

1 Identification of anthropogenic and natural inputs of sulfate into a  
2 karstic coastal groundwater system in northeast China: Evidence from  
3 major ions,  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{34}\text{S}_{\text{SO}_4}$

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20 **Abstract**

21 The hydrogeochemical processes controlling groundwater evolution in the Daweijia area of  
22 Dalian, northeast China, were characterized using hydrochemistry and isotopes of carbon and  
23 sulfur ( $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{34}\text{S}_{\text{SO}_4}$ ). The aim was to distinguish anthropogenic impacts as distinct  
24 from natural processes, with a particular focus on sulfate, which is found at elevated levels  
25 (range: 54.4 to 368.8 mg/L; mean: 174.4 mg/L) in fresh and brackish groundwater. The  
26 current investigation reveals minor seawater intrusion impact (not exceeding 5% of overall  
27 solute load), in contrast with extensive impacts observed in 1982 during the height of  
28 intensive abstraction. This indicates that measures to restrict groundwater abstraction have  
29 been effective. However, hydrochemical facies analysis shows that the groundwater remains  
30 in a state of ongoing hydrochemical evolution (towards Ca-Cl type water) and quality  
31 degradation (increasing nitrate and sulphate concentrations). The wide range of  $\text{NO}_3$   
32 concentrations (74.7-579 mg/L) in the Quaternary aquifer indicates considerable input of  
33 fertilizers and/or leakage from septic systems. Both  $\delta^{13}\text{C}$  (-14.5 ‰ ~ -5.9 ‰) and  $\delta^{34}\text{S}_{\text{SO}_4}$   
34 (+5.4 ~ +13.1‰) values in groundwater show increasing trends along groundwater flow paths.  
35 While carbonate minerals may contribute to increasing  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{34}\text{S}_{\text{SO}_4}$  values in deep  
36 karstic groundwater, high loads of agricultural fertilizers reaching the aquifer via irrigation  
37 return flow are likely the main source of the dissolved sulfate in Quaternary groundwater, as  
38 shown by distinctive isotopic ratios and a lack of evidence for other sources in the major ion  
39 chemistry. According to isotope mass balance calculations, the fertilizer contribution to  
40 overall sulfate has reached an average of 62.1% in the Quaternary aquifer, which has a strong  
41 hydraulic connection to the underlying carbonate aquifer. The results point to an alarming  
42 level of impact from the local intensive agriculture on the groundwater system, a widespread  
43 problem throughout China.

44 **Keywords:** groundwater, carbonate aquifer, seawater intrusion, anthropogenic pollution

## 45 **1. Introduction**

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

57 Coastal areas are often sites of intensive human activity, including urbanisation and  
58 agriculture. Intensive agriculture is known to be associated in some areas with salinization  
59 (e.g. Ghassemi et al, 1995; Kumar et al., 2015) and other groundwater quality issues such as  
60 addition of nitrate, sulphate and other compounds contained in fertilizers (e.g. Kaown et al,  
61 2009; Currell et al, 2010). Environmental tracers, such as stable sulfur and carbon isotopes,  
62 e.g.  $\delta^{34}\text{S}$  of dissolved  $\text{SO}_4$  ( $\delta^{34}\text{S}_{\text{SO}_4}$ ), and  $\delta^{13}\text{C}$  in dissolved inorganic carbon ( $\delta^{13}\text{C}_{\text{DIC}}$ ), and  
63 major ion chemistry have been useful in identifying sources of salinity and dissolved sulphate

64 and carbonate species in groundwater (Sánchez-Martos et al., 2002; de Montety et al., 2008;  
65 Schiavo et al., 2009; Ghiglieri et al., 2012; Kim et al., 2015) and for determining water-rock  
66 interaction processes in carbonate aquifers (e.g., carbonate mineral dissolution/precipitation,  
67 cation-exchange) (Back et al., 1979; Plummer and Sprinkle, 2001; Moral et al., 2008; Daniele  
68 et al., 2013). However, to date few areas of major anthropogenic activity and known active or  
69 previous salinization from seawater intrusion have been assessed using these tracers, in order  
70 to distinguish different water quality degradation processes, such as seawater-freshwater  
71 mixing versus input of agricultural chemicals and irrigation return flow.

72 This study focuses on the coastal carbonate aquifers around Daweijia well field, which  
73 located in the Daweijia area of Dalian City, northeast China. Most previous investigations in  
74 this area have focused on the mechanism of seawater intrusion and related water-rock  
75 interactions (Wu et al., 1994; Yang, 2011; Zhao et al., 2012), but have ignored the potential  
76 impact of anthropogenic contributions to groundwater salinity and water quality degradation.  
77 Little is known about the influence of agricultural practices on sulphur cycling and transport  
78 in this and other coastal aquifers impacted by intensive agriculture. Here, we report new data  
79 for C and S isotopes and major ions in groundwater from the Daweijia area, which gives new  
80 insight into sources of water quality degradation, including agriculture. Using chemical and  
81 isotopic tracers, this study reveals the dominant factors controlling on groundwater  
82 hydrochemistry before and after groundwater pumping in the Daweijia well field, and

83 identifies the different sources of sulfate, salinity and determines the major controls on  
84 hydrochemical evolution. Understanding these issues can help to prevent further deterioration  
85 of groundwater quality in this and other similar systems in north China and elsewhere around  
86 the world.

## 87 **2. Study area**

88 The investigated area ( $39^{\circ}10' \sim 39^{\circ}14' \text{ N}$  and  $121^{\circ}37' \sim 121^{\circ}45' \text{ E}$ ) is located in northeast  
89 China along the Bohai-Sea coast (Fig. 1). It has a catchment area of  $66 \text{ km}^2$  to the north of  
90 Dalian City (population 3.25 million), Liaoning Province. The climate is warm temperate  
91 continental monsoon, with annual average temperature of  $\sim 10^{\circ}\text{C}$ . Most of the precipitation,  
92 totalling  $\sim 600 \text{ mm}$  annually (Dalian Municipal Meteorological Bureau, 2014) falls during the  
93 June-September rainy season. The ephemeral Daweijia River runs through the region from  
94 east to west. Under natural conditions, groundwater discharged into the sea from the  
95 southeast towards the northwest (Fan, 1984).

96 The geology of the Daweijia area consists of Quaternary deposits over-lying carbonate  
97 aquifers of Paleozoic (Ordovician and Cambrian) and Proterozoic (Sinian) age. Two groups  
98 of faults are developed in this area, namely NE normal faults (F1 and F2 in Fig. 1) and EW  
99 reverse faults (F3 and F4 in Fig. 1). These structural faults cut the bedrock and are the main  
100 channel for groundwater infiltration and movement, affecting the degree of subsurface karst  
101 development (Song, 2013). The main karst development sections in the Cambrian and

102 Ordovician formation include (i) 5 to 20 m.a.s.l (meters above sea level) (near surface karst),  
103 (ii) -5 to -40 m.a.s.l (shallow karst), (iii) -50 to -85 m.a.s.l (medium depth karst), and (iv) < -  
104 90 m.a.s.l. (deep karst) (Zhao, 1991). The aquifers within the Daweijia area can be divided  
105 into upper and lower aquifer systems; the upper aquifer is composed of Quaternary sediments  
106 with variable thickness of 0-40 m. This consists of gravel, sand and clay layers and is not  
107 extensively pumped for water supply. The carbonate aquifers underlying the Quaternary  
108 deposits are mainly composed of Lower Ordovician, Middle and Upper Cambrian limestone,  
109 with major karst development in the medium section between -40 and -70 m.a.s.l (Lü et al.,  
110 1981; Zhao, 1991). The most productive carbonate aquifers are distributed along Daweijia  
111 River valley. Figures 1 and 2 show a geological map and stratigraphic cross-section of the  
112 hydrogeological system along this valley, showing natural groundwater flow from east to  
113 west (Fan, 1984). The geologic contacts and hydraulic connections between the upper and  
114 lower aquifer systems used in this study were determined from geologic logs and geophysical  
115 exploration during a previous investigation of regional hydrogeology in the Daweijia area (Lü  
116 et al., 1981; Jin and Wu, 1990).

117 Seawater intrusion was first discovered in the Dalian area in 1964. This study focuses on  
118 the coastal aquifers around Daweijia well field (Fig. 1), which was established in 1969 and  
119 formerly provided major water supply for Dalian City as the pumping rates of  $12 \sim 24 \times 10^3$   
120  $\text{m}^3/\text{d}$  in 1970 (Lü et al., 1981). With the increase of pumping rate till 1983 (up to  $4.8 \sim 6.2 \times 10^3$

121 m<sup>3</sup>/d in 1977), the average chloride concentration of groundwater from eight fixed  
122 monitoring wells increased from 380 mg/L in 1968 to 1137 mg/L in 1982 (Song, 2013),  
123 indicating the serious seawater intrusion occurred. The groundwater withdrawal of the  
124 Daweijia well field was changed from a perennial pattern to a seasonal regime with a  
125 decrease by two-thirds of the pumped volume. The abstraction increased after 1991 but was  
126 reduced again from 20 ×10<sup>3</sup> m<sup>3</sup>/d in 1995 to 4×10<sup>3</sup> m<sup>3</sup>/d in 2000 (Li et al., 2006).  
127 Alternatively, in order to reduce the threat of seawater intrusion to the aquifer, with the  
128 establishment of surface water supply projects, water supply for Dalian City from the well  
129 field has ceased since 2001, with seasonal pumping for local agricultural irrigation (Song,  
130 2013). The area is also the site of ongoing intensive agricultural activity.

131       The carbonate aquifer is pumped for agricultural and public water supply. The Daweijia  
132 well field was established in 1969 for water supply to Dalian City and at peak usage, the  
133 upper aquifer suffered extensive drawdown. Along with this, the average chloride  
134 concentration in groundwater increased from 199 mg/L in 1966 to 559 mg/L in 1991, and  
135 reached a peak of 940 mg/L in 1994. Under the restrictions on groundwater extraction  
136 enacted, the Cl value returned to 454 mg/L in 2005. This included the drastic measure of  
137 switching off the well field supplying Dalian City since 2001 (Song, 2013). Although the  
138 groundwater levels have recovered in recent years, groundwater salinity has not completely  
139 been reversed, and elevated nitrate and sulphate concentrations have continued since this time.

140 Potential causes include ‘residual’ seawater intrusion which has not yet re-equilibrated with  
141 recovered water levels and/or different sources of contamination, associated with agriculture  
142 or urban activities.

### 143 **3. Methods**

#### 144 **3.1 Sampling and analysis**

145 We collected 30 water samples during two sampling campaigns (June 2006 and August  
146 2010) for analysis of major ions and stable isotopes ( $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{34}\text{S}_{\text{SO}_4}$ ). The samples  
147 include 29 from wells and one seawater sample. Sampling wells are production wells with  
148 variable depths (8.4-128 m) and screened intervals (lengths of 2-35 m, see Table 1) and these  
149 are distributed mainly along the Daweijia River valley (Fig. 1). The screened intervals of  
150 wells in the carbonate aquifer are mainly between 65-100 m below ground surface (Table 1).  
151 Before sampling, the wells were pumped for at least for half an hour until physico-chemical  
152 parameters (e.g., water temperature, pH, electrical conductivity and dissolved oxygen)  
153 stabilised. All samples were filtered through 0.45 $\mu\text{m}$  pore-size filter paper and stored in  
154 HDPE bottles at 4°C in a cool room until analysis. The samples prepared for cation analysis  
155 were acidified to pH<2 by adding high purity  $\text{HNO}_3$ . Bicarbonate was determined in the field  
156 by titrating with 0.22N  $\text{H}_2\text{SO}_4$ . Major anions were measured by ion chromatography  
157 (SHIMADZU), and major cations were determined using ICP-AES by the Laboratory of  
158 Physics and Chemistry, Institute of Geographic Sciences and Natural Resources Research



159 (IGSNRR), Chinese Academy of Sciences (CAS). The ion balance errors of the chemical  
160 analyses were generally within  $\pm 15\%$ . The hydrogeochemical code PHREEQC-2 (version  
161 2.18.3, Parkhurst and Appelo, 1999) was used to determine the saturation indexes (SI) of  
162 calcite, dolomite and gypsum.

163 The  $\delta^{13}\text{C}$  values of dissolved inorganic carbon (DIC) in 16 water samples were  
164 measured using continuous flow on a Finnigan MAT 252 mass spectrometer, with the  
165 automated headspace analysis of the preparation device, in the State Key Laboratory of  
166 Environmental Geochemistry, Institute of Geochemistry (Guiyang), CAS. The results of  $\delta^{13}\text{C}$   
167 analysis are expressed in conventional delta ( $\delta$ ) notation, defined as  $\delta = (R_{\text{sample}} -$   
168  $R_{\text{standard}})/R_{\text{standard}} \times 1000$ , where R is the ratio of  $^{13}\text{C}/^{12}\text{C}$ . The  $\delta^{13}\text{C}$  values of dissolved  
169 inorganic carbon (DIC) are expressed relative to the standard Vienna Peedee Belemnite  
170 (VPDB), with an analytical precision of  $\pm 0.2\%$ . Samples for  $^{34}\text{S}$  in dissolved sulfate in 18  
171 groundwater samples (Table 1) were measured by a Finnigan MAT Delta-S gas mass  
172 spectrometer after on-line pyrolysis with an EA (Elemental Analyzer) in the Laboratory for  
173 Stable Isotope Geochemistry, Institute of Geology and Geophysics, CAS. The method of  
174 Halas and Szaran (1999) was used for converting precipitated  $\text{BaSO}_4$  to  $\text{SO}_2$ . The  
175 international standard against which  $\delta^{34}\text{S}$  values are referenced is the troilite (FeS) phase of  
176 the Cañon Diablo meteorite (CDT), which has a  $^{34}\text{S}/^{32}\text{S}$  abundance ratio of 0.0450 and are

177 reported as  $\delta$  (‰) difference from the standard with an analytical precision of better than or  
178 about  $\pm 0.4\%$ .

### 179 **3.2 Ionic deltas and mixing calculations**

180 To further investigate the hydrochemical behaviour of major cations and diagnose the  
181 processes modifying hydrochemical composition of groundwater in the aquifer, ionic delta  
182 values were calculated. The delta values express enrichment or depletion of particular ions  
183 relative to a conservative mixing system. These have been used in previous studies as  
184 effective indicators of groundwater undergoing freshening or salinization, along with  
185 associated water-rock interaction processes (primarily cation exchange – e.g., Appelo, 1994).  
186 Based on variations of molar Cl/Br ratios and major ions in groundwater (section 5.1), we  
187 have ruled out significant sources of Cl<sup>-</sup> other than meteoric and oceanic inputs. It is assumed  
188 in these calculations that there is no chloride input from salts in the aquifer matrix itself, and  
189 that Cl can be regarded as the most conservative species during mixing and hydrochemical  
190 evolution. The fraction of seawater ( $f_{sea}$ ) in a groundwater sample can thus be calculated  
191 using (Appelo and Postma, 2005):

$$192 \quad f_{sw} = \frac{C_{Cl,sam} - C_{Cl,f}}{C_{Cl,sw} - C_{Cl,f}} \quad (1)$$

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

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

$$198 \quad C_{i,mix} = f_{sw} \cdot C_{i,sw} + (1 - f_{sw}) \cdot C_{i,f} \quad (2)$$

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

$$202 \quad \Delta C_i = C_{i,sam} - C_{i,mix} \quad (3)$$

## 203 4. Results

### 204 4.1 Chemical analysis

205 The physical and chemical characteristics of groundwater samples from the Quaternary  
206 aquifer (QA) and the Cambrian-Ordovician carbonate aquifer (COA) in the Daweijia are  
207 compiled in Table 1. Total dissolved solids (TDS) concentrations vary from 372 to 2403  
208 mg/L, with values increasing along the main direction of groundwater flow from the east  
209 towards the sea. Groundwater pH ranges from 6.5 to 7.6 with a mean of 7.2. Dissolved  
210 oxygen concentrations range from 1.3 to 8.6 mg/L with a mean of 5.6 mg/L. The fresh (<1  
211 g/L TDS) groundwater (e.g., CG6, CG14) is characterized as Ca-HCO<sub>3</sub>(·Cl) type water,  
212 while brackish (1 to 10g/L TDS) groundwater (e.g., CG7, CG10, CG11, CG17) is  
213 predominantly Ca-Cl type in the carbonate aquifer. Brackish groundwater in the shallow

214 Quaternary aquifer was observed to be Ca-Cl-SO<sub>4</sub> type water, or near the coastline, (e.g.,  
215 QG10, QG11) Na·Ca-Cl(·HCO<sub>3</sub>) type.

216 According to mixing calculations, minor seawater intrusion near the coastline is  
217 identified (Fig. 3), however the fraction of seawater does not exceed 5% and this compares  
218 with a fraction of 20.8% observed in 1982 (Wu et al., 1994). The groundwater in this study is  
219 characterized by a wide range of sulfate concentrations between 54.4 and 368.8 mg/L, with a  
220 mean value of 174.4 mg/L. Nitrate concentrations ranged from 43.1 to 579.4 mg/L with a  
221 mean value of 206.9 mg/L, far beyond the drinking water standard (50 mg/L) in China. The  
222 investigated seawater sample also has a very high nitrate concentration of 1092 mg/L.

223 Comparing background data (1962, Lü et al., 1981) and current data (2010, in this study),  
224 the nitrate concentrations in groundwater increased from a range of 0~10.9 mg/L (n=51,  
225 mean value of 2.1 mg/L) in 1962 to a range of 43.1~579.4 mg/L (n=15, mean value of 207.1  
226 mg/L) in 2010 in the carbonate aquifer, and mean sulfate concentration increased from a  
227 range of 0~121.6 mg/L (n=64, mean value of 72.4 mg/L) in 1962 to a range of 65.1 ~ 306.9  
228 mg/L (n=15, mean value of 154.1 mg/L) in 2010. For the Quaternary aquifer, nitrate  
229 concentrations have changed from a range of 0~9.9 mg/L (n=3, mean value of 6.7 mg/L) in  
230 1962 to a range of 74.7 ~ 347.9 mg/L (n=9, mean value of 199.2 mg/L) in 2010, and sulfate  
231 from a range of 0~64.1 mg/L (n=3, mean value of 35.2 mg/L) in 1962 to a range of 54.4 ~  
232 368.8 mg/L (n= 9, mean value of 224.1 mg/L) in 2010.

233 The ionic delta values are plotted in Fig. 3, illustrating the varied distribution of  
234 geochemical types and evolution in the aquifer. Generally most groundwater samples are  
235 characterized by negative  $\Delta\text{Na}^+$  values and positive  $\Delta\text{Ca}^{2+}$  values. Some brackish  
236 groundwater samples have negative  $\Delta\text{Na}^+$  values and positive  $\Delta\text{Ca}^{2+} + \Delta\text{Mg}^{2+}$  values,  
237 displaying a deficit of  $\text{Na}^+$  with a corresponding excess in  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . There are positive  
238 values of  $\Delta\text{SO}_4^{2-}$  observed in most groundwater sample, and these are particularly high in the  
239 brackish groundwater (Fig. 3d).

#### 240 **4.2 Dissolved inorganic carbon (DIC) and $\delta^{13}\text{C}_{\text{DIC}}$**

241 Fig. 4 presents the  $\delta^{13}\text{C}_{\text{DIC}}$  isotope data and this can be used to infer the sources and  
242 evolution of dissolved inorganic carbon in the investigated groundwater (Clark and Fritz,  
243 1997). The measured  $\delta^{13}\text{C}_{\text{DIC}}$  values in groundwater range from -14.5 ‰ to -5.9 ‰ vs. PDB,  
244 with a mean value of -10.5 ‰ (Table 1). The water samples from the carbonate aquifer show  
245 a relatively narrow range of  $\delta^{13}\text{C}_{\text{DIC}}$  values (-12 to -8.4 ‰ with a mean value of -10.1 ‰, n=8)  
246 comparable to the range of  $\delta^{13}\text{C}_{\text{DIC}}$  values (-14.5 to -5.9 ‰, mean of -10.0 ‰, n=7) from the  
247 Quaternary aquifer. The waters collected in the upstream areas show  $\delta^{13}\text{C}$  values from -14.5  
248 to -12.8 ‰, while the middle area has values of -12.0 to -9.0 ‰ and the coastline values  
249 between -10.6 to -5.9 ‰ (Fig. 4, Table 1).

250 The local seawater sample (SW1) has a  $\delta^{13}\text{C}_{\text{DIC}}$  value of -3.3‰, which is relatively low  
251 compared to other reported values of modern seawater (-1~+2 ‰, Clark and Fritz, 1997).

252 Carbon in C<sub>4</sub> plants, which include maize, sugar cane and sorghum, has δ<sup>13</sup>C values that  
253 range from -10 to -16 ‰ with a mean value of ~ -12.5 ‰, while most C<sub>3</sub> plants have δ<sup>13</sup>C  
254 values that range from -24 to -30 ‰ with an average of ~ -27 ‰ (Vogel, 1993). Maize is the  
255 main agricultural product in the study area (Hu, 2010), indicating a C<sub>4</sub> vegetation source may  
256 be dominant. Carbonate dissolution and/or exchange leads to progressive enrichment of δ<sup>13</sup>C  
257 values towards the values of the mineral, usually with values between -2 and +2‰.

#### 258 **4.3 Stable isotopes of sulfate**

259 The δ<sup>34</sup>S<sub>SO<sub>4</sub></sub> compositions varied between +5.4 and +13.1‰ (Table 1). Sample CG1, with  
260 a sampling depth of 100 m and collected from the centre of a residential area, has the highest  
261 δ<sup>34</sup>S<sub>SO<sub>4</sub></sub> value (+13.1‰). The lowest δ<sup>34</sup>S<sub>SO<sub>4</sub></sub> value (+5.4 ‰) was found for sample QG3  
262 collected in an upstream area. Water samples from the carbonate aquifer are denoted with  
263 dashed line in Fig. 5 and have relatively high δ<sup>34</sup>S<sub>SO<sub>4</sub></sub> values (ranging from +6.6 to +13.1 ‰  
264 with mean value of +9.9 ‰, n=9) and low SO<sub>4</sub>/Cl ratios. The groundwater samples from the  
265 Quaternary aquifer are characterized by a relatively narrow range of δ<sup>34</sup>S<sub>SO<sub>4</sub></sub> values (ranging  
266 from +5.4 to +10.1 ‰ with mean value of +7.9 ‰, n=8) and wider range of SO<sub>4</sub>/Cl ratios.  
267 Some brackish groundwater (QG2 and QG10) from the Quaternary aquifer also shows these  
268 characteristics (Fig. 5). In general, the δ<sup>34</sup>S<sub>SO<sub>4</sub></sub> values increase with correspondingly lower  
269 SO<sub>4</sub>/Cl ratios in the direction of the coastline.

## 270 **5. Discussion**

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

### 277 **5.1 Seawater intrusion, freshening and cation exchange**

278 Widespread seawater intrusion appears to be a thing of the past, although local  
279 salinization continues around the well field. Chloride is an important index for estimating the  
280 extent of seawater intrusion, and is generally assumed to behave relatively conservatively.  
281 The molar Cl/Br ratios (based on values from this study and Yang et al, 2011) range from  
282 118.3 to 633.1 (n=11, mean value 394.3), which is generally below the oceanic ratio of ~650  
283 (Drever, 1997). As halite is Br-depleted from its mineral structure, halite precipitation may  
284 lead to depletion of the ratios, however it is unlikely that saturation with respect to halite  
285 could be reached in the groundwater (e.g., McCaffrey et al., 1987; Edmunds, 1996;  
286 Cartwright et al., 2004). Minor contamination, e.g., with pesticides such as ethyl dibromine,  
287 methyl bromide and/or preferential Cl adsorption on organic material may explain the lower  
288 than usual ratios. Overall the ratios do not indicate significant sources of additional Cl. The

289 TDS concentrations of groundwater in this study area varied within a range of 0.4-4.5 g/L in  
290 1981 (the peak period of seawater intrusion) (Lü et al., 1981). For the well CG2 located in the  
291 centre of the well field, TDS was 0.3 g/L on December 1965, 0.71 g/L on August 1981, 0.66  
292 g/L on December 1981, and up to 1.19 g/L on August 2010, an obvious increasing trend,  
293 however,  $\text{Cl}^-$  concentrations decreased from 375.6 mg/L in August 1981 to 288.4 mg/L in  
294 August 2010.. By contrast, there are much more significant increases on  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$   
295 concentrations in groundwater, which explains increasing TDS but decreasing chloride. For  
296 the well CG2,  $\text{SO}_4^{2-}$  concentration increased 5 times from 38.2 mg/L in August 1981 to 189.2  
297 mg/L in August 2010. While  $\text{NO}_3^-$  concentration increased 4 times from 64.6 mg/L in August  
298 1981 to 263.9 mg/L in August 2010 – far higher than the overall changes in TDS. These  
299 changes of different ions concentration in groundwater show that the anthropogenic input  
300 (e.g., application of agricultural fertilizer) has modified the hydrochemical composition of  
301 groundwater to great extent after the cessation of pumping in the well field.

302 The freshening of coastal aquifers can be shown using the multi-rectangular HFE-  
303 diagram (Fig. 6). This classification method proposed by Giménez-Forcada (2010) can be  
304 employed to determine the dynamics of seawater intrusion, considering the percentages of  
305 major ions, showing the intruding and freshening phases in hydrochemical facies evolution.  
306 The fresh water in the recharge area mainly belongs to the  $\text{Ca-MixHCO}_3$  (14) facies, and  
307 seawater belongs to the  $\text{Na-Cl}$  (4) facies. Most of the groundwater samples don't follow the



308 predicted succession of facies along the mixing line (4-7-10-13), and rather indicate a small  
309 degree of simple mixing between fresh and seawater components, along with inverse cationic  
310 exchange between Na and Ca. This leads to the water reaching the Ca-Cl (16) facies observed  
311 in brackish groundwater in the carbonate aquifer. The surplus  $\text{Ca}^{2+}$  from ion exchange may  
312 also cause super-saturation with respect to calcite and dolomite; consistent with the observed  
313 positive values in the majority of samples (Langmuir, 1971). Net dissolution of carbonate  
314 minerals is not evident as a major process in the groundwater, as is shown by a number of  
315 lines of evidence below (Mg/Ca ratios, stable isotopes of DIC – see Table 2). Cation  
316 exchange is thus considered crucial to the development of the Ca-Cl facies in the more  
317 evolved waters.

318 Generally most groundwater samples collected from the west of Daweijia well field are  
319 characterized by depletion of  $\text{Na}^+$  more or less balanced by equivalent enrichment of  $\text{Mg}^{2+}$   
320 plus  $\text{Ca}^{2+}$ . Both  $\Delta\text{Na}^+$  and  $\Delta\text{Mg}^{2+}$  decrease with an increasing fraction of seawater ( $f_{sw}$ ),  
321 especially for  $f_{sw} > 3\%$  (Fig. 3), which would be more characteristic of a salinization-driven  
322 base exchange process (Appelo and Postma, 2005). This may suggest a residual effect from  
323 the previous saline intrusion which is yet to re-equilibrate with the aquifer matrix. Most  
324 groundwater samples from the carbonate aquifer show  $\Delta\text{Ca}^{2+}$ ,  $\Delta\text{Mg}^{2+}$ , and  $\Delta\text{SO}_4^{2-}$  increases  
325 with salinity whereas  $\Delta\text{Na}^+$  decreases as salinity increases (Fig. 3), consistent with inverse  
326 cation exchange.

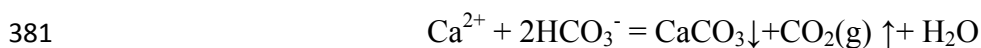
327 For fresh groundwater in the carbonate aquifer, the ionic deltas values are close to 0,  
328 indicating the modifying processes are controlled by conservative mixing and there has been  
329 little chemical interaction between the groundwater and the aquifer material. Compared to the  
330 conservative mixing, the excess of  $\text{SO}_4$  observed (positive  $\Delta\text{SO}_4^{2-}$  values) might be attributed  
331 to gypsum dissolution, under the influence of seawater intrusion (creating temporary under-  
332 saturation). However, only greater degrees of seawater intrusion can cause gypsum  
333 dissolution to result in the  $\text{SO}_4$  excess (Daniele et al., 2013), and the chloride data are  
334 inconsistent with ongoing seawater intrusion. It can therefore be inferred that there must be  
335 an additional source of  $\text{SO}_4$ . Anthropogenic fertilizer input may explain the increases in  $\text{SO}_4^{2-}$   
336 along with  $\text{NO}_3^-$  and possibly even  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  in the aquifer, as is discussed further below.

## 337 **5.2 Groundwater interaction with carbonate minerals**

338 The evolution of DIC and  $\delta^{13}\text{C}_{\text{DIC}}$  in the carbonate system begins with atmospheric  $\text{CO}_2$   
339 with  $\delta^{13}\text{C}$  value  $\sim -7\text{‰}$  VPDB, while subsequent dissolution of soil gas carbon dioxide leads  
340 to depletion of the carbon depending which source of vegetation is dominant (Clark and Fritz,  
341 1997). Concentrations of DIC in fresh and brackish groundwater were in the range of 60.1-  
342 446.5 mg/L (average 189.2 mg/L) and 46.2 - 512.7 mg/L (average 203.1 mg/L), respectively  
343 (Table 1). The  $\delta^{13}\text{C}_{\text{DIC}}$  values of groundwater ranging from  $-14.5\text{‰}$  to  $-5.9\text{‰}$  vs. PDB are  
344 similar to groundwater from carbonate aquifers in southwest China, which has typical values,  
345 ranging from  $-15.0\text{‰}$  to  $-8.0\text{‰}$  (Li et al., 2010). The  $\delta^{13}\text{C}_{\text{DIC}}$  in groundwater shows a

346 negative correlation with DIC concentration, particularly in the karst aquifer (Fig. 4). This  
347 indicates that simple, congruent dissolution of carbonate minerals is not a major source of  
348 DIC in the groundwater. Rather,  $\delta^{13}\text{C}_{\text{DIC}}$  may undergo progressive equilibration with aquifer  
349 carbonate during sequential carbonate dissolution/precipitation reactions (e.g. de-  
350 dolomitization). This is consistent with the increasing Mg/Ca ratios observed along the flow  
351 path, along with increasing  $\delta^{13}\text{C}_{\text{DIC}}$  values in the carbonate aquifer (see Fig. 7a), but no  
352 overall increase in  $\text{HCO}_3$  (Fig. 4 and Table 2). Near the coastline, the more enriched  $\delta^{13}\text{C}_{\text{DIC}}$   
353 values and lower DIC may also result due to mixing with seawater. An increasing trend in  
354  $\text{SO}_4$  and Mg concentrations and Mg/Ca ratios along the flow path are also indicative of de-  
355 dolomitization (e.g. Jones et al., 1989; Plummer et al., 1990; López-Chicano et al., 2001;  
356 Szykiewicz et al., 2012) in which the dissolution of gypsum and anhydrite lead to over-  
357 saturation and thus dolomite dissolution and calcite precipitation. For deeper carbonate  
358 groundwater underlying the Daweijia wellfield, the negative correlation between  $\text{Ca}^{2+}$  and  
359  $\delta^{13}\text{C}_{\text{DIC}}$  (Fig. 7b) also indicate that Ca enrichment in groundwater may be not attributed to  
360 carbonate dissolution. The increase in  $\delta^{13}\text{C}$  with decreasing Ca content is likely related to the  
361 incongruent reaction, which removes Ca from solution and progressively increases  $\delta^{13}\text{C}$  to  
362 equilibrate with the aquifer matrix. In the Quaternary aquifer, the minor calcite dissolution  
363 occurring could lead to increasing  $\delta^{13}\text{C}$  with increasing Ca. An alternative process may  
364 remove the  $\text{HCO}_3$  along flow paths (e.g.,  $\text{CO}_2$  de-gassing).

365 Deines et al. (1974) showed that there are significant differences in the relationships  
366 between carbon isotopic composition and chemical variables for open and closed system  
367 conditions. Based on their model (which uses similar initial conditions to the study area) the  
368 chemical and isotopic composition of groundwater at a given pH in equilibrium with a  
369 reservoir of a given  $P_{\text{CO}_2}$  and  $\delta^{13}\text{C}_r$  can be estimated. For the closed system model the  $^{13}\text{C}$   
370 content of the solution depends not only on the  $^{13}\text{C}/^{12}\text{C}$  ratio of the reservoir  $\text{CO}_2$  ( $\delta^{13}\text{C}_r$ ), but  
371 also on that of the dissolving carbonate rock ( $\delta^{13}\text{C}_{\text{rock}}$ ). The pH and  $\delta^{13}\text{C}$  values of the  
372 carbonate aquifer groundwater suggest evolution in a relatively closed system. Lower  $\delta^{13}\text{C}$   
373 value (-14.5‰) of shallow groundwater (QG4) in recharge area may be more affected by the  
374 soil  $\text{CO}_2$  in areas of intensive corn cultivation, ranging from approximately -18 to -25‰  
375 (Deines et al., 1974). In this area, the irrigation using local carbonate groundwater may have  
376 resulted in mixing between the shallow groundwater with similar values to this, and the deep  
377 water from the carbonate aquifer (with higher values), leading to the intermediate value  
378 observed. Most groundwater in the study area is supersaturated with respect to calcite and  
379 dolomite (Han et al., 2015). The hydrochemical composition of groundwater is influenced by  
380  $\text{CO}_2$  exsolution and  $\text{CaCO}_3$  precipitation, which can be described by the reaction:



382 At isotopic equilibrium  $\text{CO}_2$  is enriched in  $^{12}\text{C}$  and  $\text{CaCO}_3$  in  $^{13}\text{C}$  with respect to  $\text{HCO}_3^-$   
383 (Deines et al., 1974). Since for each mole of  $\text{CO}_2$  exsolved one mole of  $\text{CaCO}_3$  is precipitated,  
384 the kinetic isotope effects is removal of  $^{12}\text{C}$  enriched carbon from the solution, which

385 concentrates  $^{13}\text{C}$  in the remaining  $\text{HCO}_3^-$ . The enrichment of  $\delta^{13}\text{C}_{\text{DIC}}$  without change in  
386  $\text{HCO}_3^-$  content may thus be caused by  $^{12}\text{CO}_2$  loss during exsolution and  $^{13}\text{C}$  enrichment in  
387 solution. Dolomite dissolution is likely to add  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{HCO}_3^-$  to the solution, while  
388 calcite precipitation will remove DIC and retain calcite saturation, resulting in generally  
389 increasing Mg/Ca ratios along flow paths, along with increasing  $\delta^{13}\text{C}$  values (Freeze and  
390 Cherry, 1979; Edmunds et al., 1987; Cardenal et al., 1994; Kloppmann et al., 1998). The  
391 dissolution of even very small amounts of gypsum may cause this process to occur in  
392 carbonate aquifers, which usually characterized by near saturation with respect to calcite, by  
393 creating temporary under-saturation (due to the addition of calcium but not bicarbonate ion)  
394 (Plummer et al., 1990; López-Chicano et al., 2001; Moral et al., 2008; Szykiewicz et al.,  
395 2012).

396 Additionally, Sr is good proxy for Ca variations and sources with higher correlation, and  
397 the concentration of  $\text{Sr}^{2+}$  is often particularly high and frequently correlated with  $\text{SO}_4^{2-}$   
398 concentrations (Figure 8). In addition to Sr's origin from celestite, which may be present as  
399 microcrystalline inclusions in gypsum,  $\text{Sr}^{2+}$  can also occur as solid solution in carbonate  
400 minerals (Hunkeler and Mudry, 2007). Large amounts of anthropogenic chemical input will  
401 change these highly correlated relationships. Fig. 8 shows different slopes in the relationship  
402 between Cl/TDS and Sr for different water types. The chloride-rich brackish water with high  
403 Cl/TDS ratios has high Sr contents in the carbonate aquifer; in contrast, the sulphate-rich

404 brackish water with low Cl/TDS has wide range of Sr contents in the Quaternary aquifer. The  
405 higher Sr contents in the COA likely result due to enhanced from water-rock interaction  
406 (carbonate minerals dissolution), possibly enhanced by historic seawater intrusion.

407 Another possible control on the carbon chemistry of the groundwater is that active re-  
408 circulation of water is taking place in the unsaturated zone of the aquifer due to  
409 anthropogenic activity. In the local agricultural soils, CO<sub>2</sub> concentration is usually high, with  
410 a  $\delta^{13}\text{C}_{\text{DIC}}$  between -6.3 and -13.1‰ and  $\delta^{13}\text{C}$  of dissolved organic carbon between -23.2 and -  
411 21.8 ‰ (Yang, 2011). During recharge events, water dissolves the soil CO<sub>2</sub> which is involved  
412 in carbonate dissolution and becomes part of the DIC pool. If this process is conducted over  
413 successive irrigation, the HCO<sub>3</sub><sup>-</sup> concentration increases and  $\delta^{13}\text{C}_{\text{DIC}}$  will deplete owing to the  
414 dissolved biogenic CO<sub>2</sub> in soil.

### 415 **5.3 Sources of dissolved SO<sub>4</sub> to groundwater**

416 Dissolved SO<sub>4</sub><sup>2-</sup> of groundwater in the coastal aquifers might originate from several  
417 sources, potentially including (i) natural and artificial sulfates in rainwater; (ii) dissolution of  
418 sulphate-bearing evaporates (e.g. gypsum and anhydrite); (iii) seawater; (iv) anthropogenic  
419 pollutants (e.g. domestic sewage, detergent and agricultural fertilizers). The  $\delta^{34}\text{S}$  of  
420 groundwater SO<sub>4</sub> are used as a tracer to identify the sources of dissolved SO<sub>4</sub><sup>2-</sup> to the  
421 groundwater in this study. Fig. 5 shows the relation between  $\delta^{34}\text{S}_{\text{SO}_4}$  values and SO<sub>4</sub>/Cl for  
422 groundwater samples, showing typical literature values for sulfur isotopic composition of

423 major sulphate sources. Most of water samples from the Daweijia area have sulfur isotopic  
424 compositions that reflect mixed sources. The  $\delta^{34}\text{S}_{\text{SO}_4}$  values are generally lower in the  
425 upstream area (+5.4~+5.7 ‰) increasing along the groundwater flow paths towards the coast  
426 (+13.1‰). Enrichment in  $\delta^{34}\text{S}_{\text{SO}_4}$  may result from sulphate reduction, whereas sulphide  
427 oxidation generally leads to negative  $\delta^{34}\text{S}_{\text{SO}_4}$  values (Clark and Fritz, 1997). However, there  
428 are no negative  $\delta^{34}\text{S}_{\text{SO}_4}$  values observed in this study area, indicating minor or negligible  
429 sulphide (such as pyrite) oxidation occurring in the aquifer.

430  $\delta^{34}\text{S}_{\text{SO}_4}$  value of modern seawater is approximately +21‰ (Rees et al., 1978). The  
431  $\delta^{34}\text{S}_{\text{SO}_4}$  of groundwaters, ranging from +13.1 to +5.4 ‰ with a mean value of +8.9 ‰, thus  
432 generally discount this as a significant source of sulphate, consistent with the low mixing  
433 fractions calculated using Cl. The  $\delta^{34}\text{S}_{\text{SO}_4}$  values of precipitation from 8 stations in the north  
434 region of Yangtze River ranges from +4.9 ‰ to +11.0 ‰ (Hong et al., 1994). Aside from  
435 CG1, the  $\delta^{34}\text{S}_{\text{SO}_4}$  compositions of the samples overlap with the isotopic range of rainfall.  
436 However, rainfall is characterized by higher  $\text{SO}_4/\text{Cl}$  (2.26, Zhang et al., 2012) than the  
437 groundwater (0.16~0.97) and significantly lower total concentrations than are observed;  
438 indicating that this is only a partial origin of sulfate in groundwater. Sulfate minerals  
439 (gypsum, anhydrite, etc.) from marine sources typically have  $\delta^{34}\text{S}_{\text{SO}_4}$  values between +9 and  
440 +30.2‰ (Shi et al., 2004; Vitòria et al., 2004). As groundwater flows downwards into the  
441 deeper karst aquifer, the  $\delta^{34}\text{S}$  values increase and approach the values in marine evaporites,

442 part of the continuous de-dolomitization reaction discussed above. However, this can't  
443 explain the observed sulfate levels in the Quaternary aquifer (see mass balance calculations  
444 below).

445 Fertilizers have a wide range of  $\delta^{34}\text{S}_{\text{SO}_4}$  values ranging from -6.5 to +11.7 ‰, with a  
446 mean value of +3.7 ‰ and -0.8 ‰ in the northern hemisphere (Szynkiewicz et al., 2011) and  
447 China (Li et al., 2006), respectively. Apart from CG1 ( $\delta^{34}\text{S}_{\text{SO}_4}$  value of +13.1‰), the  $\delta^{34}\text{S}_{\text{SO}_4}$   
448 values of the rest groundwater samples are within the  $\delta^{34}\text{S}_{\text{SO}_4}$  ranges of known fertilizers. The  
449 isotopic  $\delta^{34}\text{S}$  values in fertilizers significantly differ from the geological  $\text{SO}_4$  inputs of  
450 sedimentary origin, and over-lap with most of the observed compositions (Fig. 5). In addition  
451 the very high nitrate concentrations observed in the groundwater (up to 625 mg/L) strongly  
452 indicate a high input of excess fertilizer residue via irrigation returns to the aquifer. This  
453 indicates that sulfate in fertilizers should be taken into account as a major contributing source  
454 of dissolved  $\text{SO}_4$  in groundwater, especially from the Quaternary aquifer. This is also  
455 confirmed by the general positive relationship between  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  concentrations (Fig.  
456 9a) and correlation (albeit weak) between  $\delta^{34}\text{S}$  values and  $\text{NO}_3^-$  concentrations in the  
457 Quaternary aquifer (Fig. 9b). It can be assumed that other anthropogenic sources of  $\text{SO}_4$  such  
458 as atmospheric deposition or detergents from domestic/wastewater sources, or pig manure are  
459 negligible in the study area.



460 Despite they clear overlap in  $\delta^{34}\text{S}$  of fertilizers and groundwater  $\text{SO}_4^{2-}$ , the  $\delta^{34}\text{S}$   
461 measured in upstream locations (e.g. QG3 and QG4) probably reflect inputs from geologic  
462  $\text{SO}_4$  sources (such as soil sulfate) (Fig. 5). In contrast, the sulfur isotope values are more  
463 consistent with marine sedimentary sources of groundwater  $\text{SO}_4$  in the carbonate aquifer, due  
464 to the sustained water-rock interaction and longer residence time. The evidence for gypsum  
465 dissolution as part of de-dolomitization in the major ion and carbon isotope data (discussed  
466 above) is also consistent with a marine evaporite source of sulphur in the deeper aquifer.

467 Both  $\delta^{13}\text{C}$  and  $\delta^{34}\text{S}_{\text{SO}_4}$  values increase along the groundwater flow path. Groundwater  
468 with low  $\delta^{13}\text{C}$  values (e.g.  $-14.5\text{‰}$ ) and  $\delta^{34}\text{S}_{\text{SO}_4}$  values (e.g.  $\sim+5.4\text{‰}$ ) represents recently  
469 recharged water, which is dominated by unsaturated zone processes and diffuse flow.  
470 Equilibration with carbonate minerals in the aquifer matrix during de-dolomitization makes  
471 an important contribution to the groundwater  $\delta^{13}\text{C}$  evolution in the karst aquifer ( $\delta^{13}\text{C}$  up to -  
472  $5.9\text{‰}$  in QG11), reaching saturation with respect to calcite and dolomite. Then, the high  
473 loads of fertilizers accessible during agricultural return flow are the most likely source of the  
474 dissolved sulfate and nitrate, particularly in the shallow Quaternary aquifer.

#### 475 **5.4 Anthropogenic contribution on groundwater chemistry and environmental** 476 **implications**

477 Fertilizers are applied beyond what is taken up by crops in the long term in many parts  
478 of China (Davidson and Wei, 2012) as evident from the high  $\text{NO}_3^-$  concentrations in

479 groundwater. The wide range of NO<sub>3</sub> concentrations, indicate considerable anthropogenic  
 480 input under human activities (e.g., fertilizer usage during irrigation, leakage from septic  
 481 system), which is responsible for the deterioration of local groundwater and near shore sea-  
 482 water quality. NO<sub>3</sub><sup>-</sup> concentrations are obviously elevated (e.g. 75-386 mg/L) in the shallow  
 483 groundwater from the Quaternary aquifer, especially near the Daweijia well field, resulting  
 484 from agricultural fertilization. Due to nitrate input from fertilizers, the relatively low nitrate  
 485 concentrations in some deep groundwater (e.g. CG4, CG14), which are located in the  
 486 upstream area, show that, compared with groundwater in the downgradient area, these waters  
 487 have locally reduced impacts from contamination. However, many deep groundwater samples  
 488 have similar ranges of NO<sub>3</sub><sup>-</sup> concentrations to shallow groundwaters, indicating that there is  
 489 hydraulic connection between shallow and deep aquifers (e.g. QG5 and CG7 in Fig. 2).

490 To quantify the fertilizers contributions to groundwater chemistry, we considered the  
 491 inputs of precipitation infiltration, seawater intrusion and evaporite dissolution into  
 492 groundwater system. We used a mass balance approach to evaluate the contribution of  
 493 different sources of sulphate to the dissolved SO<sub>4</sub><sup>2-</sup> of groundwater. The four sources of  
 494 sulphate in the dissolved SO<sub>4</sub><sup>2-</sup> of groundwater are from precipitation, seawater, fertilizer and  
 495 evaporite dissolution. The isotopic composition of groundwater sulphate ( $\delta^{34}\text{S}_{\text{SO}_4}$ ) can be  
 496 calculated by:

$$497 \quad \delta^{34}\text{S}_{\text{gw}} \times \text{SO}_{4,\text{gw}} = \delta^{34}\text{S}_{\text{prec}} \times \text{SO}_{4,\text{prec}} + \delta^{34}\text{S}_{\text{sw}} \times \text{SO}_{4,\text{sw}} + \delta^{34}\text{S}_{\text{fer}} \times \text{SO}_{4,\text{fer}} + \delta^{34}\text{S}_{\text{evp}} \times \text{SO}_{4,\text{evp}} \quad (7)$$

498 where  $\delta^{34}\text{S}_{\text{prec}}$ ,  $\text{SO}_{4,\text{prec}}$ ,  $\delta^{34}\text{S}_{\text{sw}}$ ,  $\text{SO}_{4,\text{sw}}$ ,  $\delta^{34}\text{S}_{\text{fer}}$ ,  $\text{SO}_{4,\text{fer}}$ ,  $\delta^{34}\text{S}_{\text{evp}}$ , and  $\text{SO}_{4,\text{evp}}$ , correspond to the  
 499 end member  $\delta^{34}\text{S}$  values for rainfall (+5.39‰, Hong et al., 1994), seawater (+21‰, Clark and  
 500 Fritz, 1997), fertilizer (-0.8 ‰, Li et al., 2006), and sulfate marine evaporates of Cambrian-  
 501 Ordovician age (+28‰, Clark and Fritz, 1997). The dissolved  $\text{SO}_4^{2-}$  concentration ( $\text{SO}_{4,\text{gw}}$ ) in  
 502 groundwater is the total sulphate contribution from precipitation, seawater, fertilizer and  
 503 evaporate:

$$504 \quad \text{SO}_{4,\text{gw}} = \text{SO}_{4,\text{prec}} + \text{SO}_{4,\text{sw}} + \text{SO}_{4,\text{fer}} + \text{SO}_{4,\text{evp}} \quad (8)$$

$$505 \quad \text{where } \text{SO}_{4,\text{prec}} = [\text{SO}_{4,\text{prec}}] \times R = 8.02 \text{ mg/L} \times 0.783 \quad (9)$$

$$506 \quad \text{SO}_{4,\text{sw}} = [\text{SO}_{4,\text{sw}}] \times f_{\text{sw}} = 2710 \text{ mg/L} \times f_{\text{sw}} \quad (10)$$

507 The  $\text{SO}_4^{2-}$  concentration ( $[\text{SO}_{4,\text{prec}}] = 8.02 \text{ mg/L}$ ) of the local precipitation was reported by  
 508 Zhang et al., 2012, and  $\text{SO}_4^{2-}$  concentration ( $[\text{SO}_{4,\text{sw}}] = 2710 \text{ mg/L}$ ) of the seawater referenced  
 509 from Clark and Fritz, 1997.  $R$  is the recharge rate equal to the ratio of the amount of  
 510 precipitation infiltration and the amount of the total groundwater resources in the study area.  
 511 According to the water balance calculations in the local groundwater flow system (CGS,  
 512 2007), groundwater is mainly recharged from precipitation infiltration, which occupied 78.3%  
 513 ( $R$ ) of the total recharge water volume.  $f_{\text{sw}}$  can be calculated by the equation (1) for each  
 514 groundwater sample.

515 The results of the mass balance, showing sulphate contribution to groundwater from  
516 fertilizer (assuming these end-members correspond to values in the study area) are shown in  
517 Fig. 10. In total, 4 to 22% of the dissolved  $\text{SO}_4^{2-}$  concentrations in groundwater are  
518 contributed from evaporite dissolution, whereas 30 to 75% of the dissolved  $\text{SO}_4^{2-}$   
519 concentrations in groundwater can be ascribed to input from fertilizers. According to these  
520 calculations, overall, the local application of the fertilizers is now responsible for the majority  
521 of dissolved  $\text{SO}_4^{2-}$  in groundwater. The contribution reaches on average 62.1% in the  
522 Quaternary aquifer and 48.7% in the deeper carbonate aquifer; showing that the shallow  
523 Quaternary aquifer is particularly prone to pollution by fertilizer utilization. The sulphate  
524 contributions to groundwater from seawater and precipitation are less than 10%, which is  
525 relatively lower and is consistent with the observation that pumping restrictions have  
526 effectively halted saline intrusion in the area. We analysed the sensitivity of the mass balance  
527 by changing  $\pm 10\%$  of the end-member sulfur isotope compositions of fertilizer and evaporate,  
528 respectively. We found the change on  $\delta^{34}\text{S}_{\text{fer}}$  varied the contributions from fertilizer and  
529 evaporate by  $\pm 0.1\%$  and  $\pm 0.2\%$  respectively. The  $\pm 10\%$  change in  $\delta^{34}\text{S}_{\text{evp}}$  leads to changes  
530 in the contributions from fertilizer and evaporate by  $\pm 0.4\%$  and  $\pm 2\%$ , respectively. This  
531 suggests that the results are more sensitive to  $\delta^{34}\text{S}_{\text{evp}}$  values in the mass balance.

532 Although further investigation is needed to determine the contribution of dissolved  
533 sulphate from different pollution sources (the end-member values used above are naturally

534 uncertain and may bias the overall % contributions), the current results indicate that the  
535 anthropogenic contaminant input plays dominant role in providing sulfate to the shallow  
536 groundwater (as well as nitrate), and that this influence has extended into the deeper  
537 carbonate aquifer. This widespread shift towards agricultural return flow becoming the  
538 dominant control on groundwater chemistry, particularly in shallow aquifers, is consistent  
539 with what is unfolding over many areas of northern China (Currell et al, 2012). This is a  
540 disturbing trend, particularly given the time-lags involved in groundwater systems  
541 equilibrating towards new water quality norms, which suggest significant future degradation  
542 of groundwater resources will continue to occur in these areas.

## 543 **6. Conclusions**

544 The coastal aquifer in the Daweijia area, northeast China is composed of interlayered  
545 Quaternary sedimentary and Cambrian-Ordovician carbonate rocks. The groundwater has  
546 evolved from fresh water (meteoric recharge) to brackish water in series of water types:  
547  $\text{Ca}(\cdot\text{Mg})\text{-HCO}_3\cdot\text{Cl} \rightarrow \text{Ca}\cdot\text{Na}\text{-Cl}\cdot\text{HCO}_3 \rightarrow \text{Ca}\text{-Cl} \rightarrow \text{Na}\cdot\text{Ca}\text{-Cl} \rightarrow \text{Na}\text{-Cl}$  via a combination of  
548 natural and anthropogenic processes. After the cessation of the groundwater pumping in the  
549 Daweijia well field, the TDS concentration of groundwater has increased, however, the  $\text{Cl}^-$   
550 concentrations have not, and in some areas have decreased. The major change has been large  
551 increases in  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations, which have increased several times compared to  
552 1981. This indicates that the local government efforts to restrict groundwater abstraction have

553 been effective in their purpose of limiting saline intrusion; however, water quality  
554 degradation has continued due to a new source- nitrate and sulphate contamination, largely  
555 resulting from the heavy application of agricultural fertilizers.

556       There are the increasing trends of  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{34}\text{S}_{\text{SO}_4}$  values for groundwater along the  
557 flow path. The enrichment of  $\delta^{13}\text{C}_{\text{DIC}}$  of groundwater may be caused by kinetic isotope  
558 effects as most groundwater is supersaturated with respect to calcite and dolomite, which can  
559 cause  $^{12}\text{CO}_2$  loss during exsolution and  $^{13}\text{C}$  enrichment in solution. The pH and  $\delta^{13}\text{C}$  values  
560 of the investigated groundwater suggest evolution in a closed system. The potential sources  
561 of dissolved  $\text{SO}_4^{2-}$  in the coastal aquifers include natural and artificial sulfates in rainwater,  
562 dissolution of sulfate evaporates (e.g. gypsum and anhydrite), seawater, and anthropogenic  
563 pollutants (e.g. agricultural fertilizers). We estimated the contributions of the four different  
564 sources on the dissolved sulphate in groundwater quality by using mass balance approach.  
565 Apart from seawater and precipitation (less than 10%), the fertilizer contribution in sulphate  
566 concentrations of groundwater could be as high as an average of 62.1% in the Quaternary  
567 aquifer, and 48.7% in the deeper carbonate aquifer, depending on the end-member  
568 composition used. Although the processes that affect the groundwater quality and the  
569 contribution to the dissolved sulfate of groundwater in the Daweijia area should be further  
570 evaluated by more investigation (such as nitrogen isotope data), the current research results  
571 obtained from a set of geochemical and isotopic tools show the sulfate contribution from

572 fertilizer application, compared with that from seawater intrusion and precipitation  
573 infiltration, is dominant, with a secondary source from long-term evaporite dissolution and  
574 de-dolomitization as water equilibrates with the carbonate aquifer matrix.

575 Also, there are similar ranges of  $\text{NO}_3^-$  concentrations, isotopic compositions ( $\delta^{13}\text{C}_{\text{DIC}}$   
576 and  $\delta^{34}\text{S}_{\text{SO}_4}$ ) and water type in the shallow Quaternary and deeper carbonate aquifers in most  
577 parts of the study area, indicating interaction between shallow and deep groundwater in the  
578 study area, which has implications for aquifer protection from contamination by agricultural  
579 chemicals.

580 Coastal carbonate aquifers, a prolific groundwater source worldwide, are characterized  
581 by rapid groundwater circulation and recharge and are therefore highly vulnerable to  
582 anthropogenic contamination. Human activities in heavily populated areas such as the current  
583 study are now potentially the key driver in the hydrology and hydrochemical evolution of  
584 some of these coastal aquifers, as demonstrated here. Only by strictly controlling  
585 anthropogenic land-use and water use activities can the pollution and degradation of these  
586 aquifers be prevented. Future studies could focus on the seasonal variation of sulfur and  
587 nitrogen isotopes of dissolved  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ , respectively, and more detailed analysis of  
588 these stable isotopes in soil profiles. This could provide more insight into the dynamics of  
589 contamination of this and other similar aquifers.

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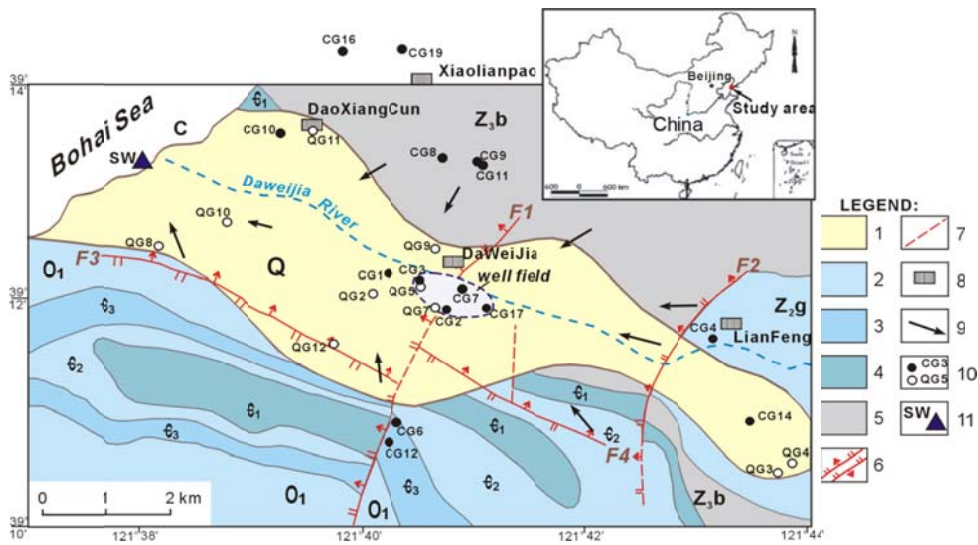
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769 FIGURES:



770

771 Fig. 1. Geological setting and water sampling locations. Geology modified after Wu and Jin  
 772 (1990). Formation note: O<sub>1</sub>- Lower Ordovician; E<sub>3</sub>-Upper Cambrian; E<sub>2</sub>-Middle Cambrian;  
 773 E<sub>1</sub>-Lower Cambrian; Z<sub>2g</sub>-Ganjingzi group of Middle Sinian; Z<sub>3b</sub>- Beishan group of Upper  
 774 Sinian. Legend: 1-Quaternary sediments; 2-thick-bedded limestone; 3-laminated limestone  
 775 with shale; 4-argillaceous limestone; 5-sandstone and shale; 6- normal/thrust fault; 7- buried  
 776 fault; 8- town location; 9- approximate groundwater flow direction; 10-sampling wells ●from  
 777 deep carbonate aquifers (depth>80 m), ○ from shallow Quaternary aquifer (depth<40 m); 11-  
 778 sampling site for seawater.

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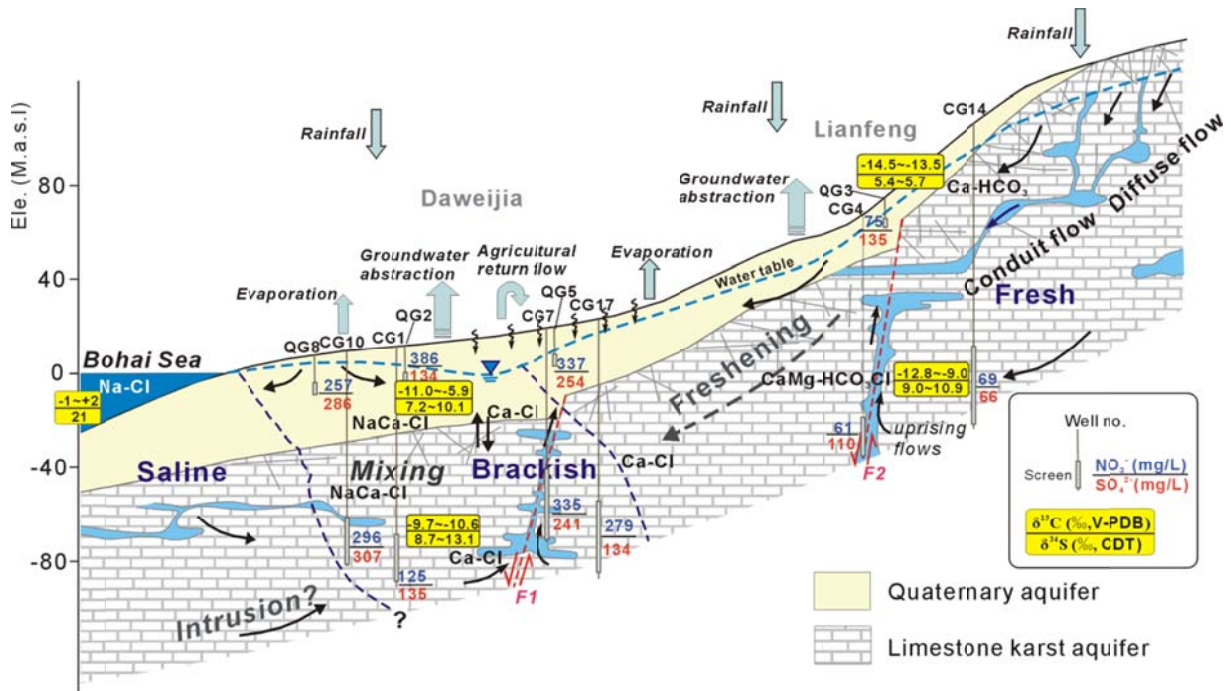
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788 Fig. 2. Conceptual model showing the hydrogeological system (modified after Yang, 2011)  
 789 and NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> concentrations and sources, with characteristic ranges of δ<sup>13</sup>C and δ<sup>34</sup>S<sub>SO4</sub>  
 790 values (showing a vertically increasing trend). Arrows in aquifers indicate general  
 791 groundwater flow direction.

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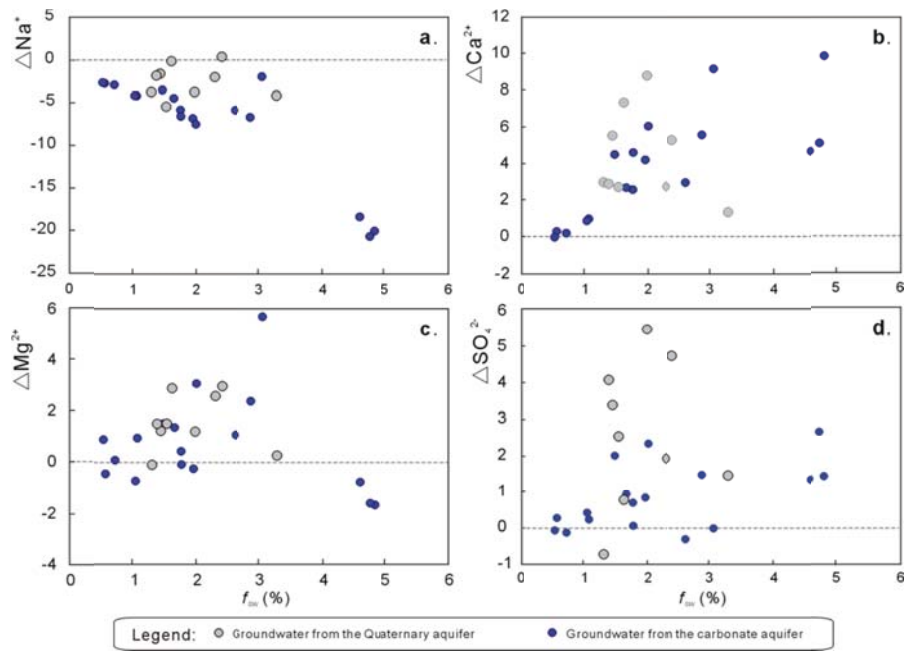
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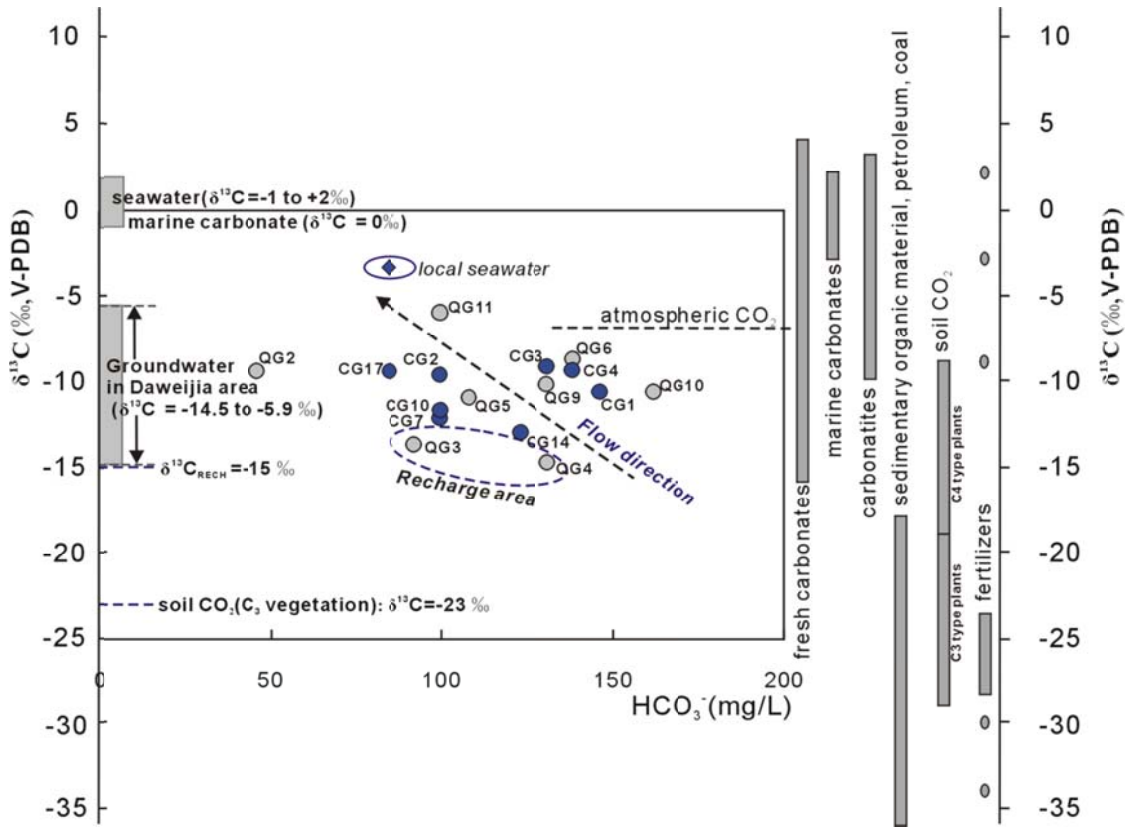


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802 Fig. 3. Graphs showing the cationic Δ-values of groundwater samples vs. fraction of seawater:

803 (a) ΔNa<sup>+</sup>; (b) ΔCa<sup>2+</sup>, (c) ΔMg<sup>2+</sup>, and (d) ΔSO<sub>4</sub><sup>2-</sup>.

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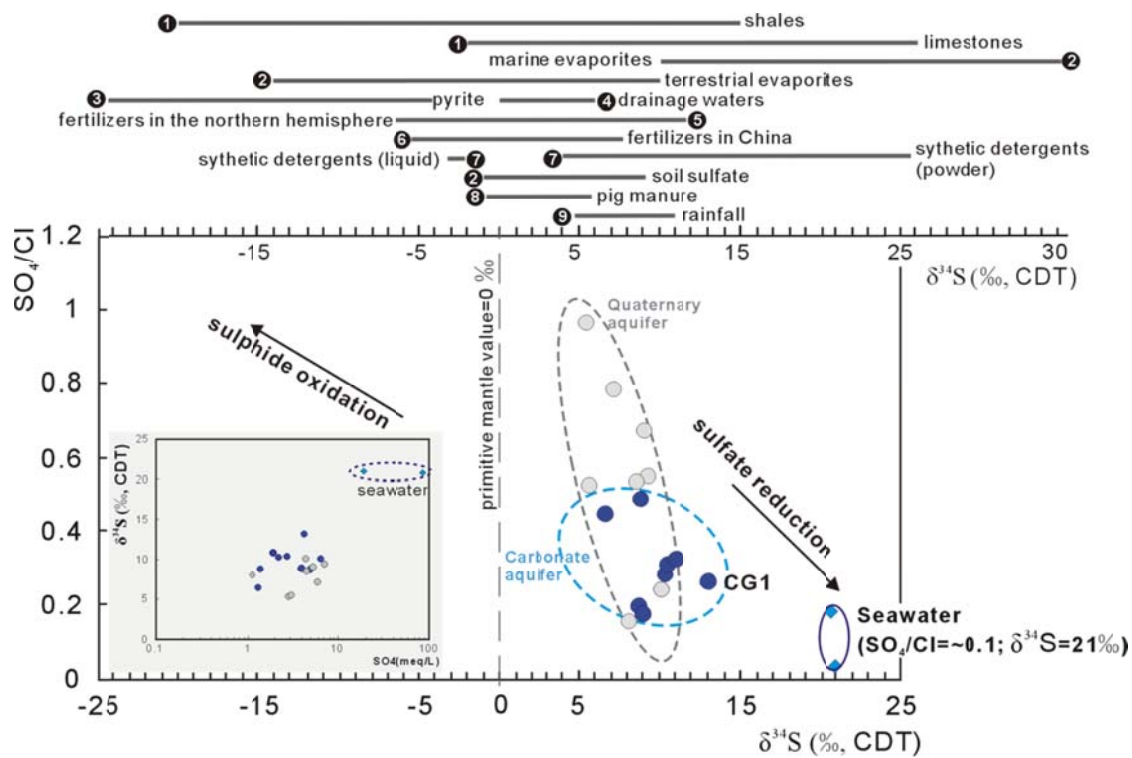
806 Fig. 4.  $\delta^{13}\text{C}_{\text{DIC}}$  vs. dissolved inorganic carbon for the groundwater samples (Aug.2009) in the

807 Daweijia area, comparing with  $\delta^{13}\text{C}$  values for the main carbon reservoirs (Vitòria et al., 2004

808 and therein). See Fig. 3 for legend.

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810

811 Fig. 5.  $\delta^{34}S$  of dissolved  $SO_4$  versus  $SO_4/Cl$  for groundwater samples from the Daweijia area

812 The range of sulfur isotopic values of some major sulfur reservoirs and selected materials is summarized from literature

813 compiled data as follows: 1-Clark and Fritz, 1997; 2- Vitória et al., 2004; 3- Szykiewicz et al., 2012; 4- Unland et al., 2012;

814 5- Szykiewicz et al., 2011; 6- Li et al., 2006; 7- Hosono et al., 2007; 8- Cravotta, 1997 and Otero et al., 2007; 9- Hong et al.,

815 1994. See Fig. 3 for legend.

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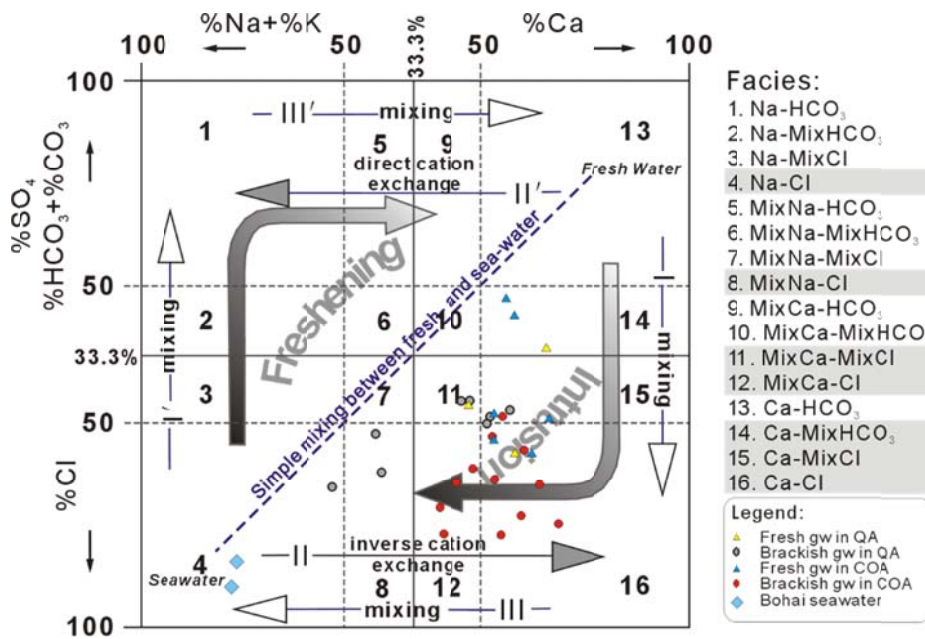
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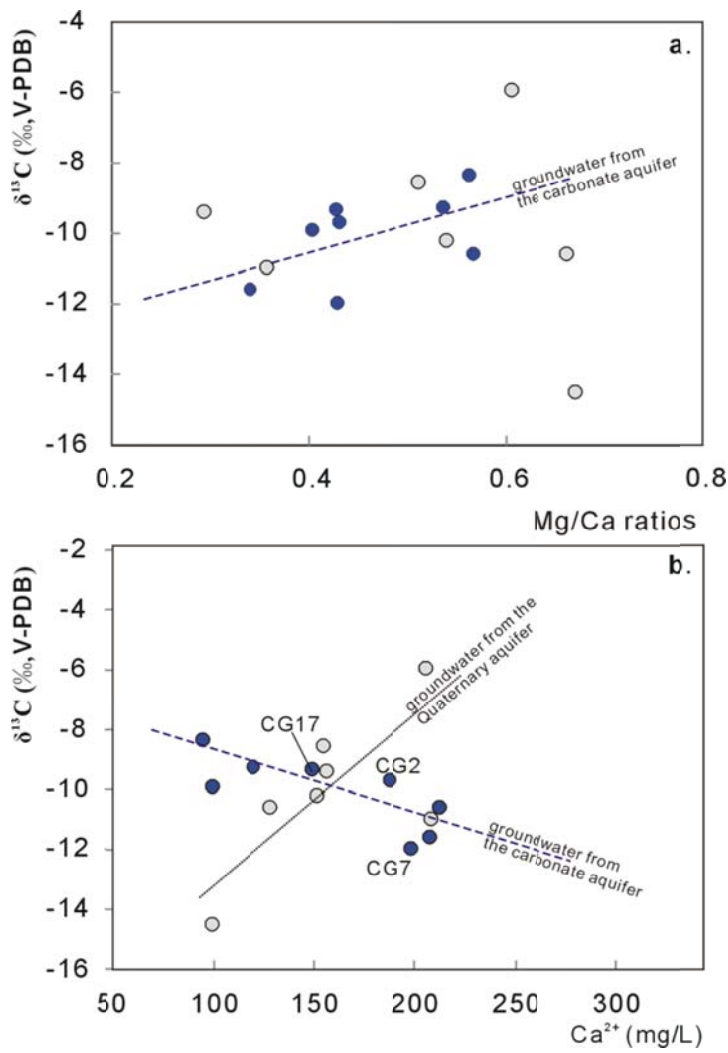
826 Fig. 6. Hydrogeochemical Facies Evolution (HFE) diagram.

827 QA-Quaternary aquifer; COA- Cambrian- Ordovician carbonate aquifer.

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832 Fig. 7. Graphs showing (a) Mg/Ca ratios (by meq/L); (b)  $\text{Ca}^{2+}$  concentrations vs.  $\delta^{13}\text{C}_{\text{DIC}}$   
833 values in different aquifers (grey- groundwater samples collected from the Quaternary aquifer;  
834 blue- groundwater samples collected from the carbonate aquifer). See Fig. 3 for legend.

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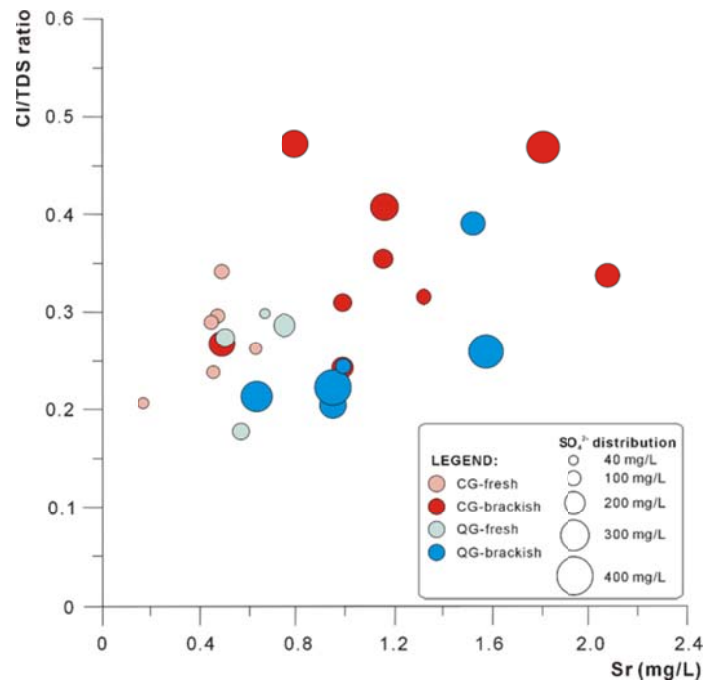
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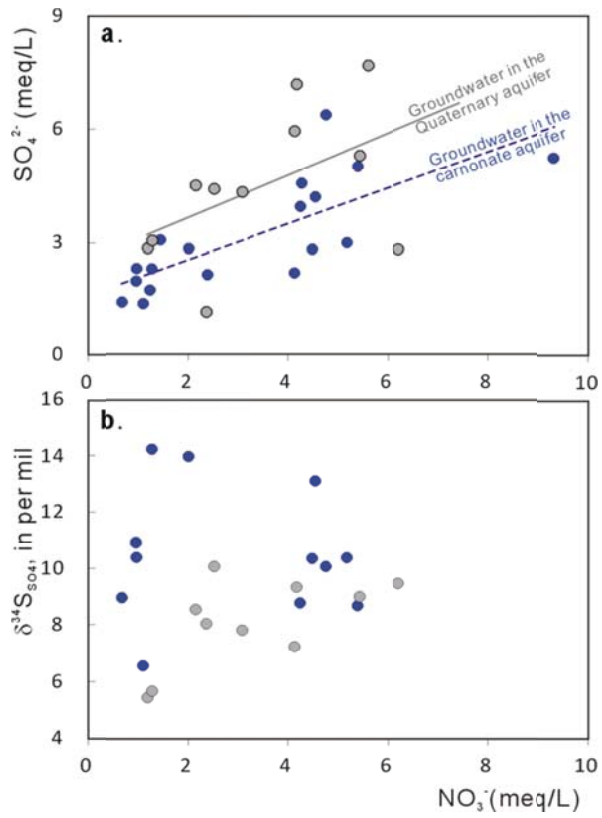


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842 Fig. 8. Plot of Cl/TDS ratio vs. Sr (mg/L) from groundwater samples in the Daweijia area. Sulphate  
843 concentration of each sample is also indicated by the size of the point. CG-groundwater from carbonate  
844 aquifer; QG-groundwater from Quaternary aquifer.

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848 Fig. 9. Bivariate plots for **a** relationship between  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentration and **b**  $\delta^{34}\text{S}_{\text{SO}_4}$

849 vs.  $\text{NO}_3^-$  concentrations. See Fig. 2 for legend.

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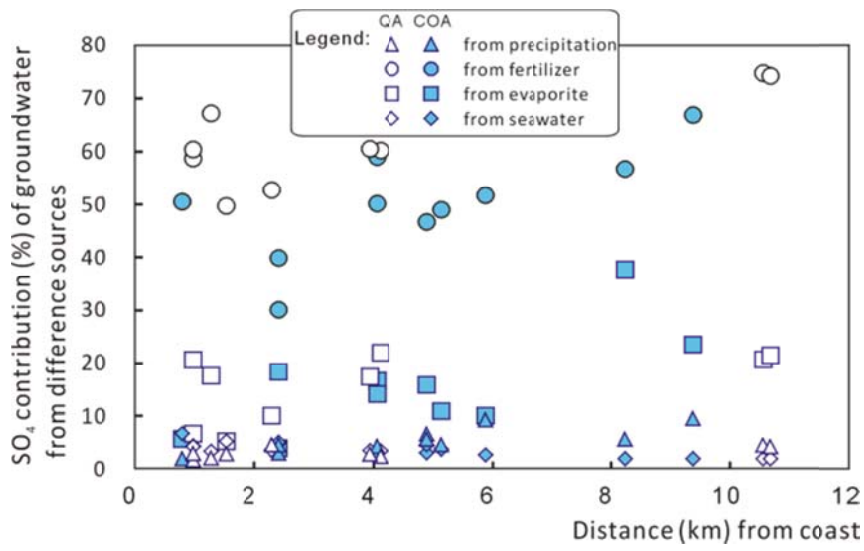
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857 Fig. 10. Calculated SO<sub>4</sub><sup>2-</sup> contribution of groundwater from four different sources (QA-  
858 groundwater from the Quaternary aquifer; COA-groundwater from the carbonate aquifer)

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860

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

Sample	Well Depth (m)	Screened Intervals (m)	EC ( $\mu\text{s}/\text{cm}$ )	pH	T ( $^{\circ}\text{C}$ )	ORP (mV)	DO (mg/L)	Ca <sup>2+</sup> (mg/L)	Na <sup>+</sup> (mg/L)	K <sup>+</sup> (mg/L)	Mg <sup>2+</sup> (mg/L)	Cl <sup>-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	HCO <sub>3</sub> <sup>-</sup> (mg/L)	Sr (mg/L)	SI <sub>cal</sub>	SI <sub>dol</sub>	SI <sub>gyp</sub>	$\delta^{34}\text{S}_{\text{SO}_4}$ (‰)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)
<b>Groundwater samples collected from the carbonate aquifer:</b>																					
CG4	100	70-95	1015	7.2	16.1	193	3.6	119.6	50.5	1.2	38.5	261.0	109.7	60.9	247.1	0.49	0.1	-0.07	-1.47	10.4	-9.3
CG16	88	58-84	715	7.5	22.4	2	5.7	100.9	26.1	4.7	16.1	112.1	82.4	77.2	101.2	0.45	0.1	-0.24	-1.58		
CG3	110	72-98	986	7.3	19.3	201	4.0	115.8	47.2	1.5	37.8	209.5	93.8	60.3	282.8	0.47	0.27	0.33	-1.55	10.9	
CG6	120	75-112	796	7.3	21.7	139	3.7	99.4	38.2	1.2	24.1	141.6	67.1	43.1	250.1	0.63	0.23	0.18	-1.41	9.0	-9.9
CG14	128	85-118	749	7.6	22.0	34	7.2	94.5	24.5	1.0	31.9	105.7	65.1	69.1	238.1	0.17	0.48	0.84	-1.75	6.6	-8.4
CG9	100	68-92	846	7.6	18.8	2	8.6	113.6	44.4	6.5	17.4	203.8	101.8	147.9	134.0	0.45	0.21	-0.14	-1.47		
CG2	120	72-107	2050	6.5	16.0	186	7.5	187.7	106.0	2.3	48.5	288.4	189.2	263.9	199.4	0.99	-0.59	-1.53	-1.12	8.8	-9.7
CG7	92	59-88	1761	6.6	17.0	222	6.6	198.5	97.8	1.0	51.1	892.9	240.5	334.7	145.9	0.79	-0.65	-1.65	-1.05	8.7	-12.0
CG17	110	68-97	1370	7.0	14.2	200	7.0	149.1	82.9	1.5	38.3	343.4	134.1	278.8	163.7	0.99	-0.31	-1.01	-1.31	10.4	-9.3
CG1	100	71-93	2280	7.2	18.2	163	5.6	212.5	184.0	3.5	72.3	561.0	201.4	282.6	282.8	2.07	0.27	0.32	-1.12	13.1	-10.6
CG8	95	65-92	1416	7.4	20.0	199	6.1	190.6	66.7	1.4	32.1	344.5	104.1	256.6	190.5	1.32	0.38	0.27	-1.35		
CG11	100	67-93	2050	7.1	15.1	2	7.6	302.8	84.3	1.7	42.3	937.3	249.9	579.4	205.4	1.16	0.14	-0.36	-0.9		
CG12	100	68-93	1362	7.3	20.0	25	7.4	183.0	81.3	1.6	31.9	380.8	146.2	90.1	318.5	1.15	0.51	0.55	-1.24		
CG19	62	43-59	1481	6.7	14.5	26	4.7	220.0	70.6	2.0	72.1	390.0	219.1	265.6	446.5	0.49	0	-0.28	-1.05		
CG10	90	59-86	1586	7.4	21.5	214	7.4	207.7	62.0	26.4	42.4	923.5	306.9	295.7	205.4	1.80	0.35	0.31	-0.95	10.1	-11.6
CG1*	100	71-93	2890	7.3	14.9			284.5	312.2	3.7	114.0	596.6	135.3	124.8	253.8	-	0.34	0.5	-1.23	14.0	
CG2*	120	72-107	2110	7.0	13.2			151.2	103.2	1.5	48.4	323.3	142.7	321.5	174.2	-	-0.33	-0.97	-1.29	10.4	
CG3*	110	72-98	2300	7.2	13.2			158.9	175.6	3.5	54.2	511.2	109.4	79.6	120.8	-	-0.28	-0.85	-1.41	14.2	
<b>Groundwater samples collected from the Quaternary aquifer:</b>																					
QG7	28	15-24	1242	7.6	13.1	2	6.7	156.2	82.1	1.0	27.5	254.5	54.4	146.6	262.0	0.66	0.56	0.55	-1.65	8.1	-9.4
QG3	8.4	6-7.5	821	7.0	18.3	52	4.4	118.3	28.6	4.0	21.6	103.3	135.4	74.7	190.5	0.57	-0.24	-0.95	-1.34	5.4	-12.8
QG4	14	7-13	912	7.5	23.0	22	3.6	99.1	42.5	13.1	40.0	203.3	145.2	80.2	241.1	0.50	0.34	0.6	-1.43	5.7	-14.5
QG5	12	7-11	1903	7.0	17.1	219	3.6	208.4	146.0	0.5	44.7	281.3	254.3	337.3	199.4	0.95	-0.03	-0.48	-0.98	9.0	-11.0
QG10	10	6-9	2210	7.2	13.9	204	5.0	128.2	286.1	12.8	51.0	640.6	211.5	156.1	309.6	1.52	0.04	-0.13	-1.27	10.1	-10.6
QG8	15	9-14	1633	7.4	16.4	16	7.8	154.6	134.5	2.7	47.5	269.8	285.9	256.9	220.3	0.63	0.31	0.33	-1.03	7.2	-8.6
QG9	20	12-17	1289	7.3	20.7	23	4.4	151.4	67.8	7.6	49.1	299.4	216.2	133.5	241.1	0.75	0.27	0.34	-1.15	8.6	-10.2
QG11	17	8-15	2780	7.4	23.2	65	1.3	205.8	295.5	11.1	74.8	469.4	344.9	259.5	291.7	1.58	0.59	1.07	-0.95	9.4	-5.9
QG12	17	12-16	2210	7.0	14.2	41	5.6	274.7	154.6	2.3	49.6	386.2	368.8	347.9	300.7	0.95	0.19	-0.16	-0.76		
QG2*	22	15-21	2310	7.0	15.2			244.9	198.5	3.6	66.3	315.7	134.2	386.3	512.7	-	0.32	0.29	-1.23	9.5	
QG11*	17	8-15	2820	7.2	13.9			153.8	229.2	4.4	69.2	448.3	207.6	190.6	200.9	-	-0.1	-0.35	-1.19	7.8	
SW1	Seawater sample		43800	7.7	26.8	171	5.0	324.5	7626.0	289.1	978.8	16683.9	4116.0	1092.0	163.7	5.81				20.8	-3.3

862 Table 2 – Summary of main hydrochemical processes occurring in the carbonate and quaternary aquifer, along with evidence used to assess the process

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Aquifer (Carb/Quat)	Process	Occurring (Y/N)?	Evidence (1)	Evidence (2)	Figure
Carbonate Aquifer	Calcite dissolution (congruent)	No	Most groundwater samples with $SI_{\text{calcite}} < 0.1$ and $\text{Ca}:\text{HCO}_3 > 1:2$	No correlation between Ca or $\text{HCO}_3$ and $\delta^{13}\text{C}$	Figure 7
	Incongruent dolomite weathering	Yes	Increase in Mg/Ca along the flow path	Increase in $\delta^{13}\text{C}$ with increasing Mg/Ca	Figure 7a
	Cation exchange	Yes	Most samples with negative $\Delta\text{Na}^+$ values and positive $\Delta\text{Ca}^{2+} + \Delta\text{Mg}^{2+}$ values	MixCa-Cl facies in HFE diagram	Figure 3; Figure 6
	Fertilizer addition	Yes	Positive correlation between $\text{NO}_3^-$ and $\text{SO}_4^{2-}$ concentrations	Mass balance results from different sources of $\delta^{34}\text{S}_{\text{SO}_4}$	Figure 9 Figure 10
	Gypsum dissolution	Yes	All water samples with $SI_{\text{gypsum}} < -0.5$	Ca/ $\text{SO}_4$ ratios $> 1$	-
Quaternary Aquifer	Calcite dissolution (congruent)	Minor	Lack of correlation between $\delta^{13}\text{C}$ and $\text{HCO}_3$ ; Increasing $\delta^{13}\text{C}$ with increasing Ca	Most groundwater samples with $SI_{\text{calcite}} < 0.1$ and $\text{Ca}:\text{HCO}_3$ around 1:2	Figure 7
	Incongruent dolomite weathering	No (apart from QG3)	$SI_{\text{dolomite}} > -0.5$ ; $\text{Mg}:\text{HCO}_3 > 1:4$	No obvious increasing trend in $\delta^{13}\text{C}$ with increasing Mg/Ca	Figure 7
	Cation exchange	Yes	Enrichment in Ca and loss of Na along flow path	$SI_{\text{calcite}}$ and $SI_{\text{dolomite}}$ close to or exceeding 0	Figure 3
	Addition of sulphate from fertilizer	Yes	Positive relationship between $\text{SO}_4$ and $\text{NO}_3$	Increasing $\delta^{34}\text{S}$ values with increasing $\text{NO}_3$ concentrations	Figure 9 Figure 10
	Gypsum dissolution	Yes	Ca: $\text{SO}_4$ close to 1	$SI_{\text{gyp}} < -0.5$	-