



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 CO₂ levels, and
51 there is no detail documents detailing the soil CO₂ concentration and its relationship with
52 global climate change in karst areas. Several problems puzzle us: Is there any difference
53 between soil profile CO₂ 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 CO₂ 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 CO₂ 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 CO₂ concentration in karst areas
61 and its potential effect on global carbon cycles, soil profile CO₂ 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 CO₂ concentration in carbonate and non-carbonate areas; (2) discuss the relationship
65 between soil CO₂ concentration and other parameters, and clarify the effect of carbonate
66 corrosion on soil CO₂; (3) develop a mathematical model of soil CO₂ transfer and
67 quantitatively evaluate the effect scale of carbonate corrosion on soil CO₂ 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**

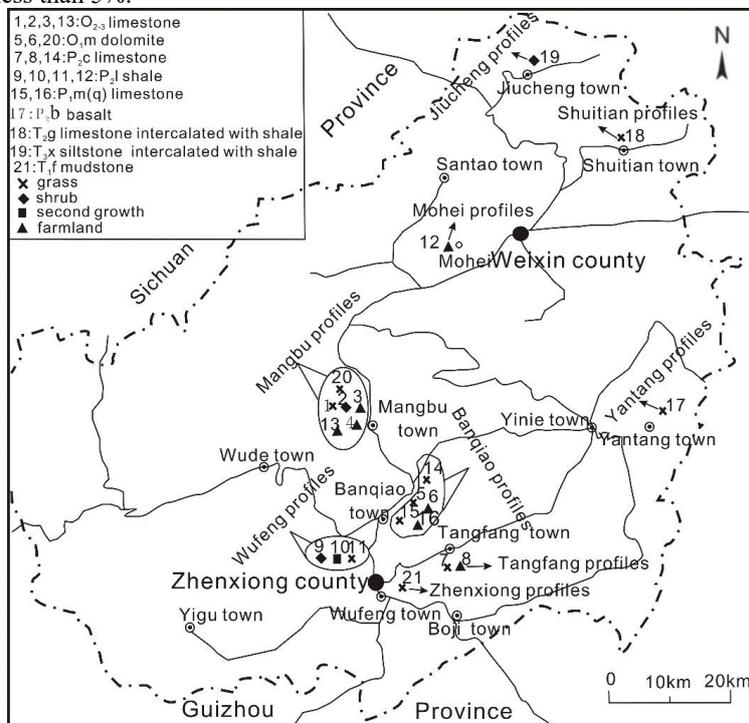
87 In order to comprehensively reveal characteristics of soil CO₂ concentration in a karst area,
88 sample sites were selected in such a way as to cover different stratigraphic units and different
89 types of vegetation. Meanwhile, profiles in carbonate and non-carbonate areas were both
90 measured. Totally, CO₂ 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 (O₁), the Middle and Upper
93 Ordovician Baota Formation (O₂₋₃), the Lower Permian Xixia and Maokou Formations



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

99 CO₂ 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 CO₂ 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 CO₂ and gathering organic carbon samples (1-Mangbu O₂₋₃ grass, 2-Mangbu O₂₋₃ shrub, 3-
 113 Mangbu O₂₋₃ farmland, 4-Mangbu O₂₋₃ farmland, 5-Banqiao O_{1m} grass, 6-Mangbu O_{1m} farmland, 7-Tangfang P_{2c} grass, 8-
 114 Tangfang P_{2c} farmland, 9-Wufeng P_{2l} shrub, 10-Wufeng P_{2l} second growth, 11-Wufeng P_{2l} grass, 12-Mohei P_{2l} farmland, 13-
 115 Mangbu O₂₋₃ farmland, 14-Banqiao P_{2c} grass, 15-Banqiao P_{1m}(q) grass, 16-Banqiao P_{1m}(q) shrub, 17-Tangfang P_{2β} grass, 18-
 116 Shuitian T_{2g} shrub, 19-Jiucheng T_{3x} shrub, 20-Mangbu O_{1m} grass, 21-Zhenxiong T_{1f} grass).



117 **3 Results**

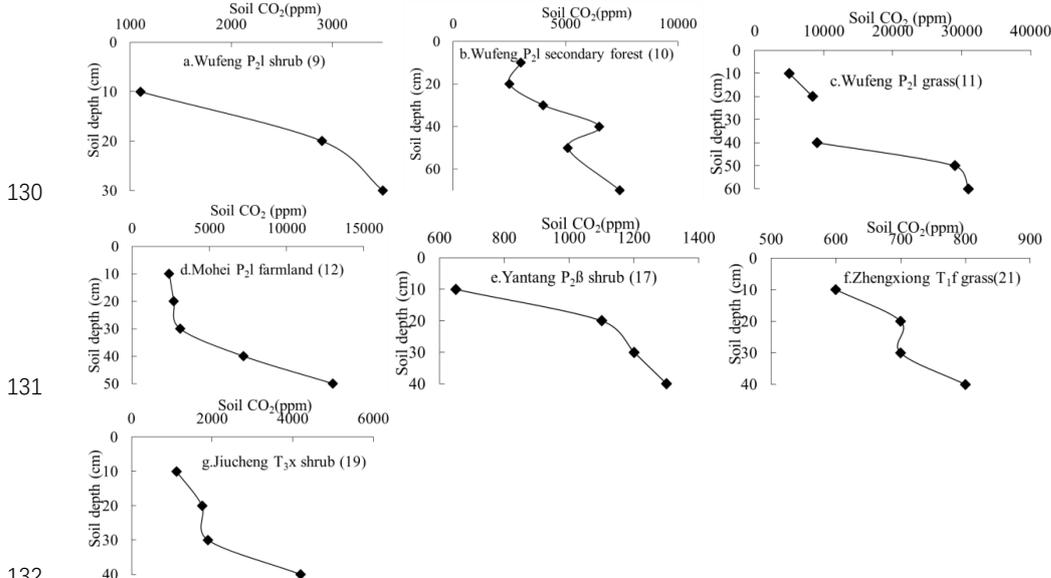
118 **3.1 Varying CO₂ concentration characteristics of soil profiles**

119 Fig. 2 shows soil profile CO₂ concentrations varying with soil depths in 7 non-carbonate
 120 areas. The data show a distinct tendency of increasing CO₂ concentration with soil depth, with
 121 R²=0.8-0.92 (Table 1).The reasons may be the higher soil bulk density, more condensed soil
 122 pores, and difficulty of CO₂ diffusion in the deeper soil. In fact, soil profile CO₂ 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 CO₂ increases
 127 with soil depth in non-carbonate areas.

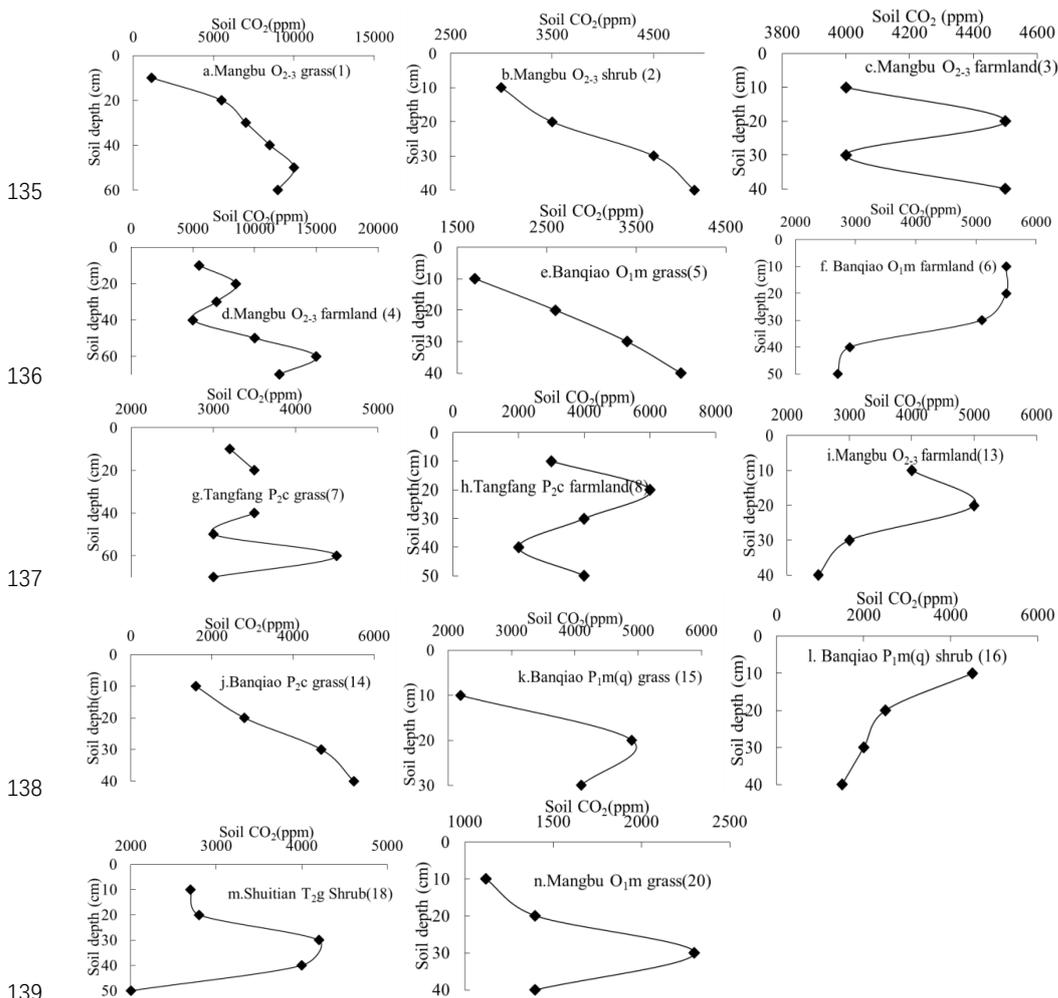
128 Table 1. Regression analysis of soil CO₂ concentration and profile depth in non-carbonate areas.

Profiles	Regression equation	R ²	P
Wufeng P ₂ l shrub (9)	$y = 0.0077x + 0.7692$	0.92	0.179
Wufeng P ₂ l second growth (10)	$y = 0.0099x - 10.595$	0.80	0.016*
Wufeng P ₂ l grass (11)	$y = 0.0015x + 11.527$	0.80	0.042*
Mohei P ₂ l farmland (12)	$y = 0.0031x + 12.239$	0.80	0.039*
Yantang P ₂ β grass (17)	$y = 0.0415x - 19.114$	0.85	0.077
Zengxiong T ₁ f grass (21)	$y = 0.15x - 70$	0.9	0.051
Jiucheng T ₃ 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 CO₂ concentration in non-carbonate areas
 133 (profile no. in brackets).
 134



139
 140 Figure 3. Varying characteristics of soil profile CO₂ concentration in carbonate areas (profile
 141 no. in brackets).

142 14 Soil profile CO₂ concentration with soil depth in carbonate areas was gained (Fig. 3). The
 143 results show a complex and inverse relationship between soil CO₂ and soil depth in carbonate areas.
 144 Most Soil profile CO₂ increases with soil depth in the upper sections, such as Mangbu O₂₋₃ grassy
 145 profile (Fig. 3a), Mangbu O₂₋₃ shrub profile (Fig. 3b), Mangbu O₂₋₃ farmland profile (Fig. 3d),
 146 Banqiao O_{1m} grassy profile (Fig. 3e), and Banqiao P_{2c} grassy profile (Fig. 3j). CO₂ concentrations
 147 decrease with soil depth when they increase from surface to a certain depth in Mangbu O₂₋₃
 148 farmland profile (Fig. 3i), Banqiao P_{1m(q)} grassy profile (Fig. 3k), Gaotian T_{2g} grassy profile (Fig.
 149 3m) and Mangbu O_{1m} grassy profile (Fig. 3n). Those of Banqiao O_{1m} farmland profile (Fig. 3f)
 150 and Banqiao P_{1m(q)} shrub profile (Fig. 3l) even decrease all along with soil depth, and two
 151 farmland profiles of Mangbu O₂₋₃ (Fig. 3c) and Tangfang P_{2c} (Fig. 3h) fluctuate, and have no
 152 regularity due to the effect of human farming activities. Generally, Except Mangbu O₂₋₃ farmland
 153 profile (Fig. 3.c) and Tangfang P_{2c} farmland profile (Fig. 3.h), which are disturbed by farming,
 154 CO₂ 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 CO₂ concentration with soil depth,
 156 because sequestration of deep soil CO₂ 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 CO₂ is
 159 consumed and CO₂ sequestration occurs, and there is no linear relationship between CO₂
 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 CO₂ concentration
 162 reaches a peak at a certain depth, and then decreases with soil depth in carbonate areas. CO₂
 163 concentration in Banqiao O_{1m} farmland profile (Fig. 3.f) and Banqiao P_{1m(q)} 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 CO₂ concentration in surface layers higher than those
 166 in bottom layers are scarcely documented in carbonate areas.

167 3.2 Relationship between soil profile CO₂ concentration and soil organic carbon

168 Soil organic carbon (SOC) was analyzed in a part of the profiles, corresponding with CO₂
 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 CO₂ concentration and SOC in shale areas is listed in
 172 Table 2. It shows a negative correlation, with high regression coefficients (R²= 0.67-0.85). An
 173 exception of 0.29 occurs in Wufeng P_{2l} secondary forest, which possibly is caused by stronger
 174 root respiration and a higher ratio of CO₂ generated by the roots. Therefore, SOC is directly
 175 affected by the release of soil CO₂, 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 CO₂
 177 concentration don't show significant regression with SOC, which means which means that soil
 178 CO₂ concentration is not only related to SOC, but also to soil respiration and microbe activities.
 179 Correlation analysis of soil CO₂ and organic carbon in carbonate areas is shown in Table 3, and
 180 the regression coefficients are irregular, and even those of Banqiao O_{1m} farmland profile and
 181 Banqiao P_{1m(q)} shrub profile are positive. Previous studies in Shilin, Lunan City and in
 182 Guizhou Plateau also showd no correlation between CO₂ concentration and SOC (Liang et al.
 183 2003).

184 Table 2. Correlation analysis of soil CO₂ and soil organic carbon in shale areas of karst.

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

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 186

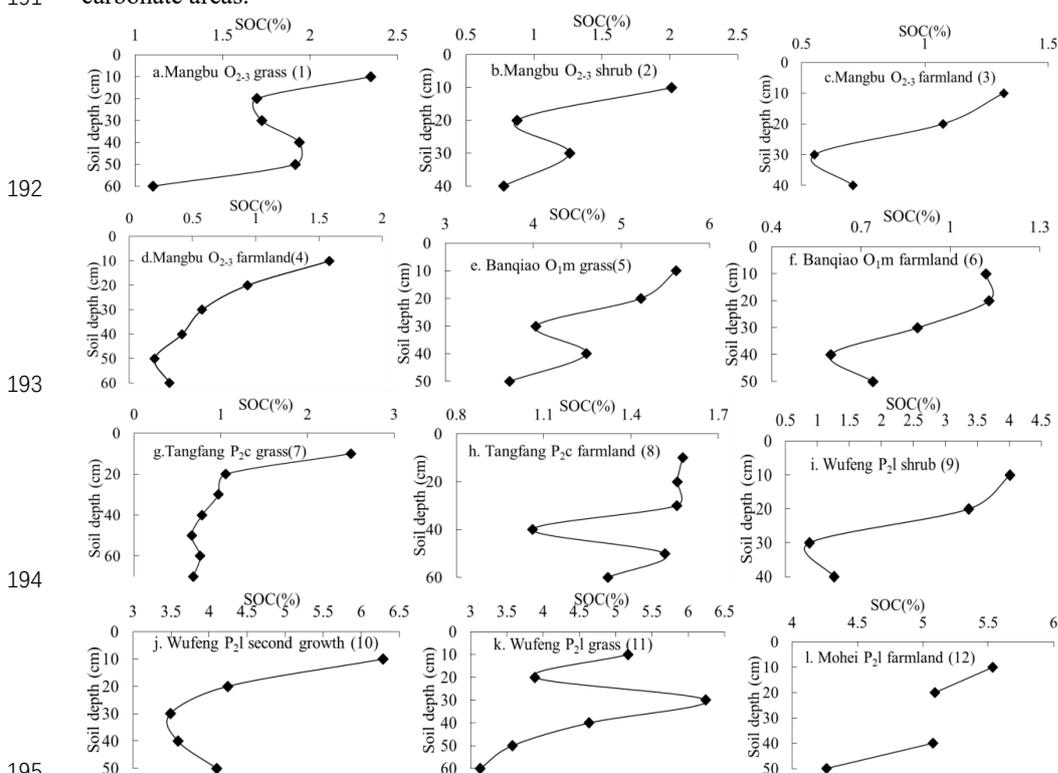
Table 3. Correlation analysis of soil CO₂ and soil organic carbon in carbonate areas of karst.

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

187 What is the reason of poor relationship between soil CO₂ and SOC in carbonate areas? The
 188 possible answer may be carbonate corrosion. By means of corrosion, deep soil CO₂ 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 CO₂ levels in
 191 carbonate areas.

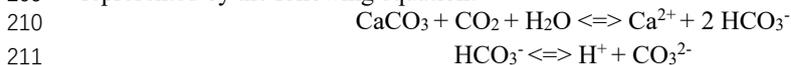


195
 196 Figure 4. Varying characteristics of soil profile organic carbon in karst areas (profile no. in
 197 brackets)

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 CO₂ and SOC. Conversely, in carbonate areas,
 203 pH generally increases with soil depth in the surface layer except in the Banqiao O_{1m} farmland
 204 profile. Moreover, from Figs. 3 and 5 it is evident that soil CO₂ concentration decreases where
 205 soil pH decreases too, and even CO₂ level in the Banqiao O_{1m} 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 CO₂ concentration in carbonate areas is related closely to soil pH.

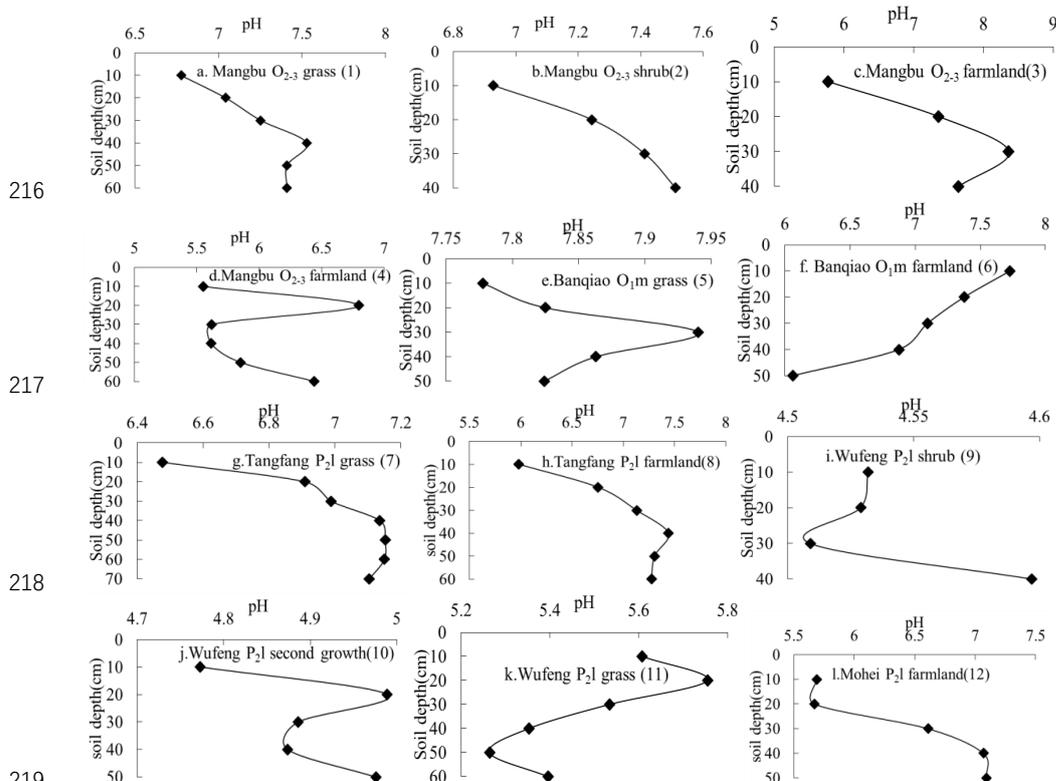
208 Chemically, with soil water and soil CO₂ added together, carbonate corrosion can be
 209 represented by the following equation:



212 By means of this reaction, deep soil CO₂ 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 CO₂ 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).
 221

222 3.4 Carbonate corrosion and the global carbon cycle

223 Many studies have observed that soil CO₂ 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 CO₂ in non-carbonate
 229 areas is found, and, furthermore, the depths with decreasing CO₂ concentrations were
 230 distinguishable in different profiles, even at only 20-30 cm depths. The decreased CO₂
 231 concentration could be attributed to decreased microbe numbers or root respiration at such depths.
 232 By comparative analysis of soil CO₂ 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.

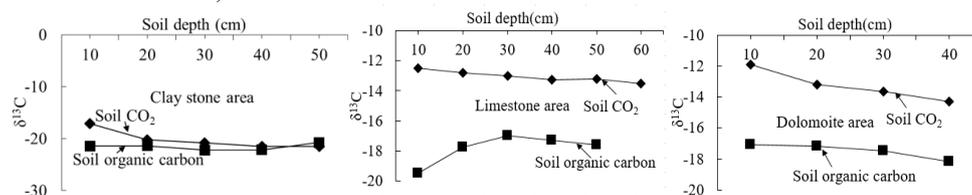
235 Soil CO₂ and SOC in non-carbonate areas have a good negative correlation, with correlation
 236 coefficients $R^2 = 0.67-0.85$, although significance is not clear because soil CO₂ is determined by
 237 not only organic matter but also by other factors, such as root respiration and microbe activities.
 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 CO₂ 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 CO₂ 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 CO₂, and
244 this may imply that H⁺ generated by carbonate corrosion mixes into the deep soil increasing
245 soil acidity.

246 Previous work has determined the imbalance between soil CO₂ produced and released in
247 carbonate areas. Pan et al (2000) observed and simulated field data in Yaji, Guangxi Province,
248 concluding that CO₂ 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 CO₂. The data account for an absorbing coefficient of 22-130 g/m²·a.

251 Isotopes can effectively trace the carbon source of soil CO₂. Fig. 6 reflects the δ¹³C value
252 of soil CO₂ and SOC overlying different bedrock according to data from Li et al. (1995). It
253 shows that in deep soil, CO₂ has a higher δ¹³C 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 CO₂ 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 δ¹³C should be more than -14‰. CaCO₃ in carbonate has δ¹³C values of -
258 3‰~+1‰. It must, therefore, possibly be recognized that carbon in CaCO₃ of carbonate bedrock
259 mixes into soil CO₂, since the corrosion reaction is reversible.



260
261 Figure 6. Varying δ¹³C of soil CO₂ 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 CO₂ concentration at the rock-soil interface in
268 carbonate areas. As a result, the decreased CO₂ level caused by corrosion will, of course,
269 impose effects on atmospheric CO₂ 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 CO₂ transfer

273 In this model, only the molecular diffusion of CO₂ 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 CO₂ diffusion, and
276 temperature gradient was neglected because of its low contribution (0.2-0.4%) to CO₂ flow.
277 Therefore, the transport of soil CO₂ 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, θ_a is the air content, θ_w is the water content, C_a is the gaseous CO₂ concentration, J_{da} is the
 282 gaseous CO₂ flow due to diffusion, J_{dw} is the dissolution CO₂ flow due to diffusion, J_{ca} is the
 283 gaseous CO₂ flow due to convection, J_{cw} is the dissolution CO₂ 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 CO₂ diffusion coefficient in soil substrate, D_w is the dissolution CO₂
 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 CO₂ 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 CO₂ diffusion coefficient in air at the reference temperature T^0 .

299 For the carbon source, the rate of CO₂ 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 CO₂ at depth of z , S_0 is the CO₂ concentration in the surface soil, z
 303 is the soil depth, and z_s is the depth gradient. It also considered the CO₂ 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 CO₂ 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 CO₂
 317 concentration (C_a) 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 θ_a , θ_w , S₀, T, and D_a of different
 320 profiles.

321 That means, it can be expressed as a linear or parabolic relationship of soil profile CO₂
 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 CO₂ concentration
 325 and soil depth.

3.6 The rough evaluation of CO₂ decreased by corrosion

327 SPSS software was used to simulate the curve of measured soil CO₂ concentration and soil depth
 328 in non-carbonate areas (Fig. 7 and Table 4), resulting in parabolas with multiple regression
 329 coefficients R²=0.8-1. Multiple regression coefficient of P_{2c} 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 CO₂ concentration.

333 Table 4. Simulated equation of measured soil CO₂ concentration and soil depth in non-carbonate areas.

Profiles	Equations	R ²	P	Simulated depth	Simulated equation by exponents
P _{2l} shrub (9)	$y = -6x^2 + 360x - 1900$	1	-	0-30 cm	$y = 702.44e^{0.0579x} (0.8681)$
P _{2l} 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 _{2l} 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 _{2c} farmland (12)	$y = 10.5x^2 - 373x + 5320$	0.9914	0.0086	0-50 cm	$y = 1221.3e^{0.0436x} (0.8877)$
P ₂ 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 _{1f} shrub (21)	$y = -4E - 15x^2 + 6x + 550$	0.9	0.3162	0-40 cm	$y = 561.25e^{0.0086x} (0.8977)$
T _{3x} 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 R² of simulated exponent in brackets.

335 In carbonate areas, however, there is no linear or parabolic relationship between soil profile
 336 CO₂ 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 CO₂ concentration in the deep soil of carbonate areas, the CO₂
 339 concentration in the surface layer can be used and to predict the CO₂ 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 CO₂ is consumed by carbonate corrosion.

344 The method of subtraction of predicted and measured values can be used to evaluate the
 345 decreased CO₂ 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 CO₂ concentration of every stratigraphic unit
 348 can be gained by taking the average (Fig. 9).

349 Table 5. The evaluated results of the decreased CO₂ concentration in carbonate areas caused
 350 by carbonate corrosion.

Profiles	O ₂₋₃ grass (1)	O ₂₋₃ shrub (2)	O ₂₋₃ farmland (3)	O ₂₋₃ farmland (4)	O _{1m} grass (5)	O _{1m} farmland (6)	P _{2c} grass (7)	P _{2c} farmland (8)	O ₂₋₃ farmland (13)	P _{2c} grass (14)	P _{1m(q)} grass (15)	P _{1m(q)} shrub (16)	T _{2g} shrub (18)	O _{1m} grass (20)
Decreased CO ₂ 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 ₂ (%)	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

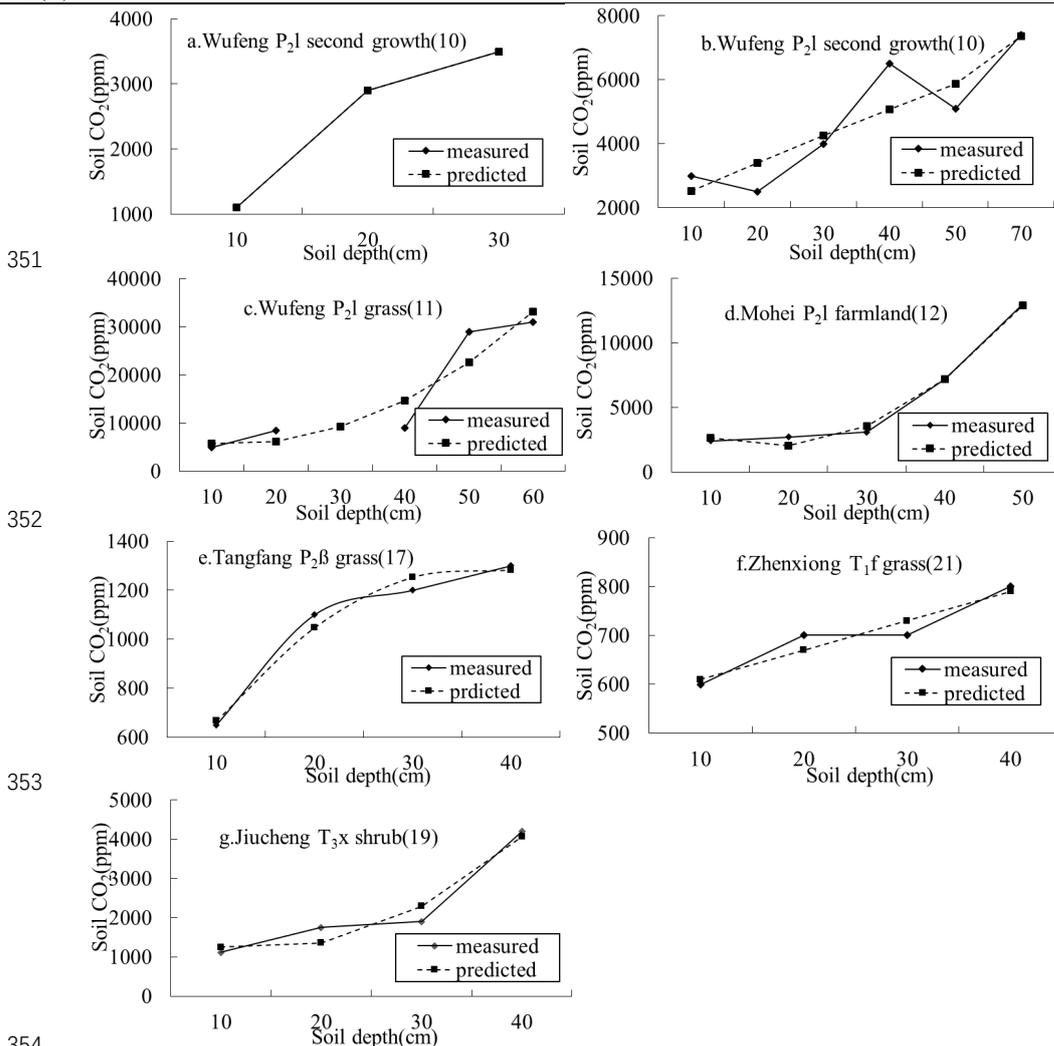
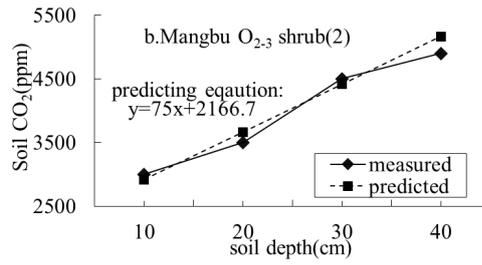
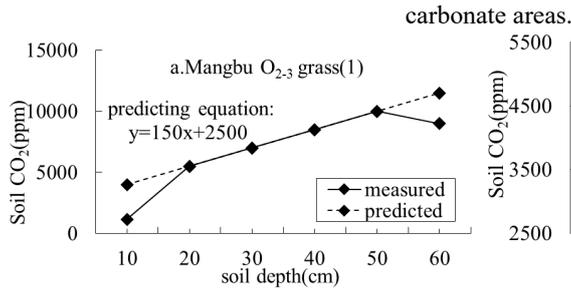


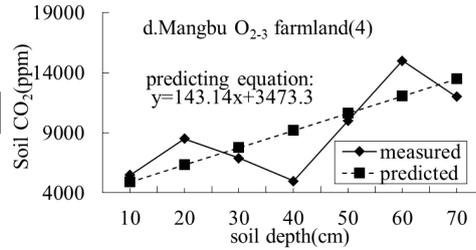
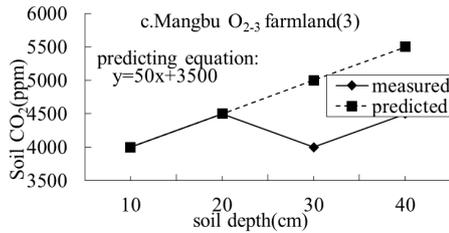
Figure 7. The measured and the simulated CO₂ concentrations of soil profiles in non-



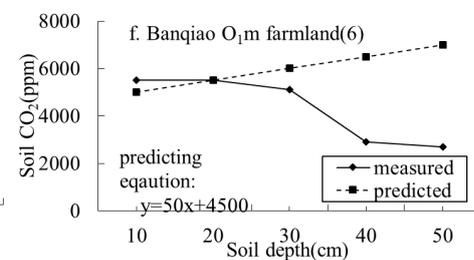
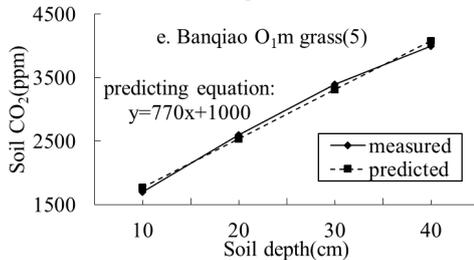
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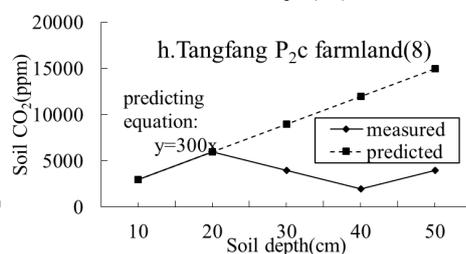
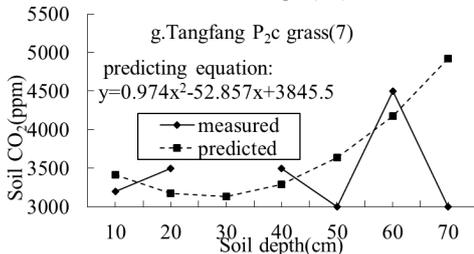
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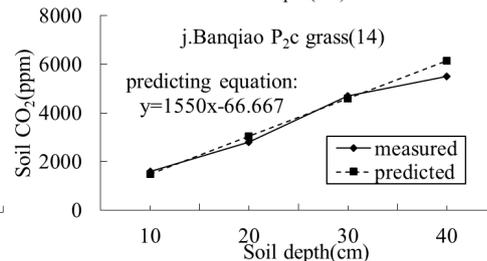
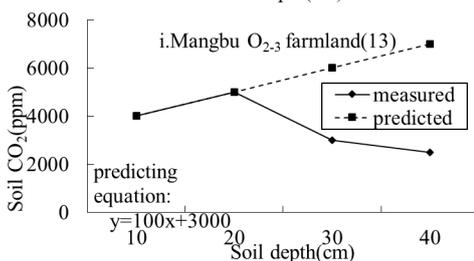
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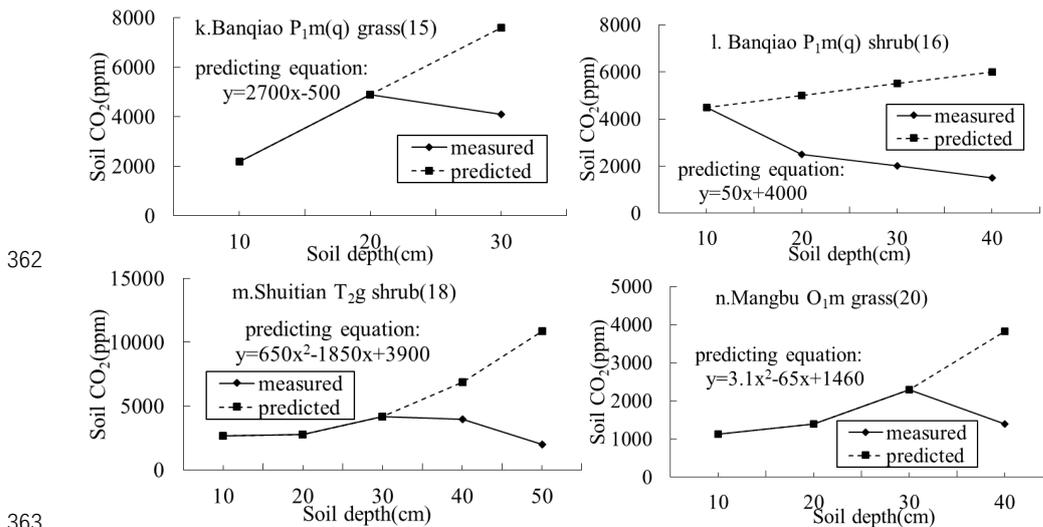
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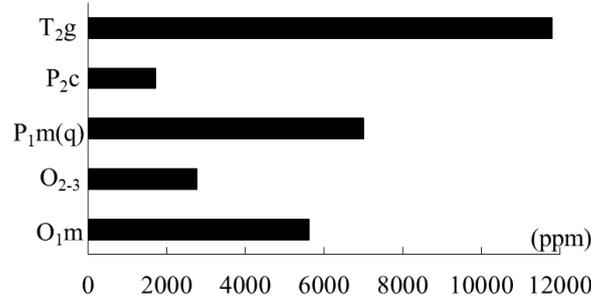


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Figure 8. The measured and predicted soil profile CO₂ concentrations in carbonate areas.



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Figure 9. The evaluation of the decreased CO₂ concentration caused by carbonate corrosion based on stratigraphic units.

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3.7 The main affecting factors of the decreased CO₂ concentration

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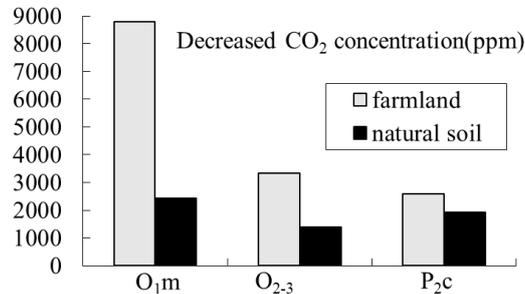
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Fig. 9 shows great dissimilarity of the decreased CO₂ concentration with different stratigraphic units in the following order: T_{2g}>P_{1m}(q)>O_{1m}>O₂₋₃>P_{2c}. Fig. 10 shows the calculated results of the decreased CO₂ concentration, respectively, in farmland and natural soil (grass and shrub) of the same stratigraphic unit. CO₂ concentration on T_{2g} and P_{1m}(q) farmland is lacking, but the comparative analysis of O_{1m}, O₂₋₃ and P_{2c} can demonstrate that the decrease of CO₂ in natural soil profiles is obviously less than that in farmland profiles. It is clear that corrosion was strengthened by farming activities and more CO₂ was consumed in the deep soil, which may be due to higher CO₂ levels and acidity caused by farming. Therefore, the decreased CO₂ concentrations of T_{2g} and P_{1m}(q) should be more than the calculated values, when farming activities are considered. The decreased CO₂ 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.

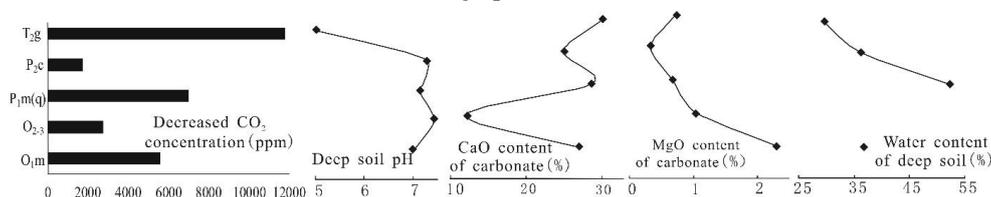
Several parameters, such as CaO and MgO contents of carbonate, water content and pH of the overlying soil, were determined to address some natural factors affecting de-creased CO₂



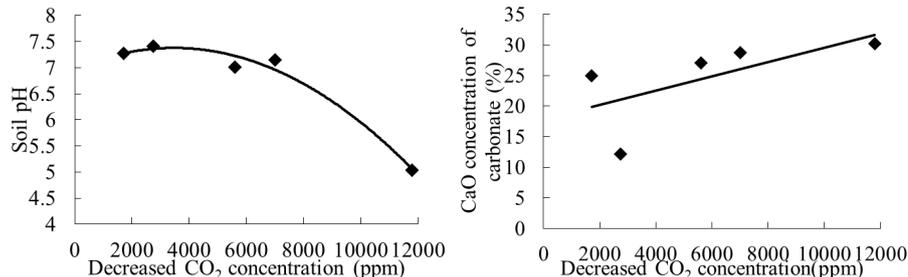
384 concentration. The parameters are shown in Fig. 11. Deep soil-pH is negatively correlated with
 385 decreased CO₂ concentration, and the stronger the soil acidity, the more the decreased CO₂
 386 concentration. Water content of deep soil does not impose effort to corrosion. CaO content of carbonate
 387 carbonate is positively correlated with the de-creased CO₂ concentration, and the more pure the
 388 CaCO₃ in carbonate rock, the stronger is the corrosion. MgO content of carbonate is not
 389 correlated with corrosion, which indicates that it is CaCO₃ corrosion and not that of MgCO₃
 390 consuming soil CO₂. Simulation by SPSS software results in an equation ($y = -3E - 08x^2 + 0.0002x + 6.976$) of decreased CO₂ 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 CO₂ 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 CaCO₃ and MgCO₃ 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 CO₂ concentration in farmland and natural soil of the same
 402 stratigraphic unit.



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 404 Figure 11. Relationship of the decreased CO₂ 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 CO₂ concentration.



408 **4 Discussion and conclusions**

409 It is not surprising that soil CO₂ 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 CO₂ 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 CO₂ 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 CO₂ in soil profiles of non-carbonate areas (mudstone, basalt, shale or siltstone
419 areas), also it seems to be reasonable to expect CO₂ 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 CO₂ 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 CO₂ decrease to microbe respiration in such shallow
423 occurrences.

424 Additionally, soil profile CO₂ only decreases in carbonate areas, and SOC content is
425 positively correlated with soil CO₂ concentration in non-carbonate areas ($R^2=0.67-0.85$),
426 although there is no significant correlation at some profiles because soil CO₂ is not only related
427 with organic carbon, but also with other factors, such as root respiration. Soil CO₂ 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 CO₂ concentrations. Furthermore, CO₂ consumed by
431 carbonate corrosion leads to uncorrelated re-relationship between soil CO₂ and organic carbon
432 levels in carbonate areas. Soil profile pH in carbonate areas always suddenly and sharply
433 decreases at the depth of CO₂ decrease, and this can be explained well by carbonate corrosion.
434 Analysis of $\delta^{13}\text{C}$ isotope, which mixes into the CO₂ 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 CO₂ 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 CO₂ is consumed in carbonate areas. Simply stated, our work strongly indicates
439 that carbonate corrosion leads to the decrease of soil profile CO₂ concentration in areas with
440 carbonate bedrock.

441 Further, a mathematical model of soil CO₂ transfer was developed, showing that soil CO₂
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 CO₂ 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 CO₂ is consumed by carbonate corrosion. In addition, the decreased
449 CO₂ concentration caused by carbonate corrosion can be evaluated by the subtraction of
450 measured and simulated CO₂. The decreased CO₂ 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 CaCO_3 systems (Jiang and Yuan, 1999).
458 Experiments and calculations indicate that 1.774×10^7 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 CO_2 concentration, and slight variations may impose great effects
463 on global carbon cycle. Several factors affecting soil 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 CO_2
466 concentration can be found. Our study argues that deep soil 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 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

476 **Acknowledgments.** The author express the heartfelt thanks to the staff of the Zhaotong Bureau of Sciences
477 and Technology, and the IGSNRR in gathering the samples, as well as Professor C B. Wood, Department of
478 Biology Faculty, Providence College, USA for correcting English grammar. This work was financially
479 supported by the Chinese National Key Natural Science Foundation (Grant No. 90202017), the Natural Science
480 Fund of Shandong Province (ZR2018MD012), 2017 Special Fund for Scientific Research of Shandong
481 Coalfield Geologic Bureau [2017(10)].

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