



Geochemical and multiple stable isotope (N, O, S) investigation on tap and bottled water from Beijing, China



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ABSTRACT

In the present study we investigated Beijing tap water from urban and suburban areas as well as bottled water from Beijing supermarkets with a focus on selected anions (Cl^- , NO_3^- , SO_4^{2-} , F^-), metals and trace elements (Al, As, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn), in order to reveal the degree of anthropogenic pollution and the ability of both water types to serve as a safe drinking water source. In addition, we applied multiple stable isotope ($\delta^{15}\text{N}_{\text{nitrate}}$, $\delta^{18}\text{O}_{\text{nitrate}}$, $\delta^{34}\text{S}_{\text{sulfate}}$, $\delta^{18}\text{O}_{\text{sulfate}}$, $\Delta^{33}\text{S}_{\text{sulfate}}$) analyses on Beijing tap water for the identification of specific pollution sources. 27% of the analyzed tap water samples show one or more constituents above the national guideline limits. 9% of the samples reveal concentrations above the NO_3^- limit, while 5% exceed the standard value for As, which makes this tap water unsuitable for daily consumption due to a serious health risk, especially for children and babies. The median concentrations of most analyzed compounds are significantly higher in Beijing tap water compared to European countries. Concentration and isotope data for tap water indicate urban sewage as the major origin of anthropogenic pollutants probably released by leaking wastewater pipes to the local groundwater as the principal tap water source. The results suggest industrial emissions and As-rich alluvial deposits as further but minor pollutant sources. In contrast, bottled water exhibits exclusively concentrations below the standard values and clearly lower median values compared to Beijing tap water. Hence, bottled water can be recommended as a valuable alternative to Beijing tap water, especially in areas where the pollutant levels in tap water are high. Moreover, the results reveal the problematic groundwater situation in Beijing and demonstrate the advantages of a combined geochemical and multiple isotope approach in order to uncover complex pollution mechanisms in metropolitan areas.

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1. Introduction

China's economy has grown rapidly in the last 30 years and became the second largest economy in the world (United Nations WESP, 2012). Beijing, China's capital city and one of its fastest-growing municipalities, represents one of the largest megacities in Asia with a total population of around 20 million residents (BMBS, 2011). Since many years the municipal government faces severe problems in respect to providing sufficient clean drinking water for all households due to an irresponsible treatment of the vital water resources of Beijing in the past 60 years. In 2007 the Chinese government tried to address the problem of insufficient drinking water quality in the Beijing area and established the new drinking water guideline GB 5749-2006 for microbial and chemical parameters, which came into effect five years later in July 2012 (MOH, 2012). The number of indicators was set up from 35 (established in 1985) to 106. Most of the new standards are much stricter than the previous ones and match international guideline limits as suggested by the

World Health Organization (WHO, 2011). However, it has yet to be proven, if the new standards are really put into practice.

Beijing tap water is mainly derived from groundwater (~80%), the rest comes from the Miyun surface water reservoir (BWG, 2012) located around 60 km northeast of the Beijing city area. After the progressive pollution of other water reservoirs, such as the Guanting dam lake 50 km northwest of Beijing city (He et al., 2011), the Miyun dam lake is the last remaining surface water reservoir, which mainly supplies water for refilling Beijing's park lakes that were once fed by springs.

Beijing's tap water is produced in numerous water plants, which are widespread all over Beijing to supply each part of Beijing with public water. Each water factory commands a groundwater well located on the site of the water plant exploiting groundwater from depths of more than 100 m in the urban area. In contrast, in the towns and villages of the rural parts of Beijing groundwater is mainly derived from depths < 120 m (Dou et al., 2006). After treatment (e.g., ozonation) the water is distributed as finish water to the private households via the city pipeline system (Wei et al., 2010).

Due to increasing pollution of surface and groundwater especially in Asian metropolitan areas (e.g., Yasuhara, 1998), bottled mineral water is

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alleged to be the safer alternative to tap water. Meanwhile most supermarkets in Beijing provide a great selection of mineral waters produced by national and international companies. The quality of these bottled waters is under permanent observation and has to comply with the national standards for natural mineral water (GB 8537-2008) (MOH, 2012).

For the present study we analyzed tap water from 56 locations in the Beijing area (Fig. 1), 12 bottled mineral waters from different national and international brands available in Beijing supermarkets, water from the Miyun dam lake, and Beijing precipitation for selected physico-chemical parameters as well as the concentrations of a number of cations, anions, metals and trace elements. The results were compared with the national guideline values for drinking water and natural mineral water as well as with European tap and bottled water. In addition, stable isotope analyses of NO_3^- for 22 tap water samples (39%) and Miyun lake water as well as of SO_4^{2-} for 34 tap water samples (61%) and Miyun lake water were conducted in order to detect the sources of these compounds. Unfortunately, no groundwater sample was allowed to be taken in the Beijing urban area due to restrictions imposed by the local government of Beijing.

The major goal of this investigation is to show if Beijing tap water represents a safe drinking water source for the local residents with respect to the analyzed compounds according to the current drinking water standards and to detect the sources of certain dissolved contaminants. Additional analyses on bottled mineral water reveal, if this water meets the standards according to the national mineral water guideline and if bottled water can serve as an appropriate alternative to Beijing tap water. The results provide guidance for the consumers in their choice for their daily drinking water source.

2. Materials and methods

2.1. Sampling

In total 56 tap water samples were collected between July and November 2012 in urban, suburban and rural areas of Beijing (Fig. 1). The random daytime samples were collected from drinking water taps in private apartments and public places (office buildings, hotels, restaurants, cafes, bars, shop kitchens). After 2 min flushing the main part of

each tap water sample was collected in a PET (polyethylene terephthalate) bottle (1.5 L), which was rinsed several times with the sample water. This fraction of the sample was prepared later in lab for analyses on 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 on anions, cations, metals and trace elements. Before sampling the tubes for analyses on 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 $\text{pH} < 2$. All subsamples were stored dark and cool immediately after sampling until further preparation in lab. On-site measurements of pH, redox potential (Eh) and electric conductivity (EC) were carried out during sampling using the electrode kit SX731 (Sanxin®).

10 of the 12 investigated bottled waters are all still mineral waters without any artificial addition of carbonate, the other two are artificially mineralized waters. All bottled waters were sold in PET bottles and purchased in three supermarkets in Beijing city in August 2012. The waters were the products of different national and international companies from China and France. The brand names in alphabetical order and the location of the springs are as follows: Evian (France, Alpes), Ganten (Guangdong province), Hosanmi (Hainan province), Kunlunshan (Qinghai province), Lanjian (Beijing municipality), Laoshan (Shandong province), Master Kong (Jilin province), Master Kong (mineralized water), Nongfu Spring (Jilin province), Quechao (mineralized water), Tibet Spring (Tibet Autonomous Region), and Yibao (Hebei province).

Moreover, water from the Miyun dam lake northeast of Beijing was collected. The water sample was taken at the southern shore of the lake distant to farms and villages. The subsampling procedure for bottled water and Miyun lake water samples for later concentration and isotope analyses was the same as for the tap water samples.

2.2. Analytical methods

Concentration measurements on anions (Cl^- , NO_3^- , SO_4^{2-} , F^-), cations (Ca^{2+} , K^+ , Mg^{2+} , Na^+), metals and trace elements (Al, As, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn) were carried out in the laboratories of

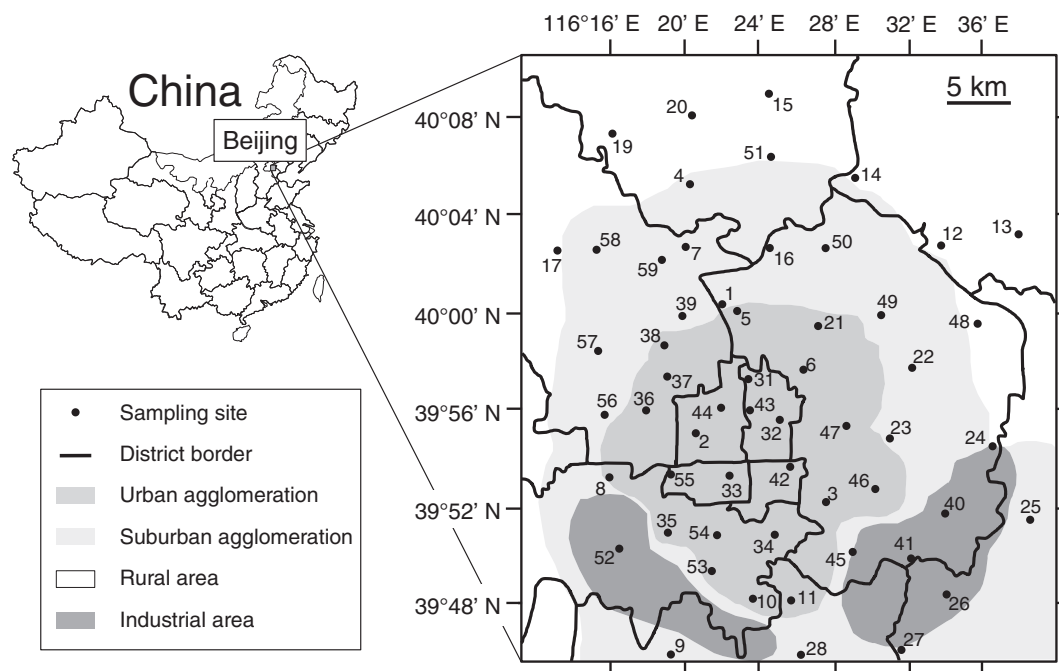


Fig. 1. Simplified map of Beijing with the locations of the tap water sampling sites and the different types of land use.

the Institute of Geographic Sciences and Natural Resources Research (IGSNRR), CAS in Beijing, China. Anions were analyzed by gas chromatography using an AMS Smartchem 300®. Analytical precision was better than $\pm 5\%$. Cation concentrations were determined by an inductively coupled plasma optical emission spectrometer (ICP-OES) with an analytical precision of $\pm 1.5\%$ on average. Concentration measurements on metals and trace elements were carried out using an inductively coupled plasma mass spectrometer (ICP-MS) with an analytical precision of $\pm 10\%$ on average. The results for each metal and trace element refer to its total abundance and do not focus on specific valence states.

The 1.5 L subsample was filtered through 0.45 μm pore-size cellulose acetate filter and 50 mL was treated with 2 mL of KOH solution in order to increase the pH to ~ 12 for later nitrogen and oxygen isotope analyses on dissolved nitrate using the bacterial denitrifier method described by Sigman et al. (2001). For later $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ 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 (e.g., Dogramaci et al., 2001). For multiple sulfur isotope measurements ($\delta^{33}\text{S}$, $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$), the precipitated BaSO_4 was converted to Ag_2S according to the Thode extraction method (Thode et al., 1961).

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

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

where R represents the $^{15}\text{N}/^{14}\text{N}$, $^{18}\text{O}/^{16}\text{O}$ or $^{34}\text{S}/^{32}\text{S}$ of the sample and the standard, respectively. N and O isotope measurements were performed in the State Key Laboratory of Environmental Geochemistry at the Institute of Geochemistry (CAS) in Guiyang, China, using an isotope ratio mass spectrometer (IRMS, Isoprime, UK) combined with a Trace Gas Pre-concentrator unit for N_2O purification. In the same laboratory O isotope ratios of sulfate were determined by elemental analyzer-isotope ratio mass spectrometry (TC/EA-IRMS, Isoprime, UK). The analytical precision of the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values is generally better than $\pm 0.3\%$ and $\pm 0.5\%$, respectively. Measurements solely for $\delta^{34}\text{S}$ were conducted using a ThermoFinnigan Delta 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 $\pm 0.3\%$. Multiple sulfur isotope measurements were carried out in the same lab with 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. $\Delta^{33}\text{S}$ values were calculated using the $\delta^{33}\text{S}$ and $\delta^{34}\text{S}$ values (Farquhar et al., 2000; Hulston and Thode, 1965) as:

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

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

3. Geographical and hydrogeological setting

Beijing is situated on the Beijing Plain, which is located in the northwest of the larger North China Plain (NCP). The Beijing Plain shows a continental semiarid climate zone with an annual mean temperature around $13\text{ }^\circ\text{C}$ and an average precipitation of $\sim 600\text{ mm}$ (Aji et al., 2008). Around 80% of the precipitation in this area occurs during the summer monsoon between June and September. The annual mean evaporation is about 1725 mm with its peak in April, May and June. The Beijing Plain is bordered in the west by the Taihang Mountains and in the north and northeast by the Yanshan Mountain Range. The

Bohai Bay as part of the East China Sea lies in a distance of around 150 km to the southeast of Beijing. The two major rivers Yongding River and Chaobai River, dammed by the Guanting Reservoir west and the Miyun Reservoir northeast of Beijing City, account for 90% of the total surface water inflow to the Beijing Plain (Zhou et al., 2012).

The bed rock of the Beijing Plain and the surrounding mountain ranges consist mainly of Archean gneisses and Proterozoic carbonates (Chen et al., 2003). The Cenozoic formation comprises thick Tertiary and Quaternary deposits, the latter with an increasing thickness from tens of meters to 500 m from the mountain area to the sea (Zhou et al., 2012). The sedimentary deposits of the Quaternary layer are classified into four aquifers based on their lithological properties and hydrodynamic conditions. The aquifers grade from a single sand–pebble–gravel aquifer at the top of the piedmont alluvio-pluvial fan to a 3–4 layered aquifer of sand–pebble–gravel and sand separated by silt and clay layers in the lowland area. The shallow aquifer ($< 100\text{ m}$ depth) is unconfined, whereas the deep aquifers ($> 100\text{ m}$) are confined (Aji et al., 2008). The recharge to the deep aquifers is mainly caused by leakage from the shallow aquifer. The general direction of the groundwater flow on the Beijing Plain is NW–SE.

4. Results and discussion

4.1. Physical–chemical parameters

The Beijing tap water samples analyzed for this study show pH values between 7.00 and 8.22 within the suggested guideline range from 6.5 to 8.5 (Table 1). The median value of 7.67 matches exactly the median value for European tap water (EGS, EuroGeoSurveys Geochemistry Expert Group, 2010). Redox potentials (Eh) from -87 to 441 mV reveal predominantly oxidizing conditions of Beijing tap water, although two samples show clearly reducing conditions. Both samples TW14 and TW13 with the lowest Eh values of -87 and -16 mV , respectively, show relatively high pH values of 8.17 and 8.11. The tap water samples display a wide range in electric conductivity (EC) from 316 to $1819\text{ }\mu\text{S}/\text{cm}$ below the official standard value of $2000\text{ }\mu\text{S}/\text{cm}$ as suggested by the national drinking water guideline. The median value of $509\text{ }\mu\text{S}/\text{cm}$ is higher than the median value for European tap water with $365\text{ }\mu\text{S}/\text{cm}$ (EGS, EuroGeoSurveys Geochemistry Expert Group, 2010). The samples TW9, 10, 11, 46 and 53 taken in the south and east of Beijing exhibit EC values above $1000\text{ }\mu\text{S}/\text{cm}$, which exceed the median value for Beijing tap water of $509\text{ }\mu\text{S}/\text{cm}$ significantly. This can be caused by human contamination transporting anthropogenic compounds to the aquifers, i.e., by percolation of polluted surface water or leaking wastewater pipes, and reaching even deeper groundwater (Virkkuntyte and Sillanpää, 2006).

The water from the Miyun dam lake shows the highest pH value (8.68), but a significantly lower EC value compared to the median value of Beijing tap water ($333\text{ }\mu\text{S}/\text{cm}$) (Table 1). As expected, rain water collected in Beijing reveals with $132\text{ }\mu\text{S}/\text{cm}$ on average the lowest EC value. It also shows the lowest pH with an average value of 6.63, which points to slightly acidic conditions in Beijing precipitation. The low pH might be caused by the large amounts of anthropogenic emissions in the Beijing air, such as SO_2 or aerosols, which lowers the air quality in the Beijing area and leads to the generation of acid rain (Xu and Han, 2009).

Physical–chemical measurements on bottled water revealed a larger range of pH values between 6.26 and 8.22 compared with Beijing tap water (Table 2). The median value of 6.87 is significantly higher compared to the median value of 5.60 for European bottled water (EGS, EuroGeoSurveys Geochemistry Expert Group, 2010), possibly caused by additions of carbonic acid to the latter. The Eh values between 30 and 128 mV indicate oxidizing conditions, which are required for mineral or mineralized drinking water. EC values between 19 and $586\text{ }\mu\text{S}/\text{cm}$ are far below the suggested guideline limit of $2000\text{ }\mu\text{S}/\text{cm}$.

Table 1

National guideline values for drinking water (GB 5749-2006), location, physical–chemical results and cation concentrations (mg/L) of Miyun lake, Beijing rain (average) and tap water samples.

ID	Latitude	Longitude	pH	Eh (mV)	EC ($\mu\text{S}/\text{cm}$)	Ca^{2+}	K^+	Mg^{2+}	Na^+
GB 5749-2006	–	–	6.5–8.5	n.e.	2000	n.e.	n.e.	n.e.	n.e.
Miyun lake	40°28'53.63"N	116°51'29.90"E	8.68	101	333	37.7	3.4	15.3	13.9
Beijing rain (average) ^a	40°0'6.75"N	116°22'43.89"E	6.63	78	132	14.8	2.9	1.2	1.2
TW1	40°0'18.61"N	116°21'54.22"E	7.57	48	438	52.2	3.4	21.5	21.4
TW2	39°54'57.01"N	116°20'38.04"E	n.d.	n.d.	n.d.	83.8	3.0	29.6	37.5
TW3	39°52'13.70"N	116°27'43.74"E	7.69	193	478	58.3	2.0	22.2	14.7
TW4	40°5'17.43"N	116°20'2.48"E	7.61	57	467	53.9	2.6	18.9	14.9
TW5	40°0'6.75"N	116°22'43.89"E	7.44	89	509	42.8	2.7	19.6	15.5
TW6	39°57'39.60"N	116°26'20.04"E	7.64	195	541	61.7	1.6	24.3	14.4
TW7	40°2'40.22"N	116°19'54.2"E	7.47	69	316	52.5	2.7	19.2	15.0
TW8	39°53'5.20"N	116°16'3.60"E	8.02	404	430	50.0	2.8	21.7	13.0
TW9	39°45'42.70"N	116°19'37.50"E	7.90	14	1469	154.8	3.5	53.7	107.9
TW10	39°48'13.60"N	116°23'54.80"E	7.28	20	1775	208.6	3.2	68.8	113.9
TW11	39°48'10.50"N	116°25'57.90"E	7.50	27	1450	175.9	3.2	59.4	72.3
TW12	40°2'57.10"N	116°33'37.90"E	7.63	50	950	81.6	2.5	24.5	28.6
TW13	40°3'27.40"N	116°37'46.40"E	8.17	–16	940	24.1	0.8	7.7	107.3
TW14	40°5'35.20"N	116°28'56.70"E	8.11	–87	782	31.2	0.7	16.2	69.9
TW15	40°9'6.10"N	116°24'11.80"E	7.83	110	677	59.6	1.2	24.4	17.0
TW16	40°2'39.60"N	116°24'9.70"E	7.97	79	422	52.1	2.8	18.4	14.6
TW17	40°2'22.00"N	116°12'58.80"E	7.77	38	402	54.6	0.5	12.6	16.8
TW19	40°7'17.00"N	116°15'47.10"E	7.96	280	378	35.4	1.3	11.4	38.0
TW20	40°8'5.50"N	116°20'2.70"E	8.09	148	402	46.0	1.3	15.6	26.1
TW21	39°59'31.30"N	116°27'5.30"E	7.89	111	407	46.8	3.0	18.6	15.9
TW22	39°57'52.30"N	116°32'10.50"E	7.78	79	412	46.7	2.8	18.1	15.2
TW23	39°54'57.00"N	116°31'5.20"E	7.88	148	467	55.6	2.5	21.9	14.7
TW24	39°54'45.20"N	116°36'36.20"E	8.22	85	467	40.9	2.2	18.4	40.8
TW25	39°51'39.10"N	116°38'41.70"E	7.97	85	475	44.9	1.1	20.8	39.4
TW26	39°48'27.60"N	116°34'18.50"E	7.92	75	555	59.2	1.5	25.8	33.6
TW27	39°46'9.50"N	116°31'53.30"E	7.95	100	441	49.7	3.0	19.7	15.4
TW28	39°45'51.50"N	116°26'33.20"E	7.86	91	817	100.7	2.1	39.2	45.1
TW31	39°57'8.90"N	116°23'18.00"E	7.52	82	424	48.4	2.7	18.5	15.5
TW32	39°55'33.10"N	116°25'11.50"E	7.71	344	483	58.2	2.1	22.9	14.9
TW33	39°53'17.30"N	116°22'28.60"E	7.54	184	456	53.5	2.4	20.8	15.8
TW34	39°50'53.80"N	116°25'1.70"E	7.55	293	535	63.1	2.5	24.4	20.0
TW35	39°50'51.90"N	116°19'15.90"E	7.57	210	516	57.2	3.1	22.7	21.8
TW36	39°55'52.70"N	116°17'56.50"E	7.45	441	855	100.1	2.5	36.4	40.8
TW37	39°57'14.10"N	116°19'3.50"E	7.56	221	569	66.3	2.6	24.6	24.0
TW38	39°58'33.20"N	116°18'52.00"E	7.36	175	425	50.5	3.0	19.3	15.7
TW39	39°59'45.10"N	116°19'46.00"E	7.71	155	467	73.3	1.9	32.2	23.5
TW40	39°51'51.70"N	116°34'7.80"E	7.67	82	669	61.2	1.9	25.0	55.3
TW41	39°49'59.10"N	116°32'30.40"E	7.67	77	636	68.6	2.2	29.9	28.7
TW42	39°53'39.70"N	116°25'45.90"E	8.00	304	484	51.4	1.6	20.4	12.6
TW43	39°55'56.50"N	116°23'29.30"E	7.70	198	562	53.5	2.4	21.4	19.6
TW44	39°56'2.80"N	116°21'59.80"E	7.71	162	611	60.0	2.5	24.5	23.6
TW45	39°50'14.10"N	116°29'13.40"E	7.00	83	845	75.1	1.9	36.0	35.5
TW46	39°52'47.70"N	116°30'21.10"E	7.11	76	1541	107.9	2.1	81.9	98.3
TW47	39°55'23.90"N	116°28'43.10"E	7.50	351	505	54.0	1.9	21.5	13.0
TW48	39°59'45.50"N	116°35'40.30"E	7.84	45	476	40.6	0.3	17.0	34.3
TW49	39°59'59.10"N	116°30'27.30"E	7.49	102	662	59.8	2.0	29.2	28.7
TW50	40°2'42.50"N	116°27'24.70"E	7.61	92	451	35.1	1.5	16.2	34.3
TW51	40°6'23.30"N	116°24'23.10"E	7.58	84	451	28.0	0.6	33.7	83.7
TW52	39°50'3.75"N	116°16'42.66"E	7.83	194	441	45.1	2.7	16.9	12.8
TW53	39°49'16.00"N	116°21'39.70"E	7.24	130	1819	183.7	3.5	66.0	88.5
TW54	39°50'43.80"N	116°21'55.10"E	7.73	160	603	58.6	2.8	22.7	21.5
TW55	39°53'16.70"N	116°19'12.35"E	7.49	135	722	68.1	3.2	26.0	29.5
TW56	39°55'39.00"N	116°15'45.70"E	7.92	184	435	43.9	2.9	16.5	12.9
TW57	39°58'18.30"N	116°15'17.40"E	7.66	120	879	89.6	2.3	34.4	30.8
TW58	40°2'27.90"N	116°15'7.20"E	7.38	108	805	107.4	1.7	18.6	24.8
TW59	40°2'2.80"N	116°18'37.70"E	7.56	112	994	100.3	2.7	43.1	36.3
Median	–	–	7.67	108	509	56.4	2.5	22.1	23.8
Min	–	–	7.00	–87	316	24.1	0.3	7.7	12.6
Max	–	–	8.22	441	1819	208.6	3.5	81.9	113.9
European tap water ^b	–	–	7.67	n.d.	365	59.5	1.6	9.6	9.5

n.e. = not established.

n.d. = not determined.

^a Unpublished data.

^b Median values of European tap water (EGS, EuroGeoSurveys Geochemistry Expert Group, 2010).

4.2. Major cation compositions

Groundwater from the mountain area of the North China Plain (NCP) is characterized by a typical $\text{Ca}-(\text{Mg})-\text{HCO}_3^-$ composition with

Ca^{2+} ($\pm \text{Mg}^{2+}$) as the dominant cations and lower Na^+ concentrations (Aji et al., 2008), which shows the influence of the Proterozoic carbonate rocks hosted by the surrounding mountain ranges. This groundwater type is also present in the Beijing urban and suburban areas on the

Table 2
National guideline values for natural mineral water (GB 8537-2008), physical–chemical results and cation concentrations (mg/L) of bottled water samples.

ID	pH	Eh (mV)	EC ($\mu\text{S}/\text{cm}$)	Ca^{2+}	K^+	Mg^{2+}	Na^+
GB 8537-2008	n.e.	n.e.	2000	n.e.	n.e.	n.e.	n.e.
BW1	7.32	30	144	13.4	1.2	2.0	4.1
BW2	7.21	91	170	10.2	3.8	8.6	8.2
BW3	6.39	89	415	11.9	1.7	4.2	72.5
BW4	6.44	85	387	50.2	0.9	11.6	8.1
BW5	7.89	89	565	34.5	1.5	31.9	26.8
BW6	6.34	94	323	29.6	1.0	6.6	18.3
BW7	7.49	90	586	75.3	1.1	25.4	6.5
BW8	8.22	128	447	23.8	8.2	11.3	50.2
BW9	6.26	111	84	6.8	2.4	0.9	6.5
BW10	6.59	121	287	10.6	3.7	7.8	36.8
BW11	6.40	126	19	0.0	3.5	0.3	0.3
BW12	7.14	98	153	14.5	0.8	5.6	4.4
Median	6.87	93	305	13.9	1.6	7.2	8.2
Min	6.26	30	19	0.0	0.8	0.3	0.3
Max	8.22	128	586	75.3	8.2	31.9	72.5
European bottled water ^a	5.60	n.d.	668	76.3	2.5	18.9	17.8

n.e. = not established.

n.d. = not determined.

^a Median values of European bottled water (EGS, EuroGeoSurveys Geochemistry Expert Group, 2010).

subsequent part of the piedmont alluvial fan of the NCP as revealed by the cation composition of Beijing tap water, which is dominated by Ca^{2+} with increases in Mg^{2+} (Table 1, Fig. 2). The results for Miyun reservoir water plot in the cluster of the tap water samples reflecting a similar cation composition compared to the local groundwater. Also the rain water from Beijing shows a similar composition of the major cations, but a clearly lower amount of Mg^{2+} ions.

The bottled water samples show a much larger variability in the concentrations of the major cations compared to Beijing tap water (Table 2). The cation compositions range from a clear Ca^{2+} to Na^+ dominance with varying Mg^{2+} concentrations (Fig. 2). The wide compositional range in cations is caused by the different source areas of the bottled water and the distinct dominant lithologies. Generally, bottled mineral water from a specific spring is characterized by a distinct and constant chemical composition, related to the respective geological and hydrological setting. Hence, these geological and hydrological conditions show a great variety among the source locations of the bottled water analyzed for this study as reflected by the different cation compositions. The cation concentrations of all bottled water samples comply with the concentration ranges as indicated by the companies, confirming the stable chemical composition of these waters.

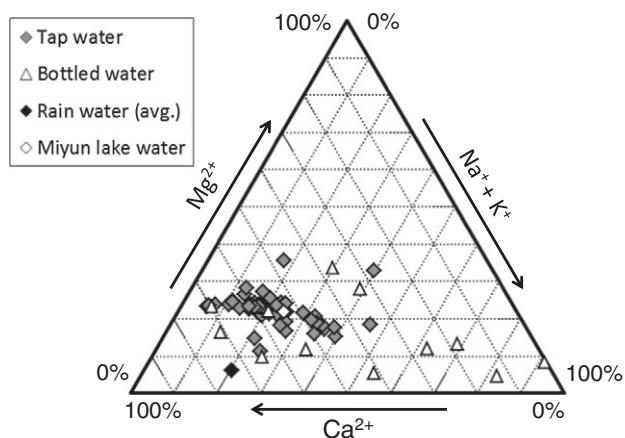


Fig. 2. Ternary diagram (Ca^{2+} , Mg^{2+} , $\text{Na}^+ + \text{K}^+$) for tap, bottled, Miyun lake and rain water (average).

4.3. Major anion compositions

4.3.1. Cl^- concentrations

Anthropogenic Cl^- sources are various, since it is one of the most widely used element in modern industrial chemistry (Eby, 2003). Natural sources of chloride can be ruled out for the Beijing area due to the lack of subsurface brines or Cl^- -rich evaporites. Also the influence of seawater by precipitation should be rather limited due to the distance of around 150 km to the East China Sea. Chloride is hydrochemically the most conservative among the common ions, since no water–rock interaction removes chloride from groundwater (Mazor, 2003). Hence, if natural sources can be ruled out, Cl^- can be used as an appropriate indicator for anthropogenic pollution on aquifers, due to the multitude of human Cl^- sources.

Chloride concentrations higher than 200 mg/L are considered to be a risk for human health and may cause an unpleasant taste of water (Versari et al., 2002). Moreover, the frequent consumption of high amounts of salt, such as NaCl, can be responsible for the development of essential hypertension and increases the risk for stroke, left ventricular hypertrophy, osteoporosis, renal stones and asthma (McCarthy, 2004).

The Beijing tap water samples show a wide range of Cl^- concentrations between 4.9 and 174.2 mg/L with a median value of 22.2 mg/L, which is clearly higher than the median value of 14.1 mg/L for European tap water (EGS, EuroGeoSurveys Geochemistry Expert Group, 2010) (Table 3). Although no sample exceeds the national guideline limit of 250 mg/L, some tap water samples from the southern and southeastern urban and suburban area (TW9, 10, 11, 46, 53) show relatively high Cl^- concentrations above 100 mg/L (Fig. 3a), which also show the highest EC values of all tap water samples analyzed for this study (Table 1). Fig. 4a reveals the strong correlation between EC and chloride concentrations suggesting the samples with the highest EC and Cl^- contents as highly affected by anthropogenic pollution.

In contrast, the Miyun lake water and Beijing precipitation reveal rather low Cl^- concentrations of 13.6 mg/L and 11.3 mg/L (average value), respectively (Table 3). The results underline that a marine influence by sea spray or Cl^- enriched marine aerosols on Beijing surface and groundwater is only minor, which is also confirmed by the results of a previous study (Xu and Han, 2009).

The Cl^- concentrations of bottled water from Beijing supermarkets vary widely from 2.0 to 56.4 mg/L (Table 4), which can be likely explained with lithological differences of the source areas of the bottled water. The maximum value is around twice the maximum value for Beijing tap water, but the median concentration for bottled water of 7.5 mg/L is clearly lower compared to the median value for Beijing tap water as well as to the median value for bottled water from Europe (18.6 mg/L) (EGS, EuroGeoSurveys Geochemistry Expert Group, 2010). Cl^- concentrations are all far below the national guideline value of 200 mg/L. Hence, the analyzed bottled water poses no health risk for the consumers with respect to dissolved chloride.

4.3.2. NO_3^- concentrations

In spite of increasing efforts to reduce nitrogen inputs into groundwater, nitrate (NO_3^-) remains one of the major pollutants of drinking water resources in many areas of the world (e.g., Widory et al., 2004). High-nitrate water poses a serious health risk, especially for children. The risk for methaemoglobinaemia in bottle-fed infants is enhanced by tap water with high nitrate concentrations, particularly in the case of simultaneous gastrointestinal infections (WHO – The World Health Organization, 2011). Methaemoglobinaemia, also known as the “blue-baby syndrome”, is caused by nitrate, which is reduced to nitrite in the infant’s stomach. The nitrite in turn oxidizes hemoglobin to methemoglobin, which is unable to transport oxygen in the veins (Sadeq et al., 2008). Consequently, the World Health Organization (WHO) and European Union (EU) have set standards for drinking water quality of 50 mg/L NO_3^- , whereas the Japanese and United States as well as the

Table 3
National guideline values for drinking water (GB 5749-2006) and anion concentrations (mg/L) of Miyun lake, Beijing rain (average) and tap water samples.

ID	NO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	F ⁻
GB 5749-2006	44	250	250	1.0
Miyun lake	5.4	45.2	13.6	0.58
Beijing rain (average) ^a	44.0	20.7	11.3	0.74
TW1	26.4	43.5	78.3	b.d.
TW2	37.1	107.2	59.8	0.22
TW3	21.1	32.4	18.9	0.32
TW4	3.5	51.0	22.5	0.32
TW5	9.3	47.4	22.0	0.34
TW6	27.4	23.7	17.2	0.38
TW7	1.4	17.0	6.4	0.28
TW8	10.5	46.1	13.7	0.28
TW9	43.0	117.9	141.9	0.32
TW10	47.6	228.8	158.6	0.18
TW11	<u>80.0</u>	117.4	138.9	0.22
TW12	19.1	42.7	41.6	0.31
TW13	0.4	16.7	18.0	0.33
TW14	0.4	10.0	4.9	0.40
TW15	8.8	13.9	8.8	0.25
TW16	9.1	42.6	19.6	0.33
TW17	19.1	13.0	18.3	0.29
TW19	2.2	26.5	6.0	0.31
TW20	5.0	20.0	7.6	0.31
TW21	4.2	48.8	20.8	0.34
TW22	3.0	47.7	20.1	0.46
TW23	18.1	33.5	18.6	0.33
TW24	2.3	28.5	9.8	0.32
TW25	2.6	28.4	8.8	0.47
TW26	20.9	31.0	22.4	0.55
TW27	9.4	46.1	18.8	0.45
TW28	39.6	65.2	76.4	0.33
TW31	3.2	49.8	21.1	0.47
TW32	23.5	30.0	19.1	0.32
TW33	11.6	44.2	21.5	0.37
TW34	21.5	45.7	26.8	0.30
TW35	13.8	60.8	28.3	0.51
TW36	38.8	89.2	56.6	0.24
TW37	15.2	62.4	33.5	0.31
TW38	<u>74.9</u>	48.4	21.7	0.47
TW39	14.8	66.2	28.3	0.29
TW40	23.8	53.7	40.5	0.51
TW41	18.6	32.5	45.8	0.43
TW42	26.1	26.7	17.9	0.34
TW43	21.3	55.5	32.9	0.43
TW44	25.8	59.2	37.7	0.44
TW45	36.4	68.2	74.5	0.50
TW46	25.8	223.0	149.6	0.71
TW47	31.2	24.1	19.7	0.52
TW48	0.6	33.4	6.1	0.45
TW49	2.3	53.4	36.9	0.43
TW50	2.3	40.2	8.1	0.58
TW51	3.2	40.6	38.0	1.13
TW52	12.1	42.2	21.3	<u>0.55</u>
TW53	<u>182.7</u>	177.3	174.2	0.34
TW54	<u>20.7</u>	65.0	37.2	0.48
TW55	33.0	78.7	54.3	0.47
TW56	10.6	43.2	21.3	0.56
TW57	28.8	108.9	66.2	0.45
TW58	45.8	46.3	60.4	0.31
TW59	<u>33.0</u>	106.9	66.3	0.53
Median	18.9	46.1	22.2	0.34 ^b
Min	0.4	10.0	4.9	b.d.
Max	182.7	228.8	174.2	1.13
Detection limit	0.05	0.01	0.01	0.004
European tap water ^c	3.9	26.9	14.1	0.09

b.d. = below detection limit.

Underlined data indicate results above drinking water guideline values.

^a Unpublished data.

^b "b.d." considered as detection limit concentration for median value calculation.

^c Median concentrations of European tap water (EGS, EuroGeoSurveys Geochemistry Expert Group, 2010).

recently established Chinese standards are 10 mg/L N_{NO₃⁻} (≈ 44 mg/L NO₃⁻) (Umezawa et al., 2009).

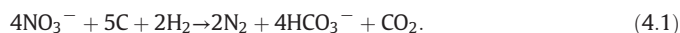
Previous studies about riverine and groundwater from the alluvial fans of the North China Plain as well as of the Taihang Mountains and Yanshan Mountains around the NCP reveal that nitrate pollution of ground- and drinking water has become a serious problem in many towns and villages in the last two decades (Ju et al., 2006; Li et al., 2008). It could be shown, that nitrate concentrations in groundwater reached maximum values up to nine times above WHO standards.

Nitrate concentrations for Beijing tap water obtained for this study range widely from 0.4 to 182.7 mg/L with a median value of 18.9 mg/L (Table 3), which is almost 5 times higher compared to the median value of 3.9 mg/L for European tap water (EGS, EuroGeoSurveys Geochemistry Expert Group, 2010). The latter one is similar to the concentration value for the Miyun lake water of 5.4 mg/L. In contrast, Beijing precipitation shows a nitrate content of 44.0 mg/L on average.

Although the majority of the tap water samples are characterized by concentrations below the national drinking water guideline limit of 44 mg/L, many samples show relatively high nitrate concentrations close to this limit. Around 46% (26 samples) of all samples reveal nitrate concentrations above 20 mg/L. Moreover, 66% (37 samples) of the tap water samples display concentrations above 10 mg/L. For comparison: concentrations above 10 mg/L occurred only in 20% of public tap water in Italy (Cidu et al., 2011). 9% (5 samples) of the Beijing tap water samples exceed the standard value up to more than 4 times with concentrations between 45.8 and 182.7 mg/L. These samples are derived from the urban and suburban area in the south (TW10, 11, 53) and northwest (TW38, 58) (Fig. 3b). Moreover, high-nitrate tap water (30–44 mg/L) could be also identified in the city center as well as from the center-near suburban area in the east and southeast.

Generally, the urban and suburban regions of Beijing, which show tap water with the highest dissolved nitrate concentrations are characterized by a relatively high population. The high population in these areas might be responsible for the release of the high amounts of dissolved nitrate and subsequent groundwater contamination. The concentration plot (Fig. 4b) reveals that tap water with increased NO₃⁻ contents show also relatively high Cl⁻ levels (except for TW38), which are interpreted as the result of human contamination. Thus, the relatively high NO₃⁻ concentrations in tap water from the urban and suburban area represent an increased health risk for the local population, primarily for infants, which may contract methaemoglobinaemia, when fed frequently by high-nitrate water. Moreover, the fact that public tap water in the Beijing urban and suburban agglomeration is commonly derived from deeper groundwater (>100 m depth) points to leakage of the shallow aquifer to the deeper groundwater. Deep groundwater pumping for the production of Beijing tap water could be the reason for the downward migration of NO₃⁻-rich water from shallow levels (Currell et al., 2010). Consequently, ongoing contamination of the deeper aquifers represents a serious threat for the future drinking water quality in the Beijing urban area.

In contrast, tap water samples from the suburban and rural area in the north, northeast and east, which host significantly less residents, show clearly lower levels of dissolved nitrate (Fig. 3b). The lowest nitrate concentrations (both 0.4 mg/L) are shown by the only two tap water samples (TW13, 14) with negative Eh values of -16 and -87 mV (Table 1) indicating reducing conditions. A reducing environment provides favorable conditions for microbial denitrifiers, which convert nitrate to N₂ using organic matter or sulfide (Clark and Fritz, 1997). This process is the stepwise reduction of nitrate (NO₃⁻) to nitrite (NO₂⁻), nitric oxide (NO), nitrous oxide (N₂O), and dinitrogen (N₂) (e.g., Sigman et al., 2001), thereby consuming organic carbon:



Hence, reducing conditions in the tap water samples TW13 and TW14 fostered the consumption of dissolved nitrate by denitrifying

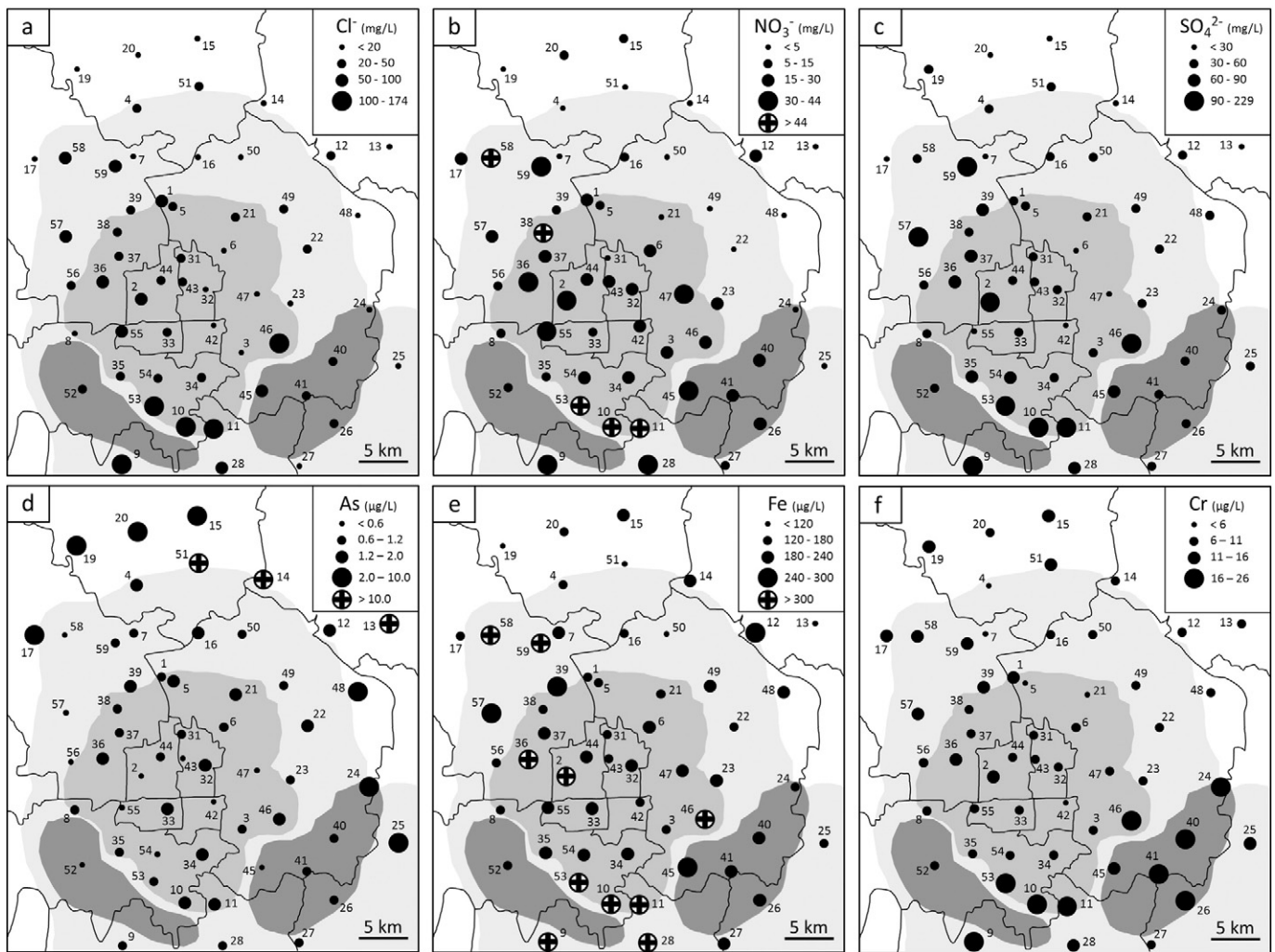


Fig. 3. Hydrochemical maps for Cl^- (a), NO_3^- (b), SO_4^{2-} (c), As (d), Fe (e) and Cr (f) concentrations in tap water. Color code for land use types as in Fig. 1.

bacteria and led to a considerable decrease of the nitrate concentration in these samples. However, aqueous environments characterized by reducing conditions represent a potential health risk, due to the possible release of contaminants, such as As, as shown by previous studies (Dou et al., 2006; Hosono et al., 2011a; Saunders et al., 2008).

In contrast to most tap water samples, the majority of bottled mineral water from Beijing supermarkets shows much lower concentrations of dissolved nitrate in a narrow range between 0.7 and 5.8 mg/L (Table 4). Only one sample (BW6) displays a much higher nitrate content (26.3 mg/L) compared to the rest of samples. All concentrations lie far below the national guideline value for natural mineral water of 44 mg/L. Also the median value of 4.1 mg/L is considerably lower compared to Beijing tap water, although almost 4 times above the median value for European bottled water of 1.1 mg/L (EGS, EuroGeoSurveys Geochemistry Expert Group, 2010). However, the high nitrate concentration of sample BW6 reveals an additional contribution by one or several sources. Due to the fact that a lithological origin of dissolved nitrate can be excluded, the nitrate contamination of sample BW6 is likely caused by agricultural or urban activities. These contaminations should be avoided and do not comply with the strict regulations for the exploitation of natural mineral water in China (MOH, 2012). Though, apart from this exception bottled water represents the healthier drinking water source with respect to dissolved nitrate compared to public tap water of Beijing. Particularly parents of infants are suggested to use rather bottled water as their daily water source for drinking and cooking

in order to avoid serious diseases for their children and babies, such as methaemoglobinaemia.

4.3.3. $\delta^{15}\text{N}_{\text{nitrate}}$ and $\delta^{18}\text{O}_{\text{nitrate}}$ for tap water and Miyun lake

In general, nitrate dissolved in surface and groundwater can originate from various sources. In urban areas municipal and industrial effluents as well as polluted precipitation represent the main nitrate sources. However, agriculture can be also a source of nitrate for urban waters due to the utilization of organic and inorganic fertilizers on farmland of the rural suburbs. Dissolved nitrate from these sources can be transported by rivers from the rural to the urban area (Choi et al., 2011). In general, different nitrate sources are characterized by their specific nitrogen ($\delta^{15}\text{N}$) and oxygen ($\delta^{18}\text{O}$) isotope signatures, and can be compared to those observed in surface and groundwater. Nitrogen and oxygen isotope ratios of dissolved nitrate have been used in numerous investigations (Deutsch et al., 2005; Hosono et al., 2010, 2011a; Yue et al., 2014a,b) to identify nitrate sources and the occurrence of microbial denitrification (nitrate reduction) under anaerobic or low-oxygen conditions, which shifts the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ signatures of the residual nitrate to higher values (e.g., Böttcher et al., 1990).

Fig. 5 shows the nitrogen and oxygen isotopic composition of dissolved nitrate from 22 of the 56 tap water samples investigated for this study as well as the isotopic ranges for the most common sources of dissolved nitrate in surface and groundwater of the Beijing area. The arrow indicates the isotopic trend in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of remaining

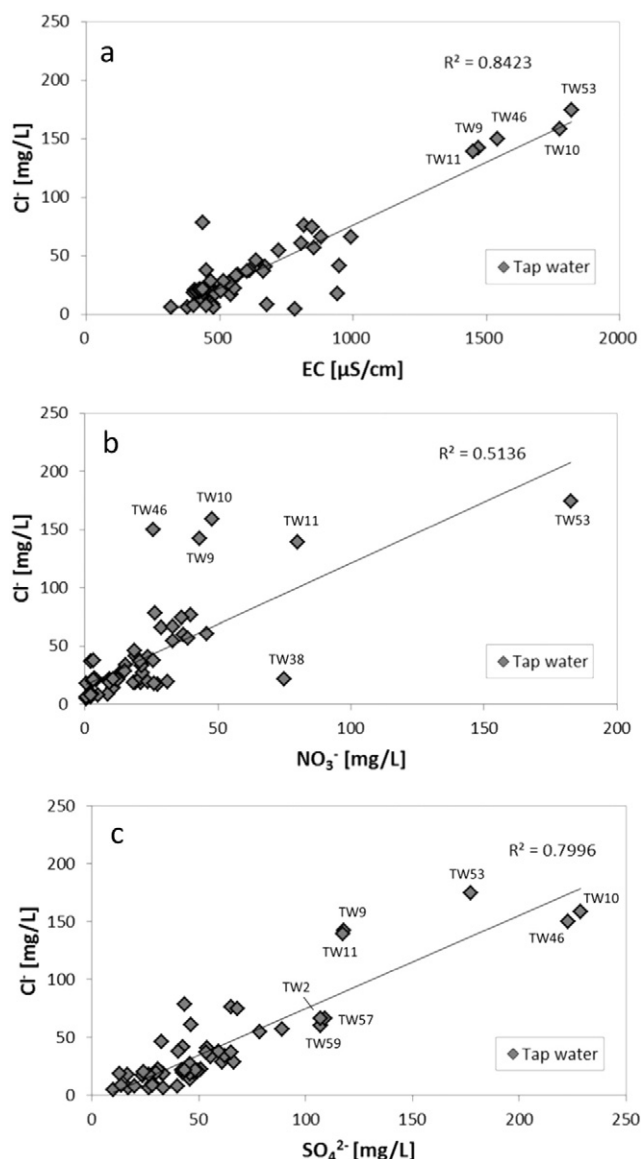


Fig. 4. Electric conductivity (EC) (a), NO_3^- (b) and SO_4^{2-} (c) concentrations vs. Cl^- concentrations for tap water.

nitrate during microbial denitrification. Tap water nitrate shows $\delta^{15}\text{N}$ values between +0.4 and +25.3‰ and $\delta^{18}\text{O}$ values between -2.7 and +13.8‰ (Table 5). This points to manure and septic waste as its predominant sources, but nitrate contributions from soil are also likely.

Due to the absence of cattle farming in the rural area around Beijing City, the data suggest wastewater from private households as the principal nitrate source. This is confirmed by the distribution map (Fig. 3b), which shows that high-nitrate tap water occurs mainly in the areas with a relatively high population. Groundwater exploited in these areas could be affected by the wastewater of the residents, which lowers the quality of the local tap water.

Urban wastewater contains usually high amounts of reduced N-containing compounds, such as ammonium (NH_4^+). During the contact with oxygen-rich water this nutrient is oxidized and increases the NO_3^- concentration by nitrification (Galloway, 2003). Rivers in urban and suburban areas receive generally high portions of raw or treated wastewater enhancing the nitrate concentration of the river water. The nitrate contaminated water can reach the aquifer through percolation and enrich the groundwater with dissolved nitrate. The dissolved nitrate concentration of groundwater can be also elevated by nitrate-rich water from leaking pipes of the public sewage network. The leakage

Table 4

National guideline values for natural mineral water (GB 8537-2008) and anion concentrations (mg/L) of bottled water samples.

ID	NO_3^-	SO_4^{2-}	Cl^-	F^-
GB 8537-2008	44	n.e.	n.e.	1.5
BW1	4.1	0.1	6.0	b.d.
BW2	4.4	8.0	2.0	0.12
BW3	5.4	20.9	8.9	0.51
BW4	5.8	41.6	17.6	0.31
BW5	3.6	47.8	56.4	0.33
BW6	26.3	18.6	36.5	1.11
BW7	4.2	13.8	9.3	0.24
BW8	1.7	35.5	5.5	1.12
BW9	1.6	2.3	2.2	0.14
BW10	1.7	5.0	10.4	0.64
BW11	0.7	1.5	3.4	0.21
BW12	4.0	4.3	5.7	0.13
Median	4.1	10.9	7.5	0.31 ^a
Min	0.7	0.1	2.0	b.d.
Max	26.3	47.8	56.4	1.12
Detection limit	0.05	0.01	0.01	0.004
European bottled water ^b	1.1	30.2	18.6	0.21

n.e. = not established.

b.d. = below detection limit.

^a "b.d." considered as detection limit concentration for median value calculation.

^b Median concentrations of European bottled water (EGS, EuroGeoSurveys Geochemistry Expert Group, 2010).

of sewer pipes is mainly caused by deterioration through age. Leakage losses represent essential factors that recharge groundwater and cause nitrate contamination (Wakida and Lerner, 2005).

Yasuhara (1998) has calculated the leakage flux of urban sewage into the ground of the Asian megacities Bangkok, Thailand (35%), Manila, Philippines (36%) and Jakarta, Indonesia (46%). This volume of sewage can make a significant contribution of dissolved ammonium and nitrate to groundwater. This effect could be even more significant for Beijing, located in a semi-arid climatic zone, due to lower annual rainfall leading to less dilution of the leaking wastewater compared to the megacities of southeast Asia, which are located in a more humid climatic zone. This is confirmed by the median nitrate concentrations of shallow groundwater (6–100 m) collected in Taipei, Taiwan (0.9 mg/L), Manila (1.2 mg/L), Bangkok (2.5 mg/L), and Jakarta (14.3 mg/L) (Hosono et al., 2011a,b; Umezawa et al., 2009). These concentrations are all below the median concentration for Beijing tap water (18.9 mg/L), which reflects the low drinking water quality in Beijing with respect to dissolved nitrate and points to the problematic situation of the local groundwater. Moreover, the subsequent pollution of the deeper groundwater by leaking shallow aquifers aggravates the situation. Hence, the combined nitrate concentration and isotope data of Beijing tap water underline the high risk of nitrate

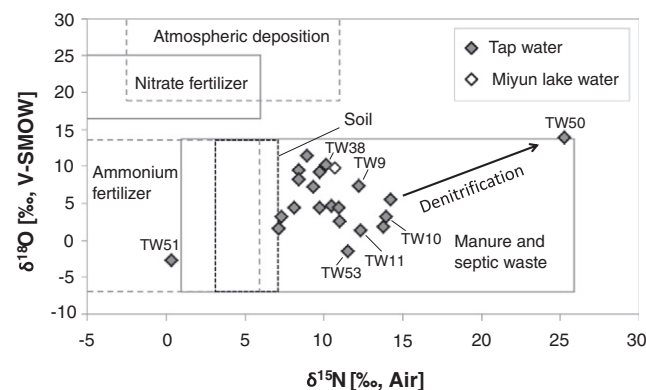


Fig. 5. $\delta^{15}\text{N}$ vs. $\delta^{18}\text{O}$ for tap and Miyun lake water. Data of possible source materials are from Kendall (1998). Errors for $\delta^{15}\text{N}$ ($\pm 0.3\text{‰}$) and $\delta^{18}\text{O}$ ($\pm 0.5\text{‰}$) are smaller than the size of the symbols.

Table 5
Isotopic compositions (‰) of dissolved nitrate and sulfate from Miyun lake, Beijing rain (average) and tap water samples.

ID	$\delta^{15}\text{N}_{\text{nitrate}}$	$\delta^{18}\text{O}_{\text{nitrate}}$	$\delta^{34}\text{S}_{\text{sulfate}}$	$\Delta^{33}\text{S}_{\text{sulfate}}$	$\delta^{18}\text{O}_{\text{sulfate}}$
Miyun lake	10.7	9.6	8.0	−0.034	6.0
Beijing rain (average) ^a			4.5	−0.129	12.6
TW1	8.1	4.4	8.1	−0.045	5.9
TW2					
TW3	7.3	3.2	6.7	−0.013	5.0
TW4	8.9	11.4	7.8	−0.049	6.3
TW5	8.4	9.4			
TW7	9.8	9.2	7.9	−0.041	6.5
TW9	12.2	7.4	9.9	−0.043	7.1
TW10	14.0	3.2	6.4	−0.037	5.5
TW11	12.3	1.4	8.2	−0.046	5.3
TW12			8.7		6.0
TW18			8.9		5.9
TW19			7.6		3.2
TW20	9.7	4.4			
TW23			8.7	−0.05	5.4
TW24	7.2	1.6			
TW25			13.1	−0.030	7.2
TW26			11.1	−0.034	5.7
TW27			7.8	−0.051	5.4
TW28	14.3	5.5	6.6	−0.034	4.9
TW29			15.1	−0.006	
TW32			8.7	−0.057	5.4
TW33			8.2	−0.047	5.9
TW34			9.2	−0.029	6.0
TW36			11.3	−0.036	5.9
TW38	10.2	10.2	7.9	−0.018	6.3
TW40	13.8	1.7			
TW41			10.2	−0.038	6.1
TW42	7.1	1.6			
TW44	9.3	7.2	7.5	0.057	5.6
TW46			−4.7	−0.095	4.4
TW48			31.6	0.026	15.3
TW49	10.5	4.6	15.4	−0.043	9.1
TW50	25.3	13.8	22.5		13.0
TW51	0.4	−2.7	17.5		10.6
TW52			7.6	−0.031	5.9
TW53	11.6	−1.5			
TW54			9.7		5.3
TW55	11.0	4.4	9.9	−0.049	5.5
TW56	11.0	2.6	7.7	−0.035	4.5
TW57			10.8	−0.024	6.7
TW58	8.4	8.2	10.2		5.1
TW59			8.1	−0.047	4.6

^a Unpublished data.

contamination by urban wastewater for aquifers beneath Asian megacities.

Only one sample (TW51), which displays the lowest $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values, is located in the compositional field for ammonium fertilizer (Fig. 5). This sample is derived from a rural site of Beijing, which is characterized by agricultural activities. The sample may have experienced some contribution of fertilizers utilized in this area, which are rich in NH_4^+ and elevate the nitrate concentration of the local tap water. Another sample (TW50) showing the highest $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ signatures may be characterized by microbial denitrification. However, although the NO_3^- concentration of this sample is relatively low (2.3 mg/L), the Eh value of 92 mV rather points to oxic than reducing conditions as favored by microbial denitrification, although nitrate reduction is possible even at higher Eh values (Rivett et al., 2008). The two samples with the lowest Eh values (TW14, 13) show also the lowest nitrate concentrations (both 0.4 mg/L), which were unfortunately too low for isotope analyses.

The data point for water from the Miyun dam lake with a $\delta^{15}\text{N}$ value of +10.7‰ and a $\delta^{18}\text{O}$ value of +9.6‰ (Table 5) plots in the cluster for tap water (Fig. 5) and reveals that even the last surface water reservoir in the Beijing area is probably affected by wastewater, although the nitrate concentration is relatively low. This wastewater might be derived from villages surrounding the lake or delivered by the tributaries.

Beijing rain water was not analyzed on N and O isotopes of dissolved nitrate.

4.3.4. SO_4^{2-} concentrations

Sulfur in natural surface and groundwater is primarily present as oxidized sulfate (SO_4^{2-}). Dissolved sulfate can have several natural and anthropogenic sources. Although SO_4^{2-} is considered as one of the least toxic anions, the frequent uptake of high amounts of sulfate may generate catharsis, dehydration and gastrointestinal irritation (Saleh et al., 2001). Moreover, the oxidation of pyrite to sulfate may lead to an intensive input of sulfate into natural waters and triggers water acidification and subsequent heavy metal release into the water environment (Norton and Vesely, 2003). Acidified tap water may also cause a release of metals from the pipeline system into the water and represents a serious health risk, when consumed frequently.

The sulfate concentrations of all tap water samples is below the national drinking water guideline limit of 250 mg/L and reach levels in a wide range between 10.0 and 228.8 mg/L with a median value of 46.1 mg/L (Table 3), which is clearly above the median value of European tap water with 26.9 mg/L (EGS, EuroGeoSurveys Geochemistry Expert Group, 2010) and Italian tap water with 26.8 mg/L (Dinelli et al., 2012). The tap water median value matches the sulfate concentration for water from the Miyun lake (45.2 mg/L), but is higher compared to the average value for rain water (20.7 mg/L). Fig. 3c reveals that the samples with the highest sulfate concentrations above 90 mg/L (TW2, 9, 10, 11, 46, 53, 57, 59) are mainly collected in the urban and suburban south, southeast and northwest, which show also relatively high concentrations of dissolved nitrate (except TW57). Moreover, particularly the samples from the south (TW9, 10, 11, 53) and southeast (TW46) display high Cl^- abundances (Fig. 4c) and were already characterized as highly affected by anthropogenic pollution, namely urban sewage, indicated by the concentrations and isotopic compositions of NO_3^- .

Furthermore, the two samples with the lowest nitrate concentrations (TW13, 14) belong to the four samples with the lowest sulfate concentrations. The very low sulfate and nitrate concentrations in the samples TW13 and TW14 might be caused by the redox conditions of the tap water. Both samples show negative Eh values, which point to reducing conditions (Table 1). Beside microbial denitrifiers, reducing conditions are also a suitable environment for sulfate reducing bacteria. In such anaerobic environments sulfate reducing microbes utilize dissolved sulfate as an electron acceptor during the oxidation of organic matter (Kendall and Doctor, 2003). This process is also known as bacterial sulfate reduction (BSR), which is characterized by the following reaction:



Thus, the low nitrate and sulfate concentrations in the tap water samples TW13 and TW14 suggest the activity of both sulfate and nitrate reducing bacteria caused by the negative redox potential.

Bottled water analyzed for this study reveals clearly lower SO_4^{2-} concentrations compared to tap water in the range from 0.1 to 47.8 mg/L (Table 4). This is also shown by the median value of 10.9 mg/L, which is lower than one fourth compared with the median value of Beijing tap water. Moreover, the median value for bottled water from Beijing is around one third of the median value of bottled water (30.2 mg/L), which can be purchased in Europe (EGS, EuroGeoSurveys Geochemistry Expert Group, 2010). The relatively wide range of dissolved sulfate concentrations in the bottled water samples of around two orders of magnitude might be related to the distinct lithological composition of the respective aquifers.

4.3.5. $\delta^{34}\text{S}_{\text{sulfate}}$ and $\delta^{18}\text{O}_{\text{sulfate}}$ for tap water and Miyun lake

Stable sulfur and oxygen isotopes of dissolved sulfate have been used as tracers for both natural and anthropogenic sulfate in rainwater, river water, sea water, rocks (oxidation of sulfide minerals, sulfate

minerals, soil sulfate) and pollutants (sewage, agrochemicals, detergents and sulfate of industrial origin) in numerous studies (Brenot et al., 2007; Hosono et al., 2010, 2011a,b; Li et al., 2014; Robinson and Bottrell, 1997). The $\delta^{34}\text{S}/\delta^{18}\text{O}$ plot (Fig. 6a) shows that each sulfate source is characterized by an individual range in $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$, which may overlap (Krouse and Mayer, 2000). Anthropogenic sources (chemical fertilizers and detergents, emissions from industry and traffic in atmospheric deposition) can be distinguished from natural sources (soil, oxidation of sulfide minerals).

Next to source identification, sulfur and oxygen isotopic compositions can be used to identify biogeochemical processes, such as bacterial sulfate reduction, in surface and subsurface waters, which may be induced by the infiltration of pollutants. The identification of these processes is relevant, because bacterially-mediated redox reactions can change the redox conditions and acidity in aqueous media significantly and govern the natural attenuation of contaminants, such as NO_3^- and SO_4^{2-} , as well as the release of heavy metals into the water. Under anaerobic conditions sulfate reducing microorganisms use SO_4^{2-} as an electron acceptor for respiration. This reaction results in the production of isotopically light H_2S (Canfield, 2001) and an enrichment in both $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ in the residual SO_4^{2-} due to isotopic fractionation (Dogramaci et al., 2001).

Sulfur and oxygen isotope measurements for sulfate from 34 tap water samples yielded $\delta^{34}\text{S}$ values between -4.7 and $+31.6\%$ and $\delta^{18}\text{O}$ values between $+3.2$ and $+15.3\%$ (Table 5). In the $\delta^{34}\text{S}/\delta^{18}\text{O}$ diagram (Fig. 6a) the isotopic composition of the majority of the tap water samples plot on or close to the fields of sulfate from atmospheric deposition and soil indicating that precipitation and soil in the Beijing area may represent sulfate sources for groundwater in the Beijing area. However, the isotopic composition of SO_4^{2-} from 3 river water samples (unpublished data) collected in the Beijing area at the discharge mouths of sewage pipes plot at the major cluster of tap water sulfate and can be used as endmember compositions for sulfate dissolved in urban sewage

of Beijing. Apparently, SO_4^{2-} from many tap water samples shows similar S and O isotopic compositions indicating urban wastewater as the major source of dissolved sulfate for Beijing tap water and confirming the major influence of sewage on Beijing ground- and tap water based on the concentration and isotope data for NO_3^- . However, minor additions of sulfate from precipitation and soil are likely. Hence, the combined results for NO_3^- and SO_4^{2-} underline that high amounts of sewage infiltrate the Beijing subsurface, probably caused by leakage of the pipeline network. This represents a significant source of contaminants for the local aquifers.

The sample from the Miyun dam lake shows a similar isotopic composition as Beijing tap water with a $\delta^{34}\text{S}$ value of $+8.0\%$ and a $\delta^{18}\text{O}$ value of $+6.0\%$ (Table 5) and plots in the tap water cluster (Fig. 6a) suggesting an influence of public sewage as previously suggested based on the isotopic composition of dissolved nitrate. However, atmospheric deposition may have also contributed to the sulfate pool in the Miyun lake. Beijing rain water samples collected in different seasons reveal average isotopic compositions of $+4.5$ and $+12.6\%$ in $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$, respectively, and plot in the field for atmospheric deposition. Sulfate containing particles and gases in the Beijing atmosphere are predominantly derived from emissions by industry, power plants, domestic heating and traffic (Li et al., 2011). A high portion of dissolved sulfate in the Beijing precipitation originates from these anthropogenic particles and gases and, consequently, shows a different sulfur and oxygen isotopic composition compared to Beijing tap water and water from the Miyun lake.

Several samples display sulfur and oxygen isotopic signatures, which do not match the composition of sulfate from Beijing sewage, atmospheric deposition or any other source material (Fig. 6a). Most of these samples form an array towards both higher $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values crossing the field for chemical detergents at the upper end. Though, most of these samples with the highest $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values show rather low sulfate concentrations below the median value of 46.1 mg/L (Table 3). This is contrary to a contribution of sulfate from additional sources, such as chemical detergents, which suggest rather higher than lower sulfate concentrations. The relatively low sulfate concentrations combined with the high $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values are suggested to be the result of bacterial sulfate reduction (BSR). This is confirmed by the very low concentrations of dissolved nitrate in these samples, since the reduction of nitrate and sulfate require comparable redox-conditions. Moreover, the sample with the second highest $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values (TW50) shows also the highest $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values. The nitrate concentration of the sample with the highest $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ (TW48) was too low for analyses of N and O isotopes.

However, the Eh values of these samples are all positive indicating rather oxidizing than reducing conditions. This may be caused by oxygenation of the water during withdrawal of the groundwater and supply to the households. The reaction of dissolved sulfide produced by BSR with dissolved metals and subsequent metal sulfide precipitation in the aquifer could have removed the sulfide from the water, so that the remaining sulfate retained its heavy isotopic composition. Unfortunately, the concentrations of dissolved sulfate of the samples TW13 and TW14 with negative Eh values were not high enough to allow isotope measurements.

4.3.6. $\Delta^{33}\text{S}_{\text{sulfate}}$ for tap water and Miyun lake

Next to $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ measurements the determination of the $\Delta^{33}\text{S}$ values was carried out for 27 tap water samples. The $\Delta^{33}\text{S}$ value represents an advanced tool in sulfur isotope geochemistry, which provides a deeper insight into chemical reactions in aqueous systems. Previous studies have shown that multiple sulfur isotope data can be used to distinguish between different organic and inorganic reactions in marine and hydrothermal environments (Ono et al., 2007; Peters et al., 2010, 2011). We applied this method for the first time on dissolved sulfate from tap water.

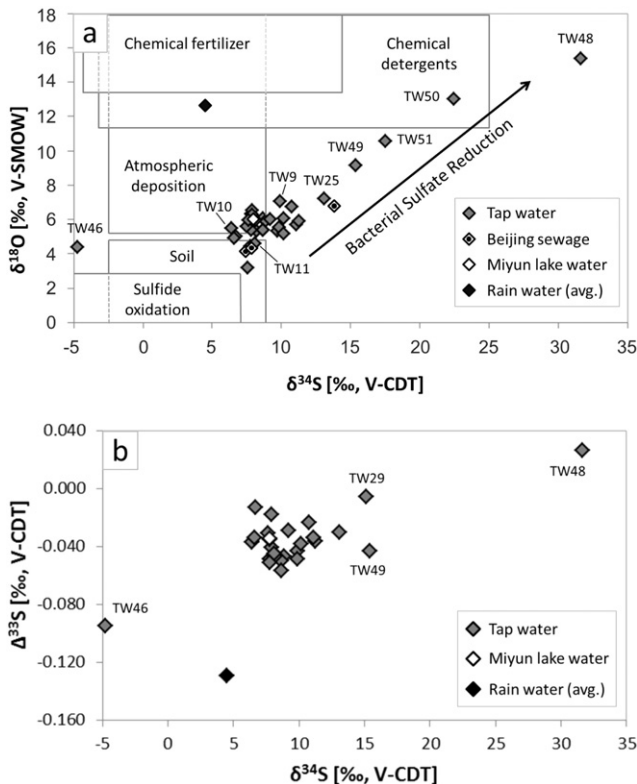


Fig. 6. $\delta^{34}\text{S}$ vs. $\delta^{18}\text{O}$ (a) and vs. $\Delta^{33}\text{S}$ (b) for tap, Miyun lake and rain water (average) as well as Beijing sewage. Data of possible source materials in (a) are from Krouse and Mayer (2000) (except for Beijing sewage). Errors for $\delta^{34}\text{S}$ ($\pm 0.3\%$) and $\delta^{18}\text{O}$ ($\pm 0.5\%$) are smaller than the size of the symbols. Errors for $\Delta^{33}\text{S}$ ($\pm 0.008\%$) are not shown.

Sulfate from Beijing tap water shows a relatively wide range in $\Delta^{33}\text{S}$ from -0.095 to $+0.026\%$ (Table 5). Miyun lake water sulfate reveals a $\Delta^{33}\text{S}$ value of -0.035% and plots in the major cluster for tap water in the $\delta^{34}\text{S}/\delta^{18}\text{O}$ diagram (Fig. 6b). In contrast, Beijing rain water displays a $\Delta^{33}\text{S}$ value of -0.129% in average, much lower and clearly distinguishable from sulfate of the majority of Beijing tap water as well as the Miyun lake. Different to Beijing tap water or water from the Miyun reservoir, sulfate from Beijing rain is mainly derived from emissions enriched in combustion products from industries and traffic. Thus, the different sulfate sources for Beijing precipitation are also reflected by the different abundances of the rare sulfur isotope ^{33}S , next to the common sulfur (^{32}S , ^{34}S) and oxygen (^{16}O , ^{18}O) isotopes.

The sulfate from some tap water samples shows compositions with a coarse trend to higher $\delta^{34}\text{S}$ with higher $\Delta^{33}\text{S}$ values as well as to lower $\delta^{34}\text{S}$ with lower $\Delta^{33}\text{S}$ values (Fig. 6b). Consequently, the sample with the highest $\delta^{34}\text{S}$ value of $+31.6\%$ (TW48) displays the highest $\Delta^{33}\text{S}$ value with $+0.026\%$, whereas the sample with the lowest $\delta^{34}\text{S}$ value of -4.7% (TW46) shows the lowest $\Delta^{33}\text{S}$ value with -0.095% . As mentioned above biological processes such as bacterial sulfate reduction affect the sulfur isotopic composition of the residual sulfate as well as the produced sulfide. Bacterial sulfate reduction is a multistep process (Brunner and Bernasconi, 2005; Johnston et al., 2007) and the fractionation factor between product (sulfide) and substrate (sulfate) depends on the magnitude of the isotope effects on ^{33}S and ^{34}S , that are intrinsic to each enzymatic reaction as well as on the relative rates of the mass flow at each branching point as shown by laboratory experiments with sulfate reducing microbes (Farquhar et al., 2007; Johnston et al., 2005). Apart from the well-known ^{34}S depletion, one characteristic feature of this flow network is that the residual sulfate yields negative $\Delta^{33}\text{S}$ values relative to the starting sulfate as well as to the produced sulfide. This has been recently confirmed by a multiple isotope study on hydrothermal barite (Eickmann et al., 2014). In contrast, the sulfur isotopic compositions for dissolved sulfate from Beijing tap water presented in this study show rather the opposite: the sulfate with the highest $\delta^{34}\text{S}$ value suggesting the highest portion of remaining sulfate from BSR shows the most positive $\Delta^{33}\text{S}$ value. In addition, the dissolved sulfate with the lowest $\delta^{34}\text{S}$ value interpreted as sulfate, which shows some contribution from re-oxidized sulfide from BSR, displays the lowest $\Delta^{33}\text{S}$ value. This is also in contrast to our expectation, because sulfide in hydrothermal areas produced by sulfate reducing microbes is characterized by positive $\Delta^{33}\text{S}$ values (e.g., Peters et al., 2011). So far, multiple sulfur isotope analyses on residual sulfate from BSR have been applied only for sulfate used in lab experiments or for sulfate from the marine or hydrothermal environment. In contrast, in this study we present for the first time multiple sulfur isotope compositions of sulfate from tap water, which is mainly derived from groundwater. This terrestrial environment is characterized by different physical and chemical conditions compared to the marine and hydrothermal environment and, hence, may host different types of sulfate reducing bacteria with different metabolic features. These different metabolic processes may lead to distinct $\Delta^{33}\text{S}$ signatures for both the produced sulfide and the residual sulfate. However, additional work has to be carried out in future in order to confirm these assumptions.

4.3.7. F^- concentrations

Sources of fluoride are predominantly natural and represented by loess, paleosols and rocks, which are rich in F^- containing minerals (e.g., fluorite, cryolite, fluorapatite), as well as salt lakes and sea water (Currell et al., 2011). Moreover, industrial emissions may enhance the fluoride concentration of local air, atmospheric deposition, water and soil (Brindha and Elango, 2011; Farooqi et al., 2007). Excessive fluoride in human bodies may cause dental and/or skeletal fluorosis, and harm the kidneys, nerves and muscles (WHO – The World Health Organization, 2011).

Beijing tap water shows F^- concentrations between <0.004 (detection limit) and 1.13 mg/L (Table 3). Although one sample (TW51)

reveals a concentration above the national guideline limit of 1.00 mg/L, the median value of 0.34 mg/L is significantly lower compared to the guideline value. Hence, the F^- content in the tap water of Beijing does not represent a serious health risk for the local population. However, the median value of Beijing tap water is almost 4 times higher than the median value of European tap water with 0.09 mg/L (EGS, EuroGeoSurveys Geochemistry Expert Group, 2010).

The Miyun lake water and Beijing precipitation reveal moderate F^- concentration of 0.58 mg/L and 0.74 mg/L (Table 3), respectively.

The bottled water samples from Beijing reveal a similar range in the F^- concentrations compared to Beijing tap water with values between <0.004 (detection limit) and 1.12 mg/L water (Table 4). All samples show concentrations below the national guideline value for natural mineral water of 1.50 mg/L. The median content of 0.31 mg/L is only slightly higher than the median concentration of European bottled water with 0.21 mg/L (EGS, EuroGeoSurveys Geochemistry Expert Group, 2010). Hence, the low to moderate F^- levels in most of both Beijing tap and bottled water neither represent a health risk for the local population nor allow a recommendation for one of the drinking water sources with respect to F^- .

4.4. Concentrations of metals and trace elements in tap and bottled water

Many heavy metals and trace elements are highly toxic for humans and may cause several types of cancer next to other negative health effects, such as skin, kidney or vascular diseases (WHO – The World Health Organization, 2011). Most natural sources of these compounds are geogenic, whereas the most important anthropogenic sources are represented by industry (e.g., smelters, metal manufacturers, coal combustion) and agriculture (agrochemicals). The results of the tap water analyses reveal partly wide ranges of the metal and trace element concentrations. In total 17 concentration values exceed the respective limits of the national drinking water guideline for As (3 samples), Fe (10 samples), Mn (3 samples) and Zn (1 sample). 75% (42 samples) of the tap water samples comply with the national standards, whereas 25% (14 samples) reveal at least one concentration value exceeding a standard limit. Except for Cu and Zn the median contents of all trace elements are above the median concentrations of European tap water.

Beijing tap water analyzed for our study exhibits As concentrations between 0.32 and 51.02 $\mu\text{g}/\text{L}$ (Table 6). The tap water of 3 samples shows As levels exceeding the national standard value up to more than 5 times and represents an increased health risk for the consumers, since the frequent ingestion of high As doses may cause several types of cancer (skin, lung, bladder, kidney) and serious skin diseases (WHO – The World Health Organization, 2011). Moreover, the median value of 1.07 $\mu\text{g}/\text{L}$ is significantly higher than the median value for European tap water of 0.19 $\mu\text{g}/\text{L}$ (EGS, EuroGeoSurveys Geochemistry Expert Group, 2010). Due to its redox sensitivity As is primarily released to groundwater under reducing conditions (Saunders et al., 2008), particularly in shallow aquifers at young (Quaternary) alluvial deltaic sediments, such as at the North China Plain. All tap water samples with relatively high arsenic concentrations above 2 $\mu\text{g}/\text{L}$ are collected in the outlying suburban and rural area of Beijing (Fig. 3d). In these areas groundwater is mainly derived from shallow depths of not more than 100 – 120 m (Dou et al., 2006) compared to the deeper origin of the groundwater (>100 m) for the tap water production in urban Beijing. In contrast to the deeper aquifers of the Beijing Plain, which consist mainly of coarse-grained sand–pebble–gravel associations (Zhou et al., 2012), the shallow alluvial sediments consist of fine-grained sediments and clays with sulfide minerals and organic matter are suggested to contain substantial amounts of As (Plant et al., 2003). Consequently, the elevated arsenic contents in the tap water of rural Beijing are probably caused by its origin from shallow As-rich aquifers. However, a contribution of As to the rural groundwater by agrochemicals (herbicides, pesticides) cannot be ruled out.

Table 6

National guideline values for drinking water (GB 5749-2006) and concentrations ($\mu\text{g/L}$) of heavy metals and trace elements of Miyun lake, Beijing rain (average) and tap water samples.

ID	Al	As	Co	Cr	Cu	Fe	Mn	Ni	Pb	Se	V	Zn
GB 5749-2006	200	10	n.e.	50 ^a	1000	300	100	20	10	10	n.e.	1000
Miyun lake	15.91	1.43	0.08	4.04	1.48	118.8	0.87	2.00	0.19	0.52	1.19	20.38
Beijing rain (average) ^b	46.19	1.84	0.27	2.32	5.56	51.8	41.71	1.85	1.01	2.26	2.19	38.69
TW1	117.25	0.66	0.27	15.47	2.42	160.3	1.54	3.20	0.36	1.30	0.91	23.79
TW2	76.58	0.45	0.17	15.61	3.47	425.9	1.93	2.23	0.62	3.77	b.d.	45.17
TW3	34.59	1.10	0.12	7.40	1.85	176.2	0.46	1.90	0.16	1.31	1.07	11.24
TW4	14.76	1.27	0.09	5.15	3.43	166.4	7.09	1.70	0.08	0.92	0.25	26.81
TW5	57.51	1.61	0.09	4.33	2.27	134.2	3.65	1.60	0.14	0.79	0.92	7.31
TW6	16.22	0.94	0.15	9.14	0.67	192.1	0.54	2.04	0.12	0.97	1.20	21.25
TW7	17.85	0.88	0.11	0.59	0.68	183.0	8.38	1.88	0.55	1.28	0.19	273.11
TW8	84.49	1.03	0.15	6.57	0.62	161.1	0.17	1.62	0.30	1.42	0.97	12.30
TW9	12.57	1.08	1.16	17.25	1.00	521.3	16.03	4.97	0.75	3.72	1.23	1203.48
TW10	7.32	1.61	0.36	23.77	8.19	706.3	0.47	6.11	0.47	4.39	2.30	33.74
TW11	7.12	1.34	0.29	19.36	1.25	569.5	0.50	5.00	0.17	4.07	2.17	7.36
TW12	17.55	1.29	0.29	10.17	0.86	277.6	1.00	3.32	0.22	1.97	1.63	16.08
TW13	11.97	51.02	0.06	9.16	0.93	91.1	54.16	0.84	0.18	0.98	b.d.	10.61
TW14	15.24	20.49	0.06	9.42	0.60	192.7	114.35	1.10	0.18	0.87	b.d.	2.93
TW15	29.19	2.64	0.09	12.20	0.93	208.9	1.79	2.56	0.26	1.08	2.22	13.10
TW16	90.36	1.36	0.10	6.11	0.64	173.7	1.11	1.84	0.18	1.69	0.76	23.68
TW17	8.31	2.19	0.07	13.34	0.35	171.9	2.70	1.57	0.23	1.53	3.03	4.15
TW19	7.97	2.87	0.05	12.05	0.47	114.5	0.42	1.16	0.29	0.64	5.20	2.90
TW20	6.14	2.87	0.06	10.49	0.28	142.5	0.22	1.51	0.15	0.90	3.44	23.94
TW21	86.51	1.34	0.08	5.02	0.43	143.0	0.89	1.37	0.12	1.38	0.51	4.59
TW22	91.62	1.37	0.09	6.06	0.52	161.9	1.32	1.58	0.22	1.44	0.47	10.09
TW23	28.02	1.05	0.12	8.29	4.10	183.8	0.41	1.88	0.32	1.36	0.88	33.99
TW24	6.18	2.51	0.05	26.63	0.84	133.2	1.03	1.28	0.13	1.29	5.58	5.15
TW25	7.10	2.27	0.06	11.61	0.36	155.4	10.15	1.30	0.23	2.07	5.76	55.84
TW26	5.83	1.06	0.08	20.53	2.36	185.8	0.09	1.72	0.28	1.46	3.54	11.01
TW27	146.64	1.11	0.12	7.38	1.08	205.9	1.20	2.52	0.36	1.35	0.68	29.36
TW28	3.56	1.17	0.16	14.24	0.84	345.1	1.86	3.23	0.61	3.03	1.89	166.50
TW31	38.59	1.06	0.11	7.52	0.40	172.1	2.75	2.40	0.44	1.27	0.35	743.00
TW32	26.82	1.25	0.14	9.80	0.45	208.4	0.87	3.05	0.31	1.63	1.11	26.81
TW33	30.20	1.21	0.12	7.72	1.24	182.5	1.45	3.03	0.14	1.56	0.81	9.44
TW34	38.21	1.24	0.15	10.30	0.83	221.1	1.07	3.47	0.60	2.39	1.04	64.61
TW35	39.32	1.01	0.14	8.11	0.54	207.7	2.31	2.59	0.34	3.12	0.66	173.51
TW36	38.31	1.43	0.22	14.95	0.73	329.8	0.54	3.35	0.19	4.21	1.56	18.17
TW37	26.30	0.93	0.13	9.78	0.50	225.2	1.40	2.29	0.06	2.81	0.49	11.05
TW38	33.22	1.01	0.10	6.86	0.71	169.3	3.28	2.86	0.23	1.78	0.25	14.64
TW39	6.35	1.42	0.12	11.69	0.90	250.9	0.54	3.12	0.16	2.09	2.35	24.49
TW40	6.85	0.80	0.09	16.39	3.04	210.3	0.52	2.03	0.21	1.66	1.79	14.52
TW41	3.64	0.74	0.10	16.21	0.62	246.5	1.77	2.70	0.33	1.62	3.09	193.26
TW42	17.90	0.43	0.10	4.46	0.46	159.0	0.23	1.52	0.11	0.84	1.06	12.87
TW43	35.83	0.55	0.11	6.18	b.d.	166.0	0.52	1.60	0.05	1.49	0.91	7.33
TW44	33.85	0.60	0.13	6.13	b.d.	189.1	1.00	1.47	0.10	1.57	0.97	14.70
TW45	16.30	0.38	0.14	13.18	b.d.	245.8	0.07	2.19	0.27	1.30	1.56	4.62
TW46	15.31	1.83	0.30	17.59	0.08	351.2	217.51	2.37	0.13	1.84	2.97	5.90
TW47	17.02	0.44	0.11	8.85	5.62	189.7	0.55	1.38	0.41	0.70	1.31	14.48
TW48	30.00	3.54	0.05	8.14	b.d.	217.1	101.23	0.86	0.05	0.75	b.d.	1.92
TW49	45.20	1.05	0.08	10.71	b.d.	186.7	1.23	1.22	0.29	1.07	2.86	9.58
TW50	43.25	1.05	0.04	10.59	0.16	112.0	0.47	0.78	0.33	0.57	3.60	7.46
TW51	19.54	46.94	0.05	11.44	0.98	103.2	17.80	1.02	0.23	0.94	2.66	65.53
TW52	38.19	0.47	0.09	6.88	b.d.	152.9	0.36	1.21	0.27	1.16	0.63	48.93
TW53	44.11	1.04	0.32	21.00	1.23	586.4	1.37	3.64	0.33	5.97	2.06	13.43
TW54	56.17	0.57	0.12	9.72	1.24	192.8	1.94	1.51	0.37	1.76	0.85	11.41
TW55	29.26	0.55	0.16	9.42	b.d.	217.6	2.04	1.37	0.17	2.44	0.89	7.32
TW56	40.78	0.32	0.10	6.30	b.d.	151.7	0.06	1.14	0.17	1.11	0.49	27.51
TW57	16.77	0.44	0.21	11.20	3.05	285.2	7.34	1.80	0.30	2.60	0.83	36.02
TW58	11.70	0.52	0.16	12.58	b.d.	339.6	1.21	2.06	1.48	1.11	1.36	836.37
TW59	4.23	0.69	0.15	14.31	b.d.	305.9	1.30	1.98	0.16	2.71	2.29	15.13
Median	26.56	1.07	0.12	9.99	0.68 ^b	189.4	1.22	1.88	0.23	1.45	1.07 ^c	14.67
Min	3.56	0.32	0.04	0.59	b.d.	91.1	0.06	0.78	0.05	0.57	b.d.	1.92
Max	146.6	51.02	1.16	26.63	8.19	706.3	217.51	6.11	1.48	5.97	5.76	1203.5
Detection limit	0.001	0.01	0.001	0.01	0.001	0.01	0.01	0.01	0.001	0.01	0.01	0.01
European tap water ^d	2.47	0.19	0.02	0.19	5.65	3.2	0.54	0.38	0.12	0.12	0.17	23.50

b.d. = below detection limit.

Underlined data indicate results above drinking water guideline values.

n.e. = not established.

^a Only for Cr⁶⁺.^b Unpublished data.^c "b.d." considered as detection limit concentration for median value calculation.^d Median concentrations of European tap water (EGS, EuroGeoSurveys Geochemistry Expert Group, 2010).

In contrast to As, Fe-rich drinking water does not represent a serious risk for human health. However, high concentrations of Fe in tap water can cause unpleasant color, odor and taste of drinking water and stain laundry and parts of the distribution system (Virkunyte and Sillanpää, 2006). Concentrations of total Fe in Beijing tap water range from 91.1 to 706.3 $\mu\text{g/L}$ (Table 6) and exceed the national guideline value in 10 samples, which account for around 18% of the tap water samples analyzed for this study. The median value of 189.4 $\mu\text{g/L}$ is almost 60 times the median concentration of European tap water of 3.2 $\mu\text{g/L}$ (EGS, EuroGeoSurveys Geochemistry Expert Group, 2010). Most of the tap water samples with the relatively high Fe concentrations ($>240 \mu\text{g/L}$) are taken in the urban and suburban south, southeast and northwest of Beijing (Fig. 3e). The samples with the highest Fe abundances in the south (TW9, 10, 11, 53) as well as TW46 in the southeast are suggested to have received substantial contributions by urban sewage based on the Cl^- concentrations. This can be also suggested for the total Cr concentrations in Beijing tap water, which show values between 0.59 and 26.63 $\mu\text{g/L}$ (Table 6). All concentrations lie below the national guideline value of 50 $\mu\text{g/L}$. However, the median value of 9.99 $\mu\text{g/L}$ is almost 50 times the median value for European tap water (EGS, EuroGeoSurveys Geochemistry Expert Group, 2010). The clear trend of the Cr and Fe concentrations (Fig. 7) for the samples from the south (TW9, 10, 11, 53) and southeast (TW46) also indicates that the Cr in these samples is mainly derived from sewage. Moreover, the Cr–Fe-plot reveals that both the high Fe tap water from the northwest (TW36, 58, 59) as well as the water of TW28 from the south lie on the same trend line with a slope of ~ 34 indicating an influence of urban wastewater on the heavy metal composition of these samples. The samples from the southeast with high Cr concentrations (TW24, 26, 40, 41) do not show any correlation with Fe, which points to a distinct source of Cr in these samples. The distribution map (Fig. 3f) shows, that these samples were collected in the southeastern part of the industrial belt suggesting the numerous metal utilizing industries based in this area as the major Cr source. Interestingly, the Cr–Fe-plot (Fig. 7) reveals another array of data points with a slope of ~ 10.7 distinct to the one for the samples affected by urban sewage. These tap water samples show only low to moderate Cr ($<11 \mu\text{g/L}$) and Fe ($\leq 221 \mu\text{g/L}$) contents and were collected all over Beijing. The clear Cr–Fe-trend might be caused by interactions of the tap water with the distribution system releasing both Cr and Fe to tap water in a relatively constant ratio but lower amounts compared to urban wastewater or the manufacturing industry at Beijing's periphery.

Next to As and Fe, only Mn and Zn show concentrations above the national guideline limits (Table 6). However, elevated Mn and Zn levels in drinking water are not harmful to humans similar to Fe and the number of samples with high Mn and Zn concentrations is rather small. Hence, these heavy metals do not represent a health risk for the Beijing residents consuming local tap water. Moreover, all bottled water samples analyzed for this study exhibit metal and trace element concentrations below the

national guideline limits for natural mineral water (Table 7) underlining that the analyzed bottled water represents a safe aliment for the habitants of Beijing. However, except for Cu and Mn the median concentrations for all of these elements are higher compared to the median values for European bottled water.

4.5. Tap water vs. bottled water and Beijing tap water vs. European tap water

The comparison between Beijing tap and bottled water reveals higher median concentrations in the tap water for all anions (Fig. 8a) as well as heavy metals and trace elements (Fig. 8b) analyzed for this study. The abundances of some compounds (NO_3^- , SO_4^- , Al, Co, Fe, Pb, V, Zn) reach values up to more than 4 times higher in tap water compared to bottled water. The higher contaminant level is caused by the different sources of both types of drinking water. Beijing tap water is predominantly derived from groundwater of the aquifers in the Beijing area, whereas the investigated bottled water originates mainly from natural springs in different provinces of China as well as the Alps in Europe.

Groundwater in densely populated areas, such as the southeast Asian megacities, is usually affected by anthropogenic pollution (e.g., Hosono et al., 2010, 2011a; Yasuhara, 1998). In this study, we have shown that the local aquifers of Beijing are also affected by human contamination as reflected by the tap water composition revealing partly heavy enrichments in anthropogenic contaminants. Urban effluents reaching the aquifers probably via leaking sewage pipes of the municipal sewer network seem to have the greatest influence on the local ground- and tap water quality. But also specific industrial branches, such as the metal utilizing industry, as well as in-house installations are suggested to release pollutants to the Beijing ground- and tap water, respectively. These contamination sources can be usually ruled out for bottled water derived from natural springs. Consequently, the median values of the analyzed inorganic compounds are generally lower for bottled water, which can serve as a valuable alternative to tap water for the residents of Beijing. With respect to specific contaminants, such as NO_3^- or As, bottled water is highly recommended to be the prime drinking water source for the local consumers, especially for children and babies.

Also the comparison with European tap water exhibits higher median concentrations for Beijing tap water of almost all analyzed constituents (Fig. 9a + b). Only the median concentrations of Cu and Zn are higher in the tap water of Beijing than in Europe. The largest differences could be shown for the median contents of Fe and Cr in Beijing tap water, which exceed the median concentrations in European tap water around 60 and 50 times, respectively. Also the median concentrations of Al and Se in tap water from Beijing are more than 10 times higher than in Europe. The median NO_3^- level is almost 5 times higher compared to tap water from Europe.

The guideline limits for European tap water according to the national and EU wide directives are very similar to the national limits of the Chinese legislation following the guideline values recommended by the WHO (Birke et al., 2010). However, most of the median concentrations of Beijing tap water obtained for this study are significantly higher compared to Europe. Beijing as one of the biggest cities in China, which is the largest developing country in the world, still faces severe environmental problems, due to its fast growth in the past decades (BMBS, 2011). The constant release of anthropogenic pollutants by human activities affected the local surface and subsurface environments heavily and deteriorated the water quality of many surface water reservoirs used in the past for drinking water production (e.g., Xue et al., 2005). Moreover, the effect of urban wastewater released to the environment by leaking sewers on groundwater was proven for many megacities in the developing countries of SE Asia (Yasuhara, 1998), which causes concern for the drinking water quality in these regions. The results obtained for this study confirm the anthropogenic influence on Beijing groundwater,

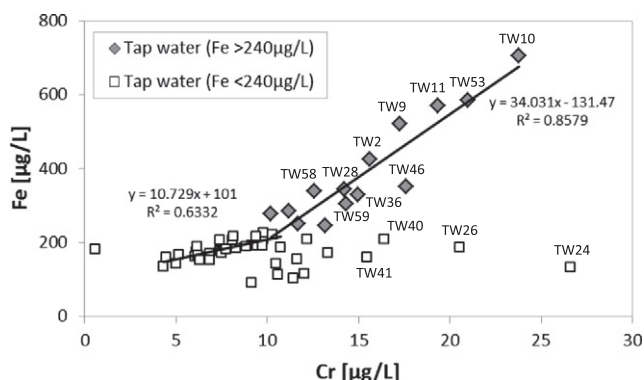


Fig. 7. Cr vs. Fe concentrations for tap water.

Table 7
National guideline values for natural mineral water (GB 8537-2008) and concentrations (µg/L) of heavy metals and trace elements of bottled water samples.

ID	Al	As	Co	Cr	Cu	Fe	Mn	Ni	Pb	Se	V	Zn
GB 8537-2008	n.e.	10	n.e.	50	1000	n.e.	400	20	10	50	n.e.	200
BW1	7.78	0.46	0.03	3.82	0.94	29.1	0.17	1.13	0.13	0.31	0.22	7.31
BW2	6.01	0.28	0.04	1.50	1.57	28.6	b.d.	0.48	0.15	0.39	3.83	7.05
BW3	4.89	1.59	0.03	27.79	1.60	37.1	b.d.	0.56	0.06	0.16	12.98	4.98
BW4	10.65	1.43	0.05	3.91	b.d.	146.0	b.d.	0.94	0.06	4.42	0.03	5.33
BW5	6.51	0.16	0.04	4.11	b.d.	101.7	b.d.	0.79	0.05	0.67	0.06	2.48
BW6	8.18	0.30	0.04	2.69	b.d.	89.9	b.d.	1.15	0.06	1.00	0.73	7.73
BW7	1.57	0.31	0.07	6.00	b.d.	225.5	b.d.	1.43	0.03	1.09	0.06	0.74
BW8	4.72	6.30	0.03	3.59	b.d.	67.6	b.d.	0.61	0.02	0.62	0.02	0.77
BW9	2.05	0.02	0.03	2.36	b.d.	20.5	b.d.	0.48	0.04	1.70	0.25	2.17
BW10	6.30	2.13	0.01	3.40	b.d.	31.6	b.d.	0.45	0.03	0.92	0.43	0.69
BW11	2.94	b.d.	0.01	0.24	b.d.	1.1	b.d.	0.29	0.03	0.74	b.d.	1.25
BW12	7.80	2.57	0.02	1.10	b.d.	39.4	b.d.	0.56	0.13	1.20	0.24	3.28
Median	6.15	0.39 ^a	0.03	3.49	– ^b	38.2	– ^b	0.59	0.05	0.83	0.23 ^a	2.88
Min	1.57	b.d.	0.01	0.24	b.d.	1.1	b.d.	0.29	0.02	0.16	b.d.	0.69
Max	10.65	6.30	0.07	27.79	1.60	225.5	0.17	1.43	0.15	4.42	12.98	7.73
Detection limit	0.001	0.01	0.001	0.01	0.001	0.01	0.01	0.01	0.001	0.01	0.01	0.01
European bottled water ^c	1.95	0.21	0.02	0.12	0.25	1.3	0.80	0.20	0.02	0.04	0.15	1.20

n.e. = not established.

b.d. = below detection limit.

^a "b.d." considered as detection limit concentration for median value calculation.

^b Number of values above detection limit too low to determine median value.

^c Median concentrations of European bottled water (EGS, EuroGeoSurveys Geochemistry Expert Group, 2010).

which represents the most important drinking water source in the Beijing area, and suggest a high contribution of urban sewage to the local aquifers probably caused by leakage of the corroding pipeline network. Hence, the better situation in the well-developed countries of Europe with respect to the quality of the municipal distribution systems, a more responsible handling of wastewater combined with a proper and permanent groundwater monitoring limits the discharge of urban effluents to the local aquifers and leads to a generally better tap water quality in European countries. However, the median concentrations for European tap water include values for drinking water derived from aquifers in non-urban and rural areas, which are mostly not so heavily

affected by anthropogenic contamination as urban areas, especially mega-cities with more than 15 million habitants, such as Beijing. This needs to be considered, when the tap water of Beijing and Europe are compared.

5. Conclusions

In the present study we applied physical-chemical and concentration measurements on a number of inorganic compounds dissolved in Beijing tap, bottled and rain water as well as water from the Miyun dam lake with the major goal to quantify the degree of contamination

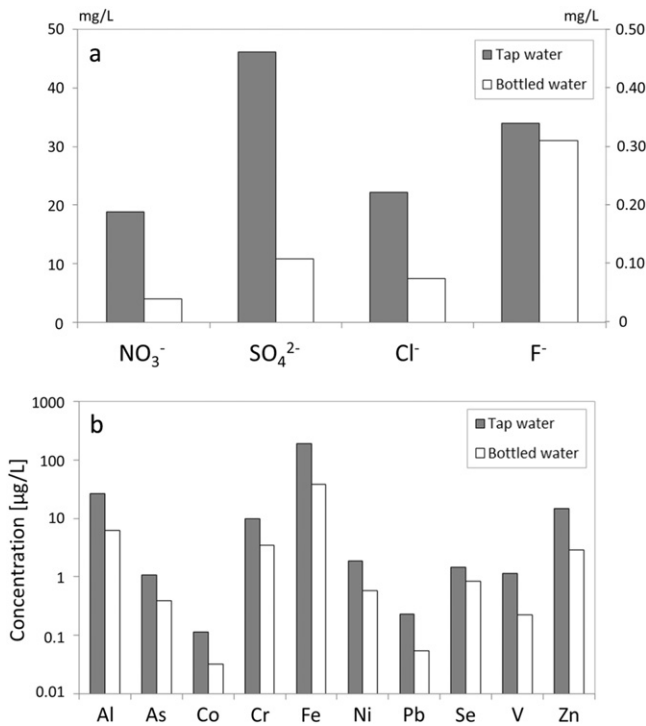


Fig. 8. Column diagrams for median concentrations of anions (a) as well as metals and trace elements (b) in tap and bottled water. The left hand y-axis in (a) refers to the NO₃⁻, SO₄²⁻ and Cl⁻ concentrations, while the right hand y-axis refers to the F⁻ concentrations.

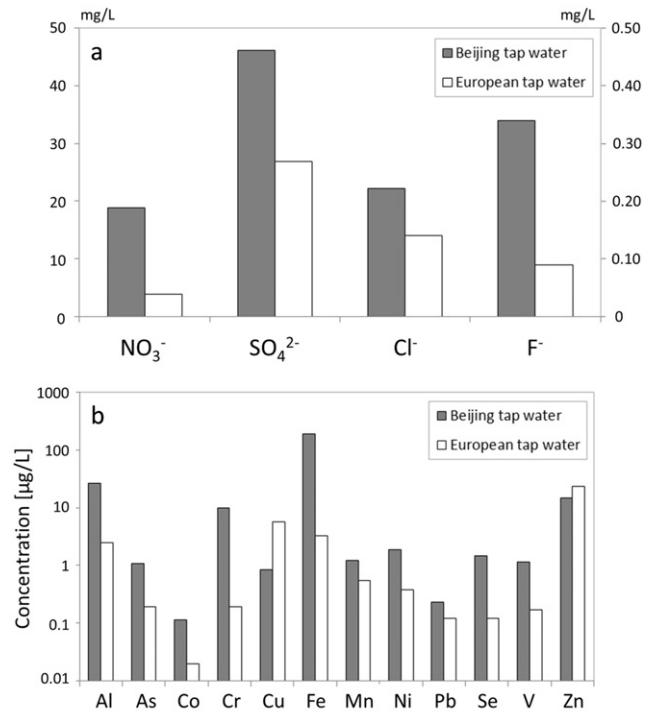


Fig. 9. Column diagrams for median concentrations of anions (a) as well as metals and trace elements (b) in tap water from Beijing and Europe (EGS, EuroGeoSurveys Geochemistry Expert Group, 2010). The left hand y-axis in (a) refers to the NO₃⁻, SO₄²⁻ and Cl⁻ concentrations, while the right hand y-axis refers to the F⁻ concentrations.

of the investigated waters. In addition, we analyzed multiple stable isotopes (N, O, S) of dissolved nitrate and sulfate of the tap water, which represents the principal drinking water source for the people of Beijing, in order to gain more information about the specific pollution sources. Although the majority of the examined tap water samples comply with the national legislation, in total 23 concentration values of 6 analyzed compounds (NO_3^- , F^- , As, Fe, Mn, Zn) in 15 samples (~27%) exceed the respective limits of the national drinking water guideline. 46% of the samples show relatively high NO_3^- concentrations of more than 20 mg/L, which reach values up to more than 4 times the guideline limit. Arsenic contents exceed the national standard value by more than 5 times. We assert that daily consumption of this tap water can be hazardous for human health and may cause serious diseases, especially for children and babies. In contrast, the concentrations of anions, metals and trace elements for all analyzed bottled water samples show values below the national guideline limits for natural mineral water. Moreover, all samples exhibit exclusively lower median abundances compared to Beijing tap water. Hence, we can recommend bottled water from Beijing supermarkets as a valuable drinking water source for the local inhabitants, especially in the areas of Beijing, where tap water is enriched in NO_3^- and As.

The concentration and isotope data reveal that certain constituents in Beijing tap water, such as Cl^- , NO_3^- , SO_4^{2-} , Cr and Fe, are mainly derived from urban sewage. Public wastewater is released to the environment probably by leaking sewage pipes contributing the local groundwater as the major source for Beijing tap water. Some pollutants were suggested to originate from further anthropogenic sources, such as the metal utilizing industry, or in-house installations. High As contents in the tap water of the outlying suburban and rural area of Beijing point to naturally occurring arsenic released from As-rich alluvial deposits and/or to anthropogenic arsenic from agrochemicals. In addition, denitrification and sulfate reduction by microbial activity under reducing conditions were identified.

Furthermore, the median concentrations of most inorganic compounds in Beijing tap water analyzed for this study (except Cu and Zn) exceed the median contents of the tap water in Europe. Hence, modernization of the local infrastructure of sewage disposal, more careful handling of public and private wastewater and independent monitoring of the groundwater status could reduce further contamination of ground- and tap water in the Beijing area. Moreover, in the outlying suburban and rural areas of Beijing the application of filter systems removing As from groundwater and the exploitation of deeper aquifers could further improve the quality of Beijing tap water and, hence, the life of the local residents.

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