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 $NaNO_3$ had a relatively little impact on carbonate weathering in comparison to those five NH_4-based fertilizers above. 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

1. Introduction

Carbonate weathering plays a significant role in consumption of atmospheric CO_2 (Kump et al., 2000; Liu et al., 2011; Liu et al., 2010). 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; 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; Song et al., 2017; Song et al., 2011; 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., 2011; Li et al., 2008); (iii) organic acid secreted by microorganisms (Lian et al., 2008); and (iv) acidic soil (such as red soil, yellow soil) (Song et al., 2014; Song et al., 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 in 1980 to 59.1 Mt in 2013 (Fig. 1). The increasing consumption of mineral fertilizers is a significant disturbance factor in carbonate weathering and the carbon cycle. Several studies have shown that nitrogen fertilizer additions increased weathering rates, and also increased the total export of DIC from agricultural watersheds (Barnes and Raymond, 2009; Gandois et al., 2011; Hamilton et al., 2007; Oh and Raymond, 2006; Perrin et al., 2008; Pierson-wickmann et al., 2009; Probst, 1986; Semhi and Suchet, 2000; West and McBride, 2005). According to estimates by Probst (1988) and Semhi et al. (2000), the contribution of N-fertilizers to carbonate dissolution was 30 % and 12-26 % in two small agricultural carbonate basins in south-western France, the Girou and the Gers, respectively (tributaries of the Garonne River). In the Garonne River Basin, which is a large basin (52,000 km^2), this contribution was estimated at 6 % by Semhi et al. (2000). Perrin et al. (2008) estimated that the contribution of N-fertilizer (usually in form of NH_4NO_3) represents up to 5.7-13.4 % and 1.6-3.8 % of the carbonate dissolution in France and across the world, respectively.

The estimates described above are largely based on calculations that assumed a single type of fertilizer (e.g. $(NH_4)_2SO_4$, NH_4NO_3, or NH_4Cl) was used throughout the whole basin that was considered. However, in actual agricultural practices, different fertilizers are usually added for different crops. The impact of these fertilizers on carbonate weathering and riverine chemical composition may be different. In the case of nitrogenous fertilizer, 100% of NO_3^- produced after the addition $(NH_4)_2SO_4$ and NH_4Cl is derived from the nitrification of NH_4^+, whilst comparatively, it is only 50 % after the addition of NH_4NO_3. Differences in NO_3^- sources may produce a deviation in the impact of N-fertilizer addition on CO_2 consumption by carbonate weathering, since the addition of different N-fertilizers (e.g. $(NH_4)_2SO_4$, NH_4NO_3, NH_4Cl, $NaNO_3$ or urea) may result in different contributions to carbonate weathering and relative products such as HCO_3^-, Ca^{2+} and Mg^{2+}. For phosphate fertilizer, the coprecipitation of phosphate ions with calcium carbonate may inhibit carbonate weathering (Kitano et al., 1978). We assume that the response of carbonate weathering to the addition of different fertilizers, such as N-fertilizer (NH_4 and NO_3), P-fertilizer and Ca/Mg fertilizer, may display differences, which are so far poorly known, but likely significant. Here we sought to understand the agricultural impact on natural carbonate weathering, and to accurately evaluate the CO_2 consumption via carbonate weathering in agricultural areas.

The carbonate-rock-tablet test is used to determine the weathering rate of carbonate rock/mineral from the laboratory to the field (Adams and Post, 1999; Dreybrodt et al., 1996; Gams, 1981; Gams, 1985; Jiang and Yuan, 1999; Liu and Dreybrod, 1997; Plan, 2005; Song et al., 2017; Song et al., 2011; Song et al., 2017; Trudgill, 1975). In the laboratory, the carbonate-rock-tablet is employed to study the kinetics of calcite dissolution/precipitation (Dreybrodt et al., 1996; Liu and Dreybrod, 1997) and determine the rate of carbonate mineral weathering in the soil column (Song et al., 2017; Song et al., 2011). In the field, it is also used to observe the rate of carbonate weathering and estimate CO_2 consumption (Jiang, 2013; Jiang and Yuan, 1999; Plan, 2005; Song et al., 2017; Song et al., 2011; Song et al., 2017). Liu (2011) argued that the carbonate-rock-tablet test may lead to deviations in estimated CO_2 consumption by carbonate weathering at the regional/global scale, in cases where there are insufficient representative data. It is nonetheless a well-established method for the comparative or simulated experiment (Song et al., 2017; Song et al., 2011;

Song et al., 2017).

A field column experiment that involved embedding carbonate-rock-tablets was carried out in a typical karst area of southwest China, in order to observe the impact of different fertilizer additions on carbonate weathering in soil.

2. Materials and Methods

2.1 The study site

This study was carried out in a typical karst area, namely the Huaxi District of Guiyang City, Guizhou Province, SW China (26°23′N, 106°40′E, 1094 m ASL). Guiyang, the capital city of Guizhou Province, is located in the central part of the province, covering an area from 26°11′00″ to 26°54′20″N and 106°27′20″ to 107°03′00″E (approximately 8,000 km^2), with elevations ranging from 875 to 1655 m ASL. Guiyang has a population of more than 1.5 million people, a wide diversity of karstic landforms, high elevations and low latitude, with a subtropical warm-moist climate, and an average annual temperature of 15.3 ℃ and annual precipitation of 1200 mm (Lang, 2006). A monsoonal climate often results in high precipitation during summer, with much less during winter, although the humidity is often high throughout most of the year (Han and Jin, 1996). Agriculture is a major land use in order to produce the vegetables and foods in the suburbs of Guiyang (Liu et al., 2006). The consumption of chemical fertilizer increased from 150 kg/ha in 1980 to 190 kg/ha in 2013 (GBS, 2014).

2.2 Soil properties

The soil used in this column experiment was yellow-brown clay, which was sampled from the B horizon (below 20 cm in depth) of yellow-brown soil profile from a cabbage-corn or capsicum-corn rotation plantation in Huaxi District. The soil was air-dried, ground to pass through a 2-mm sieve, mixed thoroughly and used for the soil columns. The soil pH ($V_{soil}:V_{water}$ = 1:2.5) was determined by pH meter. The chemical characteristics of the soil, including organic matter (OM), NH_4-N, NO_3-N, available P, available K, available Ca, available Mg, available Fe, and available S were determined according to the Agro Services International (ASI) method (Hunter, 1984). OM was extracted by using an extracting solution containing 0.2 mol l^{-1} NaOH, 0.01 mol l^{-1} EDTA, 2 % methanol, and 0.005 % Superfloc 127, and determined by the K_2CrO_7 -H_2SO_4 oxidation method. NH_4-N, NO_3-N, available Ca, and Mg were extracted by 1 mol l^{-1} KCl solution. NH_4-N and NO_3-N was determined by colorimetry method, while Ca and Mg were determined by ICP-AES (inductively coupled plasma atomic emission spectrometer). Available K, P and Fe were extracted by using an extracting solution containing 0.25 mol l^{-1} $NaHCO_3$, 0.01 mol l^{-1} EDTA, 0.01 mol l^{-1} NH_4F, and 0.005 % Superfloc 127. P was determined by spectrophotometry (colorimetry), and K and Fe were determined by atomic absorption spectrophotometry. Finally, available S was extracted by 0.1 mol l^{-1} $Ca(H_2PO_4)_2$ and 0.005 % Superfloc 127 and determined by turbidimetric method. The results are shown in Table 1.

2.3 Soil column and different fertilization treatments

In order to test the hypothesis that the impact of different chemical fertilizers on carbonate weathering may be different, columns (Ø = 20 cm, H= 15 cm) were constructed from 20 cm diameter polyvinylchloride (PVC) pipe (Fig. 2). A hole (Ø =

2 cm) was placed at the bottom of each column to discharge soil water from the soil column. A polyethylene net (Ø 0.5 mm) was placed in the bottom of the columns to prevent soil loss. A 2 cm thick filter layer, including gravel, coarse sand and fine sand, was spread over the net. Two different carbonate rock tablets were buried in the bottom of each soil column (Fig. 2). Based on the common kinds of chemical fertilizers and the main objective of this study, three types (N, P and K fertilizers) of fertilizer including 10 different fertilizers (NH_4NO_3; NH_4HCO_3; $NaNO_3$; NH_4Cl; $(NH_4)_2CO_3$; $Ca_3(PO_4)_2$; $(NH_4)_3PO_4$; fused calcium-magnesium phosphate; Urea and K_2CO_3 fertilizer) were involved in this study. As a result, eleven fertilization treatments including control treatment, each with three replicates, were set up in the field column experiment. The local practical rate of fertilizer application is approximate 160 kg N · ha^{-1} of N fertilizer, 150 kg P_2O_5 ·ha^{-1} of P fertilizer and 50 kg K · ha^{-1} of K fertilizer. In order to short the time of this experiment and make the experimental results distinct, the added amount of 10 fertilizers was increased to: (1) control without fertilizer (CK); (2) 43g NH_4NO_3 fertilizer (CF); (3) 85g NH_4HCO_3 fertilizer (NHC); (4) 91g $NaNO_3$ fertilizer (NN); (5) 57g NH_4Cl fertilizer (NCL); (6) 51g $(NH_4)_2CO_3$ fertilizer (NC); (7) 52g $Ca_3(PO_4)_2$ fertilizer (CP); (8) 15g $(NH_4)_3PO_4$ fertilizer (NP); (9) 44g fused calcium-magnesium phosphate fertilizer (Ca-Mg-P); (10) 32g Urea fertilizer (U); and (11) 10g K_2CO_3 fertilizer (PP). An aliquot of 6 kg of soil was weighed (bulk density = 1.3 g/cm^3), mixed throughly with one of the above fertilizers, and filled into its own column. This process was repeated for all three replicates of the 11 fertilizer treatments. The soil columns were labelled and placed

orderly (see Fig. 2b) at the field experiment site in Huaxi District, Guiyang for a whole year.

2.4 The rate of carbonate weathering

Two different kinds of carbonate rock tablets (2 cm × 1 cm × 0.5 cm in size) were placed in the bottom of each soil column to examine the rate of carbonate weathering in the soil. The two different kinds of carbonate rock collected from the karst area of Huaxi District were: (1) limestone with 60-65 % micrite, 30-35 % microcrystalline calcite, and 2-3 % pyrite; and (2) dolostone with 98-99 % fine crystalline dolomite, 1 % pyrite, and trace quantities organic matter. All the tablets were heated at 80 ℃ for 4 hours, weighed on a 1/10000 electronic balance in the laboratory, labeled by tying a label with fishing line, and then buried at the bottom of each soil column. After a whole year, the tablets were removed carefully, rinsed, baked and weighed.

The amount of weathering (Aw), the ratio of weathering (Rw) and the rate of weathering (Raw) for limestone and dolomite were calculated according to the weight difference of the tablets using the following formulas:

$$A\mathit{w} = (W\mathit{i}-W\mathit{f}) \tag{1}$$

$$R\mathit{w} = (W\mathit{i}-W\mathit{f})/ W\mathit{i} \tag{2}$$

$$R\mathit{aw} = (W\mathit{i}-W\mathit{f})/(S*T) \tag{3}$$

where Wi is the initial weight of the carbonate-rock-tablet, Wf is the final weight, S is the surface area of carbonate rock tablet, and T is the length of the experimental period.

2.5 Statistical analysis

Statistical analysis was performed using IBM SPSS 20.0 (Statistical Graphics Corp, Princeton, USA). All results of carbonate weathering were reported as the means ± standard deviations (SD) for the three replicates.

3. Results

3.1 Weathering rate of carbonate under different fertilized treatments

The R*w* and R*aw* of limestone and dolostone are listed in Table 2. The results show that the R*w* of limestone under urea, NH_4NO_3, NH_4Cl, $(NH_4)_2CO_3$ and NH_4HCO_3 treatments were 8.48 ± 0.96, 6.42 ± 0.28, 5.54 ± 0.64, 4.44 ± 0.81 and 4.48 ± 0.95 ‰, respectively, significantly greater than that under the control treatment 0.48 ± 0.14 ‰ (see Fig. 3). In addition, the observed R*w* of dolostone were 6.59 ± 0.67, 5.30 ± 0.87, 4.77 ± 0.78, 4.94 ± 1.91 and 3.22 ± 0.87 ‰ respectively, under these same five fertilization treatments, in contrast to -0.31 ± 0.09 ‰ in the control treatment. This clearly demonstrates that the addition of these five fertilizers increased the rate of carbonate weathering.

The remaining treatments made differences in the R*w* and R*aw* of limestone and dolostone in comparison to the control treatment (Table 2), but the differences were much smaller than the treatments with those five fertilizers as mentioned above (Fig. 3). In the $(NH_4)_3PO_4$ treatment, the R*w* were only 1.08 ± 0.34 ‰, and 0.75 ± 0.21‰ for limestone and dolomite, respectively, while the R*aw* were 4.00 ± 1.15 $g \cdot m^{-2} a^{-1}$ and 1.00 ± 1.01 $g \cdot m^{-2} a^{-1}$ for limestone and dolomite, respectively. The R*w* and R*aw* in the $NaNO_3$ treatments showed differences with the control treatment. The values, however, are much less than those under the five NH_4-based fertilizers mentioned above, exhibiting little effect of the $NaNO_3$ fertilizer addition on carbonate weathering (see Table 2 and Fig. 3). Except for the R*w* of limestone approaching zero in the $Ca_3(PO_4)_2$ treatment, all the values of R*w* and R*aw* in Ca-Mg-P, K_2CO_3 and $Ca_3(PO_4)_2$ treatments showed negative values. This indicates that the addition of Ca-Mg-P, K_2CO_3 and $Ca_3(PO_4)_2$ fertilizers led to precipitation at the surface of the carbonate mineral.

3.2 Comparison of limestone of dolomite

Fig. 3 shows that, on the whole, the ratios of dolostone weathering are smaller than those of limestone weathering except for the $(NH_4)_2CO_3$ treatment, demonstrating that dolostone weathers more slowly than limestone under fertilization effects.

In Fig. 4, we plotted the R*w* of limestone vs. dolostone tablets in a linear correlation diagram, in order to compare the weathering responses of limestone with dolostone. The results show that the R*w* of limestone and dolostone exhibit a high positive correlation (R^2=0.9773; see Fig. 4), indicating that the weathering of limestone and dolostone are similar under different treatments. Thus, we will explain the results in terms of carbonates, rather than separately discussing the individual dolostone and limestone.

4. Discussion

4.1 Kinetics of carbonate dissolution/precipitation: controlling factors

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

$$MeCO_3 \leftrightarrow Me^{2+} + CO_3^{2-} \quad (4)$$

$$MeCO_3 + H_2CO_3 \leftrightarrow Me^{2+} + 2HCO_3^- \quad (5)$$

$$MeCO_3 + H^+ \leftrightarrow Me^{2+} + HCO_3^- \quad (6)$$

where Me = Ca, Mg. As Eq. (5) describes, atmospheric/soil CO_2 is usually considered to be the natural weathering agent of carbonate. In watersheds with calcite- and dolomite-containing bedrock, H_2CO_3 formed in the soil zone usually reacts with carbonate minerals, resulting in dissolved Ca, Mg, and HCO_3^- as described in Eq. (5) (Andrews and Schlesinger, 2001; Shin et al., 2014). Although it has been proven that the reaction of carbonate dissolution is mainly controlled by the amount of rainfall (Amiotte Suchet et al., 2003; Egli and Fitze, 2001; Kiefer, 1994), in this study, we consider that the effect of rainfall is equal in each soil column, and hence is disregarded as a controlling factor in weathering rate differences among these treatments. In theory, the fertilizers could stimulate bacteria, which may increase respiration and CO_2 concentrations in the soil, as a result, probably enhance carbonate weathering as Eq. (5). However, Eq. (6) suggests that the proton from other origins, such as the nitrification processes of NH_4^+, as mentioned in the Introduction section, can play the role of weathering agent in agricultural areas. In this study, the urea, NH_4NO_3, NH_4HCO_3, NH_4Cl, and $(NH_4)_2CO_3$ amendments increased (10 to 17-fold) the natural weathering rate from 2.00 g m^{-2} a^{-1} for limestone tablets in the control treatment (Table 2). Thus, these increases are strongly related to the effect of proton release from the nitrification of NH_4^+. In contrast, carbonate precipitation will occur due to the backward reaction of Eq. (5) in the following cases: (1) the degassing of dissolved CO_2 due to dramatic changes in the parameters of the CO_2 system (such as T, pH, pCO_2, etc); (2) soil evapotranspiration; or (3) the common ion effect: the increase of Ca^{2+}, Mg^{2+} or CO_3^{2-} in a weathering-system with equilibrium between water and calcite (Calmels et al., 2014; Dreybrodt, 1998).

4.2 Main reactions and effects in different treatments

The main reactions and effects of every treatment in this study are listed in Table 3.

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

In urea ($CO(NH_2)_2$) treatment, the enzyme urease rapidly hydrolyzes the urea-N to NH_4^+ ions (Eq. (7)) when urea is applied to the soil (Soares et al., 2012).

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

Although the study of Singh et al. (2013) showed that part of NH_4^+ may be lost as ammonia (NH_3) and subsequently as nitrous oxide (N_2O) (Singh et al., 2013), the remaining ammonium (NH_4^+) is mainly oxidized during nitrification in soil by autotrophic bacteria, such as Nitrosomonas, resulting in nitrite NO_2^- and H^+ ions. Nitrite is in turn oxidized by another bacterium, such as Nitrobacter, resulting in nitrate (NO_3^-) (Eq. (8)) (Perrin et al., 2008).

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \quad (8)$$

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

(i) either by exchange process with base cations in the soil exchange complex (Eq. (9))

$$Soil - Ca + 2H^+ \rightarrow Soil - 2H^+ + Ca^{2+} \quad (9)$$

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

$$Ca_{(1-x)}Mg_xCO_3 + H^+ \rightarrow (1-x)\ Ca^{2+} + xMg^{2+} + HCO_3^- \qquad (10)$$

Consequently, by combining Eq. (8) and Eq. (10), carbonate weathering by protons produced by nitrification can be expressed as (Eq. 11) (See details in Perrin et al., 2008 and Gandois et al., 2011).

$$2Ca_{(1-x)}Mg_xCO_3 + NH_4^+ + 2O_2 \rightarrow 2(1-x)\ Ca^{2+} + 2xMg^{2+} + NO_3^- + H_2O + 2HCO_3^- \qquad (11)$$

As discussed above, provided that the loss as ammonia (NH_3) and nitrous oxide (N_2O) after hydrolyzation is disregarded in this study, the final equation of carbonate weathering in NH_4NO_3, NH_4HCO_3, NH_4Cl, $(NH_4)_2CO_3$ and urea treatments will be as follows, respectively:

$$2Ca_{(1-x)}Mg_xCO_3 + NH_4NO_3 + 2O_2 \rightarrow 2(1-x)\ Ca^{2+} + 2xMg^{2+} + 2NO_3^- + H_2O + 2HCO_3^- \qquad (12)$$

$$2Ca_{(1-x)}Mg_xCO_3 + NH_4HCO_3 + 2O_2 \rightarrow 2(1-x)\ Ca^{2+} + 2xMg^{2+} + NO_3^- + H_2O + 3HCO_3^- \qquad (13)$$

$$2Ca_{(1-x)}Mg_xCO_3 + NH_4Cl + 2O_2 \rightarrow 2(1-x)\ Ca^{2+} + 2xMg^{2+} + NO_3^- + Cl^- + H_2O + 2HCO_3^- \qquad (14)$$

$$3Ca_{(1-x)}Mg_xCO_3 + (NH_4)_2CO_3 + 4O_2 \rightarrow 3(1-x)\ Ca^{2+} + 3xMg^{2+} + 2NO_3^- + 2H_2O + 4HCO_3^- \qquad (15)$$

$$3Ca_{(1-x)}Mg_xCO_3 + CO(NH_2)_2 + 4O_2 \rightarrow 3(1-x)\ Ca^{2+} + 3xMg^{2+} + 2NO_3^- + 4HCO_3^- \qquad (16)$$

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

In the $NaNO_3$ treatment, the reaction occurs according to Eq. (17), indicating that the addition of NO_3-fertilizer does not significantly influence carbonate weathering.

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

$2HCO_3^-$ (17)

(3) Common ion effect: K_2CO_3 treatment

In the K_2CO_3 treatment, CO_3^{2-} and HCO_3^- will be produced after the addition of K_2CO_3 according to Eq. (18), hence resulting in carbonate precipitation as described in Eq. (19), due to the common ion effect.

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

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

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

In the $(NH_4)_3PO_4$ treatment, the reaction of carbonate weathering will occur according to Eq. (11) due to the nitrification of NH_4^+ ionized from the $(NH_4)_3PO_4$ fertilizer. The PO_4^{3-} anion will exert an inhibition to calcite dissolution (Kitano et al., 1978), as calcium orthophosphate (Ca-P) precipitation is produced on the surface of calcite after the addition of PO_4^{3-} in soil (reaction: $Ca + PO_4 \rightarrow Ca\text{-}P$), resulting in inhibition of the calcite dissolution (Alkattan et al., 2002; Berner and Morse, 1974; Raistrick, 1949).

(5) Complex effects: Common ion effect versus inhibition effect of PO_4 in $Ca_3(PO_4)_2$ 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 (Alkattan et al., 2002; Burton and Walter, 1990; Giannimaras and Koutsoukos, 1987; House, 1987; Ishikawa and Ichikuni, 1981; Lin and Singer, 2006; Mucci, 1986; Reddy, 1977).

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 amounts 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 added urea is 1.06 mole, while NH_4^+ ionized from added 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 R*w* 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 R*w* 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 demonstrated by many studies, from the laboratory to the field (Barnes and Raymond, 2009; Bertrand et al., 2007; Biasi et al., 2008; Errin et al., 2006; Gandois et al., 2011; Hamilton et al., 2007; Oh and Raymond, 2006; Perrin et al., 2008; Semhi and Suchet, 2000; Song et al., 2017; Song et al., 2011; West and McBride, 2005). We have noted that the R*w* 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 $(NH_4)_2CO_3$ as a typical weak acid and weak base salt, are easier to decompose and produce NH_3 and CO_2 gases according to Eq. (20) and (21) (Trypuc and Kielkowska, 1996), resulting in amounts of fertilizer-derived NH_4 that are lower than 1.07 moles.

$$NH_4HCO_3 \rightarrow NH_3 \uparrow + H_2O + CO_2 \uparrow \qquad (20)$$

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

The A*w* and R*w* 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 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).

There is no significant different between the R*w* 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 carbonate weathering, which raises a new problem. Eq. (5), usually considered as an expression for the natural weathering process of carbonate, is an important reaction in understanding the kinetics of carbonate dissolution in carbonate-dominated areas, where the molar ratio of $HCO_3^-$and Me^{2+} in the river is usually used as an indicator to make estimates of CO_2 consumption by carbonate weathering at the regional/global scale (Hagedorn and Cartwright, 2009; Li et al., 2009). In agricultural areas, the relationship between $(Ca+Mg)/HCO_3^-$ and NO_3^- is usually employed to estimate the contribution of N-fertilizer to riverine Ca^{2+}, Mg^{2+}, and alkalinity (Etchanchu and Probst, 1988; Jiang, 2013; Jiang et al., 2009; Perrin et al., 2008; Semhi and Suchet, 2000). In these studies, the nitrification described in Eq. (8) is usually considered as the unique origin of NO_3^-. According to the results of the $NaNO_3$ treatment in this study, the contribution of protons from nitrification to carbonate weathering may be overestimated, if anthropogenic NO_3^- is neglected, since the anthropogenic NO_3^- does not release the proton described in Eq. (8). For NH_4NO_3 fertilizer, Eq. (12) shows that two moles of $Ca^{2+}+Mg^{2+}$, NO_3^-, and HCO_3^- will be produced when one mole NH_4NO_3 reacts with 2 moles of carbonate, where only half of the NO_3^- originates from nitrification described as Eq. (8). This will result in an overestimation of the contribution of nitrification to carbonate weathering, and thus thereby mislead the estimation of CO_2 consumption.

At regional scales, if different fertilizers are simultaneously added to an agricultural area, the estimation of CO_2 consumption by carbonate weathering might become more complicated, since the mole ratios of Ca+Mg, HCO_3^-, and/or NO_3^- between different fertilization treatments are different (see Table 3). 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 CO_2 consumption.

4.4 The comparison with other studied results

The R*w* and R*aw* 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 R*aw*) in Nongla, Guangxi, a karst area of Southwestern China (Zhang, 2011), and with the results of 0.05-5.06 ‰ (for R*w*) and 1.08-136.90 g m^{-2} a^{-1} (for R*aw*) from the north slope of the Hochschwab Massif in Austria (Plan, 2005), as determined using the limestone tablet method. But the R*aw* of 2.00 g m^{-2} a^{-1} is lower than the results of 7.0-63.5 g m^{-2} a^{-1} for R*aw* 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 R*aw* 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 an 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 (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.

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 $NaNO_3$ had a relatively little impact 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 (Perrin et al., 2008; Semhi and Suchet, 2000).

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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

Table 2 Carbonate weathering under different fertilizer treatments

Treatment	Limestone		Dolostone	
	R*w* / ‰	Ra*w* / g m^{-2} a^{-1}	R*w* / ‰	Ra*w* / 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

R*w* - the ratio of carbonate weathering; Ra*w* - the rate of carbonate weathering; R*w* =1000 (W*i*-W*f*)/Wi and Ra*w* = (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): $Ca + PO_4 \rightarrow Ca\text{-}P$

Table 4 The amount of fertilizer-derived NH_4^+ at the initial phase of the experiment and the potential nitrogenous transformation (NH_4^+-NO_3^-)

Treatment	Molecular mass g/mol	Amount of added fertilizer /g	Molar amount of added fertilizer /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

nd=no data. The amount of added fertilizer (g) divided by its molecular mass (g/mol) is the molar amount of fertilizer (mole). The amounts of fertilizer-derived NH_4^+ are calculated by their own ionization or hydrolysis processes. The maximum of N products is estimated by their main reactions in Table 3.

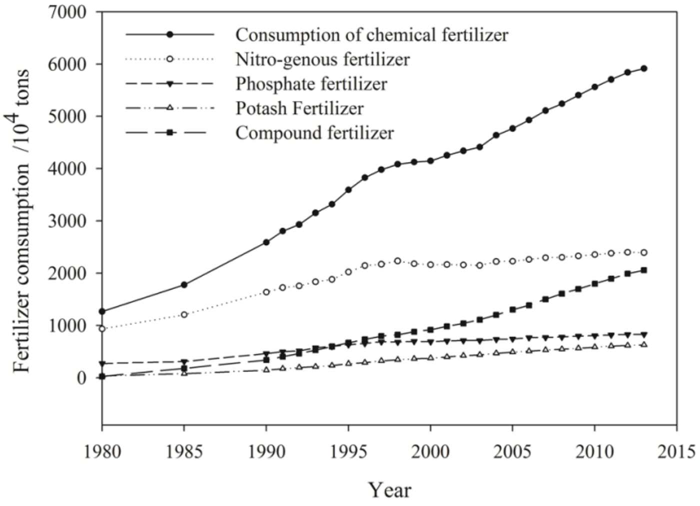

Fig. 1 The change in chemical fertilizer consumption in China during the 1980-2013 period

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/)

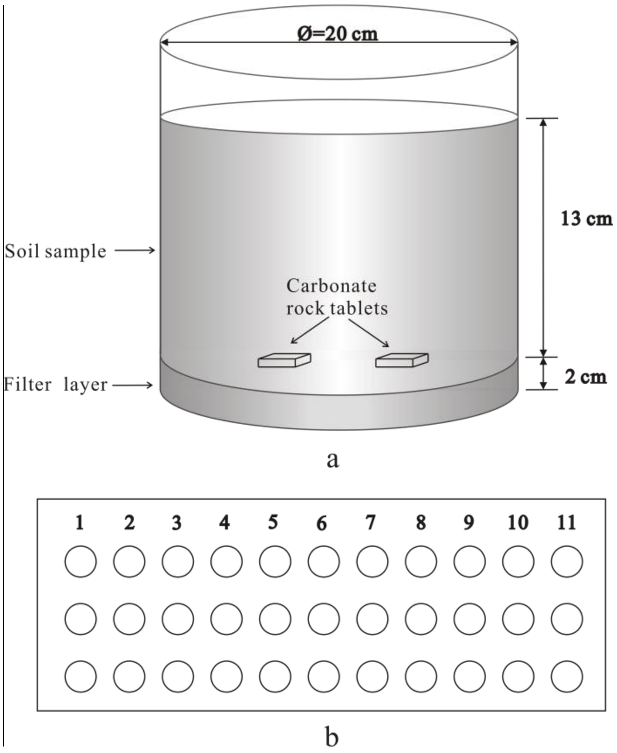

Fig. 2 Sketch of the soil column (a) and their on-site layout (b)

Fig. 2a: The filter layer (2 cm thick) consists of gravel, coarse sand and fine sand; Fig. 2b: 11 fertilization treatments with 3 replicates including: 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.

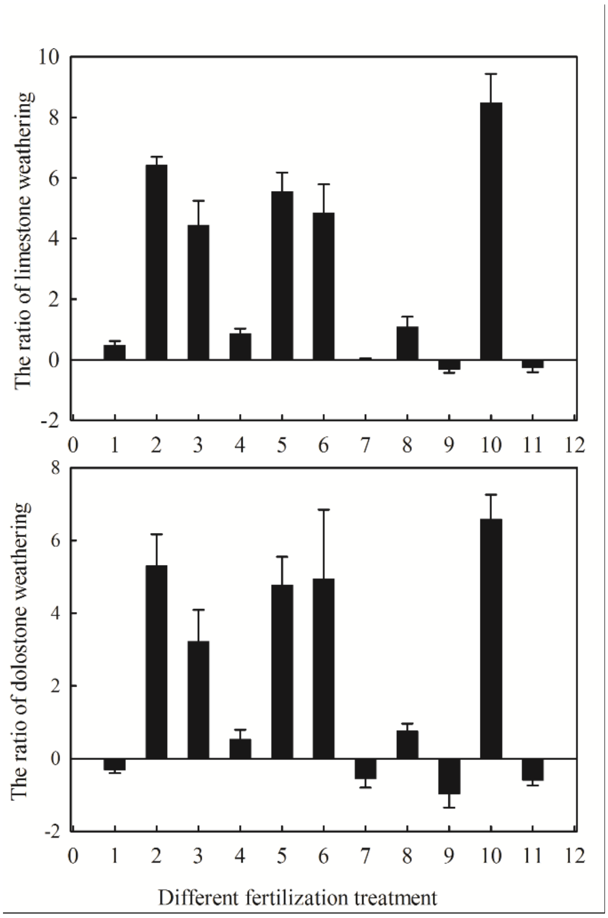

Fig. 3 The R*w* (‰) of limestone and dolostone under different fertilizer treatments

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. R*w* = 1000(W*i*-W*f*)/W*i*, where W*i* is the initial weight of the carbonate rock tablet, and W*f* is the final weight.

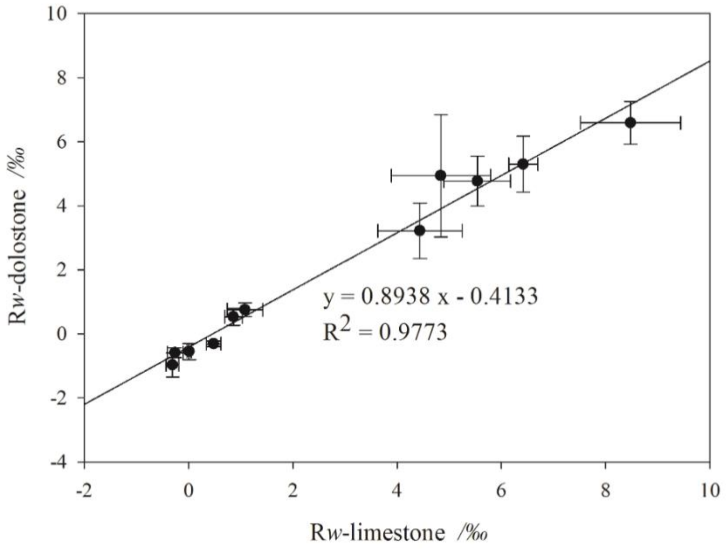

Fig. 4 The linear correlation of R*w* (‰) of limestone and dolostone

R*w* = 1000(W*i*-W*f*)/W*i*, where W*i* is the initial weight of the limestone tablet, and W*f* is the final weight.

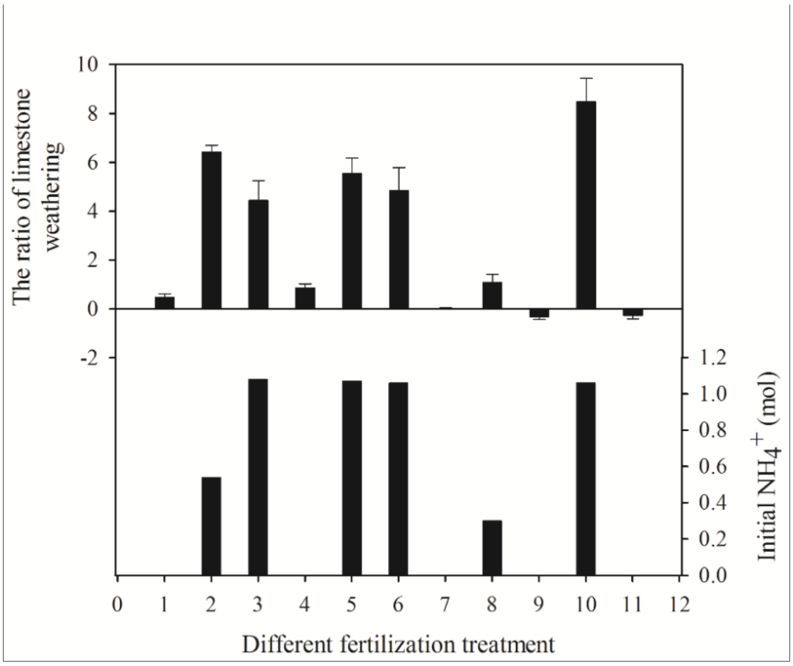

Fig. 5 The R*w* (‰) of limestone and the molar amount of produced NH_4^+ under different fertilizer treatments

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. R*w* =1000(W*i*-W*f*)/W*i*, where W*i* is the initial weight of the limestone tablet, and W*f* is the final weight.