Reviewer 1

1. In some paragraphs, the English writing may be slightly improved.
Changed in the manuscript: we have re-edited the language question by the Language Services of Elsevier.

2. In the field, how are placed the different experimental columns? Did you have a random position, mixing the different modalities?
Answer: we placed orderly the different treatments columns including replicated treatments.
Changed in the manuscript: we added "were labelled and placed orderly" to interpret this.

3. The authors mixed "perfectly" the chemical fertilizers with the sieved soils. It was not directly spread on the field/columns. This may be an artefact compared to the natural field, where fertilizers are spread on the soils, relatively far from the rock.
Answer: We agree that this design have difference from the natural field. But considering the uniformity of all treatments, the results we got are still convinced. We will consider the comparison research in terms of different way and amounts of fertilizer addition.

4. In the last part of the discussion, this point may be highlighted, as the authors compared their data with the literature… This way, their weathering rate may be (slightly) overestimated. This other point is that in the literature most studies approach the weathering estimate from riverine data as the authors discussed.
Answer: we are pleased that you agree with that.

5 - L41 – 42 : "(…) processes including the reaction between carbonates and ~~the~~ protons derived (…)".
Changed in the manuscript: We removed " the".

6 - L 45 and 47: you may be more specific on the origin of sulfuric acid, and the role of acidic soil in the carbonate – proton relationship. "Acidic soil" is still too broad.

Changed in the manuscript: changing into **"**sulfuric acid forming in the oxidation of reduced sulfuric minerals (mainly pyrite, FeS_2),……. acidic soil (such as red soil, yellow soil) "

7 - L55, you may add the increase proportion of mineral fertilizers (increase by 365%), in order to compare with the 3.3% worldwide increase… I was wondering what was the cause of such sharp increase in chemical fertilizers consumption. Is it just an effect of the increase of the size of agricultural land or is it a consequence of a change of fertilizer habit (more NO3 or NH4 fertlizers)?

Answer: The primary reasons why we set up the amount of added fertilizer in this study are: (1) the soil we used is untilled 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.

8 - L118 - 119: You worked on Guizhou area where the consumption of chemical fertilizers increased by about 26% (far less than the increase of fertilizer consumption at the scale of the whole country).
Answer: It is true that according to the 2014 Guizhou statistical yearbook.

9 - L121: Could you be more specific for the soil classification, more precise than B horizon?

Changed in the manuscript: we added ″yellow-brown clay″.

10 - L123: did you crush (ground) the sample before to pass it through 2 mm sieve? Or did you pass the air - dried soil through 2 mm sieve, and after you crushed it… this may seem to be a detail, but it is really important.
Answer: all of soil samplers we sampled were ground first, and then sieved.

11 - L141: Did you have any silt or clay loss with a 0.5 mm net at the bottom of your column? Did you add some quartz wool in addition to the sand "filter" above the PE net?
Answer: we didn't consider the clay loss with the smaller particle. We will consider the quartz wool material as the member of filters in future studies. Thank you so much for your suggestions.

12 - L142 - 143: "Two different carbonate rock tablets were buried in the bottom of each soil column"; by this, do you mean that you put only one tablet of two different carbonate rocks? So the carbonate rocks are different, or are they two aliquots of the same rock type?
Answer: yes, we placed only one tablet of each carbonate rock in one column, but we designed 3 columns for each treatment as replicates. The carbonate rocks are different absolutely got from different area.

13 - L145 - 150: How did you determine the weight of each chemical fertilizer applied on each soil experiment?
Answer: The primary reasons why we set up the amount of added fertilizer in this study are: (1) the soil we used is untilled 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.

In order to short the time of this experiment, and also considering the low nutrients of the fresh soil, we have added the amount of N, P and K fertilizer in local practical use in this manuscript like this: (N fertilizer: 160 kg N · ha-1; P fertilizer: 150 kg P2O5 · ha-1; K fertilizer: 50 kg K · ha-1). According to the chemical formula and the molecular weight of each fertilizer, we finally calculated the amount of added fertilizer for each treatment.

14 - L151 - 152: you did mix each fertilizer with air - dried soils. So the fertilizer was not spread on the column? As soil and fertilizers were perfectly mixed, did you also crush the chemical fertilizers or did you leave them in their original shapes?

Answer: All the fertilizers are small granular with homogeneous size. They were perfectly mixed with soil. Undeniably speaking, the fertilizer may be spread partly on the wall of column in some cases, but we believe that its effect on our experiment results can be ignored. We will think it about in our further researches

15 - L158 - 159: you used 2 carbonate types: a limestone and a dolostone. Did you put one tablet of each carbonate in the same column, or did you put 2 tablets of the same carbonate (in order to have duplicates) in the same column?

16 - L176: This is at this point that we know that you have triplicates. How did you obtain these triplicates: did you use different columns for replicates, or are they in the same columns… It is important in order to understand on which data you performed a statistical analysis. How many columns did you in total?

Answer for 15 and 16: we placed only one tablet of each carbonate rock in one column, but we designed 3 columns for each treatment as replicates.

17 - You should add "respectively" at the end of your sentence when you're listing some results…

Changed in the manuscript: we added it.

18 - L189: the "rest treatments"? do you mean the other chemical fertilizers other than NH_4NO_3, NH_4Cl, $(NH_4)_2CO_3$, NH_4HCO_3?

Answer: yes, it is pointing the other chemical fertilizers than urea, NH_4NO_3, NH_4Cl, $(NH_4)_2CO_3$, NH_4HCO_3.

Changed in the manuscript: The English language editor in Elsevier suggested us changing it into the remaining treatment, we did it.

19 - L206: you explain that there is no difference in the weathering behavior of limestone and dolostone, however the control experiment show different behavior. Did you test this similarity?

Answer: yes, it is true that there is a difference between limestone and dolostone in control treatment. But we plotted the Rw of limestone vs. dolostone tablets in a linear correlation diagram, the results show that the Rw of limestone and dolostone exhibit a high positive correlation (R^2=0.9773; see Fig. 4), indicating that the weathering of limestone and dolostone are similar under different treatments.

Changed in the manuscript: see the details in the manuscript.

20 - L213 - 215: you may present these 3 equations in the following order: (5) > (4) > (3), following an increasing pKa (or pH).

Changed in the manuscript: we changed it**.**

21 - L218: H2CO3 is not only formed in the soil, it is first formed in the atmosphere with the dissolution of atmospheric CO2(g) into rain droplets and rain, as CO2aq and then H2CO3. The concentration of H2CO3 is exacerbated into soil because of the presence of organic CO2 from respiration. And yes, one of the main control of carbonate dissolution is the amount of rainfall.
That's why is it important to know how the different columns were placed in the field, randomly or the same modalities were placed together (L223 - 224). If randomly, you can say that rainfall may not be consider a controlling effect for your experiment.
Answer: Thank you very much. It is true that the rainfall is a main controlling factor in the natural weathering processes. The rate of chemical weathering is higher in high-precipitation area. However, in this study, we placed orderly the different treatments columns including replicated treatments in one specific place of field. To each treatment, the precipitation is same. So we conclude that the difference in weathering rate in each treatment is not caused by the precipitation. That's what we are meaning.
Changed in the manuscript: We changed it to make it clearer, see the manuscript.

22 - L231 - 232: you may be more precise for "CO_2 degassing"… Issued from carbonate dissolution? For respiration?
Answer: In theory, the source of CO_2 dissolved in water is from respiration (common cases), deep crust (tufa formation; areas where have thermal mineral spring), artificial source (CO2 capture and storage), etc. It is another big problem. No matter where they come from, these CO_2 usually keep in their balance status in specific stratum. Some of them keep their balance in H_2O-CO_2-HCO_3-carbonate system in water. Dramatic changes in the parameters of the CO_2 system such as T, pH and/or pCO_2 can cause CO_2 degassing. Here, we just listed some cases which can result in $CaCO_3$ precipitation.

Changed in the manuscript: we added some information like this "the degassing of dissolved CO_2 due to dramatic changes in the parameters of the CO_2 system (such as T, pH, pCO_2, etc)"

23 - L244: the year of the publication from Singh et al is missing.
Changed in the manuscript: it was added.

24 - L305: you did calculate the initial fertilizer –derived NH4 per unit. But it would be interesting to have the initial rate of fertilizer spread in the field and to compare it with what it is really applied in the Chinese agricultural watersheds.
Answer: The reason why Table 4 was given is mainly to better understand the N balance of these fertilizers in their own reactions listed in table 3, to interpret how many NO_3 derived from nitrification to further evaluate the effect of fertilizer on carbonate weathering.
Yes, we believe that the comparison between the addition amount of fertilizer in this study and that in practical agricultural activity of local area is very interesting question. But it is another interesting question. It has a little difficult to do it here and make it sense since it needs another experiment design. We will consider conducting some experiment to fill the gaps between them in the future.

25 - L396 - 397: - Table 2: what is the significance of a, b, c behind the numbers

(ANOVA)?

Answer: we deleted them and plotted the Rw of limestone vs. dolostone tablets in a linear correlation diagram (R2=0.9773; see Fig. 4) instead to further explain it. See the manuscript.

Reviewer 2

1. In the methods section, very few data seem to have been collected from the soils during the experiment. For example was pH monitored? This is an important parameter and would have helped the authors determine which mechanism is responsible for their results.

Answer: Before experiment, we tested the parameter of soil we used including soil pH organic matter (OM), NH_4-N, NO_3-N, available P, available K, available Ca, available Mg, available Fe, and available S. The results were listed in Table 1.
As you mentioned, we regret pretty much that we didn't monitor their change by testing them after experiment.

2. The authors carry out experiments on soil columns in a field setting. What exactly does this mean? Some photos of the experimental setup might help explain.

Answer: The shape and inner structure of columns in this study were described in Fig. 2. We orderly placed them (11treatments*3 triplicates= 33 columns) in field (on line and row). No suitable pictures here.

3. The authors should discuss the role played by bacteria in the system. Presumably the fertilizers could have stimulated bacteria which may have increased respiration and CO2 concentrations in the soil. This might account for some of the enhanced weathering. Can this mechanism be assessed?

Answer: Thank you for your comment on this, the probability truly exits more or less here, but we think the effect on nitrification is more distinct according to the results in the urea, NH_4NO_3, NH_4HCO_3, NH_4Cl, and $(NH_4)_2CO_3$ treatments. It is very difficult to distinguish and quantify their contribution in this study. We may try to do it by some isotope methods.

Changed in the manuscript: we added relative statements in Section 4.1.
In theory, the fertilizers could stimulate bacteria, which may increase respiration and CO_2 concentrations in the soil, as a result, probable enhance carbonate weathering as Eq. (5).

4. There are no high resolution SEM images of the tablets before or after the experiment. This may help the authors understand the loss mechanisms a bit better. The authors focus solely on chemical dissolution, although recently it has been suggested that mechanical grain detachment in carbonate rocks is likely to be an important weathering pathway. Imaging might help identify such a process.

Answer: Your suggestion about SEM is very inspiring for us. We will use this method in our future study. We appreciate.

5. Why was the reason for selecting the specific amounts of fertilizer? There is no explanation at all. Does this correspond to the amounts typically applied to crops? Also if this is to simulate the agricultural application does it make sense to mix the fertilizer thoroughly into the soil?

Answer: The primary reasons why we set up the amount of added fertilizer in this study are: (1) the soil we used is untilled 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.

The amount is just for this comparison experiment. Undeniably, it is not perfect for linking this experiment with practical agricultural activities in local area. We are fixing on that. Some data and papers are in preparation.

6. What kind of limestone and dolostone were used? What was the grain size and composition for example? Again, some SEM images here would help.
Answer: As described in Methods section, the statement on carbonate rock tablets used in this study is that "Two different kinds of carbonate rock tablets (2 cm × 1 cm × 0.5 cm in size) were placed in the bottom of each soil column to examine the rate of carbonate weathering in the soil. The two different kinds of carbonate rock collected from the karst area of Huaxi District were: (1) limestone with 60-65 % micrite, 30-35 % microcrystalline calcite, and 2-3 % pyrite; and (2) dolostone with 98-99 % fine crystalline dolomite, 1 % pyrite, and trace quantities organic matter."

SEM image are a good advice for our further study. Thank you so much.

7. Although the authors use both limestone and dolostone they don't really discuss the differences in detail. For example, on the whole dolostone seems to weather more slowly than limestone, but there are some exceptions (ammonium carbonate for instance). Are the differences significant? If so, what do they mean?
Answer: Thank you for your comment on it. We note it and added some statement on it. But there are no more points to discuss further, we think.

Changed in the manuscript: We added the following statements in Section 3.2.
Fig. 3 shows that, on the whole, the ratios of dolostone weathering are smaller than those of limestone weathering except $(NH_4)_2CO_3$ treatment, exhibiting that dolostone weather more slowly than limestone under fertilization effects.
In Fig. 4, we plotted the R*w* of limestone vs. dolostone tablets in a linear correlation diagram, in order to compare the weathering responses of limestone with dolostone. The results show that the R*w* of limestone and dolostone exhibit a high positive correlation (R^2=0.9773; see Fig. 4), indicating that the weathering of limestone and dolostone are similar under different treatments. Thus, we will explain the results in terms of carbonates, rather than by way of the individual dolostone and limestone.

8. In the conclusions, the authors state that the fact that the ammonium phosphate and sodium nitrate treatments did not impact the weathering rate raises a new question. But they don't explicitly state what this question is. A similar phrase is used in the Abstract.
Changed in the manuscript: we noticed that and made it clearer, we used a colon instead of a full stop in Abstract section:
The results of $NaNO_3$ treatment raise a new question: the negligible impact of nitrate on carbonate weathering may result in overestimation of the impact of N-fertilizer on CO_2 consumption by carbonate weathering at the regional/global scale, if the effects of NO_3 and NH_4 are not distinguished.
In conclusion part: we added a pointing expression like: The question is: ……..

9. Figure 3 is a bit confusing because of all the lower case letters (a,b, bc etc) dotted all over. What do they mean? It's not explained in the caption. **Changed in the manuscript:** we deleted them and plotted the Rw of limestone vs. dolostone tablets in a linear correlation diagram (R2=0.9773; see Fig. 4) instead to further explain it. See the manuscript.

10. Finally, careful English language editing would significantly improve the paper. Apart from numerous grammatical errors, it may also help organize the discussion. For example the section 4.2 is a bit of a mess and does not flow at all.
Changed in the manuscript: we have re-edited the language question by the

Language Services of Elsevier.

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 is 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 their these discrepanciesdifferences are as of yet not still well-known so far. In this study, a field column experiment was employed conducted to explore the responses of carbonate weathering to the addition of different fertilizers addition. The eleven different treatments with three replicates including control, NH_4NO_3, NH_4HCO_3, $NaNO_3$, NH_4Cl, $(NH_4)_2CO_3$, $Ca_3(PO_4)_2$, $(NH_4)_3PO_4$, fused calcium-magnesium phosphate fertilizer (Ca-Mg-P), Urea and K_2CO_3 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 thesoil-filled columns. The results showed that the addition of urea, NH_4NO_3, NH_4HCO_3, NH_4Cl and $(NH_4)_2CO_3$ distinctly increased carbonate weathering, which was attributed to the nitrification of NH_4^+, $^+$. and tThe addition of $Ca_3(PO_4)_2$, Ca-Mg-P and K_2CO_3 induced carbonate precipitation due to the common ion effect. Whereas theThe addition of $(NH_4)_3PO_4$ and $NaNO_3$ addition did not significantly impact significantly on carbonate weathering. The results of

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NaNO$_3$ treatment seem to be raisingraise a new question: the negligiblelittle impact of nitrate on carbonate weathering may result in the overestimation of the impact of N-fertilizer on CO_2 consumption by carbonate weathering at the regional/global scale, if the effects of NO$_3$ and NH$_4$ are not distinguished. 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 CO_2 (Kump et al., 2000; Liu et al., 2010; Liu et al., 2011)(Kump et al., 2000; Liu et al., 2010; 2011)(Kump et al., 2000; Liu et al., 2010; 2011). The rRiverine hydro-chemical composition, such as the ratio of HCO_3^- and to Ca^{2+} + Mg^{2+}, is usually employed as an indicator to estimate the CO_2 consumption by natural carbonate weathering at the regional/global scale (Hagedorn and Cartwright, 2009; Li et al., 2009)(Hagedorn and Cartwright, 2009; Li et al., 2009)(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 CO_2 consumption estimation is introduced because the fluvial alkalinity, Ca^{2+} and Mg^{2+} may also be

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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-wWickmann 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)(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 forming in the oxidation of reduced sulfuric minerals (mainly pyrite, FeS_2) (Lerman and Wu, 2006; Lerman et al., 2007; Li et al., 2008; Li et al., 2009)(Lerman and Wu, 2006; Lerman et al., 2007; Li et al., 2008; Li et al., 2009)(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)(Lian et al., 2008)(Lian et al., 2008);, as well asand (iv) from acidic soil (such as red soil, yellow soil) (Chao et al., 2014; Chao et al., 2017)(Chao et al., 2014)(Chao et al., 2014). –Given the that atmospheric CO_2 is not the a unique weathering agent, differentiating the agent of carbonate weathering is more and more significant to enableimportant for the accurate budgeting of the net CO_2 consumption by carbonate weathering, especially in agricultural areas where mineral fertilizers are usedarea.

The world global average annual increase in mineral fertilizer consumption was 3.3 % from 1961 to 1997, and FAO's study predicts a 1 % increase per year until

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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~~ increasing consumption of ~~chemical~~ mineral fertilizers is a significant disturbance factor ~~of~~ in carbonate weathering and the carbon cycle. ~~Many~~ Several studies have ~~showed~~ shown that nitrogen fertilizer additions ~~aided~~ increased ~~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-~~w~~Wickmann et al., 2009; Probst, 1986; Semhi and Suchet, 2000; West and McBride, 2005)~~(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)(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,~~ ~~on~~in two small agricultural carbonate basins in south-western France, the Girou and the Gers, respectively (~~subtributary and~~ tributar~~y~~ies of the Garonne ~~river~~River~~, respectively~~). ~~For~~ In ~~lager basin level, such as~~ the Garonne ~~river~~ River ~~basin~~Basin, which is a large~~r~~ 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

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NH_4NO_3) represents up to 5.7-13.4 % and only 1.6-3.8 %– of the total CO_2 flux naturally consumed bytoof the carbonate dissolution, forin France and across the on a gglobal scale, respectively.

These estimated results estimates described above wereare usuallylargely based on calculations that assumeding that a single type of fertilizer (e.g. $(NH_4)_2SO_4$, NH_4NO_3, or NH_4Cl) was used throughout the whole basin that was considered. Howeverwere usually based on a hypothesis of individual fertilizer (e.g. $(NH_4)_2SO_4$, NH_4NO_3, or NH_4Cl) 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 % NO_3^- produced after the addition $(NH_4)_2SO_4$ and NH_4Cl is derived from the nitrification of NH_4^+, whilst comparatively, it is only 50 % after the addition of NH_4NO_3. The dDifferences of in NO_3^- sources may cause theproduce an evaluated deviation of in the impact of N-fertilizer addition on CO_2 consumption by carbonate weathering. Because, since the addition of different N-fertilizers (e.g. $(NH_4)_2SO_4$, NH_4NO_3, NH_4Cl, $NaNO_3$ or urea) may result in different contributions to carbonate weathering and relative products such as HCO_3^-, Ca^{2+} and Mg^{2+}. For phosphate fertilizer, the coprecipitation of phosphate ions with calcium carbonate may inhibit carbonate weathering (Kitano et al., 1978)(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 (NH_4 and NO_3), 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

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agricultural ~~force~~ impact on natural carbonate weathering, and to accurately evaluate the CO_2 consumption via carbonate weathering in agricultural areas.

~~Moreover, Tt~~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)~~(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 the laboratory, the carbonate-rock-tablet is employed to study the kinetics of calcite dissolution/precipitation (Dreybrodt et al., 1996; Liu and Dreybrodt, 1997)~~(Dreybrodt et al., 1996; Liu and Dreybrod, 1997)(Dreybrodt et al., 1996; Liu and Dreybrod, 1997)~~ and determine the rate of carbonate mineral weathering in the soil column (Chao et al., 2011)~~(Chao et al., 2011)(Chao et al., 2011)~~. However, in the field, it is also used to observe the rate of carbonate weathering and estimate~~d~~ CO_2 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)(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 CO_2 consumption by carbonate weathering at the regional/global scale, in ~~the~~ cases ~~of~~where there are insufficient representative data (Liu, 2011)~~(Liu, 2011)(Liu, 2011),~~. ~~our results show that~~ ~~yet i~~It is nonetheless ~~a~~the preferred ~~option~~method for the ~~condition controlled contrast~~comparative or stimulated experiment (Chao et al., 2011; ~~Chao et al.,~~ 2014; ~~Chao et al.,~~ 2017) ~~(Chao~~

~~et al., 2014; Chao et al., 2011)(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).~~

~~Thus~~Therefore~~, in order to observe their difference between the impacts of different fertilizer addition on carbonate weathering in soil, a~~ 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 impact~~s~~ 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~~ District of Guiyang ~~city~~City, Guizhou ~~province~~Province, SW China (26°23′N, 106°40′E, 1094 m ~~asl~~ASL). Guiyang, the capital city of Guizhou Province, is located in the central part of ~~The~~ the ~~Province~~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 km^2), with elevations ranging from 875 to 1655 m ~~above mean sea level~~ASL. Guiyang has a population of more than 1.5 million people, a ~~high~~ wide diversity of karstic landforms, ~~a~~ high elevations and low latitude, with a subtropical warm-moist climate, and an average annual ~~average~~ temperature of 15.3 °C and annual precipitation of 1200 mm (Lang et al., 2006)~~(Lang et al., 2006)(Lang et al., 2006)~~. A monsoonal climate often results in high precipitation during summer, with ~~and~~ much less during winter, although the humidity is often high ~~during~~ throughout most of the year (Han and Jin, 1996)~~(Han and Jin, 1996)(Han and Jin, 1996)~~. Agriculture is a major land use in order

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to produce the vegetables and foods in the suburbs of Guiyang (Liu et al., 2006)~~(Liu et al., 2006)(Liu et al., 2006)~~. The consumption of chemical fertilizer increased from ~~0.8~~ 150 kg/ha ~~Mt~~ in 1980 to ~~1.0~~190 kg/ha ~~Mt~~ in 2013 (GBS, 2014)~~(GBS, 2014)(GBS, 2014)~~.

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2.2 Soil properties

The soil used in this column experiment was ~~–~~yellow-brown clay, which sampled from the B horizon (below 20 cm in depth) of yellow-brown soil profile ~~in~~from ~~–dug from~~ a cabbage-corn or capsicum-corn rotation plantation in Huaxi ~~d~~District~~,–~~. ~~It~~The soil was air-dried, ground to pass through a 2-mm sieve, mixed thoroughly and used for the soil columns. The soil pH (V_{soil}:V_{water} = 1:2.5) ~~were~~ was determined by pH meter. The chemical characteristics of the soil, in~~–~~cluding organic matter (OM), NH_4-N, NO_3-N, available P, available K, available Ca, available Mg, ~~available S and~~ available Fe, and available S were determined according to the Agro Services International (ASI) ~~M~~method~~–~~ (Hunter, 1980)~~(Hunter, 1980)(Hunter, 1980),~~. OM was determined using an ~~where the~~ extracting solution ~~used for O.M.~~ contain~~ed~~ing 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~~ using ~~on~~ an ~~extraction~~ extracting solution of~~by–~~ 1 mol l^{-1} KCl solution, whereas available K, P and Fe were determined using an ~~extracted by~~ extracting solution containing 0.25 mol l^{-1} $NaHCO_3$, 0.01 mol l^{-1} EDTA, 0.01 mol l^{-1} NH_4F, and 0.005 % Superfloc 127~~,–~~. Finally, ~~and~~ available S was determined using an extracting solution of ~~ed by~~ 0.1 mol l^{-1} $Ca(H_2PO_4)_2$ and 0.005 % Superfloc 127. The results are shown in Table 1.

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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 polyvinylchloride (PVC) pipe (Fig. 2). A hole (Ø = 2 cm) ~~were~~ was ~~established~~ placed at the bottom of each column to discharge soil water from the ~~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 2 cm thick filter ~~sand~~ layer, ~~with 2 cm thickness~~ including gravel, coarse sand and fine sand, was spread ~~on~~over the net.~~-~~ Two different carbonate rock tablets were buried in the bottom of each soil column (Fig~~-~~. 2). ~~According to~~Based on 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 are ~~were set up~~: (1) control without fertilizer (CK); (2) 43g NH_4NO_3 fertilizer (CF); (3) 85g NH_4HCO_3 fertilizer (NHC); (4) 91g $NaNO_3$ fertilizer (NN); (5) 57g NH_4Cl fertilizer (NCL); (6) 51g $(NH_4)_2CO_3$ fertilizer (NC); (7) 52g $Ca_3(PO_4)_2$ fertilizer (CP); (8) 15g $(NH_4)_3PO_4$ fertilizer (NP); (9) 44g fused calcium-magnesium phosphate fertilizer (Ca-Mg-P); (10) 32g Urea fertilizer (U); and (11) 10g K_2CO_3 fertilizer (PP). ~~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 P· ha^{-1}; K fertilizer: 50 kg K· ha^{-1}).~~ ~~The~~An aliquot of 6 kg of soil was weighed (bulk density = 1.3 g/cm^3), mixed ~~perfect~~throughly with one of the above fertilizers,

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~~respectively,~~ and filled into its own column. This process was repeated for all three replicates of the 11 fertilizer treatments. The~~se~~ soil columns were labelled and placed orderly 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~~ placed in the bottom of each soil column to ~~explore~~ examine the rate of carbonate weathering in the soil. The two different kinds of carbonate rock collected from the karst area of Huaxi ~~d~~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 organic matter. All ~~of~~ the tablets were ~~baked~~ heated 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, ~~T~~they ~~y~~ tablets were ~~taken out~~removed carefully, rinsed, baked and weighed~~ after a whole year~~.

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

A~~c~~*w* = (W*i*-W*f*) (1)

R~~c~~*w* = (W*i*-W*f*)/ W*i* (2)

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$R_{acw} = (W_i - W_f)/(S*T)$ (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 Crorp, Princeton, USA). All results of carbonate weathering were reported as the means ± standard deviations (SD)means standard errors (SE) for the three replicationes. asStatistical analysis was performed using IBM SPSS 20.0 (Statistical Graphics Crop, Princeton, USA).

3. Results

3.1 The wWeathering rate of carbonate under different fertilized treatments

weathering of under different treatmentsThe amount (ARcw), and the ratio (Racw) and the rate (Racw) of limestone and dolostonecarbonate weatheringweare listed in Table 2. were listed The results showed that in Table 2, and the Rcw were plotted in Fig. 3. The results in Table 2 and Fig. 3 The results showed Tthe Acw, Rcw and Racw of carbonate weatheringlimestone and dolomite weathering under urea, NH_4NO_3, NH_4Cl, $(NH_4)_2CO_3$$NH_4HCO_3$, NH_4Cl and NH_4HCO_3 $(NH_4)_2CO_3$ 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, respectively, and much biggersignificantly greater than that under the control treatment 0.48 ± 0.14 ‰ (see Fig. 3,). In addition, the observed Rw of as

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~~observed in~~ dolo~~mite~~stone 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 ~~vs.~~ -0.31 ± 0.09 ‰ in the control treatment~~)~~. This ~~suggesting manifested~~clearly demonstrates that the addition of these five fertilizers ~~can aid and~~ increased the rate of ~~the chemical weathering of~~ carbonate weathering~~.~~.

The remaining ~~st~~ treatments ~~had~~made no significant differences in the R*w* and R~~*c*~~*aw* of limestone and dolo~~mite~~stone in comparison ~~with~~ to the control treatment (Fig. 3). ~~In~~ In the $(NH_4)_3PO_4$ treatment, the ~~*Acw*~~R*w*~~, and R*acw*~~ were only 1.08 ± 0.34 ‰~~, -0.0028g~~ and ~~-0.0007~~0.75 ± 0.21‰~~g~~ for limestone and dolomite, respectively, while the R*aw* were 4.00 ± 1.15 g·m^{-2}·a^{-1} ~~-1.08‰~~ and 1.00 ± 1.01~~-0.75~~ g·m^{-2}·a^{-1}~~‰~~ for limestone and dolomite, respectively~~,~~. These values are less than those under the other four NH_4-fertilizers, as mentioned above. The ~~*Acw*, *Rcw*~~ R*w* and R*a*~~*c*~~*w* in the $NaNO_3$ treatments failed to show ~~a remarkable~~ notable differences with the control treatment, ~~implying~~ exhibiting little effect of the $NaNO_3$ fertilizer addition on carbonate weathering (Fig. 3). –

~~However, e~~Except for the R*cw* of limestone approaching zero in the $Ca_3(PO_4)_2$ treatment~~ approaching zero~~, all the values of ~~the *Acw*,~~ R*cw* and R~~*ac*~~*aw*~~ of two different carbonate~~ in Ca-Mg-P~~ and~~, K_2CO_3 and $Ca_3(PO_4)_2$ treatments showed ~~a~~ negative values~~,~~. This ~~indicating~~ indicates that the addition of Ca-Mg-P~~-~~, K_2CO_3 and $Ca_3(PO_4)_2$ fertilizers ~~can lead~~led to ~~the~~ precipitation at the surface of the carbonate mineral, which can be explained by common ion effect.

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3.2 ~~The c~~Comparison of limestone of dolomite

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

In Fig. 4, we plotted the R*w* of~~In order to compare~~ ~~The result of~~ limestone ~~with~~vs. dolo~~mite~~stone tablets in a~~, we plotted Fig. 4, a~~ linear corre~~e~~lation diagram, in order to compare the weathering responses of ~~with the Rw of limestone vs. dolostone tablets~~limestone with dolostone. The results show~~s~~ that the R*w* of limestone and dolostone exhibit~~s~~ a high positive correla~~e~~tion (R^2=0.9773~~,~~; see Fig. 4), ~~suggest~~indicating that the weathering of ~~ANOVA was use the~~ limestone and dolostone are similar under different treatments ~~were similar~~. Thus, we will explain the results ~~with~~ in terms of carbonates, rather than ~~instead of~~ by way of the individual dolostone and limestone. ~~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 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**~~

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determine the rate of carbonate mineral weathering in soil column (Chao et al., 2011). However, in field, it is also used to observe the rate of carbonate weathering and estimated CO_2 consumption by carbonate weathering (Chao et al., 2014; Jiang and Yuan, 1999; Jiang et al., 2013; Plan, 2005). Although Liu (2011) argue that the carbonate-rock-tablet test may lead to the deviation of estimated CO_2 consumption by carbonate weathering at the regional/global scale in the case of insufficient representative data (Liu, 2011), 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 kKinetics 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):

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

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

$$MeCO_3 + H^+ \leftrightarrow Me^{2+} + HCO_3^- \qquad (46)$$

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

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

where Me = Ca, Mg. As Eq. (5) describes, atmospheric/soil CO_2 is usually ~~regard~~considered to be ~~as~~ the natural weathering agent of carbonate. In watersheds with calcite- and dolomite-containing bedrock, H_2CO_3 formed in the soil zone usually reacts with carbonate minerals, resulting in dissolved Ca, Mg, and HCO_3^- as described in Eq. (5) (Andrews and Schlesinger, 2001; Shin et al., 2014)~~(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)~~(Amiotte Suchet et al., 2003; Egli and Fitze, 2001; Kiefer, 1994)~~, in this study, we consider that the effect of rainfall is equal in each soil column, and hence is disregarded ~~unconsidered~~ as a controlling factor in weathering rate differences among these treatments~~in this study~~. In theory, the fertilizers could stimulate bacteria, which may increase respiration and CO_2 concentrations in the soil, as a result, probable enhance carbonate weathering as Eq. (5). However, ~~The~~ Eq. (~~4~~6) suggests that the proton from other origins, such as the nitrification processes of NH_4^+, as mentioned in the ~~i~~Introduction section, can play the role of weathering agent in agricultural areas. In this study, the urea, NH_4NO_3, NH_4HCO_3, NH_4Cl, and $(NH_4)_2CO_3$ amendments increased (10 to 17-fold) the natural weathering rate ~~of~~from 2.00 $g \cdot m^{-2} \cdot a^{-1}$ ~~from~~for limestone tablets in the control

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treatment (tTable 2). Thus, these increases are strongly relativeted to the effect of the proton released from the nitrification of NH_4^+. OnIn the contrarryst, the carbonate precipitation will occur as due to the backward reaction of the Eq. (5) in the following cases: (1) the degassing of dissolved CO_2 due to dramatic changes in the parameters of the CO_2 system (such as T, pH, *p*CO_2, etc),; (2) soil evapotranspiration; or (3) the common ion effect: the increase of Ca^{2+}, Mg^{2+} or CO_3^{2-} in a weathering-system with equilibrium between water and calcite (Calmels et al., 2014; Dreybrodt, 1988)(Calmels et al., 2014; Dreybrodt, 1988).

4.2 The mMain reactions and effects in different treatments

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

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

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

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

Although the study fromof Singh et al. (2013) 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)(Singh et al., 2013), yet the restremaining ammonium (NH_4^+) is mainly oxidized during nitrification in soil by autotrophic bacteria (, likesuch 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

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al., 2008)(Perrin et al., 2008).

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

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

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

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

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

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

Consequently, afterby combining Eq. (8) and Eq. (10) are combined, carbonate weathering by protons produced by nitrification iscan supposedly be expressed as to becomes (Eq. 11) (See details in Perrin et al., 2008 and Gandois et al., 2011).

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

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

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

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

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

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

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

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

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

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

(3) ~~The c~~Common ion effect: K_2CO_3 treatment

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

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

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

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

~~For~~In the $(NH_4)_3PO_4$ treatment, the reaction of carbonate weathering will occur according to Eq. (11) due to the nitrification of NH_4^+ ionized from the $(NH_4)_3PO_4$ fertilizer ~~will occur the nitrification~~. ~~Whilst t~~The PO_4^{3-} anion will exert an inhibition to calcite dissolution~~:~~, as calcium orthophosphate (Ca-P) precipitation is produce~~s~~d on the surface of calcite after the addition of PO_4^{3-} in soil (reaction: $Ca + PO_4 \rightarrow Ca\text{-}P$), resulting in inhibit~~ing~~ion of the calcite dissolution ~~of calcite~~.

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

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

4.3 The dDifference 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_4NO_3, NH_4HCO_3, NH_4Cl, $(NH_4)_2CO_3$ and $(NH_4)_3PO_4$ is 0.54 mole, 1.08 mole, 1.07 mole, 1.06 mole, and 0.03 mole, respectively (Table 4). The R*w* of limestone tablets and the initial amount of NH_4^+ per treatment are plotted in Fig. 45. A distinct relationship between them is observed, in that: the R*w* values in NH_4NO_3, NH_4HCO_3, NH_4Cl, $(NH_4)_2CO_3$ and urea treatments are bigg larger than in the control treatment, where the initial amount of NH_4^+ displaysyields similar results (Fig. 45). This suggests that carbonate weathering in NH_4NO_3, NH_4HCO_3, NH_4Cl, $(NH_4)_2CO_3$ and urea treatments are mainly attributed to the dissolution reaction described as Eq. (11). This process of carbonate weathering by protons released from nitrification has been proven by many studies, from the laboratory to the field (Barnes and Raymond, 2009; Bertrand et al., 2007; Biasi et al., 2008; Chao et al., 2011; Errin et al., 2006; Gandois et al., 2011; Hamilton et al., 2007; Oh and Raymond, 2006; Perrin et al., 2008; Semhi and Suchet, 2000; West and McBride, 2005)(Barnes and Raymond, 2009; Bertrand et

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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_4HCO_3 and $(NH_4)_2CO_3$ treatments are lowerless 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_4HCO_3 and $(NH_4)_2CO_3$, are easier to decompose and produce the NH_3 and CO_2 gases as followingaccording to Eq. (20) and (21), resulting in the amounts of fertilizer-derived NH_4 ofthat are lower than 1.07 moles.

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

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

The A*w* and R*w* in the $(NH_4)_3PO_4$ treatment, unlike in other NH_4-fertlizer treatments, had notdo not show a significant increase comparinged to wi the control treatment, which is not only owing to the low amount of added NH_4^+ in $(NH_4)_3PO_4$ treatment (0.3 mole,; see Table 4), but also more or less relative to the inhibition of phosphate (Chien et al., 2011; Wang et al., 2012)(Chien et al., 2011; Wang et al., 2012). After the addition of $(NH_4)_3PO_4$ in soil, calcium orthophosphate (Ca-P) precipitation will form on calcite surfaces, which is initiated with the aggregation of clusters leading to the nucleation and subsequent growth of Ca-P phases, at various pH values and ionic strengths relevant to soil solution conditions (Chien et al., 2011; Wang et al., 2012)(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, indicatinges that the addition of NO_3-fertilizer does not

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significantly influence carbonate weathering.

A notable issue herein is that the $NaNO_3$ treatment produces the same amount of NO_3^- (1.07 mole) as other NH_4 fertilizer (NH_4NO_3, NH_4HCO_3, NH_4Cl, $(NH_4)_2CO_3$ and urea), but it fails to impact on carbonate weathering, which ~~is~~ rais~~ing~~es a new problem. Eq. (5), usually considered as an expression for the natural weathering process of carbonate, is an important reaction ~~for~~ in 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 estimat~~ion~~es of CO_2 consumption by carbonate weathering at the regional/global scale (Hagedorn and Cartwright, 2009; Li et al., 2009)~~(Hagedorn and Cartwright, 2009; Li et al., 2009)~~. ~~At~~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)~~(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_4NO_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_4NO_3 reacts with 2 moles of carbonate, where only half of the NO_3^- originates from nitrification described as Eq. (8). This will result in a double overestimation o~~n~~f the contribution of ~~the~~ nitrification to carbonate weathering, and thus thereby mislead the estimation of CO_2 consumption ~~therein~~.

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At regional scales, ~~I~~if different fertilizers are~~ added~~ simultaneously added 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 ~~is~~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~~ These are~~ is~~ 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)~~(Zhang, 2011)~~, and with the results of 0.05-5.06 ‰ (for R*w*) and 1.08-136.90 g·m^{-2}·a^{-1} (for R*aw*) from the north slope of the Hochschwab ~~m~~Massif in Austr~~al~~ia (Plan, 2005)~~(Plan, 2005)~~, as determined ~~–~~using the limestone tablet method. But the R*aw* of 2.00 g·m^{-2}·a^{-1} is lower than the results ~~(~~of 7.0-63.5 g·m^{-2}·a^{-1} for R*aw*~~)~~ from Jinfo Mount~~i~~ain in Chongqing~~—of~~, China (Zhang, 2011)~~(Zhang, 2011)~~. These differences in carbonate weathering are mainly attributed to the different types of carbonate rock tablets, climate, micro-environments of soil, etc. The R*aw* of limestone in the N-fertilizers treatments ~~is~~are 20.57-34.71 g·m^{-2}·a^{-1}, similar to the weathering rate of carbonate in ~~O~~orchard (32.97 g·m^{-2}·a^{-1}) at Nongla, Manshan, Guangxi~~ of~~, China, wh~~ere~~ich usually involves~~ in~~ 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

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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)~~(Zeng et al., 2014)~~. The results from Semhi, et al. (2000) show~~s~~ th~~e~~at weathering rates of carbonate rock ~~by~~ using riverine hydro-chemical method are~~–~~ ~~about~~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 controlled~~comparative ~~contrast~~ or s~~t~~imulated experiments, while the riverine hydro-chemical method is appropriate for ~~the~~ regional investigations and estimations. According to the estimation from Yue et al. (2015), ~~T~~the enhanced HCO_3^- flux due to nitrification of NH_4^+ at Houzhai catchment of Guizhou ~~p~~Province would be 3.72 × 10^{5} kg C/year and account for 18.7 % of this flux in the entire catchment(Yue et al., 2015)~~(Yue et al., 2015)~~. This is similar to estimates from other small agricultural carbonate basins (12–26 %) in ~~S~~southwest France (Perrin et al., 2008; Semhi and Suchet, 2000)~~(Perrin et al., 2008; Semhi and Suchet, 2000)~~.

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5. Conclusions

The impact of the addition of different fertilizers (NH_4NO_3, NH_4HCO_3, $NaNO_3$, NH_4Cl, $(NH_4)_2CO_3$, $Ca_3(PO_4)_2$, $(NH_4)_3PO_4$, Ca-Mg-P, ~~U~~urea, and K_2CO_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_4NO_3, NH_4HCO_3, NH_4Cl, and $(NH_4)_2CO_3$ distinctly increased carbonate weathering, which was attributed to the nitrification of NH_4^+, ~~and~~while the addition of $Ca_3(PO_4)_2$, Ca-Mg-P and K_2CO_3 induced carbonate precipitation due to the common ion effect. ~~While t~~The addition of $(NH_4)_3PO_4$ and $NaNO_3$ ~~addition~~ did not impact significantly on carbonate weathering, where the former can be attributed to the low added amount of $(NH4)_3PO_4$,– and may be related to the inhibition of phosphate, ~~and~~ while the latter seemed to ~~be~~ raising~~e~~ a new question. The question is：~~T~~the ~~little~~minor impact of nitrate on carbonate weathering may result in the overestimation of the impact of N-fertilizer on CO_2 consumption by carbonate weathering at the regional/global scale, if the effects of NO_3 and NH_4 are not distinguished. Thus, the related anthropogenic inputs (e.g. Ca+ Mg, NH_4, NO_3^-, HCO_3^-, etc.) need to be investigated to more accurately estimate the impact of fertilization on carbonate weathering and its consumption of CO_2~~ 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):~~

~~$MeCO_3 + H^+ \rightarrow Me^{2+} + HCO_3^-$ (4)~~

~~$MeCO_3 + H_2CO_3 \rightarrow Me^{2+} + 2HCO_3^-$ (5)~~

~~$MeCO_3 \rightarrow Me^{2+} + CO_3^{2-}$ (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: s which can originate from the nitrification processes of N-fertilizerH_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 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 and 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_4NO_3, NH_4HCO_3, NH_4Cl and $(NH_4)_2CO_3$ amendment increased (10 to 17-fold) the natural weathering rate of 2.00 $g·m^{-2}·a^{-1}$ from limestone tablets in control treatment (table 2). 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

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Schlesinger, 2001).

According to the added amount of different fertilization treatment, the molar amount of added nitrogen nutrient in $NaNO_3$ treatment is 1.07mol, much bigger than in NH_4NO_3, equivalent to NH_4HCO_3 and NH_4Cl treatment. However, the A*cw* and R*cw*, and R*acw* of $NaNO_3$ treatment is far less (Fig. 3 and table 2), inhibiting that the increases of carbonate weathering rate in urea, NH_4NO_3, NH_4HCO_3, NH_4Cl and $(NH_4)_2CO_3$ amendment have no distinct relationship with enhanced microbiogenic CO_2 due to nitrogenous fertilizer amendment.

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4.3 The effect of nitrification of NH_4-fertilizer

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

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

Table 3 shows that the amount of NH_4^+ hydrolyzed from urea is 1.06 mol, while NH_4^+ ionized from NH_4NO_3, NH_4HCO_3, NH_4Cl, $(NH_4)_2CO_3$ and $(NH_4)_3PO_4$ is 0.54 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).

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

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

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

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

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

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

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

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

The R*cw* of limestone tablets and the initial concentration of NH_4^+ are plotted in Fig. 4. A distinct relationship between them is observed: the A*cw* and R*cw* 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 3.72×10^5 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_4NO_3, NH_4HCO_3, NH_4Cl, $(NH_4)_2CO_3$ and urea treatments will be followed as, respectively:

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

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

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

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

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

The *Acw* and *Rcw* in $(NH_4)_3PO_4$ 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 $(NH_4)_3PO_4$ treatment (0.3 mol, see Table 3) but also relative to the inhibition of phosphate. After the addition of $(NH_4)_3PO_4$ in soil, calcium orthophosphate (Ca-P) precipitation will form on calcite surface which is initiated with the aggregation of clusters leading to the nucleation and subsequent growth of Ca-P phases, at various pH values and ionic strengths relevant to soil solution conditions (Chien et al., 2011; Wang et al., 2012).

4.4 Little/no effect of NO_3-fertilizer on carbonate weathering and its implication to the evaluation of CO_2 consumption by carbonate weathering

In Fig. 3, the A*cw* and R*cw* without significant difference with control treatment in $NaNO_3$ treatment indicates that the addition of NO_3-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 HCO_3^- and Me^{2+} in the river as an indicator is usually used to make estimations of CO_2 consumption by carbonate weathering at the regional/global scale (Hagedorn and Cartwright, 2009; Li et al., 2009). At agricultural areas, the relationship between $(Ca+Mg)/HCO_3^-$ and NO_3^- is usually employed to estimate the contribution of N-fertilizer to riverine Ca^{2+}, Mg^{2+} and alkalinity (Etchanchu and Probst, 1988; Jiang, 2013; Jiang et al., 2009; Perrin et al., 2008; Semhi and Suchet, 2000). In these studies, the nitrification described as Eq. (8) is usually considered as the unique origin of NO_3^-. According to the result of $NaNO_3$ treatment in this study, the contribution of protons from nitrification to carbonate weathering may be overestimated if anthropogenic NO_3^- is neglected, since the anthropogenic NO_3^- does not release the proton described as Eq. (8). For NH_4NO_3 fertilizer, the (Eq. (12)) show that the two moles of $Ca^{2+}+Mg^{2+}$, NO_3^- and HCO_3^- will be produced when one mole NH_4NO_3 react with 2 moles of carbonate, where only half of NO_3^- originate from nitrification described as Eq. (8). This will result in 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 became 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_4NO_3, NH_4HCO_3, $NaNO_3$, NH_4Cl, $(NH_4)_2CO_3$, $Ca_3(PO_4)_2$, $(NH_4)_3PO_4$, Ca-Mg-P, Urea and K_2CO_3) on carbonate weathering was studied in a field column experiment with carbonate rock tablets at its bottom of each. The weathering amount and ratio of carbonate rock tablets showed that the addition of urea, NH_4NO_3, NH_4HCO_3, NH_4Cl and $(NH_4)_2CO_3$ distinctly increased carbonate weathering, which was attributed to the nitrification of NH_4^+, and the addition of $Ca_3(PO_4)_2$, Ca-Mg-P and K_2CO_3 induced carbonate precipitation due to common ion effect. While the $(NH_4)_3PO_4$ and $NaNO_3$ addition did not impact significantly on carbonate weathering, where the former can be attributed to low added amount of $(NH4)_3PO_4$, may be related to the inhibition of phosphate, and the latter seemed to be raising a new question. The little impact of nitrate on carbonate weathering may result in the overestimation of impact of N-fertilizer on CO_2 consumption by carbonate weathering at the regional/global scale if the effect of NO_3

and NH_4 are not distinguished. Thus, the related anthropogenic inputs (e.g. Ca+ Mg, NH_4, NO_3^-, HCO_3^-, etc.) need to be investigated to more accurately estimate the impact of fertilization on carbonate weathering and its CO_2 consumption. 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

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

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Table 1 Chemical composition of soil

Parameter	Unit	Values
pH	-	6.94
Content of particles (<0.01mm)	%	74
Content of particles (<0.001mm)	%	45
Organic matter	%	0.99
NH_4^+-N	mg/kg	339.87
NO_3^--N	mg/kg	569.05
Available P	mg/kg	8.18
Available K	mg/kg	56.88
Available Ca	mg/kg	3041.06
Available Mg	mg/kg	564.83
Available S	mg/kg	100.72
Available Fe	mg/kg	24.41

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Table 2 Carbonate weathering under different fertilizer treatments

Treatment	Limestone ~~Acw~~ Rw / ‰~~g~~	Limestone Raw / g·m^{-2}·a^{-1} ~~Rcw /‰~~	Dolostone ~~Acw~~ Rw / ‰~~g~~	Dolostone Raw / g·m^{-2}·a^{-1} ~~Rcw /‰~~
Control	0.~~001~~448 ± 0.14~~a~~	2.00 ± 0.58~~a0.48~~	-0.~~001~~131 ± 0.09~~a~~	-1.57 ± 0.86~~a -0.31~~
NH_4NO_3	~~0.0174~~6.42 ± 0.28~~c~~	24.86 ± 2.01~~b~~ ~~6.42~~	~~0.0144~~5.30 ± 0.87~~c~~	20.57 ± 1.15~~b5.30~~
NH_4HCO_3	~~0.0147~~4.44 ± 0.81~~b~~	21.00 ± 3.45~~b~~ ~~4.44~~	~~0.0096~~3.22 ± 0.87~~b~~	13.71 ± 3.88~~b3.22~~
$NaNO_3$	~~0.003~~10.86 ± 0.17~~a~~	4.43 ± 1.73~~a0.86~~	0.~~002~~253 ± 0.26~~a~~	3.14 ± 1.73~~a0.53~~
NH_4Cl	~~0.0149~~5.54 ± 0.64~~bc~~	21.29 ± 2.45~~b~~ ~~5.54~~	~~0.0131~~4.77 ± 0.78~~bc~~	18.71 ± 0.86~~b~~ ~~4.77~~
$(NH_4)_2CO_3$	~~0.0144~~4.48 ± 0.95~~bc~~	20.57 ± 4.46~~b~~ ~~4.84~~	~~0.0186~~4.94 ± 1.91~~bc~~	26.57 ± 7.62~~b4.94~~
$Ca_3(PO_4)_2$	~~0.0003~~0.01 ± 0.04~~a~~	0.43 ± 0.86~~a0.01~~	-0.~~001~~355 ± 0.25~~a~~	-1.86 ± 1.29~~a -0.55~~
$(NH_4)_3PO_4$	~~0.0028~~1.08 ± 0.34~~a~~	4.00 ± 1.15~~a1.08~~	~~0.0007~~0.75 ± 0.21~~a~~	1.00 ± 1.01~~a0.75~~
Ca-Mg-P	~~-0.0013~~-0.31 ± 0.12~~a~~	-1.86 ± 0.43~~a -0.31~~	-0.~~002~~297 ± 0.38~~a~~	-3.14 ± 0.72~~a -0.97~~
Urea	~~0.0243~~8.48 ± 0.96~~d~~	34.71 ± 4.32~~c~~ ~~8.48~~	~~0.0185~~6.59 ± 0.67~~d~~	26.43 ± 2.73~~c6.59~~
K_2CO_3	-0.~~000~~826 ± 0.15~~a~~	-1.14 ± 0.58~~a -0.26~~	-0.~~001~~859 ± 0.15~~a~~	-2.57 ± 0.43~~a -0.59~~

~~Acw - the amount of carbonate weathering;~~ R~~c~~w - the ratio of carbonate weathering; Ra~~c~~w - the rate of carbonate weathering; ~~Acw~~ Rw =1000 (Wi-Wf)/Wi; ~~-~~ and ~~Rcw = (Wi-Wf)/Wi,~~ Ra~~c~~w = (Wi-Wf)/(S*T), where Wi is the initial weight of the carbonate rock tablet~~s~~, and Wf is the~~ir~~ final weight. S is the surface area of carbonate ~~weathering~~ rock tablet~~s~~ (~~In this study~~here, we used ~~a same~~ S = 7 cm^2 for every tablet~~s~~), 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.~~

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~~Table 3: The main reaction and effects in fertilized treatments, and the potential nitrogenous transformation (The amount of generated NH_4^+-NO_3^-) at the initial phase of the experiment~~

~~Treatment~~	~~Main reactions and effects~~
~~1.Control~~	~~$Ca_{(1-x)}Mg_xCO_3 + CO_2 + H_2O \rightarrow (1\text{-}x)\ Ca^{2+} + xMg^{2+} + 2HCO_3^-$~~
~~2.NH_4NO_3~~	~~$2Ca_{(1-x)}Mg_xCO_3 + NH_4NO_3 + 2O_2 \rightarrow 2(1\text{-}x)\ Ca^{2+} + 2xMg^{2+} + 2NO_3^- + H_2O + 2HCO_3^-$~~
~~3. H_4HCO_3~~	~~$2Ca_{(1-x)}Mg_xCO_3 + NH_4HCO_3 + 2O_2 \rightarrow 2(1\text{-}x)\ Ca^{2+} + 2xMg^{2+} + NO_3^- + H_2O + 3HCO_3^-$~~
~~4. $NaNO_3$~~	~~$Ca_{(1-x)}Mg_xCO_3 + NaNO_3 + CO_2 + H_2O \rightarrow (1\text{-}x)\ Ca^{2+} + xMg^{2+} + Na^+ + NO_3^- + 2HCO_3^-$~~
~~5. NH_4Cl~~	~~$2Ca_{(1-x)}Mg_xCO_3 + NH_4Cl + 2O_2 \rightarrow 2(1\text{-}x)\ Ca^{2+} + 2xMg^{2+} + NO_3^- + Cl^- + H_2O + 2HCO_3^-$~~
~~6. $(NH_4)_2CO_3$~~	~~$3Ca_{(1-x)}Mg_xCO_3 + (NH_4)_2CO_3 + 4O_2 \rightarrow 3(1\text{-}x)\ Ca^{2+} + 3xMg^{2+} + 2NO_3^- + 2H_2O + 4HCO_3^-$~~
~~7. $Ca_3(PO_4)_2$~~	~~(1) Common ion effect: The $Ca_{(1-x)}Mg_xCO_3$ produces when the concentrations of Ca^{2+} and Mg^{2+} increases~~ ~~$(1\text{-}x)\ Ca^{2+} + xMg^{2+} + 2HCO_3^- \rightarrow Ca_{(1-x)}Mg_xCO_3 + CO_2 + H_2O$~~ ~~(2) Inhibition of phosphate to calcite precipitation: calcium phosphate precipitation produces on the surface of calcite after the addition of PO_4^{3-} in soil, resulting in inhibiting the precipitation of calcite~~
~~8. $(NH_4)_2PO_4$~~	~~(1) $2Ca_{(1-x)}Mg_xCO_3 + NH_4^+ + 2O_2 \rightarrow 2(1\text{-}x)\ Ca^{2+} + 2xMg^{2+} + NO_3^- + H_2O + 2HCO_3^-$~~ ~~(2) Inhibition of phosphate to calcite dissolution: calcium orthophosphate (Ca-P) precipitation produces on surface of calcite after the addition of PO_4^{3-} in soil, resulting in inhibiting the dissolution of calcite~~
~~9. Ca-Mg-P~~	~~(1) Common ion effect: The $Ca_{(1-x)}Mg_xCO_3$ produces when the concentrations of Ca^{2+} and Mg^{2+} increases~~ ~~$(1\text{-}x)\ Ca^{2+} + xMg^{2+} + 2HCO_3^- \rightarrow Ca_{(1-x)}Mg_xCO_3 + CO_2 + H_2O$~~ ~~(2) Inhibition of phosphate to calcite precipitation: calcium phosphate precipitation produces on the surface of calcite after the addition of P in soil, resulting in inhibiting the precipitation of calcite~~
~~10. Urea~~	~~$3Ca_{(1-x)}Mg_xCO_3 + CO(NH_2)_2 + 4O_2 \rightarrow 3(1\text{-}x)\ Ca^{2+} + 3xMg^{2+} + 2NO_3^- + 4HCO_3^-$~~
~~11. K_2CO_3~~	~~Common ion effect: The $Ca_{(1-x)}Mg_xCO_3$ produces when the concentration of HCO_3^- increases~~ ~~(i) $(1\text{-}x)\ Ca^{2+} + xMg^{2+} + 2HCO_3^- \rightarrow Ca_{(1-x)}Mg_xCO_3 + CO_2 + H_2O$~~ ~~(ii) $K_2CO_3 + H_2O \rightarrow 2K^+ + HCO_3^- + OH^-$~~

Table 3: –The main reaction and effects in these 11 fertilizeder treatments

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

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

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

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

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

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

~~w~~nd=~~without~~no data~~;~~. The amount of added fertilizer (g) divided by its molecular mass (g/mol) ~~wa~~is the molar amount of fertilizer (mole)~~;~~. ~~Gadf gram amount of added fertilizers (g); Maafof added fertilizers (mol).~~The amounts of fertilizer-derived NH_4^+ ~~is~~are calculated by their own ionization or hydrolysis processes. The maximum of N products is estimated by their main reactions in ~~t~~Table 3.

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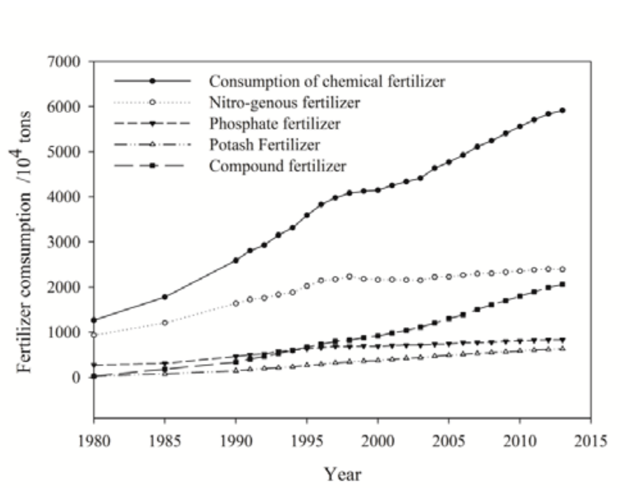

Fig. 1 The change ~~of~~ in chemical fertilizer consumption in China during the 1980-2013 period

The data were collected from National Bureau of Statistics of the People's Republic of China (NBS, 2014)~~(NBS, 2014)(NBS, 2014)~~ (http://www.stats.gov.cn/tjsj/ndsj/)

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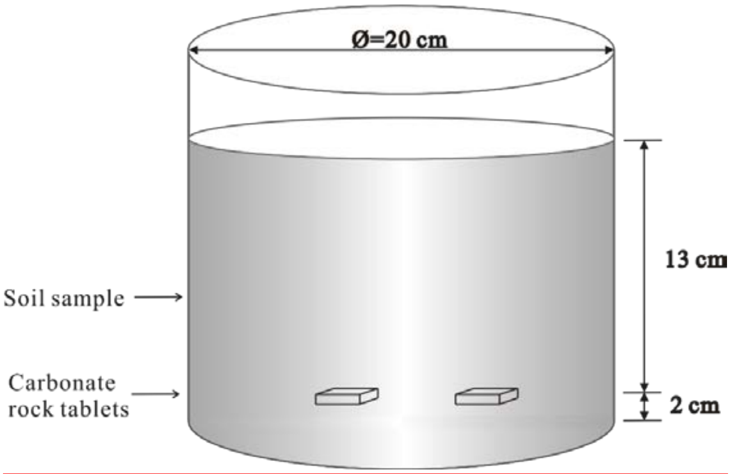

Fig. 2 Sketch ~~map~~ of the soil column with rock tablets

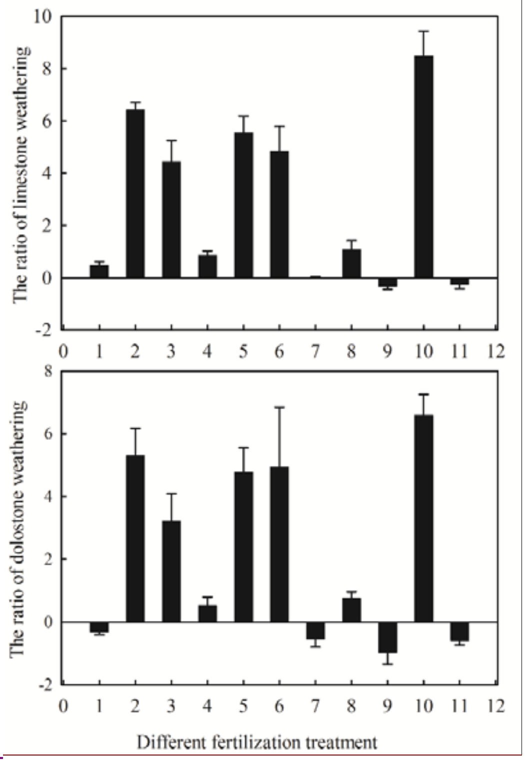

Fig. 3 The ratio of carbonate weatheringRw (‰) of limestone and dolostone –under different fertilization fertilizer treatments

(a) limestone; (b) dolostone. Treatment 1-. Control; 2-. NH_4NO_3; 3-. NH_4HCO_3; 4-. $NaNO_3$; 5-. NH_4Cl; 6-(. $(NH_4)_2CO_3$; 7-. $Ca_3(PO_4)_2$; 8-(. $(NH_4)_3PO_4$; 9-. Ca-Mg-P; 10-. Urea; 11-. K_2CO_3. Rcw = 1000(W*i*-W*f*)/W*i*, where W*i* is the initial weight of the carbonate rock tablets, and W*f* is theirir final weight. Values in each column followed by different letters are significantly (p <0.05) different based on one-way ANOVA.

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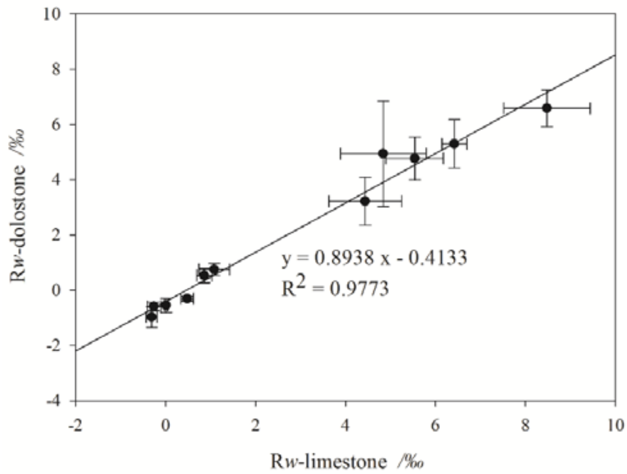

Fig. 4 The linear correlation of Rw (‰) of limestone and dolostone
Rw = 1000(Wi-Wf)/Wi, where Wi is the initial weight of the limsestone tablets, and Wf is their final weight.

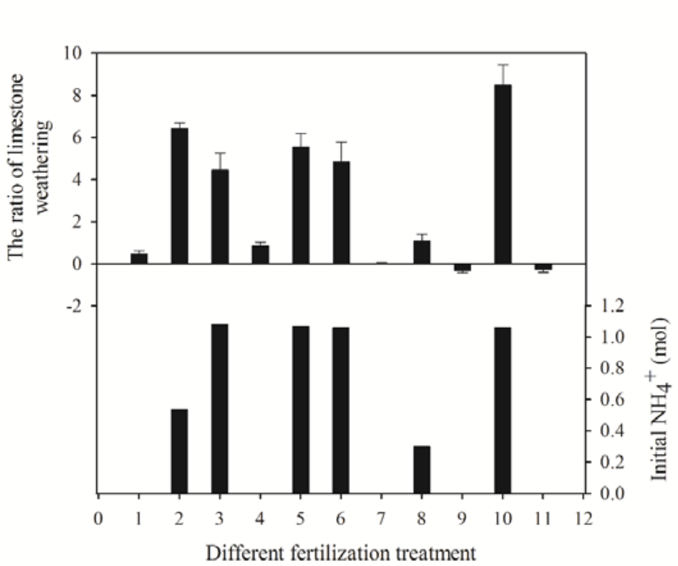

Fig. ~~4~~ 5 The R*w* (‰) of limestone ~~ratio of limestone weathering~~ and the molar amount of produced NH_4^+ under different ~~fertilization~~ fertilizer treatments

Treatment 1~~-~~. Control; 2~~-~~. NH_4NO_3; 3~~-~~. NH_4HCO_3; 4~~-~~. $NaNO_3$; 5~~-~~. NH_4Cl; 6~~(~~. $(NH_4)_2CO_3$; 7~~-~~. $Ca_3(PO_4)_2$; 8~~(~~. $(NH_4)_3PO_4$; 9~~-~~. Ca-Mg-P; 10~~-~~. Urea; 11~~-~~. K_2CO_3. R~~e~~*w* =1000(W*i*-W*f*)/W*i*, where W*i* is the initial weight of the lim~~s~~estone tablet~~s~~, and W*f* is the~~ir~~ final weight.

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