Impact of different fertilizers on the 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, are strongly influenced by anthropogenic perturbations such as agricultural fertilization since the addition of fertilizers tends to change the chemical characteristics of soil such as the pH value. Different fertilizers may exert a different impact on carbonate weathering, but these discrepancies still are not well-known so far. In this study, a field column experiment was employed to explore the responses of carbonate weathering to the addition of different fertilizers. The eleven different treatments with three replicates including control, NH₄NO₃, NH₄HCO₃, NaNO₃, NH₄Cl, (NH₄)₂CO₃, Ca₃(PO₄)₂, (NH₄)₃PO₄, fused calcium-magnesium phosphate fertilizer (Ca-Mg-P), urea and K₂CO₃ were established in this column experiment, where limestone and dolostone tablets were buried at the bottom of each to determine the weathering amount and ratio of carbonate in soil. 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 the soil-filled columns. The results showed that the addition of urea, NH₄NO₃, NH₄HCO₃, NH₄Cl and (NH₄)₂CO₃ distinctly increased carbonate weathering, which was attributed to the nitrification of NH₄⁺. The addition of Ca₃(PO₄)₂, Ca-Mg-P and K₂CO₃ induced carbonate precipitation due to the common ion effect. Whereas the addition of (NH₄)₃PO₄ and NaNO₃ addition did not significantly impact significantly on carbonate weathering. The results of
NaNO₃ treatment seem to be raising a new question: the negligible impact of nitrate on carbonate weathering may result in the overestimation of the impact of N-fertilizer on CO₂ consumption by carbonate weathering at the regional/global scale, if the effects of NO₃ and NH₄ are not distinguished. Moreover, in order to avoid misunderstanding more or less, the statement that nitrogenous fertilizer can aid carbonate weathering should be replaced by ammonium fertilizer.

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

### 1. Introduction

Carbonate weathering plays a significant role in consumption of the elevated atmospheric CO₂ (Kump et al., 2000; Liu et al., 2010; Liu et al., 2011). The riverine hydro-chemical composition, such as the ratio of HCO₃⁻ to Ca²⁺ + Mg²⁺, is usually employed as an indicator to estimate the CO₂ 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 from: (i) from the nitrification of N-fertilizer a disturbance to CO₂ consumption estimation is introduced because the fluvial alkalinity, Ca²⁺ and Mg²⁺ may also be
produced due to the reaction between carbonate and the protons which can originate from the nitrification processes 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). (i) from the sulfuric acid (Lerman and Wu, 2006; Lerman et al., 2007; Li et al., 2008; Li et al., 2009); (ii) from organic acid secreted by microorganisms (Lian et al., 2008); (iii) from the atmospheric CO$_2$ is not the unique weathering agent, differentiating the agent of carbonate weathering is more and more significant to enable important for the accurate budgeting of the net CO$_2$ consumption by carbonate weathering, especially in agricultural areas where mineral fertilizers are used. Given 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 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 chemical mineral fertilizers is a significant disturbance factor of in carbonate weathering and the carbon cycle. Many several studies have showed that nitrogen fertilizer additions aided in the dissolution of lime 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 the estimation from estimates by Probst (1988) and Semhi et al. (2000), the contribution of N-fertilizers to carbonate dissolution represents was 30% and 12-26%, respectively, in two small agricultural carbonate basins in south-western France, the Girou and the Gers, respectively (subtributary and tributaries of the Garonne river, respectively). For In larger basin level, such as the Garonne river, this contribution was estimated at 6% by Semhi et al. (2000). At national and global scales, Perrin et al. (2008) estimated that the deficit contribution of CO₂ uptake due to N-fertilizer addition (usually in form of NH₄NO₃) represents up to 5.7-13.4% and only 1.6-3.8% of the total CO₂ flux.
naturally consumed by the carbonate dissolution, for in France and across the on a global scale, respectively.

These estimated results—estimates described above were—are usually largely based on calculations that assuming that a single type of fertilizer (e.g. (NH₄)₂SO₄, NH₄NO₃, or NH₄Cl) was used throughout the whole basin that was considered. However were usually based on a hypothesis of individual fertilizer (e.g. (NH₄)₂SO₄, NH₄NO₃, or NH₄Cl) input into an agricultural basin. Nevertheless, in actual agricultural practices, at an agricultural basin, 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 In the case of nitrogenous fertilizer, 100% NO₃⁻ produced after the addition (NH₄)₂SO₄ and NH₄Cl is derived from the nitrification of NH₄⁺, whilst comparatively, it is only 50% after the addition of NH₄NO₃. The differences of NO₃⁻ sources may cause the produce an evaluated deviation of the impact of N-fertilizer addition on CO₂ consumption by carbonate weathering. Because, since the addition of different N-fertilizers (e.g. (NH₄)₂SO₄, NH₄NO₃, NH₄Cl, NaNO₃ or urea) may result in different contributions to carbonate weathering and relative products such as HCO₃⁻, Ca²⁺ and Mg²⁺. For phosphate fertilizer, the coprecipitation of phosphate ions with calcium carbonate may inhibit carbonate weathering (Kitano et al., 1978)(Kitano et al., 1978)(Kitano et al., 1978). We suppose assume that the response of carbonate weathering to the addition of different fertilizers, such as N-fertilizer (NH₄ and NO₃), P-fertilizer and Ca/Mg fertilizer, may display differences, which is are so far poorly known, so far—but likely significant. Here we sought to fully well—understand the agricultural force-impact on natural carbonate weathering, and to accurately evaluate
the CO₂ consumption via carbonate weathering in agricultural areas.

Moreover, the carbonate-rock-tablet test is used to determine the weathering rate of carbonate rock/mineral from the laboratory to the field (Chao et al., 2011; Chao et al., 2014; Dreybrodt et al., 1996; Gams, 1981; Gams, 1985; Jiang and Yuan, 1999; Liu and Dreybrodt, 1997; Plan, 2005; Trudgill, 1975). The carbonate-rock-tablet test is used to determine the weathering rate of carbonate rock/mineral from the laboratory to the field (Chao et al., 2011; Chao et al., 2014; Dreybrodt et al., 1996; Gams, 1981; Gams, 1985; Jiang and Yuan, 1999; Liu and Dreybrodt, 1997; Plan, 2005; 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 Dreybrodt, 1997) and determine the rate of carbonate mineral weathering in the soil column (Chao et al., 2011; Chao et al., 2014). However, in the field, it is also used to observe the rate of carbonate weathering and estimated CO₂ consumption by carbonate weathering (Chao et al., 2014; Jiang and Yuan, 1999; Jiang et al., 2013; Plan, 2005; Chao et al., 2014; Jiang and Yuan, 1999; Jiang et al., 2013; Plan, 2005).

Although Liu (2011) argued that the carbonate-rock-tablet test may lead to the deviations of in estimated CO₂ consumption by carbonate weathering at the regional/global scale, in the cases of where there are insufficient representative data (Liu, 2011). Our results show that yet, it is nonetheless the preferred option method for the condition-controlled contrast/comparative or simulated experiment (Chao et al., 2011; Chao et al., 2014; Chao et al., 2017) (Chao et al., 2014; Chao et al., 2011; Chao et al., 2014). Where the results...
from the carbonate-rock-tablet test is consistent to the major element geochemical
data of leachates from soil column (Chao et al., 2011).

Therefore, in order to observe their difference between the impacts of
different fertilizer addition on carbonate weathering in soil, a field column
experiment that involved embedding carbonate-rock-tablets with eleven different
treatments was carried out in a typical karst area of southwest China, in order to
observe the impacts 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 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 approximately 8,000 km²), 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 elevations and low latitude, with a subtropical warm-moist climate, and an
average annual temperature of 15.3 °C and annual precipitation of 1200 mm
(Lang et al., 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). Liu,
et al., 2006). The consumption of chemical fertilizer increased from 0.8-150 kg/ha Mt in 1980 to 1.0190 kg/ha Mt 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 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\text{soil}:V\text{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 S, and available Fe, were determined according to the Agro Services International (ASI) method (Hunter, 1980). OM was determined using an extracting solution containing 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 an extraction solution of 1 mol l$^{-1}$ KCl solution, whereas available K, P and Fe were determined using an extracting solution containing 0.25 mol l$^{-1}$ NaHCO$_3$, 0.01 mol l$^{-1}$ EDTA, 0.01 mol l$^{-1}$ NH$_4$F, and 0.005% Superfloc 127. Finally, and available S was determined using an extracting solution of 0.1 mol l$^{-1}$ Ca(H$_2$PO$_4$)$_2$ 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 fertilizers on carbonate weathering may be different, columns (Ø = 20 cm, H= 15 cm) were constructed from 20-cm diameter polyvinylchlordie (PVC) pipe (Fig. 2). A hole (Ø = 2 cm) was established at the bottom of each column to discharge soil water from the soil column. A polyethylene net mesh (Ø 0.5 mm) was placed in the bottom of the columns to prevent soil loss of the filter material. A 2 cm thick filter sand layer, with 2 cm thickness 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). According to the common kinds of chemical fertilizers and the main objective of this study, eleven fertilization treatments, each with three replicates, were set up in the field column experiment. There were set up: (1) control without fertilizer (CK); (2) 43g NH₄NO₃ fertilizer (CF); (3) 85g NH₄HCO₃ fertilizer (NHC); (4) 91g NaNO₃ fertilizer (NN); (5) 57g NH₄Cl fertilizer (NCL); (6) 51g (NH₄)₂CO₃ fertilizer (NC); (7) 52g Ca₃(PO₄)₂ fertilizer (CP); (8) 15g (NH₄)₃PO₄ fertilizer (NP); (9) 44g fused calcium-magnesium phosphate fertilizer (Ca-Mg-P); (10) 32g Urea fertilizer (U); and (11) 10g K₂CO₃ fertilizer (PP). To shorten the experiment time and enhance the effect of fertilization, the added amount of fertilizers in these treatments motioned above was increased to 30 times than its local practical amount (N fertilizer: 160 kg N·ha⁻¹·P fertilizer: 50 kg·ha⁻¹·K fertilizer: 50 kg·ha⁻¹). The aliquot of 6 kg of soil was weighed (bulk density = 1.3 g/cm³), mixed perfectly thoroughly with one of the above fertilizers, respectively, and filled into its own column. This process was repeated for all three
replicates of the 11 fertilizer treatments. These soil columns were placed at the field experiment site in Huaxi District, 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 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% power-fine crystalline dolomite, 3-5% microcrystalline calcite, 1% pyrite, and little trace quantities of organic matter. All of the tablets were baked at 80 °C for 4 hours, then weighed in a 1/10000 electronic balance in the laboratory, tied to a 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 taken out carefully, rinsed, baked and weighed after a whole year.

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

\[
A_{cw} = (W_i - W_f) \quad (1)
\]

\[
R_{cw} = (W_i - W_f) / W_i \quad (2)
\]

\[
R_{acw} = (W_i - W_f) / (S \times T) \quad (3)
\]

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 rock tablets, 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) or standard errors (SE) for the three replications, as Statistical analysis was performed using IBM SPSS 20.0 (Statistical Graphics Corp., Princeton, USA).

### 3. Results

#### 3.1 Weathering rate of carbonate under different fertilized treatments

Weathering of under different treatments The amount (AR\textsubscript{cw}) and the ratio (Ra\textsubscript{cw}) of limestone and dolostone carbonate weathering were listed in Table 2, and the AR\textsubscript{cw} and Ra\textsubscript{cw} of carbonate weathering limestone and dolomite weathering under urea, NH\textsubscript{4}NO\textsubscript{3}, NH\textsubscript{4}Cl, (NH\textsubscript{4})\textsubscript{2}CO\textsubscript{3}, NH\textsubscript{4}HCO\textsubscript{3}, NH\textsubscript{4}Cl-and NH\textsubscript{4}HCO\textsubscript{3}-(NH\textsubscript{4})\textsubscript{2}CO\textsubscript{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) positive, and much bigger significantly greater than that under the control treatment 0.48 ± 0.14 ‰ (see Fig. 3). In addition, the observed Rw of as observed in dolomite 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 the...
-0.31 ± 0.09 ‰ in the control treatment. This suggests that the addition of these five fertilizers can aid and increased the rate of the chemical weathering of carbonate weathering.

The remaining treatments had made no significant differences in the Rw and Rcw of limestone and dolomite in comparison with the control treatment (Fig. 3). In the (NH₄)₃PO₄ treatment, the Acw/Rw and Acw/Rcw were only 1.08 ± 0.34 ‰, 0.0028 ± 0.75 ‰ for limestone and dolomite, respectively. These values are less than those under the other four NH₄-fertilizers, as mentioned above. The Acw, Rw/Rw and Rcw in the NaNO₃ treatments failed to show a remarkable notable differences with the control treatment, implying exhibiting little effect of the NaNO₃ fertilizer addition on carbonate weathering (Fig. 3).

However, except for the Rw of limestone approaching zero in the Ca₃(PO₄)₂ treatment, all the values of the Acw, Rw/Rw and Rcw of two different carbonate in Ca-Mg-P and K₂CO₃ and Ca₃(PO₄)₂ treatments showed a negative values. This indicating indicates that the addition of Ca-Mg-P, K₂CO₃ and Ca₃(PO₄)₂ fertilizers can lead to the precipitation at the surface of the carbonate mineral, which can be explained by common ion effect.

3.2 The Comparison of limestone of dolomite

In Fig. 4, we plotted the Rw of limestone vs. dolomite in order to compare the result of limestone with...
dolomite tablets 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), suggesting that the weathering of ANOVA was used to determine the differences of weathering rate between limestone and dolostone.

4. Discussion

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

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

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

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

\[
\begin{align*}
\text{MeCO}_3 + H^+ &\leftrightarrow \text{Me}^{2+} + \text{HCO}_3^- \quad (4) \\
\text{MeCO}_3 + \text{H}_2\text{CO}_3 &\leftrightarrow \text{Me}^{2+} + 2\text{HCO}_3^- \quad (5) \\
\text{MeCO}_3 &\leftrightarrow \text{Me}^{2+} + \text{CO}_3^{2-} \quad (6)
\end{align*}
\]

where Me = Ca, Mg. As Eq. (5) describes, atmospheric/soil CO₂ is usually regarded considered to be as the natural weathering agent of carbonate. In watersheds
with calcite- and dolomite-containing bedrock, $\text{H}_2\text{CO}_3$ formed in the soil zone usually reacts with carbonate minerals, resulting in dissolved $\text{Ca}, \text{Mg}$, and $\text{HCO}_3^-$ 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), we consider that the effect of rainfall is equal in each soil column, and hence is disregarded as a controlling factor in this study. The Eq. (4) suggests that the proton from other origins, such as the nitrification processes of $\text{NH}_4^+$, as mentioned in the Introduction section, can play the role of weathering agent in agricultural areas. In this study, the urea, $\text{NH}_4\text{NO}_3$, $\text{NH}_4\text{HCO}_3$, $\text{NH}_4\text{Cl}$, and $(\text{NH}_4)_2\text{CO}_3$ amendments increased (10 to 17-fold) the natural weathering rate of 2.00 g m$^{-2}$ a$^{-1}$ from limestone tablets in the control treatment (Table 2). Thus, these increases are strongly related to the effect of the proton released from the nitrification of $\text{NH}_4^+$. On the contrary, the carbonate precipitation will occur due to the backward reaction of the Eq. (5) in the following cases: (1) the degassing of dissolved $\text{CO}_2$; (2) soil evapotranspiration; or (3) the common ion effect: the increase of $\text{Ca}^{2+}$, $\text{Mg}^{2+}$ or $\text{CO}_3^{2-}$ 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 are listed in...
Table 3.

(1) The nitrification in NH$_4$-fertilizer: NH$_4$NO$_3$, NH$_4$HCO$_3$, NH$_4$Cl, (NH$_4$)$_2$CO$_3$ 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):

\[
\text{CO(NH$_2$)$_2$ + 3H$_2$O \rightarrow 2NH$_4^+$ + 2OH}^- + CO$_2$ \tag{7}
\]

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$_2$O) (Singh et al., 2013), yet the remaining ammonium (NH$_4^+$) is mainly oxidized during nitrification in soil by autotrophic bacteria (e.g., such as 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):

\[
\text{NH}_4^+ + 2O_2 \rightarrow \text{NO}_3^- + H_2O + 2H^+ \tag{8}
\]

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))

\[
\text{Soil} - \text{Ca} + 2H^+ \rightarrow \text{Soil} - 2H^+ + \text{Ca}^{2+} \tag{9}
\]

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

\[
\text{Ca}_{1-x}Mg_xCO$_3$ + H$^+$ \rightarrow (1-x) \text{Ca}^{2+} + xMg^{2+} + \text{HCO}_3^- \tag{10}
\]

Consequently, after combining Eq. (8) and Eq. (10), are combined, carbonate weathering by protons produced by nitrification can supposedly be expressed as to become (Eq. (11)) (See details in Perrin et al., 2008 and Gandois et al., 2011).
\[
2\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3 + \text{NH}_4^+ + 2\text{O}_2 \rightarrow 2(1-x) \text{Ca}^{2+} + 2x\text{Mg}^{2+} + \text{NO}_3^- + \text{H}_2\text{O} + 2\text{HCO}_3^-
\] (11)

As discussed above, provided that the loss as ammonia (\(\text{NH}_3\)) and nitrous oxide (\(\text{N}_2\text{O}\)) after hydrolyzation is unconsidered in this study, the final equation of carbonate weathering in \(\text{NH}_4\text{NO}_3\), \(\text{NH}_4\text{HCO}_3\), \(\text{NH}_4\text{Cl}\), \((\text{NH}_4)_2\text{CO}_3\) and urea treatments will be as followed, respectively:

\[
2\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3 + \text{NH}_4\text{NO}_3 + 2\text{O}_2 \rightarrow 2(1-x) \text{Ca}^{2+} + 2x\text{Mg}^{2+} + 2\text{NO}_3^- + \text{H}_2\text{O} + 2\text{HCO}_3^-
\] (12)

\[
2\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3 + \text{NH}_4\text{HCO}_3 + 2\text{O}_2 \rightarrow 2(1-x) \text{Ca}^{2+} + 2x\text{Mg}^{2+} + \text{NO}_3^- + \text{H}_2\text{O} + 3\text{HCO}_3^-
\] (13)

\[
2\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3 + \text{NH}_4\text{Cl} + 2\text{O}_2 \rightarrow 2(1-x) \text{Ca}^{2+} + 2x\text{Mg}^{2+} + \text{NO}_3^- + \text{Cl}^- + \text{H}_2\text{O} + 2\text{HCO}_3^-
\] (14)

\[
3\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3 + (\text{NH}_4)_2\text{CO}_3 + 4\text{O}_2 \rightarrow 3(1-x) \text{Ca}^{2+} + 3x\text{Mg}^{2+} + 2\text{NO}_3^- + 2\text{H}_2\text{O} + 4\text{HCO}_3^-
\] (15)

\[
3\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3 + \text{CO(}\text{NH}_2\text{)}_2 + 4\text{O}_2 \rightarrow 3(1-x) \text{Ca}^{2+} + 3x\text{Mg}^{2+} + 2\text{NO}_3^- + 4\text{HCO}_3^-
\] (16)

(2) No effect of \(\text{NO}_3^-\)-fertilizer treatment: \(\text{NaNO}_3\) treatment

In the \(\text{NaNO}_3\) treatment, the reaction occurs according to as Eq. (17), indicating that the addition of \(\text{NO}_3^-\)-fertilizer does not significantly influence carbonate weathering.

\[
\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3 + \text{NaNO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow (1-x) \text{Ca}^{2+} + x\text{Mg}^{2+} + \text{Na}^+ + \text{NO}_3^- + 2\text{HCO}_3^-
\] (17)

(3) The common ion effect: \(\text{K}_2\text{CO}_3\) treatment

In the \(\text{K}_2\text{CO}_3\) treatment, \(\text{CO}_2^2^-\) and \(\text{HCO}_3^-\) will be produced after the addition of \(\text{K}_2\text{CO}_3\) according to Eq. (18) after adding \(\text{K}_2\text{CO}_3\), hence resulting in carbonate weathering.
Precipitation as described in Eq. (19), due to the common ion effect.

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

\[
(1-x)Ca^{2+} + xMg^{2+} + 2HCO_3^- \rightarrow Ca_{(1-x)}Mg_x CO_3 + CO_2 + H_2O \quad (19)
\]

(4) Complex effects: Nitrification versus inhibition effect of PO_4 in (NH_4)_2PO_4 treatments

For the (NH_4)_2PO_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)_2PO_4 fertilizer, will occur the nitrification. Whilst, the PO_4^{3-} anion will exert an inhibition to calcite dissolution, 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 → Ca-P), resulting in inhibition of the calcite 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 the Ca_3(PO_4)_2 and Ca-Mg-P treatments, on the one hand, the Ca_{(1-x)}Mg_x CO_3 is produced when the concentrations of Ca^{2+} (or/and Mg^{2+}) increases according to following Eq. (19). On the other hand, the inhibition effect of phosphate will cause that calcium phosphate precipitation to be produced on the surface of carbonate minerals after the addition of P in soil (reaction: Ca + PO_4 → Ca-P), correspondingly resulting in inhibition on 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 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$_4$NO$_3$, NH$_4$HCO$_3$, NH$_4$Cl, (NH$_4$)$_2$CO$_3$ and (NH$_4$)$_3$PO$_4$ 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. 45. A distinct relationship between them is observed, in that the $R_w$ values in NH$_4$NO$_3$, NH$_4$HCO$_3$, NH$_4$Cl, (NH$_4$)$_2$CO$_3$ and urea treatments are higher than in the control treatment, where the initial amount of NH$_4^+$ displays similar results (Fig. 45). This suggests that carbonate weathering in NH$_4$NO$_3$, NH$_4$HCO$_3$, NH$_4$Cl, (NH$_4$)$_2$CO$_3$ 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; 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 $R_w$ values in NH$_4$HCO$_3$ and (NH$_4$)$_2$CO$_3$ treatments are lower than even half of those in urea treatment in despite of adding the same amount of fertilizer-derived NH$_4$ (about approximately 1.07 mole). This is probably because the two fertilizers, NH$_4$HCO$_3$ and (NH$_4$)$_2$CO$_3$, are easier to decompose and produce the NH$_3$ and CO$_2$ gases as following according to Eq. (20) and (21), resulting in the amounts of fertilizer-derived NH$_3$ that are lower than 1.07 moles.

\[
\text{NH}_4\text{HCO}_3 \rightarrow \text{NH}_3 \uparrow + \text{H}_2\text{O} + \text{CO}_2 \uparrow \quad (20)
\]
The $A_w$ and $R_w$ in the (NH$_4$)$_3$PO$_4$ treatment, unlike in other NH$_4$-fertilizer treatments, had 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$_4$)$_3$PO$_4$ 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$_4$)$_3$PO$_4$ 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 $R_w$ without significant difference with control treatment 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$_4$NO$_3$, NH$_4$HCO$_3$, NH$_4$Cl, (NH$_4$)$_2$CO$_3$ and urea), but it fails to impact on carbonate weathering, which is raising a new problem. Eq. (5), usually considered 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 as an indicator to make estimations 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 as 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 as in Eq. (8). For NH$_4$NO$_3$ fertilizer, the (Eq. (12)) shows that the two moles of Ca$^{2+}$+Mg$^{2+}$, NO$_3^-$, and HCO$_3^-$ will be produced when one mole NH$_4$NO$_3$ reacts with 2 moles of carbonate, where only half of the NO$_3^-$ originates from nitrification described as Eq. (8). This will result in a double overestimation of the contribution of the nitrification to carbonate weathering, and thus thereby 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 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 is were 0.48‰ and 2.00 g·m$^{-2}$·a$^{-1}$, respectively, which are generally 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), with the results of 0.05-5.06‰ (for $R_w$) 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) from Jinfo Mountain in Chongqing of 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 is 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, Guangxi, China, which usually involves fertilization activities.

At larger scales, such as like 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. The estimation of Zeng, et al. (2014) estimate views that the carbon sink intensity calculated by the 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 that weathering rates of carbonate rock by 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, respectively, which are about approximately 25-35 and 2-3 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 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 of controlled comparative contrast or stimulated experiments, while the riverine hydro-chemical method is appropriate for the 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 $3.72 \times 10^5$ 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$_4$NO$_3$, NH$_4$HCO$_3$, NaN$_O_3$, NH$_4$Cl, (NH$_4$)$_2$CO$_3$, Ca$_3$(PO$_4$)$_2$, (NH$_4$)$_2$PO$_4$, Ca-Mg-P, urea, and K$_2$CO$_3$) on carbonate weathering was studied in a field column experiment with using carbonate-rock-tablets at its bottom of each. The amount of weathering amount and the ratio of weathering of carbonate rock tablets showed that the addition of urea, NH$_4$NO$_3$, NH$_4$HCO$_3$, and (NH$_4$)$_2$CO$_3$ 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$_2$CO$_3$ induced carbonate precipitation due to the common ion effect. While the addition of (NH$_4$)$_2$PO$_4$ and NaN$_O_3$ addition did not impact significantly on carbonate weathering, where the former can be attributed to the low added amount of (NH$_4$)$_2$PO$_4$ and may be related to the inhibition of phosphate, while the latter seemed to be raising a new question. The little minor impact of nitrate on
carbonate weathering may result in the overestimation of the impact of N-fertilizer on CO₂ consumption by carbonate weathering at the regional/global scale, if the effects of NO₃ and NH₄ are not distinguished. Thus, the related anthropogenic inputs (e.g., Ca+ Mg, NH₄, NO₃, HCO₃, etc.) need to be investigated to more accurately estimate the impact of fertilization on carbonate weathering and its consumption of CO₂.

4.2 The kinetics and controlled factors of carbonate weathering

Experimental studies of carbonate dissolution kinetics have shown that 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):

\[
\text{MeCO}_3^- + H^+ \rightarrow \text{Me}^{2+} + \text{HCO}_3^- \quad (4)
\]

\[
\text{MeCO}_3^- + H_2CO_3 \rightarrow \text{Me}^{2+} + 2\text{HCO}_3^- \quad (5)
\]

\[
\text{MeCO}_3^- \rightarrow \text{Me}^{2+} + \text{CO}_3^{2-} \quad (6)
\]

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

In field, carbonate dissolution is mainly controlled by the amount of rainfall (Amiotte-Suchet et al., 2003; Egli and Fitze, 2001; Kiefer, 1994), as well as impacted of soil CO$_2$ (Andrews and Schlesinger, 2001). We consider that the effect of rainfall on each soil column is same. In this study, the urea, NH$_4$NO$_3$, NH$_4$HCO$_3$, NH$_4$Cl and (NH$_4$)$_2$CO$_3$ 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). These increases may be, in the one hand, attributed to the effect of the proton released from the nitrification of NH$_4^+$. On the other hand, it may be, in theory, related to enhanced microbiogenic CO$_2$ due to nitrogenous nutrients stimulation (Eq(5)), because fertilizer application can increase soil CO$_2$ flux (Sainju et al., 2008; Bhattacharyya et al., 2013), the increased CO$_2$ can enhance carbonate dissolution rate at near neutral or alkali pH (Andrews and Schlesinger, 2001).

According to the added amount of different fertilization treatment, the molar amount of added nitrogen nutrient in NaNO$_3$-treatment is 1.07 mol, much bigger than in NH$_4$NO$_3$, equivalent to NH$_4$HCO$_3$ and NH$_4$Cl treatment. However, the A$_{cw}$ and R$_{cw}$ and R$_{aw}$ of NaNO$_3$-treatment is far less (Fig. 3 and table 2), inhibiting that the increases of carbonate weathering rate in urea, NH$_4$NO$_3$, NH$_4$HCO$_3$, NH$_4$Cl and (NH$_4$)$_2$CO$_3$-amendment have no distinct relationship with enhanced microbiogenic CO$_2$ due to nitrogenous fertilizer amendment.

4.3 The effect of nitrification of NH$_4$-fertilizer

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.,...
\[
\text{CO(NH}_2\text{)}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{NH}_4^+ + 2\text{OH}^- + \text{CO}_2 (7)
\]

Table 3 shows that the amount of \(\text{NH}_4^+\) hydrolyzed from urea is 1.06 mol, while \(\text{NH}_4^+\) ionized from \(\text{NH}_4\text{NO}_3\), \(\text{NH}_4\text{HCO}_3\), \(\text{NH}_4\text{Cl}\), \(\text{(NH}_4\text{)}_2\text{CO}_3\) and \(\text{(NH}_4\text{)}_3\text{PO}_4\) is 0.54 mol, 1.08 mol, 1.07 mol, 1.06 mol and 0.03 mol, respectively (Table 3). Although the study from Singh et al. showed that a part of \(\text{NH}_4^+\) may be lost as ammonia (\(\text{NH}_3\)) and subsequently as nitrous oxide (\(\text{N}_2\text{O}\)) (Singh et al., 2013), yet the rest ammonium (\(\text{NH}_4^+\)) is mainly oxidized in soil by autotrophic bacteria (like Nitrosomonas) during nitrification, resulting in nitrite \(\text{NO}_2^-\) and \(\text{H}^+\) ions. Nitrite is, in turn, oxidized by another bacterium, such as Nitrobacter, resulting in nitrate (\(\text{NO}_3^-\)) (Eq. (8)) (Perrin et al., 2008).

\[
\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + 2\text{H}^+ \quad (8)
\]

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

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

\[
\text{Soil-} \text{Ca} + 2\text{H}^+ \rightarrow \text{Soil-} 2\text{H}^+ + \text{Ca}^{2+} \quad (9)
\]

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

\[
\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3 + \text{H}^+ \rightarrow (1-x)\text{Ca}^{2+} + x\text{Mg}^{2+} + \text{HCO}_3^- \quad (10)
\]

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).

\[
2\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3 + \text{NH}_4^+ + 2\text{O}_2 \rightarrow 2(1-x)\text{Ca}^{2+} + 2x\text{Mg}^{2+} + \text{NO}_3^- + \text{H}_2\text{O} + 2\text{HCO}_3^- \quad (11)
\]

The Rcw of limestone tablets and the initial concentration of \(\text{NH}_4^+\) are plotted in
Fig. 4. A distinct relationship between them is observed: the $A_{cw}$ and $R_{cw}$ in NH$_4$NO$_3$, NH$_4$HCO$_3$, NH$_4$Cl, (NH$_4$)$_2$CO$_3$, and urea treatments are bigger than in control treatment, where the initial concentration of NH$_4^+$ displays similar results (Fig. 4). This suggests that carbonate weathering in NH$_4$NO$_3$, NH$_4$HCO$_3$, NH$_4$Cl, (NH$_4$)$_2$CO$_3$ 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). 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 $3.72 \times 10^5$ 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).

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$_4$NO$_3$, NH$_4$HCO$_3$, NH$_4$Cl, (NH$_4$)$_2$CO$_3$, and urea treatments will be followed as, respectively:

$$2Ca_{1+x}Mg_{x}CO_3 + NH_4NO_3 + 2O_2 \rightarrow 2(1-x)Ca^{2+} + 2xMg^{2+} + 2NO_3^- + H_2O + 2HCO_3^-$$ (12)

$$2Ca_{1+x}Mg_{x}CO_3 + NH_4HCO_3 + 2O_2 \rightarrow 2(1-x)Ca^{2+} + 2xMg^{2+} + NO_3^- + H_2O + 3HCO_3^-$$ (13)
The $\text{Ac}_w$ and $\text{Rc}_w$ in (NH$_4$)$_3$PO$_4$ treatment, unlike in other NH$_4$-fertilizer 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$_4$)$_3$PO$_4$ treatment (0.3 mol, see Table 3) but also relative to the inhibition of phosphate. After the addition of (NH$_4$)$_3$PO$_4$ 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).

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$_3^-$ has important implications on the evaluation of CO$_2$ consumption by carbonate weathering and its implication to the evaluation of CO$_2$ consumption by carbonate weathering.
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\(_4\)NO\(_3\) 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\(_4\)NO\(_3\) react with 2 moles of carbonate, where only half of NO\(_3^-\) originate from nitrification described as Eq. (8). This will result in doubled overestimation on the true contribution of the nitrification to CO\(_2\) consumption by carbonate weathering.

At regional scales, if different fertilizers are added to an agricultural area, the estimation of CO\(_2\) consumption by carbonate weathering might become more complicated, since the mole ratio of Ca+Mg, HCO\(_3^-\) and/or NO\(_3^-\) between different fertilization treatment is different (see Eq. (8)-(12)). 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. Moreover, the statement that nitrogenous fertilizer can aid carbonate weathering may result in misunderstanding more or less, it should not be nitrogenous fertilizer but, rather, ammonium fertilizer.

5. Conclusion

The impact of the addition of different fertilizer (NH\(_4\)NO\(_3\), NH\(_4\)HCO\(_3\), NaNO\(_3\), NH\(_4\)Cl, (NH\(_4\)\(_2\))CO\(_3\), Ca\(_2\)(PO\(_4\))\(_2\), (NH\(_4\)\(_2\))PO\(_4\), Ca-Mg-P, Urea and K\(_2\)CO\(_3\) on carbonate weathering was studied in a field column experiment with carbonate rock tablets at its
The weathering amount and ratio of carbonate rock tablets showed that the addition of urea, $\text{NH}_4\text{NO}_3$, $\text{NH}_4\text{HCO}_3$, $\text{NH}_4\text{Cl}$, and $(\text{NH}_4)_2\text{CO}_3$ distinctly increased carbonate weathering, which was attributed to the nitrification of $\text{NH}_4^+$ and the addition of $\text{Ca}_2(\text{PO}_4)_2$, $\text{Ca-Mg-P}$ and $\text{K}_2\text{CO}_3$-induced carbonate precipitation due to common ion effect. While the $(\text{NH}_4)_3\text{PO}_4$ and $\text{NaNO}_3$ addition did not impact significantly on carbonate weathering, where the former can be attributed to low added amount of $(\text{NH}_4)_3\text{PO}_4$, 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 $\text{N}$ fertilizer on $\text{CO}_2$ consumption by carbonate weathering at the regional/global scale if the effect of $\text{NO}_3^-$ and $\text{NH}_4^+$ are not distinguished. Thus, the related anthropogenic inputs (e.g., $\text{Ca+Mg}$, $\text{NH}_4^+$-$\text{NO}_3^-$, $\text{HCO}_3^-$, etc.) need to be investigated to more accurately estimate the impact of fertilization on carbonate weathering and its $\text{CO}_2$ consumption. Moreover, in order to avoid misunderstanding more or less, the statement that nitrogenous fertilizer can aid carbonate weathering should be replaced by ammonium fertilizer.

6. Acknowledgements

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Table 1 Chemical composition of soil

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<th>Parameter</th>
<th>Unit</th>
<th>Values</th>
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<td>Content of particles (&lt;0.01mm)</td>
<td>%</td>
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<tr>
<td>Content of particles (&lt;0.001mm)</td>
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<td>Organic matter</td>
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<tr>
<td>NO$_3^-$-N</td>
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Table 2 Carbonate weathering under different fertilizer treatments

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<thead>
<tr>
<th>Treatment</th>
<th>Limestone</th>
<th>Dolostone</th>
<th>Limestone</th>
<th>Dolostone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acc-Rw / %</td>
<td>Raw / g·m⁻²·a⁻¹</td>
<td>Acc-Rw / %</td>
<td>Raw / g·m⁻²·a⁻¹</td>
</tr>
<tr>
<td>Control</td>
<td>0.00148 ± 2.00 ± 0.58 ± 0.48</td>
<td>-0.00143 ± 1.57 ± 0.34</td>
<td>0.14 ± 0.09 ± 0.31</td>
<td></td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>0.01746 ± 24.86 ± 2.01 ± 0.28</td>
<td>0.01445 ± 20.57 ± 0.31</td>
<td>0.28 ± 0.87 ± 1.15</td>
<td></td>
</tr>
<tr>
<td>NH₄HCO₃</td>
<td>0.01934 ± 21.00 ± 3.45 ± 0.81</td>
<td>0.00363 ± 13.71 ± 0.53</td>
<td>0.17 ± 0.87 ± 3.83</td>
<td></td>
</tr>
<tr>
<td>NaNO₃</td>
<td>0.00310 ± 4.43 ± 1.73 ± 0.34</td>
<td>0.00225 ± 3.14 ± 0.53</td>
<td>0.17 ± 0.26 ± 1.73</td>
<td></td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>0.01408 ± 21.29 ± 2.45 ± 0.64</td>
<td>0.01341 ± 18.71 ± 0.86</td>
<td>0.64 ± 0.78 ± 4.22</td>
<td></td>
</tr>
<tr>
<td>(NH₄)₂CO₃</td>
<td>0.01442 ± 20.57 ± 4.46 ± 0.95</td>
<td>0.01180 ± 26.57 ± 0.64</td>
<td>0.95 ± 1.91 ± 7.62</td>
<td></td>
</tr>
<tr>
<td>Ca₄(PO₄)₂</td>
<td>0.00030 ± 0.43 ± 0.86 ± 0.01</td>
<td>-0.00135 ± 1.86 ± 0.55</td>
<td>0.04 ± 0.25 ± 1.29</td>
<td></td>
</tr>
<tr>
<td>(NH₄)₂PO₄</td>
<td>0.00028 ± 4.00 ± 1.15 ± 0.08</td>
<td>0.00020 ± 1.00 ± 0.34</td>
<td>0.34 ± 0.21 ± 1.01</td>
<td></td>
</tr>
<tr>
<td>Ca-Mg-P</td>
<td>-0.00013 ± -1.86 ± 0.43 ± 0.31</td>
<td>-0.00029 ± -2.14 ± 0.64</td>
<td>0.12 ± 0.38 ± 0.72</td>
<td></td>
</tr>
<tr>
<td>Urea</td>
<td>0.02483 ± 34.71 ± 4.32 ± 0.98</td>
<td>0.01886 ± 26.43 ± 0.55</td>
<td>0.96 ± 0.67 ± 2.73</td>
<td></td>
</tr>
<tr>
<td>K₂CO₃</td>
<td>-0.00036 ± -1.14 ± 0.58 ± 0.26</td>
<td>-0.00185 ± -2.57 ± 0.34</td>
<td>0.15 ± 0.15 ± 0.34</td>
<td></td>
</tr>
</tbody>
</table>

Acc = the amount of carbonate weathering; Rw = the ratio of carbonate weathering; Raw = the rate of carbonate weathering; Acc-Rw = Acc/1000 (Wi/Wf), and Rw = Raw/(Wi/Wf). Raw = Raw/(Wi/Wf)/S², where Wi is the initial weight of the carbonate rock tablets, and Wf is the final weight. S is the surface area of carbonate weathering rock tablets in this study, we used a same S = 7 cm² for every tablet, 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 fertilized treatments, and the potential nitrogenous transformation. (The amount of generated NH₄⁺ NO₃⁻ at the initial phase of the experiment)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Main reactions and effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Control</td>
<td>Ca₂⁺MgCO₃ + CO₃²⁻ + H₂O → (1-x)Ca²⁺ + xMg²⁺ + 2HCO₃⁻</td>
</tr>
<tr>
<td>2. NH₄NO₃</td>
<td>2Ca₂⁺MgCO₃ + NH₄NO₃ + 2O₂ → 2(1-x)Ca²⁺ + xMg²⁺ + 2NO₃⁻ + H₂O + 2HCO₃⁻</td>
</tr>
<tr>
<td>3. H₂HCO₃</td>
<td>NH₄HCO₃ → NH₄⁺ + H₂O + CO₂↑</td>
</tr>
<tr>
<td>4. NaNO₂</td>
<td>Ca₂⁺MgCO₃ + NaNO₂ + CO₂ + H₂O → (1-x)Ca²⁺ + xMg²⁺ + Na⁺ + NO₂⁻ + 2HCO₃⁻</td>
</tr>
<tr>
<td>5. NH₄Cl</td>
<td>Ca₂⁺MgCO₃ + NH₄Cl + 2O₂ → (1-x)Ca²⁺ + xMg²⁺ + NH₄⁺ + Cl⁻ + H₂O + 2HCO₃⁻</td>
</tr>
<tr>
<td>6. NH₄HCO₃</td>
<td>3Ca₂⁺MgCO₃ + (NH₄)HCO₃ → 3(1-x)Ca²⁺ + 3xMg²⁺ + 2NO₃⁻ + 2H₂O + 4HCO₃⁻</td>
</tr>
</tbody>
</table>

7. Ca₄(PO₄)₂
(1) Common ion effect: The Ca₄⁺Mg⁺₂CO₃ precipitate produces when the concentrations of Ca³⁺ and Mg²⁺ increase.
(2) Inhibition of phosphate to calcite precipitation: calcium phosphate precipitation produces on the surface of calcite after the addition of PO₄³⁻ into soil, resulting in inhibiting the precipitation of calcite.

8. (NH₄)₂PO₄
(1) Common ion effect: The Ca₄⁺Mg⁺₂CO₃ precipitate produces when the concentrations of Ca³⁺ and Mg²⁺ increase.
(2) Inhibition of phosphate to calcite precipitation: calcium phosphate precipitation produces on the surface of calcite after the addition of PO₄³⁻ into soil, resulting in inhibiting the precipitation of calcite.

9. Ca₄MgP
(1) Common ion effect: The Ca₄⁺Mg⁺₂CO₃ precipitate produces when the concentrations of Ca³⁺ and Mg²⁺ increase.
(2) Inhibition of phosphate to calcite precipitation: calcium phosphate precipitation produces on the surface of calcite after the addition of PO₄³⁻ into soil, resulting in inhibiting the precipitation of calcite.

10. Urea
3Ca₂⁺MgCO₃ + CO(NH₂)₂ + 4O₂ → 3(1-x)Ca²⁺ + 3xMg²⁺ + 2NO₃⁻ + 4HCO₃⁻ |

11. K₂CO₃
K₂CO₃ + H₂O → 2K⁺ + CO₃²⁻ + OH⁻

Table 4: The main reaction and effects in these 11 fertilizer treatments.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Main reactions and effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Control</td>
<td>Ca₂⁺MgCO₃ + CO₂ + H₂O → (1-x)Ca²⁺ + xMg²⁺ + 2HCO₃⁻</td>
</tr>
<tr>
<td>2. NH₄NO₃</td>
<td>2Ca₂⁺MgCO₃ + NH₄NO₃ + 2O₂ → 2(1-x)Ca²⁺ + xMg²⁺ + 2NO₃⁻ + H₂O + 2HCO₃⁻</td>
</tr>
<tr>
<td>3. H₂HCO₃</td>
<td>NH₄HCO₃ → NH₄⁺ + H₂O + CO₂↑</td>
</tr>
<tr>
<td>4. NaNO₂</td>
<td>Ca₂⁺MgCO₃ + NaNO₂ + CO₂ + H₂O → (1-x)Ca²⁺ + xMg²⁺ + Na⁺ + NO₂⁻ + 2HCO₃⁻</td>
</tr>
<tr>
<td>5. NH₄Cl</td>
<td>Ca₂⁺MgCO₃ + NH₄Cl + 2O₂ → (1-x)Ca²⁺ + xMg²⁺ + NH₄⁺ + Cl⁻ + H₂O + 2HCO₃⁻</td>
</tr>
<tr>
<td>6. NH₄HCO₃</td>
<td>3Ca₂⁺MgCO₃ + (NH₄)HCO₃ → 3(1-x)Ca²⁺ + 3xMg²⁺ + 2NO₃⁻ + 2H₂O + 4HCO₃⁻</td>
</tr>
<tr>
<td>7. Ca₄(PO₄)₂</td>
<td>(1) (1-x)Ca²⁺ + xMg²⁺ + 2HCO₃⁻ → Ca₁₋ₓMgₓCO₃ + CO₂ + H₂O</td>
</tr>
<tr>
<td>8. (NH₄)₂PO₄</td>
<td>(1) 2Ca₂⁺MgCO₃ + NH₄⁺ + 2O₂ → 2(1-x)Ca²⁺ + 2xMg²⁺ + NO₃⁻ + H₂O + 2HCO₃⁻</td>
</tr>
<tr>
<td>9. Ca₄MgP</td>
<td>2Ca₂⁺MgCO₃ + NH₄⁺ + 2O₂ → 2CaMgCO₃ + 2NH₄⁺ + 2O₂</td>
</tr>
<tr>
<td>10. Urea</td>
<td>3Ca₂⁺MgCO₃ + CO(NH₂)₂ + 4O₂ → 3(1-x)Ca²⁺ + 3xMg²⁺ + 2NO₃⁻ + 4HCO₃⁻</td>
</tr>
<tr>
<td>11. K₂CO₃</td>
<td>(1) (1-x)Ca²⁺ + xMg²⁺ + 2HCO₃⁻ → Ca₁₋ₓMgₓCO₃ + CO₂ + H₂O</td>
</tr>
</tbody>
</table>
(iii) $K_2CO_3 + H_2O \rightarrow 2K^+ + HCO_3^- + OH^-$

**Note:**

1. Common ion effect: The $Ca^{2+}\cdot Mg^{2+} CO_3$ 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 phosphate to 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 inhibiting of the dissolution/precipitation of calcite (for Treatment 7, 8 and 9):

   $Ca + PO_4^{3-} \rightarrow Ca-P$
Table 4: The amount of fertilizer-derived NH$_4^+$ at the initial phase of the experiment and the potential nitrogenous transformation (NH$_4^+$-NO$_3^-$)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Molecular mass (g/mol)</th>
<th>Amount of added fertilizer (g)</th>
<th>Molar amount/fertilizer-derived NH$_4^+$ (mol)</th>
<th>The maximum of N products (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$NO$_3$</td>
<td>80</td>
<td>43</td>
<td>0.54</td>
<td>0.54</td>
</tr>
<tr>
<td>NH$_4$HCO$_3$</td>
<td>79</td>
<td>85</td>
<td>1.08</td>
<td>1.08</td>
</tr>
<tr>
<td>NaNO$_3$</td>
<td>85</td>
<td>91</td>
<td>1.07</td>
<td>0.00</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>53.5</td>
<td>57</td>
<td>1.07</td>
<td>1.07</td>
</tr>
<tr>
<td>(NH$_4$)$_2$CO$_3$</td>
<td>96</td>
<td>51</td>
<td>0.53</td>
<td>1.06</td>
</tr>
<tr>
<td>Ca$_3$(PO$_4$)$_2$</td>
<td>310</td>
<td>52</td>
<td>0.17</td>
<td>0.00</td>
</tr>
<tr>
<td>(NH$_4$)$_2$PO$_4$</td>
<td>149</td>
<td>15</td>
<td>0.10</td>
<td>0.30</td>
</tr>
<tr>
<td>Ca-Mg-P</td>
<td>wind</td>
<td>44</td>
<td>wind</td>
<td>0.00</td>
</tr>
<tr>
<td>Urea</td>
<td>60</td>
<td>32</td>
<td>0.53</td>
<td>1.06</td>
</tr>
<tr>
<td>K$_2$CO$_3$</td>
<td>138</td>
<td>19</td>
<td>0.07</td>
<td>0.00</td>
</tr>
</tbody>
</table>

*Wind = without data. The amount of added fertilizer (g) divided by its molecular mass (g/mol) equals the molar amount of fertilizer (mol). Gafdi - gram amount of added fertilizers (g); Maaf - molecular amount of added fertilizers (mol). The amount of fertilizer-derived NH$_4^+$ is 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 map of the soil column with rock tablets
Fig. 3 The ratio of carbonate weathering $R_w$ (%) of limestone and dolostone under different fertilization treatments. (a) limestone; (b) dolostone. Treatment 1 - Control; 2 - NH$_4$NO$_3$; 3 - NH$_4$HCO$_3$; 4 - NaNO$_3$; 5 - NH$_4$Cl; 6 - (NH$_4$)$_2$CO$_3$; 7 - Ca$_2$(PO$_4$)$_2$; 8 - K$_2$CO$_3$; 9 - Ca-Mg-P; 10 - Urea; 11 - K$_2$CO$_3$. Values in each column followed by different letters are significantly (p <0.05). 

The ratio of carbonate weathering $R_w$ is calculated as $R_w = 1000(W_i - W_f)/W_i$, where $W_i$ is the initial weight of the carbonate rock tablets, and $W_f$ is their final weight.
带格式的：缩进：首行缩进：0 厘米，定义网格后自动调整右缩进，孤行控制。到齐到网格。
Fig. 4 The linear correlation of $R_w$ (%) of limestone and dolostone

$R_w = 1000(W_f - W_i)/W_i$, where $W_i$ is the initial weight of the limestone tablets, and $W_f$ is their final weight.
Fig. 4,5 The Rw (%) of limestone ratio of limestone weathering and the molar amount of produced NH$_4^+$ under different fertilization fertilizer treatments.

Treatment 1 - Control; 2 - NH$_4$NO$_3$; 3 - NH$_4$HCO$_3$; 4 - NaNO$_3$; 5 - NH$_4$Cl; 6 - (NH$_4$)$_2$CO$_3$; 7 - Ca$_3$(PO$_4$)$_2$; 8 - (NH$_4$)$_2$PO$_4$; 9 - Ca-Mg-P; 10 - Urea; 11 - K$_2$CO$_3$. Rw = \( \frac{1000(W_f - W_i)}{W_i} \), where $W_i$ is the initial weight of the limestone tablets, and $W_f$ is their final weight.

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| 1230 | 所有题录的数据正常 |