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Contamination patterns in river water from rural Beijing: A hydrochemical and multiple stable isotope study

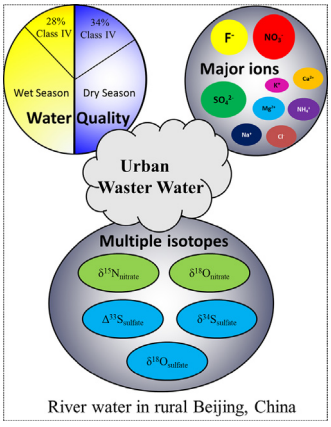
Marc Peters [a], Qingjun Guo [a,b,*], Harald Strauss [c], Rongfei Wei [a], Siliang Li [d], Fujun Yue [e]

[a] Center for Environmental Remediation, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101, China
[b] College of Resources and Environment, University of Chinese Academy of Sciences, Beijing 100190, China
[c] Westfälische Wilhelms-Universität Münster, Institut für Geologie und Paläontologie, Corrensstr. 24, 48149 Münster, Germany
[d] Institute of Surface-Earth System Science, Tianjin University, Tianjin 300072, China
[e] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

HIGHLIGHTS

- Rural Beijing river water is hazardous for human health and the aquatic ecology.
- Higher contribution of urban effluents to the downstream rivers in the rural south.
- Urban wastewater is the prime anthropogenic pollution source.
- High fluoride concentrations have a largely natural source.

GRAPHICAL ABSTRACT



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ABSTRACT

The pollution of urban river has reached a critical level. In the present study, the hydrochemical composition of local surface water collected during two seasons from the rural area around urban Beijing, China, was examined. Concentrations of selected cations and anions reveal the temporal and spatial distribution of anthropogenic and natural pollution. Multiple stable isotopes ($\delta^{15}N_{nitrate}$, $\delta^{18}O_{nitrate}$, $\delta^{34}S_{sulfate}$, $\delta^{18}O_{sulfate}$, $\Delta^{33}S_{sulfate}$) analyses were applied for detecting of specific hydrochemical processes and identifying the major sources of contamination.

Twenty-eight percent of the river water samples from the wet season and 34% from the dry season exhibit a minor water quality of class IV (poor) and below due to high pH values as well as high nitrate, sulfate and fluoride concentrations. This water is hazardous for human health and the aquatic ecology. The seemingly better river water quality in the wet season is caused by higher precipitation and, hence, dilution of the water constituents. Multiple isotopes identify urban wastewater as the prime pollution source. The higher fraction of deteriorated river water in the southern rural area (42%) compared to the north (24%) points to a higher contribution of urban effluents to the downstream rivers in the rural south. It can, thus, be concluded that less discharge of wastewater to the local surface and subsurface environments by better controls of public and private sewage disposal combined with the renewal of leaking sewer pipes would reduce the risk of anthropogenic contamination of river water.

* Corresponding author at: Center for Environmental Remediation, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101, China.
E-mail address: guoqj@igsnrr.ac.cn (Q. Guo).

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1. Introduction

Due to the rapid economic growth in China in the last 30 years, Beijing became one of the largest cities in East Asia with nearly 20 million residents (BSY, 2017). One consequence of this fast development is the precarious situation of surface water in the Beijing urban area caused by an irresponsible handling of the vital water reservoirs in this region. Discharge of private and industrial wastewater into the environment led to a significant decline of the local surface water quality with the result that tap water does not fulfill the requirements for drinking water in many parts of the Beijing urban area (He et al., 2011; Zhou et al., 2012; He et al., 2014; Peters et al., 2015; Zhang et al., 2017). Moreover, the pollution of certain river sections in urban Beijing has reached a critical level.

Around 60% of Beijing's total population lives in the suburbs as well as in towns and villages in the rural part of the Beijing municipality (BSY, 2017). High amounts of respective human emissions represent a risk for the environment and the health of the local population. In addition, the rural area around the fast growing urban sprawl of Beijing is a place of high agricultural activities with intense vegetable and fruit farming. Due to the application of fertilizer and pesticides as well as the production of manure by cattle farming, agriculture is one of the main factors for the distribution of anthropogenic pollutants to the surface water (Widory et al., 2004). Few recent studies have addressed the environmental consequences of farming activities in Beijing centering on nitrate (Su et al., 2017; Wu et al., 2018), pesticides (Wang et al., 2018; Yu et al., 2014), antibiotics (Xu et al., 2016) or heavy metals (Wu et al., 2010).

Stable isotope analyses could be applied to detect the source of specific pollutants and of the investigated water. In the previous studies, the stable isotopes have been successfully used to trace the sources and transformations of compounds in various ecosystems (Bottcher et al., 1990; Robinson and Bottrell, 1997; Balci et al., 2007; Brenot et al., 2007; Spoelstra et al., 2007; Choi et al., 2011; Lin et al., 2017; Cao et al., 2018). For example, $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ have been applied to understand the sources of nitrate pollution and denitrification processes that may take place in aquifers (Kendall, 1998, Cook and Herczeg, 2000, Nikolenko et al., 2018). $\delta^{34}S_{sulfate}$ and $\delta^{18}O_{sulfate}$ have been used to elucidate the pollution sources of dissolved sulfate (Robinson and Bottrell, 1997; Torssander et al., 2006; Otero et al., 2008; Hosono et al., 2010; Cao et al., 2018). The studies of sulfate isotopes are usually focused on the ^{32}S and ^{34}S. However, relatively little research addressing environmental issues has included the rare sulfur isotope ^{33}S and ^{36}S due to the limit of analytical technique (Hulston and Thode, 1965a, Peters et al., 2010, Han et al., 2017).

In this study, we carried out a more comprehensive hydrochemical and multiple isotope investigation focusing on diverse inorganic constituents dissolved in the river water of the Beijing countryside. The concentrations of selected pollutants allow determining the degree of contamination for the respective water in comparison to threshold values indicated in the national guideline for surface water in China (GB 3838-2002). This, in turn, allows assessing the local river water quality according to the Chinese classification system. In addition, multiple stable isotope ($\delta^{15}N_{nitrate}$, $\delta^{18}O_{nitrate}$, $\delta^{34}S_{sulfate}$, $\delta^{18}O_{sulfate}$, $\Delta^{33}S_{sulfate}$) analyses were applied for identifying the specific hydrochemical processes and major contamination sources. The overall aim of the present study is to identify the consequences of the different human activities in the rural area around Beijing city. Thereby, the distribution of contaminants in space and time were of special interest. In particular, distinguishing the river water from the northern countryside upstream of the urban center, from the southern countryside downstream of urban center, the impact of the urban effluents on the surface water quality becomes apparent. Moreover, sampling during dry and wet seasons allows to scale the seasonal effect of precipitation on the degree of contamination. Altogether, the results from this investigation could represent the base for a better water management on the Beijing countryside as well as for future measures in order to protect the rural water ecology and the health of the local residents.

2. Materials and methods

2.1. Study area

Beijing is located on the Beijing Plain, which is situated in the northwest of the larger North China Plain (NCP). The Beijing Plain is bordered by the Taihang Mountains in the west and by the Yanshan Mountain Range in the north and northeast. The Bohai Bay as part of the East China Sea is around 150 km from Beijing in southeasterly direction. The Beijing region exhibits a continental semiarid climate with an annual mean temperature of around 13 °C (Aji et al., 2008). The average precipitation is ~600 mm/year, and around 80% of this precipitation occurs during the summer monsoon between June and September. Due to the variation in precipitation the seasons in Beijing can be separated into a wet season (April–October) and a dry season (November–March).

The bed rock of the Beijing Plain and the surrounding mountain ranges is characterized by Archean gneisses and Proterozoic carbonates (Chen et al., 2003). Overlying Cenozoic deposits comprises thick Tertiary and Quaternary sediments. The thickness of these deposits increases from tens of meters to 500 m from the mountain area to the sea (Zhou et al., 2012). Within the Quaternary sedimentary deposits four aquifers are differentiated based on their distinct lithological properties and hydrodynamic conditions. The aquifers grade from a single sand-pebble-gravel aquifer at the top of the piedmont alluvio-pluvial fan in the north and west to a 3–4 layered aquifer of sand-pebble-gravel and sand in the lowland area in the south and east separated by aquitards consisting of silt and clay layers. The shallow aquifer (<50 m depth) is unconfined, whereas the deep aquifers (>50 m) are confined (Aji et al., 2008). The recharge of the deep aquifers is mainly caused by leakage from the shallow aquifer. The general direction of the river water flow on the Beijing Plain is from northwest to southeast.

Five larger and around 200 smaller rivers cross the Beijing municipality. The five main river catchments in this area are: Yongding River and Juma River in the west, Chaobai River and Beiyun River in the east as well as Jiyun River in the northeast. Many of the rivers in Beijing originate in neighboring regions, such as Hebei province, Shanxi province or Inner Mongolia Autonomous Region. These rivers are part of the much larger Hai River basin, which drains into the Bohai Sea. In the past the two major rivers Yongding River and Chaobai River, dammed by the Guanting Reservoir in the west and the Miyun Reservoir in the northeast of Beijing, accounted for 90% of the total surface water inflow to the Beijing Plain. However, due to water shortage in the Beijing area the river discharge of today is only 10% of the one in the 1950's (Zhou et al., 2012).

Wang et al. (2015) showed a clear seasonality of streamflow in the Beijing municipality throughout the year related to the variation of precipitation in the wet and dry season. During the average wet season (summer, fall), streamflow can be >10 times higher than during the average dry season (winter, spring), revealing the substantial impact of rainfall on the river water discharge as well as hydrochemical composition. Although the magnitude of seasonal variation decreased in the past 50 years possibly due to human activities and climate change, an apparent difference between wet and dry season streamflow still exists leading to lower river water levels or completely dried out rivers in the dry season compared to the wet season. In 2011 rivers north of the Beijing urban area still exhibited an up to 3 times higher average streamflow in the wet season compared to the dry season (Wang et al., 2015).

Human activities are primarily focused on the center part, southeast and east of the Beijing municipality, which are characterized by the urban agglomeration as well as the surrounding farming area with numerous smaller towns and villages. Consequently, next to the urban

region, the Beijing rural area is a source of pollutants to the environment, due to agriculture and suburban life.

2.2. Sampling

Water samples were collected from rivers and canals in the rural parts of the Beijing municipality in all five catchment areas (Fig. 1). Sampling was conducted in June and July 2013 (wet season) as well as in March 2014 (dry season). In total 43 river water samples were collected in the wet season and 38 river water samples in the dry season.

River water was sampled from the center part of each stream from road or pedestrian bridges. Samples were collected using a PE bucket (5 L), which was rinsed with the local sample water one time prior to sampling at each site. 1.5 L of the sampled water was filled in a PET (polyethylene tetraphthalate) bottle, which was also rinsed several times with the sample water. This fraction of the sample was prepared later in lab for analyses of nitrogen, oxygen and sulfur isotopes of dissolved nitrate and sulfate. Two 15 mL subsamples of each sample were filtered using 0.45 μm pore-size syringe tip filters (cellulose acetate) and collected in HDPE (high-density polyethylene) tubes for concentration measurements of selected anions and cations. Before sampling the tubes for analyses on major cations, metals and trace elements were cleaned with a 10% HNO_3 solution and filled with three drops of ultrapure HNO_3 (65%) in order to acidify the subsamples to a pH < 2. Another 50 mL subsample was taken for determining the dissolved inorganic carbon (DIC) concentration and treated with some drops of a saturated $HgCl_2$ solution after filled into the sample flask in order to terminate microbial activity. All subsamples were stored dark and cool immediately after sampling until further preparation in lab. On-site measurements of temperature, pH, redox potential (Eh) and electric conductivity (EC) were carried out during sampling using the electrode kit SX731 (Sanxin®). In addition to the river water samples, 3 rain water samples were collected on the building roof of the Institute of Geographic Sciences and Natural Resources Research (IGSNRR), Chinese Academy of Sciences (CAS) in Beijing, China, in order to quantify the concentrations of selected inorganic constituents. Sampling was carried out as mentioned above for the river water samples.

2.3. Analytical methods

Concentration measurements for cations (Ca^{2+}, K^+, Mg^{2+}, Na^+, NH_4^+) and anions (Cl^-, NO_3^-, SO_4^{2-}, F^-, DIC) were carried out in the laboratories of the IGSNRR, CAS in Beijing. Cation concentrations were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) with an analytical precision of ±1.5% on average. Anions and ammonia were analyzed by gas chromatography using an AMS Smartchem 300®. Analytical precision was better than ±5%. DIC was calculated based on the consumption of 0.1 N HCl during titration to pH 4.3. The 1.5 L subsample was filtered by 0.45 μm pore-size cellulose acetate filter and 50 mL were treated with 2 mL of KOH solution in order to raise the pH to ~12 for later nitrogen and oxygen isotope analyses on dissolved nitrate using the bacterial denitrifyer method (Sigman et al., 2001). For the $\delta^{34}S$ and $\delta^{18}O$ analyses, the dissolved sulfate was precipitated as $BaSO_4$ from the remaining part of the filtered water sample using the standard $BaCl_2$ precipitation method (Dogramaci et al., 2001). For multiple sulfur isotope measurements ($\delta^{33}S$, $\delta^{34}S$, $\Delta^{33}S$), $BaSO_4$ precipitates were converted to Ag_2S following the Thode extraction method (Thode et al., 1961).

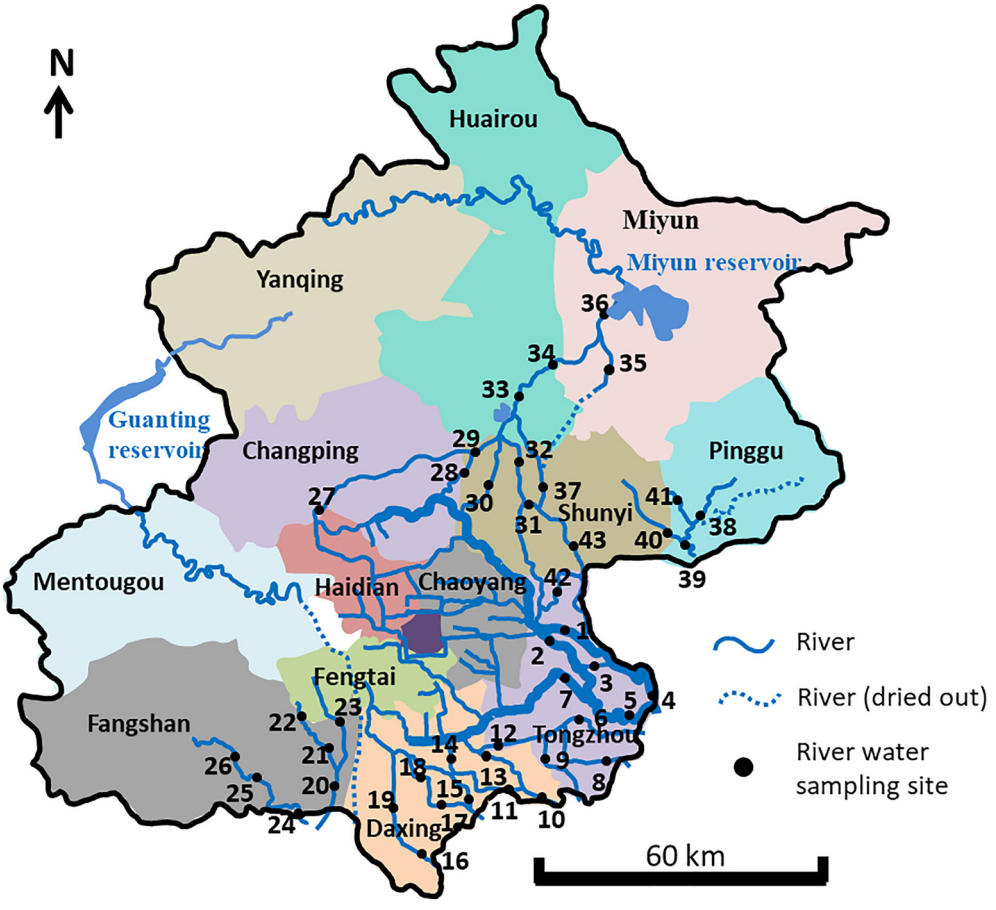

Fig. 1. Map of the Beijing municipality with the river water sampling sites.

Stable isotope ratios are reported in permil (‰) using the conventional delta notation:

$$\delta_{sample}\ (‰) = \left[\left(R_{sample} - R_{standard}\right)/R_{standard}\right] \times 1000 \quad (2.1)$$

where R represents the $^{15}N/^{14}N$, $^{18}O/^{16}O$ or $^{34}S/^{32}S$ of the sample and the standard, respectively. N and O isotope measurements were performed using an isotope ratio mass spectrometer (IRMS, Isoprime, UK) in the State Key Laboratory of Environmental Geochemistry at the Institute of Geochemistry (CAS) in Guiyang, China. O isotope ratios of sulfate were determined in the same laboratory by elemental analyzer-isotope ratio mass spectrometry (EA-IRMS, Isoprime, UK). The analytical precision of the $\delta^{15}N$ and $\delta^{18}O$ values was generally better than ±0.2‰ and ±0.3‰, respectively. Measurements solely for $\delta^{34}S$ were conducted using a ThermoFinnigan Mat Detal Plus isotope ratio mass spectrometer coupled to an elemental analyzer (EA-IRMS) at the Institut für Geologie and Paläontologie, Westfälische Wilhelms-Universität Münster, Germany. The reproducibility was better than ±0.3‰. Multiple sulfur isotope measurements were carried out in the same lab using a ThermoFinnigan Mat 253 isotope ratio mass spectrometer (IRMS). For this, Ag_2S samples were converted to SF_6 via fluorination in nickel tubes (Ono et al., 2006). The cryogenically and chromatographically purified SF_6 was introduced into the mass spectrometer via a dual inlet system and the ^{32}S, ^{33}S and ^{34}S isotopes were measured simultaneously. $\Delta^{33}S$ values were calculated using the $\delta^{33}S$ and $\delta^{34}S$ values (Hulston and Thode, 1965b; Farquhar et al., 2000) as:

$$\Delta^{33}S\ (‰) = \delta^{33}S - 1000 \times \left[\left(1 + \delta^{34}S/1000\right)^{0.515} - 1\right] \quad (2.2)$$

Analytical precision for $\Delta^{33}S$ (i.e. including fluorination) was better than ±0.008‰ (1σ).

The river water was categorized according to the classification system of the national guideline for surface water (GB 3838-2002) by single factor assessment. The quality grade of the water sample was determined by the highest concentration or value of the measured parameters.

3. Results and discussion

3.1. Physico-chemical parameters in the river water

The river water samples from the Beijing rural area show variable pH values in both seasons ranging from 7.14 to 9.98 in the wet season and from 6.83 to 9.28 in the dry season (Table 1). The median values for both seasons are 7.96 and 8.10, respectively. Six samples in the wet season and three samples in the dry season exceed the required pH range from 6 to 9 according to the Chinese surface water guideline (GB 3838-2002). This water cannot be classified into one of the five categories of the Chinese classification system and is not even appropriate to be used for agriculture or landscaping. Also the variation in the redox-potential (Eh) of the analyzed river water is relatively large with values between −182 and 117 mV in the wet season and between −83 and 140 mV in the dry season ranging from anoxic to oxic conditions. The majority of samples can be classified as suboxic considering the median Eh values of 66 and 80 mV, respectively. It is suggested that nutrient-rich anthropogenic contributions are causing the apparent O_2-depletion.

Comparable to pH and Eh, also the electric conductivity (EC) of the river water samples is highly variable with values between 235 and 1668 μS/cm in the wet season and between 405 and 2310 μS/cm in the dry season. This difference is suggested to reflect dilution by precipitation in the wet season, which is confirmed by the different EC median values of 750 and 1358 μS/cm for the wet and dry season, respectively. Similar observations were made in previous studies (Wang et al., 2015), which report an up to 3 times higher average streamflow for Beijing rivers in the wet season compared to the average streamflow in the dry season. The seasonality in the dissolved load due to the precipitation effect is also seen in the background sample with an EC value of 456 μS/cm in the wet season and 519 μS/cm in the dry season. The EC distribution map (Fig. 2a) reveals that EC values tend to be higher in river water from the rural area south of the Beijing urban area than for river water from the northern rural area. This is caused by the general NW-SE direction of the river flow on the Beijing Plain (Zhou et al., 2012). Many of the downstream rivers in the southern rural area receive contributions from

Table 1
Statistical parameters for the analyzed river water samples from rural Beijing area.

Parameter	Unit	DL	Season	Minimum	Q5	Q25	Median	Q75	Q95	Maximum
T	(°C)	—	wet	21.9	24.1	25.5	26.5	29.3	31.5	34.4
			dry	5.6	6.6	9.7	12.1	14.4	17.7	24.4
pH	—	—	wet	7.14	7.50	7.69	7.96	8.39	9.57	9.98
			dry	6.83	7.43	7.84	8.10	8.51	9.05	9.28
Eh	mV	—	wet	−182	−120	57	66	84	103	117
			dry	−83	−17	66	80	91	116	140
EC	μS/cm	—	wet	235	277	616	750	1207	1641	1668
			dry	405	467	998	1358	1627	2221	2310
Ca^{2+}	mg/L	0.01	wet	16.1	24.6	31.3	50.5	75.7	127.4	141.1
			dry	33.1	35.5	66.4	80.1	92.3	153.4	184.1
K^+	mg/L	0.1	wet	2.0	3.1	6.0	10.4	12.4	26.4	62.2
			dry	1.9	3.1	9.1	13.9	17.4	38.0	93.5
Mg^{2+}	mg/L	0.01	wet	4.3	6.5	13.7	18.7	30.6	37.6	49.9
			dry	16.0	18.4	24.9	33.6	40.7	54.4	98.2
Na^+	mg/L	0.1	wet	8.2	9.7	36.1	58.7	98.9	147.4	174.4
			dry	12.8	13.3	83.5	105.1	136.4	204.4	232.7
DIC	mg/L	0.01	wet	30.5	61.0	83.9	122.0	195.2	268.1	311.1
			dry	48.8	96.7	134.2	183.0	207.6	305.3	372.1
Cl^-	mg/L	0.01	wet	7.5	9.4	34.6	61.2	117.1	185.9	217.6
			dry	13.4	17.5	82.5	135.3	182.4	331.4	426.6
NO_3^-	mg/L	0.05	wet	b.d.	1.0	1.4	4.9	19.4	56.2	70.4
			dry	0.7	0.8	2.1	5.0	17.0	68.5	309.7
NH_4^+	mg/L	0.05	wet	b.d.	0.1	4.3	7.9	10.0	18.9	48.5
			dry	b.d.	0.1	4.4	13.5	20.8	32.7	66.1
SO_4^{2-}	mg/L	0.01	wet	11.7	20.9	48.2	76.1	105.3	246.4	363.3
			dry	11.9	22.2	73.9	124.4	165.5	322.2	568.4
F^-	mg/L	0.01	wet	0.2	0.4	0.5	0.6	0.7	0.9	3.9
			dry	0.1	0.3	0.4	0.5	0.7	1.9	2.0

DL = Detection limit, Q5 = 5th quartile, Q25 = 25th quartile, Q75 = 75th quartile, Q95 = 95th quartile, b.d. = below detection limit.

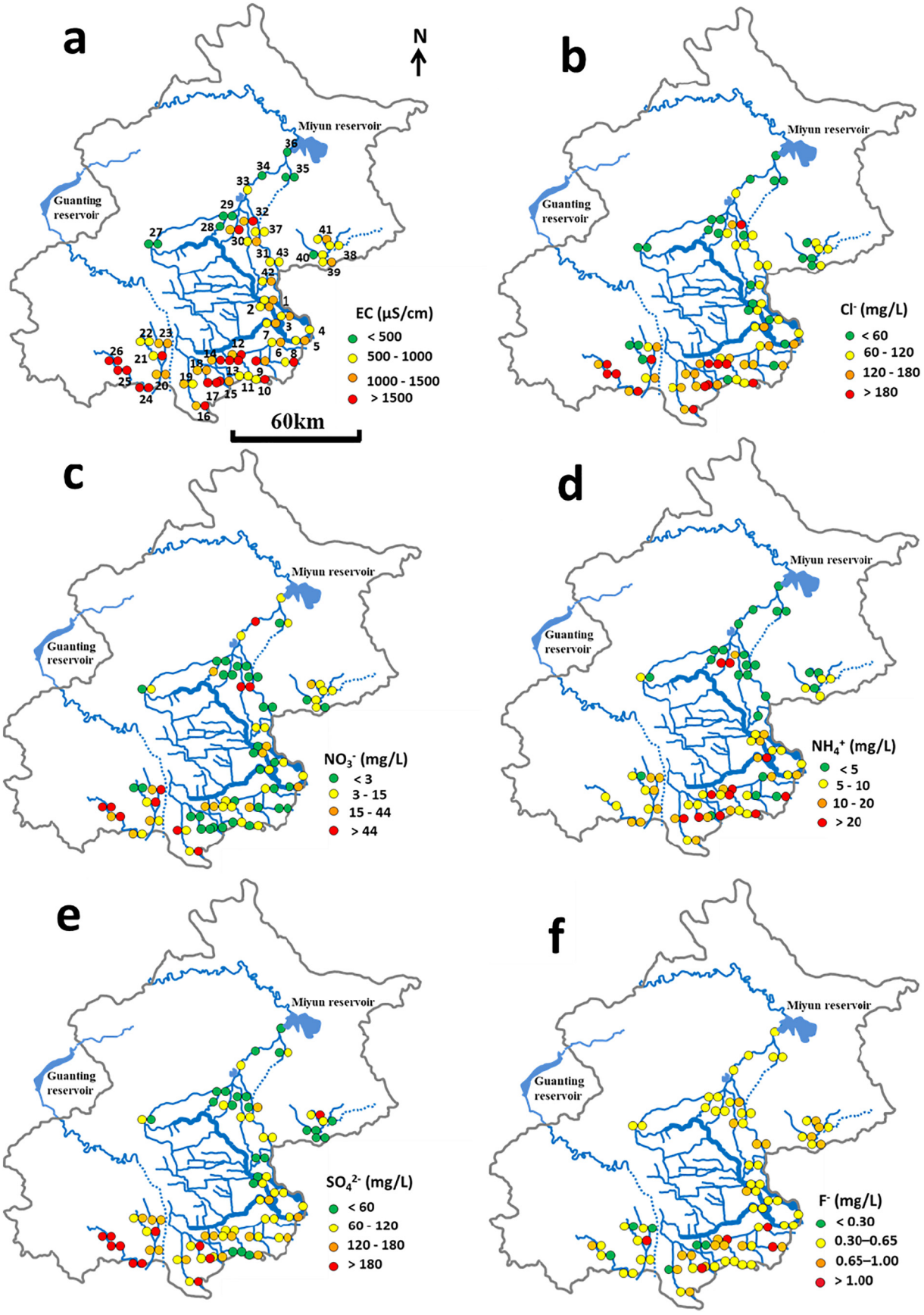

Fig. 2. Hydrochemical maps for electric conductivity (EC) (a), Cl^- (b), NO_3^- (c), NH_4^+ (d), SO_4^{2-} (e) and F^- (f) concentrations of river water samples. The left point at each sampling site refers to the wet season value and the right point to the dry season value. Single points refer to the wet season value.

other rivers, which have passed the city center with its numerous contamination sources enriching the river water with urban pollutants and increasing the concentration of total dissolved constituents. Only two river water samples from the north taken in the suburban area with a relatively high population density show also comparably high EC values above 1500 μS/cm in the dry season suggesting some input by urban wastewater increasing the dissolved load of these rivers.

3.2. Water quality and contamination patterns

In the year 2002 the national guideline on surface water quality (GB3838-2002) containing the standard values for 109 parameters was established by the Environmental Protection Administration of China. This guideline distinguishes five different functional categories regarding the official water environment protection targets (class I: very good, class II: good, class III: moderate, class IV: poor, class V: very poor). Consequently, river water can be classified according to their concentrations of dissolved constituents and/or their physicochemical characteristics.

Five of forty-three river water samples (12%) from the wet season and seven of thirty-six samples (18%) from the dry season exhibit class IV (poor) water quality (Fig. 3), which means that this water can be only used for industrial and recreational purposes and may not be touched by human bodies directly (Table 1). Moreover, 7 samples (16%) from the wet season and 6 samples (16%) from the dry season have an even lower water quality (class V, very poor). This water may not even be applied for agriculture or landscaping due to serious health risks for human beings. The number of samples with minor water quality seems to be similar in wet and dry season. However, if pH is ignored and only the concentrations of contaminants are considered, the picture changes significantly. For the wet season, the water quality of 6 samples (14%) can be categorized as class IV and only 1 sample (2%) shows a lower class V quality. In contrast, in the dry season 8 samples (21%) exhibit class IV quality and 4 samples (11%) show not even class V quality. This is a consequence of the higher concentration of dissolved pollutants for the rivers in the dry winter months compared to the wet summer month receiving higher precipitation. This dilution effect is further confirmed by the higher median values for EC and the concentrations of all analyzed compounds except fluoride in this season. Thereby, nitrate and sulfate from Beijing sewage, both being anthropogenic pollutants as well as geologically controlled pH values and fluoride concentrations are considered to be the most important factors leading to the deterioration of the river water in rural Beijing.

Focusing solely on the concentration of dissolved pollutants, 4 of 17 river water samples (24%) taken in the northern rural area can be classified as water quality class IV and below, whereas 11 of 26 river water samples (42%) collected in the southern rural area show a water quality of class IV and below. This would be consistent with a more substantial influence of the densely populated southwestern part of the Beijing rural area as well as the contribution of effluents from urban Beijing on the composition of the downstream rivers in the rural south.

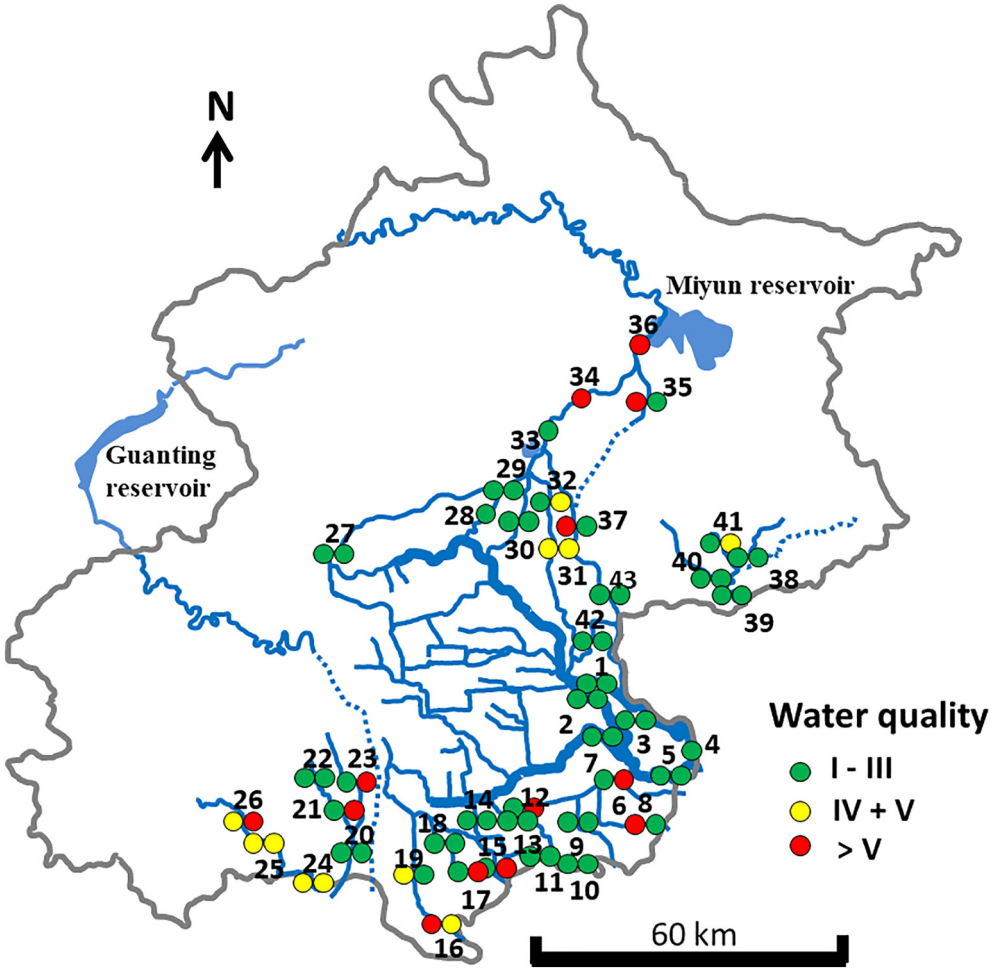

Fig. 3. Hydrochemical maps of water quality for river water samples according to Chinese classification (GB 3838–2002). The left point at each sampling site refers to the wet season value and the right point to the dry season value. Single points refer to the wet season value.

3.3. Major ion and isotopic characteristics of the river water

The river water samples show a clear trend towards higher Na^+, K^+, Cl^- and SO_4^{2-} fractions as well as lower HCO_3^- fractions in both seasons (Fig. 4). However, the higher Na^+, K^+, Cl^- and SO_4^{2-} fractions in the river water samples are probably caused by higher urban inputs into the rivers during their passage through the city area, since anthropogenic effluents, such as urban sewage, may enrich river water with these compounds (Meybeck, 2003). The urban origin of Na^+ and K^+ in the river water is also confirmed by the correlation of these concentrations with the EC values suggesting urban effluents as their major source. Hence, the rural river water seems to be affected more heavily by urban effluents than by discharge of deep groundwater confirming the conclusion based on the distribution of the EC values.

3.3.1. The Cl^- concentrations in river water

Cl^- concentrations in the rivers range from 7.5 to 217.6 mg/L in the wet season and from 13.4 to 426.6 mg/L in the dry season (Table 1). Concentration ranges together as well as median values of 61.2 and 135.3 mg/L, respectively, underline the precipitation effect by rain in the wet season as seen for the EC values. Three samples exceed 250 mg/L, which is considered as the threshold value of class III quality. All other river water samples fall into the class I category with respect to dissolved chloride. Moreover, the hydrochemical map (Fig. 2b) reveals a higher load of Cl^- for the downstream rivers in the southern rural area similar to the distribution of the EC values. Cl^- is a hydrochemically conservative ion, because it is not removed by water-rock interactions and can be used as a key indicator for anthropogenic pollution (Mazor, 2003), when natural Cl^- sources are absent as in the Beijing area. Major anthropogenic Cl^- sources are primarily represented by urban wastewater, landfills and road salts (Foppen, 2002; Ostendorf et al., 2006). In addition, Cl^- can be released to the environment in agriculture by the application of agrochemicals (e.g. fertilizers) and manure (Pionke and Urban, 1985). Although both the northern and southern rural areas are characterized by farming activities, only the downstream river water in the south experienced contributions from the Beijing urban area leading to clearly higher Cl^- concentrations compared to the upstream river water in the north. Hence, the spatial distribution of the Cl^- concentrations confirms the observations made for the EC values and prove the significant impact of urban effluents on the river water composition even in the rural area.

3.3.2. The F^- concentrations in river water

F^- concentrations in Beijing rivers range from 0.2 to 3.9 mg/L in the wet season and from 0.1 to 2.0 mg/L in the dry season (Table 1). One sample in the wet season as well as 4 samples in the dry season exceed the national standard limit of 1.5 mg/L and cannot be even classified as class V, which represents the lowest quality level of the classification system. All other river water samples display F^- concentrations below 1.0 mg/L and fall into class I with respect to dissolved fluoride. Moreover, the median values of 0.6 and 0.5 mg/L for wet and dry season, respectively, are close to the background values of 0.5 and 0.6 mg/L, respectively, indicating a natural source for F^- in most of the river water samples. A possible source could be loess, which can contain relatively high amounts of fluoride (Currell et al., 2011). Loess can be found further upstream in parts of the Beijing mountain area. The supposed natural origin of F^- is confirmed by a relatively even distribution of F^- in the rivers of the north and south (Fig. 2f) compared to the distribution of NO_3^-, NH_4^+ or SO_4^{2-}. Still, the five river water samples displaying the highest concentrations were all derived from the southern rural area. Yet, the spatial distribution of the sampling sites suggests point sources releasing higher amounts of dissolved fluoride into the rivers compared to the other sites. Besides coal combustion and industrial emissions (e.g. from cement, aluminum, steel industry), agrochemicals represent the most important anthropogenic F^- source (Farooqi et al., 2007). Industrial facilities are rare in the Beijing countryside, whereas

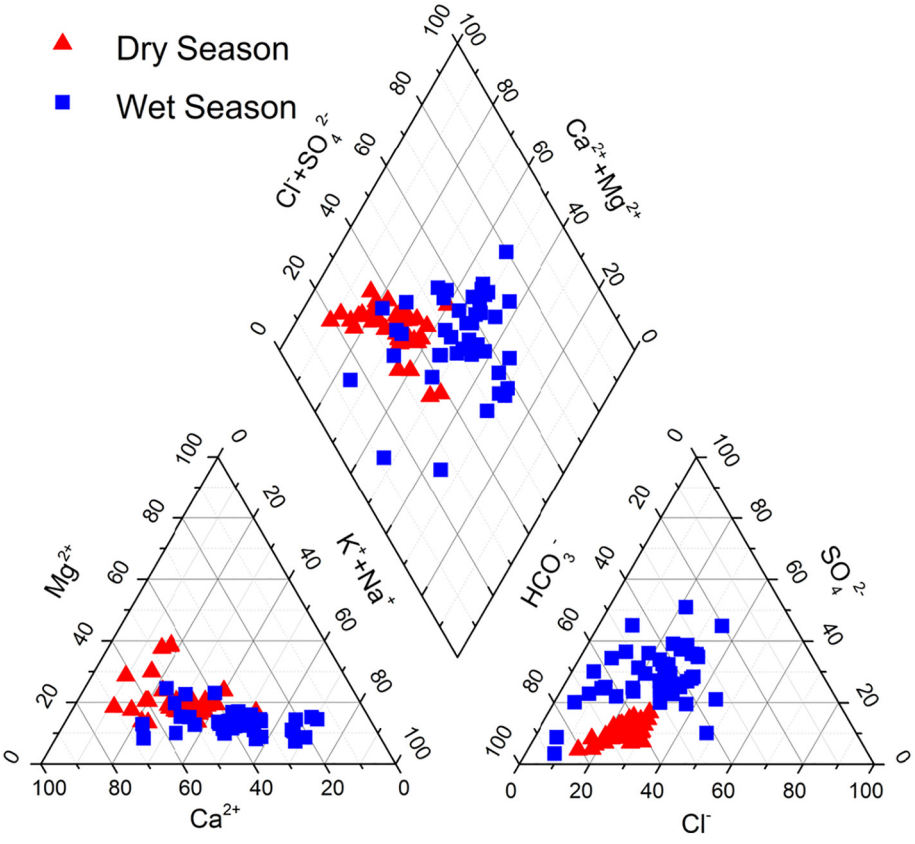

Fig. 4. Piper diagrams for river water samples collected in the wet and in the dry season.

fruit and vegetable farming is very common in the northern and southern rural area, receiving intense application of artificial fertilizers. F^- from fertilizers applied in agriculture can accumulate in the soil and pore water. Moreover, with the surface runoff the dissolved fluoride can be washed into local surface water, such as rivers and lakes. Hence, those river water samples with extraordinary high F^- concentrations may well reflect additional F^- contributions from fertilizers applied to the farmland or kept in leaking fertilizer storages.

3.3.3. The NO_3^- and NH_4^+ concentrations and the isotopic characteristics in river water

River water displays a wide range in NO_3^- concentration from below detection limit (0.05 mg/L) to 70.4 mg/L in the wet season and from 0.7 to 309.7 mg/L in the dry season (Table 1). Moreover, NH_4^+ concentrations range from below detection limit (0.05 mg/L) to 48.5 mg/L in the wet season and to 66.1 mg/L in the dry season. Four samples in the wet season and six samples in the dry season exceed a NO_3^- concentration of 44 mg/L (the class III threshold), suggesting a decreased water quality of the river water, which can be only used for industrial and agricultural use or for parks and landscaping. Seven samples with exceeding concentrations are derived from the southern and 3 from the northern rural area. Also the hydrochemical map (Fig. 2c) reveals that the upstream rivers in large parts of the rural north are less affected by NO_3^- pollution compared to the rural south as seen for Cl^-. However, in contrast to the distribution of Cl^-, the downstream rivers in the rural south and southeast are also characterized by relatively low NO_3^- concentrations in the local river water, whereas high-nitrate river water can be mainly found in the rural southwest. The distribution map for NH_4^+ (Fig. 2d) reveals that rivers in the northern rural area show, again, lower concentrations than in the rural south. However, the nitrate-poor river water in the south exhibits relatively high NH_4^+ concentrations.

The most common anthropogenic nitrate sources are municipal effluents as well as atmospheric deposition (Galloway, 2003). In addition, agrochemicals can be also a source of nitrate for urban waters. Dissolved nitrate from manure as well as inorganic fertilizers can be washed into rivers and transported from the rural to the urban area (Choi et al., 2011). N-containing organic compounds in soils represent the most prominent natural nitrate source.

Each nitrate source is characterized by its individual N and O isotope signature (Kendall, 1998; Kendall et al., 2015). The river water nitrate from rural Beijing displays $\delta^{15}N$ values between −15.7 and + 23.9‰ in the wet season and between −23.5 and +32.0‰ in the dry season (Table 2). $\delta^{18}O$ values range from −5.3 to +39.2‰ in the wet season and from −12.7 to +25.2‰ in the dry season. In a $\delta^{15}N/\delta^{18}O$ plot, especially samples from the dry season fall into or near the field of manure and septic waste (Fig. 5). Manure as a major NO_3^- source can be ruled out as livestock farming is absent in the Beijing area. Hence, human wastewater is suggested to be the prime source for dissolved nitrate in the rural rivers, especially in the dry winter months with low precipitation. This result is according with the study of Li et al. (2016), which suggested that the pollution of some rivers in Beijing ware mainly due to the untreated sewage discharge. Still, soil nitrate could have also contributed to the nitrate pool in the rivers. Moreover, the isotopic composition of NO_3^- from the wet season reveals additional NO_3^- sources, such as atmospheric deposition as well as industrial fertilizers. This is in line with the higher precipitation in this season leading to a higher input of N-containing compounds into the local rivers from the atmosphere, such as NO_x from anthropogenic emissions, like traffic. But also NO_3^- and NH_4^+ from agrochemicals, which are mainly applied in the wetter growing season, are washed into the rivers in farming areas primarily by precipitation in the rainy season. However, despite contributions from the atmosphere and from fertilizers, municipal sewage represents the major NO_3^- source in the wet season. Consequently, urban wastewater shows the highest impact on the nitrate reservoir of the rural rivers in Beijing, even if the concentrations are mostly relatively low.

Urban sewage from private households contains large amounts of NH_4^+, which oxidizes under aerobic conditions via NO_2^- to NO_3^- (nitrification) in the presence of ammonium and nitrite oxidizing microorganisms according to following reactions (Galloway, 2003):

$$2NH_4^+ + 2O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+ \quad (3.1)$$

and

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \quad (3.2)$$

Hence, the release of wastewater into oxygen-rich river water would increase the concentration of dissolved nitrate. However, low NO_3^- but relatively high NH_4^+ concentrations in the water samples from downstream rivers in the southern rural area combined with sewage as the major NO_3^- source point to the accumulation of wastewater derived NH_4^+ in suboxic river water. There, the O_2 content is rather limited due to enhanced microbial activity caused by the high amount of nutrients. Thus, oxygen-depleted downstream rivers limit the oxidation of NH_4^+ to NO_3^-. As a consequence, the NH_4^+ concentration remains relatively high due to low nitrification rates.

3.3.4. The SO_4^{2-} concentrations and isotopic characteristics in river water

Beijing rural rivers display a wide range in SO_4^{2-} concentration between 11.7 and 363.3 mg/L in the wet season and between 11.9 and 568.4 mg/L in the dry season (Table 1). Three samples in the wet and seven samples in the dry season exceed a SO_4^{2-} concentration of 250 mg/L, which represents the class III threshold. Although dissolved sulfate is not as harmful for the aquatic ecology as dissolved nitrate, this river water should only be used for industrial and agricultural purpose or for parks and landscaping. Moreover, only one river water sample from the northern rural area shows a SO_4^{2-} concentration above the respective guideline value indicating, again, the clear difference in the chemical composition of river water in the north in comparison to the south. This is discernible in the spatial distribution of riverine sulfate concentration (Fig. 2e) showing generally higher sulfate abundances in the southern rural area compared to the north with the highest values in the densely populated southwest.

River water sulfate displays $\delta^{34}S$ values between 4.9 and 31.8‰ in the wet season and between 1.0 and 27.5‰ in the dry season (Table 2). Moreover, $\delta^{18}O$ values of SO_4^{2-} range from 2.5 to 11.1‰ in the wet season and from 2.0 and 11.8‰ in the dry season. As evident by the isotopic composition (Fig. 6), Beijing sewage represents the prime sulfate source for the vast majority of samples. This underlines the high impact of urban wastewater on the local river water quality, especially in the rural south, similar to what was shown already by the concentrations and isotopic compositions of NO_3^- and NH_4^+. In addition, some river water samples exhibit a higher contribution of SO_4^{2-} from precipitation. In contrast, detergents and fertilizers do not seem to play a significant role for the sulfate pool in Beijing rivers.

Moreover, an array of data points towards higher $\delta^{34}S$ and $\delta^{18}O$ values suggesting that bacterial sulfate reduction (BSR) affects the riverine sulfate pool. In oxygen-depleted environments sulfate reducing microbes utilize dissolved sulfate as an electron acceptor during the oxidation of organic matter according to following reaction (Kendall and Doctor, 2003):

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^- \quad (3.3)$$

Due to the microbial preference for sulfate with light S and O isotopes, the isotopic composition of the remaining sulfate is shifted to more positive $\delta^{34}S$ and $\delta^{18}O$ values. Although none of the samples forming the array in the isotope plot (Fig. 6) reveals extraordinary low Eh values indicating suboxic or even anoxic conditions as required for BSR, individual samples either shows relatively low SO_4^{2-} concentrations in both seasons.

Table 2
Isotopic compositions of dissolved nitrate and sulfate from river water samples collected in rural Beijing.

ID	$\delta^{15}N_{nitrate}$		$\delta^{18}O_{nitrate}$		$\delta^{34}S_{sulfate}$		$\delta^{18}O_{sulfate}$		$\Delta^{33}S_{sulfate}$	
	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
	‰									
CW1	7.0	11.1	32.1	2.2	10.5	10.7	6.0	2.5	−0.014	−0.034
CW2	19.9	10.8	−0.2	−0.6	11.0	9.5	5.2	2.4	−0.045	
CW3	9.9	15.7	19.0	6.9	11.0	14.8	4.7	7.1		
CW4	23.9		8.5		8.5		5.0			
CW5	18.1	7.3	14.2	6.2	8.5	8.9	4.6	2.6		
CW6	12.4	−4.1	15.8	25.2	8.7	11.1	6.8	4.3		
CW7	−0.9	32.0	39.2	18.4	4.9	8.4	4.8	4.1	−0.018	−0.048
CW8	5.6		19.1		5.7	9.8	9.3	4.7		
CW9	17.8	6.1	12.5	15.3	10.9	15.0	6.6	7.1		
CW10	2.0		19.3		8.8	9.1	6.0	3.7		
CW11	−7.3	7.2	15.1	8.0	7.0	9.2	3.5	2.9		
CW12	−3.7		21.2		11.0	10.2	6.1	3.7	−0.055	−0.055
CW13		14.9		14.8	6.3	7.0	7.4	5.1	−0.040	
CW14	15.1	6.3	3.7	0.1	9.6	9.1	4.1	2.0		
CW15		5.3		5.7	11.4	11.1	4.3	2.6	−0.052	−0.042
CW16	12.7	6.2	10.6	−0.3	8.0	7.9	2.5	6.2		
CW17		2.4		14.2	7.1	1.0	7.1	8.8	−0.038	
CW18					7.0	4.8	7.5	8.1	−0.032	−0.034
CW19	13.0	8.1	5.4	8.8	7.4	9.3	3.6	3.5		
CW20	11.0	10.3	1.6	−12.7	12.1	11.9	6.1	3.5	−0.047	
CW21	12.6	10.2	8.2	4.3	12.2	12.8	6.6	11.8		
CW22	6.6	1.4	12.4	15.5	31.8	27.5	11.1	9.6	−0.076	−0.042
CW23	15.4	12.8	5.7	0.6	12.3	11.6	6.2	3.0		
CW24	18.5	17.1	7.5	6.6	8.2	10.0	7.0	5.8		
CW25		10.7		0.1		9.4		4.9		
CW26		1.4		11.9		7.6		4.5		
CW27	−15.7		13.6		7.2	7.8	4.0	3.5	−0.045	
CW28	0.4		36.6		6.6		9.5			
CW29		5.2		12.6		7.7		4.2		
CW30	−10.9		11.1		10.1		5.6		−0.039	
CW31	10.0	7.4	−5.3	−10.2	7.7	12.5	5.7	1.4		
CW32					9.4	10.0		0.8		
CW33	11.0		8.5		7.9		6.0		−0.014	
CW34	−12.3		12.7		8.3		5.7			
CW35	6.5	7.6	12.6	9.8	7.0	6.5	5.1	4.9	−0.029	
CW36	−0.1		6.4		8.1		5.9		−0.040	
CW37					8.6	8.6	5.1	8.7	−0.035	−0.016
CW38	6.7	14.1	6.4	−0.7	12.3	10.4	5.2	2.8	−0.037	−0.051
CW39	−0.6	9.3	12.8	5.0	9.7	9.0	7.2	4.8		
CW40	4.1	9.8	22.0	6.7		8.9	8.7	6.1		
CW41	6.1	16.3	11.9	15.7	6.9	2.9	7.5	9.0		
CW42		3.7		−2.2	19.0	23.8	8.7	8.9		
CW43		−23.5		19.0	5.5		5.5		−0.006	

The $\Delta^{33}S$ value for sulfate sulfur from 18 river water samples from the wet season and for 8 samples from the dry season range from −0.055 to −0.006‰ and from −0.055 to −0.016‰, respectively (Table 2). In a $\delta^{34}S/\Delta^{33}S$ plot (Fig. 7) most data points can be found in or near the field for Beijing sewage as well as for local fertilizers. Due to the wide range in $\Delta^{33}S$ values for Beijing fertilizer, the respective field overlaps widely with the field for Beijing sewage. Hence, $\Delta^{33}S$ values are consistent with and confirm urban wastewater as major

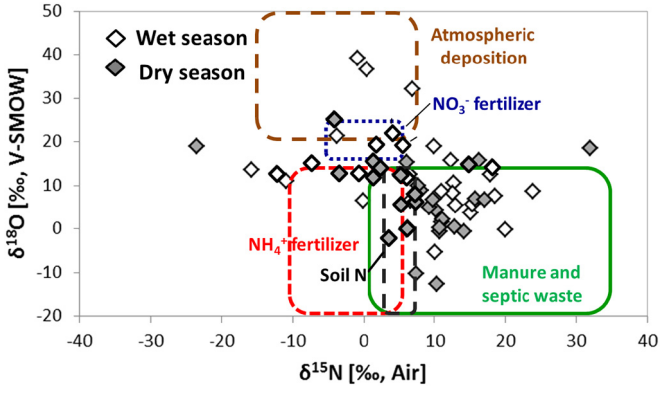

Fig. 5. $\delta^{15}N$ vs. $\delta^{18}O$ for dissolved nitrate in river water samples collected in rural Beijing as well as for different nitrate sources (the latter based on data from Kendall, 1998 and Kendall et al., 2015). Errors for $\delta^{15}N$ (±0.3‰) and $\delta^{18}O$ (±0.5‰) are smaller than the size of the symbols.

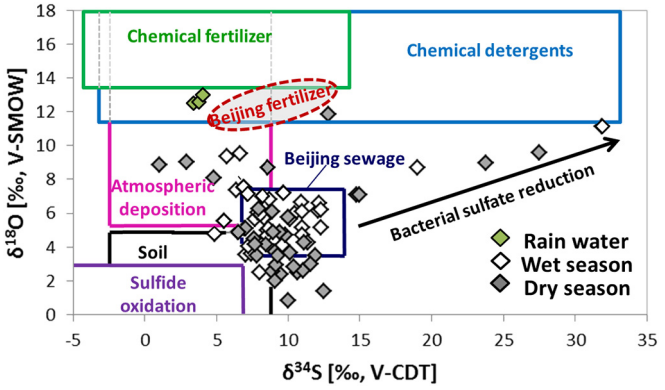

Fig. 6. $\delta^{34}S$ vs. $\delta^{18}O$ for dissolved sulfate in river water samples collected in rural Beijing as well as for sulfate sources (the latter based on data from Krouse and Mayer, 2000). Errors for $\delta^{34}S$ (±0.3‰) and $\delta^{18}O$ (±0.3‰) are smaller than the size of the symbols.

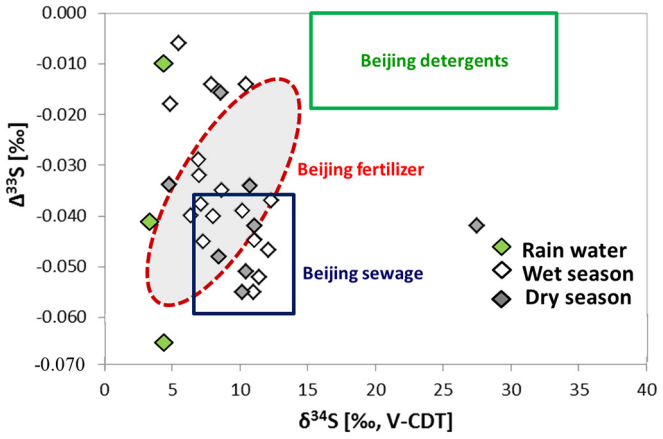

Fig. 7. $\delta^{34}S$ vs. $\Delta^{33}S$ for dissolved sulfate in river water samples collected in rural Beijing. Errors for $\Delta^{33}S$ ($\pm$0.008‰) are not shown.

sulfate source, since the $\delta^{34}S/\delta^{18}O$ plot does not reveal any significant contribution by Beijing fertilizer. In contrast, one group of samples with $\Delta^{33}S$ values above −0.020‰ and $\delta^{34}S$ values between +5 and +10‰ suggests an influence from an additional sulfate source next to Beijing sewage. In the $\delta^{34}S/\delta^{18}O$ plot the data points of some samples from this group (CW7, 18, 37, 43) can be found in or near the field for precipitation suggesting that sulfate from Beijing rain contributed to the river water sulfate of these samples. However, Beijing rain is characterized by a relatively low $\Delta^{33}S$ signature of −0.040‰ in average, which is in contradiction to the trend to higher $\Delta^{33}S$ values for these samples. Hence, future $\Delta^{33}S$ analyses on other sulfate sources should be conducted to detect their origin.

4. Conclusions

We analyzed selected physico-chemical and chemical parameters for river water samples from rural Beijing collected during different seasons in order to address the degree of inorganic pollution as well as to identify the temporal and spatial distribution of contaminants in those waters. The results were evaluated according to the national legislation for surface water quality (GB3838-2002). In addition, multiple stable isotopes were applied to trace the respective pollution sources.

In the wet season, 28% of the river water samples exhibit a low surface water quality of class IV (poor) and below, whereas in the dry season 34% fall into these water quality categories primarily due to high pH values, nitrate, sulfate and fluoride concentrations. Considering solely dissolved water pollutants, the seasonal difference in river water quality is even more obvious: 16% of the samples in the wet season and 31% of the samples in the dry season show a water quality below class V (very poor). Results indicate clearly that dilution via precipitation reduces the pollutant load, mimicking in a better water quality during the wet season. Moreover, 16% of the river water in the wet season and 16% in the dry season are even below the worst quality class V, when pH is included into the evaluation. It means that this water may not be used for any purpose, because it represents a serious risk for human health and the aquatic ecology.

Stable isotopes (N, O, S) of dissolved nitrate and sulfate point to wastewater as the dominant source of anthropogenic pollutions, while fluoride represents the major natural contaminant. The higher fraction of river water samples below class III quality in the southern rural area (42%) compared to the northern rural area (24%) reflects the influence of urban Beijing effluents and the consequence of the relatively densely populated area in the rural southwest on the water quality of southern downstream rivers.

The results of the present study provide clear evidence for a large influence of human wastewater on the river water composition in the Beijing rural area. In this region wastewater is often released as untreated sewage to surface environments leading to the quality decline of the local surface water. From this study it is clear that solely a more responsible handling of wastewater and more efficient controls on public and private sewage disposal combined with a better maintenance or renewal of the local sewer network could reduce further anthropogenic contamination. Only such measures would ultimately improve the quality of the most important water resources in the Beijing area.

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