Impact of different fertilizers on carbonate weathering in a typical karst area, Southwest China: a field column experiment

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Abstract: Carbonate weathering, as a significant vector for the movement of carbon both between and within ecosystems, is strongly influenced by agricultural fertilization, since the addition of fertilizers tends to change the chemical characteristics of soil such as the pH. Different fertilizers may exert a different impact on carbonate weathering, but these discrepancies are as of yet not well-known. In this study, a field column experiment was conducted to explore the response of carbonate weathering to the addition of different fertilizers. We compared 11 different treatments, including a control treatment, using 3 replicates per treatment. Carbonate weathering was assessed by measuring the weight loss of limestone and dolostone tablets buried at the bottom of soil-filled columns. The results show that the addition of urea, NH_4NO_3, NH_4HCO_3, NH_4Cl and $(NH_4)_2CO_3$ distinctly increased carbonate weathering, which was attributed to the nitrification of NH_4^+. The addition of $Ca_3(PO_4)_2$, Ca-Mg-P and K_2CO_3 induced carbonate precipitation due to the common ion effect. The addition of $(NH_4)_3PO_4$ and $NaNO_3$ did not significantly impact carbonate weathering. The results of $NaNO_3$ treatment raise a new question: the negligible impact of nitrate on carbonate weathering may result in overestimation of the impact of N-fertilizer on CO_2 consumption by carbonate weathering at the regional/global scale, if the effects of NO_3 and NH_4 are not distinguished.

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

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1.   Introduction

Carbonate weathering plays a significant role in consumption of atmospheric CO_2 (Kump et al., 2000; Liu et al., 2010; 2011). Riverine hydro-chemical composition, such as the ratio of HCO_3^- to $Ca^{2+} + Mg^{2+}$, is usually employed as an indicator to estimate the CO_2 consumption by natural carbonate weathering at the regional/global scale (Hagedorn and Cartwright, 2009; Li et al., 2009). However, fluvial alkalinity may also be produced by other processes including the reaction between carbonates and protons derived from: (i) the nitrification of N-fertilizer (Barnes and Raymond, 2009; Chao et al., 2011; Gandois et al., 2011; Hamilton et al., 2007; Oh and Raymond, 2006; Perrin et al., 2008; Pierson-Wickmann et al., 2009; Semhi and Suchet, 2000; West and McBride, 2005); (ii) sulfuric acid forming in the oxidation of reduced sulfuric minerals (mainly pyrite, FeS_2) (Lerman and Wu, 2006; Lerman et al., 2007; Li et al., 2008; 2009); (iii) organic acid secreted by microorganisms (Lian et al., 2008); and (iv) acidic soil (such as red soil, yellow soil) (Chao et al., 2014; 2017). Given that atmospheric CO_2 is not a unique weathering agent, differentiating the agent of carbonate weathering is important for the accurate budgeting of net CO_2 consumption by carbonate weathering, especially in agricultural areas where mineral fertilizers are used.

The global average annual increase in mineral fertilizer consumption was 3.3 % from 1961 to 1997, and FAO's study predicts a 1 % increase per year until 2030 (FAO, 2000). In China, the consumption of chemical fertilizer increased from 12.7 Mt

57 in 1980 to 59.1 Mt in 2013 (Fig. 1). The increasing consumption of mineral fertilizers

58 is a significant disturbance factor in carbonate weathering and the carbon cycle.

59 Several studies have shown that nitrogen fertilizer additions increased weathering

60 rates, and also increased the total export of DIC from agricultural watersheds (Barnes

61 and Raymond, 2009; Gandois et al., 2011; Hamilton et al., 2007; Oh and Raymond,

62 2006; Perrin et al., 2008; Pierson-Wickmann et al., 2009; Probst, 1986; Semhi and

63 Suchet, 2000; West and McBride, 2005). According to estimates by Probst (1988) and

64 Semhi et al. (2000), the contribution of N-fertilizers to carbonate dissolution was 30 %

65 and 12-26 % in two small agricultural carbonate basins in south-western France, the

66 Girou and the Gers, respectively (tributaries of the Garonne River). In the Garonne

67 River Basin, which is a large basin (52,000 km^2), this contribution was estimated at 6 %

68 by Semhi et al. (2000). Perrin et al. (2008) estimated that the contribution of

69 N-fertilizer (usually in form of NH_4NO_3) represents up to 5.7-13.4 % and 1.6-3.8 % of

70 the carbonate dissolution in France and across the global, respectively.

71 The estimates described above are largely based on calculations that assumed a

72 single type of fertilizer (e.g. $(NH_4)_2SO_4$, NH_4NO_3, or NH_4Cl) was used throughout the

73 whole basin that was considered. However, in actual agricultural practices, different

74 fertilizers are usually added for different crops. The impact of these fertilizers on

75 carbonate weathering and riverine chemical composition may be different. In the case

76 of nitrogenous fertilizer, 100 % NO_3^- produced after the addition $(NH_4)_2SO_4$ and

77 NH_4Cl is derived from the nitrification of NH_4^+, whilst comparatively, it is only 50 %

78 after the addition of NH_4NO_3. Differences in NO_3^- sources may produce an evaluated

79 deviation in the impact of N-fertilizer addition on CO_2 consumption by carbonate

80   weathering, since the addition of different N-fertilizers (e.g. $(NH_4)_2SO_4$, NH_4NO_3,

81   NH_4Cl, $NaNO_3$ or urea) may result in different contributions to carbonate weathering

82   and relative products such as HCO_3^-, Ca^{2+} and Mg^{2+}. For phosphate fertilizer, the

83   coprecipitation of phosphate ions with calcium carbonate may inhibit carbonate

84   weathering (Kitano et al., 1978). We assume that the response of carbonate

85   weathering to the addition of different fertilizers, such as N-fertilizer (NH_4 and NO_3),

86   P-fertilizer and Ca/Mg fertilizer, may display differences, which are so far poorly

87   known, but likely significant. Here we sought to fully understand the agricultural

88   impact on natural carbonate weathering, and to accurately evaluate the CO_2

89   consumption via carbonate weathering in agricultural areas.

90   The carbonate-rock-tablet test is used to determine the weathering rate of

91   carbonate rock/mineral from the laboratory to the field (Chao et al., 2011; Chao et al.,

92   2014; Dreybrodt et al., 1996; Gams, 1981; Gams, 1985; Jiang and Yuan, 1999; Liu

93   and Dreybrodt, 1997; Plan, 2005; Trudgill, 1975). In the laboratory, the

94   carbonate-rock-tablet   is   employed   to   study   the   kinetics   of   calcite

95   dissolution/precipitation (Dreybrodt et al., 1996; Liu and Dreybrodt, 1997) and

96   determine the rate of carbonate mineral weathering in the soil column (Chao et al.,

97   2011). However, in the field, it is also used to observe the rate of carbonate

98   weathering and estimate CO_2 consumption (Chao et al., 2014; Jiang and Yuan, 1999;

99   Jiang et al., 2013; Plan, 2005). Liu (2011) argued that the carbonate-rock-tablet test

100   may lead to deviations in estimated CO_2 consumption by carbonate weathering at the

101   regional/global scale, in cases where there are insufficient representative data (Liu,

102   2011). It is nonetheless the preferred method for the comparative or simulated

103   experiment (Chao et al., 2011; 2014; 2017) .

104   A field column experiment that involved embedding carbonate-rock-tablets was

105   carried out in a typical karst area of southwest China, in order to observe the impact

106   of different fertilizer additions on carbonate weathering in soil.

107   **2. Materials and Methods**

108   **2.1 The study site**

109   This study was carried out in a typical karst area, namely the Huaxi District of

110   Guiyang City, Guizhou Province, SW China (26°23′N, 106°40′E, 1094 m ASL).

111   Guiyang, the capital city of Guizhou Province, is located in the central part of the

112   province, covering an area from 26°11′00″ to 26°54′20″N and 106°27′20″ to

113   107°03′00″E (approximately 8,000 km^2), with elevations ranging from 875 to 1655 m

114   ASL. Guiyang has a population of more than 1.5 million people, a wide diversity of

115   karstic landforms, high elevations and low latitude, with a subtropical warm-moist

116   climate, and an average annual temperature of 15.3 ℃ and annual precipitation of

117   1200 mm (Lang et al., 2006). A monsoonal climate often results in high precipitation

118   during summer, with much less during winter, although the humidity is often high

119   throughout most of the year (Han and Jin, 1996). Agriculture is a major land use in

120   order to produce the vegetables and foods in the suburbs of Guiyang (Liu et al., 2006).

121   The consumption of chemical fertilizer increased from 150 kg/ha in 1980 to 190 kg/ha

122   in 2013 (GBS, 2014).

123   **2.2 Soil properties**

124   The soil used in this column experiment was yellow-brown clay, which sampled

125   from the B horizon (below 20 cm in depth) of yellow-brown soil profile from a

126   cabbage-corn or capsicum-corn rotation plantation in Huaxi District. The soil was

127 air-dried, ground to pass through a 2-mm sieve, mixed thoroughly and used for the

128 soil columns. The soil pH ($V_{soil}:V_{water} = 1:2.5$) was determined by pH meter. The

129 chemical characteristics of the soil, including organic matter (OM), NH_4-N, NO_3-N,

130 available P, available K, available Ca, available Mg, available Fe, and available S

131 were determined according to the Agro Services International (ASI) method (Hunter,

132 1980). OM was determined using an extracting solution containing 0.2 mol l^{-1} NaOH,

133 0.01 mol l^{-1} EDTA, 2 % methanol, and 0.005 % Superfloc 127. NH_4-N, NO_3-N,

134 available Ca, and Mg were determined using an extracting solution of 1 mol l^{-1} KCl

135 solution, whereas available K, P and Fe were determined using an extracting solution

136 containing 0.25 mol l^{-1} $NaHCO_3$, 0.01 mol l^{-1} EDTA, 0.01 mol l^{-1} NH_4F, and 0.005 %

137 Superfloc 127. Finally, available S was determined using an extracting solution of 0.1

138 mol l^{-1} $Ca(H_2PO_4)_2$ and 0.005 % Superfloc 127. The results are shown in Table 1.

2.3 Soil column and different fertilization treatments

140 In order to test the hypothesis that the impact of different chemical fertilizers on

141 carbonate weathering may be different, columns (Ø = 20 cm, H= 15 cm) were

142 constructed from 20 cm diameter polyvinylchloride (PVC) pipe (Fig. 2). A hole (Ø =

143 2 cm) was placed at the bottom of each column to discharge soil water from the soil

144 column. A polyethylene net (Ø 0.5 mm) was placed in the bottom of the columns to

145 prevent soil loss. A 2 cm thick filter layer, including gravel, coarse sand and fine sand,

146 was spread over the net. Two different carbonate rock tablets were buried in the

147 bottom of each soil column (Fig. 2). Based on the common kinds of chemical

148 fertilizers and the main objective of this study, eleven fertilization treatments, each

149　with three replicates, were set up in the field column experiment. There are: (1)

150　control without fertilizer (CK); (2) 43g NH_4NO_3 fertilizer (CF); (3) 85g NH_4HCO_3

151　fertilizer (NHC); (4) 91g $NaNO_3$ fertilizer (NN); (5) 57g NH_4Cl fertilizer (NCL); (6)

152　51g $(NH_4)_2CO_3$ fertilizer (NC); (7) 52g $Ca_3(PO_4)_2$ fertilizer (CP); (8) 15g $(NH_4)_3PO_4$

153　fertilizer (NP); (9) 44g fused calcium-magnesium phosphate fertilizer (Ca-Mg-P); (10)

154　32g Urea fertilizer (U); and (11) 10g K_2CO_3 fertilizer (PP). An aliquot of 6 kg of soil

155　was weighed (bulk density = 1.3 g/cm^3), mixed throughly with one of the above

156　fertilizers, and filled into its own column. This process was repeated for all three

157　replicates of the 11 fertilizer treatments. The soil columns were labelled and placed

158　orderly at the field experiment site in Huaxi District, Guiyang for a whole year.

159　**2.4 The rate of carbonate weathering**

160　　　Two different kinds of carbonate rock tablets (2 cm $\times$ 1 cm $\times$ 0.5 cm in size) were

161　placed in the bottom of each soil column to examine the rate of carbonate weathering

162　in the soil. The two different kinds of carbonate rock collected from the karst area of

163　Huaxi District were: (1) limestone with 60-65 % micrite, 30-35 % microcrystalline

164　calcite, and 2-3 % pyrite; and (2) dolostone with 98-99 % fine crystalline dolomite, 1 %

165　pyrite, and trace quantities organic matter. All the tablets were heated at 80 ℃ for 4

166　hours, weighed in a 1/10000 electronic balance in the laboratory, labeled by tying a

167　label with fishing line, and then buried at the bottom of each soil column. After a

168　whole year, the tablets were removed carefully, rinsed, baked and weighed.

169　　　The amount of weathering (Aw), the ratio of weathering (Rw) and the rate of

170　weathering (Raw) for limestone and dolomite were calculated according to the weight

171 difference of the tablets using the following formulas:

$$Aw = (Wi\text{-}Wf) \tag{1}$$

$$Rw = (Wi\text{-}Wf)/\ Wi \tag{2}$$

$$Raw = (Wi\text{-}Wf)/(S*T) \tag{3}$$

175 where Wi is the initial weight of the carbonate-rock-tablet, Wf is the final weight, S is

176 the surface area of carbonate rock tablet, and T is the length of the experimental

177 period.

2.5 Statistical analysis

179 Statistical analysis was performed using IBM SPSS 20.0 (Statistical Graphics

180 Corp, Princeton, USA). All results of carbonate weathering were reported as the

181 means ±standard deviations (SD) for the three replicates.

3. Results

3.1 Weathering rate of carbonate under different fertilized treatments

184 The Rw and Raw of limestone and dolostone are listed in Table 2. The results

185 show that the Rw of limestone under urea, NH_4NO_3, NH_4Cl, $(NH_4)_2CO_3$ and

186 NH_4HCO_3 treatments were 8.48 ±0.96, 6.42 ±0.28, 5.54 ±0.64, 4.44 ±0.81 and 4.48

187 ±0.95 ‰, respectively, significantly greater than that under the control treatment 0.48

188 ±0.14 ‰ (see Fig. 3). In addition, the observed Rw of dolostone were 6.59 ±0.67,

189 5.30 ±0.87, 4.77 ±0.78, 4.94 ±1.91 and 3.22 ±0.87 ‰ respectively, under these

190 same five fertilization treatments, in contrast to -0.31 ± 0.09 ‰ in the control

191 treatment. This clearly demonstrates that the addition of these five fertilizers increased

192 the rate of carbonate weathering.

193   The remaining treatments made no significant differences in the R*w* and R*aw* of

194   limestone and dolostone in comparison to the control treatment (Fig. 3). In the

195    $(NH_4)_3PO_4$ treatment, the R*w* were only 1.08 ± 0.34 ‰, and 0.75 ± 0.21‰ for

196   limestone and dolomite, respectively, while the R*aw* were 4.00 ± 1.15 g m^{-2} a^{-1} and

197   1.00 ± 1.01 g m^{-2} a^{-1} for limestone and dolomite, respectively. These values are less

198   than those under the other four NH_4-fertilizers, as mentioned above. The R*w* and R*aw*

199   in the $NaNO_3$ treatments failed to show notable differences with the control treatment,

200   exhibiting little effect of the $NaNO_3$ fertilizer addition on carbonate weathering (Fig.

201   3). Except for the R*w* of limestone approaching zero in the $Ca_3(PO_4)_2$ treatment, all

202   the values of R*w* and R*aw* in Ca-Mg-P, K_2CO_3 and $Ca_3(PO_4)_2$ treatments showed

203   negative values. This indicates that the addition of Ca-Mg-P, K_2CO_3 and $Ca_3(PO_4)_2$

204   fertilizers led to precipitation at the surface of the carbonate mineral, which can be

205   explained by common ion effect.

206   3.2 Comparison of limestone of dolomite

207   Fig. 3 shows that, on the whole, the ratios of dolostone weathering are smaller

208   than those of limestone weathering except $(NH_4)_2CO_3$ treatment, exhibiting that

209   dolostone weather more slowly than limestone under fertilization effects.
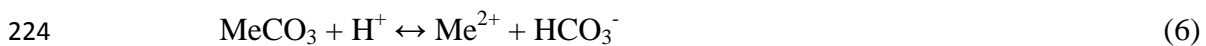
210   In Fig. 4, we plotted the R*w* of limestone vs. dolostone tablets in a linear

211   correlation diagram, in order to compare the weathering responses of limestone with

212   dolostone. The results show that the R*w* of limestone and dolostone exhibit a high

213   positive correlation ($R^2=0.9773$; see Fig. 4), indicating that the weathering of

214   limestone and dolostone are similar under different treatments. Thus, we will explain

215   the results in terms of carbonates, rather than by way of the individual dolostone and

216   limestone.

4. Discussion

4.1 Kinetics of carbonate dissolution/precipitation: controlling factors

219   Experimental studies of carbonate dissolution kinetics have shown metal

220   carbonate weathering usually depends upon three parallel reactions occurring at the

221   carbonate interface (Chou et al., 1989; Plummer et al., 1978; Pokrovsky et al., 2009):

222   $$MeCO_3 \leftrightarrow Me^{2+} + CO_3^{2-} \tag{4}$$

223   $$MeCO_3 + H_2CO_3 \leftrightarrow Me^{2+} + 2HCO_3^- \tag{5}$$

224   $$MeCO_3 + H^+ \leftrightarrow Me^{2+} + HCO_3^- \tag{6}$$

225   where Me = Ca, Mg. As Eq. (5) describes, atmospheric/soil CO_2 is usually considered

226   to be the natural weathering agent of carbonate. In watersheds with calcite- and

227   dolomite-containing bedrock, H_2CO_3 formed in the soil zone usually reacts with

228   carbonate minerals, resulting in dissolved Ca, Mg, and HCO_3^- as described in Eq. (5)

229   (Andrews and Schlesinger, 2001; Shin et al., 2014). Although it has been proven that

230   the reaction of carbonate dissolution is mainly controlled by the amount of rainfall

231   (Amiotte Suchet et al., 2003; Egli and Fitze, 2001; Kiefer, 1994), in this study, we

232   consider that the effect of rainfall is equal in each soil column, and hence is

233   disregarded as a controlling factor in weathering rate differences among these

234   treatments. In theory, the fertilizers could stimulate bacteria, which may increase

235   respiration and CO_2 concentrations in the soil, as a result, probable enhance

236   carbonate weathering as Eq. (5). However, Eq. (6) suggests that the proton from other

237   origins, such as the nitrification processes of NH_4^+, as mentioned in the Introduction

238   section, can play the role of weathering agent in agricultural areas. In this study, the

239   urea, NH_4NO_3, NH_4HCO_3, NH_4Cl, and $(NH_4)_2CO_3$ amendments increased (10 to

240   17-fold) the natural weathering rate from 2.00 g m^{-2} a^{-1} for limestone tablets in the

241   control treatment (Table 2). Thus, these increases are strongly related to the effect of

242   proton release from the nitrification of NH_4^+. In contrast, carbonate precipitation will

243   occur due to the backward reaction of Eq. (5) in the following cases: (1) the degassing

244   of dissolved CO_2 due to dramatic changes in the parameters of the CO_2 system (such

245   as T, pH, pCO_2, etc); (2) soil evapotranspiration; or (3) the common ion effect: the

246   increase of Ca^{2+}, Mg^{2+} or CO_3^{2-} in a weathering-system with equilibrium between

247   water and calcite (Calmels et al., 2014; Dreybrodt, 1988).

248   **4.2 Main reactions and effects in different treatments**

249   The main reactions and effects of every treatment in this study are listed in Table

250   3.

251   **(1) Nitrification in NH_4-fertilizer: NH_4NO_3, NH_4HCO_3, NH_4Cl, $(NH_4)_2CO_3$ and**

252   **urea**

253   In urea ($CO(NH_2)_2$) treatment, the enzyme urease rapidly hydrolyzes the urea-N

254   ($CO(NH_2)_2$) to NH_4^+ ions (Eq. (7)) when urea is applied to the soil (Soares et al.,

255   2012).

256                $CO(NH_2)_2 + 3H_2O \rightarrow 2NH_4^+ + 2OH^- + CO_2$ (7)

257   Although the study of Singh et al. (2013) showed that part of NH_4^+ may be lost as

258   ammonia (NH_3) and subsequently as nitrous oxide (N_2O) (Singh et al., 2013), the

259   remaining ammonium (NH_4^+) is mainly oxidized during nitrification in soil by

260 autotrophic bacteria, such as Nitrosomonas, resulting in nitrite NO_2^- and H^+ ions.

261 Nitrite is in turn oxidized by another bacterium, such as Nitrobacter, resulting in

262 nitrate (NO_3^-) (Eq. (8)) (Perrin et al., 2008).

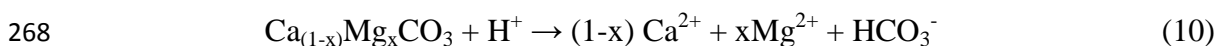263 $$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \tag{8}$$
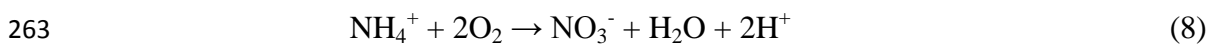
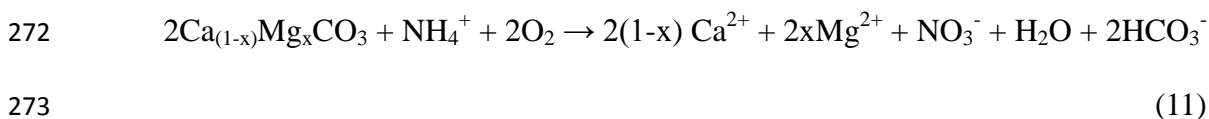264 The protons (H^+) produced by nitrification can be neutralized in two ways:

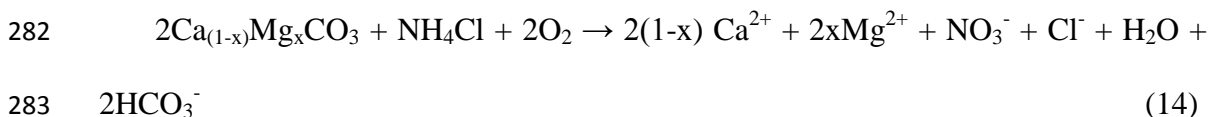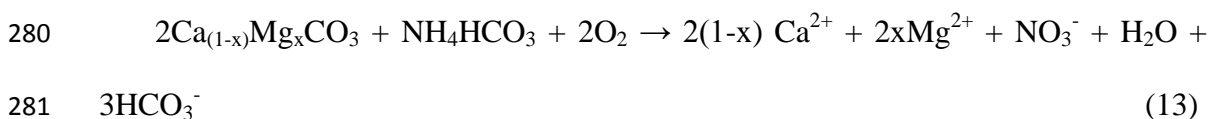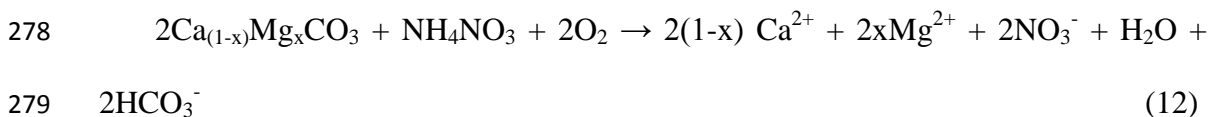265 (i) either by exchange process with base cations in the soil exchange complex

266 (Eq. (9)) $$Soil - Ca + 2H^+ \rightarrow Soil - 2H^+ + Ca^{2+} \tag{9}$$

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

268 $$Ca_{(1-x)}Mg_xCO_3 + H^+ \rightarrow (1-x)\,Ca^{2+} + xMg^{2+} + HCO_3^- \tag{10}$$
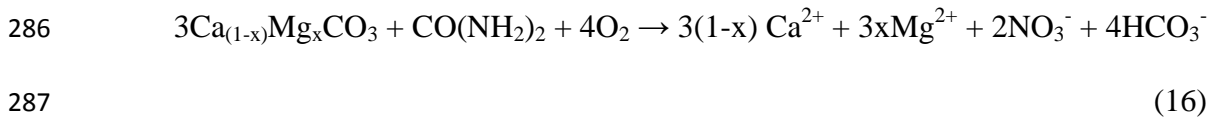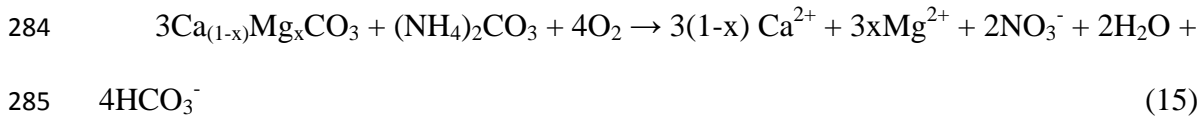
269 Consequently, by combining Eq. (8) and Eq. (10), carbonate weathering by

270 protons produced by nitrification can supposedly be expressed as (Eq. 11) (See details

271 in Perrin et al., 2008 and Gandois et al., 2011).

272 $$2Ca_{(1-x)}Mg_xCO_3 + NH_4^+ + 2O_2 \rightarrow 2(1-x)\,Ca^{2+} + 2xMg^{2+} + NO_3^- + H_2O + 2HCO_3^-$$

273 $$\tag{11}$$

274 As discussed above, provided that the loss as ammonia (NH_3) and nitrous oxide

275 (N_2O) after hydrolyzation is disregarded in this study, the final equation of carbonate

276 weathering in NH_4NO_3, NH_4HCO_3, NH_4Cl, $(NH_4)_2CO_3$ and urea treatments will be as

277 follows, respectively:

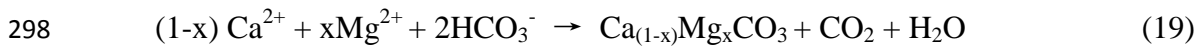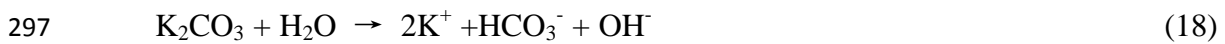278 $$2Ca_{(1-x)}Mg_xCO_3 + NH_4NO_3 + 2O_2 \rightarrow 2(1-x)\,Ca^{2+} + 2xMg^{2+} + 2NO_3^- + H_2O +$$

279 $$2HCO_3^- \tag{12}$$

280 $$2Ca_{(1-x)}Mg_xCO_3 + NH_4HCO_3 + 2O_2 \rightarrow 2(1-x)\,Ca^{2+} + 2xMg^{2+} + NO_3^- + H_2O +$$

281 $$3HCO_3^- \tag{13}$$

282 $$2Ca_{(1-x)}Mg_xCO_3 + NH_4Cl + 2O_2 \rightarrow 2(1-x)\,Ca^{2+} + 2xMg^{2+} + NO_3^- + Cl^- + H_2O +$$

283 $$2HCO_3^- \tag{14}$$

284      $3Ca_{(1-x)}Mg_xCO_3 + (NH_4)_2CO_3 + 4O_2 \rightarrow 3(1-x)\ Ca^{2+} + 3xMg^{2+} + 2NO_3^- + 2H_2O +$

285      $4HCO_3^-$ (15)

286      $3Ca_{(1-x)}Mg_xCO_3 + CO(NH_2)_2 + 4O_2 \rightarrow 3(1-x)\ Ca^{2+} + 3xMg^{2+} + 2NO_3^- + 4HCO_3^-$

287   (16)

288 **(2) No effect of NO_3-fertilizer treatment: $NaNO_3$ treatment**

289   In the $NaNO_3$ treatment, the reaction occurs according to Eq. (17), indicating that

290 the addition of NO_3-fertilizer does not significantly influence carbonate weathering.

291      $Ca_{(1-x)}Mg_xCO_3 + NaNO_3 + CO_2 + H_2O \rightarrow (1-x)\ Ca^{2+} + xMg^{2+} + Na^+ + NO_3^- +$

292 $2HCO_3^-$ (17)
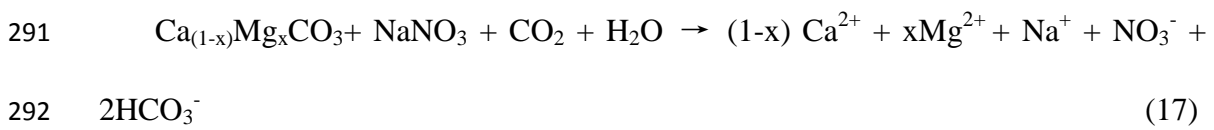
293 **(3) Common ion effect: K_2CO_3 treatment**

294   In the K_2CO_3 treatment, CO_3^{2-} and HCO_3^- will be produced after the addition of

295 K_2CO_3 according to Eq. (18), hence resulting in carbonate precipitation as described

296 in Eq. (19), due to the common ion effect.

297      $K_2CO_3 + H_2O \rightarrow 2K^+ + HCO_3^- + OH^-$ (18)

298      $(1-x)\ Ca^{2+} + xMg^{2+} + 2HCO_3^- \rightarrow Ca_{(1-x)}Mg_xCO_3 + CO_2 + H_2O$ (19)

299 **(4) Complex effects: Nitrification versus inhibition effect of PO_4 in $(NH_4)_3PO_4$**

300 **treatments**

301   In the $(NH_4)_3PO_4$ treatment, the reaction of carbonate weathering will occur

302 according to Eq. (11) due to the nitrification of NH_4^+ ionized from the $(NH_4)_3PO_4$

303 fertilizer. The PO_4^{3-} anion will exert an inhibition to calcite dissolution, as calcium

304 orthophosphate (Ca-P) precipitation is produced on the surface of calcite after the

305 addition of PO_4^{3-} in soil (reaction: $Ca + PO_4 \rightarrow Ca$-P), resulting in inhibition of the

306 calcite dissolution.

307 **(5) Complex effects: Common ion effect versus inhibition effect of PO_4 in**

Ca₃(PO₄)₂ and Ca-Mg-P treatments

In the $Ca_3(PO_4)_2$ and Ca-Mg-P treatments, on the one hand, $Ca_{(1-x)}Mg_xCO_3$ is produced when the concentrations of Ca^{2+} (or/and Mg^{2+}) increases according to Eq. (19). On the other hand, the inhibition effect of phosphate will cause calcium phosphate precipitation to be produced on the surface of carbonate minerals after the addition of P in soil (reaction: $Ca + PO_4 \rightarrow Ca\text{-}P$), resulting in inhibition the carbonate precipitation.

4.3 Difference between NH_4^+ and NO_3^- in impacts on carbonate weathering and implication on the estimation of CO_2 consumption

In order to further compare the differenceS between NH_4^+ and NO_3^- effects on carbonate weathering, the initial molar amount of fertilizer-derived NH_4 per unit in every treatment were calculated, and are listed in Table 4. The results show that the amount of NH_4^+ hydrolyzed from urea is 1.06 mole, while NH_4^+ ionized from NH_4NO_3, NH_4HCO_3, NH_4Cl, $(NH_4)_2CO_3$ and $(NH_4)_3PO_4$ is 0.54 mole, 1.08 mole, 1.07 mole, 1.06 mole, and 0.03 mole, respectively (Table 4). The Rw of limestone tablets and the initial amount of NH_4^+ per treatment are plotted in Fig. 5. A distinct relationship between them is observed, in that the Rw values in NH_4NO_3, NH_4HCO_3, NH_4Cl, $(NH_4)_2CO_3$ and urea treatments are larger than in the control treatment, where the initial amount of NH_4^+ yields similar results (Fig. 5). This suggests that carbonate weathering in NH_4NO_3, NH_4HCO_3, NH_4Cl, $(NH_4)_2CO_3$ and urea treatments are mainly attributed to the dissolution reaction described as Eq. (11). This process of carbonate weathering by protons released from nitrification has been proven by many studies, from the laboratory to the field (Barnes and Raymond, 2009; Bertrand et al., 2007; Biasi et al., 2008; Chao et al., 2011; Errin et al., 2006; Gandois et al., 2011; Hamilton et al., 2007; Oh and Raymond, 2006; Perrin et al., 2008; Semhi and Suchet,

2000; West and McBride, 2005). We have noted that the Rw values in NH_4HCO_3 and

$(NH_4)_2CO_3$ treatments are less than half those in urea treatment despite adding the

same amount of fertilizer-derived NH_4 (approximately 1.07 mole). This is probably

because the two fertilizers, NH_4HCO_3 and $(NH_4)_2CO_3$, are easier to decompose and

produce NH_3 and CO_2 gases according to Eq. (20) and (21), resulting in amounts of

fertilizer-derived NH_4 that are lower than 1.07 moles.

$$NH_4HCO_3 \; \rightarrow \; NH_3 \; \uparrow \; + H_2O + CO_2 \; \uparrow \qquad\qquad (20)$$
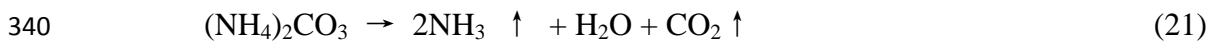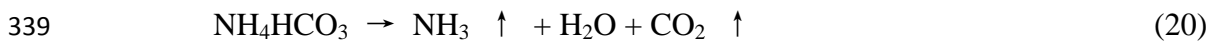
$$(NH_4)_2CO_3 \; \rightarrow \; 2NH_3 \; \uparrow \; + H_2O + CO_2 \uparrow \qquad\qquad (21)$$

The Aw and Rw in the $(NH_4)_3PO_4$ treatment, unlike in other NH_4-fertlizer

treatments, do not show a significant increase compared to the control treatment,

which is not only owing to the low amount of added NH_4^+ in $(NH_4)_3PO_4$ treatment

(0.3 mole; see Table 4), but also more or less relative to the inhibition of phosphate

(Chien et al., 2011; Wang et al., 2012). After the addition of $(NH_4)_3PO_4$ in soil,

calcium orthophosphate (Ca-P) precipitation will form on calcite surfaces, which is

initiated with the aggregation of clusters leading to the nucleation and subsequent

growth of Ca-P phases, at various pH values and ionic strengths relevant to soil

solution conditions (Chien et al., 2011; Wang et al., 2012).

However, in Fig. 3, there is no significant different between the Rw in the $NaNO_3$

treatment compared to the control treatment, indicating that the addition of

NO_3-fertilizer does not significantly influence carbonate weathering.

A notable issue herein is that the $NaNO_3$ treatment produces the same amount of

NO_3^- (1.07 mole) as other NH_4 fertilizer (NH_4NO_3, NH_4HCO_3, NH_4Cl, $(NH_4)_2CO_3$

and urea), but it fails to impact on carbonate weathering, which raises a new problem.

Eq. (5), usually considered as an expression for the natural weathering process of

357 carbonate, is an important reaction in understanding the kinetics process of carbonate

358 dissolution in carbonate-dominated areas, where the molar ratio of HCO_3^- and Me^{2+} in

359 the river is usually used as an indicator to make estimates of CO_2 consumption by

360 carbonate weathering at the regional/global scale (Hagedorn and Cartwright, 2009; Li

361 et al., 2009). In agricultural areas, the relationship between $(Ca+Mg)/HCO_3^-$ and NO_3^-

362 is usually employed to estimate the contribution of N-fertilizer to riverine Ca^{2+}, Mg^{2+},

363 and alkalinity (Etchanchu and Probst, 1988; Jiang, 2013; Jiang et al., 2009; Perrin et

364 al., 2008; Semhi and Suchet, 2000). In these studies, the nitrification described in Eq.

365 (8) is usually considered as the unique origin of NO_3^-. According to the results of the

366 $NaNO_3$ treatment in this study, the contribution of protons from nitrification to

367 carbonate weathering may be overestimated, if anthropogenic NO_3^- is neglected, since

368 the anthropogenic NO_3^- does not release the proton described in Eq. (8). For NH_4NO_3

369 fertilizer, Eq. (12) shows that two moles of $Ca^{2+}+Mg^{2+}$, NO_3^-, and HCO_3^- will be

370 produced when one mole NH_4NO_3 reacts with 2 moles of carbonate, where only half

371 of the NO_3^- originates from nitrification described as Eq. (8). This will result in a

372 double overestimation of the contribution of nitrification to carbonate weathering, and

373 thus thereby mislead the estimation of CO_2 consumption.

374   At regional scales, if different fertilizers are simultaneously added to an

375 agricultural area, the estimation of CO_2 consumption by carbonate weathering might

376 became more complicated, since the mole ratios of Ca+Mg, HCO_3^-, and/or NO_3^-

377 between different fertilization treatments are different (see Table 3). Thus, the related

378 anthropogenic inputs (e.g. Ca+Mg, NH_4, NO_3^-, HCO_3^-, etc.) need to be investigated to

379 more accurately estimate the impact of fertilization on carbonate weathering and its

380 CO_2 consumption.

381 **4.4 The comparison with other studied results**

The Rw and Raw of limestone in the control treatment in this study were 0.48 ‰ and 2.00 g m^{-2} a^{-1}, respectively. These are generally consistent with observations of 0.51-32.97 g m^{-2} a^{-1} (for Raw) in Nongla, Guangxi, a karst area of Southwestern China (Zhang, 2011), and with the results of 0.05-5.06 ‰ (for Rw) and 1.08-136.90 g m^{-2} a^{-1} (for Raw) from the north slope of the Hochschwab Massif in Austria (Plan, 2005), as determined using the limestone tablet method. But the Raw of 2.00 g m^{-2} a^{-1} is lower than the results of 7.0-63.5 g m^{-2} a^{-1} for Raw from Jinfo Mountain in Chongqing, China (Zhang, 2011). These differences in carbonate weathering are mainly attributed to the different types of carbonate rock tablets, climate, micro-environments of soil, etc. The Raw of limestone in the N-fertilizer treatments are 20.57-34.71 g m^{-2} a^{-1}, similar to the weathering rate of carbonate in orchard (32.97 g m^{-2} a^{-1}) at Nongla, Manshan, Guangxi, China, which usually involves fertilization activities.

At larger scales, such as watersheds, the weathering rate is usually estimated by using the riverine hydro-chemical method, which is inconsistent with the results from the carbonate-rock-tablet test. Zeng, et al. (2014) estimate that the carbon sink intensity calculated by the carbonate-rock-tablet test is only one sixth of that estimated using the riverine hydro-chemical method, due to its own limits in methodology (Zeng et al., 2014). The results from Semhi, et al. (2000) show that weathering rates of carbonate rock using riverine hydro-chemical method are approximately 77.5 g m^{-2} a^{-1} and 50.4 g m^{-2} a^{-1} in the upstream and downstream, respectively, of the Garonne river, France, which are approximately 25-35 times greater than that in the control treatment (2.00 g m^{-2} a^{-1} for natural weathering rate) and 2-3 times greater than in the N-fertilizer treatment (20.57-34.71 g m^{-2} a^{-1} for anthropic weathering rate) in this study. The global natural weathering rate of

carbonate reported by Amiotte Suchet, et al. (2003) is 47.8 g m^{-2} a^{-1}, which is much

higher than that we observed. Thus, we conclude that it is difficult to compare the

results from the carbonate-rock-tablet test and the riverine hydro-chemical method.

The carbonate-rock-tablet test is suitable for research on the comparative or simulated

experiments, while the riverine hydro-chemical method is appropriate for regional

investigations and estimations. According to the estimation from Yue et al. (2015), the

enhanced HCO_3^- flux due to nitrification of NH_4^+ at Houzhai catchment of Guizhou

Province would be 3.72×10^5 kg C/year and account for 18.7 % of this flux in the

entire catchment(Yue et al., 2015). This is similar to estimates from other small

agricultural carbonate basins (12–26 %) in southwest France (Perrin et al., 2008;

Semhi and Suchet, 2000).

5. Conclusions

The impact of the addition of different fertilizers (NH_4NO_3, NH_4HCO_3, $NaNO_3$,

NH_4Cl, $(NH_4)_2CO_3$, $Ca_3(PO_4)_2$, $(NH_4)_3PO_4$, Ca-Mg-P, urea, and K_2CO_3) on carbonate

weathering was studied in a field column experiment using carbonate-rock-tablets.

The amount of weathering and the ratio of weathering of carbonate rock tablets

showed that the addition of urea, NH_4NO_3, NH_4HCO_3, NH_4Cl, and $(NH_4)_2CO_3$

distinctly increased carbonate weathering, which was attributed to the nitrification of

NH_4^+, while the addition of $Ca_3(PO_4)_2$, Ca-Mg-P and K_2CO_3 induced carbonate

precipitation due to the common ion effect. The addition of $(NH_4)_3PO_4$ and $NaNO_3$

did not impact significantly on carbonate weathering, where the former can be

attributed to the low added amount of $(NH4)_3PO_4$, and may be related to the inhibition

of phosphate, while the latter seemed to raise a new question. The question is：the

minor impact of nitrate on carbonate weathering may result in the overestimation of

the impact of N-fertilizer on CO_2 consumption by carbonate weathering at the

regional/global scale, if the effects of NO_3 and NH_4 are not distinguished. Thus, the

related anthropogenic inputs (e.g. Ca+ Mg, NH_4, NO_3^-, HCO_3^-, etc.) need to be

investigated to more accurately estimate the impact of fertilization on carbonate

weathering and its consumption of CO_2.

6. Acknowledgements

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Table 1 Chemical composition of soil

Parameter	Unit	Values
pH	-	6.94
Content of particles <0.01mm	%	74
Content of particles <0.001mm	%	45
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	
	Rw / ‰	Raw / g m^{-2} a^{-1}	Rw / ‰	Raw / g m^{-2} a^{-1}
Control	0.48 ± 0.14	2.00 ± 0.58	-0.31 ± 0.09	-1.57 ± 0.86
NH_4NO_3	6.42 ± 0.28	24.86 ± 2.01	5.30 ± 0.87	20.57 ± 1.15
NH_4HCO_3	4.44 ± 0.81	21.00 ± 3.45	3.22 ± 0.87	13.71 ± 3.88
$NaNO_3$	0.86 ± 0.17	4.43 ± 1.73	0.53 ± 0.26	3.14 ± 1.73
NH_4Cl	5.54 ± 0.64	21.29 ± 2.45	4.77 ± 0.78	18.71 ± 0.86
$(NH_4)_2CO_3$	4.48 ± 0.95	20.57 ± 4.46	4.94 ± 1.91	26.57 ± 7.62
$Ca_3(PO_4)_2$	0.01 ± 0.04	0.43 ± 0.86	-0.55 ± 0.25	-1.86 ± 1.29
$(NH_4)_3PO_4$	1.08 ± 0.34	4.00 ± 1.15	0.75 ± 0.21	1.00 ± 1.01
Ca-Mg-P	-0.31 ± 0.12	-1.86 ± 0.43	-0.97 ± 0.38	-3.14 ± 0.72
Urea	8.48 ± 0.96	34.71 ± 4.32	6.59 ± 0.67	26.43 ± 2.73
K_2CO_3	-0.26 ± 0.15	-1.14 ± 0.58	-0.59 ± 0.15	-2.57 ± 0.43

Rw - the ratio of carbonate weathering; Raw - the rate of carbonate weathering; $Rw = 1000 (W_i-W_f)/W_i$ and $Raw = (W_i-W_f)/(S*T)$, where W_i is the initial weight of the carbonate rock tablet, and W_f is the final weight. S is the surface area of carbonate rock tablet (here, we used S = 7 cm^2 for every tablet), and T is the experiment period. Values are reported as means ± standard deviations, n = 3.

Table 3 The main reaction and effects in the 11 fertilizer treatments

Treatment	Main reactions and effects
1. Control	$Ca_{(1-x)}Mg_xCO_3 + CO_2 + H_2O \rightarrow (1-x) Ca^{2+} + xMg^{2+} + 2HCO_3^-$
2. NH_4NO_3	$2Ca_{(1-x)}Mg_xCO_3 + NH_4NO_3 + 2O_2 \rightarrow 2(1-x) Ca^{2+} + 2xMg^{2+} + 2NO_3^- + H_2O + 2HCO_3^-$
3. NH_4HCO_3	$NH_4HCO_3 \rightarrow NH_3\uparrow + H_2O + CO_2\uparrow$ $2Ca_{(1-x)}Mg_xCO_3 + NH_4HCO_3 + 2O_2 \rightarrow 2(1-x) Ca^{2+} + 2xMg^{2+} + NO_3^- + H_2O + 3HCO_3^-$
4. $NaNO_3$	$Ca_{(1-x)}Mg_xCO_3 + NaNO_3 + CO_2 + H_2O \rightarrow (1-x) Ca^{2+} + xMg^{2+} + Na^+ + NO_3^- + 2HCO_3^-$
5. NH_4Cl	$2Ca_{(1-x)}Mg_xCO_3 + NH_4Cl + 2O_2 \rightarrow 2(1-x) Ca^{2+} + 2xMg^{2+} + NO_3^- + Cl^- + H_2O + 2HCO_3^-$
6. $(NH_4)_2CO_3$	$(NH_4)_2CO_3 \rightarrow 2NH_3\uparrow + H_2O + CO_2\uparrow$ $3Ca_{(1-x)}Mg_xCO_3 + (NH_4)_2CO_3 + 4O_2 \rightarrow 3(1-x) Ca^{2+} + 3xMg^{2+} + 2NO_3^- + 2H_2O + 4HCO_3^-$
7. $Ca_3(PO_4)_2$	(1) $(1-x) Ca^{2+} + xMg^{2+} + 2HCO_3^- \rightarrow Ca_{(1-x)}Mg_xCO_3 + CO_2 + H_2O$ (2) $Ca + PO_4 \rightarrow Ca\text{-}P$
8. $(NH_4)_3PO_4$	(1) $2Ca_{(1-x)}Mg_xCO_3 + NH_4^+ + 2O_2 \rightarrow 2(1-x) Ca^{2+} + 2xMg^{2+} + NO_3^- + H_2O + 2HCO_3^-$ (2) $Ca + PO_4 \rightarrow Ca\text{-}P$
9. Ca-Mg-P	(1) $(1-x) Ca^{2+} + xMg^{2+} + 2HCO_3^- \rightarrow Ca_{(1-x)}Mg_xCO_3 + CO_2 + H_2O$ (2) $Ca + PO_4 \rightarrow Ca\text{-}P$
10. Urea	$3Ca_{(1-x)}Mg_xCO_3 + CO(NH_2)_2 + 4O_2 \rightarrow 3(1-x) Ca^{2+} + 3xMg^{2+} + 2NO_3^- + 4HCO_3^-$
11. K_2CO_3	(i) $(1-x) Ca^{2+} + xMg^{2+} + 2HCO_3^- \rightarrow Ca_{(1-x)}Mg_xCO_3 + CO_2 + H_2O$ (ii) $K_2CO_3 + H_2O \rightarrow 2K^+ + HCO_3^- + OH^-$

Note: (1) Common ion effect: The $Ca_{(1-x)}Mg_xCO_3$ produced when the concentrations of Ca^{2+}, Mg^{2+} and/or HCO_3^- increases (for treatment 7, 9 and 11): $(1-x) Ca^{2+} + xMg^{2+} + 2HCO_3^- \rightarrow Ca_{(1-x)}Mg_xCO_3 + CO_2 + H_2O$;

(2) Inhibition of calcite dissolution/precipitation by phosphate: calcium orthophosphate (Ca-P) precipitation produced on the surface of calcite after the addition of PO_4^{3-} in soil, resulting in the inhibition of the dissolution/precipitation of calcite (for treatment 7, 8 and 9): $Ca + PO_4 \rightarrow Ca\text{-}P$

611   Table 4 The amount of fertilizer-derived NH_4^+ at the initial phase of the experiment and the

612   potential nitrogenous transformation (NH_4^+-NO_3^-)

Treatment	Molecular mass g/mol	Amount of added fertilizer /g	Molar amount /mole	Amount of fertilizer-derived NH_4^+ /mole	The maximum of N products /mole
NH_4NO_3	80	43	0.54	0.54	1.08
NH_4HCO_3	79	85	1.08	1.08	1.08
$NaNO_3$	85	91	1.07	0.00	1.07
NH_4Cl	53.5	57	1.07	1.07	1.07
$(NH_4)_2CO_3$	96	51	0.53	1.06	1.06
$Ca_3(PO_4)_2$	310	52	0.17	0.00	0.00
$(NH_4)_3PO_4$	149	15	0.10	0.30	0.30
Ca-Mg-P	nd	44	nd	0.00	0.00
Urea	60	32	0.53	1.06	1.06
K_2CO_3	138	10	0.07	0.00	0.00

613   nd=no data. The amount of added fertilizer (g) divided by its molecular mass (g/mol) is the molar

614   amount of fertilizer (mole). The amounts of fertilizer-derived NH_4^+ are calculated by their own

615   ionization or hydrolysis processes. The maximum of N products is estimated by their main

616   reactions in Table 3.

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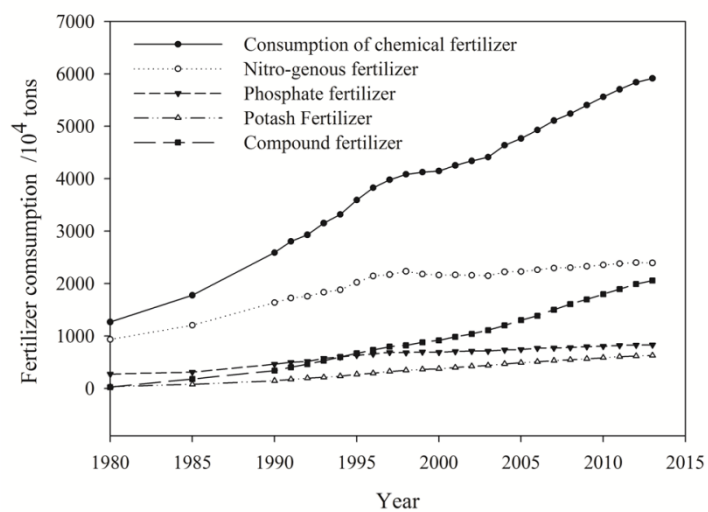
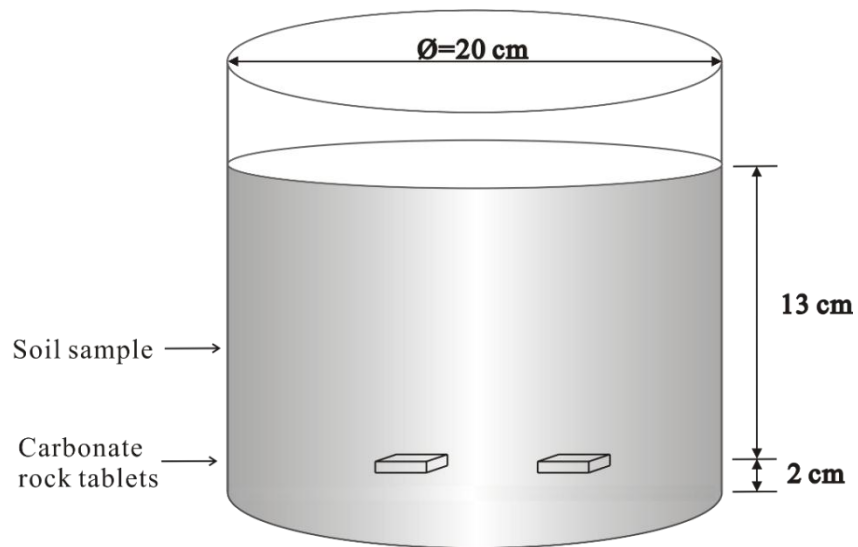Fig. 1 The change in chemical fertilizer consumption in China during the 1980-2013 period

   The data were collected from National Bureau of Statistics of the People's Republic of China

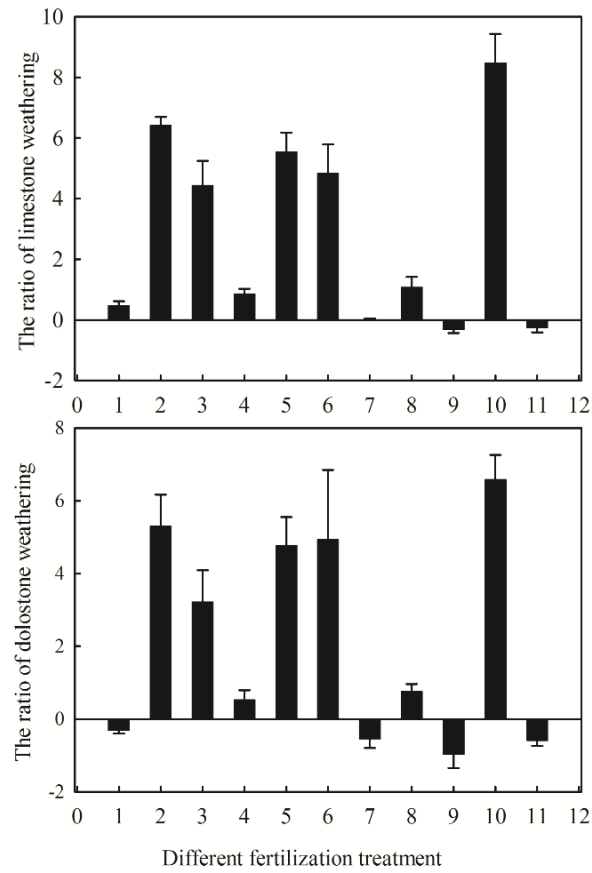(NBS, 2014) (http://www.stats.gov.cn/tjsj/ndsj/)

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Fig. 2 Sketch of the soil column with rock tablets

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Fig. 3 The Rw (‰) of limestone and dolostone under different fertilizer treatments

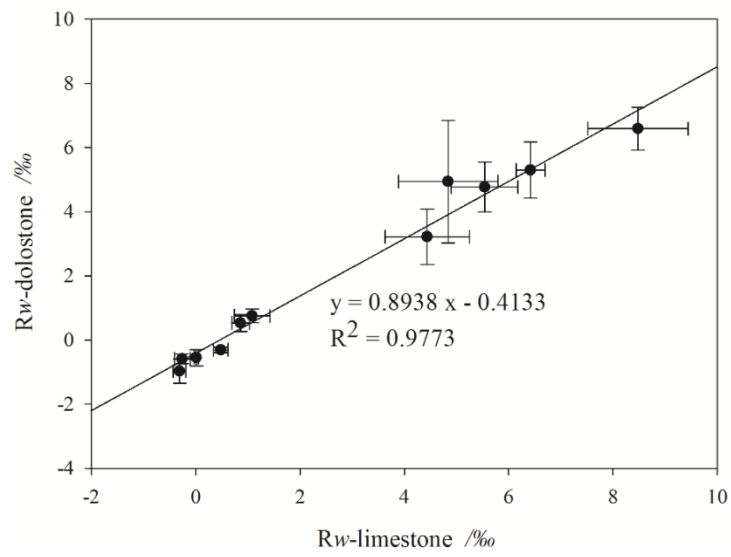Treatment 1. Control; 2. NH_4NO_3; 3. NH_4HCO_3; 4. $NaNO_3$; 5. NH_4Cl; 6. $(NH_4)_2CO_3$; 7. $Ca_3(PO_4)_2$; 8. $(NH_4)_3PO_4$; 9. Ca-Mg-P; 10. Urea; 11. K_2CO_3. Rw = 1000(Wi-Wf)/Wi, where Wi is the initial weight of the carbonate rock tablet, and Wf is the final weight.
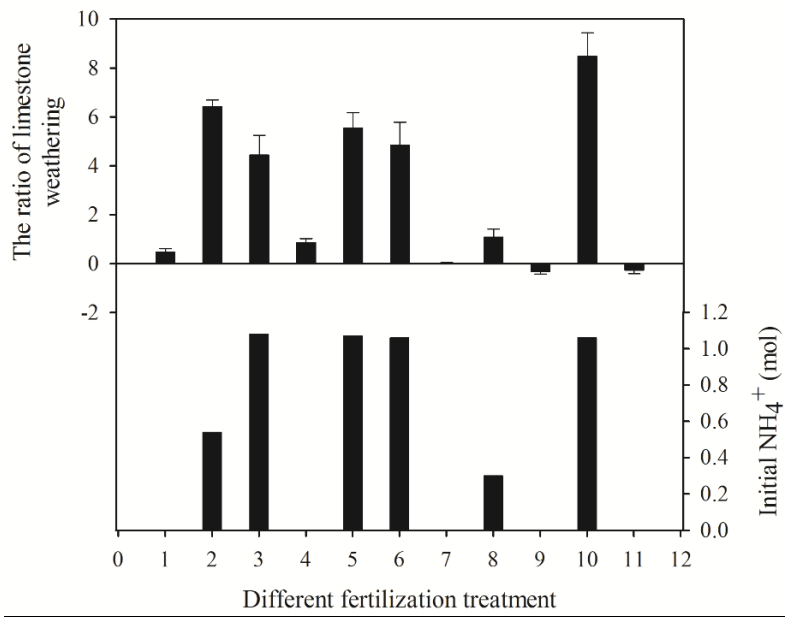
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Fig. 4 The linear correlation of Rw (‰) of limestone and dolostone

Rw = 1000(Wi-Wf)/Wi, where Wi is the initial weight of the limestone tablet, and Wf is the final weight.

Fig. 5 The Rw (‰) of limestone and the molar amount of produced NH_4^+ under different fertilizer treatments

Treatment 1. Control; 2. NH_4NO_3; 3. NH_4HCO_3; 4. $NaNO_3$; 5. NH_4Cl; 6. $(NH_4)_2CO_3$; 7. $Ca_3(PO_4)_2$; 8. $(NH_4)_3PO_4$; 9. Ca-Mg-P; 10. Urea; 11. K_2CO_3. Rw =1000(Wi-Wf)/Wi, where Wi is the initial weight of the limestone tablet, and Wf is the final weight.