at the Huangbizhuang reservoir (S1). The highest value of EC was found at S6 in both seasons. From the Huangbizhuang Reservoir (S1) to the downstream of the Xiaohe River (S12), EC values in surface water increased from 241 to 2690 µS·cm^{-1} in spring, and from 603 to 2260 µS·cm^{-1} in autumn. Comparing to spring, EC values in autumn was higher in the upper and middle reach, and lower in the lower reach (Figure 5-3).

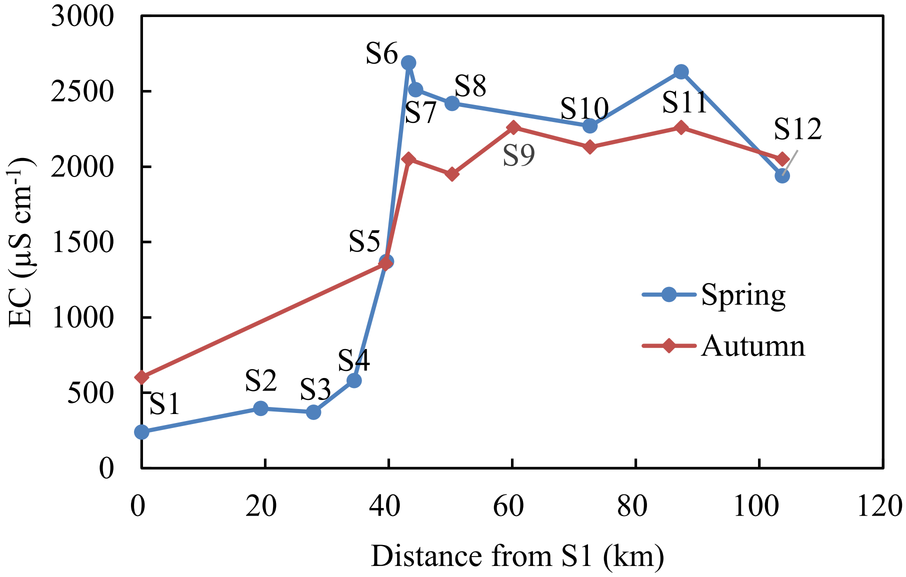


Figure 5-3 Variation of EC in surface water along the Xiaohe River.

DO concentrations in Xiaohe River ranged from 0.10 mg L^{-1} to 5.05 mg L^{-1} with an average of 2.06 mg L^{-1}. The surface water had DO value ranging from 4.20 to 5.05 mg L^{-1} before flowing into Shijiazhuang city (Figure 5-4). Because of effluents from Shijiazhuang city, DO value in the lower reach ranged from 0.10 mg L^{-1} to 2.30 mg L^{-1}, with an average of 0.60 mg L^{-1}. The lowest DO value was found at S10 in spring. Therefore, effluents of the Shijiazhuang City was responsible for the sharp declining of DO value when the river flowed into the lower reach.

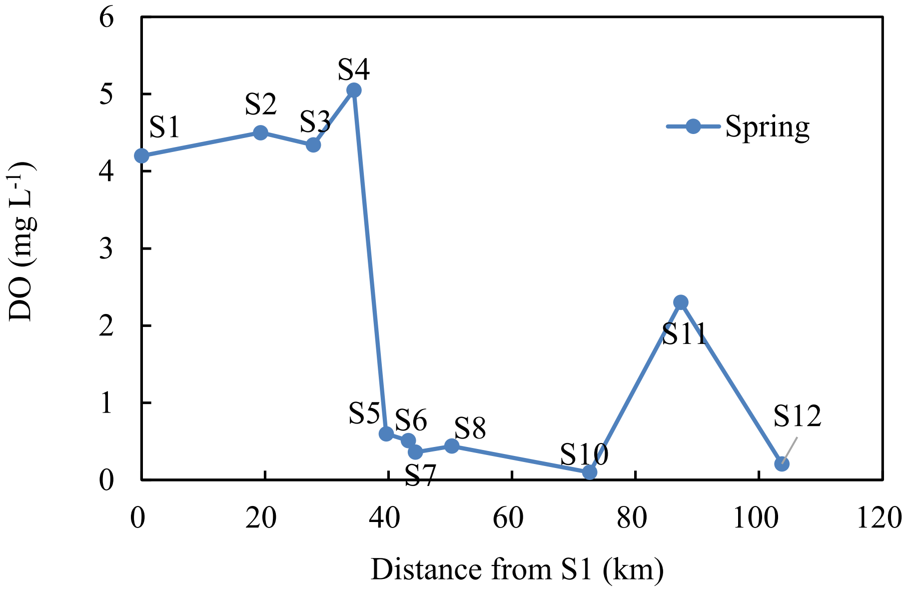


Figure 5-4 Variation of DO in surface water along the Xiaohe River in spring.

Oxidation Reduction Potential (ORP) is a measure of the tendency of a chemical species to acquire electrons and thereby be reduced. In fact, it is common to have complex non-equilibrium conditions between a large number of species, meaning that it is often not possible to make accurate and precise measurements of the reduction potential in field. However, it is usually possible to obtain an approximate value and define the conditions as being in the oxidizing or reducing regime (vanLoon and Duffy, 2011). ORP had significant changes in surface water with DO. ORP in Xiaohe River ranged from -321 mV to 497 mV with an average of -73 mV. The surface water had positive ORP value ranging from 17 to 497 mV in the upper and middle reach, and dropped to negative value in a rage from -177 mV to -321 mV in the lower reach (Figure 5-5).

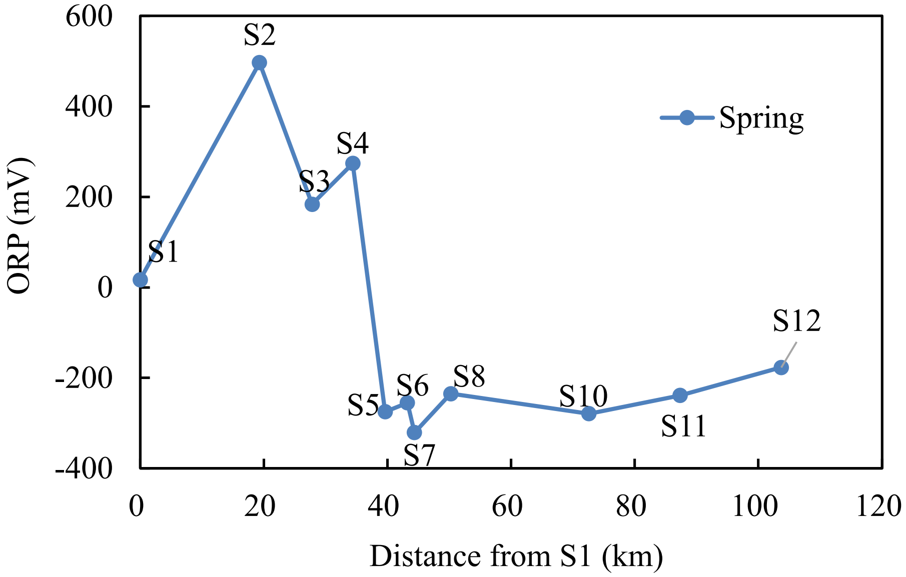


Figure 5-5 Variation of ORP in surface water along the Xiaohe River in spring.

5.4.2 Major hydrochemical composition in Xiaohe River

The chemistry of a water samples can be illustrated in the piper diagram (Figure 5-6). The cations and anions are shown by separate ternary plots. The apexes of the cation plot are Ca^{2+}, Na^{+}+K^{+}, Mg^{2+}. The sum of the concentrations of the three ions, in meq L^{-1}, is recalculated to 100% and the relative composition is plotted in the triangle. For anions, the apexes of the anion plot are SO_4^{2-}, Cl^{-}+NO_3^{-} and HCO_3^{-}. The two ternary plots are then projected onto a diamond. The diamond is a matrix transformation of a graph of the anions (SO_4^{2-} + Cl^{-}+NO_3^{-} / total cations) and cations (Ca^{2+} +Mg^{2+} / total cations).

The piper diagram shows hydrochemical characteristics of all surface water samples in the Xiaohe River in spring (March) and autumn (October) (Figure 5-6). For the major cation, in the upper reach (S1), Ca^{2+} was the dominant cation, with concentration of 30.40 mg L^{-1} in spring and 54.37 mg L^{-1} in autumn (Table 5-1). The mole equivalence ratios of total cations was decreased from 50 to 28 % for Ca^{2+} in the upper and middle reach of the Xiaohe River (S1-S6). Na^{+}+K^{+} was the dominant cation in the lower reach from S6 to S12, and the mole equivalence ratios of total cation for Na^{+}+K^{+} were 50-61% in spring and 60-68% in autumn, respectively. Mg^{2+} concentration ranging from 30.40 to 139.12 mg L^{-1} with an average of 105.10 mg L^{-1}, and it contributed to 11-30% of the total cation. Generally, for the surface water the prevalent cation were Ca^{2+} > Na^{+}+K^{+} > Mg^{2+} in the upper and middle reach (S1-S5), and Na^{+}+K^{+} > Ca^{2+} > Mg^{2+} in the lower reach of the Xiaohe River (S6-S12).

For the major anion, HCO_3^- was the dominate anion and followed by SO_4^{2-} and Cl^-. HCO_3^- ranged 63.00-913.50 mg L^{-1} with an average of 536.90 mg L^{-1}, and the mole equivalence ratios of HCO_3^- was about 42% of the total anions. SO_4^{2-} had a range from 61.22 to 752.26 mg L^{-1} with an average of 26.38 mg L^{-1}, and the mole equivalence ratio of SO_4^{2-} was about 29% of the total anions. Cl^- ranged from 16.14 to 412.32 mg L^{-1} with an average of 234.15 mg L^{-1}, and contributed about 28% of the total anion.

Stiff diagram is a graphical representation of chemical analyses, first developed by H.A. Stiff in 1951. It is widely used by hydrogeologists and geochemists to display the major ion composition of a water sample. A polygonal shape is created from three parallel horizontal axes extending on either side of a vertical zero axis. Cation are plotted in milliequivalents per liter on the left side of the zero axis, one to each horizontal axis, and anions are plotted on the right side. Stiff diagram is useful in making a rapid visual comparison between water from different sources. Stiff diagram can be used to help visualize ionically related waters from which a flow path can be determined, and if the flow path is known, to show how the ionic composition of a water body changes over space and/or time (Stiff Jr, 1951).

The Stiff diagrams show hydrochemical ionic composition of all surface water samples along the Xiaohe River in spring (March) and autumn (October) (Figure 5-7). In the upper reach, Ca^{2+} and HCO_3^- were the main ions in surface water. In spring and autumn, the mole equivalence ratios of the total cation decreased from 60 to 22 % for Ca^{2+}, and increased from 15 to 62 % for Na^+. As a result, the Xiaohe River changed from a Ca–SO_4 type in the upper reach, to a Na–Cl type in the urban reach, and finally to a Na–HCO_3 type in the lower reach of the study area.

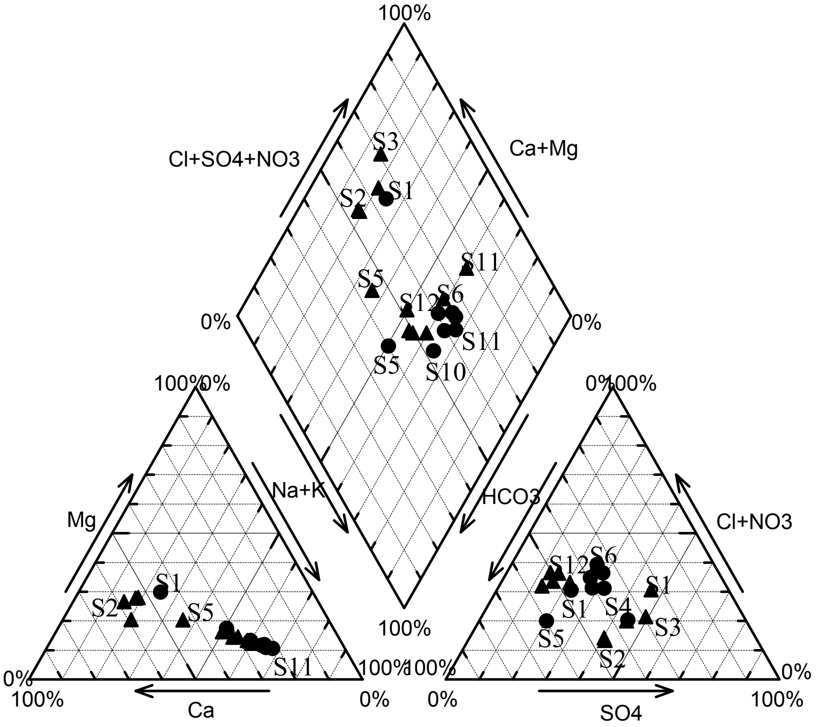


Figure 5-6 Piper diagram of surface water samples in the Xiaohe River Basin. (▲ spring; ●autumn).

Table 5-1 Concentration of major ions in surface water.

	ID	Na^+ (mg L^{-1})	K^+ (mg L^{-1})	Ca^{2+} (mg L^{-1})	Mg^{2+} (mg L^{-1})	NH_4^+ (mg L^{-1})	Cl^- (mg L^{-1})	NO_3^- (mg L^{-1})	SO_4^{2+} (mg L^{-1})	HCO_3^- (mg L^{-1})	Water type
Spring (March 2010)	S1	11.60	0.86	30.40	6.30	2.98	16.14	7.74	61.22	63.00	Ca–SO_4
	S2	27.40	1.84	74.04	22.81	0.00	25.46	14.75	140.41	198.45	Ca–HCO_3
	S3	27.64	1.79	70.54	22.26	0.00	27.34	14.13	136.52	195.3	Ca–SO_4
	S4	33.39	1.61	113.48	31.08	0.00	59.99	30.81	241.05	182.70	Ca–HCO_3
	S5	122.10	9.40	133.97	37.62	63.45	229.46	0.00	124.73	680.40	Ca–HCO_3
	S6	310.5	16.25	131.77	37.75	93.78	412.32	13.16	370.26	648.90	Na–Cl
	S7	307.52	19.40	126.93	36.74	145.01	372.63	0.00	313.42	891.45	Na–HCO_3
	S8	255.16	14.60	134.45	36.89	119.01	349.57	0.00	214.67	913.50	Na–HCO_3
	S10	281.61	15.22	136.58	39.67	102.83	371.57	0.00	179.22	878.85	Na–HCO_3
	S11	348.17	16.24	139.12	38.03	89.74	368.73	0.00	752.26	478.8	Na–SO_4
	S12	220.78	12.25	134.54	38.94	83.65	346.35	0.00	201.83	787.5	Na–HCO_3
Autumn (October 2010)	S1	32.70	1.92	54.37	21.37	nd	52.57	6.69	165.82	167.75	Ca–SO_4
	S5	141.28	36.32	89.74	29.37	nd	134.64	0.00	182.40	689.30	Na–HCO_3
	S6	291.16	34.29	102.92	29.80	nd	274.50	46.00	266.70	460.55	Na–Cl
	S8	244.61	37.13	104.29	30.94	nd	250.18	20.84	264.19	509.35	Na–HCO_3
	S9	329.34	51.21	111.54	31.39	nd	313.55	5.67	338.15	518.50	Na–Cl
	S10	294.38	45.78	100.80	30.42	nd	276.39	0.00	272.12	732.00	Na–HCO_3
	S11	359.10	53.88	108.43	31.99	nd	299.29	0.00	414.11	610.00	Na–SO_4
	S12	287.43	44.79	99.08	30.33	nd	268.26	0.00	327.05	594.75	Na–HCO_3

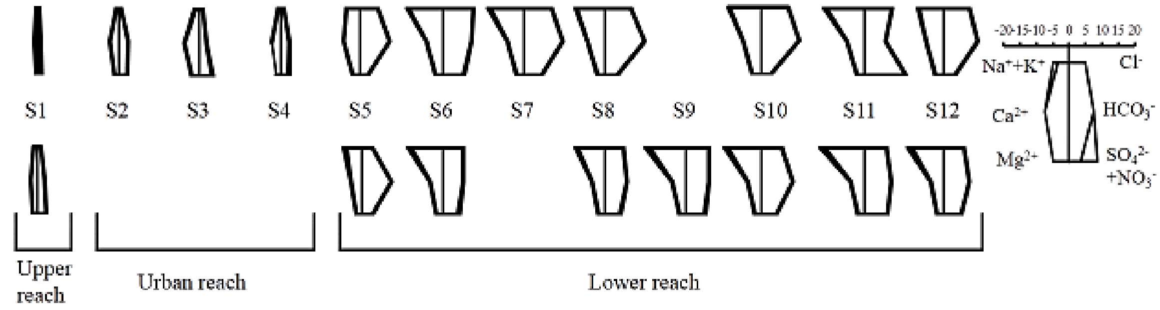


Figure 5-7 Stiff diagram of surface water samples in the Xiaohe River in spring (up) and autumn (down).

5.4.3 pH and EC in undisturbed soil cores

The soil pH is a measure of the acidity or alkalinity in the soil solution, and an important parameter to distinguish soil properties. Vertical profiles of pH and EC of soil water-solution in undisturbed soil samples were shown in Figure 5-8. The pH values in undisturbed soil cores shown a relatively stable state, ranged from 7.5 to 9.8 in wastewater irrigation area and from 9.5 to 7.8 in groundwater irrigation area, respectively. EC values ranged from 278 to 1,391 μS cm^{-1} with a mean value of 736 μS cm^{-1} in wastewater irrigation area and from 68 to 320 with a mean value of 172 μS cm^{-1} in groundwater irrigation area, respectively. EC values in wastewater irrigation area were higher than those in groundwater irrigation area. The pH and EC has obvious opposite trend, pH value increased and EC decreased with depth, and demonstrated from the surface to 0.5 m depth in wastewater irrigation area and from 1 m to 0.5 m depth in groundwater irrigation area.

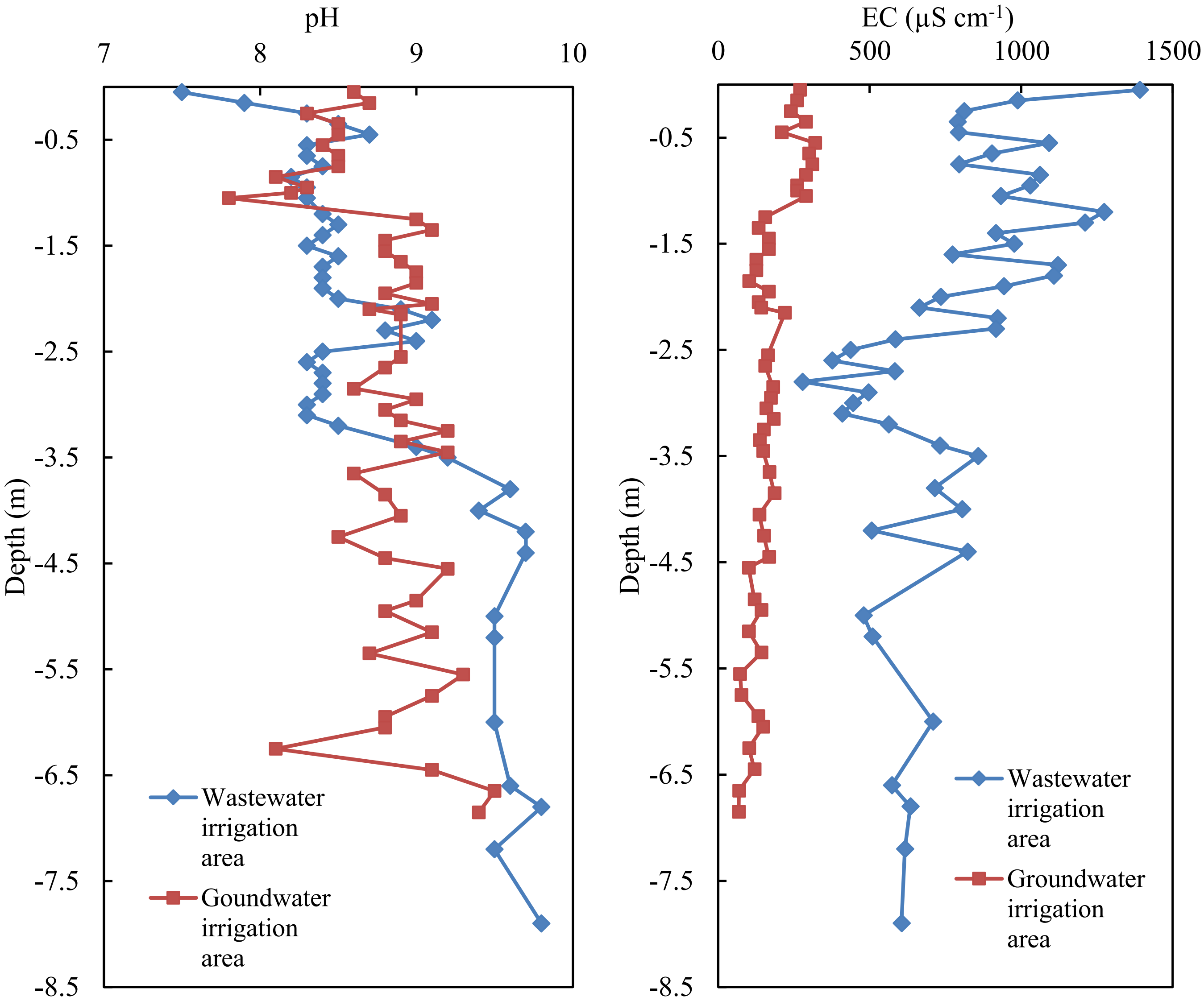


Figure 5-8 Variations of EC and pH in wastewater irrigation area and groundwater irrigation area.

5.4.4 Variation of major ions in undisturbed soil cores

The profiles of water-soluble cation K^+, Ca^{2+}, Na^+, Mg^{2+} and anions SO_4^{2-}, NO_3^-, Cl^- in undisturbed soil cores were shown in Figure 5-9 and Figure 5-10, respectively. In wastewater irrigation area, Na^+ was the dominant cation in the unsaturated zone, Na^+ concentration ranged from 66.55 to 528.71 mg kg^{-1} with an average of 305.74 mg kg^{-1}. There was a clear trend of increasing for Na^+ from surface to 0.55 depth, increased from 226.1 mg kg^{-1} to 508.6 mg kg^{-1}. From 0.55 depth to deepest, Na^+ ranged from 66.6 mg kg^{-1} to 528.7 mg kg^{-1} with an average of 296.0 mg kg^{-1}. The mole ratio of total cation for Na^+ was 51 %. Followed by Ca^{2+}, Ca^{2+} concentration decreased rapidly from 1344.9mg kg^{-1} to 339.0mg kg^{-1} from surface to 0.35 m depth and from 0.35 m depth to deepest ranged from 59.1 mg kg^{-1} to 590.0 mg kg^{-1}. The mole ratio of total cation for Ca^{2+} was 43 %. Mg^{2+} ranked third, concentration ranged from 0.5 mg kg^{-1} to 223.1 mg kg^{-1} with an average of 21.6 mg kg^{-1}. The mole ratio of total cation for Mg^{2+} was 4 %. Finally, K^+ concentration ranged from 5.3 mg kg^{-1} to 78.2 mg kg^{-1} with an average of 0.2 mg kg^{-1}. The mole ratio of total cation for K^+ was 1 %. The prevalent cations were $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ in the unsaturated zone of the wastewater irrigation area. For the major anions, the prevalent ions were $Cl^- > SO_4^{2-} > NO_3^-$. Cl^- ranged from 13.06 to 336.83 mg kg^{-1} with an average of 116.79 mg $kg^{-1}$and the mole ratio of total anions was 44 % for Cl^-. The mole ratio of total anions for SO_4^{2-} and NO_3^- were 35 % and 21 %, respectively. The trends were similar to Cl^-, SO_4^{2-} and NO_3^-, from surface to about 1 m depth was increased with increasing depth, and from about 1 m depth to 7.9 m depth was declined with increasing depth.

Comparing with the wastewater irrigation area, Ca^{2+} was the dominant cation in the groundwater irrigation area, ranging from 65.46 to 417.49 mg kg^{-1} with an average of 189.85 mg kg^{-1} and the mole ratio of total cation was 70 % for Ca^{2+}. Ca^{2+} concentration is also rapidly declined from 1.05 m to 1.25 m, decreased from 417.49 mg kg^{-1} to 173.26 mg kg^{-1}. Followed by Na^{+}, the mole ratio of total cation for Na^{+} was 13 %. Na^{+} concentration ranged from 17.59 mg kg^{-1} to 133.00 mg kg^{-1} with an average of 66.20 mg kg^{-1}. Mg^{2+} ranked third, Mg^{2+} concentration ranged from 7.18 mg kg^{-1} to 57.09 mg kg^{-1} with an average of 23.64 mg kg^{-1}. The mole ratio of total cation was 15 % for Mg^{2+}. The mole ratio of total cation for K^{+} was 1 %. Generally speaking, the prevalent cations were $Ca^{2+}>Na^{+}>Mg^{2+}>K^{+}$ in the unsaturated zone of the groundwater irrigation area. For the major anions, the prevalent ion is $SO_4^{2-}>NO_3^{-}>Cl^{-}$. The mole equivalence ratio of total anions was 73 %, 17 % and 10 % for SO_4^{2-}, NO_3^{-} and Cl^{-}, respectively. SO_4^{2-} was ranging from 4.9 to 467.6 mg kg^{-1} with an average of 116.6 mg kg^{-1}. NO_3^{-} ranged from 0.1 to 725.8 mg kg^{-1} with an average of 107.6 mg kg^{-1}.

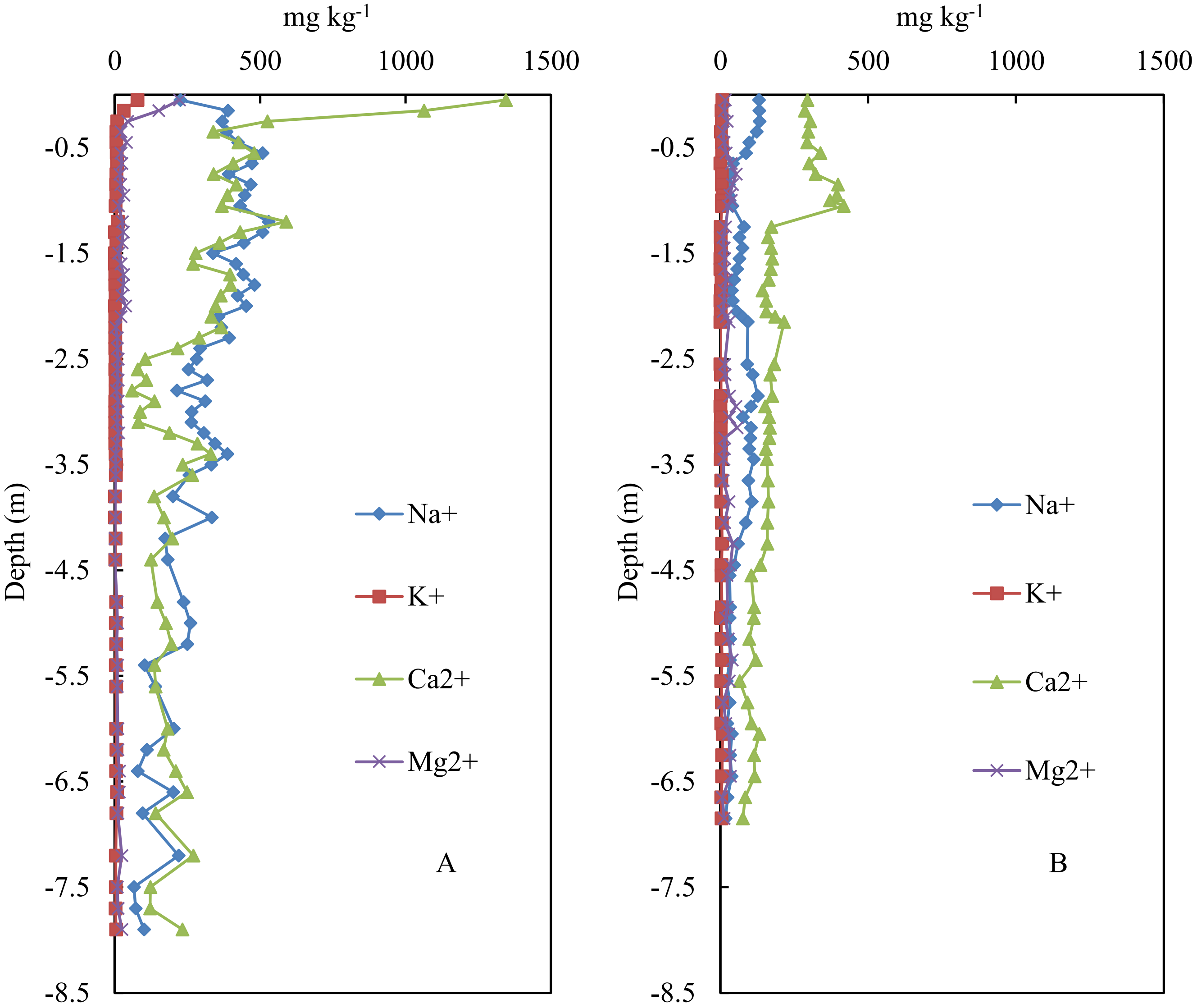


Figure 5-9 Variations in major cation in from soil core sample (A) wastewater irrigation area (B) groundwater irrigation area

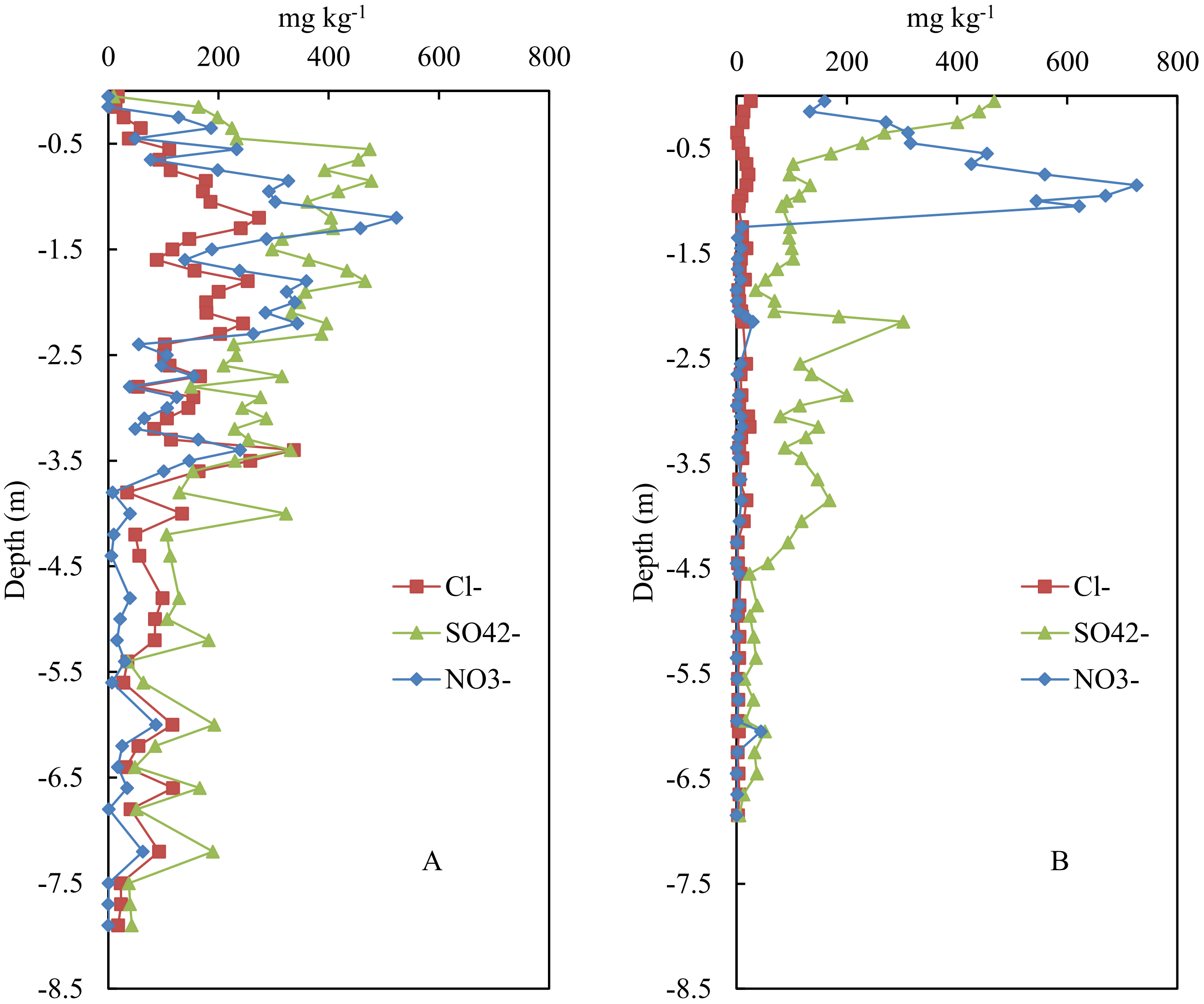


Figure 5-10 Variations in major anion in from soil core sample in (A) wastewater irrigation area and (B) groundwater irrigation area.

5.4.5 EC, DO, pH and ORP in groundwater

The EC values ranged from 399 to 1,636 µS cm^{-1} with a mean value of 916. The pH value of groundwater ranged from 6.9 to 8.5 with a mean value of 7.7. The lowest EC and pH value was found at G10 (pH=6.9) with the deepest depth. DO and ORP ranged from 1.78 mg L^{-1} to 7.35 mg L^{-1} with a mean value of 3.7 mg L^{-1} and ranged from 84 mV to 161 mV with a mean value of 126 mV, respectively (Table 5-2)

Table 5-2 EC, DO, pH, and ORP in groundwater.

ID	EC (µS cm^{-1})	DO (mg L^{-1})	pH	ORP (mV)
G2	1283	7.35	8	113
G3	784	3.51	8.2	104
G4	654	3.33	8.3	84
G5	715	1.78	8	137
G6	731	2.74	8.4	152
G7	1101	3.3	8.3	132
G11	976	3.15	8.3	161
G12	1636	3.85	8.1	116
G13	469	4.04	8.5	132
G1	846	ND	7.1	ND
G8	1252	ND	7.0	ND
G9	992	ND	7	ND
G10	399	ND	6.9	ND
G14	1156	ND	7.2	ND
G15	531	ND	6.9	ND
G16	1132	ND	7.1	ND

ND: No Data.

5.4.6 Major ions in groundwater

Table 5-3 shows concentration of major ions in groundwater, most of the groundwater samples were located in the left corner of the cation triangular chart (Figure 5-11). It was found that the cation are $Ca^{2+} > Na^{+}+K^{+} > Mg^{2+}$ in the groundwater. Comparing with the surface water, the groundwater has more Ca^{2+} ranged from 44.69 mg L^{-1} to 234.44 mg L^{-1}. In average, the mole equivalence ratio of total cation was 53% for Ca^{2+}, which is slightly higher than these in the surface water. The mole equivalence ratio of total cation for $Na^{+}+K^{+}$ ranged from 9% to 28% with an average of 17 %, lower than in the surface water. The mole equivalence ratio of total cation for Mg^{2+} ranges 21% to 38% with an average 30%. And it is found that HCO_3^- is dominating ion in the groundwater samples, HCO_3^- concentration ranged from 274.50 mg L^{-1} to 570.15 mg L^{-1} with an average of 397.17 mg L^{-1}. The mole equivalence ratio of total anions for HCO_3^- was 54%. The average concentration for Cl^- and SO_4^{2-} were 133.16 mg L^{-1} and 104.62 mg L^{-1}, respectively. The mole equivalence ratios of Cl^- and SO_4^{2-} are 26% and 15%, respectively. Groundwater in the study area is classified as the $Ca–HCO_3$ type in the Xiaohe River (Figure 5-12).

Table 5-3 Hydrochemical major ions in groundwater.

ID	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2+} (mg/L)	HCO_3^- (mg/L)	Water type
G2	107.23	1.37	186.99	74.08	239.07	108.81	205.80	491.40	Ca–HCO_3
G3	33.67	0.81	121.47	51.31	128.76	37.13	81.85	374.85	Ca–HCO_3
G4	30.92	1.00	115.14	48.70	122.92	40.33	72.90	355.95	Ca–HCO_3
G5	54.17	0.84	92.57	32.05	50.29	19.25	54.48	447.30	Ca–HCO_3
G6	28.09	0.11	126.19	39.07	117.32	32.75	80.98	346.50	Ca–HCO_3
G7	68.85	0.16	216.69	73.05	238.80	89.22	167.69	535.50	Ca–HCO_3
G11	64.33	0.69	167.69	70.39	203.19	67.65	164.63	450.45	Ca–HCO_3
G12	128.85	0.57	234.44	85.35	310.57	156.62	234.01	570.15	Ca–HCO_3
G13	19.10	0.92	78.81	35.36	54.88	28.32	33.53	318.15	Ca–HCO_3
G1	32.26	1.03	110.85	26.62	47.83	30.94	170.38	311.10	Ca–HCO_3
G8	28.65	0.80	176.60	38.44	178.62	75.80	98.93	375.15	Ca–HCO_3
G9	51.15	0.75	109.65	33.88	104.21	39.75	108.34	366.00	Ca–HCO_3
G10	27.54	0.49	44.69	11.37	8.88	4.03	11.08	274.50	Ca–HCO_3
G14	42.30	1.42	137.04	56.59	163.66	59.87	80.72	411.75	Ca–HCO_3
G15	17.73	0.53	63.16	21.51	38.19	9.42	12.29	338.55	Ca–HCO_3
G16	36.64	0.74	126.11	47.60	123.43	63.02	96.33	387.35	Ca–HCO_3

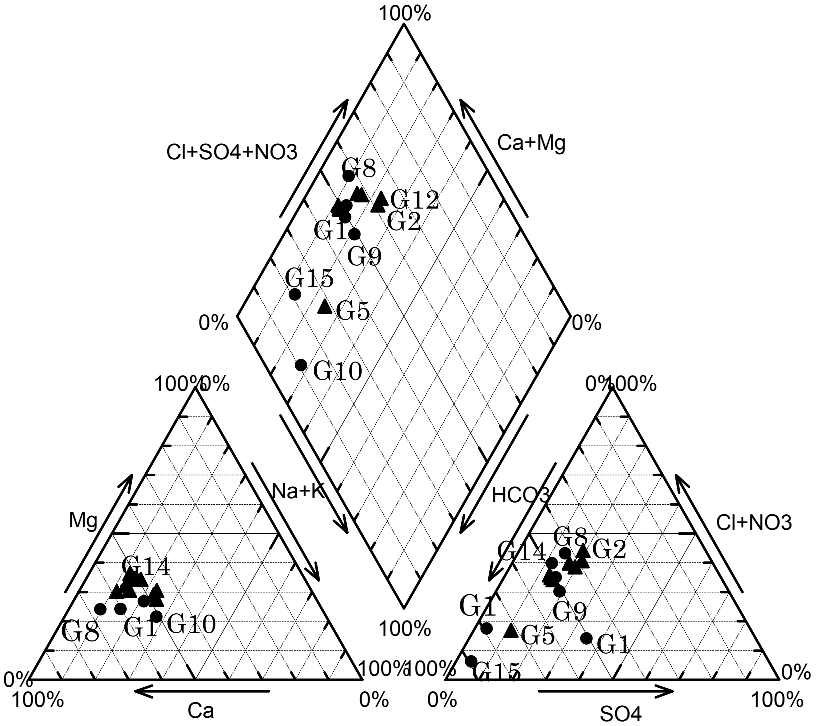


Figure 5-11 Piper diagram of groundwater in the Xiaohe River Basin.

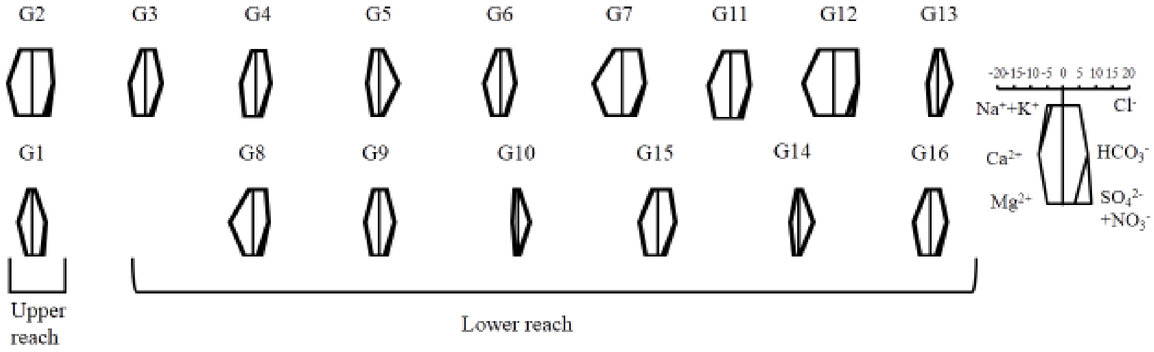


Figure 5-12 Stiff diagram of surface water samples in the Xiaohe River.

5.5 Discussion

5.5.1 Sources of major ions in Xiaohe River

Weathering and dissolution of carbonate, silicate or evaporate mineral release elements of water body. Mass balance models provide a convenient approach to inferring the sources of dissolved major ions to waters. The abundances of dissolved cations and anions in water body can be modeled in terms of the weathering of various minerals in the basin. Some weathering reactions for minerals such as Calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$) and gypsum ($CaSO_4$) can be written as the following equations (Sarin et al., 1989):

$$CaCO_3 + H_2CO_3 \leftrightarrow Ca^{2+} + 2HCO_3^- \qquad \text{(Equation 5-1)}$$

$$CaMg(CO_3)_2 + 2H_2CO_3 \leftrightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- \qquad \text{(Equation 5-2)}$$

To separate the contribution of calcite and dolomite dissolution to major ions composition in the study area, the relation between Ca^{2+} and HCO_3^- is showed in Figure 5-13. If the weathering is by carbonic acid, the mole equivalence ratio of dissolved Ca^{2+} to HCO_3^- in the waters should be 1:1 for calcite weathering and 1:2 for dolomite weathering according to Equation 5-1 and Equation 5-2. The surface water samples and some groundwater samples are plotted in the area between the 1:1 line and 1:2 line, indicating both calcite and dolomite are the sources of the major ions.

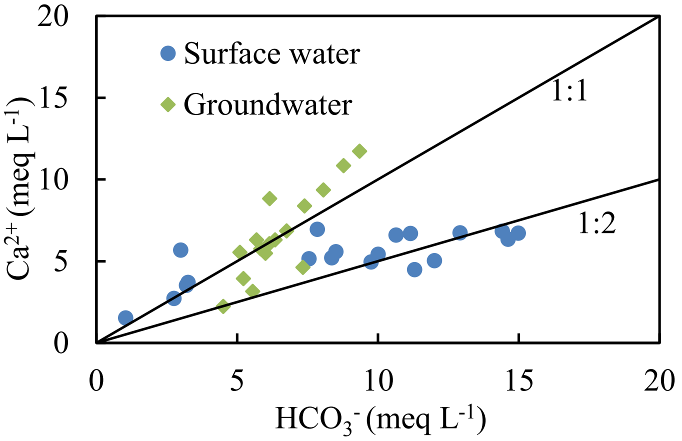


Figure 5-13 The relation between Ca^{2+}, and HCO_3^- in the Xiaohe River Basin.

5.5.2 Anthropogenic inputs

It has long been known that Cl^- in surface waters with no terrestrial sources of the element declines systematically as a function of increasing distance from the sea (Stallard and Edmond, 1981). Other possible minor sources of chloride include anthropogenic sources:

fertilisers, road salts, industrial emissions, and lithological sources. Cl^- and Na^+ concentrations reflect domestic wastewater enrichment (Panno et al., 2006a), so their changes highlight the effects of human activity on the chemical status of the Xiaohe River (Figure 5-14). The average concentration of Cl^- in surface water was 234.50 mg L^{-1} in spring and 233.67 mg L^{-1} in autumn, while the average Na^+ concentration was 176.90 mg L^{-1} in spring, and 247.50 mg L^{-1} in autumn. Na^+ and Cl^- concentrations were low in the upper reach near Shijiazhuang but rose rapidly as urban wastewater was released into the Xiaohe River in the middle reach between S4-S6. Na^+ and Cl^- concentrations in the lower reach remained relatively high compared with those in the upper reach.

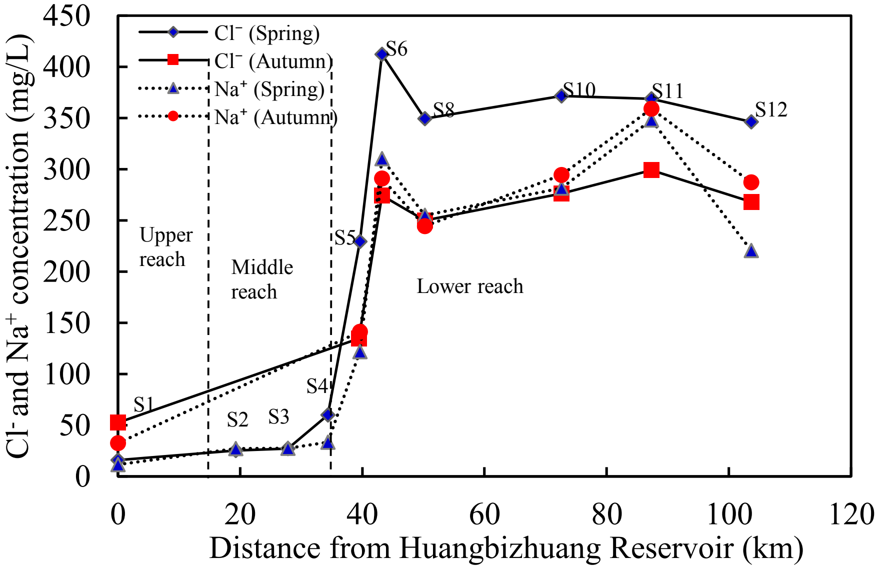


Figure 5-14 Relationship between Cl^- and Na^+ concentrations and distance from the Huangbizhuang Reservoir Dam on the Xiaohe River.

5.6 Conclusions

For the surface water, concentrations of Cl^- and Na^+ were low in the upper reach but increased rapidly in the lower reach, because of effluent from Shijiazhuang City. Na^+ and Cl^- concentrations in the upper reach remained relatively high compared with those in the upper reach, indicating the human activities are important factor to control hydrochemistry of river.

As a result, the chemical pattern of the Xiaohe River changed from a Ca-SO_4 type in the upper reach, to a Na-Cl type in the urban reach, and finally to a Na-HCO_3 type in the lower reach of the study area. For the groundwater, TDS ranged from 383 to 1721 mg L^{-1}, with an average of 916 mg L^{-1}. The hydrochemical type for all of groundwater samples are Ca-HCO_3 type. Based on the stoichiometry calculation, it is found that the dissolution of carbonates caused by carbonic acid result in the hydrochemical pattern in the Xiaohe River Basin.

For the unsaturated zone, the prevalent cations are $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and prevalent anions are $Cl^- > SO_4^{2-} > NO_3^-$ in the wastewater irrigation area. Comparing with the wastewater irrigation area, the prevalent cations are $Ca^{2+} > Na^+ > Mg^{2+} > K^+$ and the prevalent anions are $SO_4^{2-} > NO_3^- > Cl^-$ in groundwater irrigation area.

SAR value indicates that some of surface water and all of groundwater are suitable for irrigation of most crops and plow layer soil quality in groundwater irrigation area is better than wastewater irrigation area. It can be used to cultivate most crops with Low-salinity level. Both groundwater and wastewater irrigation area, salinity level of soil is greater in plow layer than the layer below.

Chapter 6 Fate and transport of nitrate

6.1 Introduction

Worldwide, nitrate concentrations have increased in both surface water and groundwater in the past decades (McIsaac et al., 2001; Orban et al., 2010; Yang et al., 2004a). Many studies were reported that elevated NO_3^- concentrations in rivers (Beaulieu et al., 2011; Mulholland et al., 2008; Paerl et al., 1998; Panno et al., 2008; Pellerin et al., 2012; Richardson et al., 2004), groundwater (Agrawal et al., 1999; Kumazawa, 2002; Li et al., 2008b; Nolan and Hitt, 2006; Weiskel and Howes, 1992; Zhang et al., 1996) and unsaturated zone (Costa et al., 2002; McMahon et al., 2006). High concentration of nitrate in rivers and groundwater has a serious threat to drinking water supplies because it may cause methemeoglobinemia in infants and be responsible for increases in stomach cancer in others (Morales-Suarez-Varela et al., 1995; Yang et al., 1998).

River systems in the NCP are important not only for providing recharge water for groundwater, but also for transporting nutrients. Owing to severe water shortages in the NCP, much of the wastewater is used for irrigation which has caused groundwater pollution problems (Chen et al., 2005a; Hu et al., 2005; Tang et al., 2004). Several studies document have shown that the elevated NO_3^- concentrations in groundwater caused by the agriculture activities is the common threaten on groundwater quality. In particular, large amounts of nitrogenous fertilizers input and low using efficiency may lead to nitrate leaching (McArthur et al., 2012; Tang et al., 2004).

$\delta^{15}N–NO_3$ have been used since the early 1970s to identify nitrate sources and indicate denitrification processes (Kohl et al., 1971). Based on the isotopic composition of N in NO_3^- is generally different among various NO_3^- sources such as atmospheric N_2, soil, chemical fertilizers, and manure (Xue et al., 2009). The $\delta^{15}N–NO_3$ evidence suggests that most of the NO_3^- in the Mississippi River is primarily derived from synthetic fertilizers and soil organic N (Panno et al., 2006b). A study using nitrogen and oxygenisotope ratios of nitrate (NO_3^-) for elucidating sources and transformations of riverine nitrate in a comparative study of 16 watersheds in the northeastern U.S.A., and provided evidence for denitrification in the form of elevated $\delta^{15}N$ nitrate values (Mayer et al., 2002).

The objectives of this chapter were to (1) study distribution and transformation of nitrate-N and ammonia-N; (2) estimate effects of wastewater irrigation on nitrate and (3) identify the nitrate sources using $\delta^{15}N–NO_3$ in the Xiaohe River basin.

6.2 Site description

The site description has been presented in chapter 2.

6.3 Sample method

The sample collection for surface and groundwater has been presented in chapter 3. The sample collection and analysis for soil samples has been presented in chapter 5.3.

6.4 Results

6.4.1 Nitrate in the Xiaohe River

In spring, Concentration of NO_3^- in the Xiaohe River from the reservoir (S1) to the urban zone (S2-S4) ranged from 7.7 mg L^{-1} (S1) to 30.8 mg L^{-1} (S4), but was not detected after the river flowed into the lower reach, except at site S6, near the outlet of sewage treatment plant (STP) outlet. In autumn, NO_3^- ranged from 6.7 mg L^{-1} (S1) to 46.0 mg L^{-1} (S6) in the upper and middle reach. Concentration of NO_3^- in spring was higher than thses in autumn (Figure 6-1). The mean values of NH_4^+ in the Xiaohe River were 63.68 mg L^{-1} in spring. Due to a large number of wastewater is discharged into rivers, ammonium became main part of nitrogen in the lower reach of the Xiaohe River. The $\delta^{15}N$-NO_3^- values in surface water ranged from +2.8 ‰ to +21.9 ‰ with an average value of +11.97 ‰.

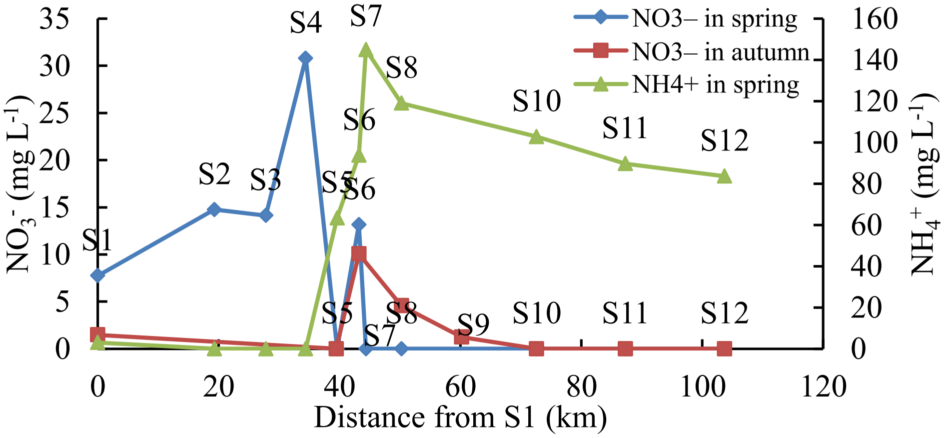


Figure 6-1 NO_3^- and NH_4^+ variation of surface water along the Xiaohe River.

Table 6-1 NO_3^- and NH_4^+ concentrations and $\delta^{15}N$-NO_3^- values in surface water in the Xiaohe River.

	ID	NH_4^+ (mg L^{-1})	NO_3^- (mg L^{-1})	$\delta^{15}N$ (‰)
Spring	S1	3.0	7.7	11.3
	S2	0.0	14.8	10.4
(March 2010)	S3	0.0	14.1	12.3
	S4	0.0	30.8	11.1
	S5	63.5	0.0	n.d.
	S6	93.8	13.2	21.9
	S7	145.0	0.0	n.d.
	S8	119.0	0.0	n.d.
	S10	102.8	0.0	n.d.
	S11	89.7	0.0	n.d.
	S12	83.7	0.0	n.d.
Autumn	S1	n.d.	6.7	12.2
	S5	n.d.	0.0	n.d.
(October 2010)	S6	n.d.	46.0	19.2
	S8	n.d.	20.8	6.5
	S9	n.d.	5.7	2.8
	S10	n.d.	0.0	n.d.
	S11	n.d.	0.0	n.d.
	S12	n.d.	0.0	n.d.

n.d.: No data

6.4.2 Soil classification and vertical profile of NO_3^- concentration in unsaturated zone

In order to evaluate behavior of nitrate and its response to the irrigation practices in study area. Water-soluble NO_3^- concentrations were measured in wastewater irrigation area and groundwater irrigation area. The mean value of NO_3^- was 137.0 mg kg^{-1} in wastewater irrigation area, and 107.7 mg kg^{-1} in groundwater irrigation area. The maximum value of

NO_3^- was found at the depth of 1.20 m in wastewater irrigation area with a value of 523.2 mg kg^{-1}, and in the depth of 0.85 m in groundwater irrigation area with a value of 725.9 mg kg^{-1} (Figure 6-2). Water-soluble NO_3^- has several peaks at different depths in wastewater area. It was found at layers 1.20 m depth, 1.60 m−1.80 m, 2.40 m−3.40 m, 3.8 m−4.0 m, 5.6 m−6 m and 6.8 m−7.2 m in depth. In groundwater irrigation area, trend of water-soluble NO_3^- was simpler than these in wastewater irrigation area. A peak value can be found at 0.85 m depth (725.9 mg kg^{-1}), and NO_3^- declined to 9.5 mg kg^{-1} from 0.85 m to 1.25 m depth. From 1.25 m depth to the deepest (6.8 m depth), nitrate content kept at a low level with small fluctuations from 0 mg kg^{-1} to 44.2 mg kg^{-1}.

6.4.3 Nitrate in groundwater

The concentrations of NO_3^- in groundwater in the Xiaohe River basin ranged from 4.0 mg L^{-1} to 156.6 mg L^{-1} with mean values of 53.9 mg L^{-1} (Table 6-2). The highest concentrations of NO_3^- in groundwater was found in G12 and the lowest was found in G10.

The $\delta^{15}N$-NO_3^- values in groundwater ranged from +6.1 ‰ to +14.7 ‰ with an average value of +9.2‰ (Table 6-2). The highest $\delta^{15}N$-NO_3^- values in groundwater were found at G6, and the lowest was found in G2.

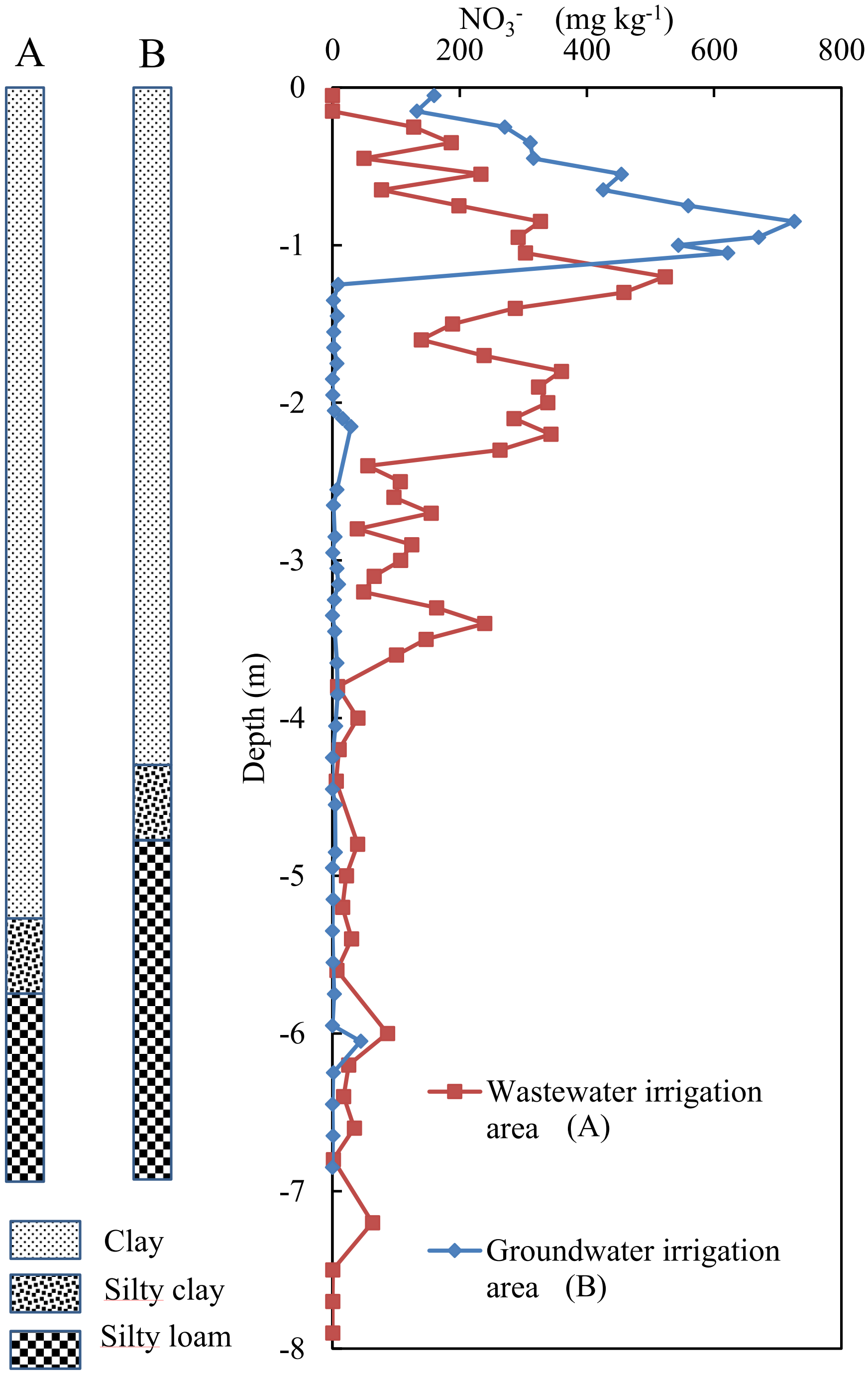


Figure 6-2 Soil classification and concentration profiles of water-soluble NO_3^- in (A) in wastewater irrigation area and soil core (B) in groundwater irrigation area.

Table 6-2 NO_3^- Concentrations and δ^{15}N-NO_3^- values in groundwater, wells information.

ID	NO_3^- (mg/L)	δ^{15}N (‰)	Distance away (m)	Well depth (m)
G2	108.8	6.1	470	70
G3	37.1	10.5	3020	50
G4	40.3	7.9	3750	30
G5	19.3	11.5	550	120
G6	32.8	14.7	1790	80
G7	89.2	9.0	730	65
G11	67.7	9.2	1100	70
G12	156.6	9.1	1980	40
G13	28.3	9.4	nd	nd
G1	30.9	7.8	5	58
G8	75.8	7.3	86	60
G9	39.8	11.4	113	75
G10	4.0	ND	244	120
G14	59.9	7.5	582	120
G15	9.4	8.0	1150	112
G16	63.0	ND	2492	80

ND: no data

6.5 Discussion

6.5.1 Redox environment in water environment

The nitrogen cycle in water environment is closely related to its redox environment. Various redox processes is the only way for NO_3^- removal from water environment, due to NO_3^- can neither to form water insoluble minerals that could precipitate, not to be adsorbed significantly (Appelo and Postma, 2005). ORP is a very important factor used to characterize redox stage in surface water and groundwater (Thayalakumaran et al., 2008). Once a relationship between the ORP and the redox species concentrations particular to an aquifer has been established, field ORP measurements can be used as indications for specific geochemical reactions (Postma et al., 1991).

In addition to the redox conditions, the fate of NO_3^- in water environment is also strongly influenced by pH. The pH-ORP diagram was used to evaluate the comprehensive effect of ORP and pH on the processes of nitrification or denitrification occurred in the Xiaohe River Basin. The *pe* is calculated from the measured values of ORP as:

$$pe = \frac{ORP*F}{2.303RT} \qquad \text{(Equation 6-1)}$$

where *F* is the Faraday's constant (96.42 kJ/Volt gram equivalent), *R* is the gas constant (8.314×10-3kJ/mol·deg), *T* is the absolute temperature in Kelvin and ORP is presented in Volt.

The possible stable reactant of the dissolved nitrogen in the surface water and the groundwater were showed by the pH-ORP diagram (Figure 6-3). Surface water has a widely distribute in the NH_4^+, N_2 and NO_3^- area of the pH-pe diagram. Surface water samples in the upper reach (S1) distribute in NO_3^- area of the pH-pe diagram, indicating the oxic region in which the stable form of nitrogen is NO_3^-. In the upper reach and middle reach (S1-S4) ORP ranged from 17 mV to 497 mV, and DO had an average of 4.5 mg L^{-1}, which indicated that surface water in the upper reach and middle reach was in the oxic condition (vanLoon and Duffy, 2011). As a result, denitrification hardly occurred in the upper reach (S1-S4) of Xiaohe River due to oxic environment. Surface water samples in the lower reach (S5-S12) distribute in NH_4^+ area of the pH-pe diagram, and ammonium (NH_4^+) concentration was high in the lower reach. It suggesting the potential contribution of mineralization of organic matter to the enhanced NH_4^+ concentration, and strong reduction condition and NH_4^+ is stable form in lower reach (S5-S12) of the Xiaohe River.

All of groundwater samples were distribute in N_2 area of the pH-pe diagram. ORP of the groundwater ranged from 84 mV to 161 mV and the mean of DO was 3.9 mg L^{-1} for the groundwater explaining most of aquifers in the Xiaohe River basin were under oxic condition. A study shown that denitrification does not occur in an aquifer with a deeper water table because there is insufficient labile organic carbon present (Starr and Gillham, 1993), A laboratory experiments shown that ORP drop below 0 mv, the nirate begin to be converted and denitrification occurred (Lee et al., 2000). Because of oxic condition and ORP above 0 mV in our study, denitrification is considered not occur in groundwater of the Xiaohe River basin.

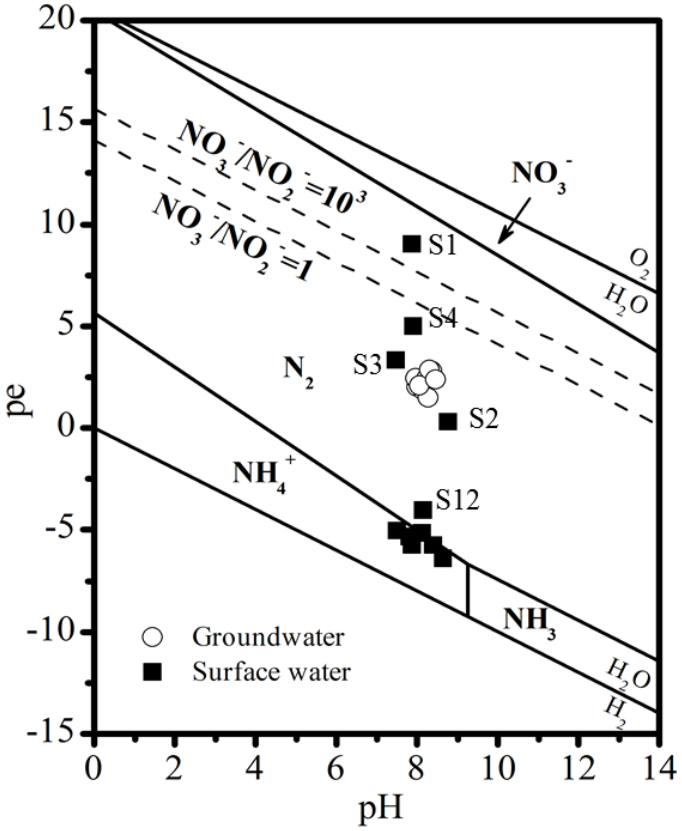


Figure 6-3 pH-pe diagram for the nitrogen in the Xiaohe River Basin.

6.5.2 Effects of wastewater irrigation

Cl^- is a conservative ion in aquifer environments and can be used in most settings to determine surface water and groundwater movement (Panno et al. 2006). Generally, Cl^- originates from natural sources and discharges of industrial, agricultural and domestic wastewaters (Tang et al. 2003). There are no natural sources of Cl^- in the aquifer, which implies that the sources of Cl^- in the Xiaohe River are anthropogenic. The relation between Cl^- and NO_3^- would offer some information to understand the effects of wastewater irrigation for nitrate in the study area. Cl^- also was used as a tracer for N transport in surface water, groundwater and soil.

Due to nitrogen is mainly in two forms NO_3^- and NH_4^+ in Xiaohe River, the relationship between NO_3^-+NH_4^+ and Cl^- was shown in Figure 6-4. The significant linearity ($R^2 = 0.896$) specifies wastewater discharged from urban areas is common source for nitrogen and Cl^- in Xiaohe River. The significant linearity ($R^2 = 0.908$) between NO_3^- and Cl^- concentrations indicates the source of NO_3^- was same with Cl^- in groundwater (Figure 6-4). It suggest that the elevated NO_3^- concentration in groundwater are related to wastewater discharged from urban, because of wastewater was used for irrigation and infiltration from the Xiaohe River channel.

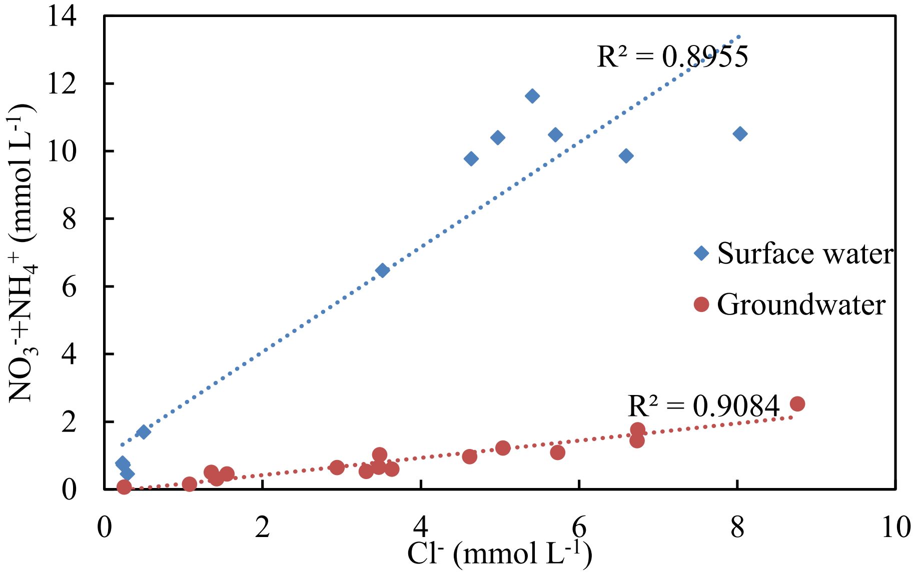


Figure 6-4 The relationship between NO_3^-+NH_4^+ and Cl^- in the surface water and groundwater.

Cl^- also can be used as a tracer for NO_3-N transport for unsaturated soil profiles, because of similarity between NO_3-N and Cl^- transport mechanisms and identical breakthrough curves for the soil (Kanwar et al., 1997). There was a good significant linearity (R^2=0.766) between water-soluble NO_3^- and Cl^- concentrations shows a common source of nitrate in unsaturated zone of wastewater irrigation area (Figure 6-5). These results suggest that the elevated water-soluble NO_3^- concentrations in unsaturated zone of wastewater irrigation area are related to wastewater discharged from the city. As a comparison, there was no correlation between water-soluble NO_3^- and Cl^- in groundwater irrigation area indicates increasing concentration of nitrate is not directly related to wastewater (Figure 6-5). These results suggest that the elevated NO_3^- concentration in the unsaturated zone of groundwater irrigation area came from nitrogen fertilizers.

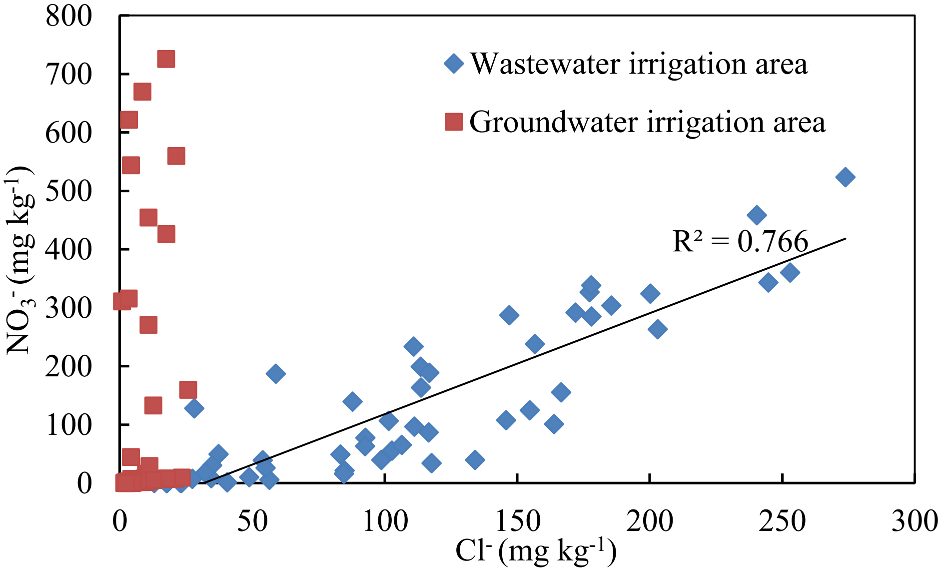


Figure 6-5 The relationship between NO_3^- and Cl^- concentrations in soil cores.

Variations of NO_3^- concentration in groundwater with well depth and distance from the river are shown in Figure 6-6. NO_3^- values (> 45 mg L^{-1}, WHO drinking water standard) mainly be found in groundwater from the wells shallower than 80 m in the adjacent area along Xiaohe River. It is reasonable to consider that the high nitrate concentration in groundwater was resulted from leaching from the riverbed or from the sewage-irrigated farmland in the study area.

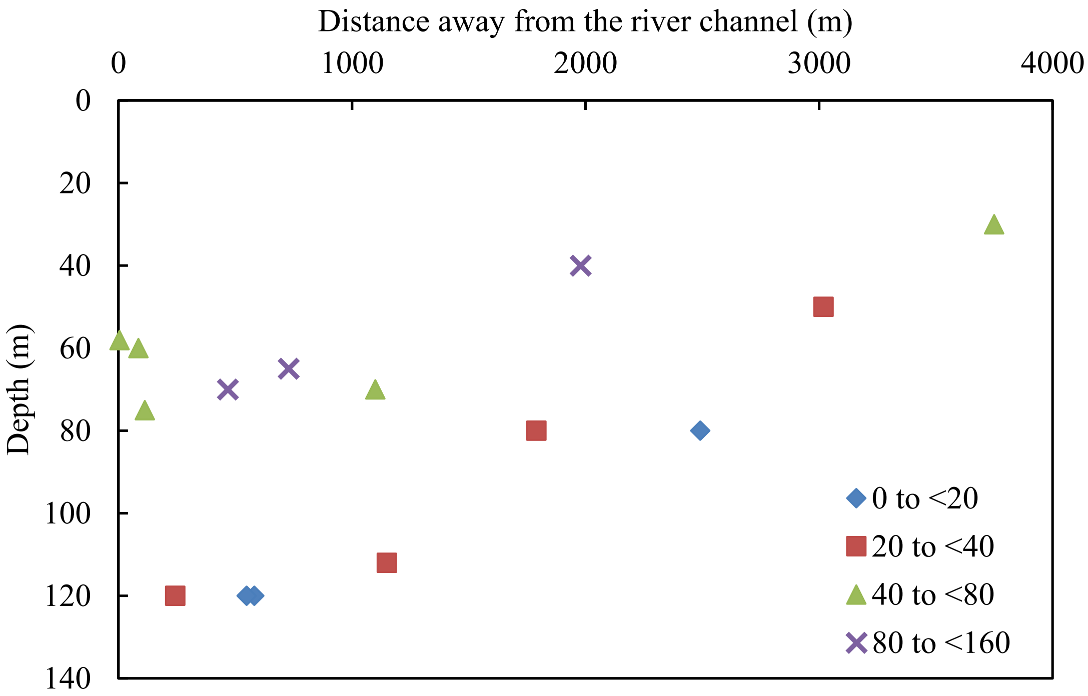


Figure 6-6 Variations in NO_3^- concentrations with well depth and distance from the river.

NO_3^- concentration of groundwater increased as the increase of contributing fraction of surface water (Figure 6-7). Contributing fractions were the average contribution of the surface water for groundwater calculated by Cl^-, δD or $\delta^{18}O$ in each site of groundwater. It indicates that the increased NO_3^- concentration in groundwater is the result of recharge from surface water. Site G1 is located in the upper reach near the Huangbizhuang Reservoir, which was not affected by sewage. Hence, even though most of the groundwater at G1 (*cf*= 89.2 %) is recharged by surface water, NO_3^- concentration is still lower.

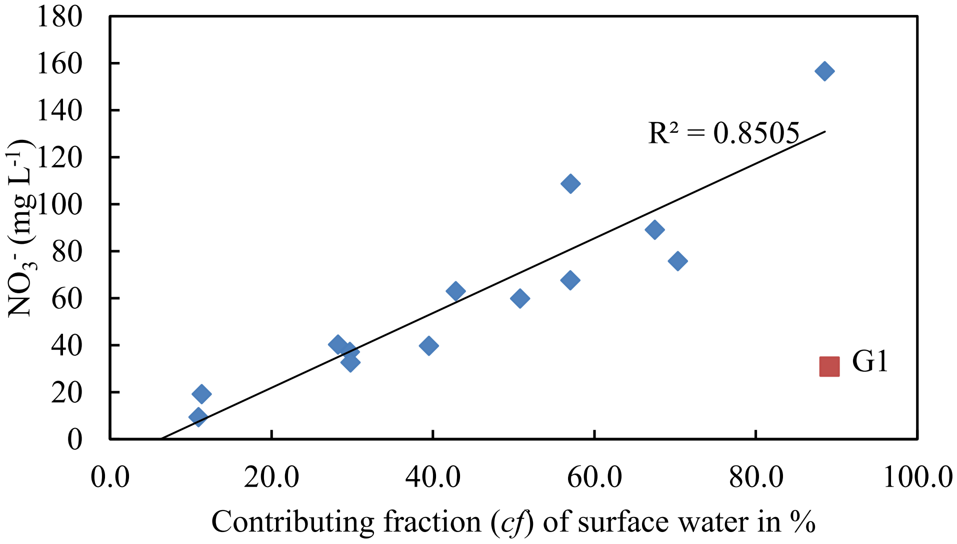


Figure 6-7 Calculated fraction (*cf*) of surface water to groundwater recharge and its relationship to NO_3^- concentrations. Contributing fractions were calculated by Cl^-, δD or $\delta^{18}O$.

In addition, the long-term effect of the Xiaohe River on groundwater can be accessed by using groundwater ages (Böhlke and Denver, 1995; Gourcy et al., 2009; Koh et al., 2006). It allowed us to determine whether groundwater containing elevated concentrations of NO_3^- was of recent origin related to anthropogenic activities (Cao et al., 2013). Based on the CFCs dating and nitrate transported by groundwater of different ages reflects pollutions caused by human activities at the recharge time. Nitrate contamination history in groundwater could be reconstruction in this study. It clearly showed that the NO_3^- in the young groundwater with the recharged age after 1975 was higher than old groundwater with the recharged age before 1975 (Figure 6-8). It was agreed with the anthropogenic activities such as wastewater irrigation which stared since 1970s in the study area.

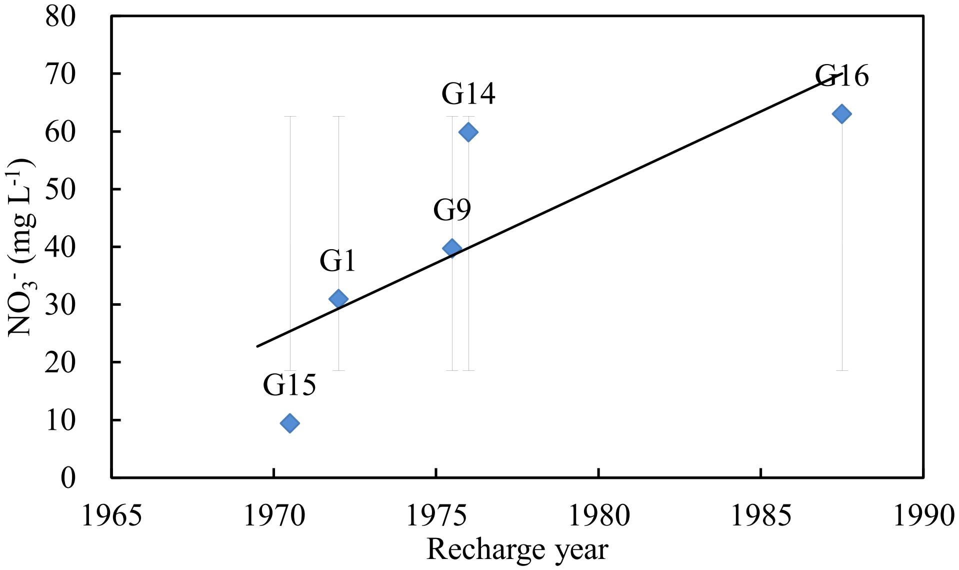


Figure 6-8 The relationship between NO_3^- concentrations and apparent ages of CFC-12.

6.5.3 Identify the nitrate sources using $\delta^{15}N–NO_3$

Nitrogen isotope ratios of nitrate ($\delta^{15}N-NO_3$) have been used since the early 1970s to identify nitrate sources and indicate denitrification processes (Kohl et al., 1971). Sources and behaviors of nitrate contamination in groundwater can be effectively distinguished by the nitrogen isotope for nitrate (δ^{15}N-NO_3) (Cao et al., 2013; Chen et al., 2006b; Kaown et al., 2009; Katz et al., 2004; Panno et al., 2001). The δ^{15}N–NO_3 can be used to help identify NO_3^- sources, because NO_3^- from different sources has characteristic δ^{15}N values (Figure 6-9). The relationship between δ^{15}N–NO_3 and residual nitrate can be used to identify N transformations by denitrification, volatilization and fractionation (Cao et al., 2013; Robinson, 2001). Surface water with high NH_4^+ concentrations is usually used to irrigate farmland, where NH_4^+ and organic nitrogen in the aerobic unsaturated zone are transformed to NO_3^- that can move into groundwater. Analyses of δ^{15}N–NO_3 are based on the principle that the three main sources of nitrate pollution have their own characteristic ranges of nitrogen isotope ratios of nitrate: N fertilizer, –6 to +6 ‰; natural soil-N (organic nitrogen), 0 to +8 ‰; and manure and sewage, +4 to +25 ‰ (Xue et al., 2009).

The δ^{15}N–NO_3 values in surface water ranged from 2.8 to 21.9 ‰. The δ^{15}N–NO_3 value from the Huangbizhuang Reservoir (S1), at 12.4 ‰, the NO_3^- concentration in reservoir water was low (6.72 mg L^{-1}), showing that it contributed little to NO_3^- in the study area. The maximum values for δ^{15}N (19.2 ‰ in autumn, 21.9 ‰ in spring) were found at the S6 near the STP drainage outlet.

The groundwater had higher NO_3^- concentrations and a narrower δ^{15}N–NO_3 range (6.1 to 14.7 ‰, with an average value of 9.2 ‰) than surface water. The δ^{15}N–NO_3 values of all groundwater samples fall within the typical range of manure sewage rather than that of synthetic fertilizer.

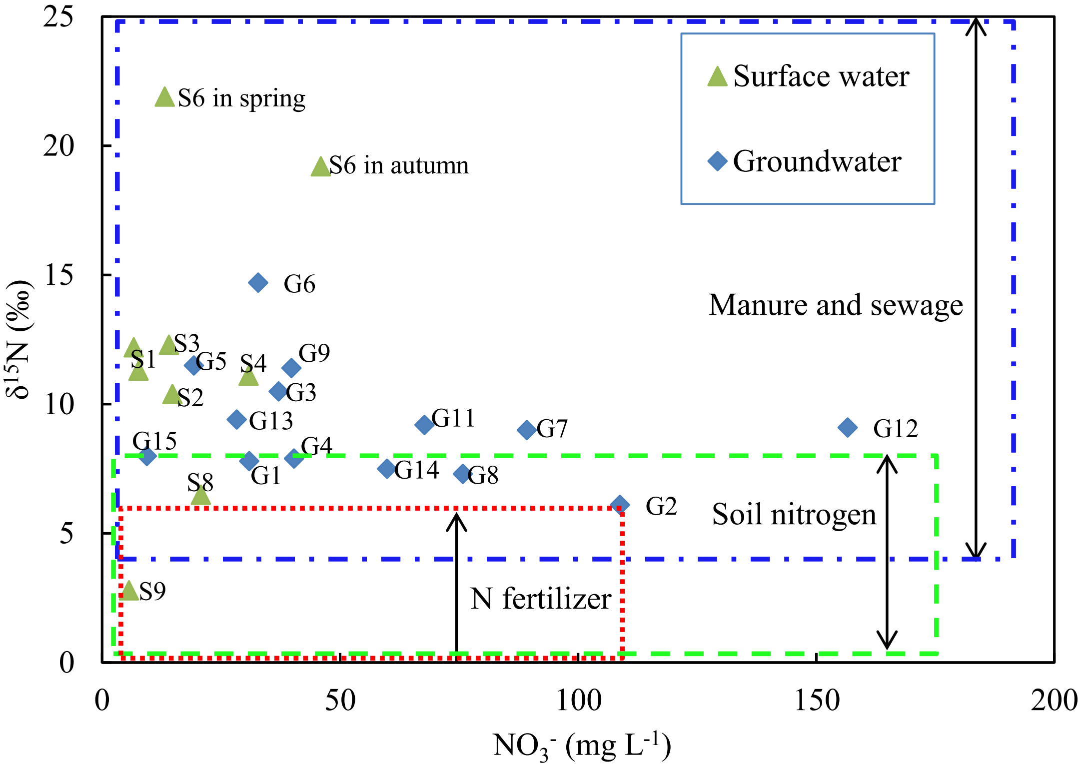


Figure 6-9 The relationship between $\delta^{15}N–NO_3^-$ and NO_3^-.

6.6 Conclusions

As a case study of the Xiaohe River basin, the distribution and transformation of nitrate-N and ammonia-N, effects of wastewater on nitrate in surface water, groundwater and soil were studied in this chapter. The main findings are as the following:

1. Under the impact of urban sewage discharged to the Xiaohe River, high concentration of nitrogen (NH_4^+–N) was found in the lower reach of the Xiaohe River. The redox analysis revealed that surface water had an oxic condition with the stable form of N was NO_3^- in

upper and middle reaches of Xiaohe River, and a strong reduction condition which are unstable for NO_3^- in the lower reach. The $\delta^{15}N$–NO_3 values highlighted manure and sewage is the main source of NO_3^- pollution in the Xiaohe River basin.

2. According to the soil column of water-soluble nitrate analysis, nitrate infiltration process was observed in the unsaturated zone. The mean concentration of NO_3^- in wastewater irrigation area was higher than groundwater irrigation area. The maximum concentration of NO_3^- (523.2 mg kg^{-1}) was found at 1.20 m depth in wastewater irrigation area was deeper than 0.85 m depth in groundwater irrigation area (725.9 mg kg^{-1}). The relationship between water-soluble NO_3^- and Cl^- concentrations showed the source of nitrate was urban effluent in wastewater irrigation area and nitrate fertilization in groundwater irrigation area. Agricultural practices were associated with high nitrate fertilization input and high contamination of nitrate of groundwater in the study area.
3. Nitrate enters the groundwater via sewage-contaminated irrigation water and infiltration from the Xiaohe River channel. More than half (56.2%) of the groundwater samples were not suitable for drinking. Especially, nitrate concentrations of all groundwater in the aquifer shallower than 80 m in depth and within a 2 km on both sides of the river exceeded the WHO drinking water standard. The significant linearity between the conservative Cl^- and NO_3^- ions indicated that wastewater was the the main source of elevated NO_3^- concentrations. DO and ORP indicated that denitrification did not dominated in groundwater of the Xiaohe River basin. The $\delta^{15}N$-NO_3 values showed that manure sewage was the main NO_3^- pollution sources in groundwater. The groundwater ages dated from CFCs data delivered useful information for evaluating NO_3^- distribution due

to long-term wastewater irrigation. It was found the NO_3^- in the young groundwater recharged year after 1975 was higher than that recharged year before. This trend was agreed with the fact that the wastewater irrigation was promoted rapidly after 1970s in the study area.

Chapter 7 Fate and transport of EDCs in surface water and groundwater

7.1 Introduction

In past decades, the environment has been continuously exposed to endocrine-disrupting chemicals (EDCs) released by urban communities and industries. The environmental behavior and fate of EDCs, such as alkylphenols (APs) and bisphenol A (BPA), have aroused serious attention in environmental research because of their estrogenic activities and ubiquity in the aquatic environment (Sumpter and Johnson, 2005).

Alkylphenol ethoxylates (APEs), which are AP metabolites, are the major constituents of APs found in surface water. APEs are widely used as non-ionic surfactants in industrial, domestic and commercial applications, such as lubricating oil additives, detergents and antistatic agents (Fenet et al., 2003). The annual worldwide APE production is estimated at approximately 650,000 tons, and 60 % of APEs are released into the aquatic environment (Guenther et al., 2002; Jobling et al., 1996). APEs are mainly composed of nonylphenol ethoxylates (NPEs) and octylphenol ethoxylates (OPEs). NPEs account for approximately 80 % of the total APE use; OPEs account for most of the remaining 20 % of APEs (Ying et al., 2002b). NP and OP are considered more toxic than their precursor APEs compounds. In China, annual APEs production is approximately 50,000 tons, which accounts for 10 % of the total global production (Fu et al., 2007).

BPA is an important intermediate that is used primarily to product polycarbonate plastic, epoxy resin and other plastic material (Kleĉka et al., 2001; Staples et al., 1998). In China, BPA production and consumption were approximately 32,000 tons and 105,000 tons, respectively, in 2001 (Zeng et al., 2006).

Most EDCs enter the aquatic environment from sewage treatment plant (STP) effluents, which led to a net accumulation in the aquatic ecosystem of urban rivers (Céspedes et al., 2008; Kang et al., 2007; Ying et al., 2002a). After entering the aquatic environment, the physicochemical properties of NP, OP and BPA play predominant roles in determining their fates in different environmental compartments. Many studies have reported on the occurrence and fate of these chemicals in a variety of environmental media including surface water, groundwater (Cailleaud et al., 2007; Latorre et al., 2003), sediments (Fu et al., 2007; Khim et al., 1999) and aquatic organisms (Belfroid et al., 2002; Pojana et al., 2007). Recently, some studies have reported that dilution might play an important role in controlling the variation of these chemicals in urban riverine systems (Gong et al., 2012; Sumpter and Johnson, 2005; Wang et al., 2012). Compared with drinking water, reclaimed water always contains high salt concentrations, nutrients and micropollutants (Yi et al., 2011).

A lot of organic pollutants such as pharmaceuticals (5930 kg/year) and most household chemicals (5660 kg/year) originated from urban wastewaters and was recharged to the Haihe River, NCP (Heeb et al., 2012). And a study clearly showed that wastewater irrigation could lead to nine organic contaminants including BPA and NP showed significantly higher concentrations in the wastewater irrigated soils than in the groundwater irrigated soils and Groundwater has been contaminated by some compounds in Hebei Province, NCP (Chen et al., 2011). However, few studies have been conducted on their behavior and ecotoxicity in urban rivers to better evaluate the issue of sewage water use in NCP.

Therefore, the objectives of this paper are as follows: (1) to assess the occurrence and distribution of EDCs (NP, OP and BPA) in surface waters, groundwater and suspended particulate matters (SPM); (2) to determine the dilution effect on the variation in EDC concentrations; and (3) to evaluate the combined effect toxicity of EDCs in the aquatic river environment.

7.2 Site description

The site description was presented in chapter 2, 10 surface water, 9 groundwater and 1 Sewage Treatment Plant (STP) effluent sample were collected for EDCs analysis (Figure 7-1).

7.3 Laboratory analysis method

The methodology was presented in Chapter 3.5.

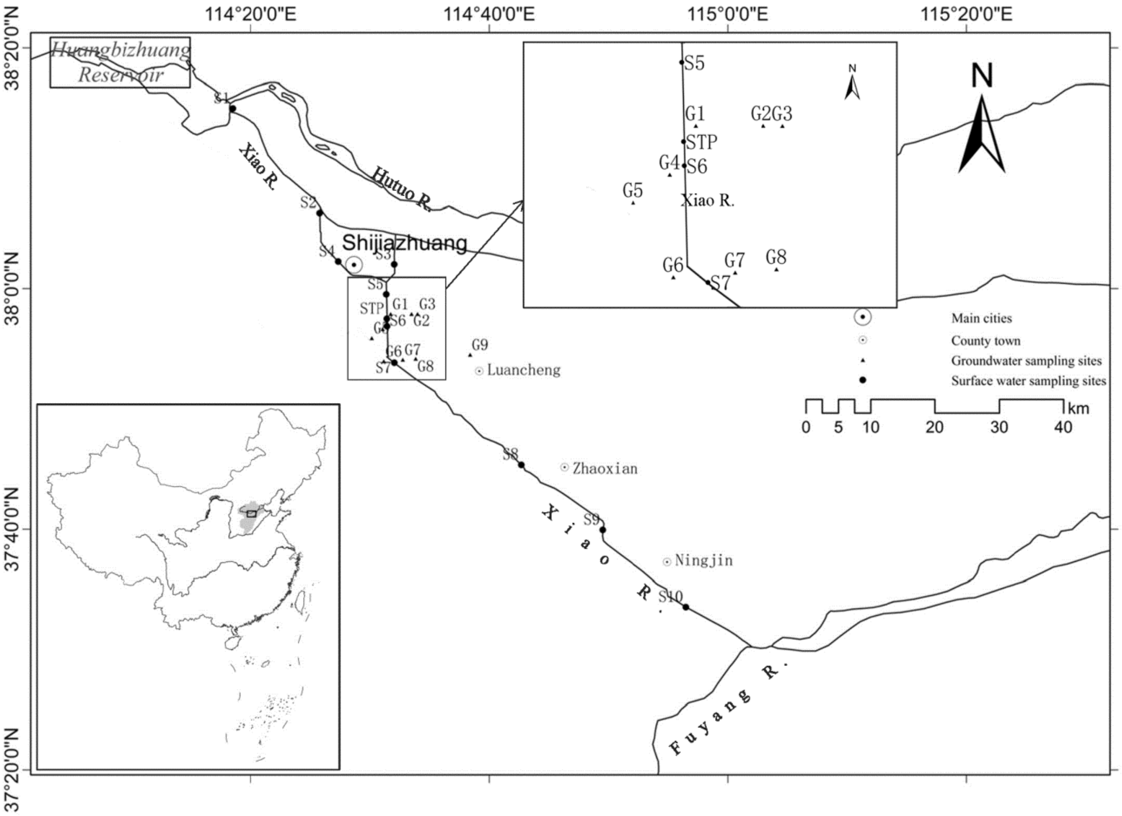


Figure 7-1 Study area and sampling locations.

7.4 Results

7.4.1 Concentrations and spatial distribution of EDCs in surface water

EDCs were detected in all samples at concentrations above their respective LOQ, which suggested that they are ubiquitous in the aquatic environment of the Xiaohe River basin. The concentrations varied from 21.6-88.8 ng L^{-1} for OP, from 38.7-1819.3 ng L^{-1} for NP and from

49.2-74.5 ng L^{-1} for BPA, with average values of 33.0, 239.5 and 151.6 ng L^{-1}, respectively. There was a significant positive correlation between the NP and OP concentrations ($R=0.906$, $p<0.01$). This implies that the NP and OP were released together into the aquatic environment and most likely underwent similar processes along the river (Watanabe et al., 2007).

Spatial distributions of the dissolved EDCs in surface water are illustrated in Figure 7-2 and show that the EDCs concentrations of the upper and middle reach river water (S1–S4) were less than those of the other areas of the Xiaohe River. NP was the predominant component of the three EDCs in the surface water with a maximum concentration of 1819.3 ng L^{-1} occurring at S5, the downstream of the Shijiazhuang urban zone and affected with a large amount of untreated wastewater from shoreline residential areas. Between sites S5 and S6, reclaimed wastewater from STP was released into the river. The concentrations of OP, NP and BPA from STP effluent were 33.0 ng L^{-1}, 239.5 ng L^{-1} and 151.6 ng L^{-1} for respectively. Those concentrations were significantly less than those of untreated wastewater. After S6, the concentrations of EDCs gradually declined. Shijiazhuang city could be considered as the major discharge source of EDCs to rivers in the study area.

As described in Chapter 5, DO concentrations ranged from 0.10-5.05 mg L^{-1} with an average concentration of 2.06 mg L^{-1} in the river. The greater DO concentration was found at the upper and middle reach sites (S1–S4) where water quality was good with the lowest total dissolved solids (TDS) value. Along the river, the DO concentration decreased dramatically to 0.5 mg L^{-1} at S5 and then decreased gradually until 0.1 mg L^{-1} at S10 (Figure 7-2). DO had a significant negative correlation with total EDCs (NP+OP+BPA) ($R= -0.779$, $p<0.01$). This was similar to the relationship of NP and DO reported in the Edogawa River

(Watanabe et al., 2007). Some studies have reported that the APEs metabolites were completely degraded to APs only under anaerobic conditions (Ying et al., 2002b). Therefore, it can be concluded that complete degradation occurred transforming APEs into APs owing to the continued lower DO concentration along the Xiaohe River.

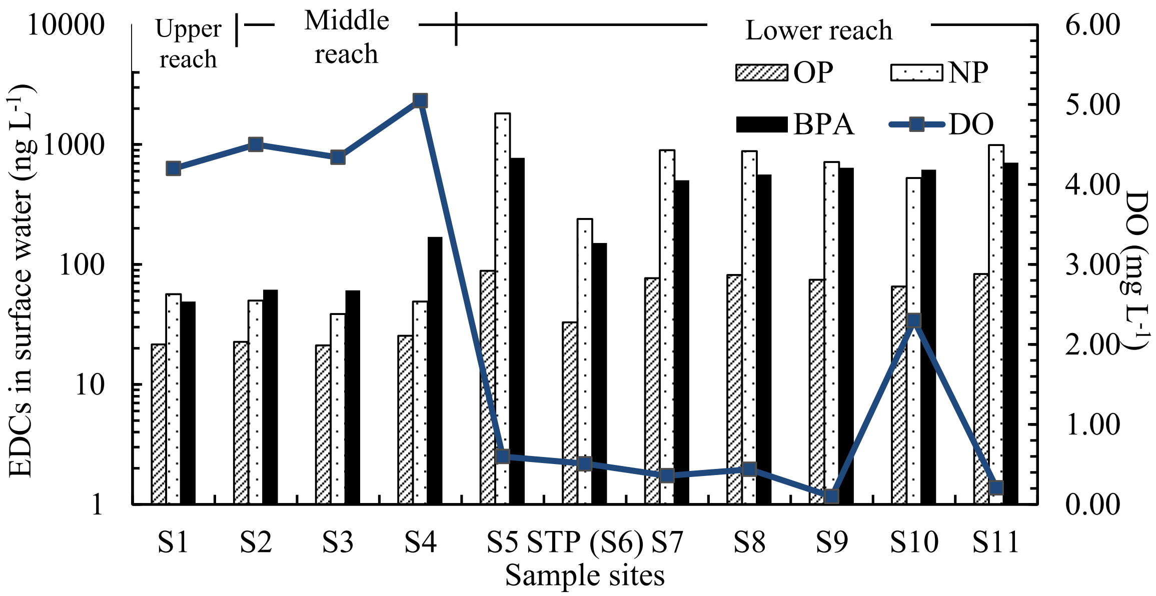


Figure 7-2 Variations of EDCs and DO in water from the Xiaohe River basin.

7.4.2 Distribution of EDCs between Dissolved and Particulate Phases

Understanding the degree of SPM-water partitioning of the organic pollutants is of importance in performing risk assessment of the river ecosystem and modeling the environmental behavior and fate of contaminants. For the particulate phase, the concentrations were in ranges of 11.9 – 19.7 ng L^{-1} for OP, 14.4 – 1196.5 ng L^{-1} for NP and

18.2 – 31.9 ngL^{-1} for BPA with average concentrations of 23.4, 785.1 and 22.5 ng L^{-1}, respectively (Figure 7-3).

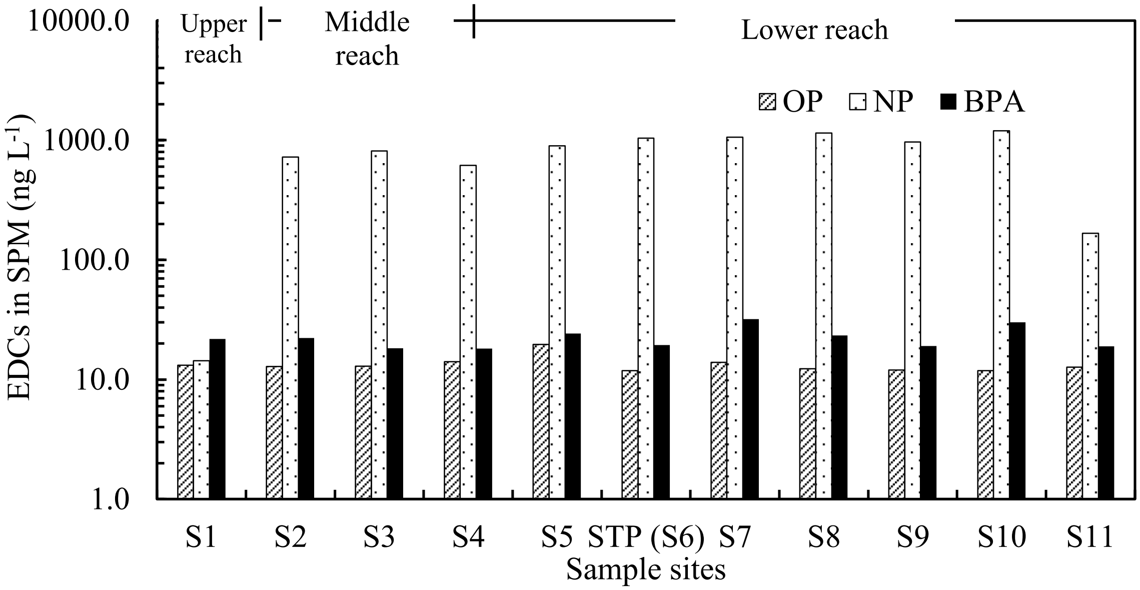


Figure 7-3 Variations of EDCs in SPM in the Xiaohe River basin.

Most APs entering the aquatic environment are highly water soluble, of which 40 – 80 % are detected in the dissolved phase and 20–60 % in SPM (Cailleaud et al., 2007; Isobe et al., 2001; Li et al., 2004). In this study, particulate OP, NP and BPA accounted for 13–38%, 20–95% and 3–31% of the total EDCs content in water bodies, respectively. Obviously, NP more readily adsorbs onto SPM than that OP or BPA, which is related to their octanol-water partition coefficients. Hence, it is reasonable to assume that as an important environmental behavior, an SPM-water partition would have a strong effect on the fates of EDCs in Xiaohe

River basin surface water. This also implies that particulate EDCs could play an important role in their transport in aquatic environments.

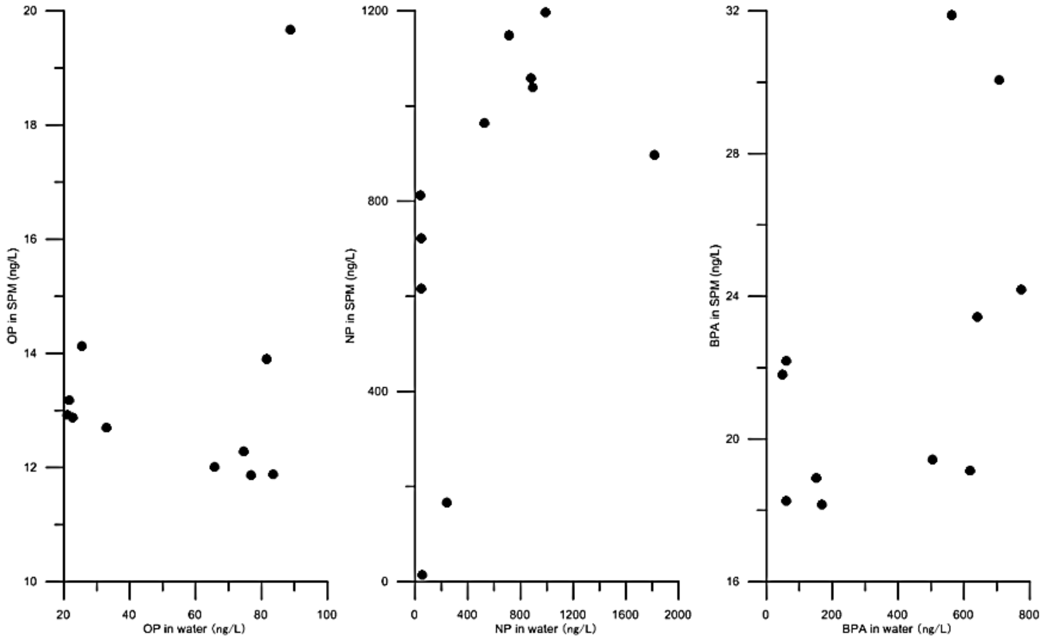


Figure 7-4 Correlations of OP (left), NP (middle) and BPA (right) between water and suspended solid.

Similar to the spatial distribution of dissolved EDCs, the lower reach particulate concentration of EDCs in lower reach was greater than that in upper reach. The correlations of EDCs between water and suspended particulate matter are shown in Figure 7-4. Both NP and OP in suspended solids dissolve easily in water, indicating that the equilibrium of NP or OP in water and suspended solids is rapidly reached in rivers. However, the correlation for BPA was so poor between water and suspended BPA that equilibrium was not reached at some sites in the study area.

Some studies have reported that the adsorption of organic contaminants to SPM is correlated with SPM's organic carbon content (Gong et al., 2012). Organic carbon (OC) contents in the dissolved phase and concentrations of dissolved organic pollutants. OC in all surface water samples from the Xiaohe River varied from 16.50 mg L^{-1} – 150.91 mg L^{-1} with a mean value of 68.89 mg/L. A positive correlation between OC and concentrations of dissolved EDCs was found (Figure 7-5). The correlation coefficient was $R = 0.78$ ($P > 0.05$) for OP, $R = 0.85$ ($P > 0.05$) for NP and $R = 0.78$ ($P > 0.05$) for BPA. These results indicate that surface water with high amounts of organic carbon was likely to adsorb more EDCs, and organic carbon plays an important role in controlling the SPM-water partition of the riverine ecosystem.

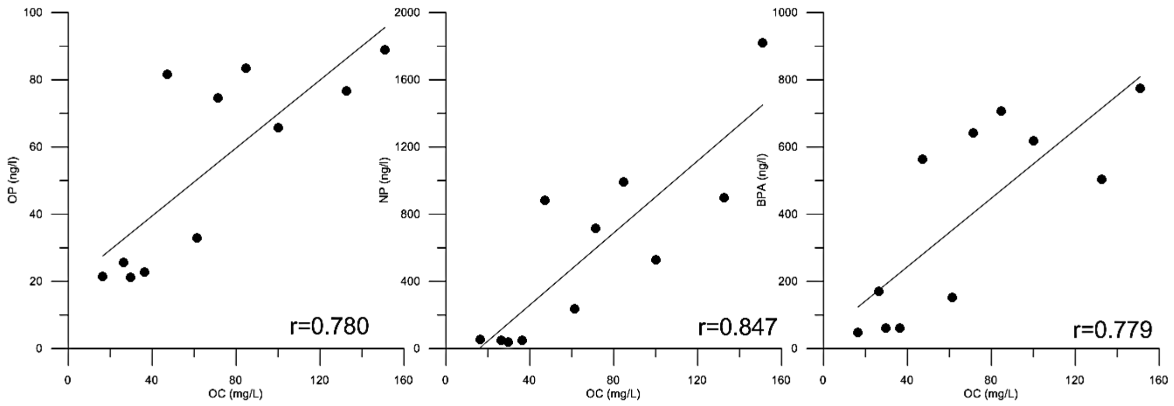


Figure 7-5 Correlations of dissolved OP (left), NP (middle) and BPA (right) and organic carbon.

7.4.3 Concentrations and spatial distribution of EDCs in groundwater

Spatial distributions of the dissolved EDCs in groundwater are illustrated in Figure 7-6. The EDCs concentrations in groundwater ranged 20.09-23.58 ng L^{-1}, 30.71-58.63 ng L^{-1}, and 36.70-137.66 ng L^{-1}, and the mean was 20.86 ng L^{-1}, 40.66 ng L^{-1} and 56.28 ng L^{-1} for OP, NP and BPA, respectively. The concentrations of OP, NP and BPA in groundwater were much less than those in the surface water.

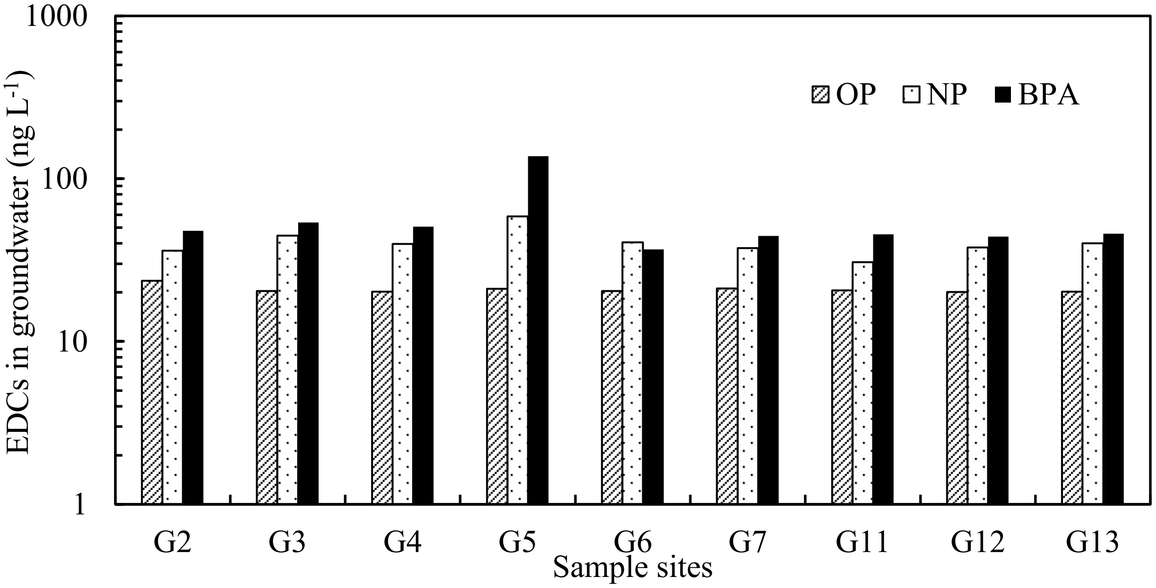


Figure 7-6 Variations of EDCs in groundwater from the Xiaohe River basin.

7.5 Discussion

7.5.1 Mixing of EDCs in surface water along the Xiaohe River

After EDCs enter into the aquatic environment, changes in phenolic EDC concentrations are associated with processes, such as dilution, photolysis, biodegradation and sorption to suspended particulate matter (SPM). Zhang et al. reported that dilution was the predominant process that affected NP and OP concentrations in surface water along the Jialu River, China, which was as high as 38.8 % for NP and 57.8 % for OP (Zhang et al., 2009b). In order to determine the fate and behavior of EDCs in the Xiaohe River, it was necessary to estimate the migration processes of EDCs in surface water along the river. Cl^- is a conservative ion that is not subject to physical, chemical, and microbiological processes and can be used as an indicator for determining surface water movement under most circumstances (Panno et al., 2006a). Generally, the origin of Cl^- is mainly from natural sources and discharges from industrial, agricultural and domestic wastewaters (Tang et al., 2003). As described in Chapter 5 and 6, potential natural sources of chloride cannot be found in the Xiaohe River basin, Cl^- can be considered as the result of anthropogenic source in the Xiaohe River basin. The significant linearity (R^2= 0.967) between total dissolved EDCs in surface water and Cl^- concentration indicates an anthropogenic source of EDCs in the Xiaohe River (Figure 7-7). S5 and S6 did not located on correlation line, due to S5 was affected by industrial wastewater and S6 was affected by STP.

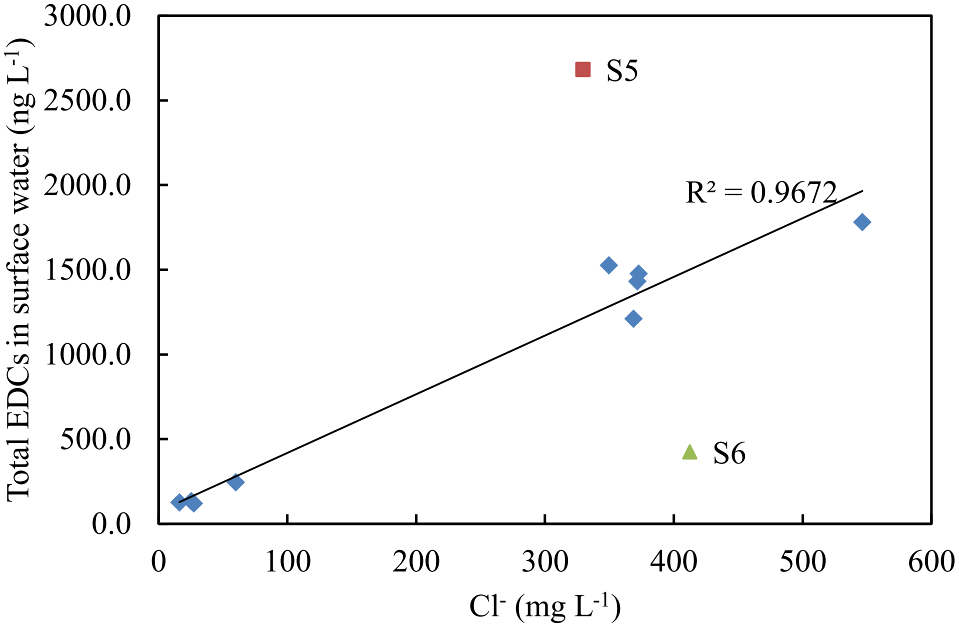


Figure 7-7 Correlations of total EDCs and Cl^- in surface water.

Therefore, percentage of water dilution at each sampling site was calculated based on the mass balance of chloride to estimate the theoretic phenolic EDC concentrations along the river by only considering dilution effect as follows:

$$Calc.-EDCs_{(n+1)} = Anal.-EDCs_n \times \frac{Cl_{(n+1)}}{Cl_n} \qquad \text{(Equation 7-1)}$$

where Anal.-$EDCs_n$ represents the analyzed concentrations of EDCs obtained by analysis at site n; Calc.- $EDCs_{(n+1)}$ is the calculated concentration of EDCs at $S_{(n+1)}$ upon considering only the mixing or dilution effect. Cl_n and Cl_{n+1} are chloride concentrations at sampling S_n and $S_{(n+1)}$, respectively.

In fact, several factors control phenolic EDC concentrations in the river, such as new sources, dilution, mixing, adsorption, biodegradation, photolysis and air–water exchange.

Therefore, (1) if the calculated value is similar to analyzed values, it indicates that the mixing effect were the predominant controlling factor on changes of EDCs concentration along the river; (2) if the calculated value is less than the analyzed one, it indicates an excess of EDCs entering the river; (3) if the calculated value is greater than the measured EDCs, it indicates that except for dilution and mixing, the combined effects of adsorption, biodegradation, photolysis and air–water exchange played an important role in decreasing the concentrations of EDCs.

The behaviors of EDCs at each sampling site along the river are shown in Figure 7-8. The agreement between the analyzed data and calculated data in upper and middle reach (S1-S4) suggested that dilution and mixing effects were the predominant processes controlling the concentration change in dissolved phenolic EDCs concentrations. Due to there is no correlation between Cl^- and EDCs, the behaviors of EDCs could not be explained use by Cl^- in site S5 and S6. The calculated data in the S10 and S11 were greater than the analyzed data, it indicates that others effects such as adsorption, biodegradation, photolysis and air–water exchange played an important role in decreasing the concentrations of EDCs. The calculated data in S8 and S12 were less than the analyzed data indicates that a source contained excess of EDCs entering the Xiaohe River.

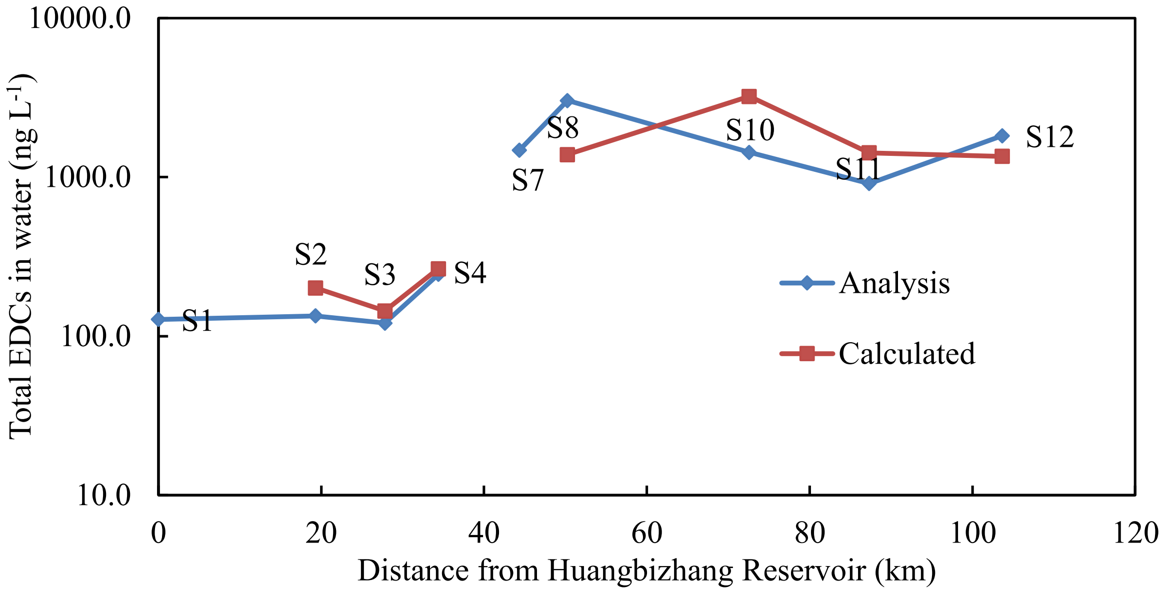


Figure 7-8 Comparison of Calc.-EDCs and Anal.-EDCs concentrations in river water along the Xiaohe River.

7.5.2 Ecotoxicity of EDCs in the Xiaohe River basin

Sharma et al. summarized the concentrations of EDCs in river water from different regions of the world and reported a level of <1 – 1440, 6 – 32800 and 0.5 – 4000 ng L^{-1} for OP, NP and BPA, respectively (Sharma et al., 2009). Concentrations of OP and NP in surface water near Tianjin city in north China were detected with concentrations of 18.0 – 31.9 ng L^{-1} and 106 – 553 ng L^{-1}, respectively. Compared with these results, the levels of NP, OP and BPA in the Xiaohe River were found to be similar to those of the other rivers (Table 7-1).

It is generally accepted that 1000 ng L^{-1} is the threshold for NP for vitellogenin induction in fish, and the lowest level in freshwater with a safety factor of 0.1 in Europe (Koschorreck et al., 2002; Renner, 1997). The Japanese Ministry of the Environment reported pedicted no-effect concentration (PNEC) on fish for NP and OP are 608 ng L^{-1} and 992 ng L^{-1}, respectively (Inudo et al., 2004; Ishibashi et al., 2004). For BPA, the freshwater PNEC of 64,000 ng L^{-1} was derived (Staples et al., 2000), and the PNEC on fish for BPA was 47 μg L^{-1} for a partial life cycle or 24.7 μg L^{-1} for a full life cycle (Belfroid et al., 2002). Based on these environmental standards, the NP concentrations observed from S5 to S10 in this study exceeded or were close to the limit and might be potentially hazardous to fish, which therefore may result in potential dietary exposure to humans.

Table 7-1 Concentrations of EDCs (ng L^{-1}) in rivers from various sites in the world.

Different water bodies	NP	OP	BPA	References
Detroit River, U.S.	269–1190	5–81		(Snyder et al., 1999)
Aire River, U.K.	<1600–53000	<1000		(Blackburn and Waldock, 1995)
Elbe River, Germany	13–53	<0.05–3.3	3.8–30	(Stachel et al., 2003)
Edogawa River, Japan	120–380	10–180		(Watanabe et al., 2007)
Pearl River, China	20–628	2–680		(Chen et al., 2006a)
Jialu River, China	75.2–1520	20.9–63.2	410–2990	(Zhang et al., 2011b)
Haihe River, China	106–296	18–20	20–8300	(Jin et al., 2004)
Xiaohe River, China	38.7–2382.4	21.2–123.4	48.2–774.5	This study

To assess the toxicity of EDCs on organisms, a concentration addition (CA) model (Equation 7-2) suggested by Sumpter et al. (2006) was used in this study. This method assesses the response of freshwater fish to a mixture of estrogenic chemicals based on concentration addition. The data about effect levels of EDCs (*k*) on freshwater fish were obtained from a toxicity database and literature (Sumpter et al., 2006; Thorpe et al., 2003).

$$k = \sum_{i=1}^{n} \frac{c_i}{EC_{x_i}} \qquad \text{(Equation 7-2)}$$

where c_i is the analyzed concentration of the individual substance present in a mixture at site i; EC_{xi} is the analyzed concentration of the single substance in a mixture *i* at effect *x* %; and *k* is the influencing factor. If $k \geq 1$, the expected mixture effect is greater than or equal to the mixture effect *x* %, and if $k < 1$, the expected mixture effect is less than the *x* % level. To classify the expected mixture effects, the EC_{10}, EC_{50} and EC_{95} values for each substance were obtained from a toxicity database and literature.

The effect is classified into five classes as follows: $k_1 \leq 0.1$ ("no effect"); $0.1 < k_1 \leq 1$ ("low effect"); $k_2 \leq 1 < k_1$ ("medium effect"); $k_3 \leq 1 < k_2$ ("high effect"); and $k_3 > 1$ ("severe effect") where

$$k_1 = \sum_{i=1}^{n} \frac{c_i}{EC_{10_i}} \qquad k_2 = \sum_{i=1}^{n} \frac{c_i}{EC_{50_i}} \qquad k_3 = \sum_{i=1}^{n} \frac{c_i}{EC_{95_i}}$$

The EC_x values of NP, OP and BPA were defined as the corresponding x% of effect concentrations. Effect concentrations of NP, OP and BPA were 7, 45 and 150 mg L^{-1}, respectively (Brian et al., 2005). In the present study, the *x* % was set to 10 %, 50 % and 95 % effect level.

According to the model, the predicted mixture effect for OP, NP and BPA to cause vitellogenin induction on fish in the study area was calculated. Mixture effect levels of EDCs in the urban area (S2–S4) were found at a low effect, and a medium effect were found at lower reach (S5–S10). Source reservoir (S1) and groundwater in the Xiaohe River basin were calculated to have no effect, and STP effluent was calculated to have a low effect. In the present study, we did not consider all of the estrogenic chemicals possibly present in the aquatic environment, which might lower the actual effect of all estrogenic chemicals compared with that of the anticipated effect.

7.6 Conclusions

High concentrations of EDCs were found in the lower reach of the Xiaohe River. Discharge of untreated wastewater was responsible for the increase of EDCs. Therefore, Shijiazhuang city can be regarded as the main discharging source of EDCs in the lower reach. The EDCs concentrations in groundwater were less than those in surface water.

The mass balance equation for chloride was used to determine the behavior of EDCs along the Xiaohe River. It was found that the mixing process plays an important role in controlling the concentrations of dissolved EDCs in upper reach, and others effects such as adsorption, biodegradation, photolysis and air–water exchange played an important role in lower reach of the Xiaohe River.

Based on environmental risk assessment of EDCs in the study area, it was found that the predicted mixture effect was low in upstream and medium in downstream urban zones. Additionally, the concentrations of EDCs in reservoir were found with no effect on fish.

Chapter 8 General discussions and conclusions

8.1 General discussions

8.1.1 Changes of hydrologic cycle structure

Anthropogenic activities will likely have a significant impact on hydrologic cycle. The natural relationship between surface water and groundwater has changed greatly in NCP, a typical arid or semi-arid regions. History of water use and changes of recharge can be explained based on Figure 8-1.

Under the natural conditions, groundwater table was shallow about 3 to 5 m in depth. The groundwater is mainly recharged by precipitation infiltration and the lateral flow from the Taihang Mountain in the piedmont alluvial plain. There was mutual recharge relationship between river water and groundwater. Water participated in hydrologic cycle is young.

Now, the natural water hydrologic cycle has been changed greatly in NCP, a typical arid or semi-arid regions. Amount of groundwater has been pumped up to meet the needs for developing industry, agriculture and urbanization, water table declined continually. Precipitation infiltration and the lateral flow could not to recharge groundwater. The interaction of surface water and groundwater has been changed to the one-way recharge from surface water to groundwater in NCP. Excessive groundwater is used to irrigate farmland, irrigation return flow could recharge to groundwater. Water participated in hydrologic cycle is changed to old.

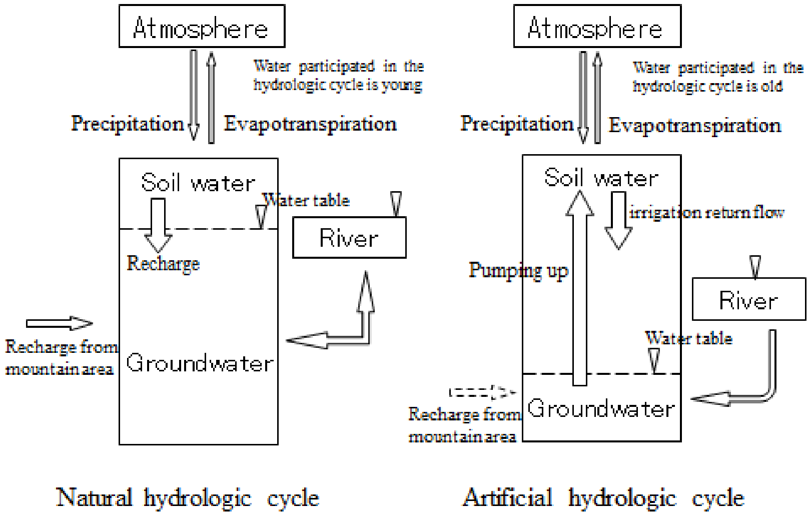


Figure 8-1 Concept map of changed hydrologic cycle structure.

8.1.2 Changes of groundwater hydrochemistry

In the past decades, the hydrochemical composition of shallow groundwater has undergone significant changes in the Shijiazhang City region. Before 1959, hydrochemical composition of groundwater remained the natural state, TDS of groundwater was 340 mg L^{-1}, NO_3^- concentration was 2.35 mg L^{-1} and pH ranged 7.5-7.8 (Zhang et al., 2009c). Hydrochemical type of groundwater was HCO_3−Ca・Mg type and began to change from 1970 in the Shijiazhuang city region.

NO_3^- concentration has increased from 2.4 mg L^{-1} in 1959 to 53.9 mg L^{-1} in 2010,at rate of 1.0 mg L^{-1} per year. The mean of NO_3^- concentration in groundwater of this study exceed

WHO drinking water standards (50 mg L^{-1}), indicating that nitrate pollution has become a serious problem threating to safe for a vast population.

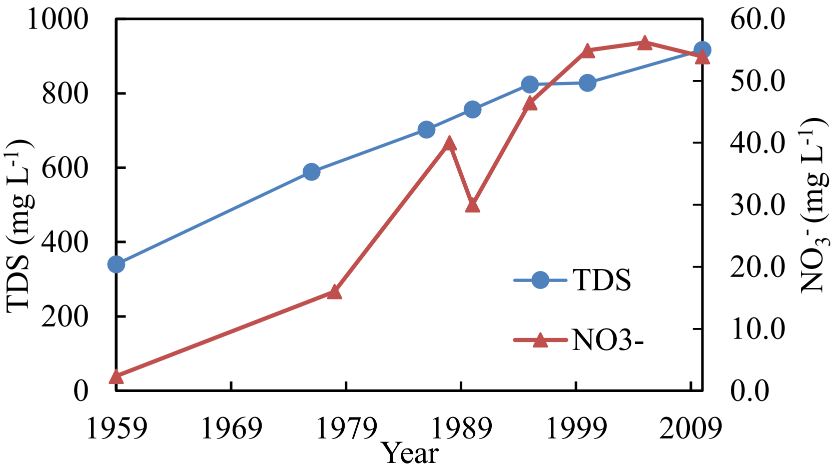


Figure 8-2 The trends of TDS and NO_3^- in the Shijiazhang City region (data from 1959 to 2009 was according to Zhang et al., 2009c)

8.1.3 Influence of different irrigation practices

Because of the use of wastewater to irrigate farmland for many years in wastewater irrigation area. It is necessary to evaluate the impact of different irrigation practices to groundwater in NCP.

In order to assess the impact of wastewater irrigation on groundwater table, the trends of monthly water table from two wells. One in wastewater irrigated area (Loudi station) and other one in the groundwater irrigated area (Luancheng station) were shown in Figure 8-3. Monthly groundwater table at the Loudi station was relatively stable within a narrow range of −1.25–+1.71 m, without responding either to high evapotranspiration in dry season and to precipitation in the rainy season. It indicates that wastewater continuously recharge to local groundwater though wastewater irrigation. A comparison with wastewater irrigation area, the groundwater table at Luancheng station fluctuated within a wider range of −2.68–+2.40 m.

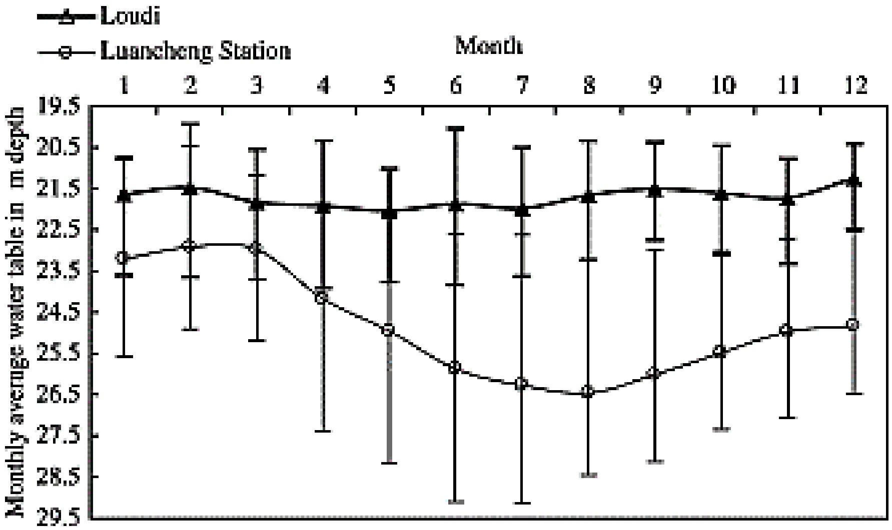


Figure 8-3 Comparison of monthly average water table levels and ranges of fluctuation (1992–1999) between wastewater irrigated site (Loudi) and groundwater irrigated site (Luancheng station), (cited from (Chen et al., 2006b)

Surface water and groundwater in the Xiaohe River basin are used for irrigation. Excessive sodium and salinity concentration in irrigation water result in salinity hazard. Sodium ion in water replacing calcium and magnesium ions in soil causes reduced permeability. Parameters such as the sodium adsorption ratio (SAR) was estimated to assess the suitability of water from the rivers for irrigation purposes. SAR parameter versus EC is very important in classifying irrigation water. The SAR parameter evaluates the sodium hazard in relation to calcium and magnesium concentrations (Glover, 1993). It can be calculated as:

$$SAR = \frac{m_{\mathrm{Na+}}}{\sqrt[2]{m_{\mathrm{Ca2+}} + m_{\mathrm{Mg2+}}}}$$

where m_i represents the concentration of ion (in mmol L^{-1}).

Figure 8-4 shows the relationship between SAR and EC. The SAR value ranges from 0.50 to 7.07 for surface water and 0.45 to 1.83 for groundwater. It is clear that surface water falling in the C2–S1 and C3–S2 area and groundwater in the C2–S1 area. According to the Glover (1993), the groundwater and the surface water in the C2–S1 makes it suitable for irrigation of most crops with little danger of development of exchangeable sodium and salinity. However, the surface water in the C3–S2 was found in the lower reach of Xiaohe River and should not be used on soils with restricted drainage.

The relationship between SAR and EC also was also used to evaluate soil quality. The SAR of soil water in plow layer (0-1 m depth) ranges from 0.017 to 0.165 falling in C2-S1 area, and in deep layer ranged from 0.001 to 0.040 falling in C2-S1 area in wastewater irrigation area. The SAR of soil water in groundwater irrigation area changed from 0.011 to 0.034 in plow layer falling in C2-S1 area, and from 0.001 to 0.050 in deep layer falling in C1-S1 area. It indicated that soil quality of plow layer in groundwater irrigation area is better than that in wastewater irrigation area, can be used to cultivate most crops with Low-salinity level. Both groundwater and wastewater irrigation area, salinity level of soil is greater in plow layer than the layer below.

50 years of wastewater irrigation result that EC of plow layer in wastewater irrigation area (965 μS cm^{-1}) was about 3 times than groundwater irrigation area (275 μS cm-1), at rate of

14 μS cm^{-1} per year. If this rate is maintained, 120 years later EC of plow layer would exceed 2750 μS cm^{-1}, and plow layer would be unsuitable for growing crops.

The most significant effect of wastewater irrigation is high NO_3^- concentration. The mean value of water-soluble NO_3^- concentrations in unsaturated zone of wastewater irrigation area (137.0 mg kg^{-1}) was higher than groundwater irrigation area (107.7 mg kg^{-1}). Wastewater irrigation result that nitrate concentrations of all groundwater in the aquifer shallower than 80 m in depth and within a 2 km on both sides of the river exceeded the WHO drinking water standard. More than half (56.2%) of the groundwater samples were not suitable for drinking.

Wastewater irrigation to groundwater had a profound influence in both quantity and quality. Wastewater irrigation is beneficial to save and recharge local groundwater in the wastewater irrigation area. Due to wastewater containing a large amount of untreated pollutants, wastewater irrigation caused multiple pollutants are infiltrated into shallow groundwater. Wastewater irrigation should be used under the scientific guidance.

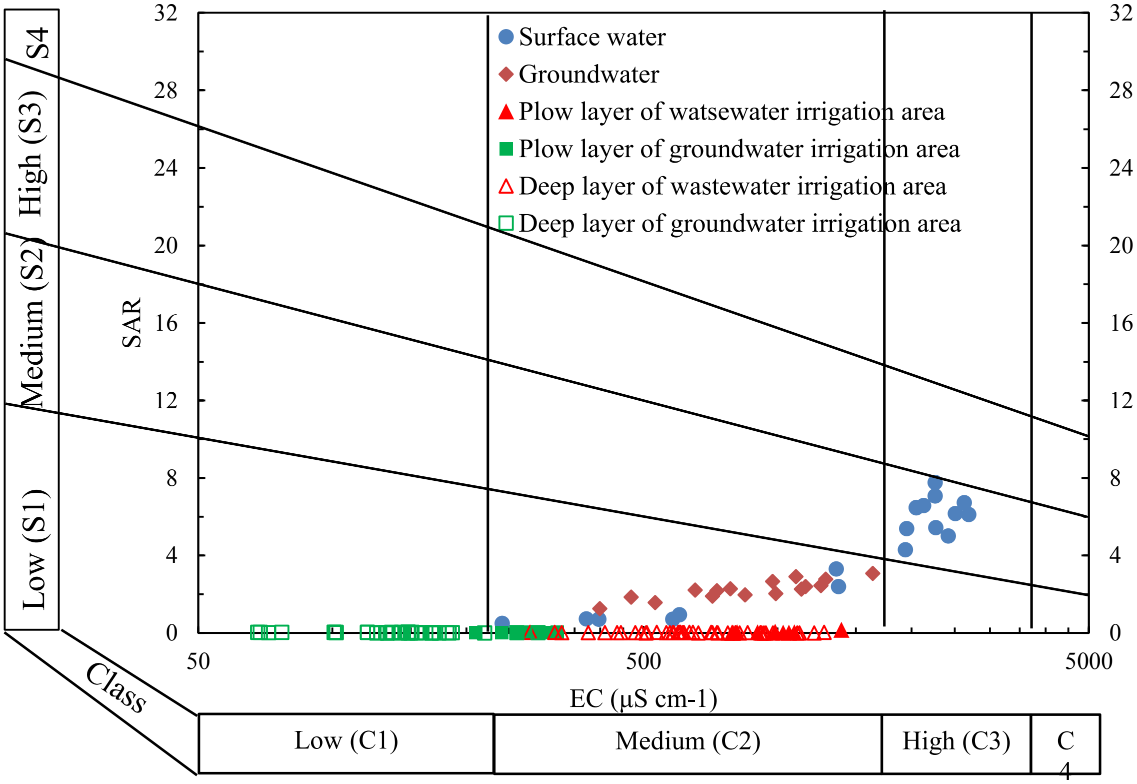


Figure 8-4 The relationship between SAR and EC characterizing the irrigation quality of surface water and groundwater and soil quality in different irrigation practices.

8.2 General conclusions

This study was carried out in artificial river of the Xiaohe River Basin in a semi-arid region of NCP, focused on different aspects to determine the changed recharge process for groundwater, soil chemistry in irrigation farmlands and the deterioration of water quality such as nitrte and EDCs contamination in water environment. Based on the results, the main conclusions are presented as follows:

1. In the NCP, surface water is the most important source of recharge for groundwater. The groundwater was approximately composed of 50–60% river water, as calculated by Cl^-, δD and $\delta^{18}O$. This finding demonstrates that rive water can be easily effect groundwater. CFCs results indicated that groundwater age varied from 22.5 to 39.5 years. The vertical flow velocity of groundwater was about 1.8–3.5 m $year^{-1}$.
2. Calcium and sodium were the dominant cation and bicarbonate were the dominant anion in most river samples. Major ions displayed clear spatial distribution with lower concentrations in the upper reach and higher in the lower reach of Xiaohe River owing to large discharges of untreated or slightly treated sewage, that is the main factor affecting surface water quality in study area. Therefore, the Xiaohe River changed from being a $Ca\text{-}SO_4$ type (natural background) in the upper reach, to a Na-Cl type in the urban area, and finally to a $Na\text{-}HCO_3$ type in the lower reach of the study area. Calcium and bicarbonate were dominant ion in groundwater, and groundwater in the Xiaohe River basin belongs to the $Ca\text{-}HCO_3$ type. Based on the EC and SAR, the groundwater and the surface water in upper reach of Xiaohe River is suitable for irrigation of most crops with little danger of development of exchangeable sodium and salinity. The surface water in lower reach of Xiaohe River cannot be used on soils without good drainage.
3. Under the impact of urban sewage discharged to the Xiaohe River, high concentration of nitrogen (NH_4^+–N) was found in the lower reach of the Xiaohe River. The redox analysis revealed that surface water had an oxic condition with the stable form of N was NO_3^- in upper and middle reaches of Xiaohe River, and a strong reduction condition which are unstable for NO_3^- in the lower reach. Nitrate enters the groundwater via sewage-

contaminated irrigation water and infiltration from the Xiaohe River channel. Especially, nitrate concentrations of all groundwater in the aquifer shallower than 80 m in depth and within a 2 km on both sides of the river exceeded the WHO drinking water standard. More than half (56.2%) of the groundwater samples were not suitable for drinking. DO and ORP indicated that denitrification did not dominated in groundwater of the Xiaohe River basin. The groundwater ages dated from CFCs data delivered useful information for evaluating NO_3^- distribution due to long-term wastewater irrigation. It was found the NO_3^- in the young groundwater recharged year after 1975 was higher than that recharged year before. This trend was agreed with the fact that the wastewater irrigation was promoted rapidly after 1970s in the study area. The significant linearity between the conservative Cl^- and NO_3^- ions indicated that wastewater was the main source of elevated NO_3^- concentrations in water body in wastewater irrigation area. The $\delta^{15}N–NO_3$ values highlighted manure and sewage is the main source of NO_3^- pollution sources in the Xiaohe River basin.

According to the soil column of water-soluble nitrate analysis, nitrate infiltration process was observed in the unsaturated zone. The mean concentration of NO_3^- in wastewater irrigation area was higher than groundwater irrigation area. The maximum concentration of NO_3^- (523.2 mg kg^{-1}) was found at 1.20 m depth in wastewater irrigation area deeper than 0.85 m depth in groundwater irrigation area (725.9 mg kg^{-1}). The relationship between water-soluble NO_3^- and Cl^- concentrations showed the source of nitrate was urban effluent in wastewater irrigation area and nitrate fertilization in groundwater irrigation area. Agricultural practices were associated with high nitrate fertilization input and high contamination of nitrate of groundwater in the study area.

4. High concentrations of EDCs were found downstream of Shijiazhuang urban centers along the Xiaohe River. Discharge of untreated wastewater was responsible for the increase of EDCs. Therefore, Shijiazhuang city can be regarded as the main discharging source of EDCs to the downstream. The EDCs concentrations in groundwater were less than those in surface water. The EDCs was found in all of groundwater samples, highlighting the need to understand their fate in aquifers.

    Based on the mass balance equation for chlorion, it found that the mixing process plays an important role in controlling the concentrations of dissolved EDCs. Using environmental risk assessment of EDCs, the predicted mixture effect was low in upper reach and medium in lower reach and urban zone in the study area. These results indicate that continuous monitoring of EDCs levels in urban rivers receiving reclaimed water is necessary because of the toxicity of EDCs on aquatic organisms and humans.

8.3 Recommendation and Future work

8.3.1 Protection of the groundwater resource

The NCP is one of the most important agricultural areas in China. Groundwater storage and quality are affected by industrial development and agricultural practices. Because plenty of water demand for industrial and domestic use and wastewater irrigation, the groundwater level is continuing decline and water quality is getting worse. The author suggests that at firstly, the management system of agricultural, industrial and domestic water use should be optimized; then, wastewater irrigation should be carried out under scientific guidance and planning of irrigation is important for saving water, and finally, the sewage treatment and monitoring should be intensified.

8.3.2 Future work

This study discussed influence of surface water to groundwater, but differences between shallow groundwater and deep groundwater has not been distinguished very well. The interaction and differences of shallow groundwater and deep groundwater should to conduct in further work. Water-rock reactions, ion exchange process and moisture migration process in unsaturated zone under different land use should be attention.

High concentration of nitrate was detected in the shallow groundwater, deep groundwater should be monitored. Effects of wastewater irrigation should be further evaluated.

Because of the presence of EDCs was found in groundwater and variation of EDCs in the unsaturated zone was not analyzed, the environmental behavior and transfer mechanism of EDCs in unsaturated zone and effects of ECDs on groundwater should be concerned.

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