Hydrol. Earth Syst. Sci., 20, 1983–1999, 2016 www.hydrol-earth-syst-sci.net/20/1983/2016/ doi:10.5194/hess-20-1983-2016 © Author(s) 2016. CC Attribution 3.0 License.





# Identification of anthropogenic and natural inputs of sulfate into a karstic coastal groundwater system in northeast China: evidence from major ions, $\delta^{13}C_{DIC}$ and $\delta^{34}S_{SO_4}$

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Received: 16 August 2015 – Published in Hydrol. Earth Syst. Sci. Discuss.: 3 November 2015 Revised: 23 March 2016 – Accepted: 25 April 2016 – Published: 17 May 2016

Abstract. The hydrogeochemical processes controlling groundwater evolution in the Daweijia area of Dalian, northeast China, were characterised using hydrochemistry and isotopes of carbon and sulfur ( $\delta^{13}C_{DIC}$  and  $\delta^{34}S_{SO_4}$ ). The aim was to distinguish anthropogenic impacts as distinct from natural processes, with a particular focus on sulfate, which is found at elevated levels (range: 54.4 to 368.8 mg  $L^{-1}$ ; mean: 174.4 mg  $L^{-1}$ ) in fresh and brackish groundwater. The current investigation reveals minor seawater intrusion impact (not exceeding 5% of the overall solute load), in contrast with extensive impacts observed in 1982 during the height of intensive abstraction. This indicates that measures to restrict groundwater abstraction have been effective. However, hydrochemical facies analysis shows that the groundwater remains in a state of ongoing hydrochemical evolution (towards Ca-Cl type water) and quality degradation (increasing nitrate and sulfate concentrations). The wide range of NO<sub>3</sub> concentrations  $(74.7-579 \text{ mg L}^{-1})$  in the Quaternary aquifer indicates considerable input of fertilisers and/or leakage from septic systems. Both  $\delta^{13}$ C (-14.5 to -5.9 ‰) and  $\delta^{34}$ S<sub>SO4</sub> (+5.4 to +13.1 %) values in groundwater show increasing trends along groundwater flow paths. While carbonate minerals may contribute to increasing  $\delta^{13}C_{DIC}$  and  $\delta^{34}S_{SO_4}$  values in deep karstic groundwater, high loads of agricultural fertilisers reaching the aquifer via irrigation return flow are likely the main source of the dissolved sulfate in Quaternary groundwater, as shown by distinctive isotopic ratios and a lack of evidence for other sources in the major ion chemistry. According to isotope mass balance calculations, the fertiliser contribution to overall sulfate has reached an average of 62.1 % in the Quaternary aquifer, which has a strong hydraulic connection to the underlying carbonate aquifer. The results point to an alarming level of impact from the local intensive agriculture on the groundwater system, a widespread problem throughout China.

# 1 Introduction

Degradation of groundwater quality, including salinisation, has become an increasingly serious global problem in coastal aquifers worldwide in recent years. With rapid economic development, population growth and increasing demand for freshwater resources, extensive groundwater withdrawals in these areas have led to water level declines and increasing groundwater salinisation (e.g. Barlow and Reichard, 2010; Han et al., 2015). Many previous studies have investigated the mechanisms of salinisation and potential sources of groundwater salinity in coastal aquifers, which can include evaporite mineral dissolution (e.g. Cardenal et al., 1994; Najib et al., 2016), downward/upward saline groundwater seepage (e.g. Guo et al., 1995; de Louw et al., 2013), brine migration (e.g. Han et al., 2011; Myshakin et al., 2015), and mixing caused by poorly constructed wells (e.g. Aunay et al., 2006), as well as "classic" seawater intrusion (e.g. Daniele et al., 2013).

Coastal areas are often sites of intensive human activity, including urbanisation and agriculture. Intensive agriculture



**Figure 1.** Geological setting and water sampling locations. Geology modified after Wu and Jin (1990). Formation note:  $O_1$  – Lower Ordovician;  $\epsilon_3$  – Upper Cambrian;  $\epsilon_2$  – Middle Cambrian;  $\epsilon_1$  – Lower Cambrian;  $Z_2g$  – Ganjingzi group of Middle Sinian;  $Z_3b$  – Beishan group of Upper Sinian. Legend: 1 – Quaternary sediments; 2 – thick-bedded limestone; 3 – laminated limestone with shale; 4 – argillaceous limestone; 5 – sandstone and shale; 6 – normal/thrust fault; 7 – buried fault; 8 – town location; 9 – approximate groundwater flow direction; 10 – sampling wells • from deep carbonate aquifers (depth > 80 m),  $\bigcirc$  from shallow Quaternary aquifer (depth < 40 m); 11 – sampling site for seawater.

is known to be associated in some areas with salinisation (e.g. Ghassemi et al., 1995; Kumar et al., 2015) and other groundwater quality issues such as addition of nitrate, sulfate and other compounds contained in fertilisers (e.g. Kaown et al., 2009; Currell et al., 2010). Environmental tracers, such as stable sulfur and carbon isotopes, e.g.  $\delta^{34}$ S of dissolved SO<sub>4</sub>( $\delta^{34}$ S<sub>SO4</sub>), and  $\delta^{13}$ C in dissolved inorganic carbon ( $\delta^{13}C_{DIC}$ ), and major ion chemistry have been useful in identifying sources of salinity and dissolved sulfate and carbonate species in groundwater (Sánchez-Martos et al., 2002; de Montety et al., 2008; Schiavo et al., 2009; Ghiglieri et al., 2012; Kim et al., 2015) and for determining water-rock interaction processes in carbonate aquifers (e.g. carbonate mineral dissolution/precipitation, cation exchange) (Back et al., 1979; Plummer and Sprinkle, 2001; Moral et al., 2008; Daniele et al., 2013). However, to date few areas of major anthropogenic activity and known active or previous salinisation from seawater intrusion have been assessed using these tracers, in order to distinguish different water quality degradation processes, such as seawater-freshwater mixing versus input of agricultural chemicals and irrigation return flow.

This study focuses on the coastal carbonate aquifers around Daweijia well field, which is located in the Daweijia area of Dalian, northeast China. Most previous investigations in this area have focused on the mechanism of seawater intrusion and related water–rock interactions (Wu et al., 1994; Yang, 2011; Zhao et al., 2012), but have ignored the potential impact of anthropogenic contributions to groundwater salinity and water quality degradation. Little is known about the influence of agricultural practices on sulfur cycling and transport in this and other coastal aquifers impacted by intensive agriculture. Here, we report new data for C and S isotopes and major ions in groundwater from the Daweijia area, which gives new insight into sources of water quality degradation, including agriculture. Using chemical and isotopic tracers, this study reveals the dominant factors controlling on groundwater hydrochemistry before and after groundwater pumping in the Daweijia well field, and identifies the different sources of sulfate, salinity and determines the major controls on hydrochemical evolution. Understanding these issues can help to prevent further deterioration of groundwater quality in this and other similar systems in north China and elsewhere around the world.

#### 2 Study area

The investigated area  $(39^{\circ}10'-39^{\circ}14' \text{ N} \text{ and } 121^{\circ}37'-121^{\circ}45' \text{ E})$  is located in northeast China along the Bohai Sea coast (Fig. 1). It has a catchment area of 66 km<sup>2</sup> to the north of Dalian (population 3.25 million), Liaoning Province. The climate is warm temperate continental monsoon, with an annual average temperature of ~ 10 °C. Most of the precipitation, totalling ~ 600 mm annually (Yang, 2011) falls during the June–September rainy season. The ephemeral Daweijia River runs through the region from east to west. Under natural conditions, groundwater discharged into the sea from the southeast towards the northwest (Fan, 1984).

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The geology of the Daweijia area consists of Quaternary deposits over-lying carbonate aquifers of Paleozoic (Ordovician and Cambrian) and Proterozoic (Sinian) age. Two groups of faults are developed in this area, namely NE normal faults (F1 and F2 in Fig. 1) and EW reverse faults (F3 and F4 in Fig. 1). These structural faults cut the bedrock and are the main channel for groundwater infiltration and movement, affecting the degree of subsurface karst development (Song, 2013). The main karst development sections in the Cambrian and Ordovician formation include (i) 5 to 20 m a.s.l. (meters above sea level) (near surface karst), (ii) -5 to -40 m a.s.l. (shallow karst), (iii) -50 to -85 m a.s.l. (medium depth karst), and (iv) < -90 m a.s.l. (deep karst) (Zhao, 1991). The aquifers within the Daweijia area can be divided into upper and lower aquifer systems; the upper aquifer is composed of Quaternary sediments with variable thickness of 0-40 m. This consists of gravel, sand and clay layers and is not extensively pumped for water supply. The carbonate aquifers underlying the Quaternary deposits are mainly composed of Lower Ordovician, Middle and Upper Cambrian limestone, with major karst development in the medium section between -40 and -70 m a.s.l. (Lü et al., 1981; Zhao, 1991). The most productive carbonate aquifers are distributed along Daweijia River valley. Figures 1 and 2 show a geological map and stratigraphic cross-section of the hydrogeological system along this valley, showing natural groundwater flow from east to west (Fan, 1984). The geologic contacts and hydraulic connections between the upper and lower aquifer systems used in this study were determined from geologic logs and geophysical exploration during a previous investigation of regional hydrogeology in the Daweijia area (Lü et al., 1981; Jin and Wu, 1990).

Seawater intrusion was first discovered in the Dalian area in 1964. This study focuses on the coastal aquifers around Daweijia well field (Fig. 1), which was established in 1969 and formerly provided major water supply for Dalian at the pumping rates of  $12-24 \times 10^3 \text{ m}^3 \text{ dav}^{-1}$  in 1970 (Lü et al., 1981). With the increase of pumping rate till 1983 (up to  $4.8-6.2 \times 10^3 \text{ m}^3 \text{ day}^{-1}$  in 1977), the average chloride concentration of groundwater from eight fixed monitoring wells increased from  $380 \text{ mg L}^{-1}$  in 1968 to 1137 mg L<sup>-1</sup> in 1982 (Song, 2013), indicating that the serious seawater intrusion occurred. The groundwater withdrawal of the Daweijia well field was changed from a perennial pattern to a seasonal regime with a decrease by two-thirds of the pumped volume. The abstraction increased after 1991 but was reduced again from  $20 \times 10^3$  m<sup>3</sup> day<sup>-1</sup> in 1995 to  $4 \times 10^3$  m<sup>3</sup> day<sup>-1</sup> in 2000 (Li et al., 2006). Alternatively, in order to reduce the threat of seawater intrusion to the aquifer, with the establishment of surface water supply projects, water supply for Dalian from the well field has ceased since 2001, with seasonal pumping for local agricultural irrigation (Song, 2013). The area is also the site of ongoing intensive agricultural activity.

The carbonate aquifer is pumped for agricultural and public water supply. The Daweijia well field was established in 1969 for water supply to Dalian and, at peak usage, the upper aquifer suffered extensive drawdown. Along with this, the average chloride concentration in groundwater increased from  $199 \text{ mg L}^{-1}$  in 1966 to  $559 \text{ mg L}^{-1}$  in 1991, and reached a peak of  $940 \text{ mg L}^{-1}$  in 1994. Under the restrictions on groundwater extraction enacted, the Cl value returned to  $454 \text{ mg L}^{-1}$  in 2005. This included the drastic measure of switching off the well field supplying Dalian since 2001 (Song, 2013). Although the groundwater levels have recovered in recent years, groundwater salinity has not completely been reversed, and elevated nitrate and sulfate concentrations have continued since this time. Potential causes include "residual" seawater intrusion which has not yet re-equilibrated with recovered water levels and/or different sources of contamination, associated with agriculture or urban activities.

## 3 Methods

# 3.1 Sampling and analysis

We collected 30 water samples during two sampling campaigns (June 2006 and August 2010) for analysis of major ions and stable isotopes ( $\delta^{13}C_{DIC}$  and  $\delta^{34}S_{SO_4}$ ). The samples include 29 from wells and one seawater sample. Sampling wells are production wells with variable depths (8.4-128 m) and screened intervals (lengths of 2-35 m; see Table 1) and these are distributed mainly along the Daweijia River valley (Fig. 1). The screened intervals of wells in the carbonate aquifer are mainly between 65 and 100 m below ground surface (Table 1). Before sampling, the wells were pumped for at least for half an hour until physico-chemical parameters (e.g. water temperature, pH, electrical conductivity and dissolved oxygen) stabilised. All samples were filtered through 0.45 µm pore-size filter paper and stored in HDPE bottles at 4 °C in a cool room until analysis. The samples prepared for cation analysis were acidified to pH < 2 by adding high purity HNO<sub>3</sub>. Bicarbonate was determined in the field by titrating with 0.22 N H<sub>2</sub>SO<sub>4</sub>. Major anions were measured by ion chromatography (SHIMADZU), and major cations were determined using ICP-AES by the Laboratory of Physics and Chemistry, Institute of Geographic Sciences and Natural Resources Research (IGSNRR), Chinese Academy of Sciences (CAS). The ion balance errors of the chemical analyses were generally within  $\pm 15$  %. The PHREEQC-2 hydrogeochemical code (version 2.18.3, Parkhurst and Appelo, 1999) was used to determine the saturation indexes (SI) of calcite, dolomite and gypsum.

The  $\delta^{13}$ C values of dissolved inorganic carbon (DIC) in 16 water samples were measured using continuous flow on a Finnigan MAT 252 mass spectrometer, with the automated headspace analysis of the preparation device, in the State



Figure 2. Conceptual model showing the hydrogeological system (modified after Yang, 2011) and NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> concentrations and sources. Characteristic ranges of  $\delta^{13}$ C and  $\delta^{34}$ S<sub>SO4</sub> values for A1, A2, B1, B2 and C are shown in Table 3. Arrows in aquifers indicate general groundwater flow direction.

Key Laboratory of Environmental Geochemistry, Institute of Geochemistry (Guiyang), CAS. The results of  $\delta^{13}$ C analysis are expressed in conventional delta ( $\delta$ ) notation, defined as  $\delta = (R_{\text{sample}} - R_{\text{standard}})/R_{\text{standard}} \times 1000$ , where R is the ratio of  ${}^{13}C/{}^{12}C$ . The  $\delta^{13}C$  values of dissolved inorganic carbon (DIC) are expressed relative to the standard Vienna Peedee Belemnite (VPDB), with an analytical precision of  $\pm 0.2$  ‰. Samples for <sup>34</sup>S in dissolved sulfate in 18 groundwater samples (Table 1) were measured by a Finnigan MAT Delta-S gas mass spectrometer after online pyrolysis with an EA (elemental analyser) in the Laboratory for Stable Isotope Geochemistry, Institute of Geology and Geographysics, CAS. The method of Halas and Szaran (1999) was used for converting precipitated BaSO<sub>4</sub> to SO<sub>2</sub>. The international standard against which  $\delta^{34}$ S values are referenced is the troilite (FeS) phase of the Cañon Diablo meteorite (CDT), which has a <sup>34</sup>S / <sup>32</sup>S abundance ratio of 0.0450 and are reported as  $\delta$  (‰) difference from the standard with an analytical precision of better than or about  $\pm 0.4$  %.

## 3.2 Ionic deltas and mixing calculations

To further investigate the hydrochemical behaviour of major cations and diagnose the processes modifying hydrochemical composition of groundwater in the aquifer, ionic delta values were calculated. The delta values express enrichment or depletion of particular ions relative to a conservative mixing system. These have been used in previous studies as effective indicators of groundwater undergoing freshening or salinisation, along with associated water–rock interaction processes (primarily cation exchange – e.g. Appelo, 1994). Based on variations of molar Cl / Br ratios and major ions in ground-

water (Sect. 5.1), we have ruled out significant sources of Cl<sup>-</sup> other than meteoric and oceanic inputs. It is assumed in these calculations that there is no chloride input from salts in the aquifer matrix itself, and that Cl can be regarded as the most conservative species during mixing and hydrochemical evolution. The fraction of seawater ( $f_{sea}$ ) in a groundwater sample can thus be calculated using (Appelo and Postma, 2005)

$$f_{\rm sw} = \frac{C_{\rm Cl,sam} - C_{\rm Cl,f}}{C_{\rm Cl,sw} - C_{\rm Cl,f}},\tag{1}$$

where  $C_{\text{Cl,sam}}$ ,  $C_{\text{Cl,fresh}}$ , and  $C_{\text{Cl,sw}}$  refer to the Cl concentration in the sample, freshwater, and seawater, respectively.

The theoretical concentration  $(C_{i,\text{mix}})$  of an ion *i* in a water sample can be calculated by comparing the measured concentration of this ion with its expected composition from conservative mixing between seawater and freshwater (Appelo and Postma, 2005):

$$C_{i,\text{mix}} = f_{\text{sw}} \cdot C_{i,\text{sw}} + (1 - f_{\text{sw}}) \cdot C_{i,\text{f}}, \qquad (2)$$

where  $C_{i,\text{sam}}$  and  $C_{i,\text{f}}$  – the measured concentration of the ion *i* in the water sample and freshwater, respectively;  $f_{\text{sw}}$  – fraction of seawater. The ionic deltas ( $\Delta C_i$ ) of ion *i* can thus be obtained by:

$$\Delta C_i = C_{i,\text{sam}} - C_{i,\text{mix}}.$$
(3)

Table 1. Hydrochemical and isotopic data of the June $2006(*)$ and August 2010 field sampling.	

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1.1																					i.												
	δ <sup>13</sup> C <sub>DIC</sub> (‰)		-9.3			-9.9	-8.4		-9.7	-12.0	-9.3	-10.6					-11.6					-9.4	-12.8	-14.5	-11.0	-10.6	-8.6	-10.2	-5.9				-3.3
	δ <sup>34</sup> S <sub>SO4</sub> (‰)		10.4		10.9	9.0	6.6		8.8	8.7	10.4	13.1					10.1	14.0	10.4	14.2		8.1	5.4	5.7	9.0	10.1	7.2	8.6	9.4		9.5	7.8	20.8
	SIgyp		-1.47	-1.58	-1.55	-1.41	-1.75	-1.47	-1.12	-1.05	-1.31	-1.12	-1.35	-0.9	-1.24	-1.05	-0.95	-1.23	-1.29	-1.41		-1.65	-1.34	-1.43	-0.98	-1.27	-1.03	-1.15	-0.95	-0.76	-1.23	-1.19	
	SIdol		-0.07	-0.24	0.33	0.18	0.84	-0.14	-1.53	-1.65	-1.01	0.32	0.27	-0.36	0.55	-0.28	0.31	0.5	-0.97	-0.85		0.55	-0.95	0.6	-0.48	-0.13	0.33	0.34	1.07	-0.16	0.29	-0.35	
	SIcal		0.1	0.1	0.27	0.23	0.48	0.21	-0.59	-0.65	-0.31	0.27	0.38	0.14	0.51	0	0.35	0.34	-0.33	-0.28		0.56	-0.24	0.34	-0.03	0.04	0.31	0.27	0.59	0.19	0.32	-0.1	
	$\mathop{\rm Sr}_{(mgL^{-1})}$		0.49	0.45	0.47	0.63	0.17	0.45	0.99	0.79	0.99	2.07	1.32	1.16	1.15	0.49	1.80	I	I	I		0.66	0.57	0.50	0.95	1.52	0.63	0.75	1.58	0.95	I	I	5.81
	$HCO_3^-$ (mg L <sup>-1</sup> )		247.1	101.2	282.8	250.1	238.1	134.0	199.4	145.9	163.7	282.8	190.5	205.4	318.5	446.5	205.4	253.8	174.2	120.8		262.0	190.5	241.1	199.4	309.6	220.3	241.1	291.7	300.7	512.7	200.9	163.7
	$\substack{NO_3^- \\ (mgL^{-1})}$		60.9	77.2	60.3	43.1	69.1	147.9	263.9	334.7	278.8	282.6	256.6	579.4	90.1	265.6	295.7	124.8	321.5	79.6		146.6	74.7	80.2	337.3	156.1	256.9	133.5	259.5	347.9	386.3	190.6	1092.0
	$\underset{(\mathrm{mg}L^{-1})}{\mathrm{so}_{4}^{2-}}$	aquifer	109.7	82.4	93.8	67.1	65.1	101.8	189.2	240.5	134.1	201.4	104.1	249.9	146.2	219.1	306.9	135.3	142.7	109.4	' aquifer	54.4	135.4	145.2	254.3	211.5	285.9	216.2	344.9	368.8	134.2	207.6	4116.0
	$cl^{-}$ (mg L <sup>-1</sup> )	he carbonate	261.0	112.1	209.5	141.6	105.7	203.8	288.4	892.9	343.4	561.0	344.5	937.3	380.8	390.0	923.5	596.6	323.3	511.2	le Quaternary	254.5	103.3	203.3	281.3	640.6	269.8	299.4	469.4	386.2	315.7	448.3	16 683.9
	$\substack{Mg^{2+}\\(mgL^{-1})}$	lected from t	38.5	16.1	37.8	24.1	31.9	17.4	48.5	51.1	38.3	72.3	32.1	42.3	31.9	72.1	42.4	114.0	48.4	54.2	ected from th	27.5	21.6	40.0	44.7	51.0	47.5	49.1	74.8	49.6	66.3	69.2	978.8
	$\overset{K^{+}}{(\operatorname{mg} L^{-1})}$	samples col	1.2	4.7	1.5	1.2	1.0	6.5	2.3	1.0	1.5	3.5	1.4	1.7	1.6	2.0	26.4	3.7	1.5	3.5	samples colle	1.0	4.0	13.1	0.5	12.8	2.7	7.6	11.1	2.3	3.6	4.4	289.1
	$\frac{\mathrm{Na}^{+}}{(\mathrm{mg}L^{-1})}$	Groundwater	50.5	26.1	47.2	38.2	24.5	44.4	106.0	97.8	82.9	184.0	66.7	84.3	81.3	70.6	62.0	312.2	103.2	175.6	Groundwater	82.1	28.6	42.5	146.0	286.1	134.5	67.8	295.5	154.6	198.5	229.2	7626.0
	$\begin{array}{c} ca^{2+}\\ (mgL^{-1})\end{array}$		119.6	100.9	115.8	99.4	94.5	113.6	187.7	198.5	149.1	212.5	190.6	302.8	183.0	220.0	207.7	284.5	151.2	158.9		156.2	118.3	99.1	208.4	128.2	154.6	151.4	205.8	274.7	244.9	153.8	324.5
	$DO \ (mg L^{-1})$		3.6	5.7	4.0	3.7	7.2	8.6	7.5	6.6	7.0	5.6	6.1	7.6	7.4	4.7	7.4					6.7	4.4	3.6	3.6	5.0	7.8	4.4	1.3	5.6			5.0
	ORP (mV)		193	7	201	139	34	0	186	222	200	163	199	0	25	26	214					6	52	22	219	204	16	23	65	41			171
	Т (°С)		16.1	22.4	19.3	21.7	22.0	18.8	16.0	17.0	14.2	18.2	20.0	15.1	20.0	14.5	21.5	14.9	13.2	13.2		13.1	18.3	23.0	17.1	13.9	16.4	20.7	23.2	14.2	15.2	13.9	26.8
	Hd		7.2	7.5	7.3	7.3	7.6	7.6	6.5	6.6	7.0	7.2	7.4	7.1	7.3	6.7	7.4	7.3	7.0	7.2		7.6	7.0	7.5	7.0	7.2	7.4	7.3	7.4	7.0	7.0	7.2	<i>T.T</i>
	$EC$ ( $\mu s  cm^{-1}$ )		1015	715	986	796	749	846	2050	1761	1370	2280	1416	2050	1362	1481	1586	2890	2110	2300		1242	821	912	1903	2210	1633	1289	2780	2210	2310	2820	43800
	Screened intervals (m)		70-95	58-84	72–98	75-112	85-118	68-92	72-107	59-88	68-97	71–93	65-92	67–93	68-93	43-59	59-86	71–93	72-107	72–98		15-24	6-7.5	7–13	7-11	6-9	9–14	12-17	8-15	12-16	15-21	8-15	ter sample
	Well depth (m)		100	88	110	120	128	100	120	92	110	100	95	100	100	62	6	100	120	110		28	8.4	14	12	10	15	20	17	17	22	17	Seawa
	Sample		CG4	CG16	CG3	CG6	CG14	CG9	CG2	CG7	CG17	CGI	CG8	CG11	CG12	CG19	CG10	CG1*	CG2*	$CG3^*$		QG7	QG3	QG4	QG5	QG10	QG8	$QG_9$	QG11	QG12	QG2*	QG11*	SW1



**Figure 3.** Graphs showing the cationic  $\Delta$  values of groundwater samples vs. fraction of seawater: (a)  $\Delta Na^+$ , (b)  $\Delta Ca^{2+}$ , (c)  $\Delta Mg^{2+}$ , and (d)  $\Delta SO_A^{2-}$ .

### 4 Results

# 4.1 Chemical analysis

The physical and chemical characteristics of groundwater samples from the Quaternary aquifer (QA) and the Cambrian-Ordovician carbonate aquifer (COA) in the Daweijia are compiled in Table 1. Total dissolved solids (TDS) concentrations vary from 372 to 2403 mg  $L^{-1}$ , with values increasing along the main direction of groundwater flow from the east towards the sea. Groundwater pH ranges from 6.5 to 7.6, with a mean of 7.2. Dissolved oxygen concentrations range from 1.3 to  $8.6 \text{ mg L}^{-1}$  with a mean of  $5.6 \text{ mg L}^{-1}$ . The fresh (< 1 g L<sup>-1</sup> TDS) groundwater (e.g. CG6, CG14) is characterised as Ca-HCO<sub>3</sub>(·Cl) type water, while brackish (1 to  $10 \text{ g L}^{-1}$  TDS) groundwater (e.g. CG7, CG10, CG11, CG17) is predominantly Ca-Cl type in the carbonate aquifer. Brackish groundwater in the shallow Quaternary aquifer was observed to be Ca-Cl·SO<sub>4</sub> type water, or near the coastline (e.g. QG10, QG11), Na Ca-Cl(·HCO<sub>3</sub>) type.

According to mixing calculations, minor seawater intrusion near the coastline is identified (Fig. 3), however the fraction of seawater does not exceed 5% and this compares with a fraction of 20.8% observed in 1982 (Wu et al., 1994). The groundwater in this study is characterised by a wide range of sulfate concentrations between 54.4 and  $368.8 \text{ mg L}^{-1}$ , with a mean value of  $174.4 \text{ mg L}^{-1}$ . Nitrate concentrations ranged from 43.1 to 579.4 mg L<sup>-1</sup>, with a mean value of 206.9 mg L<sup>-1</sup>, far beyond the drinking water standard (50 mg L<sup>-1</sup>) in China. The investigated seawater sample also has a very high nitrate concentration of 1092 mg L<sup>-1</sup>.

Comparing background data (1962, Lü et al., 1981) and current data (2010, in this study), the nitrate concentrations in groundwater increased from a range of  $0-10.9 \,\mathrm{mg}\,\mathrm{L}^{-1}$  $(n = 51, \text{ mean value of } 2.1 \text{ mg L}^{-1})$  in 1962 to a range of 43.1–579.4 mg L<sup>-1</sup> (n = 15, mean value of 207.1 mg L<sup>-1</sup>) in 2010 in the carbonate aquifer, and mean sulfate concentration increased from a range of  $0-121.6 \text{ mg L}^{-1}$  (n = 64, mean value of  $72.4 \text{ mg L}^{-1}$ ) in 1962 to a range of 65.1–  $306.9 \text{ mg } \text{L}^{-1}$  (*n* = 15, mean value of 154.1 mg L<sup>-1</sup>) in 2010. For the Quaternary aquifer, nitrate concentrations have changed from a range of 0–9.9 mg  $L^{-1}$  (n = 3, mean value of 6.7 mg L<sup>-1</sup>) in 1962 to a range of 74.7–347.9 mg L<sup>-1</sup> (n = 9, mean value of  $199.2 \text{ mg L}^{-1}$ ) in 2010, and sulfate from a range of 0–64.1 mg  $L^{-1}$  (n = 3, mean value of 35.2 mg  $L^{-1}$ ) in 1962 to a range of 54.4–368.8 mg  $L^{-1}$  (n = 9, mean value of 224.1 mg  $L^{-1}$ ) in 2010.

The ionic delta values are plotted in Fig. 3, illustrating the varied distribution of geochemical types and evolution in the aquifer. Generally most groundwater samples are characterised by negative  $\Delta Na^+$  values and positive  $\Delta Ca^{2+}$  values. Some brackish groundwater samples have negative  $\Delta Na^+$  values and positive  $\Delta Ca^{2+} + \Delta Mg^{2+}$  values, displaying



**Figure 4.**  $\delta^{13}C_{\text{DIC}}$  vs. dissolved inorganic carbon for the groundwater samples (August 2009) in the Daweijia area, comparing with  $\delta^{13}C$  values for the main carbon reservoirs (Vitòria et al. (2004) and therein). See Fig. 3 for legend.



**Figure 5.**  $\delta^{34}$ S of dissolved SO<sub>4</sub> versus SO<sub>4</sub> / Cl for groundwater samples from the Daweijia area. The range of sulfur isotopic values of some major sulfur reservoirs and selected materials is summarised from literature compiled data as follows: 1 – Clark and Fritz (1997); 2 – Vitòria et al. (2004); 3 – Szynkiewicz et al. (2012); 4 – Unland et al. (2012); 5 – Szynkiewicz et al. (2011); 6 – Li et al. (2006); 7 – Hosono et al. (2007); 8 – Cravotta (1995) and Otero et al. (2007); 9 – Hong et al. (1994). See Fig. 3 for legend.

a deficit of Na<sup>+</sup> with a corresponding excess in Ca<sup>2+</sup> and Mg<sup>2+</sup>. There are positive values of  $\Delta SO_4^{2-}$  observed in most groundwater sample, and these are particularly high in the brackish groundwater (Fig. 3d).

# 4.2 Dissolved inorganic carbon (DIC) and $\delta^{13}C_{DIC}$

Figure 4 presents the  $\delta^{13}C_{DIC}$  isotope data and this can be used to infer the sources and evolution of dissolved inorganic carbon in the investigated groundwater (Clark and Fritz, 1997). The measured  $\delta^{13}C_{DIC}$  values in groundwater range from -14.5 to -5.9% vs. PDB, with a mean value of -10.5% (Table 1). The water samples from the carbonate aquifer show a relatively narrow range of  $\delta^{13}C_{DIC}$  values (-12 to -8.4% with a mean value of -10.1%, n = 8) comparable to the range of  $\delta^{13}C_{DIC}$  values (-14.5 to -5.9%, mean of -10.0%, n = 7) from the Quaternary aquifer. The waters collected in the upstream areas show  $\delta^{13}C$  values from -14.5 to -12.8%, while the middle area has values of -12.0 to -9.0% and the coastline values between -10.6 and -5.9% (Fig. 4, Table 1).

The local seawater sample (SW1) has a  $\delta^{13}C_{\text{DIC}}$  value of  $-3.3 \,\%$ , which is relatively low compared to other reported values of modern seawater (-1 to +2 %, Clark and Fritz, 1997). Carbon in C<sub>4</sub> plants, which include maize, sugar cane and sorghum, has  $\delta^{13}C$  values that range from -10 to -16 % with a mean value of  $\sim$  -12.5 %, while most C<sub>3</sub> plants have  $\delta^{13}C$  values that range from -24 to -30 %, with an average of  $\sim$  -27 % (Vogel, 1993). Maize is the main agricultural product in the study area (Hu, 2010), indicating that a C<sub>4</sub> vegetation source may be dominant. Carbonate dissolution and/or exchange leads to progressive enrichment of  $\delta^{13}C$  values towards the values of the mineral, usually with values between -2 and +2 %.

# 4.3 Stable isotopes of sulfate

The  $\delta^{34}S_{SO_4}$  compositions varied between +5.4 and +13.1 % (Table 1). Sample CG1, with a sampling depth of 100 m and collected from the centre of a residential area, has the highest  $\delta^{34}S_{SO_4}$  value (+13.1 ‰). The lowest  $\delta^{34}S_{SO_4}$ value (+5.4 ‰) was found for sample QG3 collected in an upstream area. Water samples from the carbonate aquifer are denoted with dashed line in Fig. 5 and have relatively high  $\delta^{34}S_{SO_4}$  values (ranging from +6.6 to +13.1 ‰ with a mean value of  $+9.9 \,\%$ , n = 9) and low SO<sub>4</sub> / Cl ratios. The groundwater samples from the Quaternary aquifer are characterised by a relatively narrow range of  $\delta^{34}S_{SO4}$  values (ranging from +5.4 to +10.1 % with a mean value of +7.9 ‰, n = 8) and a wider range of SO<sub>4</sub> / Cl ratios. Some brackish groundwater (OG2 and OG10) from the Quaternary aquifer also shows these characteristics (Fig. 5). In general, the  $\delta^{34}S_{SO_4}$  values increase with correspondingly lower  $SO_4$  / Cl ratios in the direction of the coastline.

# 5 Discussion

A number of geochemical processes control the evolution of groundwater in the study area. Some of these processes show evidence of taking place in both carbonate and Quaternary aquifers, while others are more confined to one of the aquifers. The major hydrochemical processes inferred from the data are summarised in Table 2, which also includes a description of lines of evidence used to infer these (in most cases two supporting lines of evidence exist).

# 5.1 Seawater intrusion, freshening and cation exchange

Widespread seawater intrusion appears to be a thing of the past, although local salinisation continues around the well field. Chloride is an important index for estimating the extent of seawater intrusion, and is generally assumed to behave relatively conservatively. The molar Cl / Br ratios (based on values from this study and Yang et al., 2011) range from 118.3 to 633.1 (n = 11, mean value 394.3), which is generally below the oceanic ratio of  $\sim 650$  (Drever, 1997). As halite is Br-depleted from its mineral structure, halite precipitation may lead to depletion of the ratios, however it is unlikely that saturation with respect to halite could be reached in the groundwater (e.g. McCaffrey et al., 1987; Edmunds, 1996; Cartwright et al., 2004). Minor contamination, e.g. with pesticides such as ethyl dibromine, methyl bromide and/or preferential Cl adsorption on organic material may explain the lower than usual ratios. Overall the ratios do not indicate significant sources of additional Cl. The TDS concentrations of groundwater in this study area varied within a range of 0.4- $4.5 \text{ g L}^{-1}$  in 1981 (the peak period of seawater intrusion) (Lü et al., 1981). For the well CG2 located in the centre of the well field, TDS was  $0.3 \text{ g L}^{-1}$  on December 1965,  $0.71 \text{ g L}^{-1}$  on August 1981,  $0.66 \text{ g L}^{-1}$  on December 1981, and up to  $1.19 \,\mathrm{g} \,\mathrm{L}^{-1}$  on August 2010, an obvious increasing trend, however,  $Cl^-$  concentrations decreased from 375.6 mg  $L^{-1}$ in August 1981 to  $288.4 \text{ mg L}^{-1}$  in August 2010. By contrast, there are much more significant increases on  $SO_4^{2-}$  and NO<sub>3</sub><sup>-</sup> concentrations in groundwater, which explains increasing TDS but decreasing chloride. For the well CG2,  $SO_4^{2-}$ concentration increased 5 times from  $38.2 \text{ mg L}^{-1}$  in August 1981 to 189.2 mg  $L^{-1}$  in August 2010. While NO<sub>3</sub><sup>-</sup> concentration increased 4 times from  $64.6 \text{ mg L}^{-1}$  in August 1981 to 263.9 mg  $L^{-1}$  in August 2010 – far higher than the overall changes in TDS. These changes in different ion concentrations in groundwater show that the anthropogenic input (e.g. application of agricultural fertiliser) has modified the hydrochemical composition of groundwater to a great extent after the cessation of pumping in the well field.

The freshening of coastal aquifers can be shown using the multi-rectangular HFE diagram (Fig. 6). This classification method proposed by Giménez-Forcada (2010) can be employed to determine the dynamics of seawater intrusion, considering the percentages of major ions, showing the intrud-

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**Table 2.** Summary of main hydrochemical processes occurring in the carbonate and Quaternary aquifer, along with evidence used to assess the process.

Aquifer (Carb/Quat)	Process	Occurring (Y/N)?	Evidence (1)	Evidence (2)	Figure
	Calcite dissolution (congruent)	No and Ca : HCO <sub>3</sub> > 1 : 2	Most groundwater samples with SI <sub>calcite</sub> < 0.1 HCO <sub>3</sub> and $\delta^{13}$ C	No correlation between Ca and $\delta^{13}$ C	Fig. 7
	Incongruent dolomite weathering	Yes	Increase in Mg / Ca along the flow path	Increase in $\delta^{13}$ C with increasing Mg / Ca	Fig. 7a
Carbonate aquifer	Cation exchange	Yes	Most samples with negative $\Delta Na^+$ values and positive $\Delta Ca^{2+}+$ $\Delta Mg^{2+}$ values	MixCa–Cl facies in HFE diagram	Figs. 3 and 6
	Fertiliser addition	Yes	Positive correlation between $NO_3^-$ and $SO_4^{2-}$ concentrations	Mass balance results from different sources of $\delta^{34}S_{SO_4}$	Figs. 9 and 10
	Gypsum dissolution	Yes	All water samples with $SI_{gypsum} < -0.5$	$Ca / SO_4 ratios > 1$	-
	Calcite dissolution (congruent)	Minor	Lack of correlation between $\delta^{13}$ C and HCO <sub>3</sub> ; increasing $\delta^{13}$ C with increasing Ca	Most groundwater samples with SI <sub>calcite</sub> < 0.1 and Ca : HCO <sub>3</sub> around 1 : 2	Fig. 7
Quaternary aquifer	Incongruent dolomite weathering	No (apart from QG3)	SI <sub>dolomite</sub> > -0.5; Mg:HCO <sub>3</sub> > 1:4	No obvious increasing trend in $\delta^{13}$ C with increasing Mg / Ca	Fig. 7
<b>C</b>	Cation exchange	Yes	Enrichment in Ca and loss of Na along flow path	SI <sub>calcite</sub> and SI <sub>dolomite</sub> close to or exceeding 0	Fig. 3
	Addition of sulfate from fertiliser	Yes	Positive relationship between $SO_4$ and $NO_3$	Increasing $\delta^{34}$ S values with increasing NO <sub>3</sub> concentrations	Figs. 9 and 10
	Gypsum dissolution	Yes	Ca: SO <sub>4</sub> close to 1	$\mathrm{SI}_{\mathrm{gyp}} < -0.5$	_

ing and freshening phases in hydrochemical facies evolution. The freshwater in the recharge area mainly belongs to the Ca–MixHCO<sub>3</sub> (14) facies, and seawater belongs to the Na– Cl (4) facies. Most of the groundwater samples do not follow the predicted succession of facies along the mixing line (4– 7–10–13), and rather indicate a small degree of simple mixing between freshwater and seawater components, along with inverse cationic exchange between Na and Ca. This leads to the water reaching the Ca–Cl (16) facies observed in brackish groundwater in the carbonate aquifer. The surplus Ca<sup>2+</sup> from ion exchange may also cause super-saturation with respect to calcite and dolomite, consistent with the observed positive values in the majority of samples (Langmuir, 1971). Net dissolution of carbonate minerals is not evident as a major process in the groundwater, as is shown by a number of lines of evidence below (Mg / Ca ratios, stable isotopes of DIC – see Table 2). Cation exchange is thus considered crucial to the development of the Ca–Cl facies in the more evolved waters.

Generally most groundwater samples collected from west of the Daweijia well field are characterised by depletion of Na<sup>+</sup> more or less balanced by equivalent enrichment of Mg<sup>2+</sup> plus Ca<sup>2+</sup>. Both  $\Delta$ Na<sup>+</sup> and  $\Delta$ Mg<sup>2+</sup> decrease with an increasing fraction of seawater ( $f_{sw}$ ), especially for  $f_{sw} > 3\%$ (Fig. 3), which would be more characteristic of a salinisationdriven base exchange process (Appelo and Postma, 2005). This may suggest a residual effect from the previous saline intrusion which is yet to re-equilibrate with the aquifer matrix. Most groundwater samples from the carbonate aquifer show  $\Delta$ Ca<sup>2+</sup>,  $\Delta$ Mg<sup>2+</sup>, and  $\Delta$ SO<sup>2-</sup><sub>4</sub> increases with salinity,



Figure 6. Hydrogeochemical facies evolution (HFE) diagram. QA – Quaternary aquifer; COA – Cambrian–Ordovician carbonate aquifer.

whereas  $\Delta Na^+$  decreases as salinity increases (Fig. 3), consistent with inverse cation exchange.

For fresh groundwater in the carbonate aquifer, the ionic deltas values are close to 0, indicating the modifying processes are controlled by conservative mixing and there has been little chemical interaction between the groundwater and the aquifer material. Compared to the conservative mixing, the excess of SO<sub>4</sub> observed (positive  $\Delta SO_4^{2-}$  values) might be attributed to gypsum dissolution, under the influence of seawater intrusion (creating temporary undersaturation). However, only greater degrees of seawater intrusion can cause gypsum dissolution to result in the SO<sub>4</sub> excess (Daniele et al., 2013), and the chloride data are inconsistent with ongoing seawater intrusion. It can therefore be inferred that there must be an additional source of SO<sub>4</sub>. Anthropogenic fertiliser input may explain the increases in  $SO_4^{2-}$  along with  $NO_3^{-}$  and possibly even  $Ca^{2+}$  and  $Cl^{-}$  in the aquifer, as is discussed further below.

#### 5.2 Groundwater interaction with carbonate minerals

The evolution of DIC and  $\delta^{13}C_{\text{DIC}}$  in the carbonate system begins with atmospheric CO<sub>2</sub> with  $\delta^{13}C$  value  $\sim -7 \%$  VPDB, while subsequent dissolution of soil gas carbon dioxide leads to depletion of the carbon, depending on which source of vegetation is dominant (Clark and Fritz, 1997). Concentrations of DIC in fresh and brack-ish groundwater were in the range of 60.1–446.5 mg L<sup>-1</sup> (average 189.2 mg L<sup>-1</sup>) and 46.2–512.7 mg L<sup>-1</sup> (average 203.1 mg L<sup>-1</sup>), respectively (Table 1). The  $\delta^{13}C_{\text{DIC}}$  values

of groundwater ranging from -14.5 to -5.9 ‰ vs. PDB are similar to groundwater from carbonate aquifers in southwest China, which has typical values ranging from -15.0to -8.0 % (Li et al., 2010). The  $\delta^{13}C_{\text{DIC}}$  in groundwater shows a negative correlation with DIC concentration, particularly in the karst aquifer (Fig. 4). This indicates that simple, congruent dissolution of carbonate minerals is not a major source of DIC in the groundwater. Rather,  $\delta^{13}C_{DIC}$ may undergo progressive equilibration with aquifer carbonate during sequential carbonate dissolution/precipitation reactions (e.g. de-dolomitisation). This is consistent with the increasing Mg / Ca ratios observed along the flow path, along with increasing  $\delta^{13}C_{DIC}$  values in the carbonate aquifer (see Fig. 7a), but no overall increase in HCO<sub>3</sub> (Fig. 4 and Table 2). Near the coastline, the more enriched  $\delta^{13}C_{DIC}$  values and lower DIC may also result due to mixing with seawater. An increasing trend in SO<sub>4</sub> and Mg concentrations and Mg / Ca ratios along the flow path is also indicative of de-dolomitisation (e.g. Jones et al., 1989; Plummer et al., 1990; López-Chicano et al., 2001; Szynkiewicz et al., 2012) in which the dissolution of gypsum and anhydrite leads to over-saturation and thus dolomite dissolution and calcite precipitation. For deeper carbonate groundwater underlying the Daweijia well field, the negative correlation between  $Ca^{2+}$ and  $\delta^{13}C_{DIC}$  (Fig. 7b) also indicates that Ca enrichment in groundwater may be not attributed to carbonate dissolution. The increase in  $\delta^{13}$ C with decreasing Ca content is likely related to the incongruent reaction, which removes Ca from solution and progressively increases  $\delta^{13}$ C to equilibrate with the aquifer matrix. In the Quaternary aquifer, the minor cal-



**Figure 7.** Graphs showing (a) Mg / Ca ratios (by meq L<sup>-1</sup>); (b) Ca<sup>2+</sup> concentrations vs.  $\delta^{13}C_{DIC}$  values in different aquifers (grey – groundwater samples collected from the Quaternary aquifer; blue – groundwater samples collected from the carbonate aquifer). See Fig. 3 for legend.

cite dissolution occurring could lead to increasing  $\delta^{13}$ C with increasing Ca. An alternative process may remove the HCO<sub>3</sub> along flow paths (e.g. CO<sub>2</sub> de-gassing).

Deines et al. (1974) showed that there are significant differences in the relationships between carbon isotopic composition and chemical variables for open and closed system conditions. Based on their model (which uses similar initial conditions to the study area) the chemical and isotopic composition of groundwater at a given pH in equilibrium with a reservoir of a given  $P_{\rm CO_2}$  and  $\delta^{13}\rm C_r$  can be estimated. For the closed system model the  $^{13}\rm C$  content of the solution depends not only on the  $^{13}\rm C/^{12}\rm C$  ratio of the reservoir CO<sub>2</sub> ( $\delta^{13}\rm C_{rock}$ ). The pH and  $\delta^{13}\rm C$  values of the carbonate aquifer groundwater suggest evolution in a relatively closed system. Lower  $\delta^{13}\rm C$  value (-14.5 ‰) of shallow groundwater (QG4) in recharge area may be more affected by the soil CO<sub>2</sub> in areas of intensive corn cultivation, ranging from approximately -18 to -25 ‰ (Deines et al., 1974). In this area, the irrigation using local carbonate groundwater may have resulted in mixing between the shallow groundwater with similar values to this, and the deep water from the carbonate aquifer (with higher values), leading to the intermediate value observed. Most groundwater in the study area is supersaturated with respect to calcite and dolomite (Han et al., 2015). The hydrochemical composition of groundwater is influenced by CO<sub>2</sub> exsolution and CaCO<sub>3</sub> precipitation, which can be described by the reaction

$$Ca^{2+} + 2HCO_3^- = CaCO_3 \downarrow +CO_2(g) \uparrow +H_2O_3$$

At isotopic equilibrium CO<sub>2</sub> is enriched in <sup>12</sup>C and CaCO<sub>3</sub> in  ${}^{13}C$  with respect to  $HCO_3^-$  (Deines et al., 1974). Since for each mole of  $CO_2$  exsolved one mole of  $CaCO_3$  is precipitated, the kinetic isotope effects is removal of <sup>12</sup>C enriched carbon from the solution, which concentrates <sup>13</sup>C in the remaining HCO<sub>3</sub><sup>-</sup>. The enrichment of  $\delta^{13}C_{DIC}$  without change in  $HCO_3^-$  content may thus be caused by  ${}^{12}CO_2$  loss during exsolution and <sup>13</sup>C enrichment in solution. Dolomite dissolution is likely to add  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $HCO_3^-$  to the solution, while calcite precipitation will remove DIC and retain calcite saturation, resulting in generally increasing Mg / Ca ratios along flow paths, along with increasing  $\delta^{13}$ C values (Freeze and Cherry, 1979; Edmunds et al., 1987; Cardenal et al., 1994; Kloppmann et al., 1998). The dissolution of even very small amounts of gypsum may cause this process to occur in carbonate aquifers, which is usually characterised by near saturation with respect to calcite, by creating temporary under-saturation (due to the addition of calcium but not a bicarbonate ion) (Plummer et al., 1990; López-Chicano et al., 2001; Moral et al., 2008; Szynkiewicz et al., 2012).

Additionally, Sr is good proxy for Ca variations and sources with higher correlation, and the concentration of  $Sr^{2+}$  is often particularly high and frequently correlated with  $SO_4^{2-}$  concentrations (Fig. 8). In addition to Sr's origin from celestite, which may be present as microcrystalline inclusions in gypsum, Sr<sup>2+</sup> can also occur as solid solution in carbonate minerals (Hunkeler and Mudry, 2007). Large amounts of anthropogenic chemical input will change these highly correlated relationships. Figure 8 shows different slopes in the relationship between Cl / TDS and Sr for different water types. The chloride-rich brackish water with high Cl / TDS ratios has high Sr contents in the carbonate aquifer; in contrast, the sulfate-rich brackish water with low Cl / TDS has a wide range of Sr contents in the Quaternary aquifer. The higher Sr contents in the COA likely result due to enhanced from water-rock interaction (carbonate mineral dissolution), possibly enhanced by historic seawater intrusion.

Another possible control on the carbon chemistry of the groundwater is that active re-circulation of water is taking place in the unsaturated zone of the aquifer due to anthropogenic activity. In the local agricultural soils, CO<sub>2</sub> concentration is usually high, with a  $\delta^{13}$ C<sub>DIC</sub> between -6.3



**Figure 8.** Plot of Cl / TDS ratio vs. Sr (mg  $L^{-1}$ ) from groundwater samples in the Daweijia area. Sulfate concentration of each sample is also indicated by the size of the point. CG – groundwater from the carbonate aquifer; QG – groundwater from the Quaternary aquifer.

and  $-13.1 \,\%$  and  $\delta^{13}$ C of dissolved organic carbon between  $-23.2 \,\text{and} -21.8 \,\%$  (Yang, 2011). During recharge events, water dissolves the soil CO<sub>2</sub> which is involved in carbonate dissolution and becomes part of the DIC pool. If this process is conducted over successive irrigation, the HCO<sub>3</sub><sup>-</sup> concentration increases and  $\delta^{13}$ C<sub>DIC</sub> will deplete owing to the dissolved biogenic CO<sub>2</sub> in soil.

#### 5.3 Sources of dissolved SO<sub>4</sub> to groundwater

Dissolved  $SO_4^{2-}$  of groundwater in the coastal aquifers might originate from several sources, potentially including (i) natural and artificial sulfates in rainwater, (ii) dissolution of sulfate-bearing evaporates (e.g. gypsum and anhydrite), (iii) seawater, and (iv) anthropogenic pollutants (e.g. domestic sewage, detergent and agricultural fertilisers). The  $\delta^{34}$ S of groundwater SO<sub>4</sub> are used as a tracer to identify the sources of dissolved  $SO_4^{2-}$  to the groundwater in this study. Figure 5 shows the relation between  $\delta^{34}S_{SO_4}$  values and SO<sub>4</sub> / Cl for groundwater samples, showing typical literature values for sulfur isotopic composition of major sulfate sources. Most of the water samples from the Daweijia area have sulfur isotopic compositions that reflect mixed sources. The  $\delta^{34}S_{SO_4}$  values are generally lower in the upstream area  $(+5.4 \sim +5.7 \text{ }\%)$ , increasing along the groundwater flow paths towards the coast (+13.1 ‰). Enrichment in  $\delta^{34}S_{SO_4}$  may result from sulfate reduction, whereas sulfide oxidation generally leads to negative  $\delta^{34}S_{SO_4}$  values (Clark and Fritz, 1997). However, there are no negative  $\delta^{34}S_{SO_4}$  values observed in this study

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area, indicating minor or negligible sulfide (such as pyrite) oxidation occurring in the aquifer.

 $\delta^{34}S_{SO_4}$  value of modern seawater is approximately +21 ‰ (Rees et al., 1978). The  $\delta^{34}S_{SO_4}$  of groundwaters, ranging from +13.1 to +5.4 % with a mean value of +8.9 ‰, thus generally discount this as a significant source of sulfate, consistent with the low mixing fractions calculated using Cl. The  $\delta^{34}S_{SO_4}$  values of precipitation from eight stations in the northern region of the Yangtze River range from +4.9% to +11.0% (Hong et al., 1994). Aside from CG1, the  $\delta^{34}S_{SO_4}$  compositions of the samples overlap with the isotopic range of rainfall. However, rainfall is characterised by higher SO<sub>4</sub> / Cl (2.26, Zhang et al., 2012) than the groundwater  $(0.16 \sim 0.97)$  and significantly lower total concentrations than are observed, indicating that this is only a partial origin of sulfate in groundwater. Sulfate minerals (gypsum, anhydrite, etc.) from marine sources typically have  $\delta^{34}$ S<sub>SO4</sub> values between +9 and +30.2 ‰ (Shi et al., 2004; Vitòria et al., 2004). As groundwater flows downwards into the deeper karst aquifer, the  $\delta^{34}$ S values increase and approach the values in marine evaporites, part of the continuous de-dolomitisation reaction discussed above. However, this cannot explain the observed sulfate levels in the Quaternary aquifer (see mass balance calculations below).

Fertilisers have a wide range of  $\delta^{34}S_{SO_4}$  values ranging from -6.5 to +11.7 ‰, with mean values of +3.7 ‰ and -0.8 ‰ in the Northern Hemisphere (Szynkiewicz et al., 2011) and China (Li et al., 2006), respectively. Apart from CG1 ( $\delta^{34}$ S<sub>SO4</sub> value of +13.1 ‰), the  $\delta^{34}$ S<sub>SO4</sub> values of the rest groundwater samples are within the  $\delta^{34} \dot{S}_{SO_4}$  ranges of known fertilisers. The isotopic  $\delta^{34}$ S values in fertilisers significantly differ from the geological SO<sub>4</sub> inputs of sedimentary origin, and overlap with most of the observed compositions (Fig. 5). In addition, the very high nitrate concentrations observed in the groundwater (up to  $625 \text{ mg L}^{-1}$ ) strongly indicate a high input of excess fertiliser residue via irrigation returns to the aquifer. This indicates that sulfate in fertilisers should be taken into account as a major contributing source of dissolved SO<sub>4</sub> in groundwater, especially from the Quaternary aquifer. This is also confirmed by the general positive relationship between  $NO_3^-$  and  $SO_4^{2-}$  concentrations (Fig. 9a) and correlation (albeit weak) between  $\delta^{34}$ S values and NO<sub>3</sub> concentrations in the Quaternary aquifer (Fig. 9b). It can be assumed that other anthropogenic sources of SO<sub>4</sub> such as atmospheric deposition or detergents from domestic/wastewater sources, or pig manure are negligible in the study area.

Despite the clear overlap in  $\delta^{34}$ S of fertilisers and groundwater SO<sub>4</sub><sup>2-</sup>, the  $\delta^{34}$ S measured in upstream locations (e.g. QG3 and QG4) probably reflect inputs from geologic SO<sub>4</sub> sources (such as soil sulfate) (Fig. 5). In contrast, the sulfur isotope values are more consistent with marine sedimentary sources of groundwater SO<sub>4</sub> in the carbonate aquifer, due to the sustained water–rock interaction and longer resi-



**Figure 9.** Bivariate plots for (a) relationship between  $SO_4^{2-}$  and  $NO_3^-$  concentration and (b)  $\delta^{34}S_{SO_4}$  vs.  $NO_3^-$  concentrations. See Fig. 2 for legend.

dence time. The evidence for gypsum dissolution as part of de-dolomitisation in the major ion and carbon isotope data (discussed above) is also consistent with a marine evaporite source of sulfur in the deeper aquifer.

Both  $\delta^{13}$ C and  $\delta^{34}$ S<sub>SO4</sub> values increase along the groundwater flow path (Table 3). Groundwater with low  $\delta^{13}$ C values (e.g. -14.5‰) and  $\delta^{34}$ S<sub>SO4</sub> values (e.g. ~+5.4‰) represents recently recharged water, which is dominated by unsaturated zone processes and diffuse flow. Equilibration with carbonate minerals in the aquifer matrix during de-dolomitisation makes an important contribution to the groundwater  $\delta^{13}$ C evolution in the karst aquifer ( $\delta^{13}$ C up to -5.9‰ in QG11), reaching saturation with respect to calcite and dolomite. Then, the high loads of fertilisers accessible during agricultural return flow are the most likely source of the dissolved sulfate and nitrate, particularly in the shallow Quaternary aquifer.

# 5.4 Anthropogenic contribution on groundwater chemistry and environmental implications

Fertilisers are applied beyond what is taken up by crops in the long term in many parts of China (Davidson and Wei, 2012), as evident from the high NO<sub>3</sub><sup>-</sup> concentrations in groundwater. The wide range of  $NO_3^-$  concentrations indicates considerable anthropogenic input under human activities (e.g. fertiliser usage during irrigation, leakage from septic system), which is responsible for the deterioration of local groundwater and near-shore seawater quality. NO<sub>3</sub><sup>-</sup> concentrations are obviously elevated (e.g.  $75-386 \text{ mg L}^{-1}$ ) in the shallow groundwater from the Quaternary aquifer, especially near the Daweijia well field, resulting from agricultural fertilisation. Due to nitrate input from fertilisers, the relatively low nitrate concentrations in some deep groundwater (e.g. CG4, CG14), which are located in the upstream area, show that, compared with groundwater in the downgradient area, these waters have locally reduced impacts from contamination. However, many deep groundwater samples have similar ranges of  $NO_3^$ concentrations to shallow groundwaters, indicating that there is a hydraulic connection between shallow and deep aquifers (e.g. QG5 and CG7 in Fig. 2).

To quantify the fertiliser contributions to groundwater chemistry, we considered the inputs of precipitation infiltration, seawater intrusion and evaporite dissolution into groundwater system. We used a mass balance approach to evaluate the contribution of difference sources of sulfate to the dissolved  $SO_4^{2-}$  of groundwater. The four sources of sulfate in the dissolved  $SO_4^{2-}$  of groundwater are from precipitation, seawater, fertiliser and evaporate dissolution. The isotopic composition of groundwater sulfate ( $\delta^{34}S_{SO_4}$ ) can be calculated by

$$\delta^{34} S_{gw} \times SO_{4,gw} = \delta^{34} S_{prec} \times SO_{4,prec} + \delta^{34} S_{sw} \times SO_{4,sw} + \delta^{34} S_{fer} \times SO_{4,fer} + \delta^{34} S_{evp} \times SO_{4,evp},$$
(4)

where  $\delta^{34}S_{\text{prec}}$ ,  $SO_{4,\text{prec}}$ ,  $\delta^{34}S_{\text{sw}}$ ,  $SO_{4,\text{sw}}$ ,  $\delta^{34}S_{\text{fer}}$ ,  $SO_{4,\text{fer}}$ ,  $\delta^{34}S_{\text{evp}}$ , and  $SO_{4,evp}$ , correspond to the end member  $\delta^{34}S$  values for rainfall (+5.39‰, Hong et al., 1994), seawater (+21‰, Clark and Fritz, 1997), fertiliser (-0.8‰, Li et al., 2006), and sulfate marine evaporates of Cambrian–Ordovician age (+28‰, Clark and Fritz, 1997). The dissolved  $SO_4^{2-}$  concentration (SO<sub>4,gw</sub>) in groundwater is the total sulfate contribution from precipitation, seawater, fertiliser and evaporate:

$$SO_{4,gw} = SO_{4,prec} + SO_{4,sw} + SO_{4,fer} + SO_{4,evp},$$
(5)

where

$$SO_{4,prec} = [SO_{4,prec}] \times R = 8.02 \,\mathrm{mg} \,\mathrm{L}^{-1} \times 0.783$$
 (6)

$$SO_{4,sw} = [SO_{4,sw}] \times f_{sw} = 2710 \,\mathrm{mg} \,\mathrm{L}^{-1} \times f_{sw}.$$
 (7)

The  $SO_4^{2-}$  concentration ([ $SO_{4,prec}$ ] = 8.02 mg L<sup>-1</sup>) of the local precipitation was reported by Zhang et al., 2012, and

**Table 3.** Characteristic ranges of  $\delta^{13}$ C and  $\delta^{34}$ S<sub>SO4</sub> values in groundwater and seawater (showing a vertically increasing trend) (see locations in Fig. 2).

	Shallow groundwater from upperstream area (A1)	Deep groundwater from upperstream area (A2)	Shallow groundwater from downstream area (B1)	Deep groundwater from downstream area (B2)	Seawater (C)
$\delta^{13}$ C (‰,V-PDB)	-14.5 to -13.5	-12.8 to -9.0	-11.0 to -5.9	-9.7 to -10.6	-1 to +2
$\delta^{34}$ S <sub>SO4</sub> (‰, CDT)	5.4 to 5.7	9.0 to 10.9	7.2 to 10.1	8.7 to 13.1	21



**Figure 10.** Calculated  $SO_4^{2-}$  contribution of groundwater from four different sources (QA – groundwater from the Quaternary aquifer; COA – groundwater from the carbonate aquifer).

 $SO_4^{2-}$  concentration ([SO<sub>4,sw</sub>] = 2710 mg L<sup>-1</sup>) of the seawater referenced from Clark and Fritz (1997). *R* is the recharge rate equal to the ratio of the amount of precipitation infiltration and the amount of the total groundwater resources in the study area. According to the water balance calculations in the local groundwater flow system (CGS, 2007), groundwater is mainly recharged from precipitation infiltration, which occupied 78.3 % (*R*) of the total recharge water volume.  $f_{sw}$  can be calculated by Eq. (1) for each groundwater sample.

The results of the mass balance, showing sulfate contribution to groundwater from fertiliser (assuming these end members correspond to values in the study area) are shown in Fig. 10. In total, 4 to 22 % of the dissolved  $SO_4^{2-}$  concentrations in groundwater are contributed from evaporite dissolution, whereas 30 to 75% of the dissolved  $SO_4^{2-}$  concentrations in groundwater can be ascribed to input from fertilisers. According to these calculations, overall, the local application of the fertilisers is now responsible for the majority of dissolved  $SO_4^{2-}$  in groundwater. The contribution reaches on average 62.1 % in the Quaternary aquifer and 48.7 % in the deeper carbonate aquifer, showing that the shallow Quaternary aquifer is particularly prone to pollution by fertiliser utilisation. The sulfate contributions to groundwater from seawater and precipitation are less than 10%, which is relatively lower and is consistent with the observation that pumping restrictions have effectively halted saline intrusion in the area. We analysed the sensitivity of the mass balance by changing  $\pm 10\%$  of the end-member sulfur isotope compositions of fertiliser and evaporate, respectively. We found that the change in  $\delta^{34}S_{fer}$  varied the contributions from fertiliser and evaporate by  $\pm 0.1$  and  $\pm 0.2\%$ , respectively. The  $\pm 10\%$  change in  $\delta^{34}S_{evp}$  leads to changes in the contributions from fertiliser and evaporate by  $\pm 0.4$  and  $\pm 2\%$ , respectively. This suggests that the results are more sensitive to  $\delta^{34}S_{evp}$  values in the mass balance.

Although further investigation is needed to determine the contribution of dissolved sulfate from different pollution sources (the end-member values used above are naturally uncertain and may bias the overall % contributions), the current results indicate that the anthropogenic contaminant input plays a dominant role in providing sulfate to the shallow groundwater (as well as nitrate), and that this influence has extended into the deeper carbonate aquifer. This widespread shift towards agricultural return flow becoming the dominant control on groundwater chemistry, particularly in shallow aquifers, is consistent with what is unfolding over many areas of north China (Currell et al., 2012). This is a disturbing trend, particularly given the time lags involved in groundwater systems equilibrating towards new water quality norms, which suggest significant future degradation of groundwater resources will continue to occur in these areas.

# 6 Conclusions

The coastal aquifer in the Daweijia area, northeast China, is composed of interlayered Quaternary sedimentary and Cambrian–Ordovician carbonate rocks. The groundwater has evolved from freshwater (meteoric recharge) to brackish water in a series of water types: Ca(•Mg)–HCO<sub>3</sub> •Cl  $\rightarrow$  Ca• Na–Cl•HCO<sub>3</sub>  $\rightarrow$  Ca–Cl  $\rightarrow$  Na• Ca–Cl  $\rightarrow$  Na–Cl via a combination of natural and anthropogenic processes. After the cessation of the groundwater pumping in the Daweijia well field, the TDS concentration of groundwater has increased; however, the Cl<sup>-</sup> concentrations have not, and in some areas have decreased. The major change has been large increases in SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> concentrations, which have increased several times compared to 1981. This indicates that the local government efforts to restrict groundwater abstraction have been effective in their purpose of limiting saline intrusion; however, water quality degradation has continued due to a new source, nitrate and sulfate contamination, largely resulting from the heavy application of agricultural fertilisers.

There are the increasing trends of  $\delta^{13}C_{DIC}$  and  $\delta^{34}S_{SO_4}$ values for groundwater along the flow path. The enrichment of  $\delta^{13}C_{DIC}$  of groundwater may be caused by kinetic isotope effects as most groundwater is super-saturated with respect to calcite and dolomite, which can cause  ${}^{12}CO_2$  loss during exsolution and  ${}^{13}C$  enrichment in solution. The pH and  $\delta^{13}C$ values of the investigated groundwater suggest evolution in a closed system. The potential sources of dissolved  $SO_4^{2-}$ in the coastal aquifers include natural and artificial sulfates in rainwater, dissolution of sulfate evaporates (e.g. gypsum and anhydrite), seawater, and anthropogenic pollutants (e.g. agricultural fertilisers). We estimated the contributions of the four different sources of the dissolved sulfate in groundwater quality by using the mass balance approach. Apart from seawater and precipitation (less than 10%), the fertiliser contribution in sulfate concentrations of groundwater could be as high as an average of 62.1% in the Quaternary aquifer, and 48.7 % in the deeper carbonate aquifer, depending on the end-member composition used. Although the processes that affect the groundwater quality and the contribution to the dissolved sulfate of groundwater in the Daweijia area should be further evaluated by more investigation (such as nitrogen isotope data), the current research results obtained from a set of geochemical and isotopic tools show that the sulfate contribution from fertiliser application, compared with that from seawater intrusion and precipitation infiltration, is dominant, with a secondary source from long-term evaporite dissolution and de-dolomitisation as water equilibrates with the carbonate aquifer matrix.

Also, there are similar ranges of NO<sub>3</sub><sup>-</sup> concentrations, isotopic compositions ( $\delta^{13}C_{DIC}$  and  $\delta^{34}S_{SO_4}$ ) and water type in the shallow Quaternary and deeper carbonate aquifers in most parts of the study area, indicating interaction between shallow and deep groundwater in the study area, which has implications for aquifer protection from contamination by agricultural chemicals.

Coastal carbonate aquifers, a prolific groundwater source worldwide, are characterised by rapid groundwater circulation and recharge and are therefore highly vulnerable to anthropogenic contamination. Human activities in heavily populated areas such as the current study are now potentially the key driver in the hydrology and hydrochemical evolution of some of these coastal aquifers, as demonstrated here. Only by strictly controlling anthropogenic land-use and water-use activities can the pollution and degradation of these aquifers be prevented. Future studies could focus on the seasonal variation of sulfur and nitrogen isotopes of dissolved  $SO_4^{2-}$  and  $NO_3^-$ , respectively, and more detailed analysis of these stable isotopes in soil profiles. This could provide more insight into the dynamics of contamination of this and other similar aquifers.

Acknowledgements. This research was partially funded Zhu Kezhen Outstanding Young Scholars Program hv (no. 2015RC102), Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences. It was undertaken as part of a groundwater survey project entitled "Assessment of Vulnerability and Investigation of Environmental Geology in the Key Section of Circum-Bohai-Sea Region". The authors are grateful to Yang Jilong, Liu Xin, Xie Hailan and Pan Tong for their help and support during water sampling and monitoring in the field and data collection. We also want to acknowledge the constructive suggestions from Ian Cartwright and another anonymous reviewer.

Edited by: C. Stumpp

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