Dear Prof. Gerard Govers

Thank you very much for your comments and giving these great suggestions, which make this paper improved a lot.

We have done a major revision according to these suggestions, and the responses and revision descriptions are following below.

I. - The structure of the paper needs improvement. Now, there is still too much mixing of methods, results and discussion. Furthermore, the results are not all well presented: you report that dolostone and limestone tables were used but only discuss the limestone results because the dolostone results were similar. I would suggest all available data should be presented, at least in tabular form in an appendix and that at least a graph is included showing that the results are indeed similar.

**Changed:** we added some contents of statistical analysis, and analyzed the relationship between dolostone and limestone weathering based on the results of ANOVA analysis.

2 - With respect to the structure of the paper, the following guidelines may be useful to you:

Introduction: explain the state of the art.
- Weathering may be impacted by mineral fertilization
- But impact of different types of fertilizers not known
- Therefore we conducted experiments

**Changed:** we revised the section like this

3. Materials and methods:
- Description of the experimental set up
- study area, including meteo data and more info on the soil (grain size Ph, SOC content in a small table)
- columns: size, way of filling, resulting bulk density of the soil.....
- measurement procedure for the tablets and presentation of the way losses are calculated
- the description needs to include a justification of some or your decisions on the methods: why this size of columns ? Why 30 times more fertilizer ? Why did you choose this length for the measuring period ?

**Changed:** we added the description mentioned above, including grain size, bulk density.

The primary reasons why we set up the amount of added fertilizer in this study are: (1) the soil we used is untitled fresh soil which we sampled from B layer. Considering its
low nutrition, we set up a higher fertilizer amount. (2) We just want to explore the
different response of these different on carbonate weathering, and magnify and
quicken the short-term response. (3) It is a simple pre-study, but we think some
findings are worthy published especially to CO$_2$ consumption via carbonate
weathering at agricultural areas.
Considering its misleading possibility, we decided to delete the relative (30 times)
statement.

4. Results
- Presentation of the results: no discussion and no further justification of the study or
certain decision taken
- Presentation of the weathering rates
- Statistical analysis: for which treatments are rates significantly different: this can be
done with an ANOVA analysis. I suggest to include the type of tablet as a class
variable here so that we can see whether or not the results for limestone and dolostone
are similar.

Changed: we added the relative ANOVA analysis.

5. Discussion
- A key element in the discussion are the weathering reactions: I suggest to have the
generic weathering reactions in the text (paragraph 4.2) and then have the
fertilizer-specific reactions in a table. In this table you can then also indicate the
amount of NH$_4$ per mole of fertilizer
- After having done this you can proceed to discuss the differences between the
treatments. I think this is already more or less covered in the current version of the
MS but it needs to be presented more clearly.
- Then you may discuss the fact that CO$_2$ consumption by weathering may be
wrongly estimated if the contributions of (different) fertilizers is not accounted for.
- Finally you have to compare your results with other data: now, there is no
quantitative comparison whatsoever with results from other studies. Nevertheless, this
is possible: you can calculate a weathering rate from your results and make than
reasonable assumptions to make a calculation for larger areas that could be compared
to the results of earlier studies which you already cite.

Changed: we rewrite the discussion section according to these suggestions above.
Thank u again.

6. The English used is not yet up to international standards. The paper really needs a
revision by a native speaker.

Changed: we changed the mistakes you noted in pdf file and checked the language
problems for several times. PLEASE correct it if conveniently.
8. We did the edition and correction in terms of the notes in pdf file.

Thank you SO much for your favor to improve our manuscript.

Best regards,

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

Chao Song\textsuperscript{1,2}, Changli Liu\textsuperscript{1}, Guilin Han\textsuperscript{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 anthropogenic perturbations such as 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. 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 carbonate and dolomite tablets buried at the bottom of the columns. The result showed that the addition of urea, NH₄NO₃, NH₄HCO₃, NH₄Cl and (NH₄)₂CO₃ distinctly increased carbonate weathering, which was attributed to the nitrification of NH₄⁺ and the addition of Ca₃(PO₄)₂, Ca-Mg-P and K₂CO₃ induced carbonate precipitation due to 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 raise a new question: the negligible impact of nitrate.
on carbonate weathering may result in the overestimation of 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; 2011). The riverine hydro-chemical composition such as the ratio of HCO₃⁻
and to Ca²⁺ + Mg²⁺ is usually employed as an indicator to estimate the CO₂
collection 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, 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; 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 the that 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.

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 chemical-mineral fertilizer is a significant disturbance factor of carbonate weathering and carbon cycle. Many several studies showed that nitrogen fertilizer additions aided increased in-the dissolution of lime 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.,...
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 tributary of the Garonne river, respectively). For larger basin level, such as the Garonne river basin, which is larger basin (52,000 km$^2$), 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 CO$_2$ uptake due to N-fertilizer addition (usually in form of NH$_4$NO$_3$) represent up to 5.7-13.4% and only 1.6-3.8% of the total CO$_2$ flux naturally consumed by carbonate dissolution for France and on a global scale, respectively.

These estimated results described above were usually based on calculations assuming that a single type of fertilizer (e.g. (NH$_4$)$_2$SO$_4$, NH$_4$NO$_3$, or NH$_4$Cl) was used throughout the whole basin that was considered. However, were usually based on a hypothesis of individual fertilizer (e.g. (NH$_4$)$_2$SO$_4$, NH$_4$NO$_3$, or NH$_4$Cl) input into an agricultural basin. Nevertheless, 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 nitrogenous fertilizer, 100% NO$_3^-$ produced after
the addition \((\text{NH}_4)_2\text{SO}_4\) and \(\text{NH}_4\text{Cl}\) derive from the nitrification of \(\text{NH}_4^+\), comparatively, only 50% after the addition \(\text{NH}_4\text{NO}_3\). The difference of \(\text{NO}_3^-\) 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. \((\text{NH}_4)_2\text{SO}_4, \text{NH}_4\text{NO}_3, \text{NH}_4\text{Cl, NaNO}_3\) or urea) may result in different contributions to carbonate weathering and relative products such as \(\text{HCO}_3^-\), \(\text{Ca}^{2+}\) and \(\text{Mg}^{2+}\). For phosphate fertilizer, the coprecipitation 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 (\(\text{NH}_4\) and \(\text{NO}_3\)), 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 (Chao et al., 2014; Chao et al., 2011; Dreybrodt et al., 1996; Gams, 1981; Gams, 1985; Jiang and Yuan, 1999; Liu and Dreybrod, 1997; Plan, 2005; Trudgill, 1975; 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; Chao et al., 2014). 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).
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), our results show that yet it is
a preferred option for the condition controlled contrast or stimulated experiment
(Chao et al., 2014; Chao et al., 2011). 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).

Thus, in order to observe their difference between the impacts of
different fertilizer addition on carbonate weathering in soil, a field column experiment
embedding carbonate rock tablets with eleven different treatments 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-Huaxi district of
Guizhou city, Guizhou province, SW China (26°23′N, 106°40′E, 1094 m asl).

Guizhou, 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 °C 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 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 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$_4$F, and 0.005% Superfloc 127, and available S was extracted by 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 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 of soil column. A polyethylene net mesh (Ø 0.5 mm) was placed in the bottom of the columns to prevent the soil loss of the filter material. 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 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 P₀·ha⁻¹; K fertilizer: 50 kg K–ha⁻¹). The 6 kg soil was weighed (bulk density=1.3 g/cm³), 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.
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, 3-5% microcrystalline calcite, 1% pyrite and little trace quantities organic matter. All of tablets were baked heated at 80 °C 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 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:

$$A_{cw} = (W_i - W_f)$$  \hspace{1cm} (1)

$$R_{cw} = (W_i - W_f) / W_i$$  \hspace{1cm} (2)

$$R_{acw} = (W_i - W_f) / (S * T)$$  \hspace{1cm} (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. Statistical analysis was performed using IBM SPSS 20.0 (Statistical Graphics Crop, Princeton, USA).

3. Results

3.1 The weathering rate of carbonate under different fertilized treatments

The amount of weathering of under different treatments of limestone and dolostone carbonate weathering were listed in Table 2, and the weathering rate was plotted in Fig. 3. The rates of limestone and dolostone carbonate weathering under urea, \( \text{NH}_4\text{NO}_3 \), \( \text{NH}_4\text{HCO}_3 \), \( \text{NH}_4\text{Cl} \), \( (\text{NH}_4)_2\text{CO}_3 \) 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 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 suggested that the addition of these five fertilizers can aid and increased the rate of the chemical weathering of carbonate weathering.
According to the results of ANOVA analysis, the rest treatments had no significant differences (p>0.05) in the Rw and Rcw of limestone and dolomite in comparison with control treatment (Table 2). In (NH₄)₃PO₄ treatment, the \( AcwRw \) and \( Rcw \) were only 1.08±0.34‰, 0.0028g and 0.00020.75±0.21‰, 0.0001g for limestone and dolomite, 4.00±1.15 g·m\(^{-2}\)·a\(^{-1}\)‰, 0.75± 0.21 ‰ g for limestone and dolomite, respectively, less than those under other four NH₄-fertilizers as mentioned above. The \( AcwRw \), \( Rcw \) and \( Rcw \) in NaNO₃ treatment failed to show a remarkable difference with the control treatment, implying exhibiting little effect of NaNO₃ fertilizer addition on carbonate weathering (Fig. 3).

However, except the \( Rw \) of limestone in Ca₃(PO₄)₂ treatment approaching zero, all the values of \( AcwRw \), \( Rw \) and \( Rcw \) of two different carbonate in Ca-Mg-P and K₂CO₃ and Ca₃(PO₄)₂ treatments showed a negative value, indicating that the addition of Ca-Mg-P, K₂CO₃ and Ca₃(PO₄)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 result of the \( Rw \) between limestone and dolomite using one-way analysis of variance (ANOVA) was 0.320 (>0.05), suggesting that ANOVA was used to determine the differences of weathering rate between limestone and dolomite.

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 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 mineral 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), 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):

\[
\text{MeCO}_3 + H^+ \leftrightarrow \text{Me}^{2+} + \text{HCO}_3^- \tag{4}
\]

\[
\text{MeCO}_3 + \text{H}_2\text{CO}_3 \leftrightarrow \text{Me}^{2+} + 2\text{HCO}_3^- \tag{5}
\]

\[
\text{MeCO}_3 \leftrightarrow \text{Me}^{2+} + \text{CO}_3^{2-} \tag{6}
\]

where Me=Ca, Mg. As Eq. (5) describes, atmospheric/soil \(\text{CO}_2\) is usually regard 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 Ca, 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 unconsidered as a controlling factor in this study. The Eq. (4) suggests that the proton from other origins such as the nitrification processes of \(\text{NH}_3^+\), as mentioned in 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 \((\text{NH}_4)\text{}_2\text{CO}_3\) 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).
Thus these increases are strongly relative to the effect of the proton released from the nitrification of $\text{NH}_4^+$. 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 $\text{CO}_2$, (2) soil evapotranspiration or (3) 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 were listed in Table 3.

(1) The nitrification in $\text{NH}_4$-fertilizer: $\text{NH}_2\text{NO}_3$, $\text{NH}_2\text{HCO}_3$, $\text{NH}_4\text{Cl}$, (NH$_4$)$_2\text{CO}_3$ and urea

In urea (CO(NH$_2$)$_2$) treatment, the enzyme urease rapidly hydrolyzes the urea-$\text{N}^+$ (CO(NH$_2$)$_2$) to $\text{NH}_4^+$ ions (Eq. (7)) when urea is applied to the soil (Soares et al., 2012).

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

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

(ii) or via carbonate mineral dissolution (Eq. (10))
\[
\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3 + \text{H}^+ \rightarrow (1-x)\text{Ca}^{2+} + x\text{Mg}^{2+} + \text{HCO}_3^-
\] (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).
\[
2\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3 + \text{NH}_4^+ + 2\text{O}_2 \rightarrow 2(1-x)\text{Ca}^{2+} + 2x\text{Mg}^{2+} + 2\text{NO}_3^- + \text{H}_2\text{O} + 2\text{HCO}_3^-
\] (11)

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

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

(2) No effect of NO₃-fertilizer treatment: NaNO₃ treatment

In NaNO₃ treatment, the reaction occurs as Eq. (17), indicating that the addition
of NO$_3$-fertilizer does not significantly influence carbonate weathering.

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

(3) The common ion effect: K$_2$CO$_3$ treatment

In K$_2$CO$_3$ treatment, CO$_3^{2-}$ and HCO$_3^-$ will produce according to Eq. (18) after adding K$_2$CO$_3$, hence resulting in carbonate precipitation described in Eq. (19) due to the common ion effect.

\[
\text{K}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 2\text{K}^+ + \text{HCO}_3^- + \text{OH}^- \quad (18)
\]

\[
(1-x) \text{Ca}^{2+} + x\text{Mg}^{2+} + 2\text{HCO}_3^- \rightarrow \text{Ca}_{1-x}\text{Mg}_x\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \quad (19)
\]

(4) Complex effects: Nitrification versus Inhibition effect of PO$_4$ in (NH$_4$)$_3$PO$_4$ treatments

For (NH$_4$)$_3$PO$_4$ treatment, the reaction of carbonate weathering will occur according to Eq. (11) due to the nitrification of NH$_4^+$ ionized from (NH$_4$)$_3$PO$_4$ 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$_x$CO$_3$ 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$_4$NO$_3$, NH$_4$HCO$_3$, NH$_4$Cl, (NH$_4$)$_2$CO$_3$, (NH$_4$)$_3$PO$_4$ 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$_4$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 amount 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 (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$_3$ treatment are lower than even half of those in urea treatment in spite of adding the same amount of fertilizer-derived NH$_3$ (about 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 Eq. (20) and (21), resulting in the amount of fertilizer-derived NH$_3$
of lower than 1.07 moles.

\[
\text{NH}_4\text{HCO}_3 \rightarrow \text{NH}_3 \uparrow + \text{H}_2\text{O} + \text{CO}_2 \uparrow
\]  (20)

\[
(\text{NH}_4\text{H})_2\text{CO}_3 \rightarrow 2\text{NH}_3 \uparrow + \text{H}_2\text{O} + \text{CO}_2 \uparrow
\]  (21)

The Aw and Rw 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 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 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 Rw 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$_4$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 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$_4$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 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 Rw and Raw 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 Raw) in Nongla, Guangxi, a karst area of Southwestern China (Zhang, 2011) and the results of 0.05-5.06‰ (for Rw) and 1.08-136.90 g·m$^{-2}$·a$^{-1}$ (for Raw) from the north slope of the Hochschwab massif in Australia (Plan, 2005) using limestone tablet.
method. But the Raw of 2.00 g·m⁻²·a⁻¹ is lower than the results (7.0-63.5 g·m⁻²·a⁻¹ for Raw) 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 Raw 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 HCO₃⁻ flux due to
nitrification of $\text{NH}_4^+$ 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. Conclusion

The impact of the addition of different fertilizer (NH$_3$NO$_3$, NH$_2$HCO$_3$, NaNO$_3$, NH$_4$Cl, (NH$_4$)$_2$CO$_3$, Ca$_3$(PO$_4$)$_2$, (NH$_4$)$_3$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 bottom of each. The weathering amount and ratio of carbonate rock tablets showed that the addition of urea, NH$_3$NO$_3$, NH$_2$HCO$_3$, NH$_4$Cl and (NH$_4$)$_2$CO$_3$ distinctly increased carbonate weathering, which was attributed to the nitrification of $\text{NH}_4^+$, and the addition of Ca$_3$(PO$_4$)$_2$, Ca-Mg-P and K$_2$CO$_3$ induced carbonate precipitation due to common ion effect. While the (NH$_4$)$_3$PO$_4$ and NaNO$_3$ addition did not impact significantly on carbonate weathering, where the former can be attributed to low added amount of (NH$_4$)$_3$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 N-fertilizer on CO$_2$ consumption by carbonate weathering at the regional/global scale if the effect of NO$_3^-$ and NH$_3$ 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.

4.2 The kinetics and controlled factors of carbonate weathering

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):

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

\[ \text{MeCO}_3^- + \text{H}_2\text{CO}_3 \rightarrow \text{Me}^{2+} + 2\text{HCO}_3^- \] (5)

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

where Me = Ca, Mg, As. Eq. (5) describes atmospheric/soil CO$_2$ 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, which can originate from the nitrification processes of N fertilizer H$_4$^+ (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 (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., 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$_2$-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$_{acw}$ of NaNO$_2$-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.,
2012).

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

Table 3 shows that the amount of NH$_4^+$-hydrolyzed from urea is 1.06 mol, while
NH$_4^+$-ionized from NH$_4$NO$_3$, NH$_4$HCO$_3$, NH$_4$Cl, (NH$_4$)$_2$CO$_3$ and (NH$_4$)$_2$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 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).

\[
NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \]  

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))

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

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

\[
Ca_{1-x}Mg_xCO_3 + H^+ \rightarrow (1-x)Ca^{2+} + xMg^{2+} + HCO_3^- \]  

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).

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

The Rcw of limestone tablets and the initial concentration of \(NH_4^+\) are plotted in Fig. 4. A distinct relationship between them is observed: the Acw and Rcw 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 concentration 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). 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 x 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$_2$O) 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:

1. $2\text{Ca}_ {(1-x)} \text{Mg}_x \text{CO}_3 + \text{NH}_4\text{NO}_3 + 2\text{O}_2 \rightarrow 2(1-x) \text{Ca}^{2+} + 2x\text{Mg}^{2+} + 2\text{NO}_3^- + \text{H}_2\text{O} + 2\text{HCO}_3^-$ (12)
2. $2\text{Ca}_ {(1-x)} \text{Mg}_x \text{CO}_3 + \text{NH}_4\text{HCO}_3 + 2\text{O}_2 \rightarrow 2(1-x) \text{Ca}^{2+} + 2x\text{Mg}^{2+} + \text{NO}_3^- + \text{H}_2\text{O} + 3\text{HCO}_3^-$ (13)
3. $2\text{Ca}_ {(1-x)} \text{Mg}_x \text{CO}_3 + \text{NH}_4\text{Cl} + 2\text{O}_2 \rightarrow 2(1-x) \text{Ca}^{2+} + 2x\text{Mg}^{2+} + \text{NO}_3^- + \text{Cl}^- + \text{H}_2\text{O} + 2\text{HCO}_3^-$ (14)
4. $3\text{Ca}_ {(1-x)} \text{Mg}_x \text{CO}_3 + (\text{NH}_4)_2\text{CO}_3 + 4\text{O}_2 \rightarrow 3(1-x) \text{Ca}^{2+} + 3x\text{Mg}^{2+} + 2\text{NO}_3^- + 2\text{H}_2\text{O} + 4\text{HCO}_3^-$ (15)
5. $3\text{Ca}_ {(1-x)} \text{Mg}_x \text{CO}_3 + \text{CO( NH}_2)_2 + 4\text{O}_2 \rightarrow 3(1-x) \text{Ca}^{2+} + 3x\text{Mg}^{2+} + 2\text{NO}_3^- + 4\text{HCO}_3^-$ (16)
The Acw and Rcw in (NH₄)₃PO₄ treatment, unlike in other NH₄-fertilizer treatments, had not a significant increase comparing with control treatment, which is not only owing to the low amount of added NH₄⁺ in (NH₄)₃PO₄ treatment (0.3 mol, see Table 3) but also relative to the inhibition of phosphate. After the addition of (NH₄)₃PO₄ 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).

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

In Fig. 3, the Acw and Rcw without significant difference with control treatment in NaNO₃ treatment indicates that the addition of NO₃-fertilizer does not significantly influence carbonate weathering. This result 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 HCO₃⁻ and Me²⁺ in the river as an indicator is usually used to make estimations of CO₂ 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)/HCO₃⁻ and NO₃⁻ is usually employed to estimate the contribution of N-fertilizer to riverine Ca²⁺, Mg²⁺ 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 NO₃⁻. According to the result of NaNO₃ treatment in this study, the contribution of protons from nitrification to carbonate weathering may be overestimated if anthropogenic NO₃⁻ 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 double 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$^{2+}$+Mg$^{2+}$, HCO$_3^-$ and/or NO$_3^-$ between different fertilization treatment is different (see Eq. (8)-(12)). Thus, the related anthropogenic inputs (e.g. Ca$^{2+}$+Mg$^{2+}$, 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$_3$(PO$_4$)$_2$, (NH$_4$)$_4$P$_2$O$_7$, 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 bottom of each. The weathering amount and ratio of carbonate rock tablets showed that the addition of urea, NH$_4$NO$_3$, NH$_4$HCO$_3$, NH$_4$Cl and (NH$_4$)$_2$CO$_3$ 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$_2$CO$_3$ induced carbonate precipitation due to common ion effect. While the (NH$_4$)$_2$PO$_4$ and NaNO$_3$ addition did not impact
significantly on carbonate weathering, where the former can be attributed to low
added amount of (NH4)3PO4 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 CO2
consumption by carbonate weathering at the regional/global scale if the effect 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 CO2-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.

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weathering constrained by $\delta^{13}C_{DIC}$: Examples from Southwest China. Earth and Planetary Science Letters, 270(3-4): 189-199.


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<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>-</td>
<td>6.94</td>
</tr>
<tr>
<td>Content of particle (&lt;0.01mm)</td>
<td>%</td>
<td>74</td>
</tr>
<tr>
<td>Content of particle (&lt;0.001mm)</td>
<td>%</td>
<td>45</td>
</tr>
<tr>
<td>Organic matter</td>
<td>%</td>
<td>0.99</td>
</tr>
<tr>
<td>NH₄⁺-N</td>
<td>mg/kg</td>
<td>339.87</td>
</tr>
<tr>
<td>NO₃⁻-N</td>
<td>mg/kg</td>
<td>569.05</td>
</tr>
<tr>
<td>Available P</td>
<td>mg/kg</td>
<td>8.18</td>
</tr>
<tr>
<td>Available K</td>
<td>mg/kg</td>
<td>56.88</td>
</tr>
<tr>
<td>Available Ca</td>
<td>mg/kg</td>
<td>3041.06</td>
</tr>
<tr>
<td>Available Mg</td>
<td>mg/kg</td>
<td>564.83</td>
</tr>
<tr>
<td>Available S</td>
<td>mg/kg</td>
<td>100.72</td>
</tr>
<tr>
<td>Available Fe</td>
<td>mg/kg</td>
<td>24.41</td>
</tr>
</tbody>
</table>
Table 2 Carbonate weathering under different fertilizer treatments

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Limestone</th>
<th>Dolostone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{Acc-Rw} / % $</td>
<td>$\text{Raw} / $ g·m$^{-2}$·a$^{-1}$</td>
</tr>
<tr>
<td>Control</td>
<td>0.001448 ± 0.14a</td>
<td>2.00±0.58a0.48</td>
</tr>
<tr>
<td>NH$_4$NO$_3$</td>
<td>0.01746 ± 0.28c</td>
<td>24.86±2.01b 6.42</td>
</tr>
<tr>
<td>NH$_4$HCO$_3$</td>
<td>0.01424 0.81b</td>
<td>21.00±3.45b 4.44</td>
</tr>
<tr>
<td>NaNO$_3$</td>
<td>0.00310 0.17a</td>
<td>4.43±1.73a0.86</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>0.01495 0.64bc</td>
<td>21.29±2.45b 5.54</td>
</tr>
<tr>
<td>(NH$_4$)$_2$CO$_3$</td>
<td>0.01444 0.95bc</td>
<td>20.57±4.46b 4.84</td>
</tr>
<tr>
<td>Ca(NO$_3$)$_2$</td>
<td>0.00300 0.04a</td>
<td>0.43±0.86a0.04</td>
</tr>
<tr>
<td>(NH$_4$)$_2$PO$_4$</td>
<td>0.00281 0.34a</td>
<td>4.00±1.15a 0.08</td>
</tr>
<tr>
<td>Ca-Mg-P</td>
<td>-0.0013 0.12a</td>
<td>-1.86±0.43a 0.34</td>
</tr>
<tr>
<td>Urea</td>
<td>0.02438 0.96d</td>
<td>34.71±4.32c 8.48</td>
</tr>
<tr>
<td>K$_2$CO$_3$</td>
<td>-0.0008 0.15a</td>
<td>-1.14±0.58a 0.26</td>
</tr>
</tbody>
</table>

$\text{Acc-Rw}$ - the amount of carbonate weathering; $\text{Raw}$ - the ratio of carbonate weathering; $\text{Acc-Rw} = 1000 (W_i - W_f)/Wi$; $\text{Raw} = (W_i - W_f)/Wi$. $R_{aw} = (W_i - W_f)/(S*T)$, where $Wi$ 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>
<thead>
<tr>
<th>1097</th>
<th>1098</th>
</tr>
</thead>
</table>

带格式的：左
<table>
<thead>
<tr>
<th>Treatment</th>
<th>Main reaction and effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Control</td>
<td>Ca(<em>{10.7})Mg(</em>{1.7})CO(_3) + CO(_2) + H(<em>2)O → (1-x) Ca(</em>{x}) + xMg(_x) + 2HCO(_3)</td>
</tr>
<tr>
<td>2. NH(_4)NO(_3)</td>
<td>2Ca(<em>{10.7})Mg(</em>{1.7})CO(_3) + NH(_4)NO(_3) + 2O(<em>2) → 2(1-x) Ca(</em>{x}) + 2Mg(_x) + 2NO(_x) + H(_2)O + 2HCO(_3)</td>
</tr>
<tr>
<td>3. H(_2)CO(_3)</td>
<td>2Ca(<em>{10.7})Mg(</em>{1.7})CO(_3) + H(_2)CO(_3) + 2O(<em>2) → 2(1-x) Ca(</em>{x}) + 2Mg(_x) + 2NO(_x) + H(_2)O + 3HCO(_3)</td>
</tr>
<tr>
<td>4. Na(_2)NO(_3)</td>
<td>Ca(<em>{10.7})Mg(</em>{1.7})CO(_3) + Na(_2)NO(_3) + CO(_2) + H(<em>2)O → (1-x) Ca(</em>{x}) + xMg(_x) + Na(_x) + NO(_x) + 2HCO(_3)</td>
</tr>
<tr>
<td>5. NH(_4)Cl</td>
<td>2Ca(<em>{10.7})Mg(</em>{1.7})CO(_3) + NH(_4)Cl + 2O(<em>2) → 2(1-x) Ca(</em>{x}) + 2Mg(_x) + 2NO(_x) + Cl(_x) + H(_2)O + 3HCO(_3)</td>
</tr>
<tr>
<td>6. (NH(_4))(_2)CO(_3)</td>
<td>3Ca(<em>{10.7})Mg(</em>{1.7})CO(_3) + (NH(_4))(_2)CO(_3) + 4O(<em>2) → 3(1-x) Ca(</em>{x}) + 3xMg(_x) + 2NO(_x) + 2H(_2)O + 4HCO(_3)</td>
</tr>
<tr>
<td>7. Ca(_3)(PO(_4))(_2)</td>
<td></td>
</tr>
<tr>
<td>8. (NH(_4))(_2)PO(_4)</td>
<td></td>
</tr>
</tbody>
</table>

(1) Common ion effect: The Ca\(_{10.7}\)Mg\(_{1.7}\)CO\(_3\) produces when the concentrations of Ca\(_{x}\) and Mg\(_x\) increase.
(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 dissolution of calcite.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>(1) Common ion effect:</strong> The Caₓ₋₁MgₓCO₃ produces when the concentrations of Ca²⁺ and Mg²⁺ increases</td>
<td>(1-x) Ca²⁺ + xMg²⁺ + 2HCO₃⁻ → Caₓ₋₁MgₓCO₃ + CO₂ + H₂O</td>
<td>3Caₓ₋₁MgₓCO₃ + CO(NH₂)₂ + 4O₂⁻ → 3(1-x) Ca²⁺ + 3xMg²⁺ + 2NO₃⁻ + 4HCO₃⁻</td>
<td>( \text{(i)} ) ( \text{(i)} ) ( \text{(i)} ) ( \text{(i)} )</td>
</tr>
<tr>
<td><strong>(2) Inhibition of phosphate to calcite precipitation:</strong> calcium phosphate precipitation produces on the surface of calcite after the addition of P in soil, resulting in inhibiting the precipitation of calcite</td>
<td></td>
<td></td>
<td>( \text{(ii)} ) ( \text{(ii)} )</td>
</tr>
</tbody>
</table>
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 /mole</th>
<th>amount of fertilizer-derived NH$_4^+$ /mole</th>
<th>The maximum of N products /mole</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>
<td>1.08</td>
</tr>
<tr>
<td>NH$_4$HCO$_3$</td>
<td>79</td>
<td>85</td>
<td>1.08</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>
<td>1.07</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>53.5</td>
<td>57</td>
<td>1.07</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>
<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>
<td>0.00</td>
</tr>
<tr>
<td>(NH$_4$)$_3$PO$_4$</td>
<td>149</td>
<td>15</td>
<td>0.10</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Ca-Mg-P</td>
<td>/</td>
<td>44</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Urea</td>
<td>60</td>
<td>32</td>
<td>0.53</td>
<td>1.06</td>
<td>1.06</td>
</tr>
<tr>
<td>K$_2$CO$_3$</td>
<td>138</td>
<td>10</td>
<td>0.07</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Gadf—gram amount of added fertilizers (g); Maaf—molar added fertilizers (mol).
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 ratio of carbonate weathering $R_w$ (%) of limestone and dolostone under different fertilization treatment (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$_3$(PO$_4$)$_2$; 8 - (NH$_4$)$_3$PO$_4$; 9 - Ca-Mg-P; 10 - Urea; 11 - K$_2$CO$_3$. $R_w = \frac{W_i - W_f}{W_i}$, where $W_i$ is the initial weight of the carbonate rock tablets, and $W_f$ is their final weight. Different letters on each column are significantly (p < 0.05) different based on one-way ANOVA. Values in each column followed by different letters are significantly (p < 0.05) different based on one-way ANOVA.
Fig. 4 The Ru (‰) of limestone ratio of limestone weathering and the molar amount of produced \( \text{NH}_4^+ \) under different fertilization treatment. Different letters on each column are significantly (p < 0.05) different based on one-way ANOVA.