





48 content etc) and human activities, have been widely discussed (Bajracharya et al., 2000; Dai et al.  
49 2004; Jeremy et al. 2018; Fearnside, 2018). In karst areas, however, the important geological  
50 process, carbonate corrosion, has been largely ignored in discussions of soil CO<sub>2</sub> levels, and  
51 there is no detail documents detailing the soil CO<sub>2</sub> concentration and its relationship with  
52 global climate change in karst areas. Several problems puzzle us: Is there any difference  
53 between soil profile CO<sub>2</sub> concentrations in carbonate areas compared to that in non-carbonate  
54 areas? If so, is the difference caused by carbonate corrosion? By how much is it affected?  
55 Moreover, studies have revealed that there is CO<sub>2</sub> unbalance between carbon released into  
56 atmosphere and that produced by organic matter in carbonate areas (Jiang and Yuan et al. 1999;  
57 Jeremy et al. 2018), but there is no reasonable explanation. Lack of research work on these  
58 questions restricts our understanding about soil CO<sub>2</sub> transfer, limits further study of the  
59 mechanisms, and impedes learning of its significance for the carbon cycle.

60 In order to understand the varying characteristics of soil CO<sub>2</sub> concentration in karst areas  
61 and its potential effect on global carbon cycles, soil profile CO<sub>2</sub> was measured, and samples of  
62 soils and rocks were gathered in the typical karst area of Zhaotong city, Yunan Province, China.  
63 The objectives of this paper are to: (1) analyze comparatively the varying characteristics of the  
64 soil profile CO<sub>2</sub> concentration in carbonate and non-carbonate areas; (2) discuss the relationship  
65 between soil CO<sub>2</sub> concentration and other parameters, and clarify the effect of carbonate  
66 corrosion on soil CO<sub>2</sub>; (3) develop a mathematical model of soil CO<sub>2</sub> transfer and  
67 quantitatively evaluate the effect scale of carbonate corrosion on soil CO<sub>2</sub> concentration, and  
68 discuss its significance for global carbon cycle and climate change.

## 69 **2 Study area and methods**

### 70 **2.1 Study area**

71 The study area, Zhenxiong County and Weixin County in Zhaotong City, north of the Yunnan  
72 Province, China, was selected. The area contains high mountains and steep gorges. Many of the  
73 mountain peaks tower above 2000 m, and there are many different natural watersheds. The  
74 area is sub-tropical and humid. It has a plateau-climate with an average annual temperature of  
75 11.7 °C and an average precipitation of 1200 mm. Monthly precipitation is above 100 mm, and  
76 vertical climate belts with four seasons are clearly demarcated. The soil types include mainly  
77 yellow, dingy and brown earth, with a wide thickness range (from a few up to 70-80 cm). The  
78 flora is dominated by grass, shrubs, and partly by secondary forest.

79 The bedrock is composed predominantly of Mesozoic limestone and dolomite, with flysch  
80 and associated sedimentary rocks. The widely exposed strata include mainly Ordovician,  
81 Permian, Triassic, Jurassic and Quaternary units, among which only Ordovician and Permian  
82 strata appear together. Devonian strata are not present, and Precambrian, Cambrian and Silurian  
83 strata occur in limited outcrop, or as inclusions among other strata. Ordovician, Permian and  
84 Triassic rocks are mainly marine carbonate deposits, and Jurassic and Quaternary units are  
85 mainly composed of terrestrial clastic deposits.

### 86 **2.2 Sampling and analyzing methods**

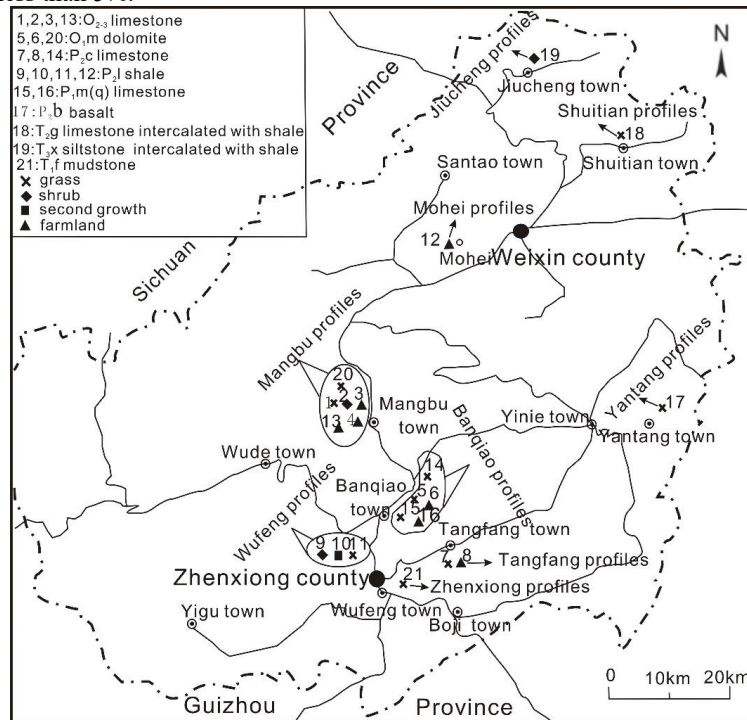
87 In order to comprehensively reveal characteristics of soil CO<sub>2</sub> concentration in a karst area,  
88 sample sites were selected in such a way as to cover different stratigraphic units and different  
89 types of vegetation. Meanwhile, profiles in carbonate and non-carbonate areas were both  
90 measured. Totally, CO<sub>2</sub> concentration of 21 soil profiles and organic carbon of 12 soil profiles  
91 were analyzed. The profile sites are shown in Fig. 1, and among these, profiles in carbonate  
92 areas include the Lower Ordovician Meitan Formation (O<sub>1</sub>), the Middle and Upper  
93 Ordovician Baota Formation (O<sub>2-3</sub>), the Lower Permian Xixia and Maokou Formations



94 (P<sub>1m</sub>(q)), the Upper Permian Changxing Formation (P<sub>2c</sub>), and the Middle Triassic Guanling  
 95 Formation (T<sub>2g</sub>). Sites in non-carbonate areas include Middle Permian basalt (P<sub>2β</sub>), shale in the  
 96 Upper Permian Longtan Formation (P<sub>2l</sub>), mudstone in the Lower Triassic Feixianguan  
 97 Formation (T<sub>1f</sub>), and siltstone intercalated with shale in the Upper Triassic Xujiahe Formation  
 98 (T<sub>3x</sub>).

99 CO<sub>2</sub> concentration within the soil pores was measured every 10 cm from the surface down  
 100 to the rock-soil interface using a GASTEC 801 instrument and 2LL or 2L CO<sub>2</sub> Detector Tube  
 101 (GASTEC Co., Japan). The profile soil samples were of one-to-one correspondence with the  
 102 gas samples and also taken every 10 cm.

103 The starting samples were air-dried naturally, and then pulverized (particle diameter <150  
 104 μm). Soil organic carbon was determined using the potassium dichromate volumetric method.  
 105 Soil pH was measured in distilled water at a solid/ solution ratio of 1/5, with the instrument  
 106 model PHS-2. Water contents of soils were synchronously measured by a cutting ring. CaO and  
 107 MgO contents of rocks were determined by Inductively Coupled Plasma-Atomic Emission  
 108 Spectrometry (ICP-AES) with a Charge Injection Detector (CID), model TJA IRIS/AP. The  
 109 standard materials (GBW07401, GBW07408) were used for quality control, with relative  
 110 deviation less than 5%.



111  
 112 FIG. 1. Sites of measuring soil CO<sub>2</sub> and gathering organic carbon samples (1-Mangbu O<sub>2-3</sub> grass, 2-Mangbu O<sub>2-3</sub> shrub, 3-  
 113 Mangbu O<sub>2-3</sub> farmland, 4-Mangbu O<sub>2-3</sub> farmland, 5-Banqiao O<sub>1m</sub> grass, 6-Mangbu O<sub>1m</sub> farmland, 7-Tangfang P<sub>2c</sub> grass, 8-  
 114 Tangfang P<sub>2c</sub> farmland, 9-Wufeng P<sub>2l</sub> shrub, 10-Wufeng P<sub>2l</sub> second growth, 11-Wufeng P<sub>2l</sub> grass, 12-Mohei P<sub>2l</sub> farmland, 13-  
 115 Mangbu O<sub>2-3</sub> farmland, 14-Banqiao P<sub>2c</sub> grass, 15-Banqiao P<sub>1m</sub>(q) grass, 16-Banqiao P<sub>1m</sub>(q) shrub, 17-Tangfang P<sub>2β</sub> grass, 18-  
 116 Shuitian T<sub>2g</sub> shrub, 19-Jiucheng T<sub>3x</sub> shrub, 20-Mangbu O<sub>1m</sub> grass, 21-Zhenxiong T<sub>1f</sub> grass).



117 **3 Results**

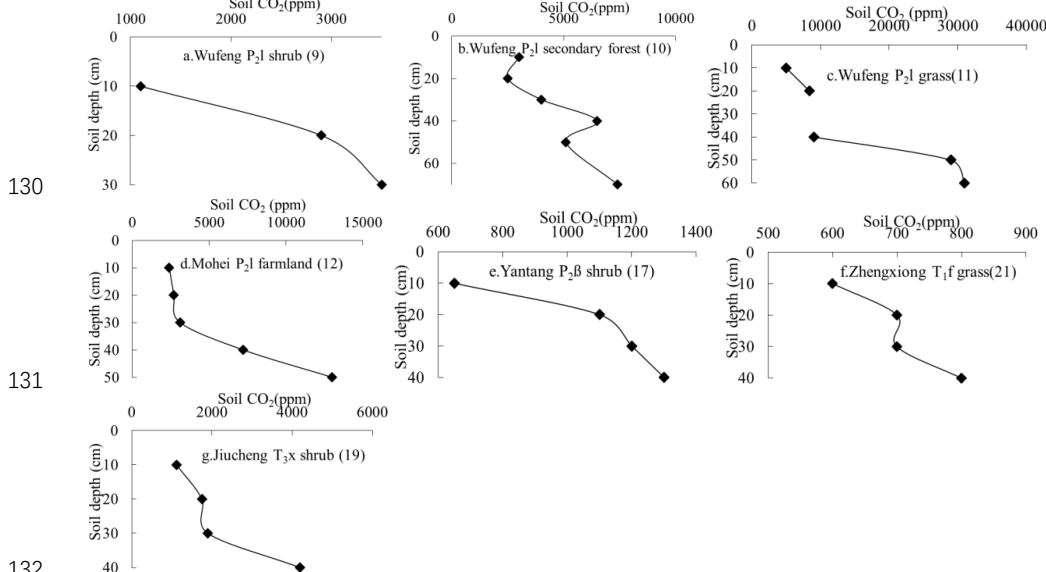
118 **3.1 Varying CO<sub>2</sub> concentration characteristics of soil profiles**

119 Fig. 2 shows soil profile CO<sub>2</sub> concentrations varying with soil depths in 7 non-carbonate  
 120 areas. The data show a distinct tendency of increasing CO<sub>2</sub> concentration with soil depth, with  
 121 R<sup>2</sup>=0.8-0.92 (Table 1).The reasons may be the higher soil bulk density, more condensed soil  
 122 pores, and difficulty of CO<sub>2</sub> diffusion in the deeper soil. In fact, soil profile CO<sub>2</sub> has been widely  
 123 reported to be correlated with soil depth by previous researches (Rustad et al. 2000; Dai et al.  
 124 2004; Malak et al. 2018) , and even the following linear equation have been developed (James  
 125 and George, 1991):  $Mean\ CO_2 = 0.035 + 0.0015(Depth)$  ( $R^2 = 0.99, P < 0.0005$ ). Our observations  
 126 in non-carbonate areas are concordant with these reports and support soil profile CO<sub>2</sub> increases  
 127 with soil depth in non-carbonate areas.

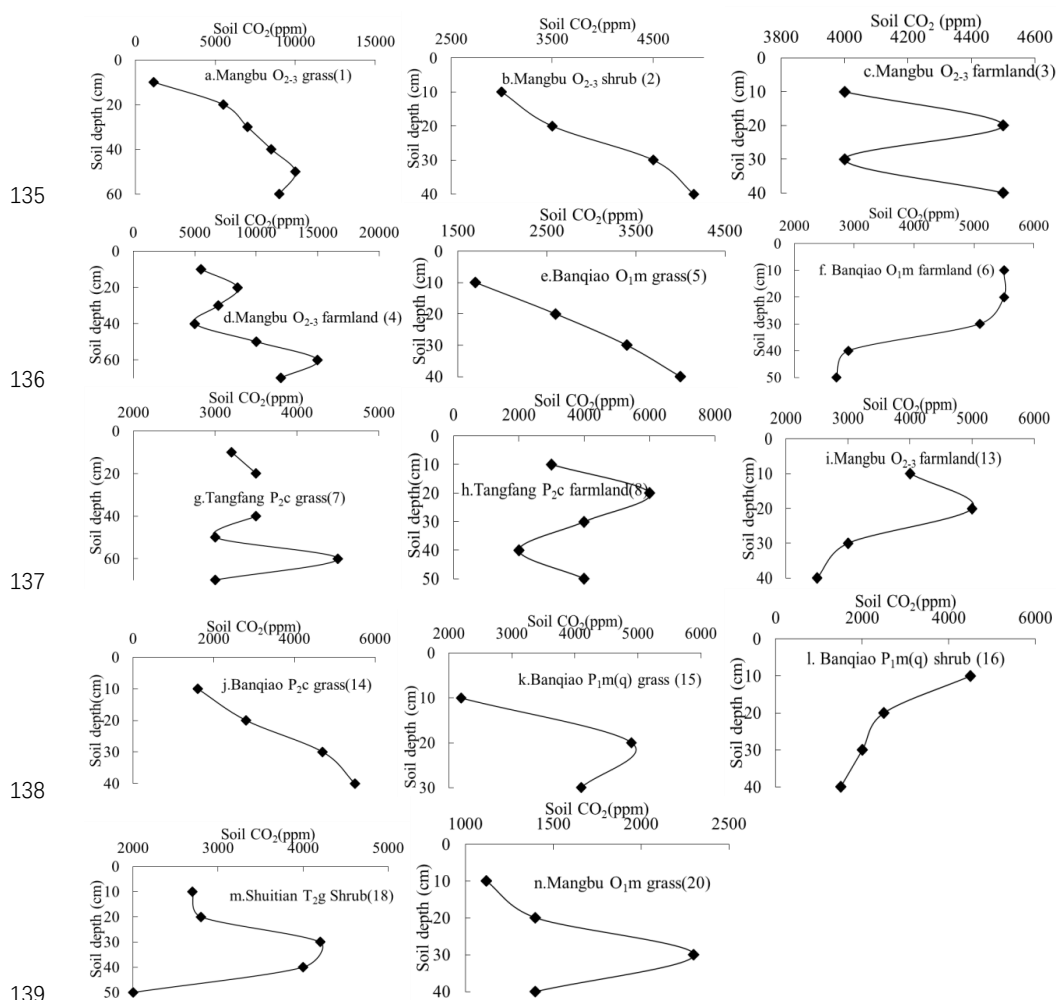
128 Table 1. Regression analysis of soil CO<sub>2</sub> concentration and profile depth in non-carbonate areas.

Profiles	Regression equation	R <sup>2</sup>	P
Wufeng P <sub>2</sub> l shrub (9)	$y = 0.0077x + 0.7692$	0.92	0.179
Wufeng P <sub>2</sub> l second growth (10)	$y = 0.0099x - 10.595$	0.80	0.016*
Wufeng P <sub>2</sub> l grass (11)	$y = 0.0015x + 11.527$	0.80	0.042*
Mohei P <sub>2</sub> l farmland (12)	$y = 0.0031x + 12.239$	0.80	0.039*
Yantang P <sub>2</sub> β grass (17)	$y = 0.0415x - 19.114$	0.85	0.077
Zengxiong T <sub>1</sub> f grass (21)	$y = 0.15x - 70$	0.9	0.051
Jiucheng T <sub>3</sub> x shrub (19)	$y = 0.0086x + 5.6875$	0.81	0.101

129 Note: ( ) means profile No., \*means significantly congressed at 0.005 level.



132 Figure 2. Varying characteristics of soil profile CO<sub>2</sub> concentration in non-carbonate areas  
 133 (profile no. in brackets).  
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 Figure 3. Varying characteristics of soil profile CO<sub>2</sub> concentration in carbonate areas (profile no. in brackets).

14 Soil profile CO<sub>2</sub> concentration with soil depth in carbonate areas was gained (Fig. 3). The results show a complex and inverse relationship between soil CO<sub>2</sub> and soil depth in carbonate areas. Most Soil profile CO<sub>2</sub> increases with soil depth in the upper sections, such as Mangbu O<sub>2-3</sub> grassy profile (Fig. 3a), Mangbu O<sub>2-3</sub> shrub profile (Fig. 3b), Mangbu O<sub>2-3</sub> farmland profile (Fig. 3d), Banqiao O<sub>1m</sub> grassy profile (Fig. 3e), and Banqiao P<sub>2c</sub> grassy profile (Fig. 3j). CO<sub>2</sub> concentrations decrease with soil depth when they increase from surface to a certain depth in Mangbu O<sub>2-3</sub> farmland profile (Fig. 3i), Banqiao P<sub>1m(q)</sub> grassy profile (Fig. 3k), Gaotian T<sub>2g</sub> grassy profile (Fig. 3m) and Mangbu O<sub>1m</sub> grassy profile (Fig. 3n). Those of Banqiao O<sub>1m</sub> farmland profile (Fig. 3f) and Banqiao P<sub>1m(q)</sub> shrub profile (Fig. 3l) even decrease all along with soil depth, and two farmland profiles of Mangbu O<sub>2-3</sub> (Fig. 3c) and Tangfang P<sub>2c</sub> (Fig. 3h) fluctuate, and have no regularity due to the effect of human farming activities. Generally, Except Mangbu O<sub>2-3</sub> farmland profile (Fig. 3.c) and Tangfang P<sub>2c</sub> farmland profile (Fig. 3.h), which are disturbed by farming, CO<sub>2</sub> concentrations of other profiles in carbonate areas all decrease with soil depth at the rock-soil



155 interface (Fig. 3.b,e,j). Moreover, there is no correlation of soil CO<sub>2</sub> concentration with soil depth,  
 156 because sequestration of deep soil CO<sub>2</sub> concentration occurs in carbonate areas. Why does the  
 157 sequestration only take place in carbonate areas, but not in non-carbonate ones? Naturally the  
 158 particular carbonate process-carbonate corrosion-is considered. That is, part of deep soil CO<sub>2</sub> is  
 159 consumed and CO<sub>2</sub> sequestration occurs, and there is no linear relationship between CO<sub>2</sub>  
 160 concentration and soil depths in carbonate areas. In fact, Buyannovsky and Wagner (1983),  
 161 Solomon and Cerling (1987), and Xu and He (1996) all reported that soil CO<sub>2</sub> concentration  
 162 reaches a peak at a certain depth, and then decreases with soil depth in carbonate areas. CO<sub>2</sub>  
 163 concentration in Banqiao O<sub>1m</sub> farmland profile (Fig. 3.f) and Banqiao P<sub>1m(q)</sub> shrub profile (Fig.3.l)  
 164 continues to decrease with depth through the integral profile, and they also had the highest  
 165 concentration at the 10cm layer. Instances of CO<sub>2</sub> concentration in surface layers higher than those  
 166 in bottom layers are scarcely documented in carbonate areas.

### 167 3.2 Relationship between soil profile CO<sub>2</sub> concentration and soil organic carbon

168 Soil organic carbon (SOC) was analyzed in a part of the profiles, corresponding with CO<sub>2</sub>  
 169 concentration. Results are given in Fig. 4 a-h, indicating profiles in carbonate areas, whereas  
 170 Fig. 4 i-l indicate those in non-carbonate (shale) areas.

171 Correlation analysis of soil profile CO<sub>2</sub> concentration and SOC in shale areas is listed in  
 172 Table 2. It shows a negative correlation, with high regression coefficients ( $R^2=0.67-0.85$ ). An  
 173 exception of 0.29 occurs in Wufeng P<sub>2l</sub> secondary forest, which possibly is caused by stronger  
 174 root respiration and a higher ratio of CO<sub>2</sub> generated by the roots. Therefore, SOC is directly  
 175 affected by the release of soil CO<sub>2</sub>, and the key problem for soil carbon storage is to slow down  
 176 the renewing of soil organic matter (Chen et al. 2002). However, the soil profile CO<sub>2</sub>  
 177 concentration don't show significant regression with SOC, which means which means that soil  
 178 CO<sub>2</sub> concentration is not only related to SOC, but also to soil respiration and microbe activities.  
 179 Correlation analysis of soil CO<sub>2</sub> and organic carbon in carbonate areas is shown in Table 3, and  
 180 the regression coefficients are irregular, and even those of Banqiao O<sub>1m</sub> farmland profile and  
 181 Banqiao P<sub>1m(q)</sub> shrub profile are positive. Previous studies in Shilin, Lunan City and in  
 182 Guizhou Plateau also showd no correlation between CO<sub>2</sub> concentration and SOC (Liang et al.  
 183 2003).

184 Table 2. Correlation analysis of soil CO<sub>2</sub> and soil organic carbon in shale areas of karst.

Profiles	Regression equation	R <sup>2</sup>	P
Wufeng P <sub>2l</sub> shrub (9)	$y = -618.67x + 4199.6$	0.67	0.387
Wufeng P <sub>2l</sub> second growth (10)	$y = -766.39x + 7548.9$	0.29	0.239
Wufeng P <sub>2l</sub> grass (11)	$y = -13093x + 69890$	0.74	0.351
Mohei P <sub>2l</sub> farmland (12)	$y = -8646.2x + 49490$	0.85	0.077

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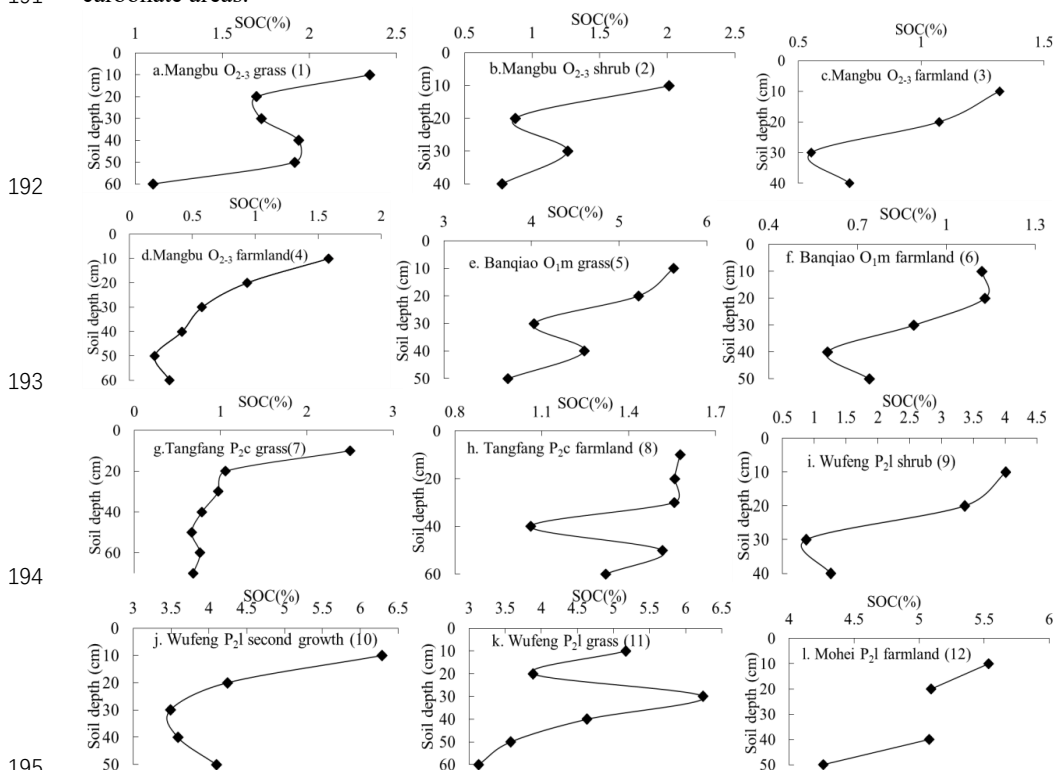
Table 3. Correlation analysis of soil CO<sub>2</sub> and soil organic carbon in carbonate areas of karst.

Profiles	Regression equation	R <sup>2</sup>
Mangbu O <sub>2-3</sub> grass (1)	$y = -4673.8x + 15214$	0.35
Mangbu O <sub>2-3</sub> shrub (2)	$y = -1054.5x + 5273.4$	0.46
Mangbu O <sub>2-3</sub> farmland (3)	$y = -61.209x + 4305.9$	0.005
Mangbu O <sub>2-3</sub> farmland (4)	$y = -3569.5x + 10875$	0.25
Banqiao O <sub>1m</sub> grass (5)	$y = -1172.2x + 8636.5$	0.68
Banqiao O <sub>1m</sub> farmland (6)	$y = 5560.6x - 639.97$	0.84
Tangfang P <sub>2c</sub> grass (7)	$y = -134.06x + 3594.1$	0.33
Tangfang P <sub>2c</sub> farmland (8)	$y = 4477.3x - 2714.1$	0.44

187 What is the reason of poor relationship between soil CO<sub>2</sub> and SOC in carbonate areas? The  
 188 possible answer may be carbonate corrosion. By means of corrosion, deep soil CO<sub>2</sub> is partly



189 consumed and its level decreases. Consequently, the relationship becomes poor. In addition,  
 190 varying characteristics of SOC cannot explain well the decrease of deep soil CO<sub>2</sub> levels in  
 191 carbonate areas.

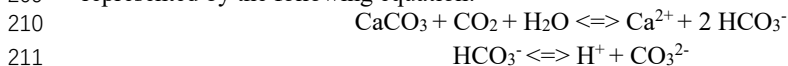


195  
 196 Figure 4. Varying characteristics of soil profile organic carbon in karst areas (profile no. in  
 197 brackets)

### 198 3.3 Varying characteristics of profile soil pH

199 Soil pH curves varying with soil depth are drawn in Fig. 5a-h, indicating carbonate profiles,  
 200 and 6i-l indicating non-carbonate (shale) profiles. In non-carbonate areas, there is a complex  
 201 relationship between pH and depths, but pH increases obviously at the rock-soil interface,  
 202 whereas pH non-significantly varied with soil CO<sub>2</sub> and SOC. Conversely, in carbonate areas,  
 203 pH generally increases with soil depth in the surface layer except in the Banqiao O<sub>1m</sub> farmland  
 204 profile. Moreover, from Figs. 3 and 5 it is evident that soil CO<sub>2</sub> concentration decreases where  
 205 soil pH decreases too, and even CO<sub>2</sub> level in the Banqiao O<sub>1m</sub> farmland profile decreases from  
 206 the surface to the bottom with soil pH through the entire profile. These observations imply that  
 207 the decrease of deep soil CO<sub>2</sub> concentration in carbonate areas is related closely to soil pH.

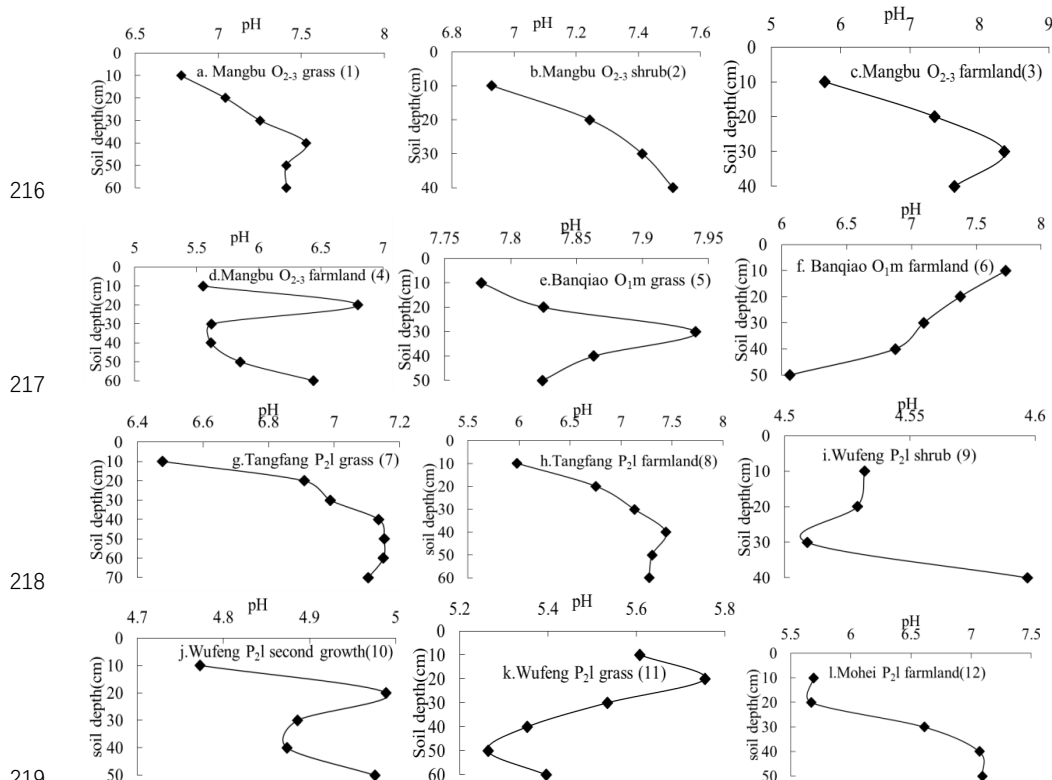
208 Chemically, with soil water and soil CO<sub>2</sub> added together, carbonate corrosion can be  
 209 represented by the following equation:



212 By means of this reaction, deep soil CO<sub>2</sub> is consumed by the corrosion of the underlying  
 213 carbonate rock, and pH decreases synchronously. This reaction cannot take place in soil over



214 areas with non-carbonate bedrock, so here the deep soil CO<sub>2</sub> concentration does not decrease,  
 215 but increases.



219 Figure 5. Soil pH of different profiles in karst area (a-h indicate those in carbonate areas, and  
 220 h-l indicate those in shale areas, profile no. in brackets).  
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### 222 3.4 Carbonate corrosion and the global carbon cycle

223 Many studies have observed that soil CO<sub>2</sub> concentration in carbonate areas decreases with depth  
 224 when it reaches a maximum at a certain soil depth in carbonate areas (Buyannovsky and  
 225 Wagner, 1983; Li et al. 1995; Xu and He, 1996; Liang et al. 2003). There has, however, been  
 226 no reasonable explanation for the observations. Li et al (1995) attributed it to less roots, and,  
 227 therefore, less root respiration in the deep soil, but there are no scientifically observed data to  
 228 support this idea, and it remains only a hypothesis. No decrease in soil CO<sub>2</sub> in non-carbonate  
 229 areas is found, and, furthermore, the depths with decreasing CO<sub>2</sub> concentrations were  
 230 distinguishable in different profiles, even at only 20-30 cm depths. The decreased CO<sub>2</sub>  
 231 concentration could be attributed to decreased microbe numbers or root respiration at such depths.  
 232 By comparative analysis of soil CO<sub>2</sub> concentration in areas of carbonate and non-carbonate  
 233 bedrock, it should be suggested that the explanation is due to the special geological process of  
 234 carbonate corrosion.

235 Soil CO<sub>2</sub> and SOC in non-carbonate areas have a good negative correlation, with correlation  
 236 coefficients  $R^2 = 0.67-0.85$ , although significance is not clear because soil CO<sub>2</sub> is determined by  
 237 not only organic matter but also by other factors, such as root respiration and microbe activities.  
 238 By contrast, such correlation in carbonate areas is poor, which was concluded also by Li et al

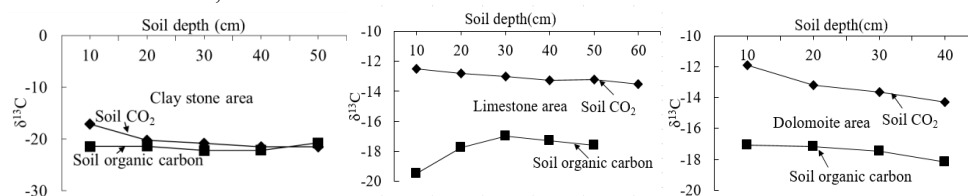




239 (1995) and Liang et al. (2003) from experiments in carbonate areas. Soil CO<sub>2</sub> of carbonate  
240 areas, in every depth at different sites, is negatively correlated with SOC, and relationship  
241 became worst with increasing soil depth. This observation means that SOC content cannot  
242 explain well the decreased CO<sub>2</sub> concentration of deep soil in carbonate areas, but rather may be  
243 related to carbonate corrosion. Soil pH in carbonate areas always decreases with soil CO<sub>2</sub>, and  
244 this may imply that H<sup>+</sup> generated by carbonate corrosion mixes into the deep soil increasing  
245 soil acidity.

246 Previous work has determined the imbalance between soil CO<sub>2</sub> produced and released in  
247 carbonate areas. Pan et al (2000) observed and simulated field data in Yaji, Guangxi Province,  
248 concluding that CO<sub>2</sub> produced by decomposition of organic matter is more than that released  
249 into the air. This confirms that the rock and the soil have an obviously “absorbing effect” for  
250 CO<sub>2</sub>. The data account for an absorbing coefficient of 22-130 g/m<sup>2</sup>·a.

251 Isotopes can effectively trace the carbon source of soil CO<sub>2</sub>. Fig. 6 reflects the δ<sup>13</sup>C value  
252 of soil CO<sub>2</sub> and SOC overlying different bedrock according to data from Li et al. (1995). It  
253 shows that in deep soil, CO<sub>2</sub> has a higher δ<sup>13</sup>C value than the SOC in limestone and dolomite  
254 areas, whereas the isotope ratios are more equivalent in clay stone areas. Such an observation  
255 may support the conclusion that that deep soil CO<sub>2</sub> in clay stone areas is mainly or completely  
256 from soil organic matter, and that in limestone and dolomite areas there must be an additional  
257 carbon source whose δ<sup>13</sup>C should be more than -14‰. CaCO<sub>3</sub> in carbonate has δ<sup>13</sup>C values of -  
258 3‰~+1‰. It must, therefore, possibly be recognized that carbon in CaCO<sub>3</sub> of carbonate bedrock  
259 mixes into soil CO<sub>2</sub>, since the corrosion reaction is reversible.



260  
261 Figure 6. Varying δ<sup>13</sup>C of soil CO<sub>2</sub> and soil organic carbon with soil depth overlying different  
262 bedrocks (data is after Li et al (1995)).

263 It has been examined that the karst carbon cycle is an important trace for the global carbon  
264 cycle and that further study is important to the hunt for “missing sink” (Jiang and Yuan, 1999).  
265 From what is presented above, with focus on the process of carbonate corrosion and comparison  
266 of different parameters in carbonate and non-carbonate areas, it is logical to conclude that  
267 carbonate corrosion causes the decreased CO<sub>2</sub> concentration at the rock-soil interface in  
268 carbonate areas. As a result, the decreased CO<sub>2</sub> level caused by corrosion will, of course,  
269 impose effects on atmospheric CO<sub>2</sub> and the karst carbon cycle. This is significantly for the  
270 potential fixation of carbon, the study of global carbon cycle balance, and the hunt for the  
271 “missing sink”.

### 272 3.5 Mathematical model of soil profile CO<sub>2</sub> transfer

273 In this model, only the molecular diffusion of CO<sub>2</sub> is considered, neglecting other processes, such  
274 as viscous flow and Knudsen diffusion in karst soil because of the weak air pressure gradient.  
275 Moreover, density gradient was regarded as the dominant dynamic of CO<sub>2</sub> diffusion, and  
276 temperature gradient was neglected because of its low contribution (0.2-0.4%) to CO<sub>2</sub> flow.  
277 Therefore, the transport of soil CO<sub>2</sub> can be described by the following one-dimensional diffusion  
278 equation according to Fick’s second law and laws of conservation of mass (Zeng and Zheng,  
279 2002), assuming horizontal homogeneity:



$$280 \quad \frac{\partial(\theta_a C_a + \theta_w C_w)}{\partial t} = -\frac{\partial(J_{da} + J_{dw} + J_{ca} + J_{cw})}{\partial z} - Q \cdot C_w + S \quad (1)$$

281 Here,  $\theta_a$  is the air content,  $\theta_w$  is the water content,  $C_a$  is the gaseous CO<sub>2</sub> concentration,  $J_{da}$  is the  
 282 gaseous CO<sub>2</sub> flow due to diffusion,  $J_{dw}$  is the dissolution CO<sub>2</sub> flow due to diffusion,  $J_{ca}$  is the  
 283 gaseous CO<sub>2</sub> flow due to convection,  $J_{cw}$  is the dissolution CO<sub>2</sub> flow due to convection,  $S$  is the  
 284 carbon source,  $Q$  is the water absorbed by roots,  $t$  is the time, and  $z$  is the space coordinate.

285 Such equation can be gained according to Fick's first law:

$$286 \quad J_{da} = -D_a \frac{\partial C_a}{\partial z} \quad J_{dw} = -D_w \frac{\partial C_w}{\partial z} \quad J_{ca} = q_a C_a \quad J_{cw} = q_w C_a \quad (2)$$

287 where  $D_a$  is the gaseous CO<sub>2</sub> diffusion coefficient in soil substrate,  $D_w$  is the dissolution CO<sub>2</sub>  
 288 diffusion coefficient in soil substrate,  $q_a$  is the soil air transference amount, and  $q_w$  is the soil  
 289 water transference amount.

290 Equation (3) can be deduced from equations (1) and (2), if it is assumed that soil water is  
 291 stable and gaseous and dissolution CO<sub>2</sub> flows are not considered:

$$292 \quad \theta_a \frac{\partial C_a}{\partial t} = D_a \frac{\partial^2 C_a}{\partial z^2} - \theta_w \frac{\partial C_w}{\partial t} - q_w \frac{\partial C_w}{\partial z} - Q \cdot C_w + S \quad (3)$$

293 Previous studies were referenced when the parameters were determined, and all the  
 294 parameters should be gained in winter of the same working period:

295  $q_w = \tau \exp(-\frac{z}{\delta})$ , presented by Yoyam et al.(1993), and

296  $Q = \frac{\tau \exp(-\frac{z}{\delta})}{\delta}$  by Warren and Michael (1984), and

297 in winter  $q_w = 0$ ,  $Q = 0$ ;  $D_a = D_a^* (\frac{\theta_a}{\theta_w}) (\frac{T}{T_0})^{1.823}$ , by Collin and Rasmuson (1988). Here,  $D_a^0$  is  
 298 the CO<sub>2</sub> diffusion coefficient in air at the reference temperature  $T^0$ .

299 For the carbon source, the rate of CO<sub>2</sub> produced by root respiration and microbes can be  
 300 expressed as follows:

$$301 \quad S(z) = S_0 \exp(-z/z_s)$$

302 where  $S(z)$  is the soil profile CO<sub>2</sub> at depth of  $z$ ,  $S_0$  is the CO<sub>2</sub> concentration in the surface soil,  $z$   
 303 is the soil depth, and  $z_s$  is the depth gradient. It also considered the CO<sub>2</sub> produced by organic  
 304 matter expressed as follows:

$$305 \quad S_{OM} = -\frac{6D_a \partial^2 C_a}{3.3 \partial z^2}.$$

306 Then equation (4) is achieved:

$$307 \quad \theta_a \frac{\partial C_a}{\partial t} = -0.82 D_a \frac{\partial^2 C_a}{\partial z^2} - \theta_w \frac{\partial C_w}{\partial t} + S_0 \exp(-z/z_s) + a \quad (4)$$

308  $\frac{\partial C_a}{\partial t}$ ,  $\frac{\partial C_w}{\partial t}$  are stable, when being from the same time and soil profile.

309 Based on the studies above, the soil profile CO<sub>2</sub> concentration varying with soil depth can be  
 310 expressed by the following equation:

$$311 \quad C_a = A \exp(Bz) + Cz + D \quad (A, B, C, D = \text{uncertain}) \quad (5)$$

312 According to Taylor formula:



313  $\exp(x) = 1 + x + \frac{1}{2!}x^2 + \dots + \frac{1}{n!}x^n + \dots$  (6), and it can be roughly expressed like the following  
 314 equation when  $x < 1$ :

315 
$$\exp(x) = \begin{cases} 1+x & (x \ll 1) \\ 1+x + \frac{1}{2!}x^2 & \end{cases} \quad (7)$$

316 When equation (7) is applied to equation (5), equation (8) can be gained to express profile CO<sub>2</sub>  
 317 concentration (C<sub>a</sub>) varying with soil depth (z):

318 
$$C_a = \begin{cases} a + bz \\ a + bz + cz^2 \end{cases} \quad (8)$$

319 Here, a, b and c are uncertain parameters, which vary with  $\theta_a$ ,  $\theta_w$ , S<sub>0</sub>, T, and D<sub>a</sub> of different  
 320 profiles.

321 That means, it can be expressed as a linear or parabolic relationship of soil profile CO<sub>2</sub>  
 322 concentration and soil depth. Actually, many observation and simulation also confirmed the  
 323 same results (James and George, 1991; Zeng and Zheng, 2002; Malak et al., 2018). Therefore,  
 324 it seems reasonable to express a linear or parabolic relationship of soil profile CO<sub>2</sub> concentration  
 325 and soil depth.

### 3.6 The rough evaluation of CO<sub>2</sub> decreased by corrosion

327 SPSS software was used to simulate the curve of measured soil CO<sub>2</sub> concentration and soil depth  
 328 in non-carbonate areas (Fig. 7 and Table 4), resulting in parabolas with multiple regression  
 329 coefficients R<sup>2</sup>=0.8-1. Multiple regression coefficient of P<sub>2c</sub> secondary forest profile shows the  
 330 lowest level at 0.79, which may be due to the different root respiration and the absorbed water  
 331 at different depths. The simulation evidences that the model is reliable and can be used to  
 332 roughly reveal the laws of soil profile CO<sub>2</sub> concentration.

333 Table 4. Simulated equation of measured soil CO<sub>2</sub> concentration and soil depth in non-carbonate areas.

Profiles	Equations	R <sup>2</sup>	P	Simulated depth	Simulated equation by exponents
P <sub>2l</sub> shrub (9)	$y = -6x^2 + 360x - 1900$	1	-	0-30 cm	$y = 702.44e^{0.0579x} (0.8681)$
P <sub>2l</sub> second growth (10)	$y = -0.1548x^2 + 92.952x + 1610$	0.7924	0.0946	0-60 cm	$y = 2320.4e^{0.0175x} (0.7784)$
P <sub>2l</sub> grass (11)	$y = 12.458x^2 - 324.64x + 7736.4$	0.8673	0.1327	0-60 cm	$y = 3456.1e^{0.0363x} (0.8601)$
P <sub>2c</sub> farmland (12)	$y = 10.5x^2 - 373x + 5320$	0.9914	0.0086	0-50 cm	$y = 1221.3e^{0.0436x} (0.8877)$
P <sub>2</sub> β grass (17)	$y = -0.875x^2 + 64.25x + 112.5$	0.9752	0.1575	0-40 cm	$y = 597.91e^{0.0217x} (0.7989)$
T <sub>1f</sub> shrub (21)	$y = -4E - 15x^2 + 6x + 550$	0.9	0.3162	0-40 cm	$y = 561.25e^{0.0086x} (0.8977)$
T <sub>3x</sub> shrub (19)	$y = 4.175x^2 - 114.85x + 1982.5$	0.93	0.2519	0-40 cm	$y = 722.96e^{0.0405x} (0.9031)$

334 Note: regression coefficients R<sup>2</sup> of simulated exponent in brackets.

335 In carbonate areas, however, there is no linear or parabolic relationship between soil profile  
 336 CO<sub>2</sub> concentration and soil depth, and the measured values are inconsistent with the simulated  
 337 ones. Linear or parabolic relationship can be found in the surface soil. Since it is carbonate  
 338 corrosion that decreases the CO<sub>2</sub> concentration in the deep soil of carbonate areas, the CO<sub>2</sub>  
 339 concentration in the surface layer can be used and to predict the CO<sub>2</sub> concentration of deep soil  
 340 based on the developed model. The predicting equation and results are listed in Fig. 8. It shows  
 341 that there is a strong difference between the measured and the predicted values, and that all the  
 342 predicted are greater than the measured ones in deep soil. It can also be deduced that deep soil  
 343 CO<sub>2</sub> is consumed by carbonate corrosion.

344 The method of subtraction of predicted and measured values can be used to evaluate the  
 345 decreased CO<sub>2</sub> concentration in carbonate areas caused by carbonate corrosion, and the results  
 346 are listed in Table 5. If synthesis factors, such as vegetation types and soil types, were



347 considered, the rough evaluation of the decreased CO<sub>2</sub> concentration of every stratigraphic unit  
 348 can be gained by taking the average (Fig. 9).

349 Table 5. The evaluated results of the decreased CO<sub>2</sub> concentration in carbonate areas caused  
 350 by carbonate corrosion.

Profiles	O <sub>2-3</sub> grass (1)	O <sub>2-3</sub> shrub (2)	O <sub>2-3</sub> farmland (3)	O <sub>2-3</sub> farmland (4)	O <sub>1m</sub> grass (5)	O <sub>1m</sub> farmland (6)	P <sub>2c</sub> grass (7)	P <sub>2c</sub> farmland (8)	O <sub>2-3</sub> farmland (13)	P <sub>2c</sub> grass (14)	P <sub>1m(q)</sub> grass (15)	P <sub>1m(q)</sub> shrub (16)	T <sub>2g</sub> shrub (18)	O <sub>1m</sub> grass (20)
Decreased CO <sub>2</sub> concentration (ppm)	2500	266.7	2000	1493.1	-	8800	1918.1	2600	7500	633.3	3500	10500	11800	2420
Percentage of total deep soil CO <sub>2</sub> (%)	21.7	5.2	19.0	6.2	-	48.9	39.0	14.4	57.7	10.3	46.0	63.6	66.3	63.4

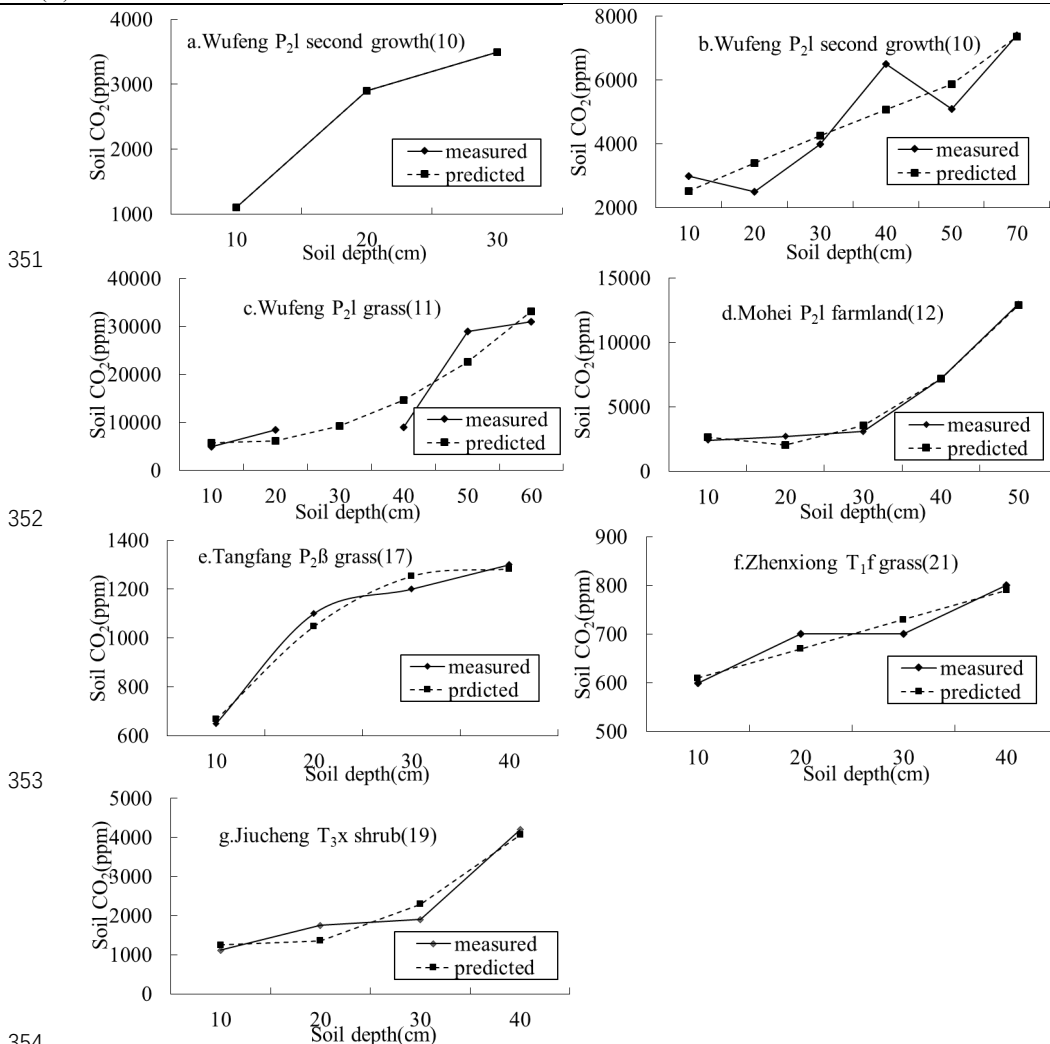
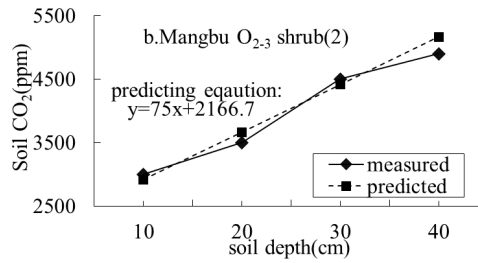
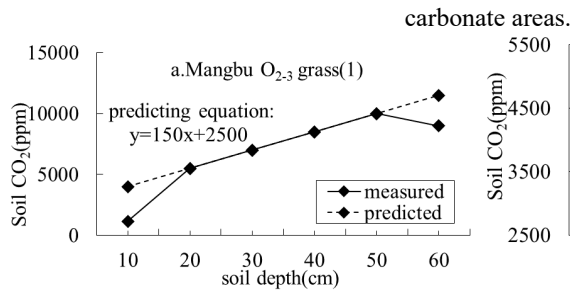


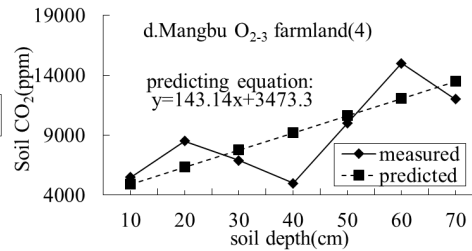
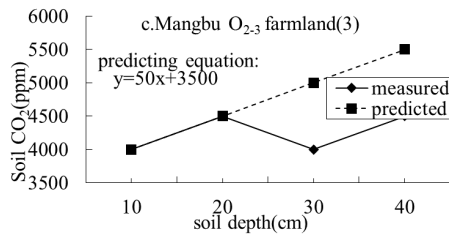
Figure 7. The measured and the simulated CO<sub>2</sub> concentrations of soil profiles in non-



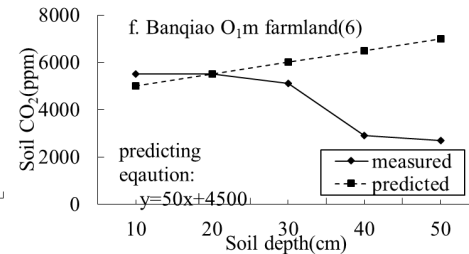
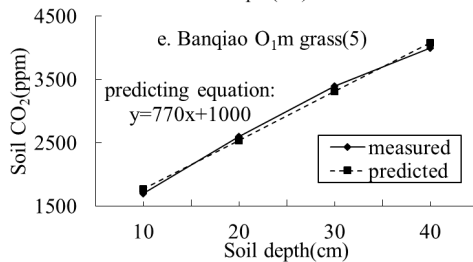
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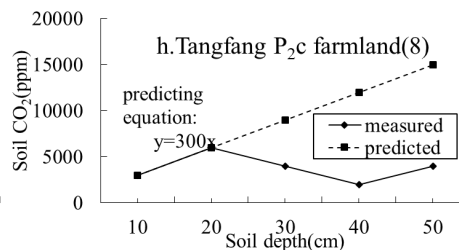
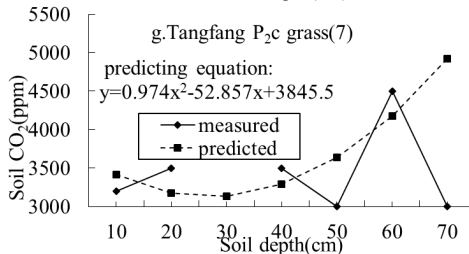
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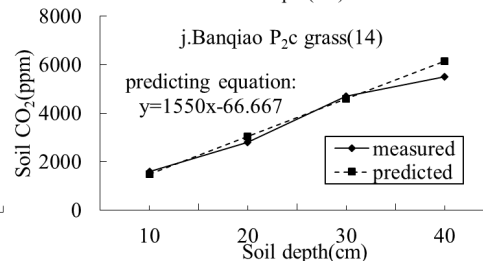
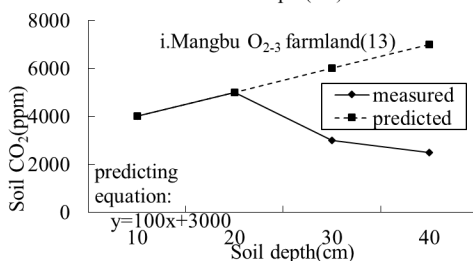
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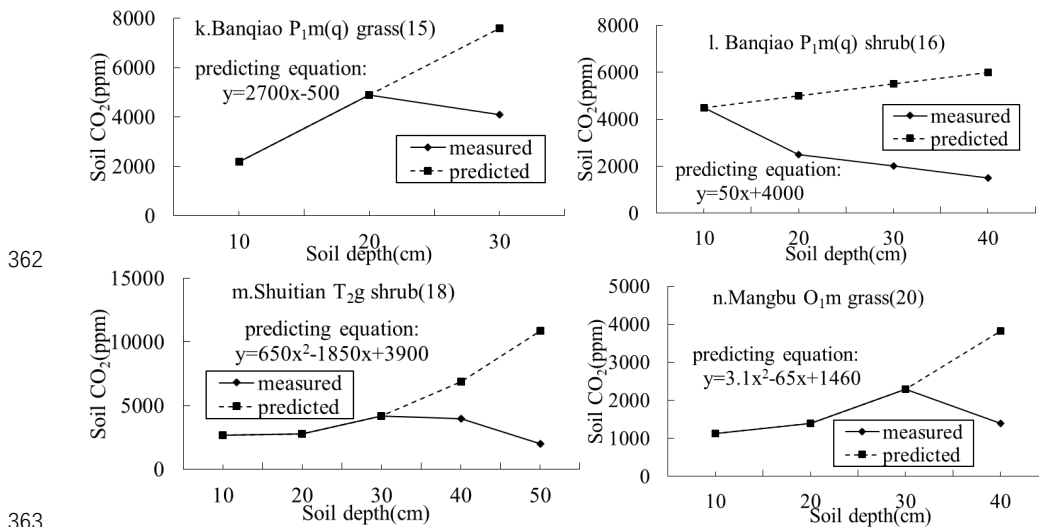
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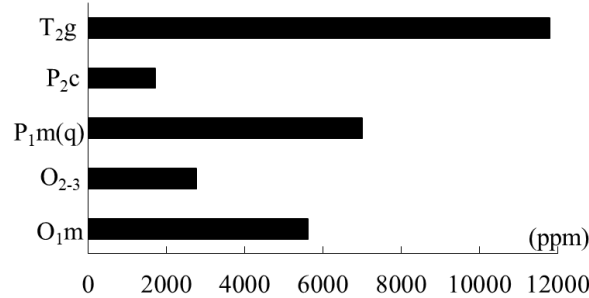


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Figure 8. The measured and predicted soil profile CO<sub>2</sub> concentrations in carbonate areas.



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Figure 9. The evaluation of the decreased CO<sub>2</sub> concentration caused by carbonate corrosion based on stratigraphic units.

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### 3.7 The main affecting factors of the decreased CO<sub>2</sub> concentration

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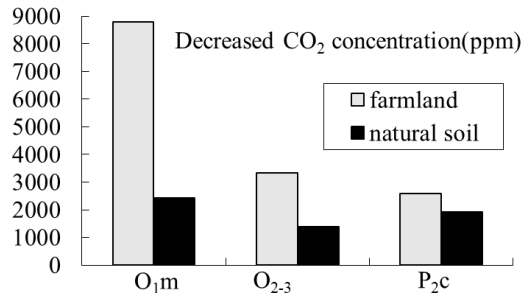
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Fig. 9 shows great dissimilarity of the decreased CO<sub>2</sub> concentration with different stratigraphic units in the following order: T<sub>2g</sub>>P<sub>1m</sub>(q)>O<sub>1m</sub>>O<sub>2-3</sub>>P<sub>2c</sub>. Fig. 10 shows the calculated results of the decreased CO<sub>2</sub> concentration, respectively, in farmland and natural soil (grass and shrub) of the same stratigraphic unit. CO<sub>2</sub> concentration on T<sub>2g</sub> and P<sub>1m</sub>(q) farmland is lacking, but the comparative analysis of O<sub>1m</sub>, O<sub>2-3</sub> and P<sub>2c</sub> can demonstrate that the decrease of CO<sub>2</sub> in natural soil profiles is obviously less than that in farmland profiles. It is clear that corrosion was strengthened by farming activities and more CO<sub>2</sub> was consumed in the deep soil, which may be due to higher CO<sub>2</sub> levels and acidity caused by farming. Therefore, the decreased CO<sub>2</sub> concentrations of T<sub>2g</sub> and P<sub>1m</sub>(q) should be more than the calculated values, when farming activities are considered. The decreased CO<sub>2</sub> concentration in different farmland profiles is remarkably distinguishable at different sites, even on their same stratigraphic units (Table 5). It seems that the degree of human activity and the quantities of imported or exported energy determine the corrosion to some degree.

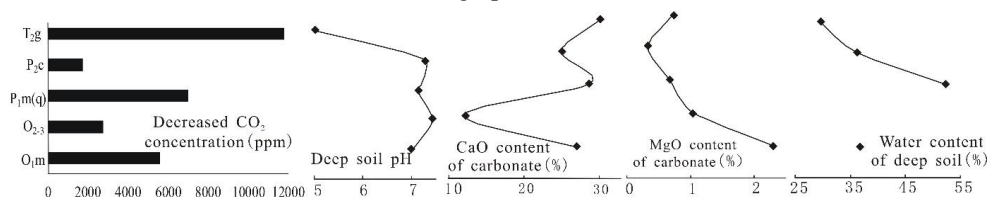
Several parameters, such as CaO and MgO contents of carbonate, water content and pH of the overlying soil, were determined to address some natural factors affecting de-creased CO<sub>2</sub>



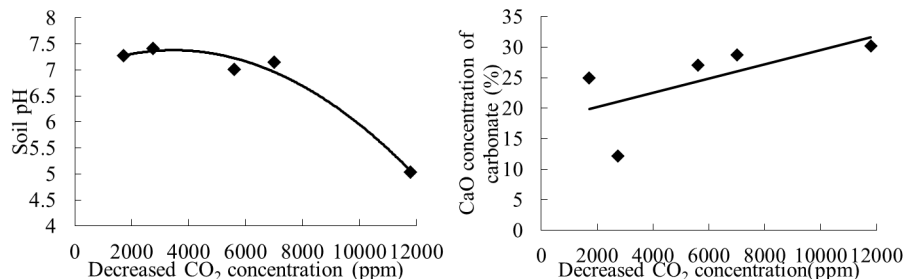
384 concentration. The parameters are shown in Fig. 11. Deep soil-pH is negatively correlated with  
 385 decreased CO<sub>2</sub> concentration, and the stronger the soil acidity, the more the decreased CO<sub>2</sub>  
 386 concentration. Water content of deep soil does not impose effort to corrosion. CaO content of carbonate  
 387 carbonate is positively correlated with the de-creased CO<sub>2</sub> concentration, and the more pure the  
 388 CaCO<sub>3</sub> in carbonate rock, the stronger is the corrosion. MgO content of carbonate is not  
 389 correlated with corrosion, which indicates that it is CaCO<sub>3</sub> corrosion and not that of MgCO<sub>3</sub>  
 390 consuming soil CO<sub>2</sub>. Simulation by SPSS software results in an equation ( $y = -3E - 08x^2 + 0.0002x + 6.976$ ) of decreased CO<sub>2</sub> concentration and soil pH with a multiple regression  
 391 coefficient  $R^2 = 0.9779$ , and a second equation ( $y = 0.0012x + 17.857$ ) of decreased CO<sub>2</sub> level and  
 392 CaO content of carbonate with a multiple regression coefficient  $R^2 = 0.4191$  (Fig. 12). A field  
 393 experiment of carbonate corrosion in the southern part of Guizhou (Nie et al. 1984), a laboratory  
 394 simulation using citric acid to corrode limestone (Cao et al., 2001), and an experimental study on  
 395 the stability of CaCO<sub>3</sub> and MgCO<sub>3</sub> under acid rain conditions (Teir et al. 2006) led to the  
 396 conclusion that corrosion is related closely with soil acidity and carbonate purity. The calculated  
 397 results can support the same conclusion and accord well with their studies, and can also easily be  
 398 confident.



400  
 401 Figure 10. The decreased CO<sub>2</sub> concentration in farmland and natural soil of the same  
 402 stratigraphic unit.



403  
 404 Figure 11. Relationship of the decreased CO<sub>2</sub> concentration and deep soil pH, water content,  
 405 CaO and MgO contents of carbonate.



406  
 407 FIG. 12. Correlation analysis of soil pH, CaO of carbonate and decreased CO<sub>2</sub> concentration.



#### 408 **4 Discussion and conclusions**

409 It is not surprising that soil CO<sub>2</sub> concentration decreases in the deep layers over carbonate  
410 bedrock areas, especially at the bottom of soil profiles, as has been observed by many  
411 experiments (Buyanovsky and Wagner, 1983; Li et al. 1995; Xu and He, 1996; Liang et al.  
412 2003), and was now supported by this paper. The explanation by some studies (Li et al., 1995)  
413 that decreased CO<sub>2</sub> is caused by decreased microbe or root respiration in deep soil, is challenged  
414 by our data. At first, one important reason leading to the earlier conclusion lies perhaps in the  
415 lack of comparative analyses of soil CO<sub>2</sub> levels in carbonate and non-carbonate areas. The  
416 underlying foundation of soluble carbonate in carbonate areas was not taken into consideration,  
417 and, most important, there was no proof or data to support this idea. Secondly, there is no  
418 decrease of CO<sub>2</sub> in soil profiles of non-carbonate areas (mudstone, basalt, shale or siltstone  
419 areas), also it seems to be reasonable to expect CO<sub>2</sub> decrease by lower microbe or root  
420 respiration rates in deep soil layers of both carbonate or non-carbonate areas. Thirdly, decrease  
421 of soil CO<sub>2</sub> takes place in 20-30 cm soil layers, and even from the soil surface in some profiles,  
422 so it may be unreasonable to attribute CO<sub>2</sub> decrease to microbe respiration in such shallow  
423 occurrences.

424 Additionally, soil profile CO<sub>2</sub> only decreases in carbonate areas, and SOC content is  
425 positively correlated with soil CO<sub>2</sub> concentration in non-carbonate areas ( $R^2=0.67-0.85$ ),  
426 although there is no significant correlation at some profiles because soil CO<sub>2</sub> is not only related  
427 with organic carbon, but also with other factors, such as root respiration. Soil CO<sub>2</sub> and organic  
428 carbon in different depths of carbonate areas are positively correlated with low correlation  
429 coefficients, but not in soil profiles of these carbonate areas. This means that organic carbon  
430 cannot be responsible for the decreased CO<sub>2</sub> concentrations. Furthermore, CO<sub>2</sub> consumed by  
431 carbonate corrosion leads to uncorrelated re-relationship between soil CO<sub>2</sub> and organic carbon  
432 levels in carbonate areas. Soil profile pH in carbonate areas always suddenly and sharply  
433 decreases at the depth of CO<sub>2</sub> decrease, and this can be explained well by carbonate corrosion.  
434 Analysis of  $\delta^{13}\text{C}$  isotope, which mixes into the CO<sub>2</sub> in deep soil layers of carbonate bedrock  
435 areas (dolomite or limestone) also demonstrates that there is another carbon source, whose  $\delta^{13}\text{C}$   
436 level is more than -14‰. In soil of clay-stone areas, however, soil CO<sub>2</sub> and soil organic carbon  
437 have the same  $\delta^{13}\text{C}$  value. This provides strong evidence that carbonate corrosion occurs, and  
438 thus deep soil CO<sub>2</sub> is consumed in carbonate areas. Simply stated, our work strongly indicates  
439 that carbonate corrosion leads to the decrease of soil profile CO<sub>2</sub> concentration in areas with  
440 carbonate bedrock.

441 Further, a mathematical model of soil CO<sub>2</sub> transfer was developed, showing that soil CO<sub>2</sub>  
442 concentration can be roughly expressed as a linear or parabolic increase with soil depth. The  
443 linear or parabolic increase can be demonstrated, strongly supported by both field data and the  
444 models. Soil CO<sub>2</sub> concentration data, collected in non-carbonate areas or in the surface soil of  
445 carbonate areas, provide additional confirmation. In the deep soil of carbonate areas, however,  
446 especially at the rock-soil interface, the simulated values are always higher than the field  
447 measurements. All of these points may also indicate that carbonate corrosion occurs in the deep  
448 soil, and that apart of soil CO<sub>2</sub> is consumed by carbonate corrosion. In addition, the decreased  
449 CO<sub>2</sub> concentration caused by carbonate corrosion can be evaluated by the subtraction of  
450 measured and simulated CO<sub>2</sub>. The decreased CO<sub>2</sub> concentration is related closely to deep soil  
451 pH and CaO content of carbonate rock (correlation coefficients, respectively,  $R^2=0.97$  and  $0.41$ ),  
452 together with farming activities, but not with deep soil water content and MgO content of  
453 carbonate. These results and conclusions can be supported by experiments, and are widely  
454 accepted by karst scholars, who add validity to our results and conclusions.

455 The carbon cycle in karst areas has attracted big attention because of the imbalance of the





456 global carbon cycle, and in recent years there has been a search to resolve the missing sink  
457 related to the absorbing and releasing of carbon in  $\text{CaCO}_3$  systems (Jiang and Yuan, 1999).  
458 Experiments and calculations indicate that  $1.774 \times 10^7$  t of carbon are absorbed by karstification  
459 in China, and that  $2.2 \times 10^8 \sim 6.08 \times 10^8$  t of carbon are drawn back from the atmosphere  
460 worldwide every year (Jiang and Yuan, 1999). It is obviously significant with regard to the  
461 increasing atmospheric temperature. Soil, as an important carbon storage area, is of great  
462 importance to atmospheric  $\text{CO}_2$  concentration, and slight variations may impose great effects  
463 on global carbon cycle. Several factors affecting soil  $\text{CO}_2$  concentration have been discussed,  
464 such as environmental ones (soil temperature, moisture, water content, etc.), microbe activities,  
465 and human activities, but no published details about the effect of carbonate corrosion on soil  $\text{CO}_2$   
466 concentration can be found. Our study argues that deep soil  $\text{CO}_2$  concentrate in carbonate areas  
467 is obviously decreased, especially at the rock-soil interface, and that this is mainly caused by  
468 carbonate corrosion. If this conclusion is correct, then naturally the atmospheric  $\text{CO}_2$  levels in  
469 carbonate areas should be affected by the corrosion, and this should be very significant in the  
470 hunting for the “missing sink”.

471

472 **Author contributions.** CQ developed the work and wrote the paper.

473

474 **Competing interests.** The author declare that he has no conflict of interest

475

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#### 483 **References**

- 484 Bajracharya, R.M., Lai, R., and Kimble, J. M.: Erosion effects on carbon dioxide concentration and carbon  
485 flux from an Chio Alfisol, *Soil Sci. Soc. Am. J.*, 64, 694-700, 2000.
- 486 Buyannovsky, G.A., and Wagner, G. H.: Annual cycles of carbon dioxide level in soil air, *Soil Sci. Soc. Am.*,  
487 47, 1139-1145, 1983.
- 488 Callendar, G. S.: The artificial production of carbon dioxide and its influence on temperature, *Q.J.R. Meteorol*  
489 *Soc.*, 64, 223-240, 1938.
- 490 Cao, J.H., Pan, G. X., and Yuan, D. X.: Simulation experiments on dissolution of calcite by citric and its  
491 karst importance, *Carsologica Sinica* (in Chinese), 20(1), 1-4, 2001.
- 492 Chen, Q.Q., Sun, Y.M., Shen, C. D., Peng, S. L., Yi, W. X., Jiang, M. T., and Li, Z. A.: Quantitative study  
493 on organic matter turnover characteristics of mountainous soil profiles in the subtropical area, south  
494 China, *Scientia Geographical Sinica* (in Chinese), 22(2), 196-201, 2002.
- 495 Collin, M., and Rasmuson, A.: A comparison of gas diffusivity models for unsaturated porous media, *Soil*  
496 *Sci. Soc Am.J.*, 52, 1559-1565, 1988.
- 497 Dai, W.H., Wang, Y. Q., Huang, Y., Liu, J., and Zhao, L.: Seasonal dynamic of  $\text{CO}_2$  concentration in Lou  
498 soil and impact by environmental factors, *Acta Pedologica Sinica* (in Chinese), 41(5), 827-831, 2004.
- 499 Fearnside, P.M.: Brazil’s Amazonian forest carbon: the key to Southern Amazonian’s significance for global  
500 climate, *Reg. Environ. Change*, 18, 47-61, 2018.
- 501 James, M.D., and George, A. B.: Spatial and temporal variations in temperate forest soil carbon dioxide  
502 during the non-growing season, *Earth Surf. Proc. Land*, 16(5), 411-426, 1991.
- 503 Jeremy, D. O., Timothy, W. L., and Christopher, M. L.: Quantifying the missing sink for global organic carbon  
504 burial during a Cretaceous oceanic anoxic event, *Earth Planet Sci Lett*, 499, 83-94, 2018.
- 505 Jiang, Z.C., and Yuan, D. X.: Dynamics features of the epikarst zone and their significance in environments



- 506 and resources, *Acta Geoscientia Sinica* (in Chinese), 20(3), 302-308, 1999.
- 507 Li, B., and Yuan, D. X.: Carbon cycle of epikarst in carbonate areas. In: Earthquake Center. carbonate and  
508 environment (Vol.1). Earthquake Press (in Chinese), Beijing, 1-15, 1995.
- 509 Liang, F.Y., Song, L. H., Tang, T., and Wang, J.: Microbial production of CO<sub>2</sub> in red soil in stone forest  
510 national park, *Carsologica Sinica* (in Chinese), 22(1), 6-11, 2003.
- 511 Malak, M.T., Nancy, J. H., Akihiro, K., and Evans, R. D.: Elevated CO<sub>2</sub> changes soil organic matter  
512 composition and substrate diversity in an arid ecosystem, *Geoderma*, 330(15), 1-8, 2018
- 513 Nie, Y.P.: A Preliminary study and test on the dissolution of carbonate rocks in south Guizhou province.  
514 *Carsologica Sinica* (in Chinese), 1, 39-45, 1984.
- 515 Pan, G.X., Cao, J. H., He, S. Y., Teng, Y. Z., and Xu, S.Y.: Sink effect of karst soil system on atmospheric  
516 CO<sub>2</sub>: evidence from field observation and simulation experiment, *Earth Science Frontiers* (in Chinese),  
517 7(4), 580-587, 2000.
- 518 Rustad, L.E., Untington, H.T.G., and Boone, R.D.: Controls on soil respiration: implications for climate  
519 change, *Biogeochemistry*, 49, 1–6, 2000.
- 520 Solomon, D.K., and Cerling, T. E.: The annual carbon dioxide cycle in a montane soil: observation, modeling  
521 and implications for weathering, *Water Resour Res*, 23, 2257-2265, 1987.
- 522 Teir, S., Eloneva, S., Fogelholm, C., and Zevenhoven, R.: Stability of calcium carbonate and magnesium  
523 carbonate in rainwater and nitric acid solutions, *Energ. Convers. Manage*, 47, 3059-3068, 2006.
- 524 Warren, W.W., and Michael, J.P.: Origin and distribution of carbon dioxide in the unsaturated zone of the  
525 southern high plains of texas, *Water Resour Res*, 20(9), 647-659, 1984.
- 526 Xu, S.Y., and He, S. Y.: The CO<sub>2</sub> regime of soil profile and its drive to dissolution of carbonate rock,  
527 *Carsologica Sinica* (in Chinese), 18(1-2), 50-57, 1996.
- 528 Yoyam, R., and Dani, O.: Stochastic modeling of unsaturated flow in heterogeneous soil with water uptake  
529 by plant roots: the parallel columns model, *Water Resour Res*, 29(3), 619-631, 1993.
- 530 Zeng, S.W., and Zheng, L. P.: Mathematical model of soil CO<sub>2</sub> transference in karst area, *Shanghai*  
531 *Environmental Sciences* (in Chinese), 21(12), 712-715, 2002.