Characteristics of soil profile CO_2 concentrations in karst areas and its significance for global carbon cycles and climate change

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Abstract: CO_2 concentrations of 21 soil profiles were measured in Zhaotong City, Yunnan Province. The varying characteristics of soil profile CO_2 concentration are distinguishable between carbonate and non-carbonate areas. In non-carbonate areas, soil profile CO_2 concentrations increase and show significant positive correlations with soil depth. In carbonate areas, however, deep soil CO_2 concentrations decrease and have no significant correlations with soil depth. Soil organic carbon is negatively correlated with soil CO_2 concentrations in non-carbonate areas. In carbonate areas, such relationships are not clear. It means the special geological process in carbonate areas- carbonate corrosion- absorbs part of the deep soil profile CO_2. Isotope and soil pH data also support such process.

Mathematical model simulating soil profile CO_2 concentration was proposed. In non-carbonate areas, the measured and the simulated values are almost equal, while the measured CO_2 concentrations of deep soils are less than the simulated in carbonate areas. Such results also indicate the occurrence of carbonate corrosion and the consuming of deep soil CO_2 in carbonate areas. The decreased CO_2 concentration was roughly evaluated based on stratigraphic unit and farming activities. Soil pH and the purity of $CaCO_3$ in carbonate bedrock deeply affect the corrosion. The corrosion in carbonate areas decreases deep soil CO_2 greatly (accounting for 5.2-66.3%, with average of 36%), and naturally affects the soil CO_2 released into the atmosphere. Knowledge of this process is important for karst carbon cycles and global climate changes, and it may be a potential part of the "missing sink".

Key words: soil CO_2; carbonate corrosion; global carbon cycles; karst areas

1 Introduction

In recent years, there has been increasing world-wide concern about carbon exchange among the atmosphere, the ocean and terrestrial ecosystems. Specifically, there have been ongoing questions regarding the problem of carbon flux, or carbon source versus carbon sink. The missing carbon sink has puzzled scientists since Callendar (1938) presented the imbalance of absorbed and released CO_2. The missing sink reaches as much as 1.7 Pg, accounting for as much as 24% of total carbon (Sundquist, 1993). There are differing viewpoints regarding the spatial distribution and absorption strength of the missing sink in terrestrial ecosystems (Fan et al. 1998; Potter and Klooster, 1999). The carbon cycle in karst areas has attracted great interest due to the absorbed and released CO_2 via carbonate corrosion and its share in regulating atmospheric CO_2 (Li and Yuan, 1995; Martin et al. 2013). Therefore, some scholars have looked for the "missing sink" within the absorbed and released carbon in karst systems, and the estimated values reach a dominating part (almost 1/3) of the missing sink (Jiang and Yuan, 1999).

Soil carbon, with storage of 1300-2000 Pg C, and as much as 2-3 times of vegetation storage, plays an important role in maintaining carbon balance (Fearnside, 2018), so that a slight change imposes a great effect on the atmospheric CO_2 concentration. Several factors

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48 affecting soil CO_2 concentration, such as environmental factors (soil temperature, moisture and
49 water content etc) and human activities, have been widely discussed (Bajracharya et al. 2000;
50 Dai et al. 2004; Owens et al. 2018; Fearnside, 2018). In karst areas, however, the important
51 geological process, carbonate corrosion, has been largely ignored in discussions of soil CO_2
52 levels, and there is no documents detailing the soil CO_2 concentration and its relationship
53 with global climate change in karst areas. Several problems puzzle us: Is there any difference
54 between soil profile CO_2 concentrations in carbonate areas and those in non-carbonate areas? If
55 so, is the difference caused by carbonate corrosion? By how much is it affected? Moreover,
56 studies have revealed that there is CO_2 unbalance between carbon released into atmosphere and
57 that produced by organic matter in carbonate areas (Jiang and Yuan et al. 1999; Pan et al.
58 2000), but there is no reasonable explanation. Lack of research work on these questions
59 restricts our understanding about soil CO_2 transfer, limits further study of the mechanisms, and
60 impedes learning of its significance for the carbon cycle.

61 In order to understand the varying characteristics of soil CO_2 concentration in karst areas
62 and its potential effect on global carbon cycles, soil profile CO_2 was measured, and samples
63 of soils and rocks were gathered in the typical karst area of Zhaotong city, Yunan Province,
64 China. The objectives of this paper are to: (1) analyze comparatively the varying characteristics
65 of the soil profile CO_2 concentration in carbonate and non-carbonate areas; (2) discuss the
66 relationship between soil CO_2 concentration and other parameters, and clarify the effect of
67 carbonate corrosion on soil CO_2; (3) develop a mathematical model of soil CO_2 transfer and
68 quantitatively evaluate the effect scale of carbonate corrosion on soil CO_2 concentration, and
69 discuss its significance for global carbon cycle and climate change.

70 2 Study area and methods

71 2.1 Study area

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

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

86 2.2 Sampling and analyzing methods

87 In order to comprehensively reveal characteristics of soil CO_2 concentration in karst area,
88 soil profiles of different stratigraphic units and vegetation types were selected. And profiles
89 in carbonate or non-carbonate areas were both involved. Totally, CO_2 concentration of 21
90 soil profiles and organic carbon of 12 soil profiles were analyzed. The profile sites are shown in
91 Fig. 1, and among these, profiles in carbonate areas include the Lower Ordovician Meitan
92 Formation (O_1), the Middle and Upper Ordovician Baota Formation (O_{2-3}), the Lower
93 Permian Xixia and Maokou Formations ($P_1m(q)$), the Upper Permian Changxing Formation

94 (P2c), and the Middle Triassic Guanling Formation (T2g). Sites in non-carbonate areas include
95 Middle Permian basalt (P2β), shale in the Upper Permian Longtan Formation (P2l), mudstone
96 in the Lower Triassic Feixianguan Formation (T1f), and siltstone intercalated with shale in the
97 Upper Tirassic Xujiahe Formation (T3x).

98   CO_2 concentration within the soil pores was measured every 10 cm from the surface
99 down to the rock-soil interface using a GASTEC 801 instrument and 2LL or 2L CO_2 Detector
100 Tube (GASTEC Co., Japan). The profile soil samples were of one-to-one correspondence
101 with the gas samples and also taken every 10 cm.

102   The starting samples were air-dried naturally, and then pulverized (particle diameter <150
103 μm). Soil organic carbon was determined using the potassium dichromate volumetric method.
104 Soil pH was measured in distilled water at a solid/ solution ratio of 1/5, with the instrument
105 model PHS-2. Water contents of soils were synchronously measured by a cutting ring. CaO and
106 MgO contents of rocks were determined by Inductively Coupled Plasma-Atomic Emission
107 Spectrometry (ICP-AES) with a Charge Injection Detector (CID), model TJA IRIS/AP. The
108 standard materials (GBW07401, GBW07408) were used for quality control, with relative
109 deviation less than 5%.
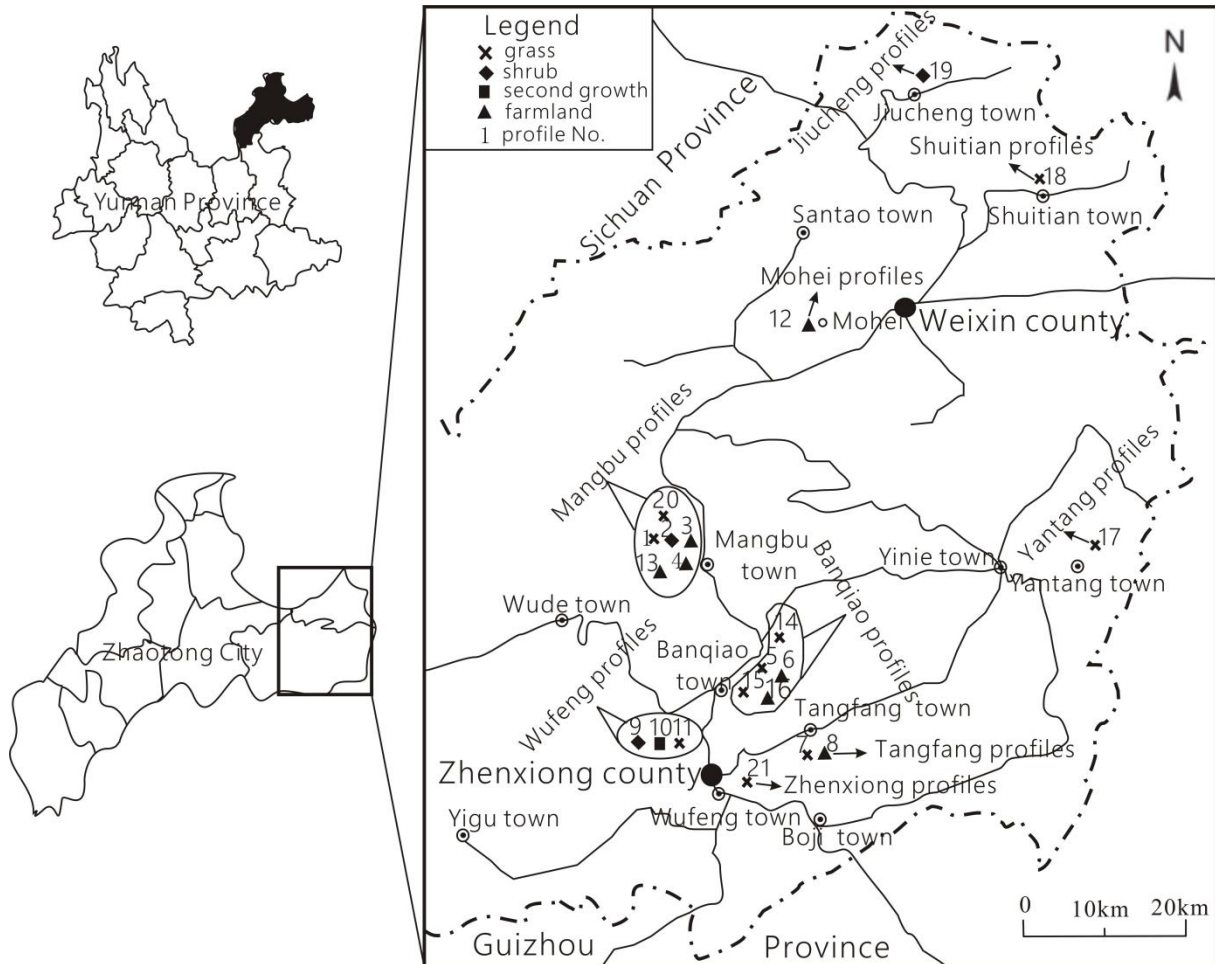
110
111   FIG.1. Sites of measuring soil CO_2 and gathering organic carbon samples (1-Mangbu O_{2-3} grass, 2-Mangbu O_{2-3} shrub,

112   3-Mangbu O_{2-3} farmland, 4-Mangbu O_{2-3} farmland, 5-Banqiao O_1m grass, 6-Mangbu O_1m farmland, 7-Tangfang P_2c grass,

113   8-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,

114   13-Mangbu O_{2-3} farmland, 14-Banqiao P_2c grass, 15-Banqiao $P_1m(q)$ grass, 16-Banqiao $P_1m(q)$ shrub, 17-Tangfang $P_2β$ grass,

18-Shuitian T_2g shrub, 19-Jiucheng T_3x shrub, 20-Mangbu O_1m grass, 21-Zhenxiong T_1f grass).

3 Results

3.1 Varying CO_2 concentration characteristics of soil profiles

Fig. 2 shows soil profile CO_2 concentrations varying with soil depths in 7 non-carbonate areas. The data show a distinct tendency of increasing CO_2 concentration with soil depth, with $R^2=0.8$-0.92 (Table 1).The reasons may be the higher soil bulk density, more condensed soil pores, and difficulty of CO_2 diffusion in the deeper soil. In fact, soil profile CO_2 has been widely reported to be correlated with soil depth by previous researches (Rustad et al. 2000; Dai et al. 2004; Malak et al. 2018) , and even the following linear equation have been developed (James and George, 1991): *Mean $CO_2=0.035+0.0015(Depth)$ ($R^2=0.99$, $P<0.05$)*. Our observations in non-carbonate areas are concordant with these reports and support soil profile CO_2 increases with soil depth in non-carbonate areas.

Table 1. Regression analysis of soil CO_2 concentration and profile depth in non-carbonate areas.

Profiles	Regression equation	R^2	P
Wufeng P_2l shrub (9)	y = 0.0077x + 0.7692	0.92	0.179
Wufeng P_2l second growth (10)	y = 0.0099x - 10.595	0.80	0.016*
Wufeng P_2l grass (11)	y = 0.0015x + 11.527	0.80	0.042*
Mohei P_2l farmland (12)	y = 0.0031x + 12.239	0.80	0.039*
Yantang $P_2\beta$ grass (17)	y = 0.0415x - 19.114	0.85	0.077
Zengxiong T_1f grass (21)	y = 0.15x - 70	0.9	0.051
Jiucheng T_3x shrub (19)	y = 0.0086x + 5.6875	0.81	0.101

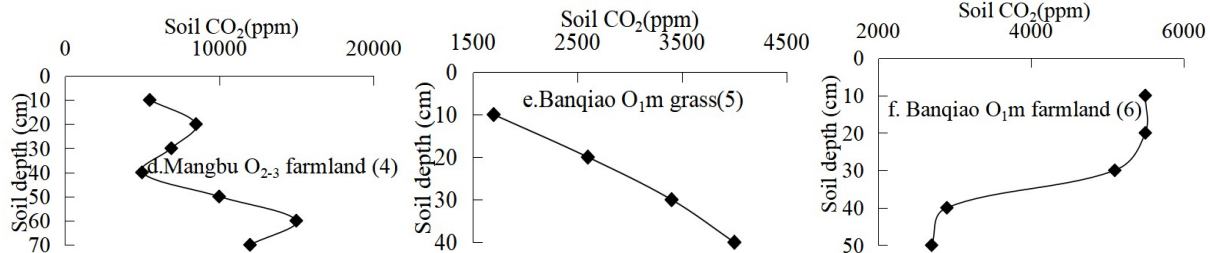Note: ( ) means profile No., *means significant correlation at 0.05 level.
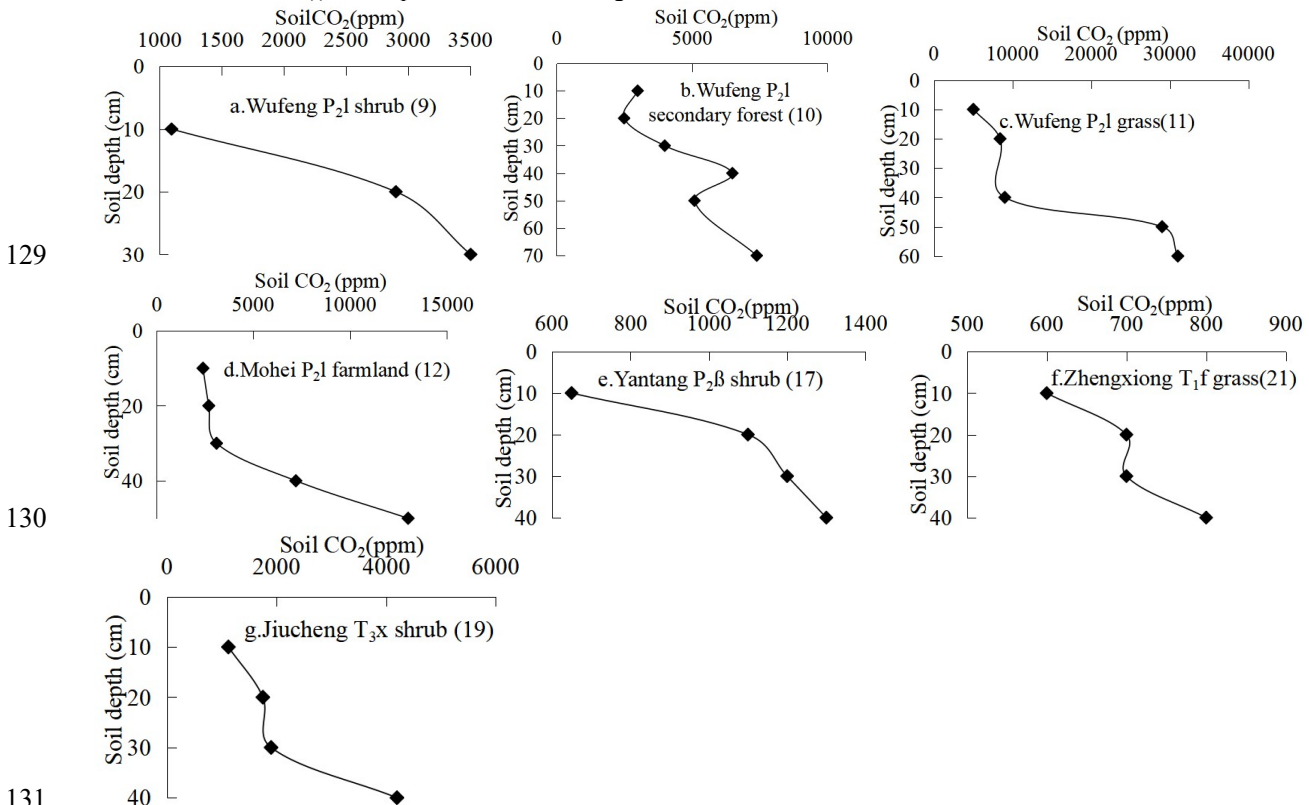
Figure 2. Varying characteristics of soil profile CO_2 concentration in non-carbonate areas (profile no. in brackets).
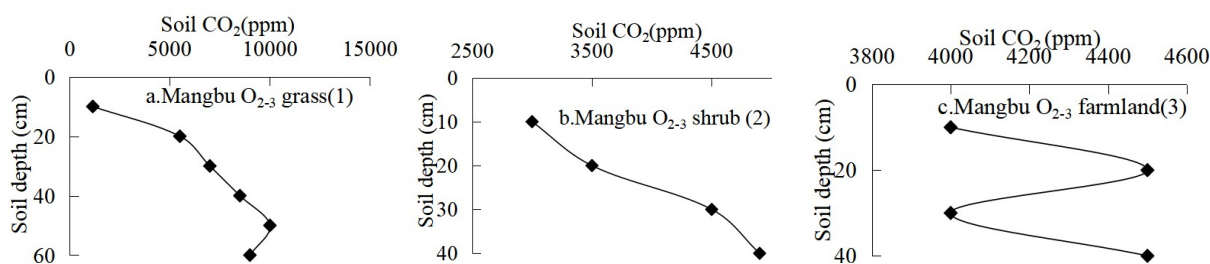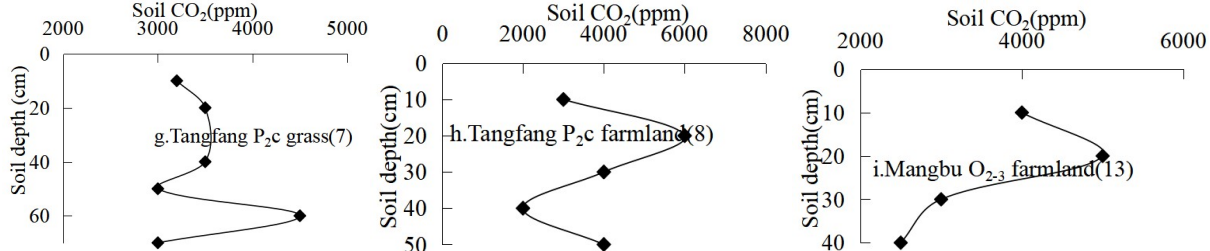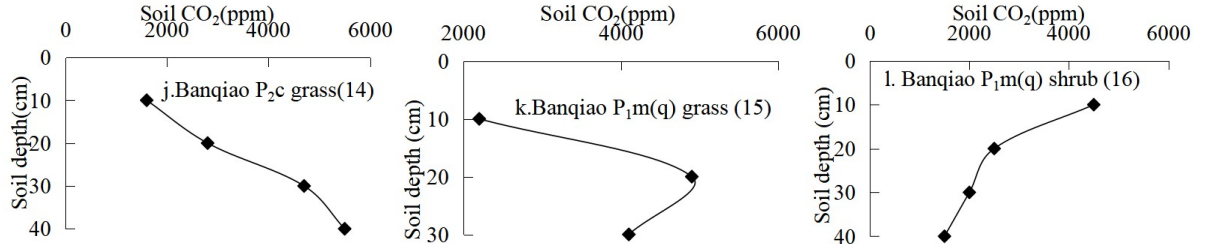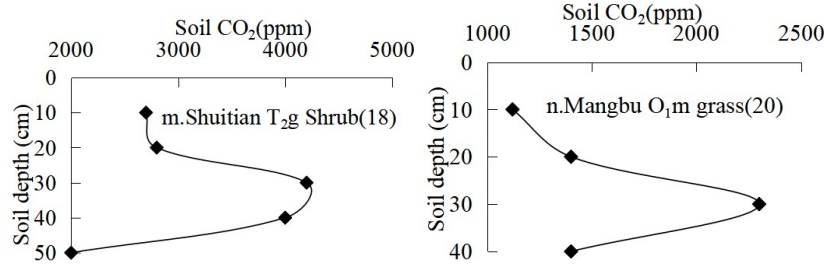
Figure 3. Varying characteristics of soil profile CO_2 concentration in carbonate areas (profile no. in brackets).

14 Soil profile CO_2 concentration with soil depth in carbonate areas was gained (Fig. 3). The results show a complex and inverse relationship between soil CO_2 and soil depth in carbonate areas. Most Soil profile CO_2 increases with soil depth in the upper sections, such as Mangbu O_{2-3} grassy profile (Fig. 3a), Mangbu O_{2-3} shrub profile (Fig. 3b), Mangbu O_{2-3} farmland profile (Fig. 3d), Banqiao O_1m grassy profile (Fig. 3.e), and Banqiao P_2c grassy profile (Fig. 3j). CO_2 concentrations decrease with soil depth when they increase from surface to a certain depth in Mangbu O_{2-3} farmland profile (Fig. 3i), Banqiao $P_1m(q)$ grassy profile (Fig. 3k), Gaotian T_2g grassy profile (Fig. 3m) and Mangbu O_1m grassy profile (Fig 3n). Those of Banqiao O_1m farmland profile (Fig. 3f) and Banqiao $P_1m(q)$ shrub profile (Fig. 3l) even decrease all along with soil depth, and two farmland profiles of Mangbu O_{2-3} (Fig. 3c) and Tangfang P_2c (Fig. 3h) fluctuate, and have no regularity due to the effect of human farming activities. Generally, Except

153　Mangbu O_{2-3} farmland profile (Fig. 3.c) and Tangfang P_2c farmland profile (Fig. 3.h), which are
154　disturbed by farming, CO_2 concentrations of other profiles in carbonate areas all decrease with
155　soil depth at the rock-soil interface (Fig. 3.b,e,j). Moreover, there is no correlation of soil CO_2
156　concentration with soil depth, because sequestration of deep soil CO_2 concentration occurs in
157　carbonate areas. Why does the sequestration only take place in carbonate areas, but not in
158　non-carbonate ones? Naturally the particular carbonate process-carbonate corrosion-is
159　considered. That is, part of deep soil CO_2 is consumed and CO_2 sequestration occurs, and there is
160　no linear relationship between CO_2 concentration and soil depths in carbonate areas. In fact,
161　Buyannovsky and Wagner (1983), Solomon and Cerling (1987), and Xu and He (1996) all
162　reported that soil CO_2 concentration reaches a peak at a certain depth, and then decreases with
163　soil depth in carbonate areas. CO_2 concentration in Banqiao O_1m farmland profile (Fig. 3.f) and
164　Banqiao $P_1m(q)$ shrub profile (Fig.3.l) continues to decrease with depth through the integral
165　profile, and they also had the highest concentration at the 10cm layer. Instances of CO_2
166　concentration in surface layers higher than those in bottom layers are scarcely documented in
167　carbonate areas.

168　**3.2 Relationship between soil profile CO_2 concentration and soil organic carbon**

169　Soil organic carbon (SOC) was analyzed in a part of the profiles, corresponding with CO_2
170　concentration. Results are given in Fig.4, among which, Fig. 4 a-h indicate profiles in
171　carbonate areas and Fig. 4 i-l indicate those in non-carbonate (shale) areas.
172　　Correlation analysis of soil profile CO_2 concentration and SOC in shale areas is listed in
173　Table 2. CO_2 shows decreasing tendency with increasing of SOC, with high regression
174　coefficients (R^2= 0.67-0.85). An exception of 0.29 occurs in Wufeng P_2l secondary forest,
175　which possibly is caused by stronger root respiration and a higher ratio of CO_2 generated by the
176　roots. Therefore, SOC is directly affected by the release of soil CO_2, and the key problem for
177　soil carbon storage is to slow down the renewing of soil organic matter (Chen et al. 2002).
178　The reason for non-significance ($P>0.05$) may be that soil CO_2 concentration is related not only
179　to SOC, but also to soil respiration and microbe activities. However, there is no such tendency
180　in carbonate areas as that in shale areas (Table 3), and even those of Banqiao O_1m farmland
181　profile and Banqiao $P_1m(q)$ shrub profile show increasing tendency. Previous studies in
182　carbonate areas as Shilin, Lunan City and Guizhou Plateau also showed no correlation
183　between CO_2 concentration and SOC (Liang et al. 2003).

184　　Table 2. Correlation analysis of soil CO_2 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

185

186　　Table 3. Correlation analysis of soil CO_2 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 CO_2 and SOC in carbonate areas?
188 The possible answer may be carbonate corrosion. By means of corrosion, deep soil CO_2 is
189 partly consumed and its level decreases. Consequently, the relationship becomes poor. In
190 addition, varying characteristics of SOC cannot explain well the decrease of deep soil CO_2
191 levels in carbonate areas.

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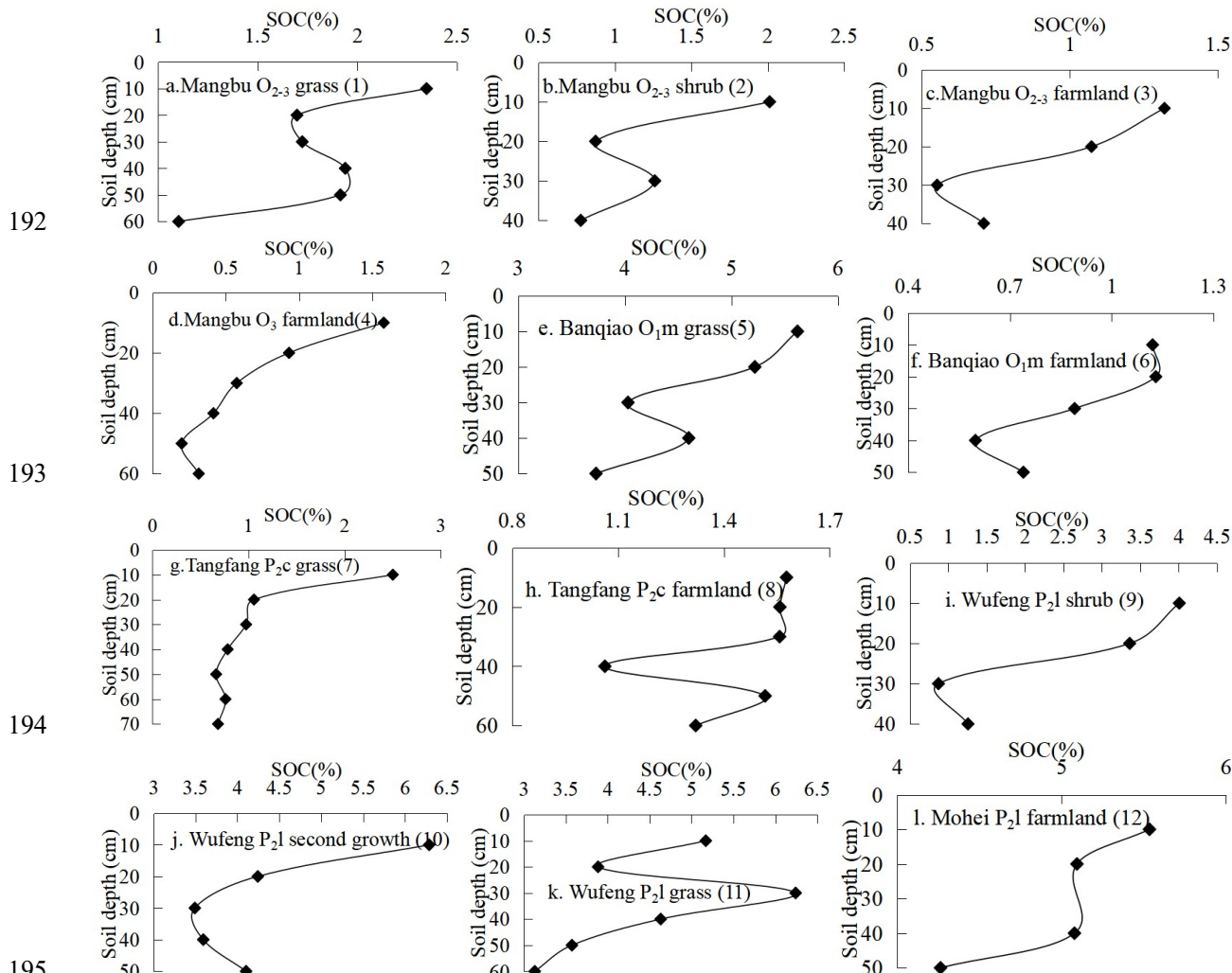
196 Figure 4. Varying characteristics of soil profile organic carbon in karst areas (profile no. in
197 brackets)

## 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_2 and SOC. Conversely, in carbonate
203 areas, pH generally increases with soil depth in the surface layer except in the Banqiao O_1m
204 farmland profile. Moreover, from Figs. 3 and 5 it is evident that soil CO_2 concentration
205 decreases where soil pH decreases too, and even CO_2 level in the Banqiao O_1m farmland profile
206 decreases from the surface to the bottom with soil pH through the entire profile. These
207 observations imply that the decrease of deep soil CO_2 concentration in carbonate areas is
208 related closely to soil pH.
209 Chemically, with soil water and soil CO_2 added together, carbonate corrosion can be

210 represented by the following equation:

$$CaCO_3 + CO_2 + H_2O <=> Ca^{2+} + 2\,HCO_3^-$$

$$HCO_3^- <=> H^+ + CO_3^{2-}$$
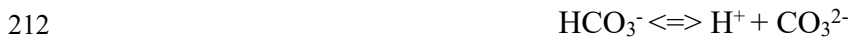
213 By means of this reaction, deep soil CO_2 is consumed by the corrosion of the underlying
214 carbonate rock, and pH decreases synchronously. This reaction cannot take place in soil over
215 areas with non-carbonate bedrock, so here the deep soil CO_2 concentration does not
216 decrease, but increases.

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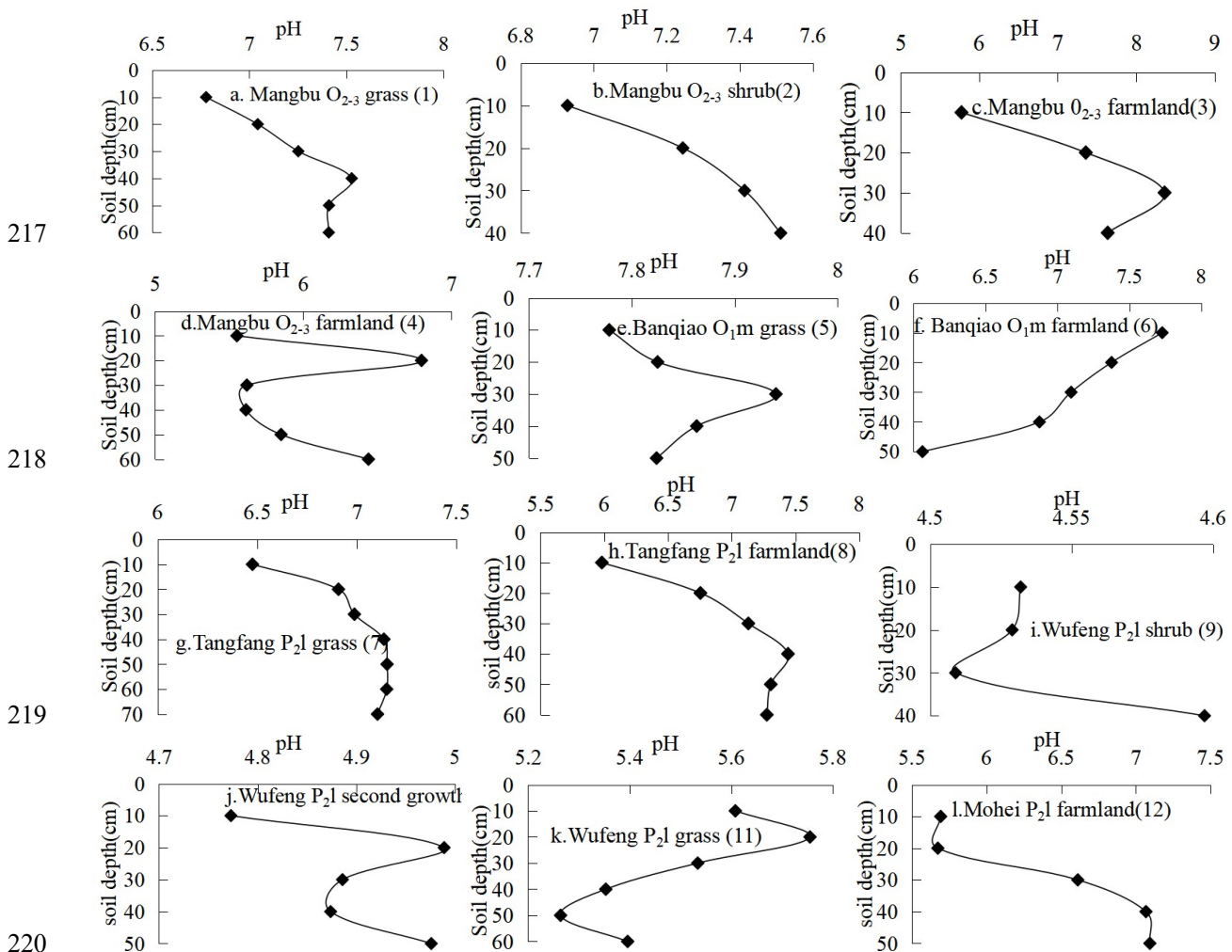
221 Figure 5. Soil pH of different profiles in karst area (a-h indicate those in carbonate areas, and
222 h-l indicate those in shale areas, profile no. in brackets).

3.4 Carbonate corrosion and the global carbon cycle

224 Many studies have observed that soil CO_2 concentration in carbonate areas decreases with
225 depth when it reaches a maximum at a certain soil depth in carbonate areas (Buyannovsky
226 and Wagner, 1983; Li et al. 1995; Xu and He, 1996; Liang et al. 2003). There has, however,
227 been no reasonable explanation for the observations. Li et al (1995) attributed it to less roots,
228 and, therefore, less root respiration in the deep soil, but there are no scientifically observed
229 data to support this idea, and it remains only a hypothesis. No decrease in soil CO_2 in
230 non-carbonate areas is found, and, furthermore, the depths with decreasing CO_2 concentrations
231 were distinguishable in different profiles, even at only 20-30 cm depths. The decreased CO_2
232 concentration could be attributed to decreased microbe numbers or root respiration at such
233 depths. By comparative analysis of soil CO_2 concentration in areas of carbonate and

234 non-carbonate bedrock, it should be suggested that the explanation is due to the special
235 geological process of carbonate corrosion.
236   Soil CO_2 and SOC in non-carbonate areas have a good negative correlation, with
237 correlation coefficients R^2= 0.67-0.85, although significance is not clear because soil CO_2 is
238 determined by not only organic matter but also by other factors, such as root respiration and
239 microbe activities. By contrast, such correlation in carbonate areas is poor, which was
240 concluded also by Li et al (1995) and Liang et al. (2003) from experiments in carbonate
241 areas. Soil CO_2 of carbonate areas, in every depth at different sites, is negatively correlated
242 with SOC, and relationship became worst with increasing soil depth. This observation means
243 that SOC content cannot explain well the decreased CO_2 concentration of deep soil in
244 carbonate areas, but rather may be related to carbonate corrosion. Soil pH in carbonate areas
245 always decreases with soil CO_2, and this may imply that H^+ generated by carbonate corrosion
246 mixes into the deep soil increasing soil acidity.
247   Previous work has determined the imbalance between soil CO_2 produced and released in
248 carbonate areas. Pan et al (2000) observed and simulated field data in Yaji, Guangxi Province,
249 concluding that CO_2 produced by decomposition of organic matter is more than that released
250 into the air. This confirms that the rock and the soil have an obviously "absorbing effect" for
251 CO_2. The data account for an absorbing coefficient of 22-130 $g/m^2 \cdot a$.
252   Isotopes can effectively trace the carbon source of soil CO_2. Fig. 6 reflects the $\delta^{13}C$ value
253 of soil CO_2 and SOC overlying different bedrock according to data from Li et al. (2001). It
254 shows that in deep soil, CO_2 has a higher $\delta^{13}C$ value than the SOC in limestone and dolomite
255 areas, whereas the isotope ratios are more equivalent in clay stone areas. Such an observation
256 may support the conclusion that that deep soil CO_2 in clay stone areas is mainly or completely
257 from soil organic matter, and that in limestone and dolomite areas there must be an additional
258 carbon source whose $\delta^{13}C$ should be more than -14‰ . $CaCO_3$ in carbonate has $\delta^{13}C$ values of
259 -3‰~+1‰. It must, therefore, possibly be recognized that carbon in $CaCO_3$ of carbonate
260 bedrock mixes into soil CO_2, since the corrosion reaction is reversible.
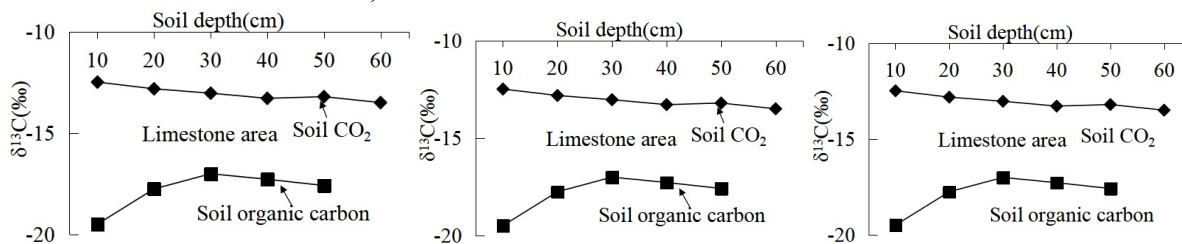
262 Figure 6. Varying $\delta^{13}C$ of soil CO_2 and soil organic carbon with soil depth overlying different
263 bedrocks (data is after Li et al (2001)).
264   It has been examined that the karst carbon cycle is an important trace for the global
265 carbon cycle and that further study is important to the hunt for "missing sink" (Jiang and
266 Yuan,1999). From what is presented above, with focus on the process of carbonate corrosion
267 and comparison of different parameters in carbonate and non-carbonate areas, it is logical to
268 conclude that carbonate corrosion causes the decreased CO_2 concentration at the rock-soil
269 interface in carbonate areas. As a result, the decreased CO_2 level caused by corrosion will, of
270 course, impose effects on atmospheric CO_2 and the karst carbon cycle. This is significantly
271 for the potential fixation of carbon, the study of global carbon cycle balance, and the hunt for
272 the "missing sink".

273 **3.5 Mathematical model of soil profile CO_2 transfer**

274 In this model, only the molecular diffusion of CO_2 is considered, neglecting other processes,

275 such as viscous flow and Knudsen diffusion in karst soil because of the weak air pressure
276 gradient. Moreover, density gradient was regarded as the dominant dynamic of CO_2
277 diffusion, and temperature gradient was neglected because of its low contribution (0.2-0.4%) to
278 CO_2 flow. Therefore, the transport of soil CO_2 can be described by the following
279 one-dimensional diffusion equation according to Fick's second law and laws of conservation of
280 mass (Zeng and Zheng, 2002), assuming horizontal homogeneity:

281 $$\frac{\partial(\theta_a C_a + \theta_w C_w)}{\partial t} = -\frac{\partial(J_{da} + J_{dw} + J_{ca} + J_{cw})}{\partial z} - Q \cdot C_w + S \quad (1)$$

282 Here, θ_a is the air content, θ_w is the water content, C_a is the gaseous CO_2 concentration, J_{da} is
283 the gaseous CO_2 flow due to diffusion, J_{dw} is the dissolution CO_2 flow due to diffusion, J_{ca} is the
284 gaseous CO_2 flow due to convection, J_{cw} is the dissolution CO_2 flow due to convection, S is
285 the carbon source, Q is the water absorbed by roots, t is the time, and z is the space
286 coordinate.
287 　　Such equation can be gained according to Fick's first law:

288 $$J_{da} = -D_a \frac{\partial C_a}{\partial z} \quad J_{dw} = -D_w \frac{\partial C_w}{\partial z} \quad J_{ca} = q_a C_a \quad J_{cw} = q_w C_a \quad (2)$$

289 where D_a is the gaseous CO_2 diffusion coefficient in soil substrate, D_w is the dissolution CO_2
290 diffusion coefficient in soil substrate, q_a is the soil air transference amount, and q_w is the soil
291 water transference amount.
292 　　Equation (3) can be deduced from equations (1) and (2), if it is assumed that soil water is
293 stable and gaseous and dissolution CO_2 flows are not considered:

294 $$\theta_a \frac{\partial C_a}{\partial t} = D_a \frac{\partial^2 C_a}{\partial z^2} - \theta_w \frac{\partial C_w}{\partial t} - q_w \frac{\partial C_w}{\partial z} - Q \cdot C_w + S \quad (3)$$

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

297 $q_w = \tau \exp(-\frac{z}{\delta})$, presented by Yoyam et al.(1993), and

298 $Q = \dfrac{\tau \exp(-\frac{z}{\delta})}{\delta}$ by Warren and Michael (1984), and

299 in winter $q_w = 0$, $Q = 0$; $D_a = D_a^\circ (\frac{\theta_a}{\theta_w})(\theta_a)(\frac{T}{T_0})^{1.823}$, by Collin and Rasmuson (1988). Here, D_a^0 is
300 the CO_2 diffusion coefficient in air at the reference temperature T^0.
301 　　For the carbon source, the rate of CO_2 produced by root respiration and microbes can be
302 expressed as follows:
303 $S(z) = S_0 \exp(-z/z_s)$
304 where $S(z)$ is the soil profile CO_2 at depth of z, S_0 is the CO_2 concentration in the surface soil,
305 z is the soil depth, and z_s is the depth gradient. It also considered the CO_2 produced by organic
306 matter expressed as follows:

307 $S_{OM} = -\dfrac{6 D_a \partial^2 C_a}{3.3 \partial z^2}$.

308 　　Then equation (4) is achieved:

309 $$\theta_a \frac{\partial C_a}{\partial t} = -0.82 D_a \frac{\partial^2 C_a}{\partial z^2} - \theta_w \frac{\partial C_w}{\partial t} + S_o \exp(-z/z_s) + a \quad (4)$$

310 $\dfrac{\partial Ca}{\partial t}, \dfrac{\partial Cw}{\partial t}$ are stable, when being from the same time and soil profile.

311 Based on the studies above, the soil profile CO_2 concentration varying with soil depth can
312 be expressed by the following equation:

313 $C_a = A\exp(Bz) + Cz + D$ (A, B, C, D = uncertain) (5)

314 According to Tailor formula:

315 $\exp(x) = 1 + x + \dfrac{1}{2!}x^2 + \cdots\cdots + \dfrac{1}{n!}x^n + \cdots\cdots$ (6), and it can be roughly expressed like the following
316 equation when x<1:

317 $\exp(x) = \begin{cases} 1 + x \\ 1 + x + \dfrac{1}{2!}x^2 \end{cases} \quad (x \ll 1)$ (7)

318 When equation (7) is applied to equation (5), equation (8) can be gained to express profile
319 CO_2 concentration (C_a) varying with soil depth (z):

320 $C_a = \begin{cases} a + bz \\ a + bz + cz^2 \end{cases}$ (8)

321 Here, a, b and c are uncertain parameters, which vary with θ_a, θ_w, S_0, T, and D_a of different
322 profiles.

323 That means, it can be expressed as a linear or parabolic relationship of soil profile CO_2
324 concentration and soil depth. Actually, many observation and simulation also confirmed the
325 same results (James and George, 1991; Zeng and Zheng, 2002; Malak et al., 2018). Therefore,
326 it seems reasonable to express a linear or parabolic relationship of soil profile CO_2
327 concentration and soil depth.

3.6 The rough evaluation of CO_2 decreased by corrosion

329 SPSS software was used to simulate the curve of measured soil CO_2 concentration and soil depth
330 in non-carbonate areas (Fig. 7 and Table 4), resulting in parabolas with multiple regression
331 coefficients R^2=0.8-1. Multiple regression coefficient of P_2c secondary forest profile shows
332 the lowest level at 0.79, which may be due to the different root respiration and the absorbed
333 water at different depths. The simulation evidences that the model is reliable and can be used
334 to roughly reveal the laws of soil profile CO_2 concentration.

335 Table 4. Simulated equation of measured soil CO_2 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 ß 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	$y=722.96e^{0.0405x}(0.9031)$

336 Note: regression coefficients R^2 of simulated exponent in brackets.

337 In carbonate areas, however, there is no linear or parabolic relationship between soil profile
338 CO_2 concentration and soil depth, and the measured values are inconsistent with the simulated
339 ones. Linear or parabolic relationship can be found in the surface soil. Since it is carbonate
340 corrosion that decreases the CO_2 concentration in the deep soil of carbonate areas, the CO_2

concentration in the surface layer can be used and to predict the CO_2 concentration of deep soil based on the developed model. The predicting equation and results are listed in Fig. 8. It shows that there is a strong difference between the measured and the predicted values, and that all the predicted are greater than the measured ones in deep soil. It can also be deduced that deep soil CO_2 is consumed by carbonate corrosion.

The method of subtraction of predicted and measured values can be used to evaluate the decreased CO_2 concentration in carbonate areas caused by carbonate corrosion, and the results are listed in Table 5. If synthesis factors, such as vegetation types and soil types, were considered, the rough evaluation of the decreased CO_2 concentration of every stratigraphic unit can be gained by taking the average (Fig. 9).

Table 5. The evaluated results of the decreased CO_2 concentration in carbonate areas caused 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

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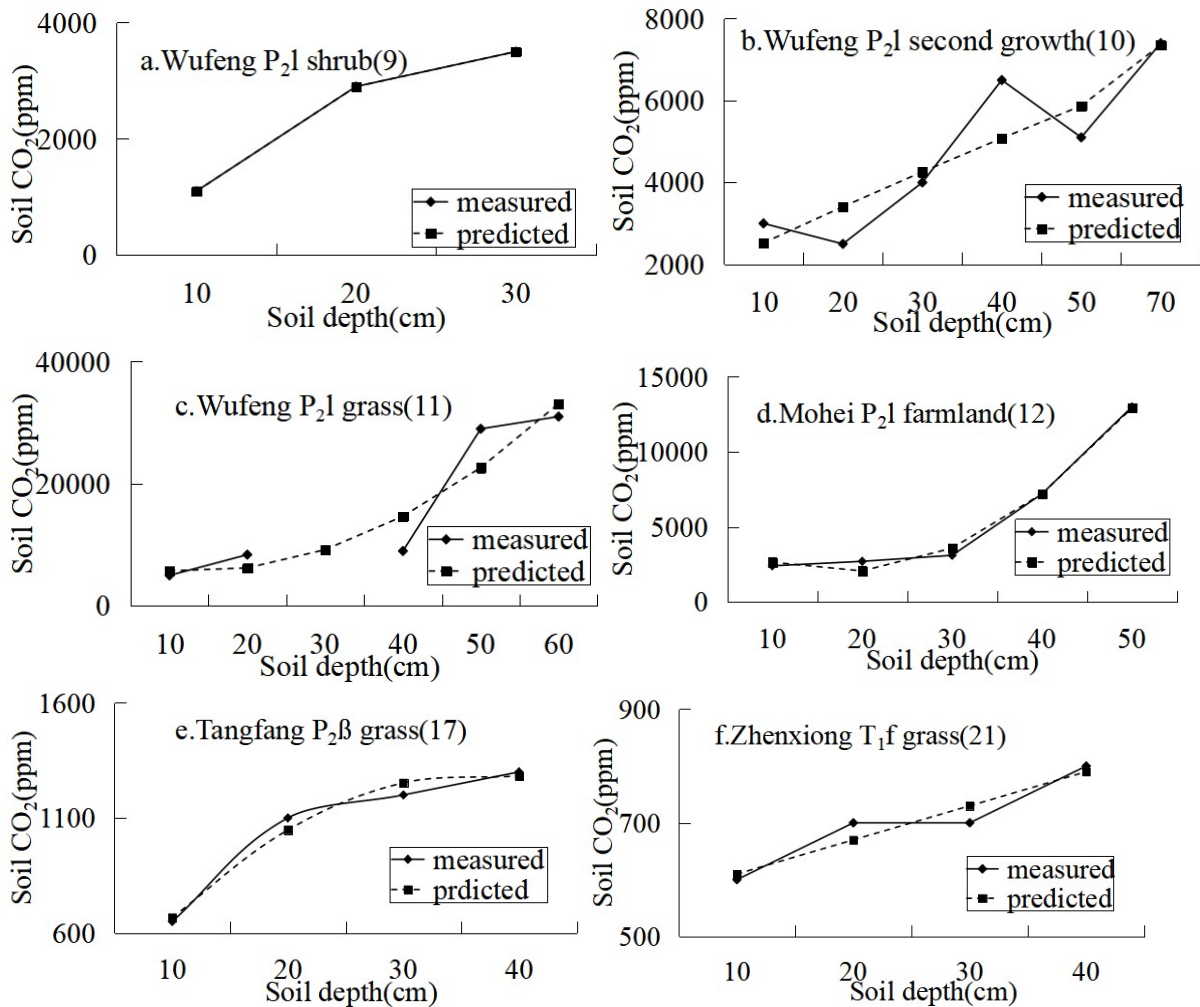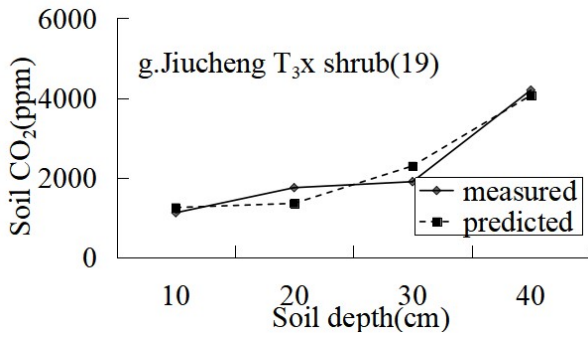
358 Figure 7. The measured and the simulated CO_2 concentrations of soil profiles in
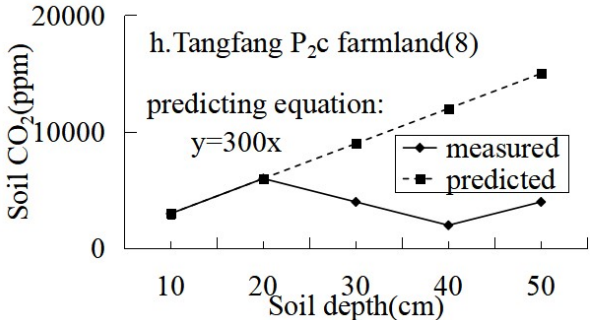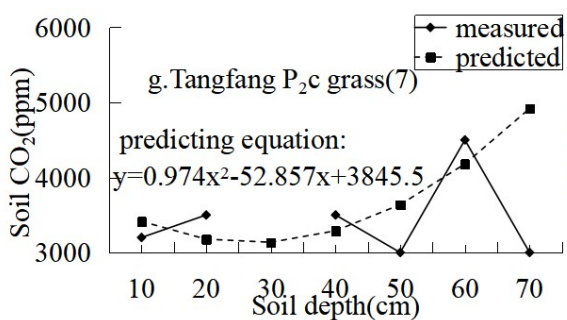359 non-carbonate areas.
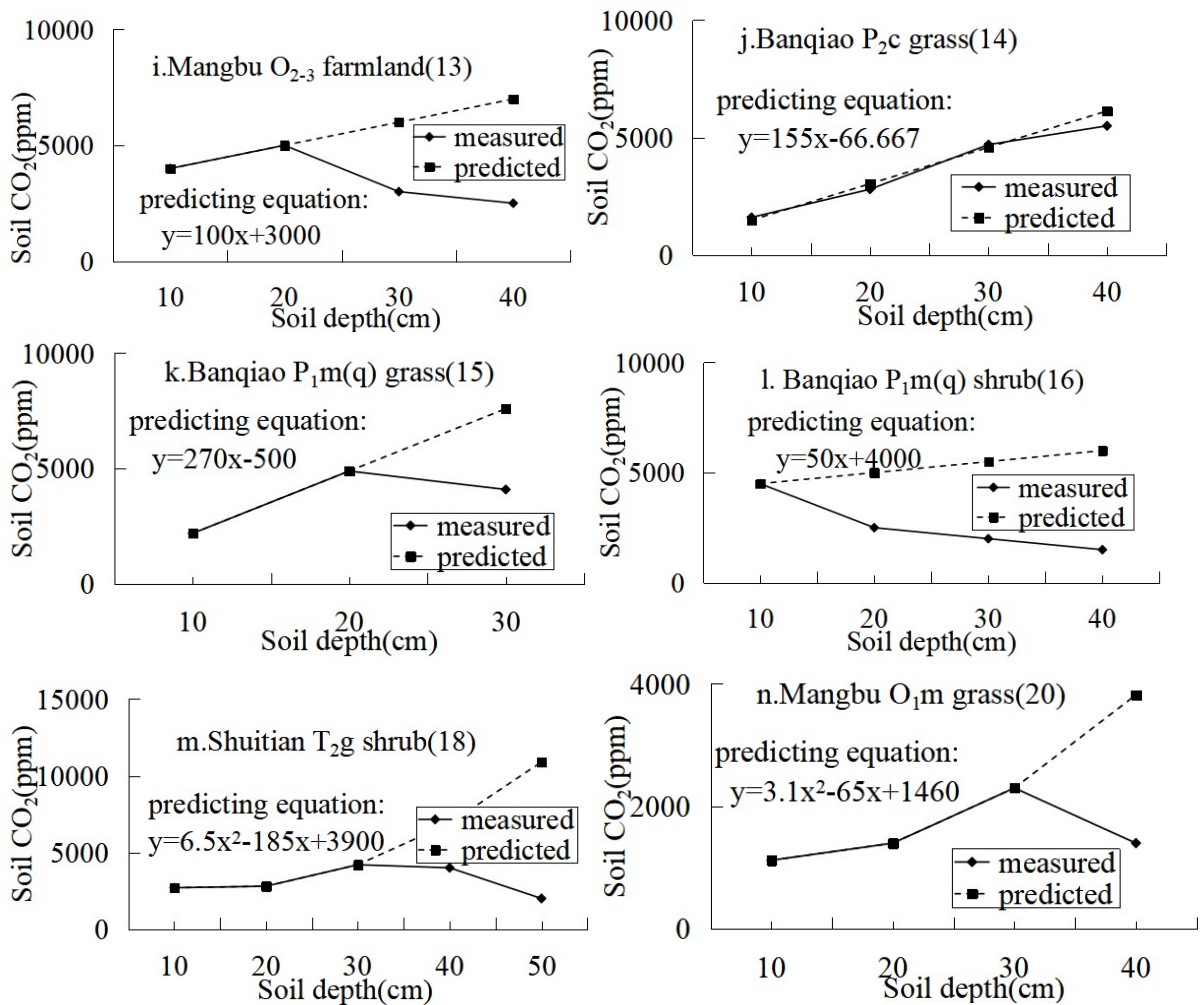

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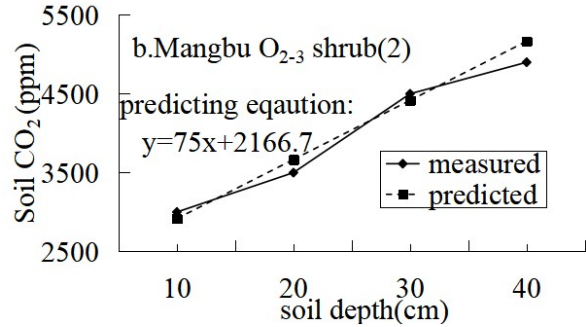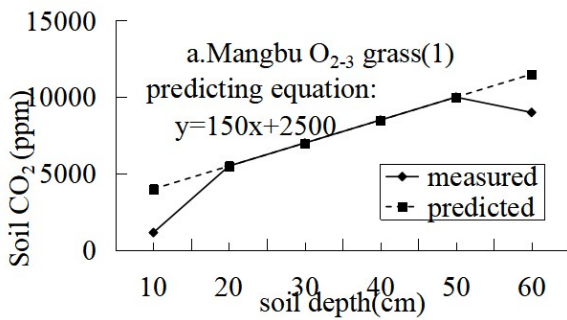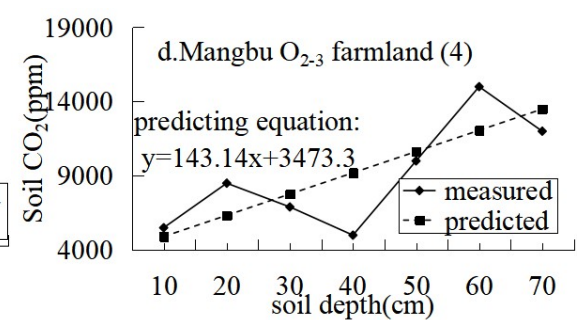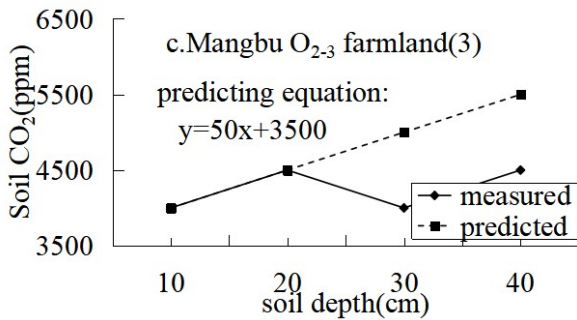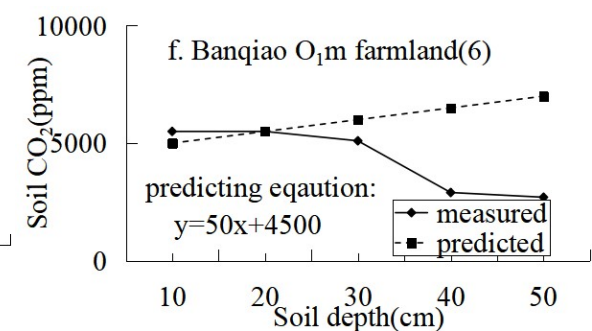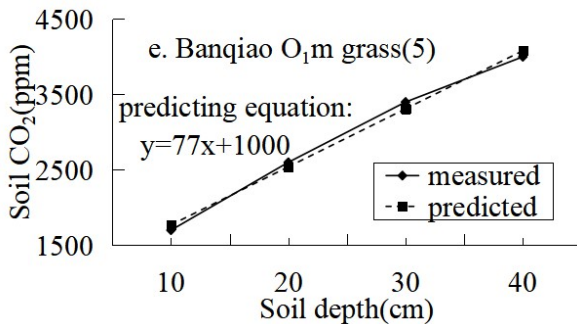
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Figure 8. The measured and predicted soil profile CO_2 concentrations in carbonate areas.
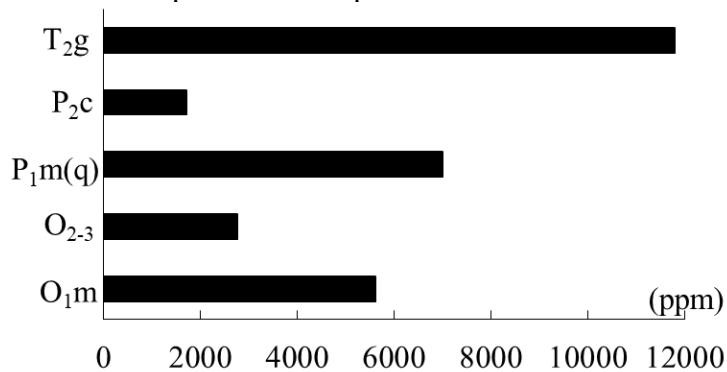

Figure 9. The evaluation of the decreased CO_2 concentration caused by carbonate corrosion based on stratigraphic units.

### 3.7 The main controlling factors of decreased CO_2 concentration

Fig. 9 shows great dissimilarity of the decreased CO_2 concentration with different stratigraphic units in the following order: $T_2g>P_1m(q)>O_1m>O_{2-3}>P_2c$. Fig. 10 shows the calculated results of the decreased CO_2 concentration, respectively, in farmland and natural soil (grass and shrub) of the same stratigraphic unit. CO_2 concentration on T_2g and $P_1m(q)$ farmland is lacking, but the comparative analysis of O_1m , O_{2-3} and P_2c can demonstrate that the decrease of CO_2 in natural soil profiles is obviously less than that in farmland profiles. It is clear that

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corrosion was strengthened by farming activities and more CO_2 was consumed in the deep soil, which may be due to higher CO_2 levels and acidity caused by farming. Therefore, the decreased CO_2 concentrations of T_2g and $P_1m(q)$ should be more than the calculated values, when farming activities are considered. The decreased CO_2 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_2 concentration. The parameters are shown in Fig. 11. Deep soil-pH is negatively correlated with decreased CO_2 concentration, and the stronger the soil acidity, the more the decreased CO_2 concentration. Water content of deep soil does not impose effort to corrosion. CaO content of carbonate is positively correlated with the de-creased CO_2 concentration, and the more pure the $CaCO_3$ in carbonate rock, the stronger is the corrosion. MgO content of carbonate is not correlated with corrosion, which indicates that it is $CaCO_3$ corrosion and not that of $MgCO_3$ consuming soil CO_2. Simulation by SPSS software results in an equation ($y=-3E-08x^2+0.0002x+6.976$) of decreased CO_2 concentration and soil pH with a multiple regression coefficient $R^2=0.9779$, and a second equation ($y=0.0012x +17.857$) of decreased CO_2 level and CaO content of carbonate with a multiple regression coefficient $R^2 = 0.4191$ (Fig. 12). A field experiment of carbonate corrosion in the southern part of Guizhou (Nie et al.1984), a laboratory simulation using citric acid to corrode limestone (Cao et al., 2001), and an experimental study on the stability of $CaCO_3$ and $MgCO_3$ under acid rain conditions (Teir et al. 2006) led to the conclusion that corrosion is related closely with soil acidity and carbonate purity. The calculated results can support the same conclusion and accord well with their studies, and can also easily be confident.
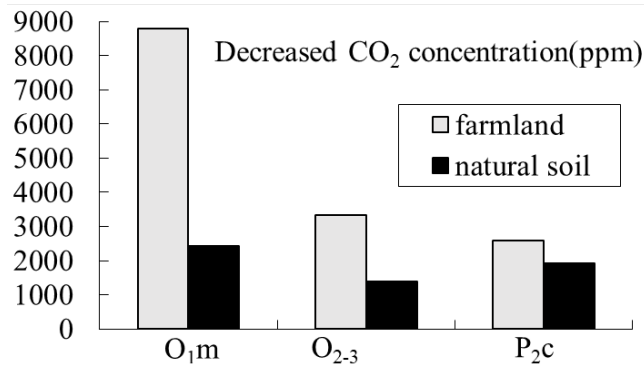
Figure 10. The decreased CO_2 concentration in farmland and natural soil of the same stratigraphic unit.
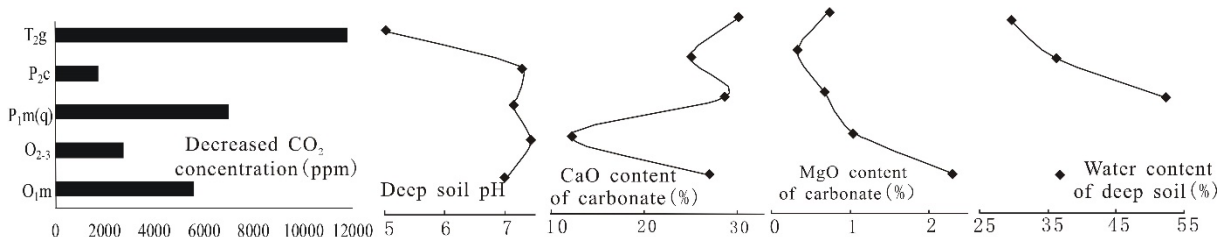
Figure 11. Relationship of the decreased CO_2 concentration and deep soil pH, water content, CaO and MgO contents of carbonate.
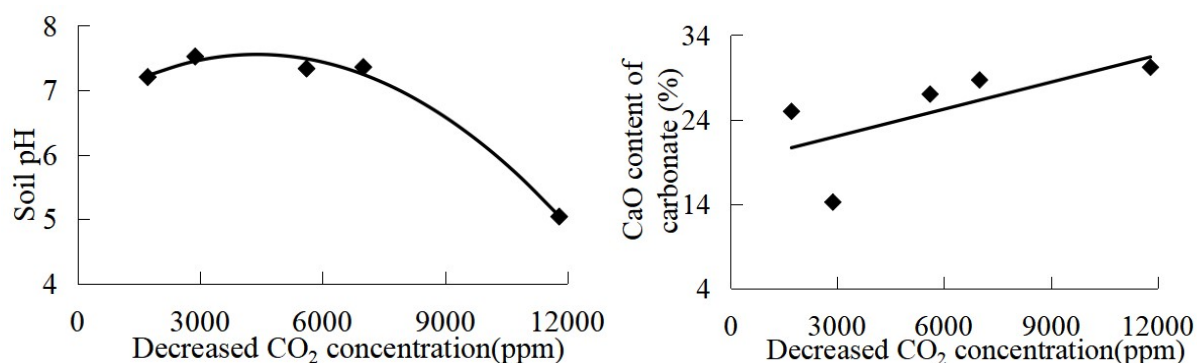
FIG. 12. Correlation analysis of soil pH, CaO of carbonate and decreased CO_2 concentration.

4 Discussion and conclusions

It is not surprising that soil CO_2 concentration decreases in the deep layers over carbonate bedrock areas, especially at the bottom of soil profiles, as has been observed by many experiments(Buyannovsky and Wagner, 1983; Li et al. 1995; Xu and He, 1996; Liang et al. 2003), and was now supported by this paper. The explanation by some studies (Li et al., 1995) that decreased CO_2 is caused by decreased microbe or root respiration in deep soil, is challenged by our data. At first, one important reason leading to the earlier conclusion lies perhaps in the lack of comparative analyses of soil CO_2 levels in carbonate and non-carbonate areas. The underlying foundation of soluble carbonate in carbonate areas was not taken into consideration, and, most important, there was no proof or data to support this idea. Secondly, there is no decrease of CO_2 in soil profiles of non-carbonate areas (mudstone, basalt, shale or siltstone areas), also it seems to be reasonable to expect CO_2 decrease by lower microbe or root respiration rates in deep soil layers of both carbonate or non-carbonate areas. Thirdly, decrease of soil CO_2 takes place in 20-30 cm soil layers, and even from the soil surface in some profiles, so it may be unreasonable to attribute CO_2 decrease to microbe respiration in such shallow occurrences.

Additionally, soil profile CO_2 only decreases in carbonate areas, and SOC content is positively correlated with soil CO_2 concentration in non-carbonate areas (R^2=0.67-0.85), although there is no significant correlation at some profiles because soil CO_2 is not only related with organic carbon, but also with other factors, such as root respiration. Soil CO_2 and organic carbon in different depths of carbonate areas are positively correlated with low correlation coefficients, but not in soil profiles of these carbonate areas. This means that organic carbon cannot be responsible for the decreased CO_2 concentrations. Furthermore, CO_2 consumed by carbonate corrosion leads to uncorrelated relationship between soil CO_2 and organic carbon levels in carbonate areas. Soil profile pH in carbonate areas always suddenly and sharply decreases at the depth of CO_2 decrease, and this can be explained well by carbonate corrosion. Analysis of $\delta^{13}C$ isotope, which mixes into the CO_2 in deep soil layers of carbonate bedrock areas (dolomite or limestone) also demonstrates that there is another carbon source, whose $\delta^{13}C$ level is more than -14‰. In soil of clay-stone areas, however, soil CO_2 and soil organic carbon have the same $\delta^{13}C$ value. This provides strong evidence that carbonate corrosion occurs, and thus deep soil CO_2 is consumed in carbonate areas. Simply stated, our work strongly indicates that carbonate corrosion leads to the decrease of soil profile CO_2 concentration in areas with carbonate bedrock.

Further, a mathematical model of soil CO_2 transfer was developed, showing that soil CO_2 concentration can be roughly expressed as a linear or parabolic increase with soil depth. The linear or parabolic increase can be demonstrated, strongly supported by both field data and the

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models. Soil CO_2 concentration data, collected in non-carbonate areas or in the surface soil of carbonate areas, provide additional confirmation. In the deep soil of carbonate areas, however, especially at the rock-soil interface, the simulated values are always higher than the field measurements. All of these points may also indicate that carbonate corrosion occurs in the deep soil, and that apart of soil CO_2 is consumed by carbonate corrosion. In addition, the decreased CO_2 concentration caused by carbonate corrosion can be evaluated by the subtraction of measured and simulated CO_2. The decreased CO_2 concentration is related closely to deep soil pH and CaO content of carbonate rock (correlation coefficients, respectively, R^2=0.97 and 0.41), together with farming activities, but not with deep soil water content and MgO content of carbonate. These results and conclusions can be supported by experiments, and are widely accepted by karst scholars, who add validity to our results and conclusions.

The carbon cycle in karst areas has attracted big attention because of the imbalance of the global carbon cycle, and in recent years there has been a search to resolve the missing sink related to the absorbing and releasing of carbon in $CaCO_3$ systems (Jiang and Yuan, 1999). Experiments and calculations indicate that 1.774×10^7 t of carbon are absorbed by karstification in China, and that $2.2 \times 10^8 \sim 6.08 \times 10^8$ t of carbon are drawn back from the atmosphere worldwide every year (Jiang and Yuan, 1999). It is obviously significant with regard to the increasing atmospheric temperature. Soil, as an important carbon storage area, is of great importance to atmospheric CO_2 concentration, and slight variations may impose great effects on global carbon cycle. Several factors affecting soil CO_2 concentration have been discussed, such as environmental ones (soil temperature, moisture, water content, etc.), microbe activities, and human activities, but no published details about the effect of carbonate corrosion on soil CO_2 concentration can be found. Our study argues that deep soil CO_2 concentrate in carbonate areas is obviously decreased, especially at the rock-soil interface, and that this is mainly caused by carbonate corrosion. If this conclusion is correct, then naturally the atmospheric CO_2 levels in carbonate areas should be affected by the corrosion, and this should be very significant in the hunting for the "missing sink".

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

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

References

Bajracharya, R.M., Lai, R., and Kimble, J. M.: Erosion effects on carbon dioxide concentration and carbon flux from an Chio Alfisol, Soil Sci. Soc. Am. J, 64, 694-700, 2000.

Buyannovsky, G.A., and Wagner, G. H.: Annual cycles of carbon dioxide level in soil air, Soil Sci. Soc. Am, 47, 1139-1145, 1983.

Callendar, G. S.: The artificial production of carbon dioxide and its influence on temperature, Q.J.R. Meteorol Soc, 64, 223-240,1938.

494 Cao, J.H., Pan, G. X., and Yuan, D. X.: Simulation experiments on dissolution of calcite by citric and its
495   karst importance, Carsologica Sinica (in Chinese), 20(1), 1-4, 2001.
496 Chen, Q.Q., Sun, Y.M., Shen, C. D., Peng, S. L., Yi, W. X., Jiang, M. T., and Li, Z. A.: Quantitative study
497   on organic matter turnover characteristics of mountainous soil profiles in the subtropical area, south
498   China, Scientia Geographical Sinica (in Chinese), 22(2), 196-201, 2002.
499 Collin, M., and Rasmuson, A.: A comparison of gas diffusivity models for unsaturated porous media, Soil
500   Sci. Soc Am.J, 52, 1559-1565, 1988.
501 Dai, W.H., Wang, Y. Q., Huang, Y., Liu, J., and Zhao, L.: Seasonal dynamic of CO_2 concentration in Lou
502   soil and impact by environmental factors, Acta Pedologica Sinica (in Chinese), 41(5), 827-831, 2004.
503 Dyer, J. M., and Brook, G. A.: Spatial and temporal variations in temperate forest soil carbon dioxide
504   during the non-growing season, Earth Surf. Proc. Land, 16(5), 411-426, 1991.
505 Fan, S., Gloor, M., Mahlman, J., Pacala, S., Sarmiento, J., Takahashi, T., and Tans, P.: A large terrestrial
506   carbon sink in North American implied by atmospheric and oceanic carbon dioxide data and models,
507   Science, 282, 442-446, 1998.
508 Fearnside, P.M.: Brazil's Amazonian forest carbon: the key to Southern Amazonian's significance for global
509   climate, Reg. Environ. Change, 18, 47-61, 2018.
510 Jiang, Z.C., and Yuan, D. X.: Dynamics features of the epikarst zone and their significance in environments
511   and resources, Acta Geoscientia Sinica (in Chinese), 20(3), 302-308, 1999.
512 Li, B., and Yuan, D. X.: Carbon cycle of epikarst in carbonate areas. In: Earthquake Center. carbonate and
513   environment (Vol.1). Earthquake Press (in Chinese), Beijing, 1-15, 1995.
514 Li, T. Y., Wang, S. J., and Zheng, L. P.: Comparative study on CO2 sources in soil developed on carbonate
515   rock and non-carbonate rock in Central Guizhou, Science in China Series D-Eearth Sciences, 45(8),
516   673-679, 2002.
517 Liang, F.Y., Song, L. H., Tang, T., and Wang, J.: Microbial production of CO_2 in red soil in stone forest
518   national park, Carsologica Sinica (in Chinese), 22(1), 6-11, 2003.
519 Martin, J. B., Brown, A., and Ezell, J. : Do carbonate karst terrains affect the global carbon cycle? Acta
520   Carsologica, 42(2-3), 187-196, 2013.
521 Nie, Y.P.: A Preliminary study and test on the dissolution of carbonate rocks in south Guizhou province.
522   Carsologica Sinica (in Chinese), 1, 39-45, 1984.
523 Owens, J. D., Lyons, T. W., and Lowery, C. M.: Quantifying the missing sink for global organic carbon
524   burial during a Cretaceous oceanic anoxic event, Earth Planet Sci Lett, 499, 83-94, 2018.
525 Pan, G.X., Cao, J. H., He, S. Y., Teng, Y. Z., and Xu, S.Y.: Sink effect of karst soil system on atmospheric
526   CO_2: evidence from field observation and simulation experiment, Earth Science Frontiers (in Chinese),
527   7(4), 580-587, 2000.
528 Potter, C. S., and Klooster, S.A.: North American carbon sink, Science, 283, 1815, 1999.
529 Rubin, Y., and Or, D.: Stochastic modeling of unsaturated flow in heterogeneous soil with water uptake by
530   plant roots: the parallel columns model, Water Resour Res, 29(3), 619-631, 1993.
531 Rustad, L.E., Huntington, T.G., and Boone, R.D.: Controls on soil respiration: implications for climate
532   change, Biogeochemistry, 49, 1–6, 2000.
533 Solomon, D.K., and Cerling, T. E.: The annual carbon dioxide cycle in a montane soil: observation,
534   modeling and implications for weathering, Water Resour Res, 23, 2257-2265, 1987.
535 Sundquist, E. T.: The global carbon budget, Science, 259, 934-941, 1993.
536 Teir, S., Eloneva, S., Fogelholm, C. J., and Zevenhoven, R.: Stability of calcium carbonate and magnesium
537   carbonate in rainwater and nitric acid solutions, Energ. Convers. Manage, 47, 3059-3068, 2006.
538 Tfaily, M. M., Hess, N. J., Koyama, A., and Evans, R. D.: Elevated CO_2 changes soil organic matter
539   composition and substrate diversity in an arid ecosystem, Geoderma, 330(15), 1-8, 2018
540 Wood, W.W., and Petraitis, M. J.: Origin and distribution of carbon dioxide in the unsaturated zone of the
541   southern high plains of texas, Water Resour Res, 20(9), 647-659, 1984.
542 Xu, S.Y., and He, S. Y.: The CO_2 regime of soil profile and its drive to dissolution of carbonate rock,
543   Carsologica Sinica (in Chinese), 18(1-2), 50-57, 1996.
544 Zeng, S.W., and Zheng, L. P.: Mathematical model of soil CO_2 transference in karst area, Shanghai
545   Environmental Sciences (in Chinese), 21(12), 712-715, 2002.