

1 **Responses to Referee 1**

2 **Comment 1:** Could authors provide the ratio of the nitrate fertilizer vs. total nitrogen
3 fertilizers in studied area, or China, or whole world? It is important for the
4 significance of the manuscript and the experiment.

5 Answer: Yes, it is very important, but we can't find the specific published data about
6 it. Only one figure we can calculate according to a reference published in 2008 is that
7 the global production of NH_4NO_3 accounts for 10% of the total N fertilizers, and
8 about 4% in China. But we think this figure is not fit to be cited in this manuscript.
9 We think that this study only focused on the relative potential mechanism, and the
10 study on the estimation of the impacts will be considered in the future.

11 **Comment 2:** Could authors compare results with data by Prof. Yuan DX's group
12 paper ?

13 Answer: We have cited the relative result from Prof. Yuan Dx's group in this study,
14 such as the papers from Jiang Z., et al.; Liu Z., et al. and Jiang Y., et al.. In fact, we are
15 familiar with them and their study focuses, we know that their studies are a little bit
16 different from ours so far.

17 **Comment 3:** The manuscript need more detail for the experiment. L134-L139: Please
18 give a detail introduction for the added amount of fertilizers in these treatments. It
19 seems that the added amount of nitrogen is slight difference.

20 (1) What's the proportion of these eleven fertilization treatments in local practical
21 use?

22 Answer: The added amounts of these 11 fertilizers were designed only by the
23 average amount of N, P and K fertilizer in the local practical use.

24 Changed in the manuscript: We have added the amount of N, P and K fertilizer in
25 local practical use in this manuscript like this: N fertilizer: $160 \text{ kg N} \cdot \text{ha}^{-1}$; P fertilizer:
26 $150 \text{ kg P}_2\text{O}_5 \cdot \text{ha}^{-1}$; K fertilizer: $50 \text{ kg K} \cdot \text{ha}^{-1}$)

27 (2) Why choose the added amount of fertilizers are 30 times than its local practical
28 amount? The application fertilizers in local practical may change two or three times to
29 use. Do you think the added fertilizers by one time may affect the result?

30 Answer: Because the added amount of fertilizer can magnify and quicken the
31 fertilization effect in the short-term according to another experiment from us, and
32 can't affect the phenomenon we want to observe in this study. Another paper of ours
33 (in preparation) about a series of different amount of fertilizer addition will discuss
34 this issue.

35 (3) Why don't authors set different height for this experiment, which might be more
36 interesting?

37 Answer: Thank you for your good suggestion. This study is conducted as a simply
38 start. The suggestion on different height must be interesting. We are considering that
39 in further study.

40 (4) Does author consider that the land use influences the carbonate weathering in the
41 experiment?

42 Answer: In fact, there are some good studies to be published about that around the
43 world. But most of them are conducted by the search and evaluation of riverine

44 hydro-geochemical data. Because of this, we did this study from another angle, and
45 hope to connect them in the future.

46 **Comment 4:** The authors made three replications. So please show the data errors for
47 each average value.

48 Answer: Fig.3 has showed these error bars. We will add them in Table 2.

49 Changed in the manuscript: The error data have been added in Table 2.

50 **Comment 5:** Could you assess the variation of nitrate fertilizer change in the
51 column. Then understand the balance between acid producing and carbonate
52 weathering together.

53 Answer: We tried our best to explain the chemical process of N fertilizer in section
54 4.3 with relative chemical reactions.

55 **Comment 6:** Line 15-17, the sentence has too many “different”s. Please revise it.

56 Changed in the manuscript: We use “these discrepancies” instead of “their
57 differences”.

58 **Comment 7:** In section 2.2, could authors provide details about abbreviation of OM,
59 ASI method and others when you write that at the first time. Please check that in
60 whole manuscript.

61 Changed in the manuscript: We have changed this.

62 **Comment 8:** L162-166 It seems Table 2 and Fig3 are repeated.

63 Changed in the manuscript: We deleted the relative data in Table 2, and leave the Fig.
64 3 because the figure is easier to see. And we also changed corresponding texts.

65 **Comment 9:** L182-L197 This paragraph can be removed to the introduction.

66 Changed in the manuscript: We moved them to the introduction.

67 **Comment 10:** L213-L219 It is repeated the introduction (L49-L54).

68 Answer: Because they are for elaborating different problem, we think we should put
69 one of them another way.

70 Changed in the manuscript: We changed the statements in section 4.2.

71 **Comment 11:** Major conclusion might be revised. Ammonium fertilizer mainly
72 includes NH_4NO_3 , NH_4Cl , $(\text{NH}_4)_2\text{CO}_3$ fertilizers, not includes urea fertilizer. I
73 suggest reductive nitrogenous fertilizer could enhance carbonate weathering via
74 nitrification.

75 Changed in the manuscript: Yes, the statement that nitrogenous fertilizer can aid
76 carbonate weathering should be replaced by ammonium fertilizer” in this manuscript
77 is not precise. We deleted it.

78

79 **Responses to Referee 2**

80 **Comment 1** - The authors did not present very well the process/method of weathering
81 which has been used in this experiment: (1) did the authors perform a leaching of the
82 soil column? How are the fertilizers introduced in the soil column? Are spread mixed
83 with soil or spread in solutions? The lack of explanation of the method used does not
84 allow us to assess the results at their fair value. There is also a lack of discussion and
85 comparison of numerical values obtained in other experiments and in natural and
86 agricultural catchments. The carbonate weathering is only estimated based on the
87 weight of each rock tablets. It is not checked by the geochemistry of both rock tablets
88 and the potential weathering/soil solution. Indeed, it would have been interesting to
89 have an estimation of the chemical weathering.

90 Answer: The fertilizer was mixed with soil before filling in columns.

91 Changed in the manuscript: We added a sentence to explain this. The soil was
92 weighed, mixed perfectly with above fertilizer, respectively, and filled in its own
93 column.

94 **Comment 2** – To speed up the carbonate weathering, the fertilizers were introduced
95 by increasing their amount by 30 times (Why 30 times?). It is a bit problematic,
96 because the authors changed the soil/fertilizers ratio compared to
97 “natural/anthropogenic” ratio? What is this ratio in the local agricultural catchments?
98 What are the specificities these local catchments compared to national Chinese
99 catchments and worldwide catchments?

100 Answer: Because the added amount of fertilizer can magnify and quicken the
101 fertilization effect in the short-term according to another experiment from us, and
102 can't affect the phenomenon we want to observe in this study. Another paper of ours
103 (in preparation) about a series of different amount of fertilizer addition will discuss
104 this issue. The added amounts of these 11 fertilizers were designed only by the
105 average amount of N, P and K fertilizer in the local practical use.

106 Changed in the manuscript: We have added the amount of N, P and K fertilizer in
107 local practical use in this manuscript like this: (N fertilizer: $160 \text{ kg N} \cdot \text{ha}^{-1}$; P fertilizer:
108 $150 \text{ kg P}_2\text{O}_5 \cdot \text{ha}^{-1}$; K fertilizer: $50 \text{ kg K} \cdot \text{ha}^{-1}$)

109 **Comment 3** – The variability of the experimental replicates should be shown
110 (average and standard deviations), presented and discussed. This can be presented in
111 Table 2.

112 Answer: We did it.

113 **Comment 4** – In general, the authors used limestone and dolostone tablets. They did
114 not discuss the results of dolostone tablets, only those from limestone tablets. In the
115 discussion, the difference or similarity between dolostone and limestone is erased as
116 the authors discuss about carbonates. More attention, or at least an explanation about
117 the use of the general term of “carbonates” instead of the difference between
118 dolostone and limestone should be given.

119 Answer: The difference between limestone and dolostone is not noteworthy, so we
120 use carbonate instead. Yes, we need to give some sentences to explain this.

121 Changed in the manuscript: We added the statement “The result between limestone

122 and dolostone weathering under different fertilization treatment were similar. We will
123 explain the results with carbonates instead of individual dolostone and limestone.” in
124 this manuscript to explain

125 **Comment 5:** In several times in the manuscript (last sentence of the abstract, first
126 paragraph of the results, and the last sentence of the conclusion) the authors used the
127 expression “can aid carbonate weathering”: they should precise if the fertilizers
128 enhance, increase, or decrease carbonate weathering.

129 Changed in the manuscript: The statement that nitrogenous fertilizer can aid carbonate
130 weathering should be replaced by ammonium fertilizer” in this manuscript is not
131 precise. We deleted it. And we replaced the rest aids with the word “increase”.

132 **Comment 6:** Introduction: - L.43 - The authors should add references showing the
133 relationship between carbonate weathering and climate in addition to Liu et al. (2010,
134 2011); for example Kump et al., 2000). –

135 Changed in the manuscript: We added it.

136 **Comment 7:** L.47 - The authors should precise that the disturbance of CO₂
137 consumption disturbance may be overestimated at a local scale by taking into account
138 Ca²⁺ and Mg²⁺ produced by a natural carbonate weathering and those produced
139 indirectly by anthropogenic activities in the watershed. And what about this
140 disturbance at a global scale?

141 Answer: Here, we are just trying to introduce the potential disturbance at the
142 regional/global scales by summarizing and classifying some references in the 1st
143 paragraph. And the specific disturbances from fertilizer addition were further
144 discussed in the 2nd paragraph.

145 **Comment 8:** 2.2. Soil properties : - At which depth did the authors sample their soils?
146 - Should precise pH(H₂O) - Precise what OM means: organic matter I suppose. -
147 Precise what ASI method means. - What is the soil typology?

148 Answer: The pH had been listed in Table 1.

149 Changed in the manuscript: The meanings of OM and ASI have been added. We
150 changed the statement “The soil used in this column experiment was sampled from
151 the B horizon (below 20 cm in depth) of yellow-brown soil in a cabbage-corn or
152 capsicum-corn rotation plantation in Huaxi district.” to explain the soil samples and
153 typology.

154 **Comment 9:** 2.3. Soil column - What is the filter material?

155 Answer: Yes, it is a misleading expression here.

156 Changed in the manuscript: It has been changed into: A Polyethylene net (Ø 0.5 mm)
157 was placed in the bottom of the columns to prevent soil loss. A filter sand layer with 2
158 cm thickness including gravel, coarse sand and fine sand was spread on the net.

159 **Comment 10:** What kind of carbonate rocks did the authors use for their experiment?
160 Are they reference rocks or rocks from karst area of HuaXi district?

161 Answer: yes, it was collected from karst area of Huaxi district.

162 Changed in the manuscript: We added this information in this manuscript.

163 **Comment 11:** How did the authors deposit each fertilizer in the column? In liquid or
164 solid form? At which temperature has the experiment been performed? - Did you
165 leach the soil column with a solution? If yes, with which solution?

166 Answer: The soil fertilizer was weighed and mixed with soil before filling in columns.
167 Changed in the manuscript: We added a sentence to explain this. The soil was
168 weighed, mixed perfectly with above fertilizer, respectively, and filled in its own
169 column.

170 **Comment 12:** - In figure 2: the authors draw 3 rock tablets, while the authors put only
171 2 rock tablets at the bottom of the column. Should change it.

172 Changed in the manuscript: We have changed this.

173 **Comment 13:** - Did the authors perform the same experiment without rock tablets if
174 they leach their column in order to observe the leaching solution of the column?

175 Answer: We didn't design that in this study. We didn't collect the soil solution. The
176 leaching depended on the rainfall.

177 **Comment 14:**- Did the authors put the 2 different rock tablets (calcite and dolomite)
178 in the same column?

179 Answer: Yes, we did.

180 **Comment 15:** The authors should explain the reason of the fertilizer weight use in the
181 experiment.

182 Answer: Because the added amount of fertilizer can magnify and quicken the
183 fertilization effect in the short-term according to another experiment from us, and
184 can't affect the phenomenon we want to observe in this study. Another paper of ours
185 (in preparation) about a series of different amount of fertilizer addition will discuss
186 this issue. The added amounts of these 11 fertilizers were designed only by the
187 average amount of N, P and K fertilizer in the local practical use.

188 Changed in the manuscript: We have added the amount of N, P and K fertilizer in
189 local practical use in this manuscript like this: N fertilizer: $160 \text{ kg N} \cdot \text{ha}^{-1}$; P fertilizer:
190 $150 \text{ kg P}_2\text{O}_5 \cdot \text{ha}^{-1}$; K fertilizer: $50 \text{ kg K} \cdot \text{ha}^{-1}$)

191 **Comment 16:** 3. Results - L.164-165: Do not repeat Table 2 and Fig. 3. You may
192 write: "The results are presented in Table 2 and in Figure 3.

193 Changed in the manuscript: We have changed this.

194 **Comment 17:** 4. Discussion - 4.1.: the first paragraph (L. 182-197) is quite general
195 and it would be worthy to move it either in the introduction, or at least in the
196 Materials and Methods section.

197 Changed in the manuscript: We moved them to the introduction.

198 **Comment 18:** 4.1. L.213-219: It is exactly the same text as in the introduction (L.
199 48-54) The authors may express their idea at least a little bit differently.

200 Answer: Because they are for elaborating different problem, we think we should put
201 one of them another way.

202 Changed in the manuscript: We changed the statements in section 4.2.

203 **Comment 19:** Information about soils and soil solutions are needed in order to
204 understand their chemical evolution during the carbonate weathering. - Would it be
205 possible to present the chemistry of each fertilizer used in this experiment? This can
206 be added in supplementary information.

207 Answer: yes, it is very important. Most of them have been discussed in section 4.2
208 and 4.3 so far. And we are doing some further research on that.

209 |

210 **Impact of different fertilizers on the carbonate weathering in a typical karst area,**

211 **Southwest China: a field column experiment**

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222 **Abstract:** Carbonate weathering, as a significant vector for the movement of carbon
223 both between and within ecosystems, are strongly influenced by anthropogenic
224 perturbations such as agricultural fertilization. Different fertilizer may exert a
225 different impact on carbonate weathering, but ~~their~~ ~~these discrepancies~~ ~~differences~~ are
226 not still well-known so far. In this study, a field column experiment was employed to
227 explore the responses of carbonate weathering to different fertilizer addition. The
228 eleven different treatments with three replicates including control, NH_4NO_3 ,
229 NH_4HCO_3 , NaNO_3 , NH_4Cl , $(\text{NH}_4)_2\text{CO}_3$, $\text{Ca}_3(\text{PO}_4)_2$, $(\text{NH}_4)_3\text{PO}_4$, fused
230 calcium-magnesium phosphate fertilizer (Ca-Mg-P), Urea and K_2CO_3 were
231 established in this column experiment, where limestone and dolostone tablets were
232 buried at the bottom of each to determine the weathering amount and ratio of
233 carbonate in soil. The result showed that the addition of urea, NH_4NO_3 , NH_4HCO_3 ,
234 NH_4Cl and $(\text{NH}_4)_2\text{CO}_3$ distinctly increased carbonate weathering, which was
235 attributed to the nitrification of NH_4^+ , and the addition of $\text{Ca}_3(\text{PO}_4)_2$, Ca-Mg-P and
236 K_2CO_3 induced carbonate precipitation due to common ion effect. Whereas the
237 $(\text{NH}_4)_3\text{PO}_4$ and NaNO_3 addition did not impact significantly on carbonate weathering.
238 The results of NaNO_3 treatment seem to be raising a new question: the little impact of
239 nitrate on carbonate weathering may result in the overestimation of impact of
240 N-fertilizer on CO_2 consumption by carbonate weathering at the regional/global scale
241 if the effect of NO_3 and NH_4 are not distinguished. ~~Moreover, in order to avoid~~
242 ~~misunderstanding more or less, the statement that nitrogenous fertilizer can aid~~
243 ~~carbonate weathering should be replaced by ammonium fertilizer.~~

244 **Keywords:** Carbonate weathering; Column experiment; Nitrogenous fertilizer;
245 Phosphate fertilizer; Southwest China

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250 1. Introduction

251 Carbonate weathering plays a significant role in consumption of the elevated
252 atmospheric CO₂ ([Kump et al., 2000; Liu et al., 2010; 2011](#))(~~[Liu et al., 2010; 2011](#)~~).

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253 The riverine hydro-chemical composition such as the ratio of HCO₃⁻ and Ca²⁺+Mg²⁺
254 is usually employed as an indicator to estimate the CO₂ consumption by carbonate
255 weathering at the regional/global scale (Hagedorn and Cartwright, 2009; Li et al.,
256 2009). However, a disturbance to CO₂ consumption estimation is introduced because
257 the fluvial alkalinity, Ca²⁺ and Mg²⁺ may also be produced due to the reaction
258 between carbonate and the protons which can originate from the nitrification
259 processes of N-fertilizer (Barnes and Raymond, 2009; Chao et al., 2011; Gandois et
260 al., 2011; Hamilton et al., 2007; Oh and Raymond, 2006; Perrin et al., 2008;
261 Pierson-wickmann et al., 2009; Semhi and Suchet, 2000; West and McBride, 2005),
262 from the sulfuric acid (Lerman and Wu, 2006; Lerman et al., 2007; Li et al., 2008; Li
263 et al., 2009), from organic acid secreted by microorganisms (Lian et al., 2008), as well
264 as from acidic soil(Chao et al., 2014). Given the atmospheric CO₂ is not the unique
265 weathering agent, differentiating the agent of carbonate weathering is more and more

266 significant to enable the accurate budgeting of the net CO₂ consumption by carbonate,
267 especially in agricultural area.

268 The world average annual increase in fertilizer consumption was 3.3% from 1961
269 to 1997, and FAO's study predicts a 1% increase per year until 2030 (FAO, 2000).
270 For China, the consumption of chemical fertilizer increased from 12.7 Mt in 1980 to
271 59.1 Mt in 2013 (Fig. 1). The Increasing consumption of chemical fertilizer is a
272 significant disturbance factor of carbonate weathering and carbon cycle. Many studies
273 showed that nitrogen fertilizer additions ~~aided~~ increased in the dissolution of lime and
274 increase the total export of DIC from agricultural watersheds (Barnes and Raymond,
275 2009; Gandois et al., 2011; Hamilton et al., 2007; Oh and Raymond, 2006; Perrin et
276 al., 2008; Pierson-wickmann et al., 2009; Probst, 1986; Semhi and Suchet, 2000; West
277 and McBride, 2005). According to the estimation from Probst (1988) and Semhi et al.
278 (2000), the contribution of N-fertilizers to carbonate dissolution represents 30% and
279 12-26%, respectively, on two small agricultural carbonate basins in south-western
280 France, the Girou and the Gers (subtributary and tributary of the Garonne river,
281 respectively). For larger basin level, such as the Garonne river basin, this contribution
282 was estimated at 6% by Semhi et al. (2000). At national and global scales, Perrin et al.
283 (2008) estimated that the deficit of CO₂ uptake due to N-fertilizer addition (usually in
284 form of NH₄NO₃) represent up to 5.7-13.4% and only 1.6-3.8% of the total CO₂ flux
285 naturally consumed by carbonate dissolution, for France and on a global scale,
286 respectively.

287 |
288 These estimated results were usually based on a hypothesis of individual fertilizer

289 (e.g. $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , or NH_4Cl) input into an agricultural basin. Nevertheless, at
290 an agricultural basin, different fertilizers are usually added for different crops in actual
291 agricultural practices. The impact of these fertilizers on carbonate weathering and
292 riverine chemical composition may be different. For nitrogenous fertilizer, 100% NO_3^-
293 produced after the addition $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl derive from the nitrification of
294 NH_4^+ , comparatively, only 50% after the addition NH_4NO_3 . The difference of NO_3^-
295 source may cause the evaluated deviation of the impact of N-fertilizer addition on
296 CO_2 consumption by carbonate weathering. For phosphate fertilizer, the
297 coprecipitation of phosphate ions with calcium carbonate may inhibit carbonate
298 weathering (Kitano et al., 1978). We suppose that the response of carbonate
299 weathering to the addition of different fertilizer such as N-fertilizer (NH_4 and NO_3),
300 P-fertilizer and Ca/Mg fertilizer may display difference, which is poorly known so far
301 but significant to well understand the agricultural force on natural carbonate
302 weathering and accurately evaluate the CO_2 consumption via carbonate weathering in
303 agricultural area.

304 Moreover, The carbonate-rock-tablet test is used to determine the weathering
305 rate of carbonate rock/mineral from laboratory to field (Gams, 1981; Chao et al., 2011;
306 Trudgill, 1975; Chao et al., 2014; Dreybrodt et al., 1996; Gams, 1985; Jiang and Yuan,
307 1999; Liu and Dreybrodt, 1997; Plan, 2005). In laboratory, the carbonate-rock-tablet is
308 employed to study the kinetics of calcite dissolution/precipitation (Dreybrodt et al.,
309 1996; Liu and Dreybrodt, 1997) and determine the rate of carbonate mineral
310 weathering in soil column (Chao et al., 2011). However, in field, it is also used to
311 observe the rate of carbonate weathering and estimated CO_2 consumption by
312 carbonate weathering (Chao et al., 2014; Jiang and Yuan, 1999; Jiang et al., 2013;
313 Plan, 2005). Although Liu (2011) argue that the carbonate-rock-tablet test may lead to

314 the deviation of estimated CO₂ consumption by carbonate weathering at the
315 regional/global scale in the case of insufficient representative data (Liu, 2011), our
316 results show that it is a preferred option for the condition controlled contrast or
317 stimulated experiment (Chao et al., 2011; Chao et al., 2014), where the result from the
318 carbonate-rock-tablet test is consistent to the major element geochemical data of
319 leachates from soil column(Chao et al., 2011).

320 ~~ThusTherefore, in order to observe their difference between the impacts of~~
321 ~~different fertilizer addition on carbonate weathering in soil,~~ a field column experiment
322 ~~embedding carbonate rock tablets with eleven different treatments~~ was carried out in a
323 typical karst area of southwest China to observe the impacts of different fertilizer
324 addition on carbonate weathering in soil.

325 **2. Materials and Methods**

326 **2.1 The study site**

327 This study was carried out in a typical karst area, the ~~HuaXi~~-Huaxi district of
328 Guiyang city, Guizhou province, SW China (26°23'N, 106°40'E, 1094 m asl).
329 Guiyang, the capital city of Guizhou Province, is located in the central part of The
330 Province, covering an area from 26°11'00" to 26°54'20"N and 106°27'20" to
331 107°03'00"E, with elevations ranging from 875 to 1655 m above mean sea level.
332 Guiyang has a population of more than 1.5 million people, a high diversity of karstic
333 landforms, a high elevation and low latitude, with a subtropical warm-moist climate,
334 annual average temperature of 15.3 °C and annual precipitation of 1200 mm (Lang et
335 al., 2006). A monsoonal climate often results in high precipitation during summer and
336 much less during winter, although the humidity is often high during most of the year

337 (Han and Jin, 1996). Agriculture is a major land use in order to produce the vegetables
338 and foods in the suburb of Guiyang (Liu et al., 2006). The consumption of chemical
339 fertilizer increased from 0.8 Mt in 1980 to 1.0 Mt in 2013 (GBS, 2014).

340 **2.2 Soil properties**

341 The soil used in this column experiment was sampled from the B horizon (below
342 20 cm in depth) of yellow-brown soil in ~~–dug from~~ a cabbage-corn or capsicum-corn
343 rotation plantation in Huaxi district. ~~It was~~ air-dried, ground to pass through a 2-mm
344 sieve, mixed thoroughly and used for soil columns. The pH ($V_{\text{soil}}:V_{\text{water}} = 1:2.5$) were
345 determined by pH meter. The chemical characteristics of soil including organic
346 matter (OM), $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, available P, available K, available Ca, available Mg,
347 available S and available Fe were determined according to the Agro Services
348 International (ASI) Method (Hunter, 1980), where the extracting solution used for
349 ~~O-M~~ contained 0.2 mol l^{-1} NaOH, 0.01 mol l^{-1} EDTA, 2% methanol and 0.005%
350 Superfloc 127, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, available Ca and Mg were determined based on
351 extraction by 1 mol l^{-1} KCl solution, available K, P and Fe were extracted by
352 extracting solution containing 0.25 mol l^{-1} NaHCO_3 , 0.01 mol l^{-1} EDTA, 0.01 mol l^{-1}
353 NH_4F , and 0.005% Superfloc 127, and available S was extracted by 0.1 mol l^{-1}
354 $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and 0.005% Superfloc 127. The results are shown in Table 1.

355 **2.3 Soil column and different fertilization treatments**

356 In order to test the hypothesis that the responses of the impact of different
357 chemical fertilizer on carbonate weathering may be different, columns ($\text{Ø}=20\text{cm}$, $H=$
358 15cm) were constructed from 20-cm diameter polyvinylchloride (PVC) pipe (Fig. 2).

359 A hole ($\varnothing=2$ cm) were established at the bottom of each column to discharge soil
360 water from ~~of~~ soil column. A Polyethylene net mesh (\varnothing 0.5 mm) was placed in the
361 bottom of the columns to prevent ~~the soil loss of the filter material~~. A filter sand layer
362 with 2 cm thickness including gravel, coarse sand and fine sand was spread on the
363 net. Two different carbonate rock tablets were buried in the bottom of each soil
364 column (Fig .2). According to common kinds of chemical fertilizer and the main
365 objective of this study, eleven fertilization treatments with three replicates in the field
366 column experiment were set up: (1)control without fertilizer (CK); (2)43g NH_4NO_3
367 fertilizer (CF); (3)85g NH_4HCO_3 fertilizer (NHC); (4)91g NaNO_3 fertilizer (NN);
368 (5)57g NH_4Cl fertilizer (NCL); (6)51g $(\text{NH}_4)_2\text{CO}_3$ fertilizer (NC); (7)52g $\text{Ca}_3(\text{PO}_4)_2$
369 fertilizer (CP); (8)15g $(\text{NH}_4)_3\text{PO}_4$ fertilizer (NP); (9)44g fused calcium-magnesium
370 phosphate fertilizer (Ca-Mg-P); (10) 32g Urea fertilizer (U) and (11) 10g K_2CO_3
371 fertilizer (PP). To shorten the experiment time and enhance the effect of fertilization,
372 the added amount of fertilizers in these treatments motioned above was increased to
373 30 times than its local practical amount (N fertilizer: $160 \text{ kg N} \cdot \text{ha}^{-1}$; P fertilizer: 150
374 $\text{kg P}_2\text{O}_5 \cdot \text{ha}^{-1}$; K fertilizer: $50 \text{ kg K} \cdot \text{ha}^{-1}$). The soil was weighed, mixed perfectly with
375 above fertilizer, respectively, and filled in its own column. These soil columns were
376 placed at the field experiment site in Guiyang of Southwestern China for a whole
377 year.

378 2.4 The rate of carbonate weathering

379 Two different kinds of carbonate rock tablets (2 cm \times 1 cm \times 0.5 cm in size) were
380 established in the bottom of each soil column to explore the rate of carbonate

带格式的：上标

带格式的：下标

带格式的：下标

381 weathering in soil. The two different kinds of carbonate rock collected from karst area
382 of Huaxi district were (1) limestone with 60-65% micrite, 30-35% microcrystalline
383 calcite and 2-3% pyrite and (2) dolostone with 98-99% power crystal dolomite, 3-5%
384 microcrystalline calcite, 1% pyrite and little organic matter. All of tablets were baked
385 at 80 °C for 4 hours then weighed in a 1/10000 electronic balance in the laboratory,
386 tied to a label with fishing line and buried at the bottom of each soil column. They
387 were taken out carefully, rinsed, baked and weighed after a whole year.

388 The amount of carbonate weathering (A_{cw}), the ratio of carbonate weathering
389 (R_{cw}) and the rate of carbonate weathering (R_{acw}) were calculated according to the
390 weight difference of the tablets using the following formulas:

$$391 \quad A_{cw} = (W_i - W_f) \quad (1)$$

$$392 \quad R_{cw} = (W_i - W_f) / W_i \quad (2)$$

$$393 \quad R_{acw} = (W_i - W_f) / (S \cdot T) \quad (3)$$

394 where W_i is the initial weight of the carbonate rock tablets, W_f is their final weights,
395 S is the surface area of carbonate weathering tablets, and T is the experiment period.

396 **3. Results**

397 The amount (A_{cw}), the ratio (R_{cw}) and the rate (R_{acw}) of carbonate weathering
398 were listed in Table 2, and ~~the R_{cw} were plotted in~~ Fig. 3. The results ~~in Table 2 and~~
399 Fig. 3 between limestone and dolostone weathering under different fertilization
400 treatment were similar. We will explain the results with carbonates instead of
401 individual dolostone and limestone. The results showed ~~the~~ A_{cw} , R_{cw} and R_{acw} of
402 carbonate weathering under urea, NH_4NO_3 , NH_4HCO_3 , NH_4Cl and $(\text{NH}_4)_2\text{CO}_3$

403 treatments were positive, and much bigger than that under the control treatment,
404 suggesting that the addition of these fertilizers can aid and increase the chemical
405 weathering of carbonate. In $(\text{NH}_4)_3\text{PO}_4$ treatment, the A_{cw} , and R_{cw} were only
406 -0.0028g and -0.0007g for limestone and dolomite, -1.08% and -0.75% for limestone
407 and dolomite, respectively, less than those under other four NH_4 -fertilizers as
408 mentioned above. The A_{cw} , R_{cw} and R_{acw} in NaNO_3 treatment failed to show a
409 remarkable difference with control treatment, implying little effect of NaNO_3 fertilizer
410 addition on carbonate weathering (Fig. 3).

411 However, except the R_{cw} of limestone in $\text{Ca}_3(\text{PO}_4)_2$ treatment approaching zero,
412 the A_{cw} , R_{cw} and R_{acw} of two different carbonate in Ca-Mg-P and K_2CO_3 and
413 $\text{Ca}_3(\text{PO}_4)_2$ treatments showed a negative value, indicating that the addition of
414 Ca-Mg-P, K_2CO_3 and $\text{Ca}_3(\text{PO}_4)_2$ fertilizers can lead to the precipitation at the surface
415 of carbonate mineral, which can be explained by common ion effect.

417 4. Discussion

418 4.1 The carbonate rock tablet test: the validation of this experiment

419 ~~The carbonate rock tablet test is used to determine the weathering rate of~~
420 ~~carbonate rock/mineral from laboratory to field (Gams, 1981; Chao et al., 2011;~~
421 ~~Trudgill, 1975; Chao et al., 2014; Dreybrodt et al., 1996; Gams, 1985; Jiang and Yuan,~~
422 ~~1999; Liu and Dreybrodt, 1997; Plan, 2005). In laboratory, the carbonate rock tablet is~~
423 ~~employed to study the kinetics of calcite dissolution/precipitation (Dreybrodt et al.,~~
424 ~~1996; Liu and Dreybrodt, 1997) and determine the rate of carbonate mineral~~
425 ~~weathering in soil column (Chao et al., 2011). However, in field, it is also used to~~

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426 ~~observe the rate of carbonate weathering and estimated CO₂ consumption by~~
427 ~~carbonate weathering (Chao et al., 2014; Jiang and Yuan, 1999; Jiang et al., 2013;~~
428 ~~Plan, 2005). Although Liu (2011) argue that the carbonate rock tablet test may lead to~~
429 ~~the deviation of estimated CO₂ consumption by carbonate weathering at the~~
430 ~~regional/global scale in the case of insufficient representative data (Liu, 2011), our~~
431 ~~results show that it is a preferred option for the condition controlled contrast or~~
432 ~~stimulated experiment (Chao et al., 2011; Chao et al., 2014), where the result from the~~
433 ~~carbonate rock tablet test is consistent to the major element geochemical data of~~
434 ~~leachates from soil column(Chao et al., 2011).~~

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435 In this study, every procedure to establish soil column with carbonate rock tablets
436 in the bottom of each was strictly same, including the size of column, the preparation
437 and column filling of soil sample, the setting and test of carbonate rock tablets, etc.
438 Moreover, three replicates of each treatment were designed. We consider the
439 experiment design can meet the objective of this study and the results of
440 carbonate-rock-tablet test are therefore valid and credible.

441 **4.2 The kinetics and controlled factors of carbonate weathering**

442 Experimental studies of carbonate dissolution kinetics have shown metal
443 carbonate weathering usually depends upon three parallel reactions occurring at the
444 carbonate interface (Chou et al., 1989; Plummer et al., 1978; Pokrovsky et al., 2009):



448 where Me=Ca, Mg. As Eq. (5) describes, atmospheric/soil CO₂ is usually regarded as
449 the natural weathering agent of carbonate, whereas many studies have exposed that
450 carbonate weathering can occur due to the reaction (Eq. (4)) between carbonate and
451 ~~the other~~ proton contributors, as mentioned in introduction section: ~~s which can~~
452 ~~originate from~~ the nitrification processes of N-fertilizer H₄⁺ (Semhi and Suchet, 2000;
453 ~~West and McBride, 2005; Oh and Raymond, 2006; Hamilton et al., 2007; Perrin et al.,~~
454 ~~2008; Barnes and Raymond, 2009; Pierson-wickmann et al., 2009; Chao et al., 2011;~~
455 ~~Gandois et al., 2011), from~~ the sulfuric acid-acid, (Lerman and Wu, 2006; Lerman et
456 ~~al., 2007; Li et al., 2008; Li et al., 2009), from~~ organic acid secreted by
457 microorganisms (~~Lian et al., 2008~~), ~~as well and as from~~ acidic soil (Chao et al., 2014).

458 In field, carbonate dissolution is mainly controlled by the amount of rainfall
459 (Amiotte Suchet et al., 2003; Egli and Fitze, 2001; Kiefer, 1994), as well as impacted
460 of soil CO₂ (Andrews and Schlesinger, 2001). We consider that the effect of rainfall
461 on each soil column is same. In this study, the urea, NH₄NO₃, NH₄HCO₃, NH₄Cl and
462 (NH₄)₂CO₃ amendment increased (10 to 17-fold) the natural weathering rate of 2.00
463 g m⁻² a⁻¹ from limestone tablets in control treatment (table 2). These increases may be,
464 in the one hand, attributed to the effect of the proton released from the nitrification of
465 NH₄⁺. On the other hand, it may be, in theory, related to enhanced microbiogenic CO₂
466 due to nitrogenous nutrients stimulation (Eq(5)), because fertilizer application can
467 increase soil CO₂ flux (Sainju et al., 2008; Bhattacharyya et al., 2013), the increased
468 CO₂ can enhance carbonate dissolution rate at near neutral or alkali pH (Andrews and
469 Schlesinger, 2001).

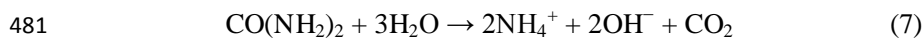
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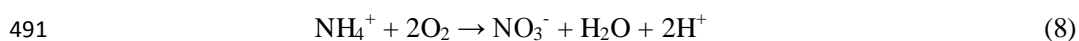
470 According to the added amount of different fertilization treatment, the molar
471 amount of added nitrogen nutrient in NaNO₃ treatment is 1.07mol, much bigger than
472 in NH₄NO₃, equivalent to NH₄HCO₃ and NH₄Cl treatment. However, the *Acw* and
473 *Rcw*, and *Racw* of NaNO₃ treatment is far less (Fig. 3 and table 2), inhibiting that the
474 increases of carbonate weathering rate in urea, NH₄NO₃, NH₄HCO₃, NH₄Cl and
475 (NH₄)₂CO₃ amendment have no distinct relationship with enhanced microbiogenic
476 CO₂ due to nitrogenous fertilizer amendment.

477 **4.3 The effect of nitrification of NH₄-fertilizer**

478 In urea (CO(NH₂)₂) treatment, the enzyme urease rapidly hydrolyzes the urea-N
479 (CO(NH₂)₂) to NH₄⁺ ions (Eq. (7)) when urea is applied to the soil (Soares et al.,
480 2012).

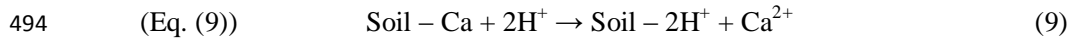


482 Table 3 shows that the amount of NH₄⁺ hydrolyzed from urea is 1.06 mol, while
483 NH₄⁺ ionized from NH₄NO₃, NH₄HCO₃, NH₄Cl, (NH₄)₂CO₃ and (NH₄)₃PO₄ is 0.54
484 mol, 1.08 mol, 1.07 mol, 1.06 mol and 0.03 mol, respectively (Table 3). Although the
485 study from Singh et al showed that a part of NH₄⁺ may be lost as ammonia (NH₃) and
486 subsequently as nitrous oxide (N₂O) (Singh et al., 2013), yet the rest ammonium
487 (NH₄⁺) is mainly oxidized in soil by autotrophic bacteria (like Nitrosomonas) during
488 nitrification, resulting in nitrite NO₂⁻ and H⁺ ions. Nitrite is, in turn, oxidized by
489 another bacterium, such as Nitrobacter, resulting in nitrate (NO₃⁻) (Eq. (8)) (Perrin et
490 al., 2008).

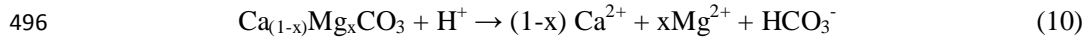


492 The protons (H^+) produced by nitrification can be neutralized in two ways:

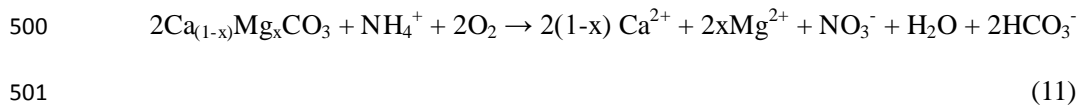
493 (i) either by exchange process with base cations in the soil exchange complex



495 (ii) or via carbonate mineral dissolution (Eq.(10))



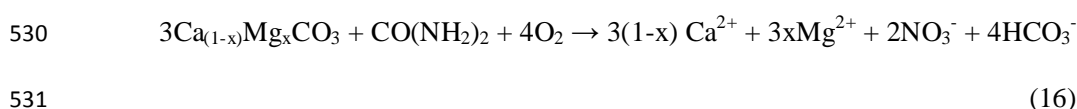
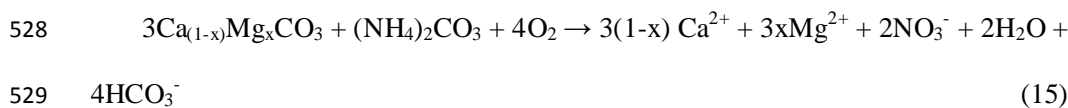
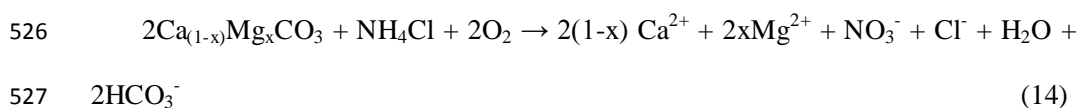
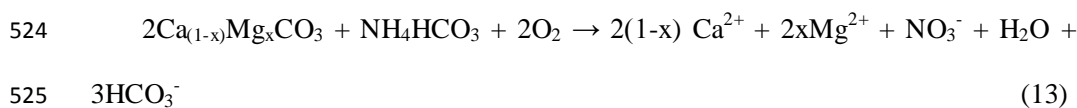
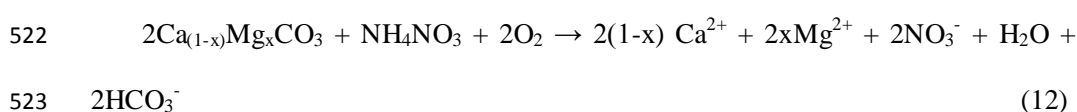
497 Consequently, after Eq. (8) and Eq. (10) are combined, carbonate weathering by
498 protons produced by nitrification is supposed to becomes (Eq. 11) (See details in
499 Perrin et al., 2008 and Gandois et al., 2011).



502 The R_{cw} of limestone tablets and the initial concentration of NH_4^+ are plotted in
503 Fig. 4. A distinct relationship between them is observed: the A_{cw} and R_{cw} in NH_4NO_3 ,
504 NH_4HCO_3 , NH_4Cl , $(NH_4)_2CO_3$ and urea treatments are bigger than in control
505 treatment, where the initial concentration of NH_4^+ displays similar results (Fig. 4).
506 This suggests that carbonate weathering in NH_4NO_3 , NH_4HCO_3 , NH_4Cl , $(NH_4)_2CO_3$
507 and urea treatments are mainly attributed to the dissolution reaction described as Eq.
508 (11). This process of carbonate weathering by protons from nitrification has been
509 proven by many studies, from laboratory to field (Semhi and Suchet, 2000; Bertrand
510 et al., 2007; Oh and Raymond, 2006; Errin et al., 2006; Hamilton et al., 2007; Biasi et
511 al., 2008; Perrin et al., 2008; Barnes and Raymond, 2009; Chao et al., 2011; West and
512 McBride, 2005; Gandois et al., 2011). According to the estimation from Yue et al.
513 (2015), The enhanced HCO_3^- flux due to nitrification of NH_4^+ at Houzhai catchment
514 of Guizhou province would be 3.72×10^5 kg C/year and account for 18.7% of this

515 flux in the entire catchment(Yue et al., 2015). This is similar to estimates from other
 516 small agricultural carbonate basins (12–26%) in Southwest France (Semhi and Suchet,
 517 2000; Perrin et al., 2008).

518 As discussed above, provided that the loss as ammonia (NH₃) and nitrous oxide
 519 (N₂O) after hydrolyzation is unconsidered in this study, the final equation of
 520 carbonate weathering in NH₄NO₃, NH₄HCO₃, NH₄Cl, (NH₄)₂CO₃ and urea treatments
 521 will be followed as, respectively:



532 The *A_{cw}* and *R_{cw}* in (NH₄)₃PO₄ treatment, unlike in other NH₄-fertilizer
 533 treatments, had not a significant increase comparing with control treatment, which is
 534 not only owing to the low amount of added NH₄⁺ in (NH₄)₃PO₄ treatment (0.3 mol,
 535 see Table 3) but also relative to the inhibition of phosphate. After the addition of
 536 (NH₄)₃PO₄ in soil, calcium orthophosphate (Ca-P) precipitation will form on calcite
 537 surface which is initiated with the aggregation of clusters leading to the nucleation
 538 and subsequent growth of Ca-P phases, at various pH values and ionic strengths

539 relevant to soil solution conditions (Chien et al., 2011; Wang et al., 2012).

540 **4.4 Little/no effect of NO₃-fertilizer on carbonate weathering and its implication**
541 **to the evaluation of CO₂ consumption by carbonate weathering**

542 In Fig. 3, the A_{cw} and R_{cw} without significant difference with control treatment
543 in NaNO₃ treatment indicates that the addition of NO₃-fertilizer does not significantly
544 influence carbonate weathering. This result is raising a new problem.

545 Eq. (5), usually as an expression for the natural weathering process of carbonate,
546 is an important reaction for understanding the kinetics process of carbonate
547 dissolution in carbonate-dominated areas, where the molar ratio of HCO₃⁻ and Me²⁺ in
548 the river as an indicator is usually used to make estimations of CO₂ consumption by
549 carbonate weathering at the regional/global scale (Hagedorn and Cartwright, 2009; Li
550 et al., 2009). At agricultural areas, the relationship between (Ca+Mg)/HCO₃⁻ and NO₃⁻
551 is usually employed to estimate the contribution of N-fertilizer to riverine Ca²⁺, Mg²⁺
552 and alkalinity (Etchanchu and Probst, 1988; Jiang, 2013; Jiang et al., 2009; Perrin et
553 al., 2008; Semhi and Suchet, 2000). In these studies, the nitrification described as Eq.
554 (8) is usually considered as the unique origin of NO₃⁻. According to the result of
555 NaNO₃ treatment in this study, the contribution of protons from nitrification to
556 carbonate weathering may be overestimated if anthropogenic NO₃⁻ is neglected, since
557 the anthropogenic NO₃⁻ does not release the proton described as Eq. (8). For NH₄NO₃
558 fertilizer, the (Eq. (12)) show that the two moles of Ca²⁺+Mg²⁺, NO₃⁻ and HCO₃⁻ will
559 be produced when one mole NH₄NO₃ react with 2 moles of carbonate, where only
560 half of NO₃⁻ originate from nitrification described as Eq. (8). This will result in
561 doubled overestimation on the true contribution of the nitrification to CO₂
562 consumption by carbonate weathering.

563 At regional scales, If different fertilizers are added to an agricultural area, the

564 estimation of CO₂ consumption by carbonate weathering might become more
565 complicated, since the mole ratio of Ca+Mg, HCO₃⁻ and/or NO₃⁻ between different
566 fertilization treatment is different (see Eq. (8)-(12)). Thus, the related anthropogenic
567 inputs (e.g. Ca+Mg, NH₄, NO₃⁻, HCO₃⁻, etc.) need to be investigated to more
568 accurately estimate the impact of fertilization on carbonate weathering and its CO₂
569 consumption. ~~Moreover, the statement that nitrogenous fertilizer can aid carbonate~~
570 ~~weathering may result in misunderstanding more or less, it should not be nitrogenous~~
571 ~~fertilizer but, rather, ammonium fertilizer.~~

572 **5. Conclusion**

573 The impact of the addition of different fertilizer (NH₄NO₃, NH₄HCO₃, NaNO₃,
574 NH₄Cl, (NH₄)₂CO₃, Ca₃(PO₄)₂, (NH₄)₃PO₄, Ca-Mg-P, Urea and K₂CO₃) on carbonate
575 weathering was studied in a field column experiment with carbonate rock tablets at its
576 bottom of each. The weathering amount and ratio of carbonate rock tablets showed
577 that the addition of urea, NH₄NO₃, NH₄HCO₃, NH₄Cl and (NH₄)₂CO₃ distinctly
578 increased carbonate weathering, which was attributed to the nitrification of NH₄⁺, and
579 the addition of Ca₃(PO₄)₂, Ca-Mg-P and K₂CO₃ induced carbonate precipitation due
580 to common ion effect. While the (NH₄)₃PO₄ and NaNO₃ addition did not impact
581 significantly on carbonate weathering, where the former can be attributed to low
582 added amount of (NH₄)₃PO₄, may be related to the inhibition of phosphate, and the
583 latter seemed to be raising a new question. The little impact of nitrate on carbonate
584 weathering may result in the overestimation of impact of N-fertilizer on CO₂
585 consumption by carbonate weathering at the regional/global scale if the effect of NO₃
586 and NH₄ are not distinguished. Thus, the related anthropogenic inputs (e.g. Ca+ Mg,

587 NH₄, NO₃⁻, HCO₃⁻, etc.) need to be investigated to more accurately estimate the
588 impact of fertilization on carbonate weathering and its CO₂ consumption. ~~Moreover,~~
589 ~~in order to avoid misunderstanding more or less, the statement that nitrogenous~~
590 ~~fertilizer can aid carbonate weathering should be replaced by ammonium fertilizer.~~

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Table 1 Chemical composition of soil

Parameter	Unit	Values
pH	-	6.94
Organic matter	%	0.99
NH ₄ ⁺ -N	mg/kg	339.87
NO ₃ ⁻ -N	mg/kg	569.05
Available P	mg/kg	8.18
Available K	mg/kg	56.88
Available Ca	mg/kg	3041.06
Available Mg	mg/kg	564.83
Available S	mg/kg	100.72
Available Fe	mg/kg	24.41

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Table 2 Carbonate weathering under different fertilizer treatments

Treatment	Limestone		Dolostone	
	Acw/g	Racw/ g m ⁻² a ⁻¹ Rew/%	Acw/g	Racw/ g m ⁻² a ⁻¹ Rew/ /%
Control	0.0014 _± 0.0004	2.00±0.58 0.48	-0.0011 _± 0.0006	-1.57±0.86 -0.31
NH ₄ NO ₃	0.0174 _± 0.0014	24.86±2.01 6.42	0.0144 _± 0.0008	20.57±1.15 5.30
NH ₄ HCO ₃	0.0147 _± 0.0024	21.00±3.45 4.44	0.0096 _± 0.0027	13.71±3.88 3.22
NaNO ₃	0.0031 _± 0.0012	4.43±1.73 0.86	0.0022 _± 0.0012	3.14±1.73 0.53
NH ₄ Cl	0.0149 _± 0.0017	21.29±2.45 5.54	0.0131 _± 0.0006	18.71±0.86 4.77
(NH ₄) ₂ CO ₃	0.0144 _± 0.0031	20.57±4.46 4.84	0.0186 _± 0.0053	26.57±7.62 4.94
Ca ₃ (PO ₄) ₂	0.0003 _± 0.0006	0.43±0.86 0.01	-0.0013 _± 0.0009	-1.86±1.29 -0.55
(NH ₄) ₃ PO ₄	0.0028 _± 0.0008	4.00±1.15 1.08	0.0007 _± 0.0007	1.00±1.01 0.75
Ca-Mg-P	-0.0013 _± 0.0003	-1.86±0.43 -0.31	-0.0022 _± 0.0005	-3.14±0.72 -0.97
Urea	0.0243 _± 0.0030	34.71±4.32 8.48	0.0185 _± 0.0019	26.43±2.73 6.59
K ₂ CO ₃	-0.0008 _± 0.0004	-1.14±0.58 -0.26	-0.0018 _± 0.0003	-2.57±0.43 -0.59

1035 Acw - the amount of carbonate weathering; Rcw - the ratio of carbonate weathering; Racw - the rate of
 1036 carbonate weathering; $Acw = (W_i - W_f)$; $Rcw = (W_i - W_f)/W_i$; $Racw = (W_i - W_f)/(S \cdot T)$, where W_i is the
 1037 initial weight of the carbonate rock tablets, and W_f is their final weight. S is the surface area of
 1038 carbonate weathering tablets, and T is the experiment period.

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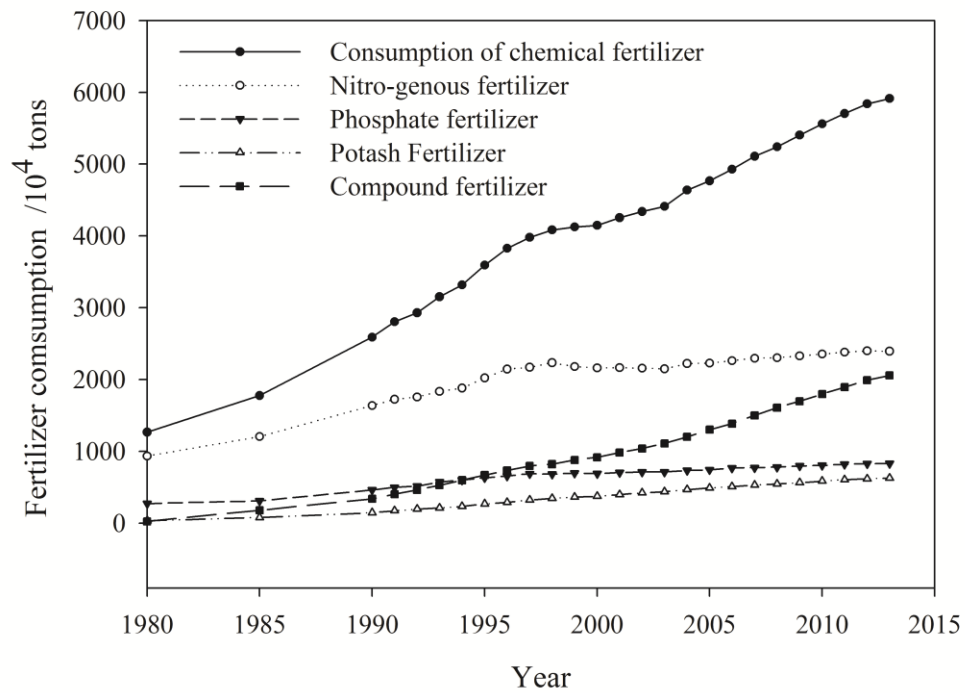
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Table 3: The amount of generated NH_4^+ at the initial phase of the experiment

Treatment	Relative molecular mass /g/mol	Amount of added fertilizer /g	Molar concentration /mol	Initial NH_4^+ /mol
NH_4NO_3	80	43	0.54	0.54
NH_4HCO_3	79	85	1.08	1.08
NaNO_3	85	91	1.07	0.00
NH_4Cl	53.5	57	1.07	1.07
$(\text{NH}_4)_2\text{CO}_3$	96	51	0.53	1.06
$\text{Ca}_3(\text{PO}_4)_2$	310	52	0.17	0.00
$(\text{NH}_4)_3\text{PO}_4$	149	15	0.10	0.30
Ca-Mg-P	/	44	0.00	0.00
Urea	60	32	0.53	1.06
K_2CO_3	138	10	0.07	0.00

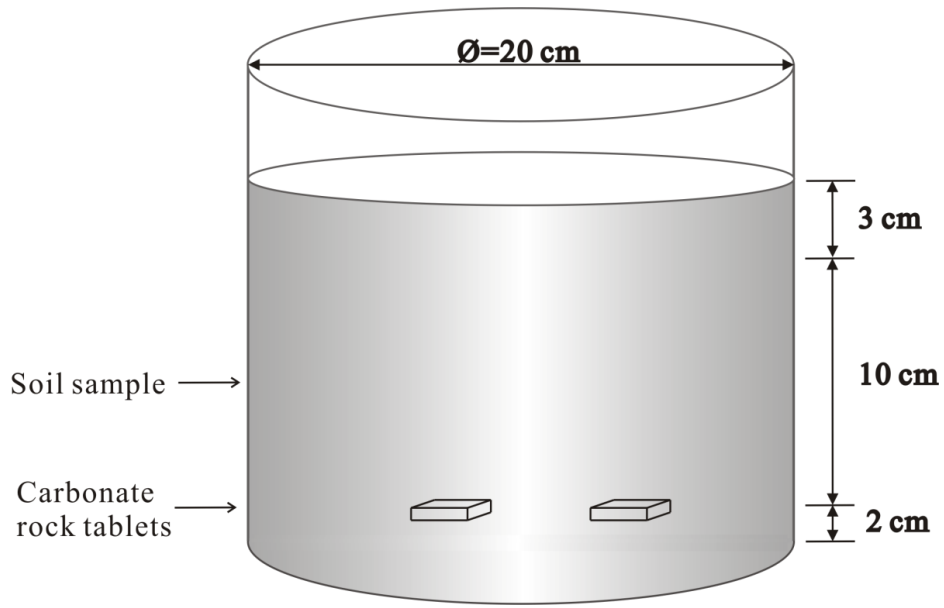
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 1046 Fig. 1 The change of chemical fertilizer consumption in China during 1980-2013
 1047 The data were collected from National Bureau of Statistics of the People's Republic of China
 1048 (NBS, 2014) (<http://www.stats.gov.cn/tjsj/ndsj/>)
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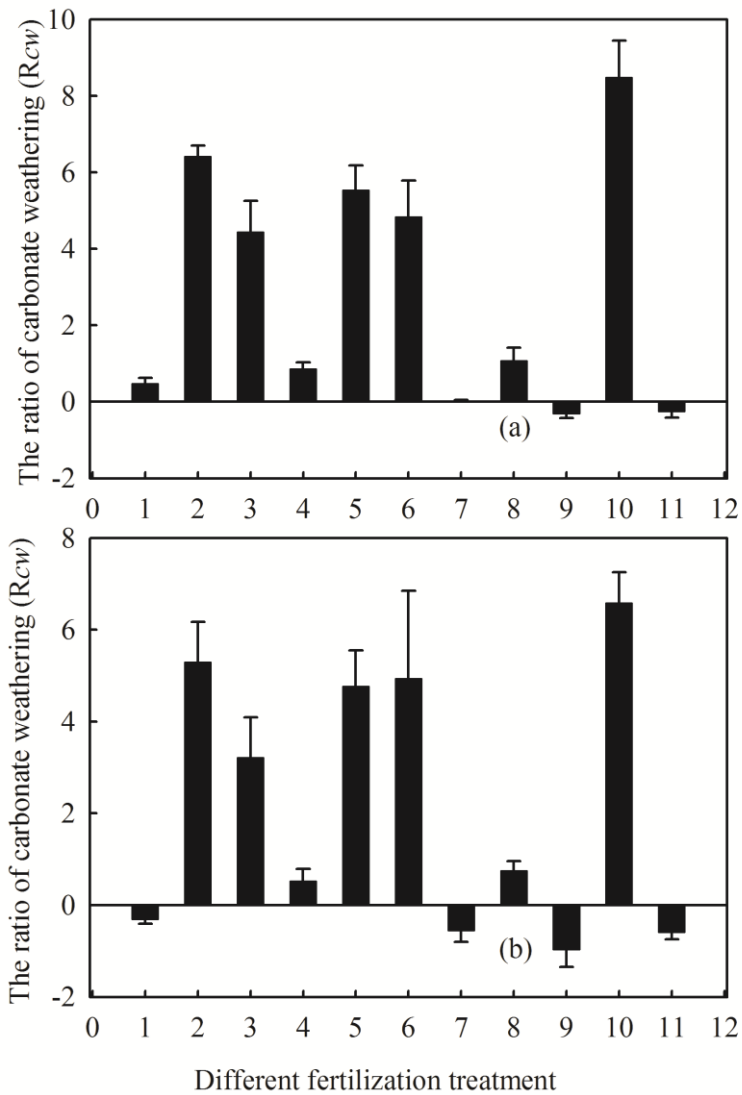
Fig. 2 Sketch map of the soil column

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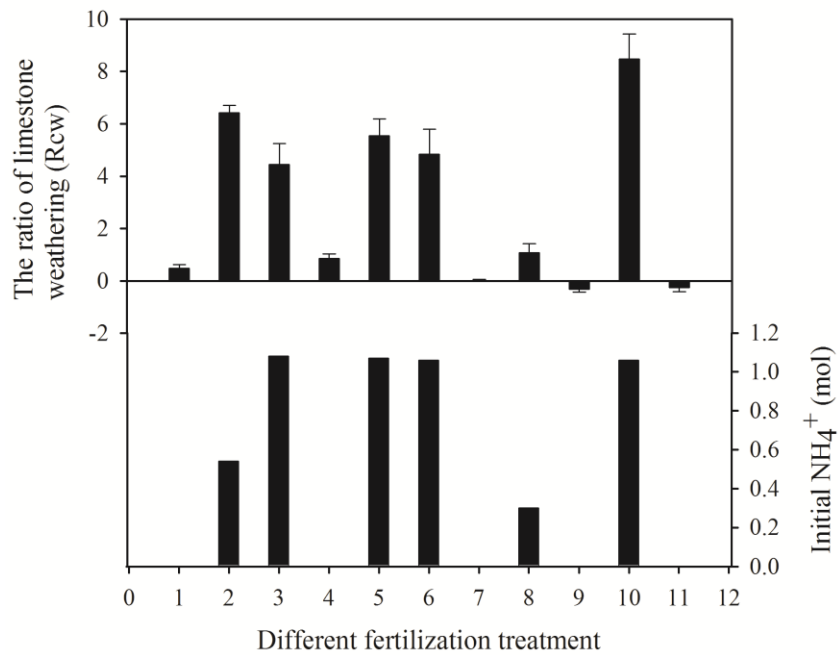
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Fig. 3 The ratio of carbonate weathering under different fertilization treatment (a)-limestone; (b)-dolostone. Treatment 1-Control; 2- NH_4NO_3 ; 3- NH_4HCO_3 ; 4- NaNO_3 ; 5- NH_4Cl ; 6- $(\text{NH}_4)_2\text{CO}_3$; 7- $\text{Ca}_3(\text{PO}_4)_2$; 8- $(\text{NH}_4)_3\text{PO}_4$; 9-Ca-Mg-P; 10-Urea; 11- K_2CO_3 . $R_{cw} = (W_i - W_f) / W_i$, where W_i is the initial weight of the carbonate rock tablets, and W_f is their final weight.



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Fig. 4 The ratio of limestone weathering and the molar amount of produced NH₄⁺ under different fertilization treatment

Treatment 1-Control; 2-NH₄NO₃; 3-NH₄HCO₃; 4-NaNO₃; 5-NH₄Cl; 6-(NH₄)₂CO₃; 7-Ca₃(PO₄)₂; 8-(NH₄)₃PO₄; 9-Ca-Mg-P; 10-Urea; 11-K₂CO₃. $R_{cw} = (W_i - W_f) / W_i$, where W_i is the initial weight of limestone tablets, and W_f is their final weight.