

Characterizing the heterogeneity of karst critical zone and its hydrological function: an integrated approach

Journal:	<i>Hydrological Processes</i>
Manuscript ID	HYP-18-0002.R1
Wiley - Manuscript type:	Special issue: Water in the Critical Zone
Date Submitted by the Author:	13-May-2018
Complete List of Authors:	Chen, Xi; State Key Laboratory of Hydrology-Water Resources and Hydraulic Engineering, Hohai University Zhang, Zhicai; Hohai University, State Key Laboratory of Hydrology-Water Resources and Hydraulic Engineering Soulsby, Chris; University of Aberdeen, School of Geosciences Cheng, Qin-Bo; Hohai University, College of Hydrology and Water Resources Binley, Andrew; Lancaster University, Lancaster Environment Centre Jiang, Rui; Hohai University, State Key Laboratory of Hydrology-Water Resources and Hydraulic Engineering Tao, Min; Hohai University, State Key Laboratory of Hydrology-Water Resources and Hydraulic Engineering
Keywords:	Cockpit karst, critical zone, hydrological functions, geophysical survey, tracers

SCHOLARONE™
Manuscripts

1
2
3 1 **Characterizing the heterogeneity of karst critical zone and its hydrological function: an**
4
5 2 **integrated approach**
6

7 3

8
9 4 Xi Chen^{1,2*}, Zhicai Zhang^{2,3}, Chris Soulsby³, Qinbo Cheng^{2,4}, Andrew Binley⁴, Rui Jiang²,
10 5 Min Tao²
11 6

12 7 1: Institute of Surface-Earth System Science, Tianjin University, Tianjin China

13 8 2: State Key Laboratory of Hydrology-Water Resources and Hydraulic Engineering, Hohai
14 9 University, Nanjing 210098, China

15 10 3: School of Geosciences, University of Aberdeen, Aberdeen AB24 3UF, United Kingdom

16 11 4: Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, United
17 12 Kingdom
18 13

19 14 *Corresponding author E-mail: xichen@hhu.edu.cn
20 15

21 16 Submitted to Special issue: Water in the Critical Zone
22 17
23 18
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 19 **Abstract**

4
5 20 Spatial heterogeneity in the subsurface of karst environments is high, as evidenced by the
6
7 21 multi-phase porosity of carbonate rocks and complex landform features that result in marked
8
9 22 variability of hydrological processes in space and time. This includes complex exchange of
10
11 23 various flows (e.g. fast conduit flows and slow fracture flows) in different locations. Here, we
12
13 24 integrate various “state-of-the-art” methods to understand the structure and function of this
14
15 25 poorly-constrained critical zone environment. Geophysical, hydrometric and tracer tools are
16
17 26 used to characterize the hydrological functions of the cockpit karst critical zone in the small
18
19 27 catchment of Chenqi, Guizhou province, China. Geophysical surveys, using electrical
20
21 28 resistivity tomography (ERT), inferred the spatial heterogeneity of permeability in the
22
23 29 epikarst and underlying aquifer. Water tables in depression wells in valley bottom areas, as
24
25 30 well as discharge from springs on steeper hillslopes and at the catchment outlet, showed
26
27 31 different hydrodynamic responses to storm event rainwater recharge and hillslope flows.
28
29 32 Tracer studies using water temperatures and stable water isotopes (δD and $\delta^{18}O$) could be
30
31 33 used alongside insights into aquifer permeability from ERT surveys to explain site- and
32
33 34 depth-dependent variability in the groundwater response in terms of the degree to which “new”
34
35 35 water from storm rainfall recharges and mixes with “old” pre-event water in karst aquifers.
36
37 36 This integrated approach reveals spatial structure in the karst critical zone and provides a
38
39 37 conceptual framework of hydrological functions across spatial and temporal scales.
40
41 38 Key words: Cockpit karst; critical zone; hydrological functions; geophysical survey; tracers;
42
43 39 stable isotopes.
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1 Introduction

Karst covers ~10% of the continents and about one quarter of the global population is completely or partially dependent on drinking water from karst aquifers (Ford and Williams, 2013). The southwest China karst region is one of the largest continuous karst areas, covering ~540×10³ km² over eight provinces. The karst terrain displays a geomorphic transition as the topography gradually descends by 2,000 metres over 700 kilometres from the western Yunnan-Guizhou Plateau to the eastern Guangxi Basin. Cockpit karst is a specific geomorphology found in some tropical areas underlain by limestone formations. Conical hills and star shaped valleys are characteristic of such karst landscapes. Due to the distinct nature of karst geology and geomorphology in the humid tropics and subtropics, spatial heterogeneity in the subsurface is high, evidenced by specific landforms features (e.g. heavily fractured outcrops, sinkholes etc.) and complex subterranean conduit networks. This leads to highly dynamic variability of hydrological processes in space and time. This heterogeneity in karstic environments and their rapidly evolving nature makes them extremely vulnerable to natural and anthropogenic hazards. Hillslope springs and groundwater in valley bottom depressions in cockpit karst areas are the main water resources for local agriculture, industry and domestic use. However, the high hydrological variability results in vulnerability to the frequent occurrences of floods and droughts. Consequently, understanding the karst critical zone, its structures and hydrological functions in the southwest karst region of China is essential to mitigate natural disasters and adapt appropriate management strategies for sustainable water resource utilization.

1
2
3
4 61 Hydrological responses to rainfall in cockpit karst areas can be conceptualised as in Fig 1.
5
6 62 The hydrological processes include rainfall infiltration in the soil and epikarst, water storage
7
8 63 and flow in the transmissive zone, and hydrological connectivity between hillslope and
9
10
11 64 depression units. To consider the effects of marked heterogeneity in the profile of the karst
12
13
14 65 critical zone on hydrological function, the profile can be sub-divided into soil, epikarst,
15
16 66 unsaturated and phreatic zones (Perrin et al., 2003). On the hillslope, since the permeability
17
18 67 usually reduces with the depth (Williams, 1983) or less permeability layers underlie the
19
20
21 68 epikarst zone, infiltrated water usually flows out as a spring. The phreatic zone is regarded as
22
23
24 69 a transmissive zone through its well-developed conduit network (e.g. Emblanch et al., 2003;
25
26 70 Perrin et al., 2003). Nevertheless, it is extremely heterogeneous in space. For example, the
27
28
29 71 solutional conduits in karst aquifers connect with intergranular pores and fractures (often
30
31
32 72 termed as matrix porosity), showing dual or even triple porosity zones (Worthington et al.,
33
34 73 2017). Thus, karst aquifers are often conceptualized as dual porosity systems as residence
35
36 74 times in the matrix are several orders of magnitude longer than those in the conduits
37
38
39 75 (Goldscheider and Drew, 2007). However, even for the matrix porosity at a specific site,
40
41
42 76 fracture apertures can widely vary, e.g. 0.01–0.1 mm (Long et al. 1982; Hyman et al. 2015);
43
44 77 and for larger conduits, the density and connectivity with the surrounding fractures can vary
45
46
47 78 greatly due to heterogeneity in the stratigraphy and geologic structure. Consequently, the
48
49 79 characterization of the functioning of such complex systems remains a great challenge.

50
51
52 80 Hydrometric observations and tracer investigations are traditional and effective
53
54 81 approaches to inferring flow processes within karst systems (Fig 1). Water table response is

1
2
3
4 82 particularly sensitive to changes in hydrometeorological forcing because of the direct
5
6 83 connectivity of the water table with the ground surface in surficial and shallow aquifers
7
8
9 84 (Winter, 1999; Healy and Cook, 2002; Sophocleous, 2002; Lee et al., 2006). The water-table
10
11 85 rise and fall during a specific storm period can be translated into a corresponding amount of
12
13
14 86 groundwater recharge and discharge (Sophocleous, 1991; Xie and Yuan, 2010; Fan et al, 2014;
15
16 87 Biswas et al, 2017). In karst areas, abundant springs on hillslopes and at catchment outlets
17
18
19 88 reflect regional flow accumulation along conduits and underground channels. Spring
20
21 89 hydrographs can be used to characterize karst systems (Kovacs and Perrochet, 2008) and
22
23
24 90 better understand system behavior during floods (Winston and Criss, 2004) or droughts
25
26
27 91 (Fiorillo, 2009).

28
29 92 As water flowing through soils or fractures carries sensible heat that can affect
30
31 93 subsurface water temperatures on mixing (Anderson, 2005; Rau et al., 2014), distributed
32
33
34 94 temperature measurements can provide excellent indications of flow and connectivity. Using
35
36
37 95 water temperature as a tracer can thus help assess groundwater flow, groundwater-surface
38
39 96 water exchanges (Becker et al., 2004; Niswonger et al., 2005; Lowry et al., 2007; Irvine et al,
40
41
42 97 2015), flow paths, mixing effects and residence times (Sun et al., 2016). This is especially
43
44
45 98 useful in karst aquifers as fast flows overcome limitation of heat tracing at lower velocities
46
47 99 (Rau et al., 2010, Rau et al., 2014). As rainwater may has different temperatures to
48
49
50 100 groundwater, the arrival of new recharge at a karst spring is evidenced by changing water
51
52 101 temperature (Ford and Williams, 2013). Subsurface temperature variability can thus be used
53
54
55
56
57
58
59
60

1
2
3
4 102 to assess the degree of connectivity and relative importance of mixing (Hartmann et al., 2014;
5
6 103 Mudarra et al., 2014).

7
8 104 Isotope studies have also substantially increased our understanding of detailed
9
10
11 105 hydrological flow paths and mixing processes in the critical zone (Sprenger et al., 2017, 2018).
12
13 106 Stable isotopes of water ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) have also been widely used to provide insight into the
14
15
16 107 functioning of karst systems (Barberá and Andreo, 2012; Mudarra and Andreo, 2011), the
17
18 108 mixing of water from different sources (Aquilina et al., 2006; Plummer et al., 1998), and the
19
20 109 their residence times (Batiot et al., 2003; Long and Putnam, 2004). Due to the high degree of
21
22 110 variability of karst systems, continuous monitoring or event-based high-frequency sampling is
23
24 111 essential, but logistically challenging (Goldscheider and Drew, 2007).

25
26
27
28
29 112 Hydrometric monitoring and tracer studies provide direct observations of
30
31 113 hydro-dynamics which can indirectly hypothesize karst critical zone structures. However,
32
33 114 explaining hydrological variability and identifying controls rely on detail information on karst
34
35 115 hydrogeological properties in space. For example, Lee and Krothe (2001) used dissolved
36
37 116 inorganic carbon (DIC) and $\delta^{13}\text{C}$ as tracers for conceptualizing hydrological functions
38
39 117 using a four-component mixing model (rain, soil water, epikarstic water and diffuse phreatic
40
41 118 water) for a karstic flow system. Similarly, Jiang et al. (2008) inferred runoff response
42
43 119 thresholds in the epikarst by monitoring the spring's discharge, pH, electrical conductivity,
44
45 120 temperature and rainfall. Increasingly, however, geophysical techniques are being used to
46
47 121 provide more direct evidence about the geological setting of a karst system. Survey
48
49 122 techniques, such as ground penetrating radar (GRP) and electrical resistivity tomography
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4 123 (ERT), provide an efficient means of describing the karst structure, mapping karst conduits
5
6 124 (Carrière et al., 2013; Martínez-Moreno et al., 2014) and defining the soil-rock interface
7
8
9 125 (Chalikakis et al., 2011). Such geological evidence is crucial for delineating hydraulic
10
11 126 structures, such as complex subsurface drainage networks in the karst which can link local
12
13
14 127 fissure and fracture networks with the dominant large conduit systems (Chalikakis et al, 2011;
15
16 128 Hartmann et al., 2014; Binley et al., 2015). These insights can be particularly powerful if
17
18
19 129 geophysical approaches are integrated with hydrometric and tracer observations and at the
20
21 130 same study site (e.g. Soulsby et al., 2016).

22
23
24 131 Different methodologies have advantages and limitations (see Goldscheider and Drew,
25
26 132 2007) so isolated measurements and observations are inadequate for characterizing a karst
27
28
29 133 system. Although many researchers apply combinations of such methods for assessing the
30
31 134 hydrology karst areas, they seldom integrate insights from multi-scale distributed geophysical
32
33
34 135 surveys, hydrometric observations and tracer investigations. Consequently, in the southwest
35
36
37 136 karst region of China, we lack a conceptual framework that characterizes spatial heterogeneity
38
39 137 hydrological functioning at multiple scales and/or in different geographic regions.

40
41
42 138 The overall aim of this study was to integrate these approaches to visualize the complex
43
44 139 heterogeneity in karst critical zone and its effect on hydrological functions. By so doing, the
45
46
47 140 study will also help identify dominant processes to incorporate in the structure of hydrological
48
49
50 141 models. We based the investigation in the long-term study site of Chenqi in the cockpit karst
51
52 142 region of Guizhou province, southwest China. Our objectives were to: (1) undertake
53
54
55 143 geophysical surveys using electrical resistivity tomography to characterize the structure of the
56
57
58
59
60

1
2
3
4 144 karst critical zone and identify variations in the permeability which define fast and slow flow
5
6 145 domains in karst aquifers. (2) Monitor groundwater levels in wells and discharge from
7
8 146 hillslope springs and the catchment outlet to characterize the spatial and temporal variations
9
10
11 147 of hydrodynamic response to rainfall events. (3) Use stable isotopes of water ($\delta^{18}\text{O}$ and $\delta^2\text{H}$)
12
13 148 qualitatively understand how “new” event water from rainwater and “old” pre-event water
14
15 149 from low permeability aquifers recharges mix and contribute to catchment discharge,
16
17 150 particularly during heavy rainfall in the vertical profiles. Improved conceptualization of a dual
18
19 151 flow system that accounts for local aquifer heterogeneity influences on the hydrological
20
21 152 connection between fast and slow reservoirs is proposed.
22
23
24
25
26
27
28

29 154 **2 Study area, data and methods**

30 155 **2.1 Study catchment**

31
32
33
34 156 The study was focused in the small (1.2km²) Chenqi catchment, located in the Puding
35
36 157 Karst Ecohydrological Observation Station, Guizhou Province, southwest China (Fig. 2). It is
37
38 158 a typical cockpit karst landscape, with surrounding conical hills separated by star shaped
39
40 159 valleys. Surface elevation ranges from 1320m at the catchment outlet to a maximum of 1500
41
42 160 m. Geological strata in the basin include dolostone, thick and thin limestone, marlite and
43
44 161 Quaternary soil (profiles of A-A' and B-B' in Fig 2). Limestone formations form the higher
45
46 162 elevation areas with 150-200 m thickness, which lie above an impervious marlite formation.
47
48 163 The Quaternary soils are irregularly developed on carbonate rocks and unevenly distributed,
49
50 164 with outcrops of carbonate rocks covering 10-30% of the catchment. Dominant vegetation
51
52
53
54
55
56
57
58
59
60

1
2
3
4 165 ranges from deciduous broad-leaved forest on the upper and middle parts of the steep
5
6 166 hillslopes and corn and rice paddy at the low of the gentle hillslopes and depression.
7

8
9 167 The catchment is located in a region with a subtropical wet monsoon climate with mean
10
11 168 annual temperature of 20.1°C, highest in July and lowest in January. Annual mean
12
13 169 precipitation is 1140 mm, almost all falling in a distinct wet season from May to September
14
15
16 170 and a dry season from October to April next year. Average monthly humidity is high, ranging
17
18
19 171 from 74% to 78%.

20 21 172 **2.2 ERT survey in the valley depression**

22
23
24 173 Electrical resistivity tomography (ERT) was used to survey the geological properties
25
26 174 along five transects crossing the depression (Fig 3). The surveyed profiles were located
27
28
29 175 adjacent to four observation wells (see below) and three sinkholes to identify the geological
30
31
32 176 controls on groundwater dynamics. The surveys were carried out in spring 2017 using a
33
34 177 Syscal Pro (Iris Instruments, France) resistivity meter with electrode spacing between 2 and
35
36 178 5m. We used a dipole-dipole electrode configuration (see for example, Binley, 2015) with
37
38
39 179 dipole spacings of one, two and three times the electrode separation and up to 20 levels. The
40
41
42 180 dipole-dipole configuration was selected to allow sensitivity of lateral variation in resistivity.
43
44
45 181 Inversion of the ERT data was carried out using the code R2
46
47 182 (<http://www.es.lancs.ac.uk/people/amb/Freeware/R2/R2.htm>). The resulting composite ERT
48
49 183 image is shown in Fig 3. The resistivity ranges from ~15 Ωm to ~8000 Ωm . Based on ERT
50
51
52 184 surveys carried out adjacent to outcrops in neighbouring areas of the catchment we interpret
53
54
55 185 the ERT results in Fig 3 as: (i) an upper layer consisting of moist soils or extensively
56
57
58
59
60

1
2
3
4 186 fractured rock (resistivity $<100 \Omega\text{m}$, blue in Fig. 3); (ii) carbonate rock with a high secondary
5
6 187 porosity (and hence permeability) ($100 \Omega\text{m} < \text{resistivity} < 1000 \Omega\text{m}$, green/yellow in Fig. 3);
7
8
9 188 (iii) an underlying carbonate rock with low secondary porosity and hence relatively low
10
11 189 permeability (resistivity $>1000 \Omega\text{m}$, red in Fig. 3).

12
13
14 190 The ERT image shows that the depression aquifer is highly heterogeneous in both the
15
16 191 horizontal direction and vertical direction. Based on our interpretation of the ERT image: well
17
18 192 W1 is surrounded by the less permeable aquifer (red colour) and its upper layer of carbonate
19
20 193 rock appears particularly impermeable; wells W3 and W4 are located in the higher
21
22 194 permeability area (blue colour); well W5 is located in the less permeable aquifer and its top
23
24 195 soils (blue colour) and the carbonate rock in the upper layer (yellow colour) is relatively more
25
26 196 permeable than that in the deep layer (red colour). The relatively permeable upper layer at W5
27
28 197 appears much thinner than those at other wells.

29
30
31
32
33
34 198 In a previous study, a GPR MALA Professional Explorer (ProEx) System was used for
35
36 199 investigation of the fracture zone thickness on the hillslope. The epikarst thickness on the
37
38 200 hillslope was identified to be in a range of 7.6~12.56 m. Along the hillslope, the thickness and
39
40 201 the epikarst zone at the lower areas is deeper than in the upper areas (Zhang et al. 2013).

41 42 43 44 202 **2.3 Hydrometric observations**

45
46
47 203 In the Chenqi catchment, groundwater levels in the valley depression were routinely
48
49 204 monitored at the four wells (W1, W3, W4 and W5) with depth to ground surface of 35, 23, 13
50
51 205 and 16 m, respectively. The well screening was installed over the whole depth for each of the
52
53 206 wells to reflect local flow exchanges at various depths. Flows discharging from a hillslope
54
55
56
57
58
59
60

1
2
3
4 207 spring (HS) at the foot of the eastern steep hillslope and leaving the catchment outlet were
5
6 208 measured by v-notch weirs (Fig. 2). The water level and temperature at each well, the
7
8
9 209 hillslope spring and the catchment were automatically recorded by HOBO U20 water level
10
11 210 logger (Onset Corporation, USA) with a time interval of 15 minutes. Additionally, an
12
13
14 211 automatic weather station was set on the upper hillslope to record precipitation, air
15
16 212 temperature, and air humidity and pressure.

17
18
19 213 Data collection ran from 28 July 2016 to 30 October 2017. Hourly variations of rainfall,
20
21 214 discharge from the hillslope spring and catchment outlet, as well as water levels in the four
22
23
24 215 wells are shown in Fig 4, and their corresponding temperature are shown in Fig 5. Statistical
25
26 216 characteristics of water levels, flow discharges and temperatures are summarized in Table 1
27
28
29 217 and Table 2.

30 31 218 **2.4 Stable isotope analysis**

32
33
34 219 For isotope analysis, the hillslope spring (HS), groundwater from outlet and rainfall were
35
36
37 220 sampled at daily intervals during the wet season from June to August 2017. Additionally, they
38
39 221 were intensively sampled during eight rainfall events in the wet season using an autosampler
40
41
42 222 set to hourly intervals. Depression groundwater was sampled from the four wells during four
43
44 223 rainfall events within the study period; in each event, water samples were collected before,
45
46
47 224 during and after rainfall. At each well, water was sampled from multiple depths with a
48
49 225 depth-specific sampler to give a profile of the isotopic composition of the groundwater
50
51
52 226 column. All water samples (1695 replicates) were collected by 5 ml glass vials. The stable
53
54
55 227 isotopic composition of $\delta^2\text{H}$ (δD) and $\delta^{18}\text{O}$ ratios were determined using the MAT 253 laser
56
57
58
59
60

1
2
3
4 228 isotope analyser (the instrument precision $\pm 0.5\%$ for $\delta^2\text{H}$ and $\pm 0.1\%$ for $\delta^{18}\text{O}$). Isotope ratios
5
6 229 are reported in the d-notation using the Vienna Standard Mean Ocean Water standards
7
8
9 230 (Coplen, 1994). The analyzed results of the isotopic values are shown in Figs 6-8.

10
11 231

12 13 14 232 **3 Results**

15 16 233 **3.1 Hydroclimatic and groundwater variability in the depression**

17
18
19 234 Generally, the hydrometric observations reveal sharp rises and falls in water level at the
20
21 235 four wells in response to rainfall events (Fig. 4). However, the magnitude of the water table
22
23
24 236 response and the rate of the water table recessions exhibit differences at the four wells, which
25
26
27 237 indicates spatial differences in the groundwater response to recharge and attenuation of the
28
29 238 hydrograph. The magnitude of the temporal dynamic is larger and more attenuated at W3 and
30
31
32 239 W4 in the low electrical resistivity (interpreted higher permeability) areas, and abrupt at W1
33
34 240 and W5 where particularly heavy rainfall is needed to produce a large water table rise. These
35
36
37 241 differences are apparent in the coefficient of variation (CV) of water level data for W3 and
38
39 242 W4 (0.21 and 0.61, respectively), whilst the CV of W1 and W5 is only 0.03 and 0.07,
40
41
42 243 respectively (see Table 1).

43
44 244 Temporal variability in temperature clearly demonstrates that groundwater dynamics at
45
46
47 245 W3 and W4 are more directly influenced by hydroclimate variability compared with W1 and
48
49 246 W5 (Fig 5). The former wells show marked temperature excursions towards air temperatures
50
51
52 247 in response to rainfall events, whilst the latter wells exhibit highly attenuated temperatures
53
54
55 248 typical of deeper groundwater. As shown in Table 2, the CV of water temperature at W3 and

1
2
3
4 249 W4 is 0.026 and 0.036, while the CV of W1 and W5 is only 0.004 and 0.012, respectively.
5
6 250 The sharp rise and drop of water temperature at W3 and W4 during rainfall is clearly
7
8
9 251 consistent with the fast arrival of freshly infiltrated rainwater. In contrast, the limited seasonal
10
11 252 fluctuation of water temperatures at W1 and W5 indicate little evidence of rainfall recharge
12
13
14 253 consistent with the interpreted low permeability in the upper layers (high resistivity zone in
15
16 254 Fig 3).

17
18
19 255 As shown in Fig. 6 and Table 3, temporal variations of rainfall δD and $\delta^{18}O$ at Chenqi
20
21 256 are marked, ranging from -120.2 to -17.9‰ for δD and from -16.4 to 0‰ for $\delta^{18}O$. The δD
22
23
24 257 and $\delta^{18}O$ responses amongst the depression wells are attenuated or damped but they are
25
26
27 258 markedly different in this restricted area due to spatial heterogeneity of the karst aquifer
28
29 259 (Table 3 and Fig 6). In terms of the temporal changes in δD and $\delta^{18}O$, values tended to
30
31
32 260 become more negative in response to direct effects of rainwater recharge into the aquifer
33
34
35 261 during storm events. Compared with isotope values at W1 and W5, groundwater at W3 and
36
37 262 W4 is clearly receiving rainfall that has marked changes in isotope values evident in the
38
39
40 263 variability in Fig 6 and the large range in Table 3. Groundwater at W5 is the most stable (Fig
41
42 264 6) and has the lowest range in Table 3 implying a limited influence of new recharge from
43
44
45 265 rainfall. However, W1 is close to the catchment outlet and the high permeability of its lower
46
47 266 aquifer inferred from the ERT survey may allow exchange with the subsurface flow leaving
48
49
50 267 the catchment (Fig 3). The isotopic signatures of groundwater at W1 show intermediate
51
52 268 isotopic values compared to the upper catchment (lower than the most stable water at W5 and
53
54
55
56
57
58
59
60

1
2
3
4 269 higher than those at W3 and W4 where the direct rainfall influence is evident), suggesting that
5
6 270 groundwater at W1 likely reflects mixing of flow paths from the upper depression.
7

8
9 271 However, at the different stages of the storm event response (e.g. the sharp rises and falls
10
11 272 in water level before and after rainfall), the degree of “new” event water recharge from
12
13 273 rainfall and “old” water release from previous storage amongst the four wells differed
14
15 274 according to the δD values from the depression aquifer (Fig 7). Generally, recharge of new
16
17 275 rainfall occurs in the early recession phase of the groundwater response, and the release of
18
19 276 previously stored (old) water occurs later in the recession. The impact of infiltrating new
20
21 277 water in the early recession can be distinguished from changes of the δD values before rainfall
22
23 278 and in the early recession in Fig 7; for rainfall events No. 1 and 4, as the rainwater δD values
24
25 279 are much more negative than those of the groundwater. The subsequent decline of the δD
26
27 280 values in these depression wells indicates the ingress of isotopically depleted (newer)
28
29 281 rainwater. However, for rainfall event No 3, as the rainwater δD is more enriched than
30
31 282 groundwater, the rise of the δD values at these depression wells also indicates the impact of
32
33 283 more enriched rainwater recharge.
34
35
36
37
38
39
40

41
42 284 In the later recession, the effects of recent recharge generally decline. Hence, the δD
43
44 285 values of groundwater increase again for rainfall events No 2 and 4. This would be consistent
45
46 286 with the release of older water into aquifer. As shown in Fig 7, changes of the δD values in
47
48 287 the three events are evident for wells W3, W4 and W5, but the changes become less
49
50 288 distinguishable for well W1 close to the catchment outlet (Fig 7). This also indicate that
51
52
53
54
55
56
57
58
59
60

1
2
3
4 289 groundwater at the catchment outlet can be attributed by regional flow that endures a
5
6 290 relatively high mixture of event new water with storage old water.
7

8 291 **3.2 Hillslope-depression flow connectivity**

9
10
11 292 Hillslope-depression flow connectivity can be identified from temporal variability in
12
13
14 293 water table levels, temperatures and isotopic tracers at W4 located at the base of a steep
15
16 294 hillslope and the hillslope spring (HS). Despite the marked response to rainfall events, the
17
18
19 295 water level at W4 recesses much more slowly after rainfall ceases compared to the other wells
20
21 296 (Fig 4). The slow recession in this interpreted high permeability area possibly arises from
22
23
24 297 some additional water from upslope areas that continues to recharge the depression aquifer
25
26 298 after rainfall ceases.

27
28
29 299 Water temperatures and isotopic values at W4 and the hillslope spring (HS) further provided
30
31 300 evidence for hillslope contributions to the depression. Water temperatures at both sites show a
32
33
34 301 similar pattern of the seasonal variations with air temperature and fluctuations with rainfall
35
36
37 302 (see Fig 5), i.e. higher in the summer season and lower in the winter season. Water isotopic
38
39 303 values at W4 are closest to these at the hillslope spring (HS), particularly, during the rainfall
40
41
42 304 period (see the yellow for W4 and the green for HS in Fig 6 and mean values in Table 3).
43
44 305 Additionally, in the winter season, water temperature at W4 is more attenuated and lags
45
46
47 306 behind that of the hillslope spring, which indicate that the hillslope flow is faster than the
48
49
50 307 depression groundwater flow at W4. In the summer season, the response of water temperature
51
52 308 to rainfall at W4 is more marked than those of the hillslope spring, which indicate that the
53
54
55 309 depression groundwater flow at W4 could receive hillslope flow as well as rainfall recharge.
56
57
58
59
60

3.3 Effect of vertical heterogeneity on hydrological functions

The ERT survey demonstrates strong vertical heterogeneity of the karst aquifer at each site (Fig 3). The δD values at various depths to groundwater table (the uncertainty bar in Fig 7) illustrates the effect of vertical heterogeneity on hydrological functions. For the four wells, the range of the vertical variation in δD is generally much higher for W1 and W3 in the central and outlet depression, than the wells of W4 and W5 at the upper depression. This is consistent with groundwater in the upper depression areas mixing more effectively in a vertical direction than groundwater in the center and catchment outlet.

The isotopic values prior to rainfall and at the early and late stages of the recession for rainfall event 4 (12 to 14 August 2017) in Fig 8 further demonstrate the control of vertical heterogeneity in aquifer structure on hydrological function. The event has a total rainfall of 36.8 mm and the rainfall δD value ranging between -109.8 and -74.8‰ with a mean of -90.7‰, with the most negative values coinciding with peak rainfall. The event-scale changes in the vertical distribution of the δD values are different for the four wells.

(1) *WI*: there is little vertical variation of the δD values before rainfall (Fig 8a(i), which indicates strong pre-event vertical mixing. Early in the recession when groundwater levels rapidly decline, the mean δD value declined from -60.5 to -61.6‰ (Fig 8a(i)), indicating some new water influence. Moreover, the flow paths of the new water ingress can be identified from the vertical variation of the δD values (see 13/8 line in Fig 8a(ii)), i.e. at the depths of 7-8m and below 18m where the δD values rapidly decline. These depths correspond to low resistivity regions indicative of high permeable layers (green in Fig 8a(iii)). Since the

1
2
3
4 331 temperature variation in Fig 5 and ERT image in Fig 8a(iii) suggest that the lower layer at W1
5
6 332 receives little rainfall recharge, the decline of the δD values seems most likely explained by
7
8 333 exchange of groundwater in the high permeability depths with the regional flow (affected by
9
10
11 334 new rainfall). Between the two higher permeability layers, water in the less permeability layer
12
13 335 (yellow in Fig 8a(iii)) changes only little, indicating that flow exchange between the
14
15
16 336 permeable and less permeable layers is weak.

17
18
19 337 Later in the recession, the δD value increases to -60.8‰, which is close to the
20
21 338 pre-rainfall value. At this time, vertical variations on 14 August (Fig 8a(ii)) demonstrate that
22
23 339 the δD value in the lower permeable layer (below 18m) recovers close to pre-event conditions.
24
25
26 340 Surprisingly, the δD values in the upper less permeable layer (the depth of 7.5 m) become
27
28 341 much less negative. This suggests that there may be release or displacement of older water,
29
30
31 342 possibly attributable to antecedent storage from the upper less permeable layer (Fig 8a(iii)).

32
33
34 343 (2) **W3**: temporal variation of δD values over the three periods (Fig.8b(i)) is similar but
35
36 344 more marked than that at W1. Vertical variation at W3 (Fig 8b(ii)) is very different over the
37
38 345 three periods. Before the rainfall on 12 August, the δD values generally are less negative
39
40
41 346 throughout the water column. The more negative values in the upper profile may reflect more
42
43 347 recent depleted rainfall and increasingly older water with depth. This seems consistent with
44
45 348 the decreasing permeability with depth at W3 implied by the less resistive upper profile and
46
47 349 more resistive deeper layers (Fig 8b(iii)).

48
49
50
51
52 350 In the early recession on 13 August, δD values (Fig 8b(ii)) become more negative and
53
54 351 almost uniform in vertical distribution. This implies that new water from recharge of
55
56
57
58
59
60

1
2
3
4 352 rainwater rapidly mixes with older pre-event water in storage. In the later recession,
5
6 353 groundwater isotope values recover indicating lessening influence of new water, though
7
8
9 354 values do not recover to pre-rainfall levels. Meanwhile, groundwater in the upper aquifer (e.g.
10
11 355 above 8m) still remains negative with continued new water influence. This suggests that the
12
13
14 356 upper, more permeable (i.e. with lower resistivity) aquifer stores more new water during
15
16 357 rainfall and releases this thereafter.

18
19 358 (3) *W4*: as shown in Fig.8c(i), the water level recession is slower than the other wells but
20
21 359 the mean of the δD value declines greatly from -59‰ before rainfall to -67‰ in the early
22
23
24 360 recession and then recovers to -65.9‰ in the later recession. The marked decline of δD is
25
26 361 again consistent with substantial influence of event water ingress. Prior to rainfall when
27
28
29 362 groundwater level is low (>4m in depth), the vertical distribution of the δD is nearly uniform
30
31 363 (Fig 8c(ii)). In the early recession when water levels remain high, groundwater in the upper
32
33
34 364 aquifer (above the depth of 3.5) tends to be more negative indicating event new water
35
36 365 influence.

38
39 366 In the later recession, the δD values below 3.5m become a little more negative, whilst the
40
41
42 367 upper aquifer remains the same. As *W4* is located at the foot of a steep hillslope, it is likely
43
44
45 368 that lateral flow from the hillslope contributes recharge since the ERT image suggests that this
46
47 369 is a high permeability area strongly connected to the hillslope flow path (Fig 3 and Fig
48
49 370 8c(iii)).

51
52 371 (4) *W5*: The water level and isotopic response at *W5* contrasts markedly to the other
53
54
55 372 wells, i.e. a transient fluctuation of water level and abrupt change in δD (Fig 8d(i)). The

1
2
3
4 373 unresponsive groundwater likely reflects that the well is located in an impervious (high
5
6 374 resistivity) area (Fig 8d(iii)). After the water level decline, groundwater has a limited decrease
7
8
9 375 in δD (from -58 to -58.4‰) in the early post-event period, and continuous decrease (to
10
11 376 -59.6‰) later. The continuous decrease of δD values indicates a longer memory of the much
12
13
14 377 less permeability aquifer to the limited recharge.

15
16 378 Before rainfall, the vertical values of δD are highly varied; water in the upper layer has
17
18
19 379 less negative values of δD , whilst waters at depths of 7.4m and below 8m have more negative
20
21 380 values of δD (Fig 8d(ii)). The much older water in the upper layer suggests strong evaporative
22
23
24 381 effect in the non-rainfall period since the top soils and the upper permeability rock layer are
25
26 382 thin (Fig 8d(iii)) and thus evaporative effect is strong. Marked changes of the δD values in the
27
28
29 383 lower depths (e.g. below 7.4m) reflects that there are still some permeable fractures, in which
30
31 384 new water could be arrival. After the end of the brief water table response, the vertical δD
32
33
34 385 values (13 August in Fig 8d(ii)) in the lower layer (e.g. below 7.4m) are more negative than
35
36 386 the upper layer. This would imply that after a short response to rainfall (Fig 8d(i)), event “new”
37
38
39 387 water in the upper layer rapidly mixes with the surrounding “old” water, but “new water” still
40
41
42 388 ingresses into the lower depths. In the later post-event period, the relatively uniform vertical
43
44 389 values of δD (14 August in Fig 8d(ii)) show recharged event water mixing in the whole
45
46
47 390 profile.

49 391 **4 Discussion and conclusions**

52 392 **4.1 Discussion**

55 393 **4.1.1 Conceptualizing hydrological functions in cockpit karst catchment**

394 Variation in hydrological functions (rainfall recharge, horizontal and vertical flow
 395 exchange at sites and hillslope-depression connectivity) in the heterogenous subsurface of our
 396 cockpit karst catchment can be summarized as in Fig 9. Fast and frequent rainwater recharge
 397 I_f into the epikarst zone on the hillslope (HS) and permeable depression (e.g. W3 and W4)
 398 leads to local flow being “active” and young, whilst infrequent rainwater recharge into the
 399 less permeable depression (e.g. W1 and W5) leads to local flow being less active or inactive
 400 and “old”. For the hillslope-depression-outlet connectivity, the mean isotopic value at outlet
 401 (δD) is between relatively “new” water from fast flows in HS and high permeability
 402 depression areas (W3 and W4) (δD_f) and “old” water from slow flows in low permeability
 403 depression areas (W1 and W5) (δD_s). Thus, outlet water (Q and δD) can be viewed as a
 404 mixture of hillslope (Q_f and δD_f) and depression flow (Q_s and δD_s) at various sites.

405 Fig 8 shows that temporal change in hydrological functions is closely linked to vertical
 406 heterogeneity with different composition of the active, less active and inactive areas. The
 407 structure of the vertical profile can be generalized as Fig 9 and classified into two types: (a)
 408 profiles consisting of two different permeability layers, e.g. a high permeability layer
 409 confined by a lower permeability layer at W1 and a high permeability layer with limited
 410 thickness perched on a less permeability layer at W5. (b) profiles comprising one layer but
 411 their permeability decreasing with depth, e.g. at W3 and W4. Here, the profile flow function
 412 can be still illustrated by exchange of fast and slow flow reservoirs (Fig 9) but the relative
 413 contribution of fast and slow flow reservoirs is a function of depth h , i.e. $Q\delta D(h) = Q_f \delta D_f$
 414 $(h) + Q_s \delta D_s(h)$, in where flows and isotopic values in each reservoir are influenced by rainfall

1
2
3
4 415 recharge I_f and water exchange between fast and slow reservoirs $Q_E = K_E(h)(WT_f - WT_s)$ (WT_f
5
6 416 and WT_s represent water table in the fast and slow reservoirs, respectively, and K_E is exchange
7
8 417 coefficient).

10
11 418 Such depth variability of hydrological function can be used to explain the hydrological
12
13 419 response of the observation wells (Fig 9). The profile depth h at W1 and W5 can be divided
14
15 420 into two homogenous layers (h_1 and h_2). At W1, we can hypothesize that recharge of the fast
16
17 421 flow reservoir (I_f) is negligible due to the upper confining layer. The fast flow Q_f can be
18
19 422 highly connected with the regional flow but has limited exchange with the slow flow reservoir
20
21 423 Q_s i.e. Q_E is small, evidenced by little change of the δD value in the less permeable layer for
22
23 424 W1 in Fig 8a(i). At W5, groundwater in the profile is dominated by the slow reservoir Q_s in
24
25 425 the lower layer ($h_2 \gg h_1$). Before rainfall, when the water level WT_s is low, limited perched
26
27 426 water Q_f in the upper layer ingresses into the slow reservoir (Q_E can be neglected). During
28
29 427 rainfall when the upper water table WT_f rises higher than the low water table WT_s , pressure
30
31 428 drives new event water Q_f into the slow reservoir in a short time (Q_E is slight and transient).
32
33 429 After rainfall when a short pulse of water table variation ends ($WT_f \leq WT_s$), the pressured
34
35 430 new water in the slow reservoir Q_s is slowly released.
36
37
38
39
40
41
42
43

44 431 The hydrological functions in the profiles W3 and W4 can be still conceptualized into
45
46 432 the fast and slow flow reservoirs in which fast flow contribution (Q_f) to the whole profile flow
47
48 433 gradually reduces with depth whilst the slow flow contribution (Q_s) increases. As the profile
49
50 434 is highly permeable and unconfined, direct recharge into the fast reservoir (I_f) and new event
51
52 435 water quickly mixes with pre-event water in the vertical direction under $WT_f > WT_s$ during
53
54
55
56
57
58
59
60

1
2
3
4 436 rainfall (large Q_E). In the later recession when water table is low and $WT_f < WT_s$, the older
5
6 437 water in the slow flow reservoir is mostly released from the lower layers (Fig.9b), i.e. less
7
8 438 negative $\delta D_s(h)$ and larger Q_s in $Q\delta D(h) = Q_f\delta D_f(h) + Q_s\delta D_s(h)$. The unconfined aquifer at W4
9
10 439 is similar to W3 but the aquifer at W4 receives direct recharge (I_f) and inputs from hillslope
11
12 440 flow (Q_h) during events when water levels are high, then quickly infiltrates into the low slow
13
14 441 reservoir (large Q_E). After rainfall, the upper fast reservoir retains a water level higher than
15
16 442 the slow reservoir ($WT_f > WT_s$) since the hillslope flow (Q_h) continually inputs into the
17
18 443 aquifer (evidenced by more negative of the δD values in Fig 7c(ii)).

19
20
21
22
23
24 444 In any specific landscape unit (e.g. depression), outlet flow Q comes from fast and slow
25
26 445 flow composition at various sites, i.e. $Q = \sum_1^n Q_f + \sum_1^n Q_s$, and $Q\delta D = \sum_1^n Q_f\delta D_f + \sum_1^n Q_s\delta D_s$,
27
28 446 where n is the total number of the sites. Meanwhile, in each reservoir, the discharge ($\sum_1^n Q_f$
29
30 447 or $\sum_1^n Q_s$) and the mass ($\sum_1^n Q_f\delta D_f$ or $\sum_1^n Q_s\delta D_s$) are influenced by rainfall recharge I_f and
31
32 448 flow exchange Q_E . More specifically, considering vertical heterogeneity at the sites, outlet
33
34 449 flows Q and mass $Q\delta D$ can be expressed by: $\sum_1^n \sum_1^{n1} Q_f + \sum_1^n \sum_1^{n2} Q_s$ and $\sum_1^n \sum_1^{n1} Q_f \delta D_f +$
35
36 450 $\sum_1^n \sum_1^{n2} Q_s \delta D_s$, respectively, where $n1$ and $n2$ are the respective number of permeable and less
37
38 451 permeable layers in a profile.

452 4.1.2 Benefits of an integrated approach

453 Karst aquifers have distinct hydraulic structures and behaviors and therefore require
454 specific investigation methods (Goldscheider and Drew 2007). Capturing the hydrological
455 functions requires hydrometric observations and tracer sampling at sub-hourly intervals as
456 shown in our study. Current techniques that deploy loggers with the capacity to monitor in

1
2
3
4 457 real-time and the capability to transfer data remotely are particularly useful (Luhmann et al.,
5
6 458 2015). In general, monitoring water level data is easy and cheap and it reflects the relatively
7
8 459 strong control of rainfall frequency on hydrograph shape. Nevertheless, it has limited value in
9
10
11 460 interpreting karst aquifer structures (Jeannin and Sauter, 1998) and identifying the
12
13
14 461 contributions of event and pre-event water. The non-conservative nature of water temperature
15
16 462 facilitates insights into conduit size, and the damping and retardation in porous media via an
17
18
19 463 analysis of input and output thermographs (Covington et al., 2011, 2012; Luhmann et al.,
20
21 464 2012; Birk et al., 2014; Luhmann et al., 2015). However, reliable identification of the
22
23
24 465 hydrological functions from input and output thermographs need integrate information on
25
26 466 heat exchange within karst conduits that may introduce a retardation in the residence times
27
28
29 467 (Luhmann et al., 2015). Comparison of the temporary variation of isotopic values in rainfall
30
31 468 with the observed variability in karst spring waters allows not only quantification of mixing
32
33
34 469 processes in discharge as shown in our study, but also to quantify transit time distributions
35
36
37 470 (Hu et al., 2015) and determine groundwater ages.

38
39 471 Selecting representative sites is challenging and important in capturing the large-scale
40
41
42 472 hydrological functions in the karst catchment due to strong heterogeneity, hydraulic
43
44
45 473 discontinuity and anisotropy. Traditionally, tracing and hydrometric observations have been
46
47 474 mostly undertaken in the conduit network to study the rapid flow (Goldscheider et al. 2008)
48
49
50 475 and at outlet springs for the overall characterization of karst systems (Kovacs and Perrochet,
51
52 476 2008). However, fractured rocks in the karst critical zone have the permeability ranging over
53
54
55 477 several orders of magnitude. Even at small spatial scales (e.g. the four wells in our study
56
57
58
59
60

1
2
3
4 478 catchment), there is relatively less active subsurface flow in the high permeability zones, and
5
6 479 relatively active subsurface flow in the less permeable zones. Additionally, our analyzed
7
8
9 480 results of new event water recharge and the degree of mixing with pre-event old water
10
11 481 indicates that water samples at representative depths to characterize subsurface inflows to
12
13
14 482 wells are necessary for assessing different flow paths in the karst and temporal changes in
15
16 483 their hydrological dynamics.

17
18
19 484 A key contribution of this study was to show how geophysical techniques like ERT
20
21 485 surveys can help identifying structural differences which can be incorporated in designing
22
23
24 486 targeted monitoring networks. ERT images combined with tracer characteristics of subsurface
25
26 487 water and the associated mixing processes identify which depths/sites in the catchment are
27
28
29 488 representative for monitoring in order to reliably quantify fast and slow flows. As shown in
30
31 489 Fig 8, water sampling at permeable layers/sites during rainfall events are required for
32
33
34 490 capturing variability of the hydrological functions in the karst catchment. If the permeability
35
36 491 varies with depth, water sampling at various depths are particularly important for quantifying
37
38
39 492 the depth-dependent variability of the hydrological function.

40
41
42 493 Moreover, ERT images combined with details observations provide insights into how to
43
44 494 conceptualize complex karst systems for lumped and distributed modeling. ERT images
45
46
47 495 provide high-resolution visualization of the subsurface, and the relationship between these
48
49
50 496 images and parameters affecting flow and transport (Hubbard et al., 1999). The spatially
51
52 497 distributed information from geophysics and isotopic characterisation of subsurface water and
53
54
55 498 the associated mixing processes facilitate tracing water flow sources (e.g. rainfall recharge

1
2
3
4 499 and exchange between high and low permeable sites/layers). This understanding can inform
5
6 500 hydrological model structures at different scales (e.g. as conceptualized fast and slow flow
7
8
9 501 reservoirs) and their hydrological connectivity (e.g. hillslope-depression-outlet). The inferred
10
11 502 hydrologic characteristics can be then used either independently or combined with direct
12
13
14 503 hydrologic observations to constrain hydrologic properties and reduce uncertainty in
15
16 504 hydrological models (Hinnell et al., 2010).

19 505 **4.2 Conclusions**

21 506 Understanding the function of the water cycle is a key issue for critical zone science
22
23
24 507 since water is a unifying theme for understanding complex environmental systems (Lin, 2010).
25
26 508 Nevertheless, it is a significant challenge to identify active subsurface processes that
27
28
29 509 determine water flows and travel times. In this study, geophysical, hydrometric and tracer
30
31
32 510 tools are used to characterize the hydrological function of the cockpit karst critical zone in the
33
34 511 small catchment of Chenqi, Guizhou province, China. The ERT surveys (Fig 2) identified
35
36
37 512 structural features that likely control aquifer permeability and the heterogeneity in observed
38
39 513 hydrodynamic response. Hydrometric observations and using water temperatures (Figs 2 and
40
41
42 514 3) as a tracer clearly identified rainfall recharge and flow recession induced by new rainwater
43
44 515 recharge and the constraints of aquifer permeability. Stable water isotopes (δD and $\delta^{18}O$) (Fig
45
46
47 516 5) largely corroborated geophysical, hydrometric and thermal data and provided detail
48
49 517 qualitative insight into event water recharge into, and pre-event storage release from, the
50
51
52 518 heterogeneous aquifer. In particular, this information can help identify flow paths of new

1
2
3
4 519 event water recharging through high permeability zones in both horizontal and vertical
5
6 520 directions in the catchment.
7

8
9 521 The study illustrated that even in a highly heterogeneous catchment, hydrological functions
10
11 522 can be conceptualized simply into fast and slow flow reservoirs. Nevertheless, using such a
12
13 523 dual flow system in simulation of hydrological processes should be based on detail
14
15
16 524 observations at representative sites within a catchment. Particularly, since hydrological
17
18
19 525 functions can vary with depth, observations and water sampling from various permeability
20
21 526 layers are extremely important.
22

23 527 **Acknowledgments**

24
25 528 This research was supported by The UK-China Critical Zone Observatory (CZO)
26
27
28 529 Programme (41571130071), the National Natural Scientific Foundation of China (41571020),
29
30
31 530 National 973 Program of China (2015CB452701), the National Key Research and
32
33 531 development Program of China (2016YFC0502602), the Fundamental Research Funds for the
34
35 532 Central Universities (2016B04814) and the UK Natural Environment Research Council
36
37
38 533 (NE/N007425/1 & NE/N007409/1). We thank the editor and the two anonymous reviewers
39
40
41 534 for their constructive comments on the earlier manuscript, which lead to an improvement of
42
43 535 the paper.
44

45 536

46
47 537
48
49
50
51
52
53
54
55
56
57
58
59
60

REFERENCES

- 538
- 539 Anderson MP. 2005. Heat as a ground water tracer. *Ground Water* 43 (6): 951–968 DOI:
- 540 10.1111/j.1745-6584.2005.00052.x
- 541 Aquilina L, Ladouche B, Dörfli N. 2006. Water storage and transfer in the epikarst of
- 542 karstic systems during high flow periods. *Journal of Hydrology* 327 (3–4): 472–485 DOI:
- 543 10.1016/j.jhydrol.2005.11.054
- 544 Barberá JA, Andreo B. 2012. Functioning of a karst aquifer from S Spain under highly
- 545 variable climate conditions, deduced from hydrochemical records. *Environmental Earth*
- 546 *Sciences* 65 (8): 2337–2349 DOI: 10.1007/s12665-011-1382-4
- 547 Batiot C, Emblanch C, Blavoux B. 2003. Total Organic Carbon (TOC) and magnesium
- 548 (Mg²⁺): two complementary tracers of residence time in karstic systems. *Comptes Rendus*
- 549 *Geoscience* 335 (2): 205–214 DOI: 10.1016/S1361-0713(03)00027-0
- 550 Becker MW, Georgian T, Ambrose H, Siniscalchi J, Fredrick K. 2004. Estimating flow and
- 551 flux of ground water discharge using water temperature and velocity. *Journal of Hydrology*
- 552 296 (1–4): 221–233 DOI: 10.1016/j.jhydrol.2004.03.025
- 553 Binley, A, 2015, Tools and Techniques: DC Electrical Methods, In: *Treatise on Geophysics*,
- 554 2nd Edition, G Schubert (Ed.), Elsevier., Vol. 11, 233-259,
- 555 doi:10.1016/B978-0-444-53802-4.00192-5.
- 556 Binley A, Hubbard SS, Huisman JA, Revil A, Robinson DA, Singha K, Slater LD. 2015. The
- 557 emergence of hydrogeophysics for improved understanding of subsurface processes over

- 1
2
3
4 558 multiple scales, Water Resources Research, 51(6), 3837-3866,
5
6 559 DOI:10.1002/2015WR017016
7
8 560 Biswas H, Sena DR, Kumar G, Lakaria BL, Raizada A, Kumar S, Mishra PK. 2017. Effect of
9
10 561 water storage structures on groundwater recharge in India. Groundwater for Sustainable
11
12 562 Development 4: 49–56 DOI: 10.1016/j.gsd.2017.01.002
13
14 563 Birk S, Wagner T, Mayaud C. 2014. Threshold behavior of karst aquifers: The example of the
15
16 564 Lurbach karst system (Austria). Environmental Earth Sciences 72 (5): 1349–1356 DOI:
17
18 565 [10.1007/s12665-014-3122-z](https://doi.org/10.1007/s12665-014-3122-z)
19
20 566 Carrière SD, Chalikakis K, Sénéchal G, Danquigny C, Emblanch C. 2013. Combining
21
22 567 Electrical Resistivity Tomography and Ground Penetrating Radar to study geological
23
24 568 structuring of karst Unsaturated Zone. Journal of Applied Geophysics 94: 31–41 DOI:
25
26 569 [10.1016/j.jappgeo.2013.03.014](https://doi.org/10.1016/j.jappgeo.2013.03.014)
27
28 570 Chalikakis K, Plagnes V, Guerin R, Valois R, Bosch FP. 2011. Contribution of geophysical
29
30 571 methods to karst-system exploration: An overview. Hydrogeology Journal 19 (6): 1169–
31
32 572 1180 DOI: [10.1007/s10040-011-0746-x](https://doi.org/10.1007/s10040-011-0746-x)
33
34 573 Coplen TB. 1994. Reporting of stable hydrogen, carbon, and oxygen isotopic abundances
35
36 574 (Technical Report). Pure and Applied Chemistry 66 (2): 273–276 DOI:
37
38 575 [10.1351/pac199466020273](https://doi.org/10.1351/pac199466020273).
39
40 576 Covington MD, Luhmann AJ, Gabrovec F, Saar MO, Wicks CM. 2011. Mechanisms of heat
41
42 577 exchange between water and rock in karst conduits. Water Resources Research 47 (10) DOI:
43
44 578 [10.1029/2011WR010683](https://doi.org/10.1029/2011WR010683).
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4 579

5
6 580 Covington MD, Luhmann AJ, Wicks CM, Saar MO. 2012. Process length scales and
7
8 581 longitudinal damping in karst conduits. *Journal of Geophysical Research: Earth Surface* 117
9
10
11 582 (1) DOI: 10.1029/2011JF002212.

12
13 583 Emblanch C, Zuppi GM, Mudry J, Blavoux B, Batiot C. 2003. Carbon 13 of TDIC to quantify
14
15 584 the role of the unsaturated zone: The example of the Vaucluse karst systems (Southeastern
16
17
18 585 France). *Journal of Hydrology* 279 (1–4): 262–274 DOI: 10.1016/S0022-1694(03)00180-X

19
20
21 586 Fan J, Oestergaard KT, Guyot A, Lockington DA. 2014. Estimating groundwater recharge
22
23 587 and evapotranspiration from water table fluctuations under three vegetation covers in a
24
25 588 coastal sandy aquifer of subtropical Australia. *Journal of Hydrology* 519 (PA): 1120–1129
26
27
28 589 DOI: 10.1016/j.jhydrol.2014.08.039

29
30
31 590 Field MS. 1993. Karst Hydrology and Chemical Contamination. *Journal of Environmental*
32
33 591 *Systems* 22 (1): 1–26 DOI: 10.2190/X7MV-C93E-66GK-BFH7

34
35
36 592 Ford D, Williams P. 2013. *Karst Hydrogeology and Geomorphology*. DOI:
37
38 593 10.1002/9781118684986

39
40
41 594 Goldscheider N, Drew D. 2007. *Methods in Karst Hydrogeology*. Taylor & Francis Group,
42
43 595 Leiden, NL.

44
45
46 596 Hartmann A, Goldscheider N, Wagener T, Lange J, Weiler M. 2014. Karst water resources in
47
48 597 a changing world: Approaches, of hydrological modeling. *Review of Geophysics* (1): 1–25
49
50
51 598 DOI: 10.1002/2013RG000443

- 1
2
3
4 599 Healy RW, Cook PG. 2002. Using groundwater levels to estimate recharge. *Hydrogeology*
5
6 600 *Journal* 10 (1): 91–109 DOI: 10.1007/s10040-001-0178-0
7
8
9 601 Hinnell AC, Ferr TPA, Vrugt JA, Huisman JA, Moysey S, Rings J, Kowalsky MB. 2010.
10
11 602 Improved extraction of hydrologic information from geophysical data through coupled
12
13 603 hydrogeophysical inversion. *Water Resources Research* 46 (4) DOI:
14
15 604 10.1029/2008WR007060.
16
17
18 605 Hu K, Chen H, Nie Y, Wang K. 2015. Seasonal recharge and mean residence times of soil
19
20 606 and epikarst water in a small karst catchment of southwest China. *Scientific Reports* 5 DOI:
21
22 607 10.1038/srep10215.
23
24
25 608 Hubbard SS, Rubin Y, Majer E. 1999. Spatial correlation structure estimation using
26
27 609 geophysical and hydrogeological data. *Water Resources Research* 35 (6): 1809–1825 DOI:
28
29 610 10.1029/1999WR900040.
30
31
32 611 Hyman JD, Painter SL, Viswanathan H, Makedonska N, Karra S. 2015. Influence of injection
33
34 612 mode on transport properties in kilometer-scale three-dimensional discrete fracture networks.
35
36 613 *Water Resources Research* 51 (9): 7289–7308 DOI: 10.1002/2015WR017151.
37
38
39 614 Irvine DJ, Cranswick RH, Simmons CT, Shanafield MA, Lutz LK. 2015. The effect of
40
41 615 streambed heterogeneity on groundwater-surface water exchange fluxes inferred from
42
43 616 temperature time series. *Water Resources Research* 51 (1): 198–212 DOI:
44
45 617 10.1002/2014WR015769
46
47
48 618 Jeannin PY, Sauter M. 1998. Analysis of karst hydrodynamic behaviour using global
49
50 619 approaches: A review. *Bull/d’Hydrogéologie* 16: 31–48.
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4 620 Jiang G, Guo F, Wu J, Li H, Sun H. 2008. The threshold value of epikarst runoff in forest
5
6 621 karst mountain area. *Environmental Geology* 55 (1): 87–93 DOI:
7
8 622 10.1007/s00254-007-0967-4.
9
10
11 623 Kovács A, Sauter M. 2007. Modelling karst hydrodynamics. In: Goldscheider N, Drew D
12
13 624 (eds) *Methods in karst hydrogeology*, vol 26. International Contribution to Hydrogeology,
14
15 625 Heise, Hanover, Germany, pp 201–220
16
17
18 626 Lee LJE, Lawrence DSL, Price M. 2006. Analysis of water-level response to rainfall and
19
20 627 implications for recharge pathways in the Chalk aquifer, SE England. *Journal of Hydrology*
21
22 628 330 (3–4): 604–620 DOI: 10.1016/j.jhydrol.2006.04.025
23
24
25
26 629 Lin H. 2010. Earth's Critical Zone and hydrogeology: concepts, characteristics, and
27
28 630 advances. *Hydrol. Earth Syst. Sci.*, 14, 25–45
29
30
31 631 Long JCS, Remer JS, Wilson CR, Witherspoon PA. 1982. Porous media equivalents for
32
33 632 networks of discontinuous fractures. *Water Resources Research* 18 (3): 645–658 DOI:
34
35 633 10.1029/WR018i003p00645.
36
37
38
39 634 Long AJ, Putnam LD. 2004. Linear model describing three components of flow in karst
40
41 635 aquifers using 18O data. *Journal of Hydrology* 296 (1–4): 254–270 DOI:
42
43 636 10.1016/j.jhydrol.2004.03.023
44
45
46
47 637 Lowry CS, Walker JF, Hunt RJ, Anderson MP. 2007. Identifying spatial variability of
48
49 638 groundwater discharge in a wetland stream using a distributed temperature sensor. *Water*
50
51 639 *Resources Research* 43 (10) DOI: 10.1029/2007WR006145
52
53
54
55
56
57
58
59
60

- 1
2
3
4 640 Luhmann AJ, Covington MD, Alexander SC, Chai SY, Schwartz BF, Groten JT, Alexander
5
6 641 EC. 2012. Comparing conservative and nonconservative tracers in karst and using them to
7
8 642 estimate flow path geometry. *Journal of Hydrology* 448–449: 201–211 DOI:
9
10 643 10.1016/j.jhydrol.2012.04.044.
11
12
13 644 Luhmann AJ, Covington MD, Myre JM, Perne M, Jones SW, Alexander EC, Saar MO. 2015.
14
15 645 Thermal damping and retardation in karst conduits. *Hydrology and Earth System Sciences*
16
17 646 19 (1): 137–157 DOI: 10.5194/hess-19-137-2015.
18
19
20
21 647 Martínez-Moreno FJ, Galindo-Zaldívar J, Pedrera A, Teixido
22
23 648 T, Ruano P, Peña JA, González-Castillo L, Ruiz-Constán A, López-Chicano M,
24
25 649 Martín-Rosales W. 2014. Integrated geophysical methods for studying the karst system of
26
27 650 Gruta de las Maravillas (Aracena, Southwest Spain). *Journal of Applied Geophysics* 107:
28
29 651 149–162 DOI: 10.1016/j.jappgeo.2014.05.021
30
31
32
33 652 Mudarra M, Andreo B, Marín AI, Vadillo I, Barberá JA. 2014. Combined use of natural and
34
35 653 artificial tracers to determine the hydrogeological functioning of a karst aquifer: the
36
37 654 Villanueva del Rosario system (Andalusia, southern Spain). *Hydrogeology Journal* 22 (5):
38
39 655 1027–1039 DOI: 10.1007/s10040-014-1117-1
40
41
42
43 656 Mudarra M, Andreo B. 2011. Relative importance of the saturated and the unsaturated zones
44
45 657 in the hydrogeological functioning of karst aquifers: The case of Alta Cadena (Southern
46
47 658 Spain). *Journal of Hydrology* 397 (3–4): 263–280 DOI: 10.1016/j.jhydrol.2010.12.005
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4 659 Niswonger RG, Prudic DE, Pohl G, Constantz J. 2005. Incorporating seepage losses into the
5
6 660 unsteady streamflow equations for simulating intermittent flow along mountain front streams.
7
8 661 Water Resources Research 41 (6): 1–16 DOI: 10.1029/2004WR003677.
9
10
11 662 Perrin J, Jeannin PY, Zwahlen F. 2003. Epikarst storage in a karst aquifer: A conceptual
12
13 663 model based on isotopic data, Milandre test site, Switzerland. Journal of Hydrology 279 (1–
14
15 664 4): 106–124 DOI: 10.1016/S0022-1694(03)00171-9.
16
17
18 665 Plummer LN, Busenberg E, McConnell JB, Drenkard S, Schlosser P, Michel RL. 1998. Flow
19
20 666 of river water into a Karstic limestone aquifer. 1. Tracing the young fraction in groundwater
21
22 667 mixtures in the Upper Floridan Aquifer near Valdosta, Georgia. Applied Geochemistry 13
23
24 668 (8): 995–1015 DOI: 10.1016/S0883-2927(98)00031-6
25
26
27 669 Rau GC, Andersen MS, McCallum AM, Acworth RI. 2010. Analytical methods that use
28
29 670 natural heat as a tracer to quantify surface water-groundwater exchange, evaluated using
30
31 671 field temperature records. Hydrogeology Journal 18 (5): 1093–1110 DOI:
32
33 672 10.1007/s10040-010-0586-0
34
35
36 673 Rau GC, Andersen MS, McCallum AM, Roshan H, Acworth RI. 2014. Heat as a tracer to
37
38 674 quantify water flow in near-surface sediments. Earth-Science Reviews 129: 40–58 DOI:
39
40 675 10.1016/j.earscirev.2013.10.015
41
42
43 676 Sophocleous M. 2002. Interactions between groundwater and surface water: The state of the
44
45 677 science. Hydrogeology Journal 10 (1): 52–67 DOI: 10.1007/s10040-001-0170-8
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4 678 Sophocleous MA. 1991. Combining the soilwater balance and water-level fluctuation
5
6 679 methods to estimate natural groundwater recharge: Practical aspects. *Journal of Hydrology*
7
8 680 124 (3–4): 229–241 DOI: 10.1016/0022-1694(91)90016-B
9
10
11 681 Soulsby C, Bradford J, Dick J, McNamara JP, Geris J, Lessels J, Blumstock M, Tetzlaff D.
12
13 682 2016. Using geophysical surveys to test tracer-based storage estimates in headwater
14
15 683 catchments. *Hydrological Processes* 30 (23): 4434–4445 DOI: 10.1002/hyp.10889
16
17
18 684 Sprenger M, Tetzlaff D, Soulsby C. 2017. Soil water stable isotopes reveal evaporation
19
20 685 dynamics at the soil-plant-atmosphere interface of the critical zone. *Hydrology and Earth*
21
22 686 *System Sciences* 21 (7): 3839–3856 DOI: 10.5194/hess-21-3839-2017
23
24
25 687 Sprenger M, Tetzlaff D, Buttle JM, Snelgrove J, Laudon H, Mitchell C, Weiler M, Soulsby C.
26
27 688 2018. Measuring and modelling stable isotopes of mobile and bulk soil water. *Vadose Zone*
28
29 689 *Journal*. DOI: 10.2136/vzj2017.08.0149.
30
31
32 690 Sun Z, Ma R, Wang Y, Ma T, Liu Y. 2016. Using isotopic, hydrogeochemical-tracer and
33
34 691 temperature data to characterize recharge and flow paths in a complex karst groundwater
35
36 692 flow system in northern China. *Hydrogeology Journal* 24 (6): 1393–1412 DOI:
37
38 693 10.1007/s10040-016-1390-2
39
40
41 694 Winter TC. 1999. Relation of streams, lakes, and wetlands to groundwater flow systems.
42
43 695 *Hydrogeology Journal* 7 (1): 28–45 DOI: 10.1007/s100400050178
44
45
46 696 Xie Z, Yuan X. 2010. Prediction of water table under stream-aquifer interactions over an arid
47
48 697 region. *Hydrological Processes* 24 (2): 160–169 DOI: 10.1002/hyp.7434
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4 698 Williams PW. 1983. The role of the subcutaneous zone in karst hydrology. *Journal of*
5
6 699 *Hydrology* 61 (1–3): 45–67 DOI: 10.1016/0022-1694(83)90234-2.
7
8
9 700 Worthington SRH, Jeannin P-Y, Alexander EC, Davies GJ, Schindel GM. 2017. Contrasting
10
11 701 definitions for the term ‘karst aquifer’. *Hydrogeology Journal* 25 (5): 1237–1240 DOI:
12
13 702 10.1007/s10040-017-1628-7.
14
15
16 703 Zhang Z, Chen X, Chen X, Shi P. 2013. Quantifying time lag of epikarst-spring hydrograph
17
18 704 response to rainfall using correlation and spectral analyses. *Hydrogeology Journal* 21 (7):
19
20 705 1619–1631 DOI: 10.1007/s10040-013-1041-9.
21
22
23
24 706 Zhang Z, Chen X, Soulsby C. 2017. Catchment-scale conceptual modelling of water and
25
26 707 solute transport in the dual flow system of the karst critical zone. *Hydrological Processes* 31
27
28 708 (19): 3421–3436 DOI: 10.1002/hyp.11268
29
30
31
32 709

Table 1 Statistical summary of water level and flow discharge

	Water Level (m)				Flow discharge (m ³ /s)	
	W1	W3	W4	W5	Hillslope	Outlet
Min	1267.4	1272.6	1280.0	1276.4	0	0
Max	1275.9	1279.9	1285.2	1284.0	1.4×10^{-3}	0.15
Range	8.5	7.3	5.2	7.6	1.4×10^{-3}	0.15
Mean	1273.6	1275.9	1281.8	1278.9	8.5×10^{-5}	4.7×10^{-3}
Cv	0.03	0.21	0.61	0.07	1.73	2.83

Table 2 Statistical summary of air and water temperature

	Air	W1	W3	W4	W5	Hillslope	Outlet
T_{\min} °C	0	17.2	16.4	16.1	16.8	8.8	14.1
T_{\max} °C	35.6	17.5	22	19.6	17.5	21.1	21.3
Range	35.6	0.3	5.6	3.5	0.7	12.3	7.2
T_{mean} °C	16.8	17.3	17.9	17.3	17.1	16.8	17.1
Cv	0.421	0.004	0.026	0.036	0.012	0.16	0.08

Table 3 Statistical summary of isotope data for rainfall, hillslope spring (HS), catchment outlet and depression wells

Obs	Period	δD (‰)					$\delta^{18}O$ (‰)				
		Max	Min	Range	Cv	Mean	Max	Min	Range	Cv	Mean
Rainfall	12/6~13/8	-17.9	-120.2	-102.3	-0.30	-73.2	0	-16.4	-16.4	-0.29	-9.9
outlet	12/6~14/8	-46.9	-73.1	-26.2	-0.06	-61.9	-5.1	-10.6	-5.5	-0.09	-8.7
HS	12/6~14/8	-51.8	-77	-25.2	-0.04	-64.3	-5.9	-10.8	-4.9	-0.06	-9.3
W1	6/7~20/8	-50.7	-65.7	-15	-0.03	-60.8	-6.3	-9.6	-3.3	-0.05	-8.7
W3	6/7~20/8	-56.1	-73.6	-17.5	-0.06	-62.4	-7.4	-10	-2.6	-0.06	-8.7
W4	6/7~20/8	-55	-70.2	-15.2	-0.07	-62.5	-7.9	-10.1	-2.2	-0.07	-8.9
W5	6/7~20/8	-55.7	-67.5	-11.8	-0.03	-58.7	-7.9	-10.1	-2.2	-0.04	-8.5

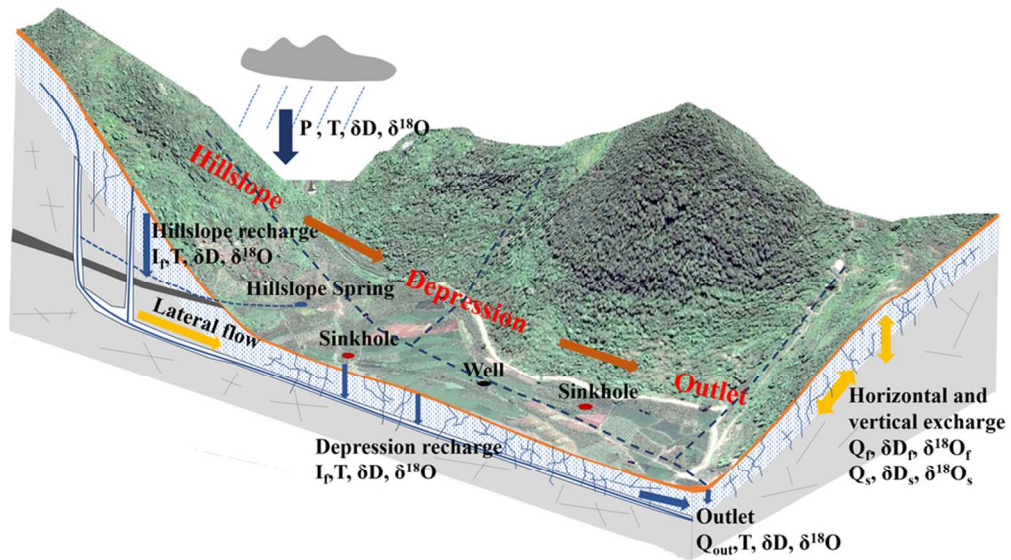


Figure 1 Sketch map of karst hydrological processes.

43x24mm (600 x 600 DPI)

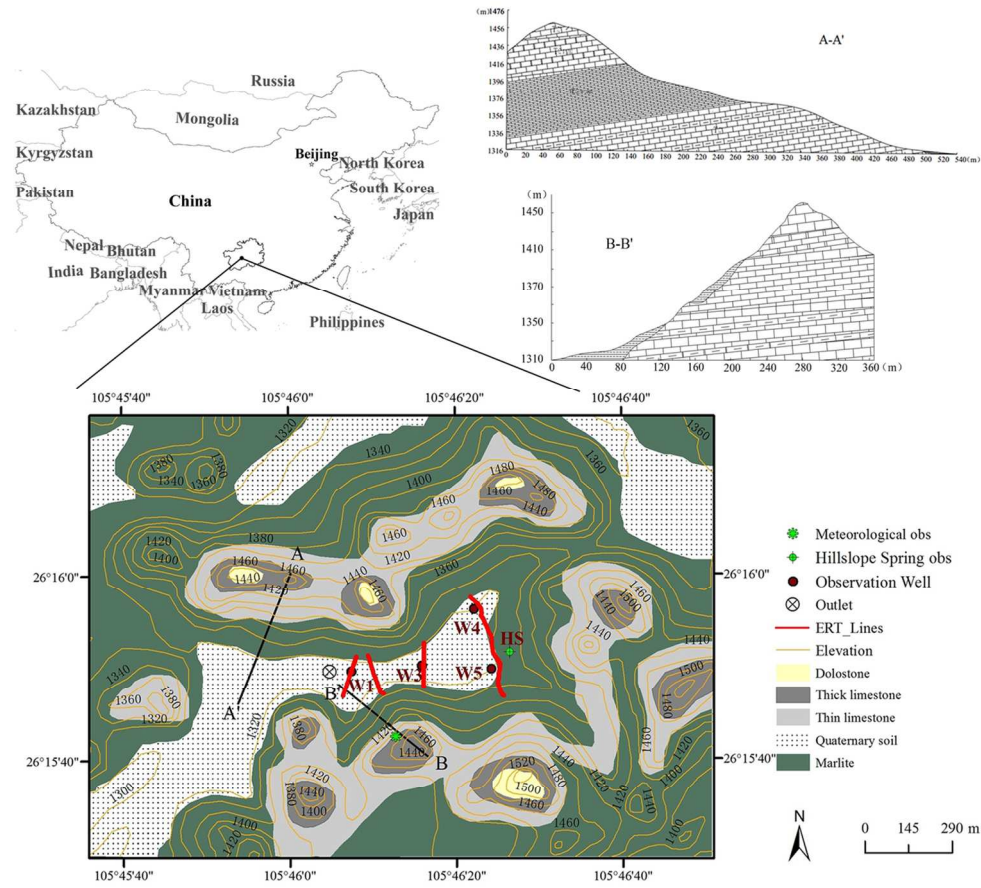


Figure 2 Map of geomorphology and hydrological monitoring locations in the Chenqi catchment.

59x53mm (600 x 600 DPI)



1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

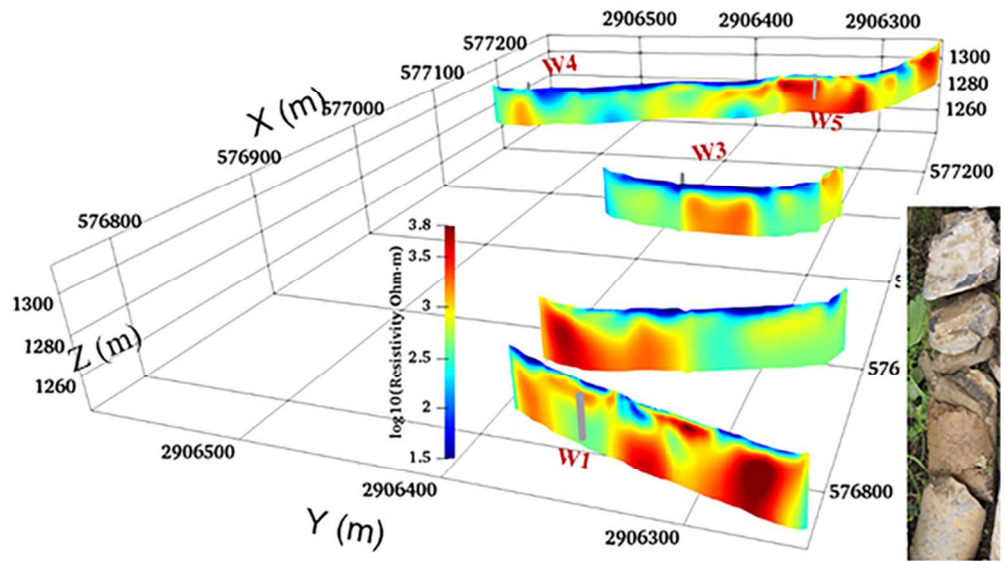


Figure 3 ERT image in the study depression corresponding to the survey profiles in Fig 1.

37x21mm (600 x 600 DPI)

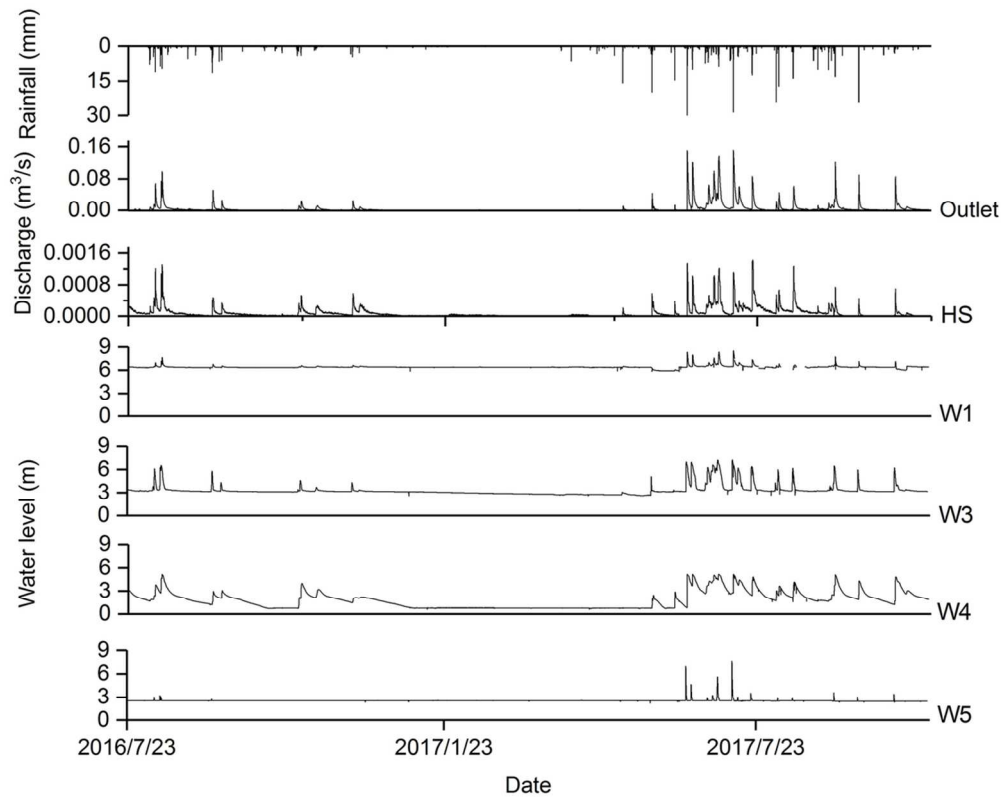


Figure 4 Variations of flow discharge for hillslope spring (HS) and catchment outlet and water levels at depression wells (W1, W3, W4 and W5).

52x41mm (600 x 600 DPI)

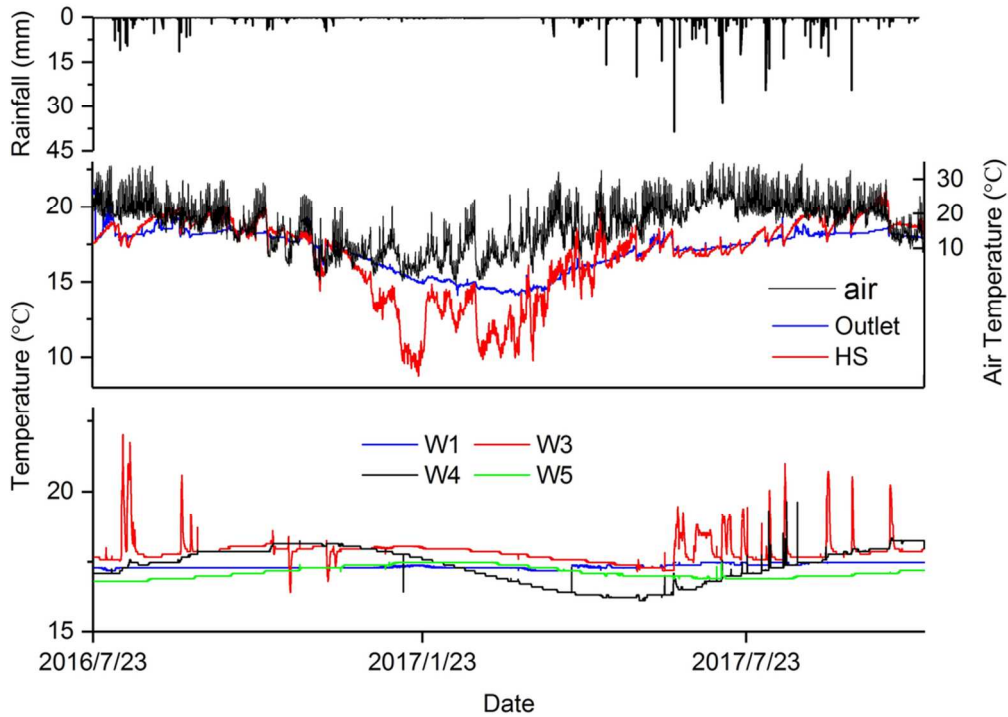


Figure 5 Variations of air temperature and water temperatures for hillslope spring (HS), outlet discharge and depression wells (W1, W3, W4 and W5).

46x33mm (600 x 600 DPI)

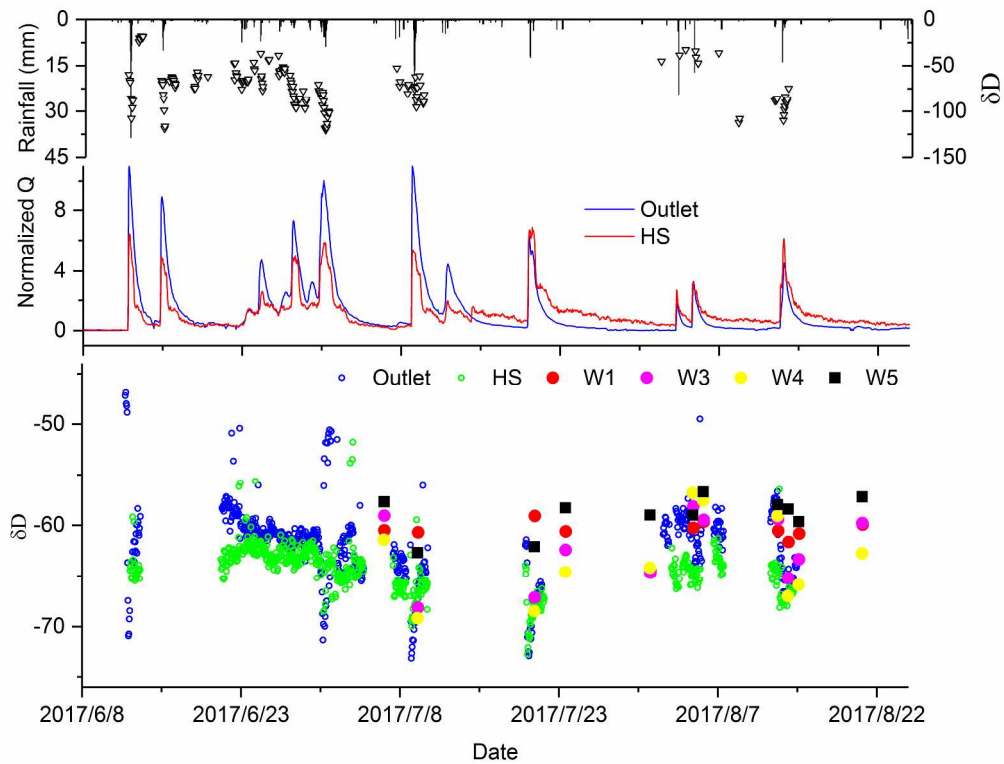


Figure 6 Variation of the δD values for rainfall, hillslope spring (HS), catchment outlet and depression wells.

148x113mm (600 x 600 DPI)

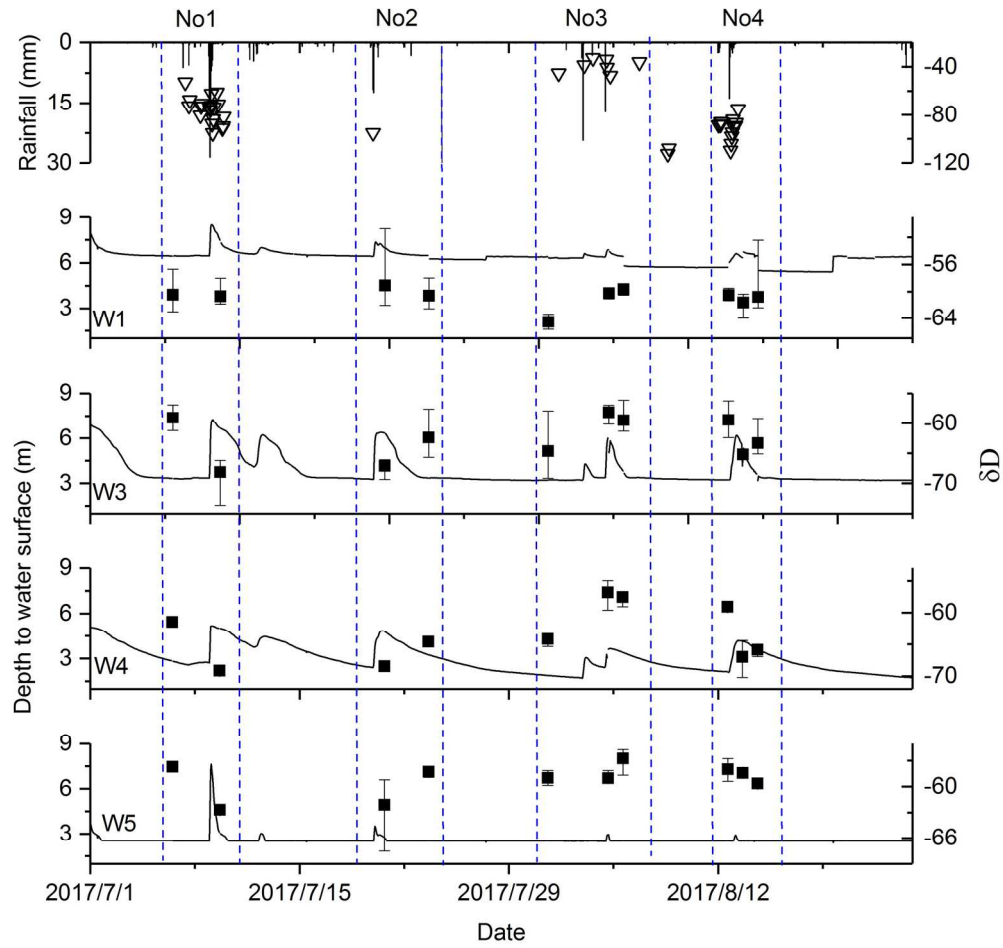
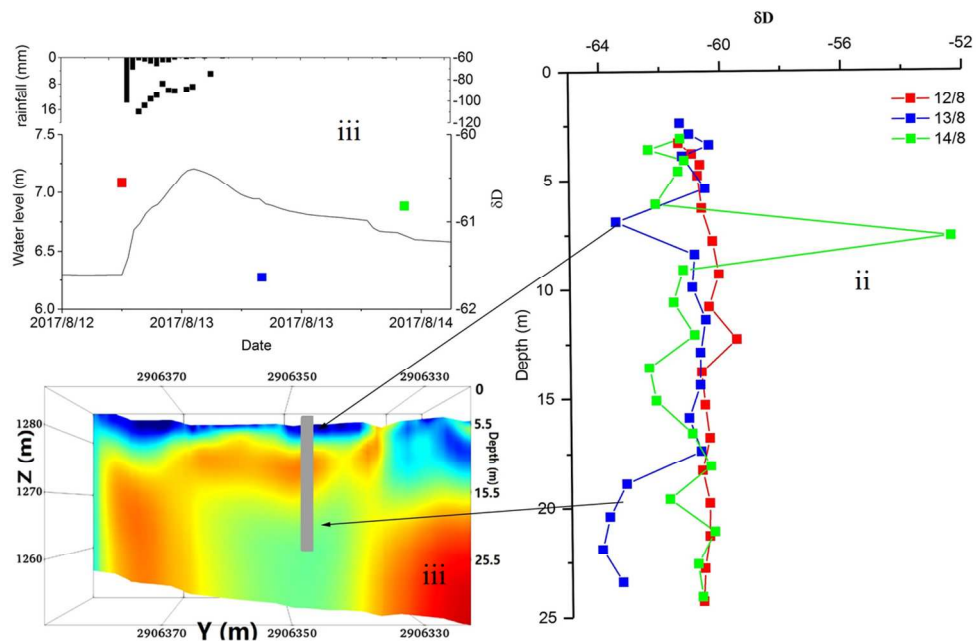


Figure 7 Variability of the δD values for depression wells (the bar represents range of δD values along various depths to water surface; black block represents its mean value; solid line represents depth to water table).

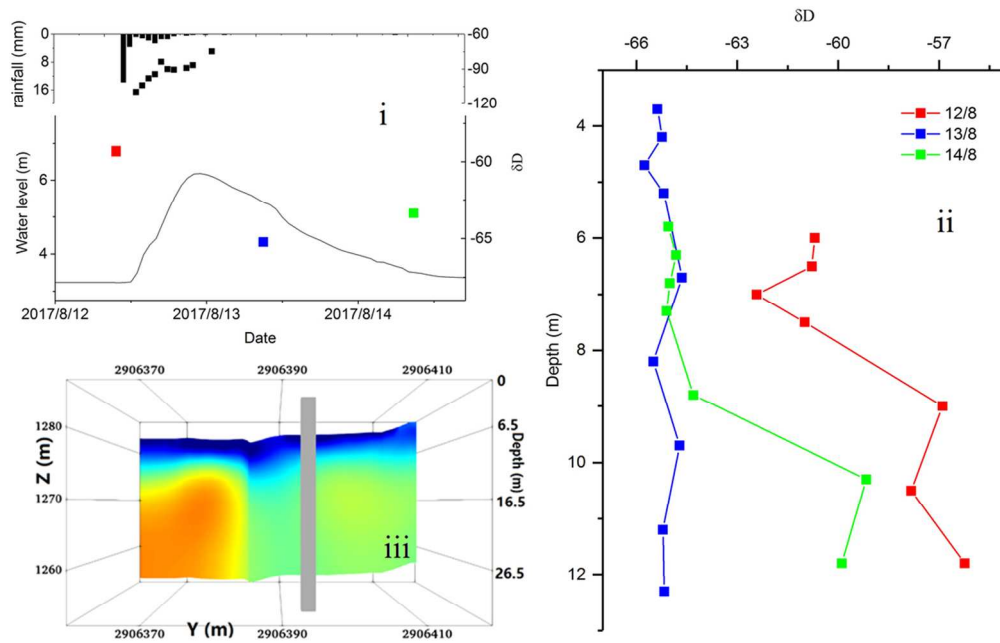
85x80mm (600 x 600 DPI)



(a)

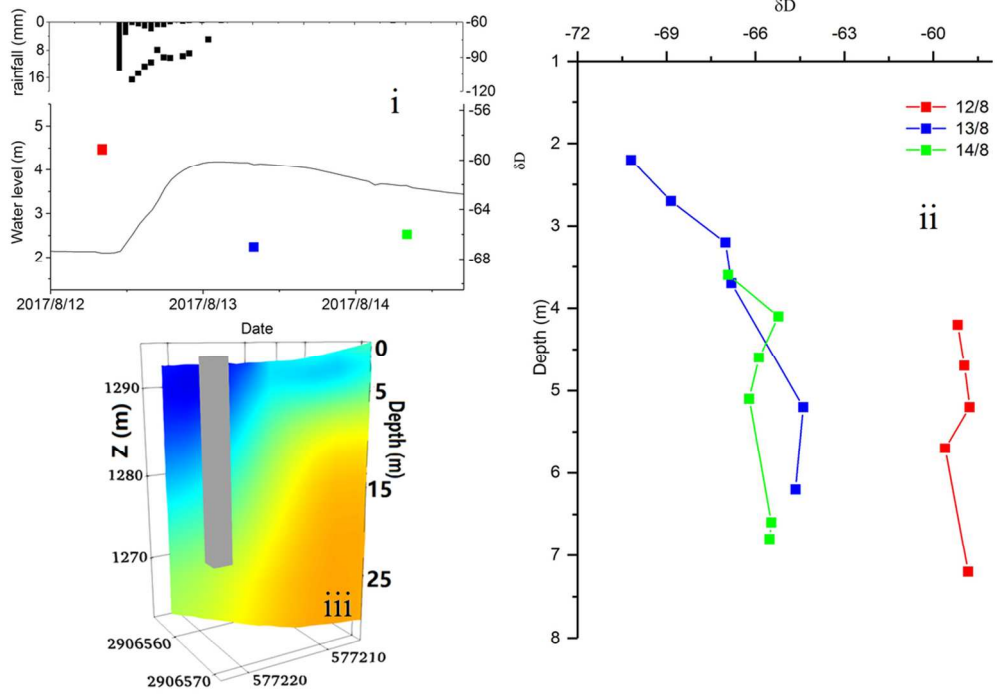
54x35mm (600 x 600 DPI)

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60



(b)

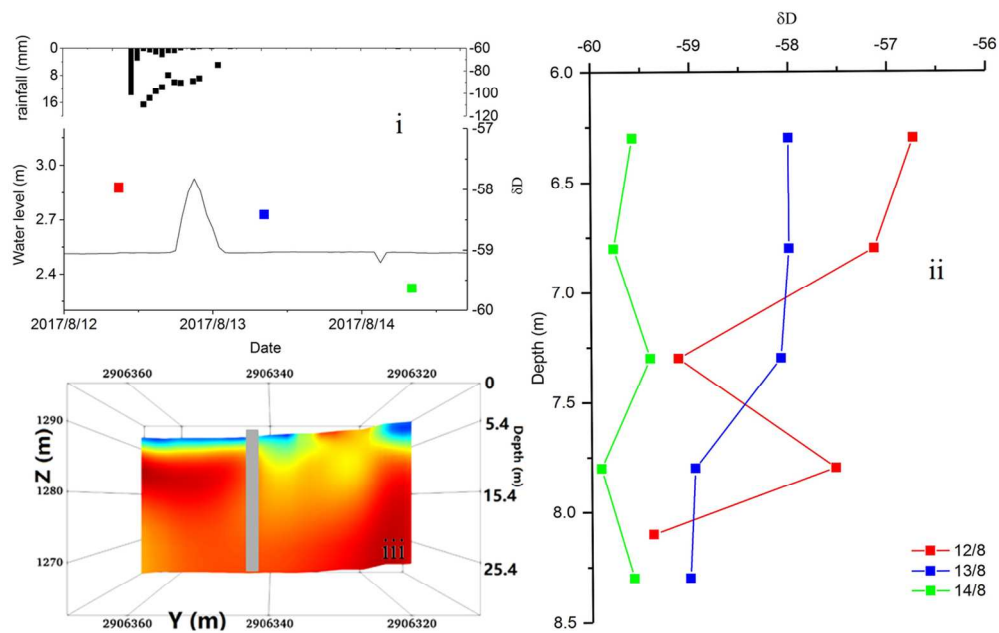
52x36mm (600 x 600 DPI)



(c)

51x39mm (600 x 600 DPI)

view



(d)

Figure 8 Variability of rainfall, water level and δD values (i), vertical distribution of groundwater δD values (ii) and ERT image (iii) of W1 (a), W3 (b), W4(c) and W5(d). The colour dots in the (i) plots are the mean δD value of different depths.

58x40mm (600 x 600 DPI)

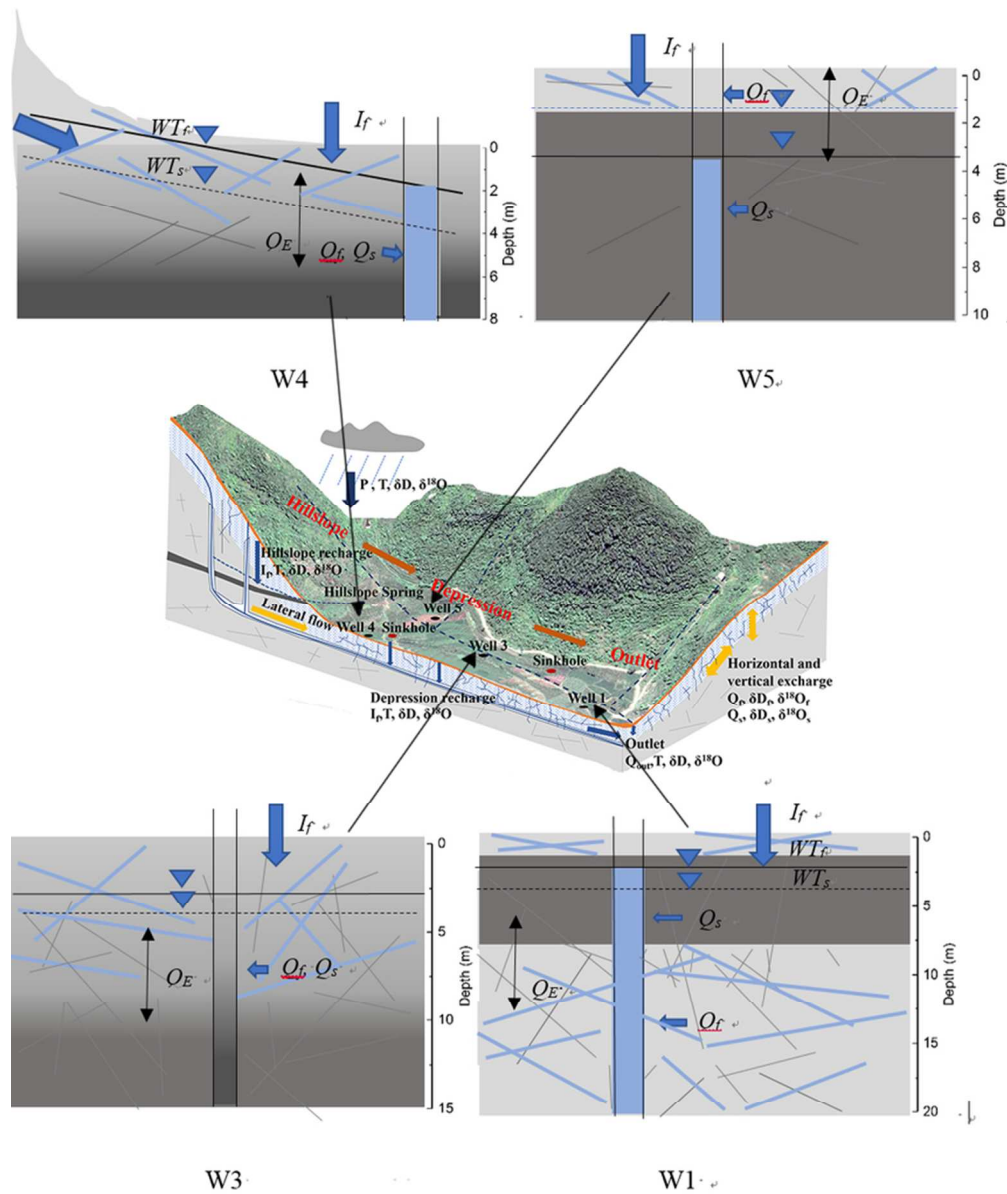


Figure 9 Conceptual model of groundwater aquifer at depression wells of W1, W3, W4 and W5. The high permeability layers in the grey color areas and low permeability layers in the deep grey color areas. WT_f on solid lines is water table of fast flow reservoir, WT_s on dotted lines is water table of slow flow reservoir, Q_E is exchange flow between fast (Q_f) and slow flow (Q_s) reservoirs and I_f is rainfall recharge.

36x43mm (600 x 600 DPI)