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Geographical detection of groundwater pollution vulnerability and

2 hazard in karst areas of Guangxi Province, China

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Abstract: Groundwater pollution is a critical concern in karst areas. This study used 13 the PLEIK (P: protective cover; L: land use; E: epikarst development; I: infiltration 14 conditions; K: karst development) method to assess the vulnerability of groundwater 15 pollution in Guangxi Province, which is the largest karst area in China. The pollution 16 sources and attenuation consist of groundwater pollution hazards. The attributions for 17 the vulnerability and hazard were measured using the geodetector method from 18 geographical information system in Luzhai County in Guangxi. The results confirmed 19 that the vulnerability of groundwater pollution was higher in karst areas than in non-20 karst areas. In Guangxi, 36.35% of the groundwater samples were polluted. A total of 21 49.73% of the areas in Luzhai County contained hazardous levels of pollution. The 22 risk assessment map, which interacted with the vulnerability and hazards, was 58.2% 23 similar to the groundwater pollution distribution. The influence of the hazard on 24 groundwater pollution was 2.6 times that of the vulnerability. It is crucial to control 25 pollution sources to prevent groundwater pollution. 26

27

28 Main finding:

The influence of the hazard on groundwater pollution was 2.6 times that of the vulnerability in the karst areas of Guangxi Province, China.

31

Keywords: PLEIK; Geodetector; covered karst area; vulnerability assessment;
hazard assessment

34 **1 Introduction**

Karst is a specific type of terrain that develops over limestone and dolomite due to 35 the dissolution of carbonate rocks from erosion and subsequent physicochemical 36 processes (Zwahlen et al., 2004; Darnault, 2008). The soil layers of karst areas in 37 southwest China are thin with a surface-ground bilayer structure, which makes it easy 38 for pollutants to enter aquifers through the weak overlying strata and sinkholes (Li et 39 al., 2018). Once contaminated, karst groundwater resources are difficult to salvage 40 without expending significant efforts and costs (Zwahlen et al., 2004; Wang et al., 41 2012; Guo et al., 2007). Groundwater contamination in karst areas has become an 42 increasingly critical issue. Intrinsic vulnerability, hazard and risk assessments are 43 crucial tools to ensuring groundwater protection (Wang et al., 2012; Zhang et al., 44 2016). 45

The intrinsic vulnerability of groundwater is determined by the geological and 46 hydrogeological characteristics of an area. Intrinsic vulnerability is, however, 47 independent of the contaminants' nature and scenario (Zwahlen et al., 2004). Because 48 the karst groundwater system has a complicated structure, diverse types of karst areas 49 have different hydrological characteristics (Zou et al., 2014). One of the most widely 50 used intrinsic vulnerability models is DRASTIC, which is a generic model built by the 51 US EPA that incorporates various physical components of both aquifers and the 52 overlying substrate (Beynen et al., 2012). The DRASTIC method has some limitations 53 when applied to karstic aquifers due to the surface-ground bilayer structure in karst 54 areas (Polemio et al., 2009). Because the conduit network and the connected joints 55 and fractures divide a more compact zone of limestone in karst areas, the EPIK 56 method was developed for karst aquifers by taking the karst network into 57 consideration (Hamdan et al., 2016). European approaches for the protection of karst 58 groundwater were developed in the COST Action 620 project, where the COP method 59 first assessed the vulnerability of karst regions based on an origin-pathway-target 60 model (Entezari et al., 2016). The EPIK model can be applied to the bare karst area in 61 South China, which has a rich karst surface zone and network, whereas the COP 62

model better suits North China's shallow buried karst area with a weak karst surface
zone (Zou et al., 2014). The PLEIK model was the best fit for examining the covered
karst in China because it highlighted protective cover and land use patterns (Zou et
al., 2014; Wen et al., 2016; Dai et al., 2015).

Hazard assessment quantifies the potential degree of harmfulness for each type of 67 hazard and is determined using the toxicity and quantity of dangerous substances 68 (Zwahlen et al., 2004). There are three methods for such an assessment. First is the 69 70 spatial analysis of the positions and types of pollution, including those from overlying and buffer sources (Li et al., 2018; Kazakis et al., 2015). Alternatively, the weighted 71 sum model accounts for the different parameters of pollution sources, including land 72 use, pollutant amounts, toxicity, and mobility (Bai et al., 2012; Zhang et al., 2016). 73 Finally, the product model takes not only the attributes of pollution sources into 74 consideration but also their attenuation, infiltration, technical status, and control 75 policy (Li et al., 2017; Andreo et al., 2006; Shrestha et al., 2016; Wang et al., 2012). 76 The parameters of each method are adjustable according to the available data. 77

78 As vulnerability and hazard assessment methods become more widely used, doubts have increased regarding their applicability, accuracy, and reliability (Wang et 79 al., 2012; Iva'n et al., 2017). Few researchers have validated assessment results. 80 Shrestha et al. (2016) used Pearson's r correlation coefficient to perform a statistical 81 comparison of the vulnerability and risk using an observed nitrate level. The results 82 indicated that the correlation coefficient is positive for risk and negative for 83 vulnerability. Cui et al. (2016) contrasted the pollution risk and distribution maps 84 qualitatively, which displayed a coherent distribution. Li et al. (2017) identified 85 inconsistencies in the relationship between the risk map and organic contamination. 86 However, the explanatory power of the vulnerability and pollutant sources for 87 groundwater pollutant concentration is still relatively unexplored. 88

In this study, the PLEIK method was used to assess the vulnerability of covered karst areas in southwestern China. We evaluated the hazard map of pollutant sources using the geostatistical method from geographical information science. Utilizing the CCME WQI method (Wang et al. 2018), we then evaluated the groundwater pollutant

93 classes based on the field sampling. Finally, the geographical detector method (Wang 94 et al. 2010) was used to quantitatively evaluate the relationships between the 95 groundwater pollution classes, the vulnerability, and the hazard. The results revealed 96 the explanatory power of the vulnerability, the hazard, and their interactions 97 concerning groundwater pollution, which should greatly aid groundwater protection 98 and management efforts.

99

2 Material and Methods

101 **2.1 Study area**

Guangxi Province lies in southern China and occupies a total area of 236.7 102 thousand square kilometres. It spans from 20.90° N to 26.38° N in latitude and 103 104.47° E to 112.07° E in longitude under a subtropical monsoon climate (Figure 1). 104 In Guangxi, there are large areas of well-developed tropical karst landscape from the 105 northeast to the southwest. The aquifer rock formations are divided into five 106 categories, including loose rock formations, pure carbonate rock formations, impure 107 carbonate rock formations, clastic rock formations, and intrusive rock formations. 108 Correspondingly, the types of groundwater in Guangxi contain pore water in loose 109 rock, pore water in clastic rock, fissure-cavern water, and bedrock fissure water. The 110 main source of groundwater is precipitation; however, other sources exist, including 111 the river water supply, irrigation sources, and other miscellaneous water sources in the 112 karst area. Groundwater in Guangxi is shallow freshwater and is mainly used in 113 industrial and agricultural production as well as domestic drinking water. Therefore, it 114 115 is crucial to protect groundwater from pollution.

116

117 **2.2 Data**

There were a total of 1029 field samples that were used to evaluate the groundwater pollution in Guangxi Province (Figure 1). The analysis indexes had 30 items, including 8 inorganic indicators (NH4+, As, Cd, Cr6+, Pb, Hg, NO2- and NO3-), 2 organic indicators (trichloromethane and tetrachloromethane), 16 volatile

indicators (1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, 122 1.2dichloroethane, 1,1,2-trichloroethane, 1,2-dichloropropane, tribromomethane, 123 chloroethylene, 1,1-dichloroethylene, chlorobenzene, o-dichlorobenzene, 124 pdichlorobenzene, methylbenzene, ethylbenzene, xylene and styrene) and 4 semi-125 volatile indicators (BHC, y-BHC, DDT and HCB). These samples covered all 126 hydrogeological units in the study area, which controlled the main underground rivers 127 and karst springs in the basin. 128



129 130

Fig. 1. Study area and field sample distribution

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132 **2.3 Methods**

133 **2.3.1 PLEIK**

The vulnerability of covered karst areas were assessed using five factors:
protective cover (P), land use (L), epikarst development (E), infiltration conditions (I)
and karst development (K).

P encompasses all geotechnical layers above the groundwater table, including theoverlying non-karst strata and karst strata above the groundwater table. In karst areas,

P has a significant defensive effect against pollution. Once pollutants get through the 139 protective cover, they quickly and heavily contaminate the groundwater. One of the 140 most important parameters for the protective cover is the soil thickness. The thinner 141 the protective cover's soil, the more vulnerable the covered karst area becomes. The 142 soil thickness was divided into four categories (Table 1). Another crucial attribute of 143 the protective cover is the degradation ability of the soil. The stronger the degradation 144 ability is, the lower the vulnerability. The cation exchange capacity (CEC) was 145 selected as a proxy to reflect the protective cover's degradation ability. The soil 146 thickness and CEC were connected to quantify the protective cover's effectiveness 147 using a rating matrix (Table 1). 148

L incorporates the impacts of human activities on covered karst areas into a vulnerability assessment. More human activity leads to higher vulnerability. Land use was divided into six classes and scored (Table 1).

E is located under any consolidated soil (Doerfliger et al., 1999) and has important pondage action for karst water systems. A number of factors—including the lithology, rock structure, and hydrodynamic conditions—can affect its development. More highly developed epikarst contributes to a higher vulnerability rating. Epikarst development can be measured and scored based on its specific type of carbonate rocks (Table 1).

I concerns the recharge type and recharge intensity (RI) of the karst aquifer. The more concentrated the recharge and the larger the intensity, the higher the vulnerability. The recharge type depends on the slope and its vegetation, which we classified into four categories (Table 1). Like the soil thickness and CEC, we also quantified the infiltration conditions using a rating matrix based on the recharge type and intensity (Table 1).

K is a network of solution openings greater than 10 mm in diameter. This size is
the effective minimum aperture for turbulent flow (Doerfliger et al., 1999).
Groundwater runoff moduli can be used to reflect the karst development of an aquifer.
The smaller the modulus, the stronger the karst network development, which results in
a higher vulnerability (Table 1).

169		Т	able 1 Classi	fications a	nd scores of P, L	, E, I, K a	and VI			
	Class	Protective	cover thickn	esses		Score	Score matrix (CEC(meq/100 g))			
		Α	В			<10	10~100	100~200	>200	
	P ₁	0~20 cm	0~2	20 cm		1	3	5	7	
Р	P ₂	20~100 cm	20	~100 cm		2	4	6	8	
	P ₃	100~150 cr	n 10	0 cm		3	5	7	9	
	P ₄	>150 cm	>1	00 cm or r	non-karst strata	4	6	8	10	
	Class	Land use				Score				
	L ₁	Forest				10				
	L ₂	Grass land				8				
L	L ₃	Garden land	d			6				
	L ₄	Farmland				4				
	L ₅	Bare land				2		-		
	L ₆	Urban and	industrial land	1		1				
	Class	Epikarst d	evelopment			Score				
	E ₁	Limestone	continuum			1				
	E ₂	Limestone	with dolomite	•		3				
Ε	E ₃	Limestone	dolomite inter	raction		5				
	E ₄	Impure carl	oonate			7				
	E ₅	Impure and	non-carbona	te interacti	ion	9				
	E ₆	Non-carbor	nate			10				
	Class	Infiltration	conditions			Score	matrix (R	I(mm/d))		
		C (m)	D (m)	Е	F	<9.9	10~	24.9 >2	25	
	I ₁	2000	2000	-	-	4	2	1		
I	I.	2000~4000	2000~4000	>10%	Farmland	- 6	4	3		
-	12			>25%	Grassland	0		5		
	T.	2000~4000	-	<10%	Farmland	- 8	6	5		
	13			<25%	Grassland	0	0	5		
	I_4	The rest of th	e catchment			10	8	7		
	Class	Moduli (L	$\cdot s^{-1} \cdot km^{-2}$)		Score				
	K ₁	<1				1-3				
K	K ₂	1~7				4-5				
	K ₃	7~15				6-8				
	K ₄	>15				9-10				
	Class	Vulnerabil	ity Degree			Score				
	VI ₁	Higher				1-2				
	VI ₂	High				2-4				
VI	VI ₃	Medium				4-6				
	VI ₄	Low				6-8				
	VI ₅	Lower				8-10				

FDI EIV алл 1.1 1 01 · c 1

Notes: A= Soil covered on the limestone; B= Soil covered on low permeability bottom;

C= Sinkhole; D= Subterranean stream; E= Slope; F= Vegetation

The vulnerability index (VI) was generated using the weighted sum of five factors (Eq. (1)).

$$VI = w_1 * P + w_2 * L + w_3 * E + w_4 * I + w_5 * K$$
(1)

P, L, E, I, and K serve as the factors' scores. Lower scores indicate higher vulnerability. $w_1, w_2, w_3, w_4, and w_5$ are the respective weights for each factor, and the fuzzy comprehensive evaluation method determines each weight (Zou et al., 2014). Equation 2 illustrates the final weighted vector.

$$w = (0.29, 0.24, 0.20, 0.16, 0.11)$$
(2)

Each factor's score—and, essentially, the range of VI—fell in the range of 1 to 180 10. The vulnerability was then divided into five classes (Table 1). Lower values 181 correspond to higher vulnerability.

182

183 **2.3.2 CCME WQI**

To evaluate the groundwater, we used the CCME WQI method to integrate the parameters into a single index (Eq. (3)). The index ranges from 0 (worst water quality) to 100 (best water quality) (Wang et al., 2018).

Here, F_1 is the percentage of indicators that do not meet the standard limits at least 188 once, F_2 represents the percentage of field samples that do not meet the standard 189 limits, and F_3 represents the average excess multiple for each sample (Terrado et al., 190 2010; Wang et al., 2018). In this study, the CCME WQI was used to calculate the 191 integrated pollution concentration of the field samples. The pollution samples were 192 defined as those whose monitoring indicators exceeded the national standard of class 193 III for groundwater quality. The standard limits used in the formula were the national 194 standard for groundwater quality of class III (GBT 14848-2017). For the 195 196 classification, the range of categories can be modified for each case study (Terrado et al., 2010). In this study, the CCME WQI values have been divided into five 197 categories: poor (0-44), marginal (44.1-64), fair (64.1-79), good (79.1-99.9) and no 198

199 pollution (100)

200

209

201 **2.3.3 Geographical detector**

The geographical detector method proposed by Wang et al. (2010; 2016; 2017) was used to compare the spatial consistency of the vulnerability, hazard, and risk maps versus the pollution concentrations in field samples. Higher similarity in the spatial distribution increases the reliability of the assessment map. The factor detector can be used to evaluate these similarities (Eq. (4)). If the assessment map can reflect the actual vulnerability and risk, the variance in the samples' pollution within strata is less than that between the strata.

$$q = 1 - \frac{\sum_{h=1}^{L} N_h \sigma_h^2}{N \sigma^2} \tag{4}$$

L represents the number of strata. N_h represents the total number of field samples in stratum h, and N is the total number of field samples in the population. σ_h^2 and σ^2 represent the variances. The value of q is within [0,1]. The larger the value, the stronger the explanatory power of the assessment map.

The natural environment's inherent vulnerability and the hazardous pollution from human activities directly and interactively influence groundwater pollution. The interactive detector can help evaluate the interaction (Table 2). $q(X1 \cap X2)$ represents the interactive explanatory power of the vulnerability and hazard assessment maps on groundwater pollution.

- 219
- 220

Table 2 Interaction relationship	ps for two factors
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Description	Interaction
$q(X1 \cap X2) < Min(q(X1),q(X2))$	Weaken, nonlinear
$Min(q(X1),q(X2)) < q(X1 \cap X2) < Max(q(X1),q(X2))$	Weaken, uni-
$q(X1 \cap X2) > Max(q(X1),q(X2))$	Enhance, bi-
$\mathbf{q}(\mathbf{X1} \cap \mathbf{X2}) = \mathbf{q}(\mathbf{X1}) + \mathbf{q}(\mathbf{X2})$	Independent
$q(X1 \cap X2) > q(X1) + q(X2)$	Enhance, nonlinear

3 Results and Discussion

3.1 Vulnerability assessment

224 Factor P considered the protective cover's permeability, soil thickness, and CEC. In the study area, most soil covered the limestone directly, and so the P class was 225 determined by the soil thickness according to Table 1. For coastal areas in southern 226 Guangxi, the soil type was latosol with a thickness of more than 1.5 metres, which 227 228 falls in category P₄. Latosol is also a heavy clay soil with strong adsorption, meaning that the CEC is low—less than 5 meq/100 g. According to Table 1, the P score for 229 these areas is 4. For the southern subtropics in central Guangxi, the soil type was 230 latored soil with a thickness of less than 1.5 metres, which falls in category P₃. The 231 CEC here lies between 5 and 10 meq/100 g, which grants these areas a P score of 3. 232 Red soil with a thickness of less than 1 metre comprises the main soil type in the low 233 hills of central and northern Guangxi and in the southern high altitude areas reaching 234 350 to 800 metres. In mid-mountain zones with an altitude of 800 to 1300 metres, the 235 236 soil type is mountainous yellow soil—also with a thickness of less than 1 metre. The Nanling mountainous region (at an altitude of 1400 to 1800 metres) has a mountain 237 yellow brown soil type with a thickness of less than 1 metre. For the karst area in 238 Guangxi, the soil type is limestone soil, which has a thickness between 0.3 and 0.4 239 metre. Those areas all belong to category P2. The CEC is more than 10 meq/100 g. 240 Therefore, the P score for those areas is 4. There are small areas in the northeast of 241 Guangxi whose soil type is meadow soil, which has a thickness of less than 0.1 metre. 242 They belong to category P1. The CEC is more than 10 meq/100 g. Therefore, the P 243 244 score for the areas is 3. Figure 2(A) shows the final classification for factor P in the study area. 245

Factor L signifies the land use type. Forested regions—which are mainly distributed in the north, east and southwest—cover 116,147 square kilometres, or 48.89%, of the total study area. Farmland takes second place with 42,471 square kilometres, which occupies 17.88% of the total area. Grassland areas cover 28,944 square kilometres, which comprises 12.18% of the study area. Most study areas have

grass lands. Bare land covers 23,518 square kilometres and comprises 9.90% of the total area, and it is most common in the central western areas. Urban and industrial land covers 9097 square kilometres and comprises 3.8% of the total area. Finally, garden land covers 5088 square kilometres and comprises 2.14% of the total area. Figure 2(B) shows the final classification for factor L in the study area.

Factor E considered the type of carbonate rocks. Limestone continuum, limestone 256 with dolomite, and limestone dolomite interaction are classified as pure carbonate 257 rocks, and the impure carbonate interlayer is less than 10% of the total. The E scores 258 were 1, 3 and 5. Impure carbonate and non-carbonate interaction occur in epibolite. 259 The former has an impure carbonate interlayer that is more than 50% of its total and a 260 non-carbonate interlayer that is less than 15% of its total, such as the carbonate rocks 261 with clasolite. The latter has an impure carbonate interlayer that is more than 50% of 262 its total and a non-carbonate interlayer that is more than 30% of its total, such as 263 sandstone, conglomerate and igneous rock. The E scores were 7 and 9. Non-carbonate 264 includes shale and mudstone with scores of 10. Figure 2(C) shows the final 265 266 classification for factor E in the study area.

Factor I considered the recharge type and intensity. The I classes in the study area were divided based on the results in Table 1. The recharge intensity refers to the average rainfall per day. In the study area, precipitation occurs more frequently in the eastern hills towards the windward slopes than in the western basin area on the leeward slopes. According to local weather stations, the average daily rainfall was less than 9.9 mm. In Table 1, the scores of classes I_1 , I_2 , I_3 , and I_4 were 4, 6, 8, and 10, respectively. Figure 2(D) shows the final classification for factor I in the study area.

Factor K considered the groundwater runoff modulus. The modulus in most areas measured between $7\sim 15 \text{ L} \cdot s^{-1} \cdot km^{-2}$, which was less than 1 in the limestone areas. The classes of factor K were divided into K₁, K₂, K₃, and K₄ and the scores were 3, 5, 8 and 10, respectively. Figure 2(E) illustrates the final classification for factor K in the study area.

The VI was generated using a weighted sum of these five factors. The scores ranged between 2 and 10. The vulnerabilities were then divided into four classes

according to Table 1. Figure 2(F) shows the final vulnerability assessment map. As
expected, the vulnerabilities in most areas of Guangxi can be classified as low. The
karst area, however, has high vulnerability, as shown in Figure 2(F).



284 285

Fig. 2. Classifications for the P, L, E, I, and K factors and the vulnerability assessment results.

3.2 Hazard assessment of groundwater pollution

In this study, the pollution sources were collected from 2011 to 2014. The categories of analysis included industrial, mineral, agricultural, and domestic pollution sources. There were a total of 249 pollution sources, including 99 industrial and mineral pollution sources, 46 domestic pollution sources, and 104 agricultural pollution sources. The sources spanned 28 countries but were mostly concentrated in

the northeastern portion of the study area. The pollution sources in other countries were not available. Luzhai County contained 28 pollution sources in total and was selected to assess the hazard (Figure 3).



Buffer analysis in geographical information system was used to evaluate the influence degrees of pollution sources. The influence scopes and intensities were scored according to the types of pollution sources (Table 3). Longer distances from pollution sources lessened the influence degree of the pollution. The scores were added up when more than one pollution source overlapped (Li et al., 2018).

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Table 3 Influence scopes and sco	ores of pollution source	S
Category	Influence scopes	Scores
Industrial and mineral pollution source	0-2000 m	3
	2000-4000 m	2
	4000-6000 m	1
Agricultural pollution source	0-2000 m	5
	2000-4000 m	3
	4000-6000 m	1
Domestic pollution source	0-2000 m	8
	2000-4000 m	5
	4000-6000 m	2

305

The hazard in Luzhai County was assessed using a buffer analysis method. The pollution sources' influence in adjacent countries was also considered. As shown in Figure 4, the hazard was divided into five classes: very low, low, moderate, high, and

very high. Areas out of the buffer zone were defined as no hazard areas. Statistically,
50.23% of areas had no hazard and 42.08% had very low hazard. Other pollution
classes made up less than 10% of the sample. They were 4.64%, 2.18%, 0.54% and
0.33% for the classes of low, moderate, high and very high, respectively. The
pollution degree for Luzhai County was optimistic.



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Fig. 4. Hazard assessment map for study area

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318 **3.3 Integrated groundwater pollution**

Using the CCME WQI method, we combined the different indicators into one index. A total of 30 indicators were integrated, including 8 inorganic regular indexes, 2 organic regular indexes, 16 volatile organic compound non-regular indexes and 4 semi-volatile organic compound non-regular indexes. The groundwater standard of class III was used as the standard limit to evaluate the excess multiple and the pollution degree while considering the pollution type and load simultaneously. Table 4 lists the name of each indicator and their standard limit.

326

2	2	7
Э	2	1

1	Table 4 Indicators and standard limits			
Category	Name	Standard limit		
Inorganic	NH4+	0.05		
(mg/L)	As	0.01		
	Cd	0.005		
	Cr6+	0.05		
	Pb	0.01		

Hg 0.001	
NO2- 1	
NO3- 20	
Trichloromethane 60	ganic
Tetrachloromethane 2	g/L)
1,1,1-Trichloroethane 2000	latile
Trichloroethylene 70	g/L)
Tetrachloroethylene 40	
1,2-Dichloroethane 30	
1,1,2-Trichloroethane 5	
1,2-Dichloropropane 5	
Tribromomethane 100	
Chloroethylene 5	
1,1-Dichloroethylene 30	
Chlorobenzene 300	
o-Dichlorobenzene 1000	
pDichlorobenzene 300	
Methylbenzene 700	
Ethylbenzene 300	
Xylene 500	
Styrene 20	
ile BHC 5	ni-volatile
γ-BHC 2	g/L)
DDT 1	
HCB 1	

328

From a total of 1029 field samples, 374 exceeded the class III groundwater standards. The main pollutant indicators included NH4+, As, Cd, Pb, Hg, NO2-, NO3- and HCB. A total of 306 samples were polluted only by one excessive item, 63 samples were polluted by two items, and there were 5 samples polluted by three items simultaneously. HCB was the highest indicated pollutant and was found in 213 samples. Heavy metal pollution (Hg, Cd, Pb and As) was less, and its components polluted just 2, 2, 12 and 17 samples, respectively.

Figure 5 displays the samples' pollutant classes, which were calculated using the CCME WQI method. A total of 655 samples were not contaminated and comprised 63.65% of the total samples. A total of 309 samples belonged to pollution class IV and were slightly polluted. Fifty-nine samples belonged to pollution class III and were moderately polluted. Four samples belonged to pollution class II and were heavy

- polluted. Only 2 samples belonged to pollution class I and were severely polluted. In
 general, the pollution is less in the study area. The pollutant samples mostly lied in the
- karst area where the vulnerability was high.



344 345

Fig. 5. Classification of the field samples

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347 **3.4 Explanatory power evaluation**

The geodetector method was used to evaluate the explanatory power of the hazard and vulnerability assessment maps for groundwater pollution in Luzhai County. For groundwater pollution that is measured using the CCME WQI, the q values for the hazard and vulnerability assessment maps were 0.378 and 0.144, respectively. The combined value of hazard and vulnerability was 0.582, which is a nonlinear enhancement based on Table 2.

Groundwater pollution was determined both by the aquifer's intrinsic characteristics—which were relatively static—and the existence of potentially polluting activities—which were dynamic and easily controlled (Saidi S. et al., 2010; Saidi S. et al., 2011; Wang et al., 2012). For the polluting activities, various types of pollution sources were selected in the study, including industrial and mineral pollution

sources, domestic pollution sources, and agricultural pollution sources. These 359 pollution sources released different kinds of compounds, which caused the 360 groundwater pollution. For example, industrial and mineral pollution sources typically 361 release heavy metals, such as As, Cd, Cr6+, Pb, and Hg. The domestic pollution 362 sources include NH4+, NO2-, and NO3-. The agricultural pollution sources mainly 363 released organic compounds and heavy metals. Although there might be other 364 compounds released by the pollution sources, which were not assessed in the study, 365 the most important compounds have been included and taken into consideration in the 366 study area. The explanatory power for the hazard and vulnerability assessment maps 367 indicated that hazard influenced groundwater pollution 2.6 times more than 368 vulnerability. Hazard was generated by human activities, while vulnerability reflected 369 the intrinsic attributes of the hydrogeological characteristics (Andreo et al., 2006). 370 These results confirm the importance of controlling human impacts on groundwater 371 protection efforts. 372

On the other hand, the explanatory power also evaluated the effectiveness of the 373 374 hazard and vulnerability assessment maps. The hazard assessment results had a 37.8% similarity with groundwater pollution, whereas the vulnerability assessment results 375 had a 14.4% similarity. With respect to their combined effect, the hazard and 376 vulnerability assessment had a 58.2% similarity with groundwater pollution. The 377 explanatory power was in high contrast to former research (Shrestha et al., 2016). 378 Other studies (Torres et al., 2018; Alfy et al., 2017) have also researched the influence 379 of hydrogeological and anthropogenic factors on groundwater pollution. The main 380 influential factors in various areas were different, depending on the geology types, the 381 382 types of pollutants, the evaluation methods and so on. Han et al. (2016) reviewed the contamination of water pollution in China and indicated that the major sources of 383 groundwater pollution included municipal and industrial wastewater discharge and 384 agricultural fertilizers, which were the crucial pollution sources that were considered 385 in this article when assessing the hazard. Due to the limited available data, the hazard 386 assessment only considered the types of pollution sources and the damping effect with 387 distance. Sudden natural catastrophes, inconsistent operating procedures (Li et al., 388

2012), and the pollutant amounts and toxicity (Bai et al., 2012; Zhang et al., 2016) could also generate hazards. There may be some impact on the explanatory power of the hazard assessment results. More detailed data could be used to further assess the explanatory power of hazard on groundwater pollution.

393

4 Conclusions

For the vulnerability assessment, the PLEIK method effectively assessed the 395 vulnerability in covered karst areas, which highlighted the importance of protective 396 cover and land use. While assessing the hazard of groundwater pollution, 50.23% of 397 the areas in Luzhai County displayed no hazard. A total of 36.35% of the groundwater 398 samples were polluted in the study area. The geodetector method evaluated the 399 vulnerability and hazard assessment maps and assessed their explanatory power for 400 groundwater pollution quantitatively. The explanatory power for the hazard and 401 vulnerability assessment maps showed that they have a combined 58.2% similarity 402 with actual groundwater pollution. Hazard influenced groundwater pollution 2.6 times 403 more than vulnerability. These results suggest that controlling pollution sources is 404 more crucial and more effective to prevent groundwater pollution than reducing 405 vulnerability. 406

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415 **References**

- 416 Alfy, M. E., Lashin, A., Abdalla, F., & Al-Bassam, A. 2017. Assessing the hydrogeochemical
- 417 processes affecting groundwater pollution in arid areas using an integration of geochemical
- 418 equilibrium and multivariate statistical techniques. Environmental Pollution, 229, 1-11
- Andreo, B., Goldscheider, N., Vadillo, I., Vías, J. M., Neukum, C., & Sinreich, M., et al. 2011.
- 420 Karst groundwater protection: first application of a pan-european approach to vulnerability, hazard
- and risk mapping in the sierra de libar (southern spain). Science of the Total Environment, 357(1),
 54-73.
- 423 Baalousha, H. M. 2016. Groundwater vulnerability mapping of qatar aquifers. Journal of African
- 424 Earth Sciences, 124, 75-93.
- 425 Bai, L. P., Wang, Y. Y., & Li, F. S. 2011. Research on gis-based risk assessment method of
- groundwater pollution and its application. Advanced Materials Research, 356-360(356-360), 819824.
- 428 Beynen, P. E. V., Niedzielski, M. A., Bialkowska-Jelinska, E., Alsharif, K., & Matusick, J. 2012.
- 429 Comparative study of specific groundwater vulnerability of a karst aquifer in central florida.
- 430 Applied Geography, 32(2), 868-877.
- 431 Cui, Y. F., Jiang-Tao, H. E., Wang, M. L., Zhao, Y. K., & Wang, F. 2016. Exploration of risk
- 432 assessment method towards groundwater contamination in karst region:a case study in disu
 433 underground river system basin. Carsologica Sinica, 35(4):372-383.
- Dai, C. H., Hai-Bing, L. I., Pan, Z., Zhao, S. J., & Huang, S. C. 2015. Comparison of the rekst
- 435 model with pleik model in performing the antifouling analysis of karstic groundwater: a case study
- 436 in the xiangxi dalongdong underground river. Carsologica Sinica, 34(4):354-361.
- 437 Darnault, C. J. G. 2011. Karst aquifers: hydrogeology and exploitation. Nato Security Through
 438 Science, 203-226.
- 439 Entezari, M., Yamani, M., & Aghdam, M. J. 2016. Evaluation of intrinsic vulnerability, hazard
- 440 and risk mapping for karst aquifers, khorein aquifer, kermanshah province: a case study.
- 441 Environmental Earth Sciences, 75(5), 1-10.
- 442 Guo, Q., Wang, Y., Gao, X., & Ma, T. 2007. A new model (drarch) for assessing groundwater
- 443 vulnerability to arsenic contamination at basin scale: a case study in taiyuan basin, northern china.

- 444 Environmental Geology, 52(5), 923-932.
- 445 Hamdan, I., Margane, A., Ptak, T., Wiegand, B., & Sauter, M. 2016. Groundwater vulnerability
- 446 assessment for the karst aquifer of tanour and rasoun springs catchment area (nw-jordan) using
- 447 cop and epik intrinsic methods. Environmental Earth Sciences, 75(23), 1474.
- Han, D., Currell, M. J., & Cao, G. 2016. Deep challenges for china's war on water pollution.
- 449 Environmental Pollution, 218(218), 1222-1233.
- 450 Iván, V., & Mádl-Szőnyi, J. 2017. State of the art of karst vulnerability assessment: overview,
- 451 evaluation and outlook. Environmental Earth Sciences, 76(3), 112.
- 452 Kazakis, N., Oikonomidis, D., & Voudouris, K. S. 2015. Groundwater vulnerability and pollution
- 453 risk assessment with disparate models in karstic, porous, and fissured rock aquifers using remote
- sensing techniques and gis in anthemountas basin, greece. Environmental Earth Sciences, 74(7),
- 455 6199-6209.
- 456 Li, B., Zeng, Y. F., Zhang, B. B., & Wang, X. Q. 2018. A risk evaluation model for karst
- groundwater pollution based on geographic information system and artificial neural network
 applications. Environmental Earth Sciences, 77(9), 344.
- Li, H., Yu, X., Zhang, W., Ying, H., Yu, J., & Zhang, Y. 2017. Risk assessment of groundwater
- 460 organic pollution using hazard, intrinsic vulnerability, and groundwater value, suzhou city in461 china. Exposure & Health(4), 1-17.
- 462 Polemio, M., Casarano, D., & Limoni, P. P. 2009. Karstic aquifer vulnerability assessment
- 463 methods and results at a test site (apulia, southern italy). Natural Hazards & Earth System
- 464 Sciences & Discussions, 9(4), 1461-1470.
- Saidi, S., Bouri, S., & Dhia, H. B. 2010. Groundwater vulnerability and risk mapping of the hajebjelma aquifer (central tunisia) using a gis-based drastic model. Environmental Earth Sciences,
 59(7), 1579-1588.
- 468 Saidi, S., Bouri, S., Dhia, H. B., & Anselme, B. 2011. Assessment of groundwater risk using
- 469 intrinsic vulnerability and hazard mapping: application to souassi aquifer, tunisian sahel.
 470 Agricultural Water Management, 98(10), 1671-1682.
- 471 Shrestha, S., Semkuyu, D. J., & Pandey, V. P. 2016. Assessment of groundwater vulnerability and
- risk to pollution in kathmandu valley, nepal. Science of the Total Environment, 556, 23-35.
- 473 Terrado, M., Barceló, D., Tauler, R., Borrell, E., Campos, S. D., & Barceló, D. 2010. Surface-

- 474 water-quality indices for the analysis of data generated by automated sampling networks. Trac
- 475 Trends in Analytical Chemistry, 29(1), 40-52.
- 476 Torres, N. I., Xue, Y., Padilla, I. Y., Macchiavelli, R. E., Ghasemizadeh, R., & Kaeli, D., et al.
- 477 2018. The influence of hydrogeological and anthropogenic variables on phthalate contamination in
- 478 eogenetic karst groundwater systems. Environmental Pollution, 237, 298-307.
- 479 Wang, J., He, J., & Chen, H. 2012. Assessment of groundwater contamination risk using hazard
- 480 quantification, a modified drastic model and groundwater value, beijing plain, china. Science of
- 481 the Total Environment, 432(16), 216-226.
- 482 Wang, J., Hu, M., Zhang, F., & Gao, B. 2018. Influential factors detection for surface water
- 483 quality with geographical detectors in china. Stochastic Environmental Research & Risk
- 484 Assessment (4), 1-13.
- 485 Wang, J.F., Li, X.H., Christakos, G., Liao, Y.L., Zhang, T., Gu, X., Zheng, X.Y. 2010.
- 486 Geographical detectors-based health risk assessment and its application in the neural tube defects
- 487 study of the Heshun Region, China. International Journal of Geographical Information Science
- 488 24(1): 107-127.
- Wang, J.F., Zhang, T.L., Fu, B.J. 2016. A measure of spatial stratified heterogeneity. Ecological
 Indicators 67(2016): 250-256.
- Wang, J.F, Xu, C.D. 2018. Geodetector: principle and prospective. Acta Geographica Sinica
 72(1): 116-134.
- Wen, Y., Lu, L. I., Zhao, L., & Zhao, K. 2016. Study on groundwater pollution risk assessment in
 Chongqing. Environmental Pollution & Control, 38(3), 90-98.
- Ying, L., Li, J., Chen, S., & Diao, W. 2012. Establishing indices for groundwater contamination
 risk assessment in the vicinity of hazardous waste landfills in china. Environmental Pollution,
 165(6), 77-90.
- 498 Zhang, B., Li, G., Cheng, P., Yeh, T. C. J., & Hong, M. 2016. Landfill risk assessment on
- groundwater based on vulnerability and pollution index. Water Resources Management, 30(4),1465-1480.
- 501 Zou, S. Z., Li, L. J., Lu, H. P., Liu, Q. Q., Su, C. T., & Zhu, D. N. 2014. The vulnerability
- assessment method of karst groundwater. Acta Geoscientica Sinica, 35(2), 262-268.
- 503 Zwahlen, F. 2003. Vulnerability and risk mapping for the protection of carbonate (karst) aquifers.

- 504 European Commission, Directorate-General XII Science, Research and Development, Brussels,
- 505 pp. 297.

- 1. CCME WQI was used to evaluate the integrated groundwater pollutant classes.
- 2. Geodetector method was used to detect the effect degree of V and H quantitatively
- 3. Hazard influence on the groundwater pollution was 2.6 times that of vulnerability.

