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

Chao Song [1, 2], Changli Liu [1], Guilin Han [2]

1. The Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences, Shijiazhuang, 050803, Hebei, China

2. School of Water Resources and Environment, China University of Geosciences (Beijing), Beijing, 100083, China.

Corresponding Author：

1. Chao Song

Email: chao-song@qq.com

Tel/Fax: +86-18931852527

Abstract: Carbonate weathering, as a significant vector for the movement of carbon both between and within ecosystems, are strongly influenced by agricultural fertilization since the addition of fertilizers tends to change the chemical characteristics of soil such as pH value. Different fertilizers may exert a different impact on carbonate weathering, but these discrepancies are not still well-known so far. In this study, a field column experiment was conducted to explore the responses 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 carbonate and dolomite tablets buried at the bottom of the columns. The result 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^+. The addition of $Ca_3(PO_4)_2$, Ca-Mg-P and K_2CO_3 induced carbonate precipitation due to 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 the overestimation of 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., 2010; 2011). The 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 the protons derived (i) from 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) from the sulfuric acid (Lerman and Wu, 2006; Lerman et al., 2007; Li et al., 2008; Li et al., 2009), (iii) from organic acid secreted by microorganisms (Lian et al., 2008) as well as (iv) from acidic soil (Chao et al., 2014). Given that atmospheric CO_2 is not the unique weathering agent, differentiating the agent of carbonate weathering is important for the accurate budgeting of the net CO_2 consumption by carbonate weathering, especially in agricultural areas where mineral fertilizers are used.

The world 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). For 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 fertilizer is a significant disturbance factor of carbonate weathering and carbon cycle. Several studies showed that nitrogen fertilizer additions increased weathering rates and 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 (subtributary and tributary of the Garonne river, respectively). For the Garonne river basin, which is larger 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) represent up to 5.7-13.4% and 1.6-3.8% to carbonate dissolution for France and on a global scale, respectively.

The estimates described above were usually based on calculations assuming that 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, different fertilizers are usually added for different crops in actual agricultural practices. The impact of these fertilizers on carbonate weathering and riverine chemical composition may be different. For nitrogenous fertilizer, 100% NO_3^- produced after the addition $(NH_4)_2SO_4$ and NH_4Cl derive from the nitrification of NH_4^+, comparatively, only 50% after the addition NH_4NO_3. The difference of NO_3^- source may cause the evaluated deviation of the impact of N-fertilizer addition on CO_2 consumption by carbonate weathering. Because 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 coprecipitaion of phosphate ions with calcium carbonate may inhibit carbonate weathering (Kitano et al., 1978). We suppose that the response of carbonate weathering to the addition of different fertilizer such as N-fertilizer (NH_4 and NO_3), P-fertilizer and Ca/Mg fertilizer may display difference, which is poorly known so far but significant to well understand the agricultural force on natural carbonate weathering and accurately evaluate the CO_2 consumption via carbonate weathering in agricultural area.

Moreover, the carbonate-rock-tablet test is used to determine the weathering rate of carbonate rock/mineral from laboratory to field (Gams, 1981; Chao et al., 2011; Trudgill, 1975; Chao et al., 2014; Dreybrodt et al., 1996; Gams, 1985; Jiang and Yuan, 1999; Liu and Dreybrod, 1997; Plan, 2005). In 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 soil column (Chao et al., 2011). However, in field, it is also used to observe the rate of carbonate weathering and estimated CO_2 consumption by carbonate weathering (Chao et al., 2014; Jiang and Yuan, 1999; Jiang et al., 2013; Plan, 2005). Although Liu (2011) argue that the carbonate-rock-tablet test may lead to the deviation of estimated CO_2 consumption by carbonate weathering at the regional/global scale in the case of insufficient representative data (Liu, 2011), yet it is a preferred option for the condition controlled contrast or stimulated experiment (Chao et al., 2011; Chao et al., 2014).

Therefore, a field column experiment embedding carbonate rock tablets was carried out in a typical karst area of southwest China to observe the impacts of different fertilizer addition on carbonate weathering in soil.

2. Materials and Methods

2.1 The study site

This study was carried out in a typical karst area, 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 (about 8,000 km^2), with elevations ranging from 875 to 1655 m above mean sea level. Guiyang has a population of more than 1.5 million people, a high diversity of karstic landforms, a high elevation and low latitude, with a subtropical warm-moist climate, annual average temperature of 15.3 ℃ and annual precipitation of 1200 mm (Lang et al., 2006). A monsoonal climate often results in high precipitation during summer and much less during winter, although the humidity is often high during most of the year (Han and Jin, 1996). Agriculture is a major land use in order to produce the vegetables and foods in the suburb 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 sampled from the B horizon (below 20 cm in depth) of yellow-brown soil in a cabbage-corn or capsicum-corn rotation plantation in Huaxi district. It was air-dried, ground to pass through a 2-mm sieve, mixed thoroughly and used for soil columns. The pH (V_{soil}:V_{water} = 1:2.5) were determined by pH meter. The chemical characteristics of soil including organic matter (OM), NH_4-N, NO_3-N, available P, available K, available Ca, available Mg, available S and available Fe were determined according to the Agro Services International (ASI)

Method (Hunter, 1980), where the extracting solution used for OM contained 0.2 mol l^{-1} NaOH, 0.01 mol l^{-1} EDTA, 2% methanol and 0.005% Superfloc 127, NH_4-N, NO_3-N, available Ca and Mg were determined based on extraction by 1 mol l^{-1} KCl solution, available K, P and Fe were extracted by 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, and available S was extracted by 0.1 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

In order to test the hypothesis that the responses of the impact of different chemical fertilizer on carbonate weathering may be different, columns (Ø=20cm, H= 15cm) were constructed from 20-cm diameter polyvinylchloride (PVC) pipe (Fig. 2). A hole (Ø=2 cm) were established at the bottom of each column to discharge soil water from soil column. A polyethylene net (Ø 0.5 mm) was placed in the bottom of the columns to prevent soil loss. A filter sand layer with 2 cm thickness including gravel, coarse sand and fine sand was spread on the net. Two different carbonate rock tablets were buried in the bottom of each soil column (Fig .2). According to common kinds of chemical fertilizer and the main objective of this study, eleven fertilization treatments with three replicates in the field column experiment were set up: (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). The 6 kg soil was weighed (bulk density=1.3 g/cm^3), mixed perfectly with above fertilizer, respectively, and filled in its own column. These soil columns were placed at the field experiment site in Guiyang of Southwestern China 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 established in the bottom of each soil column to explore the rate of carbonate weathering in soil. The two different kinds of carbonate rock collected from 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% power crystal dolomite, , 1% pyrite and trace quantities organic matter. All of tablets were heated at 80 ℃ for 4 hours then weighed in a 1/10000 electronic balance in the laboratory, tied to a label with fishing line and buried at the bottom of each soil column. They were taken out carefully, rinsed, baked and weighed after a whole year.

The amount of weathering (A*w*), the ratio of weathering (R*w*) and the rate of weathering (R*aw*) for limestone and dolomite were calculated according to the weight difference of the tablets using the following formulas:

$$Aw = (Wi - Wf) \quad (1)$$

$$Rw = (Wi - Wf)/ Wi \quad (2)$$

$$Raw = (Wi - Wf)/(S*T) \quad (3)$$

where W*i* is the initial weight of the carbonate rock tablets, W*f* is their final weights, S is the surface area of carbonate weathering tablets, and T is the length of the experimental period.

2.4 Statistical analysis

Statistical analysis was performed using IBM SPSS 20.0 (Statistical Graphics Crop, Princeton, USA). All results of carbonate weathering were reported as the means±standard deviations (SD) for the three replications. One-way analysis of variance (ANOVA) was used to determine the differences of weathering rate between limestone and dolostone.

3. Results

3.1 The weathering rate of carbonate under different fertilized treatments

The R*w* and R*aw* of limestone and dolostone were listed in Table 2. The results showed 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‰ (mean±SD, $p<0.05$), much bigger than that under the control treatment 0.48±0.14‰ (see Fig. 3) as observed in dolomite (6.59±0.67, 5.30±0.87, 4.77±0.78, 4.94±1.91 and 3.22±0.87‰ under these five fertilization treatments vs. -0.31±0.09‰ in control treatment). This manifested that the addition of these five fertilizers increased the rate of carbonate weathering.

According to the results of ANOVA analysis, the rest treatments had no significant differences ($p>0.05$) in the R*w* and R*cw* of limestone and dolomite in comparison with control treatment (Table 2). In $(NH_4)_3PO_4$ treatment, the R*w*, and R*aw* were only 1.08±0.34‰ and 0.75±0.21‰ for limestone and dolomite, 4.00±1.15 g m^{-2} a^{-1} and 1.00±1.01 g m^{-2} a^{-1} for limestone and dolomite, respectively, less than those under other four NH_4-fertilizers as mentioned above. The R*w* and R*aw* in $NaNO_3$ treatment failed to show a remarkable difference with the control treatment, exhibiting little effect of $NaNO_3$ fertilizer addition on carbonate weathering (Fig. 3). Except the R*w* of limestone in $Ca_3(PO_4)_2$ treatment approaching zero, all the values of R*w* and R*aw* in Ca-Mg-P, K_2CO_3 and $Ca_3(PO_4)_2$ treatments showed a negative value, indicating that the addition of Ca-Mg-P , K_2CO_3 and $Ca_3(PO_4)_2$ fertilizers can lead to the precipitation at the surface of carbonate mineral, which can be explained by common ion effect.

3.2 The comparison of limestone of dolomite

The statistical significance of the R*w* between limestone and dolomite using one-way analysis of variance (ANOVA) was 0.320 (>0.05), suggesting that the results between limestone and dolostone weathering under different treatments were similar. We will explain the results with carbonates instead of individual dolostone and limestone.

4. Discussion

4.1 The 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):

$$MeCO_3 + H^+ \leftrightarrow Me^{2+} + HCO_3^- \qquad (4)$$

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

$$MeCO_3 \leftrightarrow Me^{2+} + CO_3^{2-} \qquad (6)$$

where Me=Ca, Mg. As Eq. (5) describes, atmospheric/soil CO_2 is usually regard as 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)(Shin et al., 2014; Andrews and Schlesinger, 2001). 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), we consider that the effect of rainfall is equal in each soil column and hence unconsidered as a controlling factor in this study. The Eq. (4) suggests that the proton from other origins such as the nitrification processes of NH_4^+, as mentioned in 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 $(NH_4)_2CO_3$ amendment increased (10 to 17-fold) the natural weathering rate of 2.00 g m^{-2} a^{-1} from limestone tablets in control treatment (table 2). Thus these increases are strongly relative to the effect of the proton released from the nitrification of NH_4^+. On the contrary, the carbonate precipitation will occur as due to the backward reaction of the Eq. (5) in following cases: (1) the degassing of dissolved CO_2, (2) soil evapotranspiration or (3) 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, 1988).

4.2 The main reactions and effects in different treatments

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

(1) The 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 ($CO(NH_2)_2$) 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 from Singh et al showed that a part of NH_4^+ may be lost as ammonia (NH_3) and subsequently as nitrous oxide (N_2O) (Singh et al., 2013), yet the rest ammonium (NH_4^+) is mainly oxidized in soil by autotrophic bacteria (like Nitrosomonas) during nitrification, 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))

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

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

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

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

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

As discussed above, provided that the loss as ammonia (NH_3) and nitrous oxide (N_2O) after hydrolyzation is unconsidered 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 followed as, respectively:

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

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

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

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

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

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

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

$$Ca_{(1-x)}Mg_xCO_3 + NaNO_3 + CO_2 + H_2O \rightarrow (1-x)\ Ca^{2+} + xMg^{2+} + Na^+ + NO_3^- + 2HCO_3^- \quad (17)$$

(3) The common ion effect: K_2CO_3 treatment

In K_2CO_3 treatment, CO_3^{2-} and HCO_3^- will produce according to Eq. (18) after adding K_2CO_3, hence resulting in carbonate precipitation 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

For $(NH_4)_3PO_4$ treatment, the reaction of carbonate weathering will occur according to Eq. (11) due to the nitrification of NH_4^+ ionized from $(NH_4)_3PO_4$ fertilizer will occur the nitrification. Whilst the PO_4^{3-} anion will exert an inhibition to calcite dissolution: calcium orthophosphate (Ca-P) precipitation produces on the surface of calcite after the addition of PO_4^{3-} in soil, resulting in inhibiting the dissolution of calcite.

(5) Complex effects: Common ion effect versus Inhibition effect of PO_4 in $Ca_3(PO_4)_2$ and Ca-Mg-P treatments

In $Ca_3(PO_4)_2$ and Ca-Mg-P treatments, on the one hand, the $Ca_{(1-x)}Mg_xCO_3$ produces when the concentrations of Ca^{2+} (or/and Mg^{2+}) increases as following Eq. (19). On the other hand, the inhibition effect of phosphate will cause that calcium phosphate precipitation produces on the surface of carbonate mineral after the addition of P in soil, correspondingly resulting in inhibiting the carbonate precipitation.

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

In order to further compare the difference 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 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 3). The R*w* of limestone tablets and the initial amount of NH_4^+ are plotted in Fig. 4. A distinct relationship between them is observed: the R*w* in NH_4NO_3, NH_4HCO_3, NH_4Cl, $(NH_4)_2CO_3$ and urea treatments are bigger than in control treatment, where the initial amount of NH_4^+ displays similar results (Fig. 4). 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 from nitrification has been proven by many studies, from laboratory to field (Semhi and Suchet, 2000; Bertrand et al., 2007; Oh and Raymond, 2006; Errin et al., 2006; Hamilton et al., 2007; Biasi et al., 2008; Perrin et al., 2008; Barnes and Raymond, 2009; Chao et al., 2011; West and McBride, 2005; Gandois et al., 2011). We have noted that the R*w* values in NH_4HCO_3 and $(NH_4)_2CO_3$ treatment are lower than even half of those in urea treatment in spite of adding the same amount of fertilizer-derived NH_4 (about 1.07 mole). This is probably because the two fertilizers, NH_4HCO_3 and $(NH_4)_2CO_3$, are easier to decompose and produce the NH_3 and CO_2 gases as following Eq. (20) and (21), resulting in the amount of fertilizer-derived NH_4 of lower than 1.07 moles.

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

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

The A*w* and R*w* in $(NH_4)_3PO_4$ treatment, unlike in other NH_4-fertlizer treatments, had not a significant increase comparing with 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 surface 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, the R*w* without significant difference with control treatment in $NaNO_3$ treatment indicates 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 is raising a new problem. Eq. (5), usually as an expression for the natural weathering process of carbonate, is an important reaction for understanding the kinetics process of carbonate dissolution in carbonate-dominated areas, where the molar ratio of $HCO_3^-$and Me^{2+} in the river as an indicator is usually used to make estimations of CO_2 consumption by carbonate weathering at the regional/global scale (Hagedorn and Cartwright, 2009; Li et al., 2009). At 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 as Eq. (8) is usually considered as the unique origin of NO_3^-. According to the result of $NaNO_3$ 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 as Eq. (8). For NH_4NO_3

fertilizer, the (Eq. (12)) show that the two moles of Ca^{2+}+Mg^{2+}, NO_3^- and HCO_3^- will be produced when one mole NH_4NO_3 react with 2 moles of carbonate, where only half of NO_3^- originate from nitrification described as Eq. (8). This will result in a double overestimation on the contribution of the nitrification to carbonate weathering and thus mislead the estimation of CO_2 consumption therein.

At regional scales, If different fertilizers are added simultaneously to an agricultural area, the estimation of CO_2 consumption by carbonate weathering might became more complicated, since the mole ratio of Ca+Mg, HCO_3^- and/or NO_3^- between different fertilization treatment is 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 control treatment in this study is 0.48‰ and 2.00 g m^{-2} a^{-1}, which is consistent with the 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 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 Australia (Plan, 2005) using limestone tablet method. But the R*aw* of 2.00 g m^{-2} a^{-1} is lower than the results (7.0-63.5 g m^{-2} a^{-1} for R*aw*) from Jinfo Mountian in Chongqing of China (Zhang, 2011). These differences in carbonate weathering are mainly attributed to the different type of carbonate rock tablet, climate, micro-environment of soil, etc. The R*aw* of limestone in N-fertilizers treatment is 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 of China where usually involves in fertilization activities.

At larger scales like watershed, the weathering rate is usually estimated by using the riverine hydro-chemical method, which is inconsistent with the results from carbonate-rock-tablet test. The estimation of Zeng, et al. (2014) views that the carbon sink intensity calculated by carbonate rock tablet test is only one sixth of that estimated by using the riverine hydro-chemical method due to its own limits in methodology (Zeng et al., 2014). The results from Semhi, et al. (2000) shows the weathering rates of carbonate rock by using riverine hydro-chemical method are about 77.5 g m^{-2} a^{-1} and 50.4 g m^{-2} a^{-1} in upstream and downstream of the Garonne river, France, respectively, which are about 25-35 and 2-3 times than that in control treatment (2.00 g m^{-2} a^{-1} for natural weathering rate) and 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}, is much higher than that we observed. Thus, we conclude that it is difficult to compare between the results from the carbonate-rock-tablet test and the riverine hydro-chemical method. The carbonate-rock-tablet test is suitable for the research on the condition controlled contrast or stimulated experiment, while the riverine hydro-chemical method is appropriate for the regional investigation and estimation. 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 (Semhi and Suchet, 2000; Perrin et al., 2008).

5. Conclusion

The impact of the addition of different fertilizer (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 with carbonate rock tablets at its bottom of each. The weathering amount and ratio 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^+, and the addition of $Ca_3(PO_4)_2$, Ca-Mg-P and K_2CO_3 induced carbonate precipitation due to common ion effect. While the $(NH_4)_3PO_4$ and $NaNO_3$ addition did not impact significantly on carbonate weathering, where the former can be attributed to low added amount of $(NH4)_3PO_4$, may be related to the inhibition of phosphate, and the latter seemed to be raising a new question. The little impact of nitrate on carbonate weathering may result in the overestimation of impact of N-fertilizer on CO_2 consumption by carbonate weathering at the regional/global scale if the effect 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 CO_2 consumption.

6. Acknowledgements

This study is supported jointly by the Basic Science Research Fund from the Institute of Hydrogeology and Environmental Geology (Grant No. SK201208), the Chinese National Natural Science Foundation (No. 41403107 and No. 41325010), and the China Geological Survey Projects (No. 12120113005900).

References:

Amiotte Suchet, P., Probst, J.L. and Ludwig, W., 2003. Worldwide distribution of continental rock lithology: Implications for the atmospheric/soil CO_2 uptake by continental weathering and alkalinity river transport to the oceans. Global Biogeochemical Cycles, 17(2): 1-13.

Andrews, J.A. and Schlesinger, W.H., 2001. Soil CO_2 dynamics, acidification, and chemical weathering in a temperate forest with experimental CO_2 enrichment. Global Biogeochem. Cycles, 15: 149-162.

Barnes, R.T. and Raymond, P.A., 2009. The contribution of agricultural and urban activities to inorganic carbon fluxes within temperate watersheds. Chemical Geology, 266(3-4): 318-327.

Bertrand, I., Delfosse, O. and Mary, B., 2007. Carbon and nitrogen mineralization in acidic, limed and calcareous agricultural soils: Apparent and actual effects. Soil Biology and Biochemistry, 39(1): 276-288.

Biasi, C. et al., 2008. Direct experimental evidence for the contribution of lime to CO_2 release from managed peat soil. Soil Biology and Biochemistry, 40(10): 2660-2669.

Calmels, D., Gaillardet, J. and François, L., 2014. Sensitivity of carbonate weathering to soil CO_2 production by biological activity along a temperate climate transect. Chemical Geology, 390(0): 74-86.

Chao, S., Changli, L., Junkun, W., Yun, Z. and Hongbing, H., 2011. Impact of the Addition of a Compound Fertilizer on the Dissolution of Carbonate Rock Tablets: a Column Experiment. Applied Geochemistry, 26(S): 170-173.

Chao, S., Changli, L., Yun, Z. and Hongbing, H., 2014. Impact of animal manure addition on agricultural lime weathering in acidic soil: pH dependence and CO_2 independence of agricultural lime weathering. Procedia Earth and Planetary Science(10): 405-409.

Chien, S.H., Prochnow, L.I., Tu, S. and Snyder, C.S., 2011. Agronomic and environmental aspects of phosphate fertilizers varying in source and solubility: an update review. Nutrient Cycling in Agroecosystems, 89(2): 229-255.

Chou, L., Garrels, R.M. and Wollast, R., 1989. Comparative study of the kinetics and mechanisms of dissolution of carbonate minerals. Chemical Geology, 78(3-4): 269-282.

Dreybrodt, W., 1988. Processes in karst systems: physics, chemistry, and geology. Springer-Verlag Berlin Heidelberg, 0-288 pp.

Dreybrodt, W., Lauckner, J., Zaihua, L., Svensson, U. and Buhmann, D., 1996. The kinetics of the reaction $CO_2 + H_2O \rightarrow H^+ + HCO_3^-$ as one of the rate limiting steps for the dissolution of calcite in the system H_2O-CO_2-$CaCO_3$. Geochimica et Cosmochimica Acta, 60(18): 3375-3381.

Egli, M. and Fitze, P., 2001. Quantitative aspects of carbonate leaching of soils with differing ages and climates. Catena, 46(1): 35-62.

Errin, A.S.P., Robst, A.P. and Robst, J.L.P., 2006. Impact of nitrogen fertilizers on natural weathering processes : Evident role on CO_2 consumption The oxygen isotopic composition of Precambrian cherts, Goldschmidt Conference, pp. 2332-2332.

Etchanchu, D. and Probst, J., 1988. Evolution of the chemical composition of the Garonne River water during the period 1971-1984. Hydrological sciences journal, 33(3): 243-256.

Gams, I., 1981. Comparative research of limestone solution by means of standard tablets, Proceedings of the 8th International Congress of Speleology Bowling Green, Kentucky, pp. 273-275.

Gams, I., 1985. International comparative measurements of surface solution by means of standard limestone tablets. Razpr IV Razeda Sazu, 26: 361-386.

Gandois, L., Perrin, A.S. and Probst, A., 2011. Impact of nitrogenous fertiliser-induced proton release on cultivated soils with contrasting carbonate contents: A column experiment. Geochimica et Cosmochimica Acta, 75: 1185-1198.

GBS, 2014. 2014 Guizhou Statistical Yearbook. Statistical Press of China, Beijing.

Hagedorn, B. and Cartwright, I., 2009. Climatic and lithologic controls on the temporal and spatial variability of CO_2 consumption via chemical weathering: An example from the Australian Victorian Alps. Chemical Geology, 260(3-4): 234-253.

Hamilton, S.K., Kurzman, A.L., Arango, C., Jin, L. and Robertson, G.P., 2007. Evidence for carbon sequestration by agricultural liming. Global Biogeochemical Cycles, 21(GB2021): 1-12.

Han, Z. and Jin, Z., 1996. Hydrogeology of Guizhou Province, China. Seismic Publication, Beijing.

Hunter, A.H., 1980. Laboratory and greenhouse techniques for nutrient survey to determine the soil amendments required for optimum plant growth. Mimeograph. Agro Service International (ASI), Florida, USA.

Jiang, Y., 2013. The contribution of human activities to dissolved inorganic carbon fluxes in a karst underground river system: Evidence from major elements and $\delta^{13}C_{DIC}$ in Nandong, Southwest China. Journal of Contaminant Hydrology, 152(0): 1-11.

Jiang, Y., Wu, Y., Groves, C., Yuan, D. and Kambesis, P., 2009. Natural and anthropogenic factors affecting the groundwater quality in the Nandong karst underground river system in Yunan, China. Journal of Contaminant Hydrology, 109(1-4): 49-61.

Jiang, Z. and Yuan, D., 1999. CO_2 source-sink in karst processes in karst areas of China. Episodes, 22(1): 33-35.

Jiang, Z., Lian, Y. and Qin, X., 2013. Carbon cycle in the epikarst systems and its ecological effects in South China. Environmental earth sciences, 68(1): 151-158.

Kiefer, R.H., 1994. Temporal cycles of karst denudation in northwest Georgia, USA. Earth Surface Processes and Landforms, 19(3): 213-232.

Kitano, Y., Okumura, M. and Idogaki, M., 1978. Uptake of phosphate ions by calcium carbonate. Geochemical Journal(12): 29-37.

Kump, L.R., Brantley, S.L. and Arthur, M.A., 2000. Chemical weathering, atmospheric CO_2, and climate. Annual Review of Earth and Planetary Sciences, 28(1): 611-667.

Lang, Y., Liu, C., Zhao, Z., Li, S. and Han, G., 2006. Geochemistry of surface and ground water in Guiyang, China: Water/rock interaction and pollution in a karst hydrological system. Applied Geochemistry, 21(6): 887-903.

Lerman, A. and Wu, L., 2006. CO_2 and sulfuric acid controls of weathering and river water composition. Journal of Geochemical Exploration, 88(1-3): 427-430.

Lerman, A., Wu, L. and Mackenzie, F.T., 2007. CO_2 and H_2SO_4 consumption in weathering and material transport to the ocean, and their role in the global carbon balance. Marine Chemistry, 106(1-2): 326-350.

Li, S., Calmels, D., Han, G., Gaillardet, J. and Liu, C., 2008. Sulfuric acid as an agent of carbonate weathering constrained by $\delta^{13}C_{DIC}$: Examples from Southwest China. Earth and Planetary Science Letters, 270(3-4): 189-199.

Li, S., Xu, Z., Wang, H., Wang, J. and Zhang, Q., 2009. Geochemistry of the upper Han River basin, China: 3: Anthropogenic inputs and chemical weathering to the dissolved load. Chemical Geology, 264(1-4): 89-95.

Lian, B., Chen, Y., Zhu, L. and Yang, R., 2008. Effect of Microbial Weathering on Carbonate Rocks. Earth Science Frontiers, 15(6): 90-99.

Liu, C., Li, S., Lang, Y. and Xiao, H., 2006. Using $\delta^{15}N$- and $\delta^{18}O$-Values To Identify Nitrate Sources in Karst Ground Water, Guiyang, Southwest China. Environmental Science & Technology, 40(22): 6928-6933.

Liu, Z. et al., 2010. Wet-dry seasonal variations of hydrochemistry and carbonate precipitation rates in a travertine-depositing canal at Baishuitai, Yunnan, SW China: Implications for the formation of biannual laminae in travertine and for climatic reconstruction. Chemical Geology, 273(3-4): 258-266.

Liu, Z., 2011. " Method of maximum potential dissolution" to calculate the intensity of karst process and the relevant carbon sink: With discussions on methods of solute load and carbonate-rock-tablet test. Carsologica Sinica, 30(4): 79-82.

Liu, Z. and Dreybrod, W., 1997. Dissolution kinetics of calcium carbonate minerals in H_2O-CO_2 solutions in turbulent flow: The role of the diffusion boundary layer and the slow reaction $H_2O + CO_2 \leftrightarrow H^+ + HCO_3^-$. Geochimica et Cosmochimica Acta, 61(14): 2879-2889.

Liu, Z., Dreybrodt, W. and Liu, H., 2011. Atmospheric CO_2 sink: silicate weathering or carbonate weathering? Applied Geochemistry, 26(S): 292-294.

NBS, 2014. 2014 Statistical Yearbook. Statistical Press of China, Beijing.

Oh, N. and Raymond, P.A., 2006. Contribution of agricultural liming to riverine bicarbonate export and CO_2 sequestration in the Ohio River basin. Global Biogeochemical Cycles, 20: 1-17.

Perrin, A., Probst, A. and Probst, J., 2008. Impact of nitrogenous fertilizers on carbonate dissolution in small agricultural catchments: Implications for weathering CO_2 uptake at regional and global scales. Geochimica et Cosmochimica Acta, 72(13): 3105-3123.

Pierson-wickmann, A., Aquilina, L., Martin, C., Ruiz, L. and Molénat, J., 2009. High chemical weathering rates in first-order granitic catchments induced by agricultural stress. Chemical Geology, 265: 369-380.

Plan, L., 2005. Factors controlling carbonate dissolution rates quantified in a field test in the Austrian alps. Geomorphology, 68(3-4): 201-212.

Plummer, L.N., Wigley, T. and Parkhurst, D.L., 1978. The kinetics of calcite dissolution in CO_2-water systems at 5 to 60 ℃ and 0.0 to 1 atm CO_2. American Journal of Science, 278: 179-216.

Pokrovsky, O.S., Golubev, S.V., Schott, J. and Castillo, A., 2009. Calcite, dolomite and magnesite dissolution kinetics in aqueous solutions at acid to circumneutral pH, 25 to 150 ℃ and 1 to 55 atm pCO_2: New constraints on CO_2 sequestration in sedimentary basins. Chemical Geology, 265(1-2): 20-32.

Probst, J., 1986. Dissolved and suspended matter transported by the Girou River (France): mechanical and chemical erosion rates in a calcareous molasse basin. Hydrological Sciences Journal, 31(1): 61-79.

Semhi, K. and Suchet, A., 2000. Impact of nitrogen fertilizers on the natural weathering-erosion processes and fluvial transport in the Garonne basin. Applied Geochemistry, 15(6): 865-878.

Shin, W., Ryu, J., Mayer, B., Lee, K. and Lee, S., 2014. Natural and anthropogenic sources and processes affecting water chemistry in two South Korean streams. Science of The Total Environment, 485: 270-280.

Singh, J., Kunhikrishnan, A., Bolan, N.S. and Saggar, S., 2013. Impact of urease inhibitor on ammonia and nitrous oxide emissions from temperate pasture soil cores receiving urea fertilizer and cattle urine. Science of The Total Environment, 465(0): 56-63.

Soares, J.R., Cantarella, H. and Menegale, M.L.D.C., 2012. Ammonia volatilization losses from surface-applied urea with urease and nitrification inhibitors. Soil Biology and Biochemistry, 52(0): 82-89.

Trudgill, S.T., 1975. Measurement of erosional weight loss of rock tablets. British Geomorphological Research Group Technical Bulletin, 17: 13-20.

Wang, L., Ruiz-Agudo, E., Putnis, C.V., Menneken, M. and Putnis, A., 2012. Kinetics of Calcium Phosphate Nucleation and Growth on Calcite: Implications for Predicting the Fate of Dissolved

Phosphate Species in Alkaline Soils. Environmental Science & Technology, 46(2): 834-842.
West, T.O. and McBride, A.C., 2005. The contribution of agricultural lime to carbon dioxide emissions in the United States: dissolution, transport, and net emissions. Agriculture, Ecosystems and Environment, 108(2): 145-154.
Yue, F.J., Li, S.L., Liu, C.Q., Lang, Y.C. and Ding, H., 2015. Sources and transport of nitrate constrained by the isotopic technique in a karst catchment: an example from Southwest China. Hydrological Processes, 29(8): 1883-1893.
Zeng, C., Zhao, M., Yang, R. and Liu, Z., 2014. Comparison of karst processes-related carbon sink intensity calculated by carbonate rock tablet test and solute load method: a case study in the Chenqi karst spring system. Hydrogology & Engineering Geology, 41(1): 106-111.
Zhang, C., 2011. Carbonate rock dissolution rates in different landuses and their carbon sink effect. Chinese Science Bulletin, 56(35): 3759-3765.

Table 1 Chemical composition of soil

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

R*w* - the ratio of carbonate weathering; Ra*w* - the rate of carbonate weathering; R*w* =1000 (W*i*-W*f*)/Wi; Ra*w* = (W*i*-W*f*)/(S*T), where W*i* is the initial weight of the carbonate rock tablets, and W*f* is their final weight. S is the surface area of carbonate weathering tablets, and T is the experiment period. Values are reported as means±standard deviations, n=3. Values in each column followed by different letters are significantly ($p < 0.05$) different based on one-way ANOVA.

Table 3: The main reaction and effects in these fertilized 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) Common ion effect: The $Ca_{(1-x)}Mg_xCO_3$ produces when the concentrations of Ca^{2+} and Mg^{2+} increases $(1-x)\ Ca^{2+} + xMg^{2+} + 2HCO_3^- \rightarrow Ca_{(1-x)}Mg_xCO_3 + CO_2 + H_2O$ (2) Inhibition of phosphate to calcite precipitation: calcium phosphate precipitation produces on the surface of calcite after the addition of PO_4^{3-} in soil, resulting in inhibiting the precipitation of calcite
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) Inhibition of phosphate to calcite dissolution: calcium orthophosphate (Ca-P) precipitation produces on the surface of calcite after the addition of PO_4^{3-} in soil, resulting in inhibiting the dissolution of calcite
9. Ca-Mg-P	(1) Common ion effect: The $Ca_{(1-x)}Mg_xCO_3$ produces when the concentrations of Ca^{2+} and Mg^{2+} increases $(1-x)\ Ca^{2+} + xMg^{2+} + 2HCO_3^- \rightarrow Ca_{(1-x)}Mg_xCO_3 + CO_2 + H_2O$ (2) Inhibition of phosphate to calcite precipitation: calcium phosphate precipitation produces on the surface of calcite after the addition of P in soil, resulting in inhibiting the precipitation of calcite
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	Common ion effect: The $Ca_{(1-x)}Mg_xCO_3$ produces when the concentration of HCO_3^- increases (i) $(1-x)\ Ca^{2+} + xMg^{2+} + 2HCO_3^- \rightarrow Ca_{(1-x)}Mg_xCO_3 + CO_2 + H_2O$ (ii) $K_2CO_3 + H_2O \rightarrow 2K^+ + HCO_3^- + OH^-$

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 /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	/	44	0.00	0.00	0.00
Urea	60	32	0.53	1.06	1.06
K_2CO_3	138	10	0.07	0.00	0.00

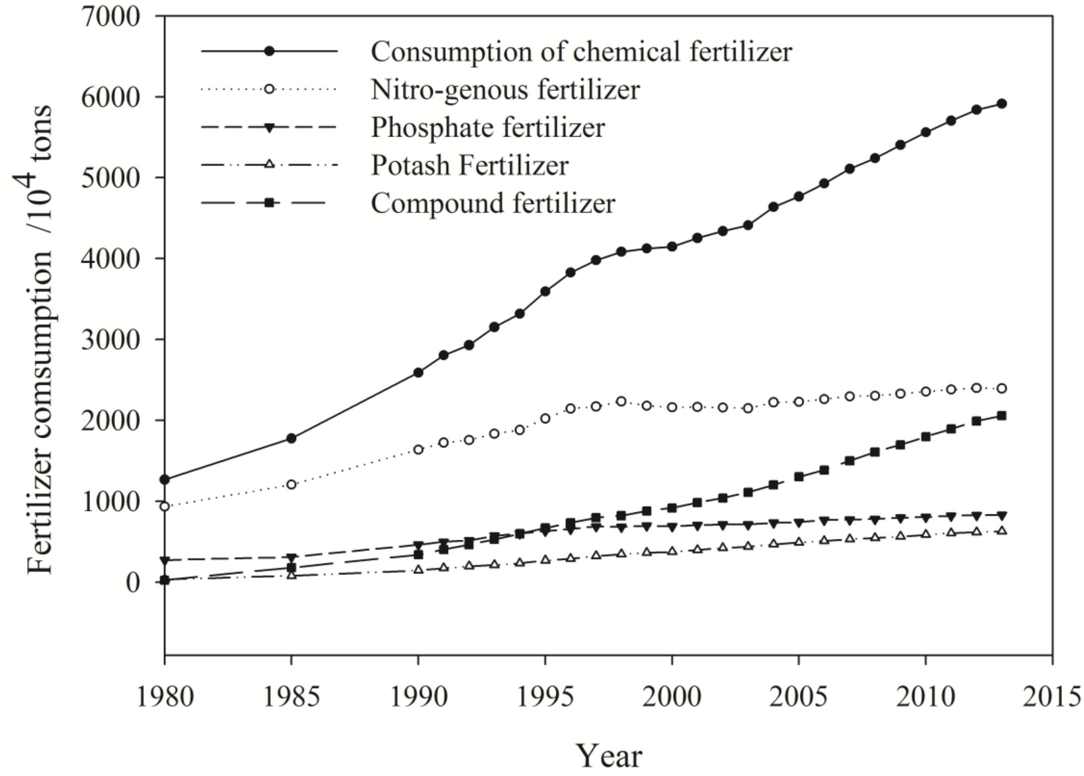

Fig. 1 The change of chemical fertilizer consumption in China during 1980-2013

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/)

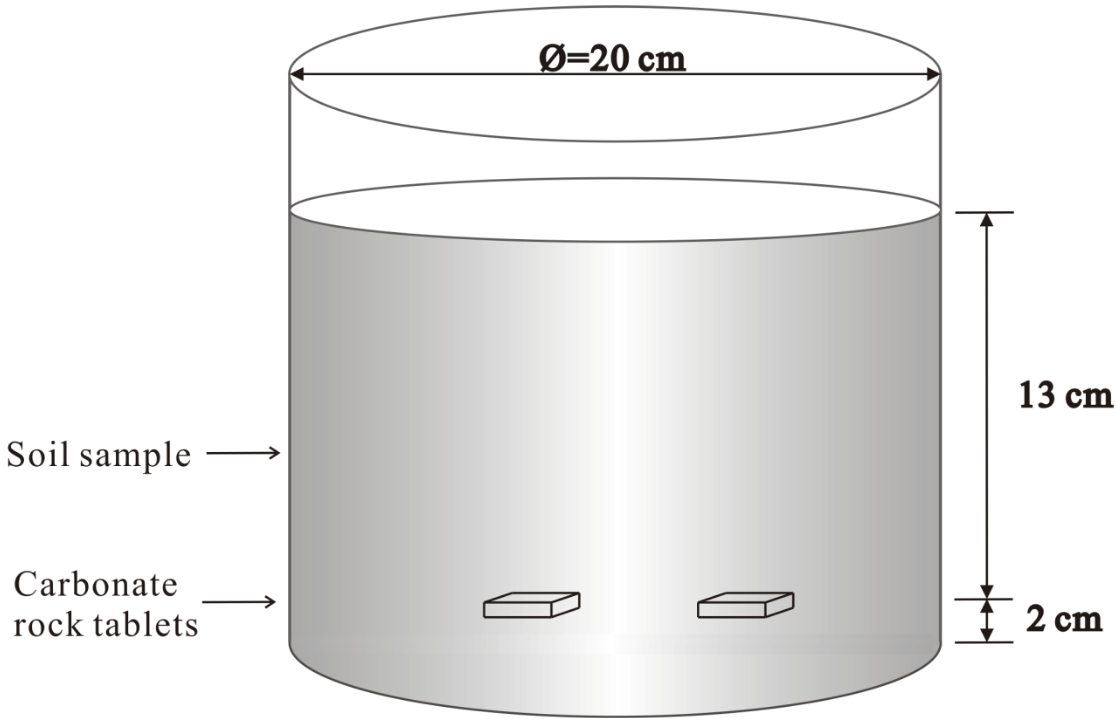

Fig. 2 Sketch map of the soil column

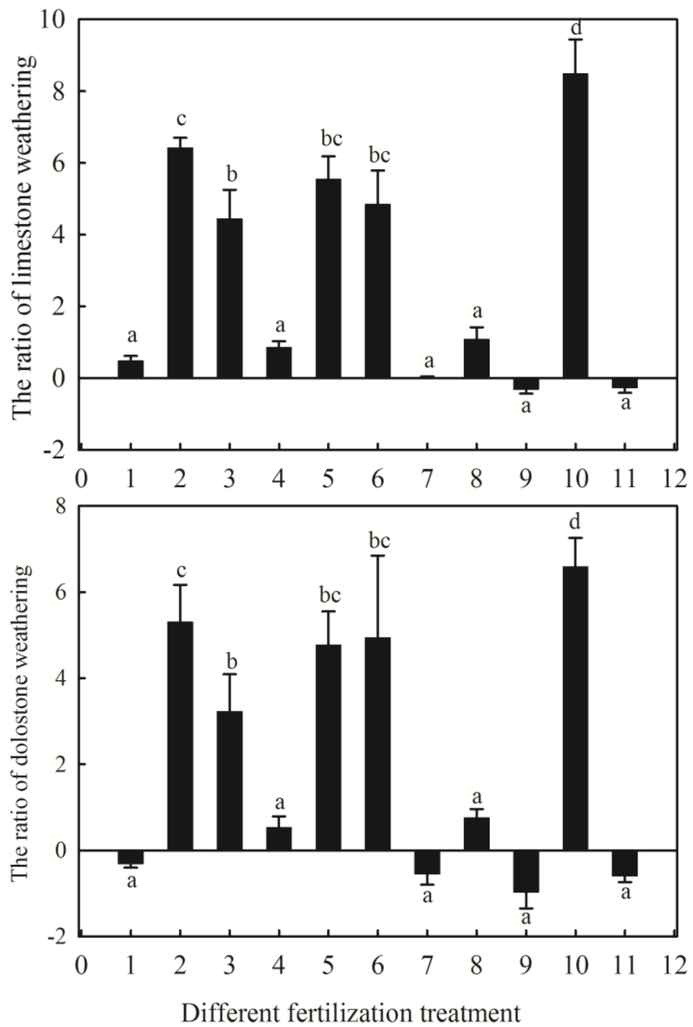

Fig. 3 The R*w* (‰) of limestone and dolostone under different fertilization treatment

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 W*i* is the initial weight of the carbonate rock tablets, and W*f* is their final weight. Different letters on each column are significantly ($p < 0.05$) different based on one-way ANOVA.

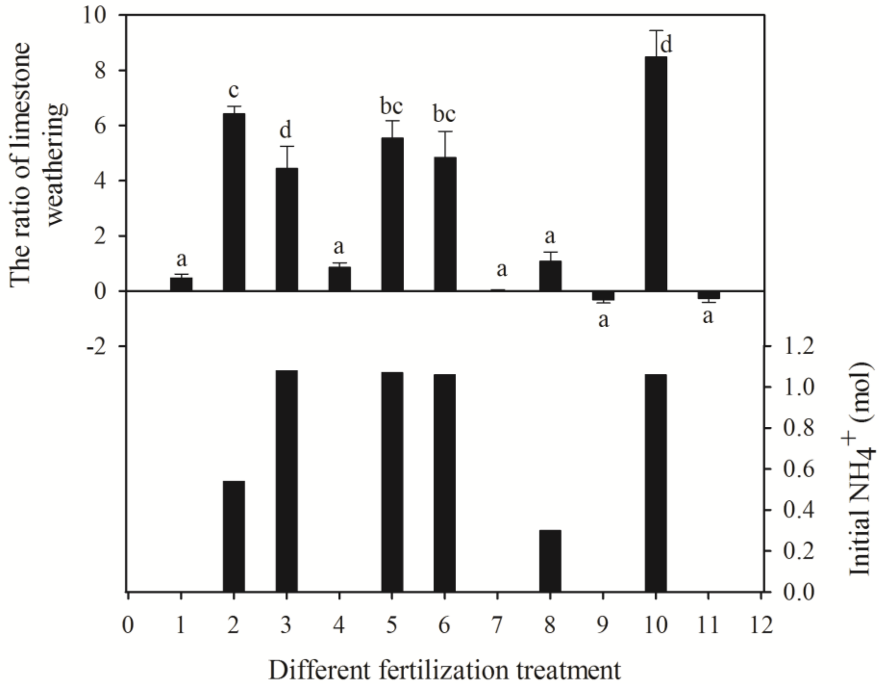

Fig. 4 The R*w* (‰) of limestone and the molar amount of produced NH_4^+ under different fertilization treatment

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 limsestone tablets, and W*f* is their final weight. Different letters on each column are significantly (p <0.05) different based on one-way ANOVA.