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Water chemical composition of reclaimed water irrigation district, China

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Abstract: Reuse of municipal treated wastewater is an important way for water-saving irrigation in water deficient region, which both increase the water available amounts and reduce the pollutant discharge. Assessing the water chemical characteristics of surface water bodies and its affection on groundwater salinity pollution is essential for security utilization of treated wastewater in the reclaimed water irrigation district (RWID). The southeast suburb agricultural district is a unique region in Beijing with large scale reclaimed water utilization since 2002, and experiencing greatly water chemistry change. The chemistry of major ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, SO_4^{2-}, NO_3^-, and Cl^-) in the water of RWID is analyzed, based on samples from 11 sites of surface water, 3 reclaimed water plants, and 30 sites of groundwater of Beijing southeast suburb RWID in 2011. The surface water composition is predominated by Na^+, Ca^{2+}, SO_4^{2-}, and HCO_3^-, characteristic with high pH value, EC, mineralization, and salinity relative to global median and other world rivers. High concentration of Na^+ and SO_4^{2-}mainly caused by the effluent, and ternary ions demonstrate that the water are mainly controlled by the weathering of carbonates characteristic as high concentration of Ca^{2+} and HCO_3^-. TDS concentration versus the weight ratios of Na^+/ (Na^++ Ca^{2+}) ternary ions demonstrate that the surface water chemical composite pattern are mainly controlled by evaporation and crystallization processes. The groundwater composition is dominated by Na^+, Cl^-, and SO_4^{2-}. Most variables of groundwater samples are under the maximum desirable limits of Class Ⅲ standard of Chinese water standard. The local sand-layer soil profile with coarse and fine minerals tends to accelerate the ion-exchange adsorption and denitrification processes during groundwater recharge, and the probability of salinity and nitrogen pollution risk is low. The groundwater pollution constrained in a certain area and not suitable as drinking water sources, and water pollution control should be improved to stop the pollution extend.

Key words: Reclaimed water utilization; Agricultural region; Stream water; Groundwater; Beijing

1. INTRODUCTION

In rural-urban continuum, reclaimed water such as treated wastewater is an important non-conventional water resource for irrigation (Pedrero et al. 2010). The municipal wastewater has been recycled in agricultural for centuries as a means of disposal in cities worldwide (AATSE, 2004; Pedrero et al. 2010). The reclaimed water irrigation district (RWID) subject to severe anthropogenic pressure and natural processes such as intensively intrusion of effluent pollutant, soil pollution, and salinization of groundwater. The major chemical composition of surface water could reveal the nature of weathering, patterns and linkages between evaporation and anthropogenic processes on a regional scale (Gibbs, 1970; Brennan and Lowenstein, 2002). Especially for RWID, quantifying the major-ions composition of surface water bodies has broad implications, e.g., water quality type, hydrogeology characteristics, natural processes and anthropogenic influences for water chemistry. Furthermore, the groundwater is saline relative to the overlying irrigation reclaimed water due to absorption of Na^+ onto the clay and release of Ca^{2+} into the recharging water (Kass et al. 2005; Rebhun, 2004).

The southeastern suburb RWID of Beijing comprised by Xinhe and Nanhongmen agricultural region, is one of the biggest RWID in China (Liu et al. 2009). Studies have been undertaken to understand the effects of reclaimed water utilization on environment (Liu et al. 2009; Wu, 2009;

Wu et al. 2009). Generally, the reclaimed water come from wastewater contained relative high concentration of chemical ions and its irrigation could results some extent of pollution risk (Nurizzo et al. 2005). However, studies suggested that the reclaimed water is treated with kinds of hydrochemical processes, and characteristic with relative low content of pollutants that under the maximum desire limits of Chinese state standard for irrigation water and the environmental pollution risk (Yi et al. 2011). In this agricultural region, the surface hydrologic network is entirely artificially controlled by irrigation/drainage canals. The water sources consist with treated reclaimed water, land surface runoff, and stream flow from upper reach. The water quality is characteristic with high chemistry concentration and spatial and temporal variation, which is combined controlled by the precipitation, soil erosion, weathering patterns, and anthropogenic activities. However, most of studies have historically focused on spot experiment focus on eutrophication, heavy metal (Zhang et al. 2011a), organically pollutants (Vanderzalm et al. 2006) of the water body for a single stream or spot, few studies have focus on the regional water chemistry investigation .

In this study, the major ionic composition (Ca, Mg, Na, K, HCO_3, SO_4, and Cl), pH value, electric conductivity (EC), and total dissolved solids (TDS) of 11 sites of surface water, 3 reclaimed water plants, and 30 sites of groundwater were investigated in the southeastern RWID in 2011 of Beijing. The patterns indicative of their source were also investigated, and the control mechanisms of ion chemistry in different water bodies of the RWID. We also study the chemistry ions sources of groundwater and assess the salt pollution risk in the reclaimed water irrigated district.

2. MATERIALS AND METHODOLOGY

2.1. Site description

The study area situates in southeast suburb of Beijing city with a temperate semi-arid continental monsoon climate. The agricultural region is 373km^2 comprised with Xinhe and Nanhongmen agricultural region located in Tongzhou and Daxing district of Beijing, respectively (Figure 1). The mean annual temperature is 11.6℃. The mean annual precipitation is 577.9mm (1951~2010) with 78% happened during the flood season from June to September. The predominant soil type is cinnamon soil characteristic as sandy loam soil.

The irrigation district located in the plain area of Beiyun watershed, and the main rivers of the area are the Beiyun main channel, the Liangshui river, the Feng river, and the Fenggangjian river (Figure 1). The Beiyun River is one the biggest river in Beijing city originates from Wenyu River in northern Yan mountainous area. Beiyun River is the only river which originates in the border and it never runs dry (Zhang et al. 2010). As a result, Beiyun River is usually called the mother river of Beijing. However, the river experiencing a prolonged river drought and the mean annual runoff is 0.931 billion m^3/a between 1961 to1998 (Fu, 2006). However, the runoff has decreased to 0.52 billion m^3/a in the recent 12 years (1999-2011). The RWID is a relative flat region, which has an average elevation of 50m above the sea level. The over layer soil profile depth is mainly from 20m to 50m and characteristic with sand-layered soil (Figure 2). The area in its northwest is higher than its southeast and the streamflow diverted to the southeast followed the regional topography.

Reclaimed water is the most important water source in the area which contributed to more than 62.5% of the available water resource in the area (Pan et al. 2012). The treated reclaimed water mostly discharged by three most important wastewater treated plans, i.e., the Gaobeidian, the Xiaohongmen, and the Huangcun effluent treatment plant. The Gaobeidian plant designed capable to treat wastewater 1 million m^3/d, in which 0.55 million m^3/d supplied to the irrigation district through Tonghuibei irrigation canal, and followed by Liangshuihe river, Tonghuinan irrigation canal, and Fenggangjian river mainly covered Xinhe agricultural district. The Xiaohongmen plant has treated capacity of 0.6 million m^3/d wastewater supported to the Nanhongmen agricultural district through Liangfeng and Beiyechang irrigation canal each day. The Huangcun plant has treated capacity about 0.08 million m^3/d, and its treated reclaimed water is discharged in the Xinfeng River for irrigation and landscape in Nanhongmen agricultural district. Other small wastewater treatment plants and equipments managed by local town and village government scattered in the agricultural district with total treated capacity no more than 80 thousand m^3/d and the treated water effluent in the nearby river and drainage canal for landscape utilization.

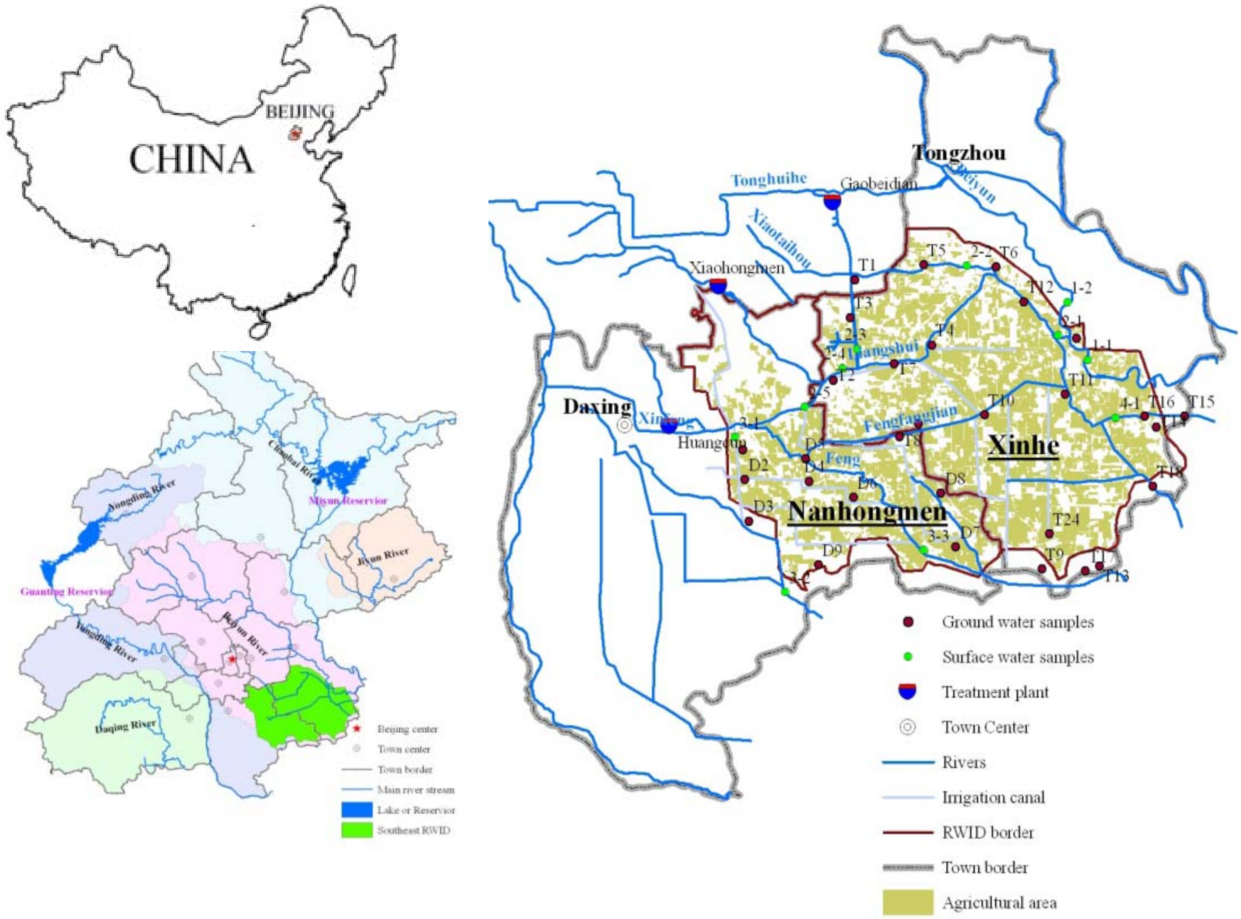

Figure 1. Study area and sample points.

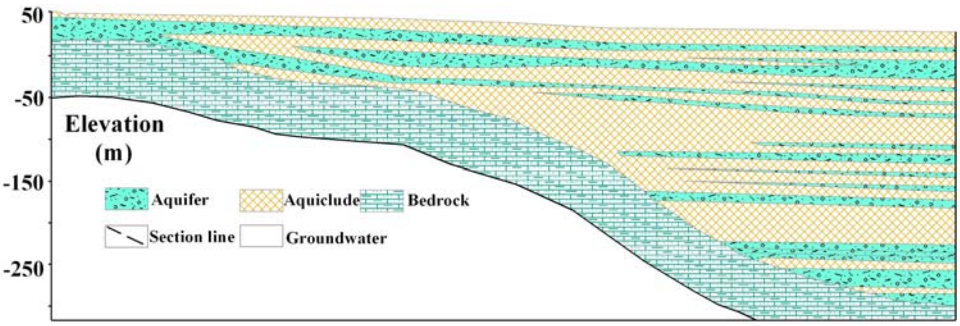

Figure 2. Zoning map of hydraulic hydrologic geology in study area.

2.2. Sampling and analysis

We performed the sampling since March of 2011 from total 34 sits include 11 surface water sits, 3 reclaimed water plants, and 30 groundwater sits (Figure 1). For the water plants and surface water sits, we sampled every 3~4 weeks. Many floodgates and artificial drainage/irrigation canals have been constructed in this region are used to store water in the non-irrigation season for groundwater recharging and sluice in the irrigation season. Therefore, the average of samples value in flood summer season (from June to September) was chosen for surface water chemical analysis. For the groundwater, we sampled 2 times each year along the river and main canals. The groundwater major elements chemistry analyzed based on the sampling in October of 2011. The monitoring well depth is 80 m under the land surface.

The water samples were collected and sent to the Institute of Geophysical and Geochemical Exploration (IGEE) of Chinese Academy of Geological Sciences (CAGS) for analysis. Electrical conductivity (EC) and pH were measured by using pH/ISE meter (005909) and EC/DDSJ-308A meter (610708070071). Other ions were determined by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS).

3. RESULTS

3.1. Major ions composition of surface water

The pH value varied from 7.5 at the inlet of Beiyechang irrigation canal (site 3-1) to 8.5 at Fengheying floodgates (site 3-3) with a mean value of 7.9 in the RWID and surface water characterized as slightly alkaline. The EC value varied from 828 us/cm at Majuqiao floodgates (site 2-4) to 1564us/cm at Shaobingzhuang floodgates (site 2-5) with a mean value 1112 us/cm. The total dissolved solids (TDS) represents the concentration of dissolved salt varied from 839mg/L at Yulinzhuang floodgates (site 1-1) to 1383mg/L at Shaobingzhuang floodgates (site 2-5) with mean value 992mg/L. Totally, the RWID surface water is characteristic with relative high pH value, EC, and salinity (Table 1). This is due to the fact that great deal of effluent from urban area into the surface rivers and irrigation canals.

Table 1. Statistical information of tested items of surface water samples in RWID (mg/L).

	Min	Max	Mean	Standard deviation	Coefficient of variation
pH	7.5	8.5	7.9	0.26	0.03
EC	828	1564	1112	247	0.22
Ca^{2+}	69.06	118.76	89.00	15.55	0.17
Mg^{2+}	36.23	62.76	52.82	7.52	0.14
Na^{+}	106.46	244.04	149.36	38.85	0.26
K^{+}	16.98	27.95	21.86	3.94	0.18
HCO_3^-	226.00	769.00	439.60	141.94	0.32
SO_4^{2-}	50.80	127.00	98.99	20.65	0.21
Cl^-	60.70	204.00	135.28	46.12	0.34
NO_3^-	0.44	11.20	5.54	3.70	0.67
TDS	839	1383	992	173.59	0.17

Sodium and Ca^{2+} are the most abundant cations with concentrations of 106.46-244.04mg/L and 69.06-118.76mg/L, respectively. Potassium is the least abundant major cation with average concentration of 16.98-27.95mg/L. Bicarbonate is the most abundant anion, and its concentration ranges from 226 to 769mg/L, and the values of Cl^-, the second most abundant anion, varied from 60.7 to 204mg/L, and values of SO_4^{2-} varied from 50.8 to 127mg/L, NO_3^- has a constant low concentration in the different water bodies of the RWID basin, and its average concentration varied from 0.44 to 11.2mg/L.

Sodium (the most abundant cation) and Ca^{2+} (the second abundant cation) contribute 41%-60% and 21%-34%, respectively, to major cations budget in the RWID surface water. Bicarbonate and Cl^- account for 42%-74% and 17%-23%, respectively, of total anions. Therefore, the water composition of the RWID is dominated by Na^+, Ca^{2+}, HCO_3^-, and Cl^-. Sodium and Ca^{2+} comprise 68%-81% of total cations, while the sum of HCO_3^- and Cl^- account for 75%-91% of total anions.

Relationships between ions, EC, and TDS were examined for all surface water sampling sites (Table 2). EC and TDS have significant positive correlations with most major ions exception with NO_3^-. There are also significant positive relationships between Na^+ and K^+, K^+ and SO_4^{2-}, Ca^{2+} and HCO_3^-, $Mg^{2+}$and Ca^{2+}, Ca^{2+} and HCO_3^-, and its shown that the correlated parent ions have similar sources. Totally, there are two sources of surface water ions which one is predominated by Na^+, Cl^-, and $SO_4^{2-}$and another one is Ca^{2+} and HCO_3^-.

Table 2. Pearson correlation matrix for surface water major ions, pH, EC, and TDS of RWID.

	pH	EC	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	TDS
pH	1										
EC	-0.01	1									
Ca^{2+}	-0.16	0.81**	1								
Mg^{2+}	0.14	0.70*	0.75*	1							
Na^+	0.36	0.43	0.20	0.23	1						
K^+	0.39	0.27	0.11	0.27	0.55	1					
HCO_3^-	-0.42	0.44	0.63	0.43	-0.16	-0.65*	1				
SO_4^{2-}	0.15	0.40	0.39	0.16	0.33	0.67*	-0.26	1			
Cl^-	0.57	0.60	0.52	0.55	0.24	0.37	0.10	0.65*	1		
NO_3^-	-0.43	-0.41	-0.18	-0.56	-0.54	-0.38	-0.01	-0.35	-0.59	1	
TDS	-0.11	0.77**	0.87**	0.67*	0.23	-0.20	0.84**	0.20	0.55	-0.35	1

* *Correlation is significant at the 0.05 level*
** *Correlation is significant at the 0.01 level*

3.2. Major ions composition of groundwater

For 30 samples of groundwater, sodium is the most abundant cations with mean value 179.93mg/L and maximum 449.15mg/L. Bicarbonate is the most abundant anions with mean value of 524.17 mg/L. The concentration of K^+ and NO_3^- characteristic with significant coefficient of variation (CV) with more than 1, but keep in relative low concentration with 2.02mg/L and 2.67mg/L, respectively, which have limited effects on water chemistry. The concentration of Na^+, Cl^-, SO_4^{2-} is extremely high and its CV value are more than 0.5, they predominated the groundwater chemistry. The water characteristic as slightly alkaline with mean pH value 7.52 and maximum is 8.0. The average TDS value is 883mg/L and minimum value is 373mg/L.

By comparison with the groundwater quality class Ⅲ of Chinese State Standards (CSS) (Table 3), most variables are under the maximum desirable limits of CSS standards. The pH values for all samples are under the desirable limits. The SO_4^{2-} concentration is 322mg/L at TZ01 over 29% of CSS standards. The Cl^- concentration is 291mg/L at TZ23 over 16% of CSS standards. The NO_3^- concentration is 31.3mg/L at DX05 over 56% of CSS standards. The TDS for 7 samples are over CSS standards with maximum 1439mg/L. It has been reported that high contents of SO_4^{2-} in drinking water could cause diarrhoea, dehydration or weight loss, and high NO_3^- concentrations could result in birth malformation, hypertension and high-Fe haemoglobin (Zhang et al. 2011b). These suggest that groundwater pollution constrained in a certain area and not suitable as drinking water sources, and water pollution control should be improved to stop the pollution extend.

Relationships between ions, pH, EC, and TDS were also examined for all 30 groundwater samples in 2011 (Table 4). Na^+ and Mg^{2+} have significant positive correlation with correlation coefficient of 0.51. Cl^- and SO_4^{2-}, Cl^- and HCO_3^- also have significant positive correlation with correlation coefficient of 0.46. Besides, the significant positive correlation also detected among HCO_3^- and Ca^{2+}, SO_4^{2-} and Mg^{2+}, Cl^- and Na^+. TDS has significant positive correlation with major ions except with K^+, and suggest that the water mineralization is synthetic controlled by multiple major ions. Therefore, the groundwater composition in the RWID is predominated by Na^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, and SO_4^{2-}. EC value has similar positive relationships as TDS, while pH has negative relationships with major ions.

Table 3. Statistical information of groundwater chemical characteristics and comparison with WHO(2006) and Chinese State Santdard (CSS) for drinking water (mg/L).

Parameters	Min	Max	Avg	CV	CSS	WHO (2006)	
						Max desirable	Max permissible
pH	7.10	8.00	7.52	0.02	6.5~8.5	7.0~8.5	6.2~9.5
EC	659	2110	1389	0.28	——	750	1500
Ca^{2+}	35.16	182.44	98.55	0.32	——	75	250
Mg^{2+}	12.05	160.76	87.65	0.42	——	30	150
Na^+	49.16	449.15	179.93	0.51	200	50	200
K^+	0.55	10.89	2.02	1.25	——	100	250
HCO_3^-	216.00	757.00	524.17	0.21	——	300	600
SO_4^{2-}	17.10	322.00	119.10	0.59	≤250	250	600
Cl^-	14.30	291.00	124.99	0.51	≤250	250	600
NO_3^-	0.25	31.30	2.67	2.51	≤50	250	600
TDS	373	1439	883	0.32	≤1000	600	1000

Table 4. Correlation matrix for groundwater major ions, pH, EC, and TDS of RWID.

	pH	EC	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	TDS
pH	1										
EC	0.51**	1.00									
Ca^{2+}	-0.68**	0.48**	1.00								
Mg^{2+}	-0.454*	0.78**	0.36	1.00							
Na^+	-0.10	0.75**	-0.01	0.51**	1.00						
K^+	-0.12	-0.01	0.28	-0.24	-0.03	1.00					
HCO_3^-	-0.56**	0.70**	0.41*	0.67**	0.47**	0.11	1.00				
SO_4^{2-}	-0.22	0.68**	0.32	0.65**	0.57**	-0.15	0.28	1.00			
Cl^-	-0.12	0.74**	0.12	0.39*	0.79**	0.07	0.46*	0.46*	1.00		
NO_3^-	-0.51*	0.265	0.58**	0.22	-0.13	0.04	0.03	0.16	-0.28	1.00	
TDS	-0.53**	0.95**	0.58**	0.80**	0.70*	-0.07	0.64**	0.78**	0.62**	0.39*	1.00

* *Correlation is significant at the 0.05level*
** *Correlation is significant at the 0.01 level*

4. DISCUSSION

4.1. Water quality assessment and major ions origin

The mean value of surface water TDS in RWID is higher than the Yellow River with 205.9mg/L, the Yangtze River with 486mg/L, and other world rivers with mean value of 65mg/L (Zhang et al. 2011b). In order to shown the effects of discharged wastewater into water streams, we also compared the major-ions concentration with Chaobai River and Wenyu River based on the report of Fan et al. (2010). The Chaobai River located in northern mountainous area of Beijing and Hebei province. The river consists of two tributaries, the Chao River and the Bai River, and their confluence is at the Miyun Reservoir the main water source of Beijing (Wang et al. 2009). The predominated anthropogenic activities are agricultural cultivation with much less effluent than the down municipal area of Beijing. In that case, the major ions concentration of the Chaobai River represents the scenario of low intensity of human activity intensity and seldom effluent in the mountainous area. The average TDS concentration of Chaobai stream water (avg.=281mg/L) is lowest in Beijing area. Wenyu River is the upper basin of Beiyun River receives the effluent from Changping, Shungyi, and Chaoyang district of Beijing. The Wenyu River main channel has moderate TDS value (avg.=546.5mg/L) of Beijing area. As Figure 3 shown that the significantly increase ions are Na^+ among cations and SO_4^{2-} among anions as the effluent increase from urban area. Concluded, the relative high concentration of Na^+ and SO_4^{2-} is caused by the great deal of effluent in the RWID water streams, while the high concentration of Ca^{2+} and HCO_3^- is due to soil and mineral erosion as land surface rainfall-runoff processes.

The Chinese water standards for irrigation water quality suggested permitted limited value with pH between 5.5~8.5, Cl^- concentration under 350mg/L, and TDS concentration under 1000mg/L for saline soil and 2000mg/L for non-saline soil. By comparison with samples value in Table 1, the surface water is suitable for utilization as irrigation water sources. The surface water throughout the study area also under the Chinese water standard for centralized drinking water source with SO_4^{2-} under 250mg/L, Cl^- under 250mg/L, and NO_3^- under 10mg/L.

It is well known that weathering of different parent rocks (e.g., carbonates, silicates and evaporites) yields different combinations of dissolved cations and anions (Garrels and Mackenzie, 1971; Zhang et al. 2011b). For instance, Na^+ and K^+ are supplied by the weathering of evaporites and silicates, Ca^{2+} and Mg^{2+} are supplied by the weathering of carbonates, silicates and evaporites, HCO_3^- by carbonates and silicates, SO_4^{2-} and Cl^- by evaporites. To explore the relative importance of different weathering regimes, ternary plots of cations (Ca-Na+K-Mg) as well as anions (HCO_3^--Cl^--SO_4^{2-}) were constructed (Figure 3). The sites fall in the cluster towards the $Na^+ + K^+$ apex and HCO_3^- apex, indicating that the RWID stream water is dominated by the weathering of evaporates in nature condition.

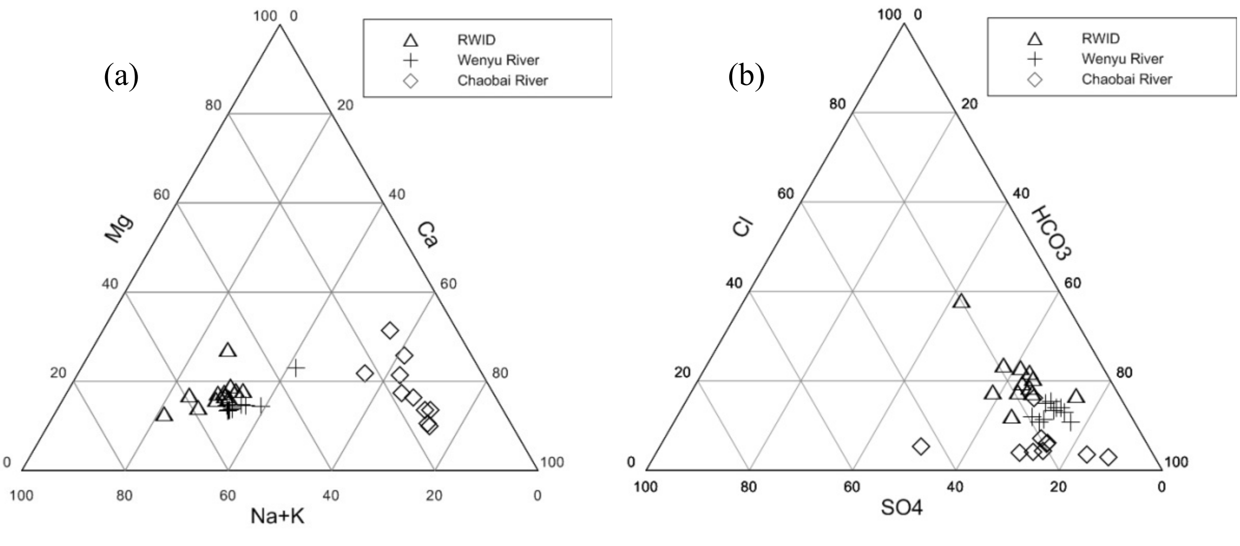

Figure 3. Trilinear diagram of ion chemistry for water samples of the RWID, the Wenyu River, and the Chaobai River.

Average NO_3^- concentration is 5.54mg/L, which is less than the mean value of 3 wastewater treated water plant with mean value 10.6mg/L and the Chaobai River of 15.7mg/L. This is due the fact that the NO_3^- is more suitable for organic oxidation than SO_4^{2-}under anaerobic condition, which can decrease the concentration of NO_3^- and increase the concentration of HCO_3^- (Li et al. 2010). As result, the surface water classified as Na^+-HCO_3^--SO_4^{2-} type. It is also leads to less NO_3^- concentration for surface water samples than discharged reclaimed water from wastewater treated plant, and also less than Chaobai River samples. As the Table 2 shown, the NO_3^- is characteristics as negative correlations with other major ions.

For the groundwater genesis coefficient Na^+/Cl^- mainly reflects the enrichment degree of sodium. Faye et al. (2005) suggested that ratio of dissolved species versus chloride concentrations to explain the possibility of mixing between waters composition determined by water–rock interactions and saline surface water. For sea water the average Na^+/Cl^- ratio is around 0.86, and for light mineralization water with Na^+/Cl^- ratio is higher than 0.86, while for high mineralization water with Na^+/Cl^- ratio less than 0.86 (Faye et al. 2005). Most sites of RWID fall over the isometric line of Na^+/Cl^-, indicating that the effluent increases the Na^+ concentration and the groundwater is characteristic as high mineralization (Figure 4a). However, the coefficient of Na^+/Cl^- is decreases as the TDS value increase shown in Figure 4b, indicating that the Na^+ replaces gradually Ca^{2+} and Mg^{2+} absorpted in the exchange clay mineral surface. The Na^+ concentration decreases and Cl^- concentration increases caused calcium carbonate precipitate and also enrich Cl^- and decrease the coefficient of Na^+/Cl^-.

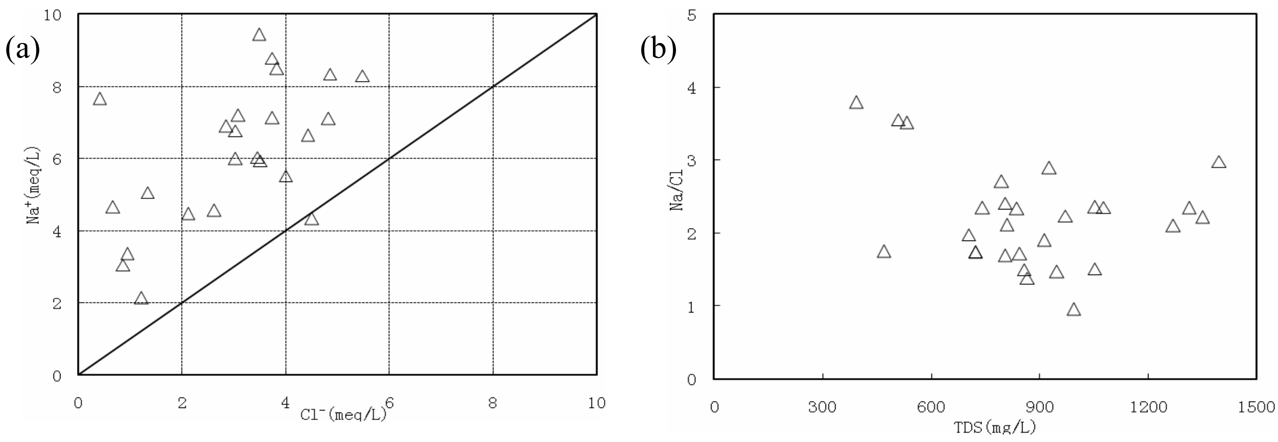

Figure 4. The molar ratio coefficient of Na^+/Cl^- and Na^+/Cl^- versus total dissolved solids (TDS) of ground water samples in the RWID.

4.2. Mechanisms controlling the surface water ions chemistry of the RWID

4.2.1. Weathering

Gibbs (1970) suggested that a simple plot of TDS versus the weight ratio of $Na^+/(Na^++Ca^{2+})$ or $Cl^-/(Cl^-+HCO_3^-)$ could provide information on the relative importance of the three major-natural mechanism controlling surface water chemistry, which include atmospheric precipitation, evaporation and fractional crystallization, and rock weathering (Zhang et al. 2011b). TDS concentration less than 10 mg/L coupled with relative high weight ratio of $Cl^-/(Cl^-+HCO_3^-)$ and $Na^+/(Na^++Ca^{2+})$ more than 1, suggesting atmospheric precipitation is the dominate mechanism. TDS concentration between 70~300 mg/L coupled with weight ratio of $Cl^-/(Cl^-+HCO_3^-)$ and $Na^+/(Na^++Ca^{2+})$ less than 0.5, suggesting rock weathering is the dominate mechanism. TDS concentration more than 300 mg/L coupled with extremely high weight ratio of $Cl^-/(Cl^-+HCO_3^-)$ and $Na^+/(Na^++Ca^{2+})$, suggesting evaporation and fractional crystallization is the dominate mechanism (Gibbs, 1970; Chen et al. 2005).

TDS concentrations versus weight ratio of $Cl^-/(Cl^-+HCO_3^-)$ or $Na^+/(Na^++Ca^{2+})$ for RWID, Chaobai River, Wenyu River simples have been plotted together (Figure 5). TDS of Chaobai River varied from 237~402mg/L and the ratio of $Cl^-/(Cl^-+HCO_3^-)$ and $Na^+/(Na^++Ca^{2+})$ less than 20%, suggesting that the basin is typically controlled by rock weathering processes. Wenyu River characterized with relative high TDS from 309~612mg/L and the ratio of $Na^+/(Na^++Ca^{2+})$ and $Cl^-/(Cl^-+HCO_3^-)$ is 42~56% and 12.2~19.5%, respectively. The Wenyu basin is dominated by both rock weathering and evaporation and fractional crystallization processes. For the RWID, TDS varied from 800 to 1400mg/L and the ratio $Na^+/(Na^++Ca^{2+})$ and $Cl^-/(Cl^-+HCO_3^-)$ is between 56~74% and 10.9~47.4%, respectively. The dominated natural mechanism is evaporation processed. Plus, the RWID located in downstream plain of the Beingyun River watershed, where the land surface evaporation capacity is higher than the mountainous area. The extremely high Na^+ concentration reflects the effect of effluent from urban area.

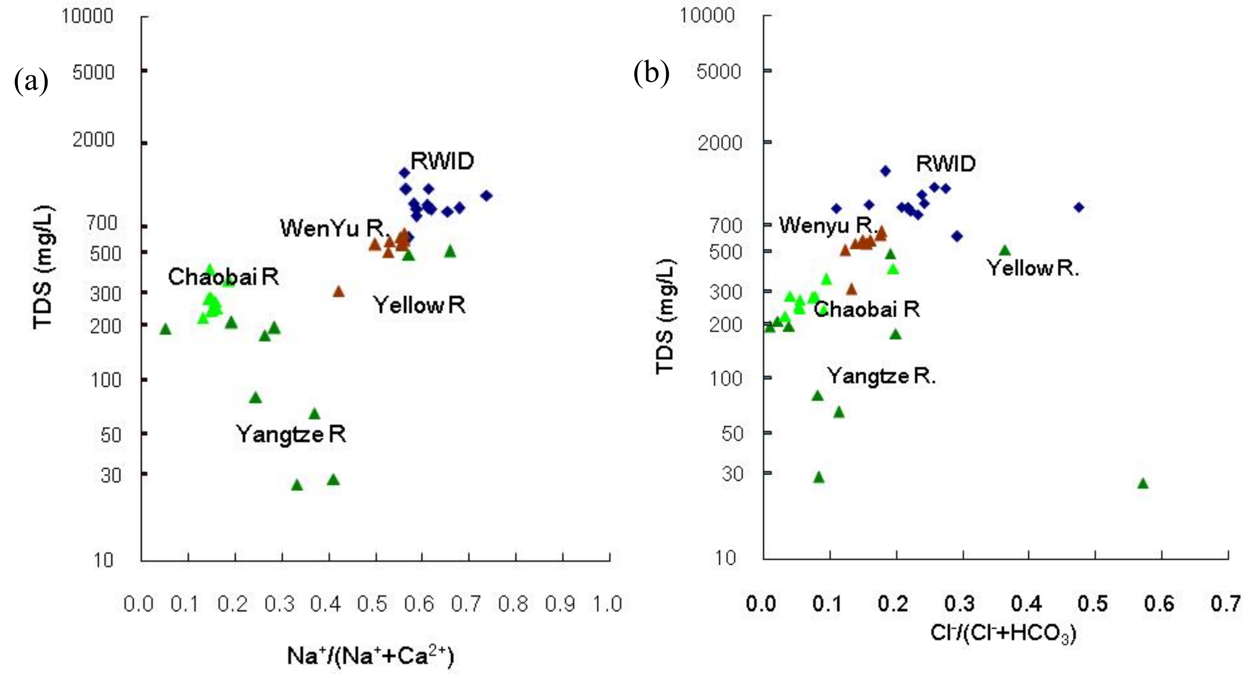

Figure 5. Gibbs map of stream water samples in the RWID and other rivers from literature in China.

4.2.2. Salt circulation

The urbanization and agricultural cultivation accelerate the natural processes of surface water quality degrade, and the surface water quality controlled by both point and non-point pollution. The major ions concentration for RWID is higher than Chaobai River, Yangtze River, Yellow River, and other world rivers. Stream water was characteristic as extremely high salt water. Naturally, Cl^- is a conservative element and the stream flow salt come from sea salt through sea evaporation, land precipitation, and runoff generation in the land surface.

The average residence time of sea salt in the atmosphere is about 3 days (Junge. 1972). As a result, the contribution of cyclic salts to riverine dissolved salt loads is expected to decrease with increasing the distance from the sea (Zhang et al. 2011b). The Chaobai River, Wenyu River, and Beiyun River located in similar longitude. However, The average Cl^- concentration is 12.36mg/L, 53.79mg/L, 135mg/L for Chaobai River, Wenyu River (Fan et al. 2010), and the RWID, respectively. Conclusively, the Cl^- concentration in the RWID shows obvious higher amounts than Chaobai River and Wenyu River. Based on the Cl^- balance with $\frac{Q_u}{Q_v} = \frac{C_v - C_t}{C_t - C_u}$, in which Q is amount of flow, C is concentration of Cl^-, t is water body after mixing, u is water source one, and v is water source two. We evaluated the runoff originates from rainfall runoff accounts for the total streamflow of the Chaobai River, Wenyu River, RWID comprise 78.35%, 9.58%, and 3.67%, respectively. As Figure 6 shown, the molar concentration ratio of Cl^- versus Na^+ for RWID, Chaobai River, and Wenyu River has been plotted together. Samples for Chaobai River and Wenyu River is around the the isometric line of Cl^-/Na^+, while RWID samples significantly fall over the isometric line of Cl^-/Na^+.

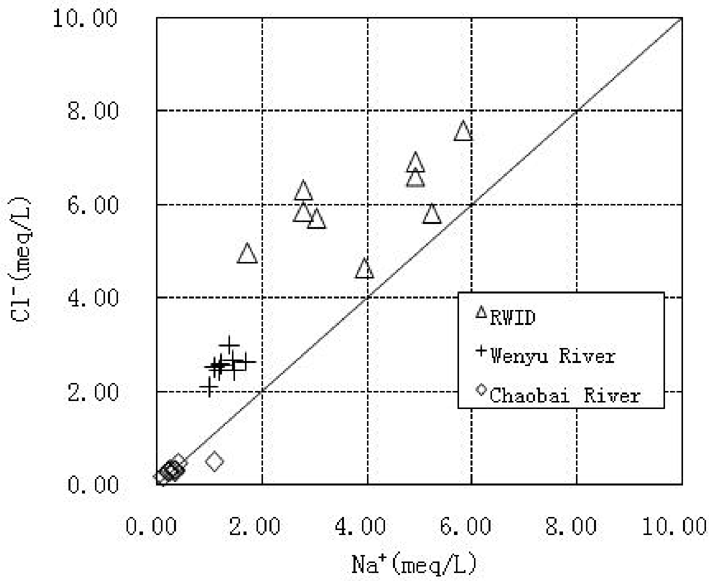

Figure 6. The molar concentration ratio of Cl^- versus Na^+ of stream water samples in the RWID, the Wenyu River, and the Chaobai River.

4.3. Spatial and temporal Distribution of surface major ions chemistry

The distribution of major ions is multiple influenced by natural processes and anthropogenic activity. There is less ions concentration in the main channel of Beiyun River and Feng River. Beiyun River is the only river never runs dry in Beijing area, and its TDS concentration is 547mg/L samples at Beiguan floodgates the junction point between Wenyu River and Beiyun main channel (Fan et al., 2010). The samples shown that in the middle point of Beiyun main channel i,e., the Yulinzhuang floodgate (sits 1-1) with TDS 839mg/L increase 53% higher than Beiguan floodgate due to the discharge of reclaimed water along the channel. For the Feng River, the reclaimed water originates from Nanhongmen wastewater treated plant and used for irrigation and ecological, and there are not great inflow of wastewater along the river channel maintain the major-ions concentration in a relative low level than other rivers. The Major-ions concentration at sites of Liangshui River, Xinfeng River, and Long River were relative high.

For the groundwater, the southern water has a lower concentration of TDS (Figure 7). This coincides with the southern irrigation canals are seasonal drying in the non-irrigation season and limited recharge groundwater aquifers. In contrast, the northern water has high concentrations of ions. This results mainly from the infiltration of surface reclaimed water. Furthermore, along the river channels the groundwater TDS concentration keeps in relative high level.

For temporal variation, the TDS concentrations in the agricultural areas exhibited gradual seasonal changes (Figure 8). In the rainy season, the TDS concentration was significantly lower than dry season. None of the regional average value of surface samples over the 1000mg/L. Other chemical ions showed a similar pattern of seasonal change in the agricultural area.

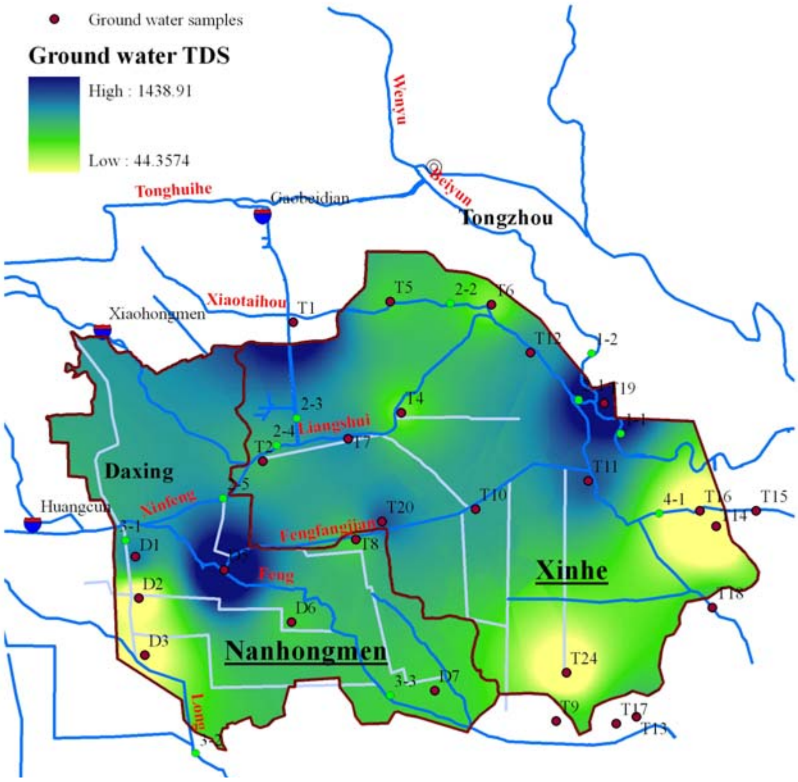

Figure 7. Spatial variation of groundwater TDS (mg/L) in the RWID.

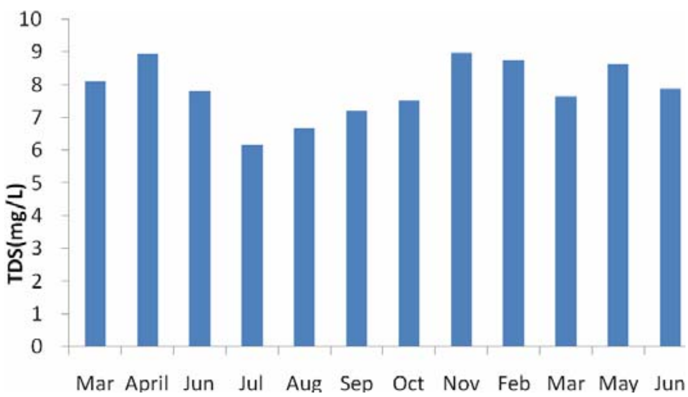

Figure 8. Seasonal changes of the stream water TDS(mg/L) in the RWID.

4.4 Groundwater pollution risk

The average major ions concentration ratio of groundwater to surface water is shown in Table 5. The pH decreases slightly while EC increases 25% as the surface water infiltrated through the soil profile. Among the cations, the average Ca^{2+}, Mg^{2+}, and Na^{+} concentration increase, while K^{+} decreases 90%. This is due the fact the K^{+} has a relative higher adsorptive affinity than Na^{+} and tends to exchange with Ca^{2+}, Mg^{2+} of clay minerals. As the increase of sodium absorption ratio (SAR) and infiltration depth, Ca^{2+}, Mg^{2+} was adopted by clay mineral and Na^{+} was released to leaching water. Ca^{2+} is much more tends to exchange adsorption than Mg^{2+}. As a result, Mg^{2+} is the most increasing cation and followed by Na^{+}, while average Ca^{2+} concentration kept in a relative stable level between ground and surface water. This result also been supported by soil column leaching experiments by Wu (2009).

Among the anions, average HCO_3^- and SO_4^{2-} concentration increased, while Cl^- and NO_3^- decreased. The atmospheric soluble CO_2 is the most important source for groundwater carbonic acid as the stream water infiltration. The composition of carbonic acid i.e., relative percentage of among HCO_3^-, CO_3^{2-}, and H_2CO_3 in groundwater is significantly affected by the pH value. The pH value is 7.52 characteristic as slightly alkaline leads to the HCO_3^- is the predominant components of carbonic acid in groundwater. The average SO_4^{2-} concentration in groundwater is 20% higher than stream water, indicating that the sub-sulfide was oxidized to high valence as the stream water infiltration.

As the Cl^- and NO_3^- are the most important external input indicative and conservative chemical pollution ions of groundwater (Yin et al., 2012). The Cl^- is a relative stable isotopic and its ratio of groundwater to surface water concentration is 0.92, indicating that the stream reclaimed water has been infiltrated to deep saturate layer and the concentration decreased as the groundwater table decreasing (Wu, 2009). The average concentration of Cl^- is 124.99mg/L closed to the groundwater background value of 128.8mg/L. For the average NO_3^- concentration, the ratio of groundwater to surface water is 0.48. This is due to denitrification happens as the stream reclaimed water go through unsaturated aquifer layer. The local sand-layer soil with coarse and fine minerals tends accelerate the denitrification processes to decrease the nitrogen concentration and reduce the nitrogen pollution risk (Hooda et al. 2003, Wu et al. 2009; Zou et al. 2002).

Totally, the average TDS concentration in groundwater is 882mg/L range of 373-1439mg/L decrease with 11% of stream water with 993mg/L range of 839-1383mg/L. After soil profile leaching, slightly decrease in groundwater TDS indicating that low probability of groundwater salt pollution. However, there is great uncertainty of different ions chemical variation as the stream reclaimed water infiltration and need further study. Totally, based on the major ions composition variation analysis, there is limited risk of groundwater pollution in RWID.

Table 5. The ratio of water chemical compositions of groundwater to surface water (C_G/C_S)

	pH	EC	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	TDS
C_G/C_S	0.96	1.25	1.11	1.66	1.20	0.09	1.19	1.20	0.92	0.48	0.89

5. SUMMARY

For the RWID, the surface water is predominant composited by Na^+, Ca^{2+}, SO_4^{2-}, and HCO_3^-, and characteristic with relative high pH, EC, mineralization, salt concentration. Great deal of reclaimed water discharged in the RWID caused increasing of Na^+ and SO_4^{2-} significantely compared with other rivers. Among the natural processes, carbonate minerals erosion caused a relative high Ca^{2+} and HCO_3^- concentration in stream water. The evaporation and crystallization processes are predominate weathering mechanism for water major ions chemistry variation. The water salt is mainly contributed by the effluent from urban area.

In the RWID groundwater, water pollution is constrained in a certain area and not suitable as drinking water sources, and water pollution control should be improved to stop the pollution extend. Most groundwater samples are under the CSS permitted maximum limits. Complex ions exchange processes happened during the stream reclaimed water infiltration. Groundwater mineralization is dominated by the synthetic effects of Na^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^- and SO_4^{2-}.

The groundwater of RWID is recharged by surface stream water and irrigation recovery water. The local sand-layer soil with coarse and fine minerals filtrate the pollutants and decrease the probability of pollution risk. There are complicated ions exchange among Ca^{2+}, Mg^{2+}, Na^+, and K^+, and the TDS decrease 11% after the leaching processes. Otherwise, the unsaturated aquifer layer tends accelerate the denitrification processes to decrease the nitrogen concentration and reduce the nitrogen pollution risk.

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