Responses to Referee 1

Comment 1: Could authors provide the ratio of the nitrate fertilizer vs. total nitrogen fertilizers in studied area, or China, or whole world? It is important for the significance of the manuscript and the experiment.

Answer: Yes, it is very important, but we can't find the specific published data about it. Only one figure we can calculate according to a reference published in 2008 is that the global production of NH_4NO_3 accounts for 10% of the total N fertilizers, and about 4% in China. But we think this figure is not fit to be cited in this manuscript. We think that this study only focused on the relative potential mechanism, and the study on the estimation of the impacts will be considered in the future.

Comment 2: Could authors compare results with data by Prof. Yuan DX's group paper ?

Answer: We have cited the relative result from Prof. Yuan Dx's group in this study, such as the papers from Jiang Z., et al.; Liu Z., et al. and Jiang Y., et al.. In fact, we are familiar with them and their study focuses, we know that their studies are a little bit different from ours so far.

Comment 3: The manuscript need more detail for the experiment. L134-L139: Please give a detail introduction for the added amount of fertilizers in these treatments. It seems that the added amount of nitrogen is slight difference.

(1) What's the proportion of these eleven fertilization treatments in local practical use?

Answer: The added amounts of these 11 fertilizers were designed only by the average amount of N, P and K fertilizer in the local practical use.

Changed in the manuscript: 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 $\cdot$ha^{-1}; P fertilizer: 150 kg P_2O_5 $\cdot$ha^{-1}; K fertilizer: 50 kg K $\cdot$ha^{-1})

(2) Why choose the added amount of fertilizers are 30 times than its local practical amount? The application fertilizers in local practical may change two or three times to use. Do you think the added fertilizers by one time may affect the result?

Answer: Because the added amount of fertilizer can magnify and quicken the fertilization effect in the short-term according to another experiment from us, and can't affect the phenomenon we want to observe in this study. Another paper of ours (in preparation) about a series of different amount of fertilizer addition will discuss this issue.

(3)Why don't authors set different height for this experiment, which might be more interesting?

Answer: Thank you for your good suggestion. This study is conducted as a simply start. The suggestion on different height must be interesting. We are considering that in further study.

(4)Does author consider that the land use influences the carbonate weathering in the experiment?

Answer: In fact, there are some good studies to be published about that around the world. But most of them are conducted by the search and evaluation of riverine hydro-geochemical data. Because of this, we did this study from another angle, and hope to connect them in the future.

Comment 4: The authors made three replications. So please show the data errors for each average value.

Answer: Fig.3 has showed these error bars. We will add them in Table 2.

Changed in the manuscript: The error data have been added in Table 2.

Comment 5: Could you assess the variation of nitrate fertilizer change in the column. Then understand the balance between acid producing and carbonate weathering together.

Answer: We tried our best to explain the chemical process of N fertilizer in section 4.3 with relative chemical reactions.

Comment 6: Line 15-17, the sentence has too many “different”s. Please revise it.

Changed in the manuscript: We use “these discrepancies” instead of “their differences”.

Comment 7: In section 2.2, could authors provide details about abbreviation of OM, ASI method and others when you write that at the first time. Please check that in whole manuscript.

Changed in the manuscript: We have changed this.

Comment 8: L162-166 It seems Table 2 and Fig3 are repeated.

Changed in the manuscript: We deleted the relative data in Table 2, and leave the Fig. 3 because the figure is easier to see. And we also changed corresponding texts.

Comment 9: L182-L197 This paragraph can be removed to the introduction.

Changed in the manuscript: We moved them to the introduction.

Comment 10: L213-L219 It is repeated the introduction (L49-L54).

Answer: Because they are for elaborating different problem, we think we should put one of them another way.

Changed in the manuscript: We changed the statements in section 4.2.

Comment 11: Major conclusion might be revised. Ammonium fertilizer mainly includes NH4NO3, NH4Cl, (NH4)2CO3 fertilizers, not includes urea fertilizer. I suggest reductive nitrogenous fertilizer could enhance carbonate weathering via nitrification.

Changed in the manuscript: Yes, the statement that nitrogenous fertilizer can aid carbonate weathering should be replaced by ammonium fertilizer” in this manuscript is not precise. We deleted it.

Responses to Referee 2

Comment 1 - The authors did not present very well the process/method of weathering which has been used in this experiment: (1)did the authors perform a leaching of the soil column? How are the fertilizers introduced in the soil column? Are spread mixed with soil or spread in solutions? The lack of explanation of the method used does not allow us to assess the results at their fair value. There is also a lack of discussion and comparison of numerical values obtained in other experiments and in natural and agricultural catchments. The carbonate weathering is only estimated based on the weight of each rock tablets. It is not checked by the geochemistry of both rock tablets and the potential weathering/soil solution. Indeed, it would have been interesting to have an estimation of the chemical weathering.

Answer: The fertilizer was mixed with soil before filling in columns.

Changed in the manuscript: We added a sentence to explain this. The soil was weighed, mixed perfectly with above fertilizer, respectively, and filled in its own column.

Comment 2 – To speed up the carbonate weathering, the fertilizers were introduced by increasing their amount by 30 times (Why 30 times?). It is a bit problematic, because the authors changed the soil/fertilizers ratio compared to "natural/anthropogenic" ratio? What is this ratio in the local agricultural catchments? What are the specificities these local catchments compared to national Chinese catchments and worldwide catchments?

Answer: Because the added amount of fertilizer can magnify and quicken the fertilization effect in the short-term according to another experiment from us, and can't affect the phenomenon we want to observe in this study. Another paper of ours (in preparation) about a series of different amount of fertilizer addition will discuss this issue. The added amounts of these 11 fertilizers were designed only by the average amount of N, P and K fertilizer in the local practical use.

Changed in the manuscript: 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 $\cdot ha^{-1}$; P fertilizer: 150 kg $P_2O_5 \cdot ha^{-1}$; K fertilizer: 50 kg K $\cdot ha^{-1}$)

Comment 3 – The variability of the experimental replicates should be shown (average and standard deviations), presented and discussed. This can be presented in Table 2.

Answer: We did it.

Comment 4 – In general, the authors used limestone and dolostone tablets. They did not discuss the results of dolostone tablets, only those from limestone tablets. In the discussion, the difference or similarity between dolostone and limestone is erased as the authors discuss about carbonates. More attention, or at least an explanation about the use of the general term of "carbonates" instead of the difference between dolostone and limestone should be given.

Answer: The difference between limestone and dolostone is not noteworthy, so we use carbonate instead. Yes, we need to give some sentences to explain this.

Changed in the manuscript: We added the statement "The result between limestone and dolostone weathering under different fertilization treatment were similar. We will explain the results with carbonates instead of individual dolostone and limestone." in this manuscript to explain

Comment 5: In several times in the manuscript (last sentence of the abstract, first paragraph of the results, and the last sentence of the conclusion) the authors used the expression "can aid carbonate weathering": they should precise if the fertilizers enhance, increase, or decrease carbonate weathering.

Changed in the manuscript: The statement that nitrogenous fertilizer can aid carbonate weathering should be replaced by ammonium fertilizer" in this manuscript is not precise. We deleted it. And we replaced the rest aids with the word "increase".

Comment 6: Introduction: - L.43 - The authors should add references showing the relationship between carbonate weathering and climate in addition to Liu et al. (2010, 2011); for example Kump et al., 2000). –

Changed in the manuscript: We added it.

Comment 7: L.47 - The authors should precise that the disturbance of CO_2 consumption disturbance may be overestimated at a local scale by taking into account Ca^{2+} and Mg^{2+} produced by a natural carbonate weathering and those produced indirectly by anthropogenic activities in the watershed. And what about this disturbance at a global scale?

Answer: Here, we are just trying to introduce the potential disturbance at the regional/global scales by summarizing and classifying some references in the 1^{st} paragraph. And the specific disturbances from fertilizer addition were further discussed in the 2^{nd} paragraph.

Comment 8: 2.2. Soil properties : - At which depth did the authors sample their soils? - Should precise pH(H2O) - Precise what OM means: organic matter I suppose. - Precise what ASI method means. - What is the soil typology?

Answer: The pH had been listed in Table 1.

Changed in the manuscript: The meanings of OM and ASI have been added. We changed the statement "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." to explain the soil samples and typology.

Comment 9: 2.3. Soil column - What is the filter material?

Answer: Yes, it is a misleading expression here.

Changed in the manuscript: It has been changed into: A Polyethylene net (Ø 0.5 mm) was placed in the bottom of the columns to prevent soil loss. A filter sand layer with 2 cm thickness including gravel, coarse sand and fine sand was spread on the net.

Comment 10: What kind of carbonate rocks did the authors use for their experiment? Are they reference rocks or rocks from karst area of HuaXi district?

Answer: yes, it was collected from karst area of Huaxi district.

Changed in the manuscript: We added this information in this manuscript.

Comment 11: How did the authors deposit each fertilizer in the column? In liquid or solid form? At which temperature has the experiment been performed? - Did you leach the soil column with a solution? If yes, with which solution?

Answer: The soil fertilizer was weighed and mixed with soil before filling in columns. Changed in the manuscript: We added a sentence to explain this. The soil was weighed, mixed perfectly with above fertilizer, respectively, and filled in its own column.

Comment 12: **-** In figure 2: the authors draw 3 rock tablets, while the authors put only 2 rock tablets at the bottom of the column. Should change it.

Changed in the manuscript: We have changed this.

Comment 13: **-** Did the authors perform the same experiment without rock tablets if they leach their column in order to observe the leaching solution of the column?

Answer: We didn't design that in this study. We didn't collect the soil solution. The leaching depended on the rainfall.

Comment 14:**-** Did the authors put the 2 different rock tablets (calcite and dolomite) in the same column?

Answer: Yes, we did.

Comment 15: The authors should explain the reason of the fertilizer weight use in the experiment.

Answer: Because the added amount of fertilizer can magnify and quicken the fertilization effect in the short-term according to another experiment from us, and can't affect the phenomenon we want to observe in this study. Another paper of ours (in preparation) about a series of different amount of fertilizer addition will discuss this issue. The added amounts of these 11 fertilizers were designed only by the average amount of N, P and K fertilizer in the local practical use.

Changed in the manuscript: 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 $\cdot$ ha^{-1}; P fertilizer: 150 kg P_2O_5 $\cdot$ ha^{-1}; K fertilizer: 50 kg K $\cdot$ ha^{-1})

Comment 16: 3. Results - L.164-165: Do not repeat Table 2 and Fig. 3. You may write: "The results are presented in Table 2 and in Figure 3.

Changed in the manuscript: We have changed this.

Comment 17: 4. Discussion - 4.1.: the first paragraph (L. 182-197) is quite general and it would be worthy to move it either in the introduction, or at least in the Materials and Methods section.

Changed in the manuscript: We moved them to the introduction.

Comment 18: 4.1. L.213-219: It is exactly the same text as in the introduction (L. 48-54) The authors may express their idea at least a little bit differently.

Answer: Because they are for elaborating different problem, we think we should put one of them another way.

Changed in the manuscript: We changed the statements in section 4.2.

Comment 19: Information about soils and soil solutions are needed in order to understand their chemical evolution during the carbonate weathering. - Would it be possible to present the chemistry of each fertilizer used in this experiment? This can be added in supplementary information.

Answer: yes, it is very important. Most of them have been discussed in section 4.2 and 4.3 so far. And we are doing some further research on that.

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

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Abstract: Carbonate weathering, as a significant vector for the movement of carbon both between and within ecosystems, are strongly influenced by anthropogenic perturbations such as agricultural fertilization. Different fertilizer may exert a different impact on carbonate weathering, but their these discrepanciesdifferences are not still well-known so far. In this study, a field column experiment was employed to explore the responses of carbonate weathering to different fertilizer 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. The result showed that the addition of urea, NH_4NO_3, NH_4HCO_3, NH_4Cl and $(NH_4)_2CO_3$ distinctly increased carbonate weathering, which was attributed to the nitrification of NH_4^+, and the addition of $Ca_3(PO_4)_2$, Ca-Mg-P and K_2CO_3 induced carbonate precipitation due to common ion effect. Whereas the $(NH_4)_3PO_4$ and $NaNO_3$ addition did not impact significantly on carbonate weathering. The results of $NaNO_3$ treatment seem 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. 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; 2011)~~(Liu et al., 2010; 2011)~~. The riverine hydro-chemical composition such as the ratio of HCO_3^- ~~and~~ $Ca^{2+}+Mg^{2+}$ is usually employed as an indicator to estimate the CO_2 consumption by carbonate weathering at the regional/global scale (Hagedorn and Cartwright, 2009; Li et al., 2009). ~~However,~~ a disturbance to CO_2 consumption estimation is introduced because the fluvial alkalinity, Ca^{2+} and Mg^{2+} 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), 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). Given ~~the~~ atmospheric CO_2 is not the unique weathering agent, differentiating the agent of carbonate weathering is ~~more and more~~

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significant to enable the accurate budgeting of the net CO_2 consumption by carbonate, especially in agricultural area.

The world average annual increase in 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 fertilizer is a significant disturbance factor of carbonate weathering and carbon cycle. Many studies showed that nitrogen fertilizer additions aided increased in the dissolution of lime and increase the total export of DIC from agricultural watersheds (Barnes and Raymond, 2009; Gandois et al., 2011; Hamilton et al., 2007; Oh and Raymond, 2006; Perrin et al., 2008; Pierson-wickmann et al., 2009; Probst, 1986; Semhi and Suchet, 2000; West and McBride, 2005). According to the estimation from Probst (1988) and Semhi et al. (2000), the contribution of N-fertilizers to carbonate dissolution represents 30% and 12-26%, respectively, on two small agricultural carbonate basins in south-western France, the Girou and the Gers (subtributary and tributary of the Garonne river, respectively). For lager basin level, such as the Garonne river basin, this contribution was estimated at 6% by Semhi et al. (2000). At national and global scales, Perrin et al. (2008) estimated that the deficit of CO_2 uptake due to N-fertilizer addition (usually in form of NH_4NO_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 were 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, 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 $(NH_4)_2SO_4$ and NH_4Cl derive from the nitrification of NH_4^+, comparatively, only 50% after the addition NH_4NO_3. The difference of NO_3^- source may cause the evaluated deviation of the impact of N-fertilizer addition on CO_2 consumption by carbonate weathering. For phosphate fertilizer, the coprecipitaion of phosphate ions with calcium carbonate may inhibit carbonate weathering (Kitano et al., 1978). We suppose that the response of carbonate weathering to the addition of different fertilizer such as N-fertilizer (NH_4 and NO_3), P-fertilizer and Ca/Mg fertilizer may display difference, which is poorly known so far but significant to well understand the agricultural force on natural carbonate weathering and accurately evaluate the CO_2 consumption via carbonate weathering in agricultural area.

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

~~Thus~~Therefore, ~~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 Guiyang city, Guizhou province, SW China (26°23′N, 106°40′E, 1094 m asl). Guiyang, the capital city of Guizhou Province, is located in the central part of The Province, covering an area from 26°11′00″ to 26°54′20″N and 106°27′20″ to 107°03′00″E, with elevations ranging from 875 to 1655 m above mean sea level. Guiyang has a population of more than 1.5 million people, a high diversity of karstic landforms, a high elevation and low latitude, with a subtropical warm-moist climate, annual average temperature of 15.3 ℃ and annual precipitation of 1200 mm (Lang et al., 2006). A monsoonal climate often results in high precipitation during summer and much less during winter, although the humidity is often high during most of the year

(Han and Jin, 1996). Agriculture is a major land use in order to produce the vegetables and foods in the suburb of Guiyang (Liu et al., 2006). The consumption of chemical fertilizer increased from 0.8 Mt in 1980 to 1.0 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 ~~dug from~~ 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 in~~-~~cluding 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 O~~.~~M~~.~~ contained 0.2 mol l^{-1} NaOH, 0.01 mol l^{-1} EDTA, 2% methanol and 0.005% Superfloc 127, NH_4-N, NO_3-N, available Ca and Mg were determined based on extraction by 1 mol l^{-1} KCl solution, available K, P and Fe were extracted by extracting solution containing 0.25 mol l^{-1} $NaHCO_3$, 0.01 mol l^{-1} EDTA, 0.01 mol l^{-1} NH_4F, and 0.005% Superfloc 127, and available S was extracted by 0.1 mol l^{-1} $Ca(H_2PO_4)_2$ and 0.005% Superfloc 127. The results are shown in Table 1.

2.3 Soil column and different fertilization treatments

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

A hole (Ø=2 cm) were established at the bottom of each column to discharge soil water from 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 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 $\cdot ha^{-1}$; P fertilizer: 150 kg P_2O_5 $\cdot ha^{-1}$; K fertilizer: 50 kg K $\cdot ha^{-1}$). The soil was weighed, mixed perfectly with above fertilizer, respectively, and filled in its own column. These soil columns were placed at the field experiment site in Guiyang of Southwestern China for a whole year.

2.4 The rate of carbonate weathering

Two different kinds of carbonate rock tablets (2 cm × 1 cm × 0.5 cm in size) were established in the bottom of each soil column to explore the rate of carbonate

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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~~ organic matter. All of tablets were ~~baked~~ at 80 ℃ for 4 hours then weighed in a 1/10000 electronic balance in the laboratory, tied to a label with fishing line and buried at the bottom of each soil column. They were taken out carefully, rinsed, baked and weighed after a whole year.

The amount of carbonate weathering (A*cw*), the ratio of carbonate weathering (R*cw*) and the rate of carbonate weathering (Ra*cw*) were calculated according to the weight difference of the tablets using the following formulas:

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

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

$$Ra_{cw} = (W_i - W_f)/(S*T) \quad (3)$$

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

3. Results

The amount (A*cw*), the ratio (R*cw*) and the rate (Ra*cw*) of carbonate weathering were listed in Table 2~~,~~ and ~~the Rcw were plotted in~~ Fig. 3. The results ~~in Table 2 and Fig. 3~~ between limestone and dolostone weathering under different fertilization treatment were similar. We will explain the results with carbonates instead of individual dolostone and limestone. The results showed ~~T~~the A*cw*, R*cw* and Ra*cw* of carbonate weathering under urea, NH_4NO_3, NH_4HCO_3, NH_4Cl and $(NH_4)_2CO_3$

treatments were positive, and much bigger than that under the control treatment, suggesting that the addition of these fertilizers ~~can aid and~~ increase ~~the chemical weathering of~~ carbonate. In $(NH_4)_3PO_4$ treatment, the A*cw*, and R*cw* were only -0.0028g and -0.0007g for limestone and dolomite, -1.08‰ and -0.75‰ for limestone and dolomite, respectively, less than those under other four NH_4-fertilizers as mentioned above. The A*cw*, R*cw* and Ra*cw* in $NaNO_3$ treatment failed to show a remarkable difference with control treatment, implying little effect of $NaNO_3$ fertilizer addition on carbonate weathering (Fig. 3).

However, except the R*cw* of limestone in $Ca_3(PO_4)_2$ treatment approaching zero, the A*cw*, R*cw* and Ra*cw* of two different carbonate in Ca-Mg-P and K_2CO_3 and $Ca_3(PO_4)_2$ treatments showed a negative value, indicating that the addition of Ca-Mg-P , K_2CO_3 and $Ca_3(PO_4)_2$ fertilizers can lead to the precipitation at the surface of carbonate mineral, which can be explained by common ion effect.

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~~

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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.

4.2 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):

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

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

$$MeCO_3 \rightarrow Me^{2+} + CO_3^{2-} \quad (6)$$

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).

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 $g \cdot m^{-2} \cdot a^{-1}$ 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).

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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 Ra*cw* 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.

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).

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

Table 3 shows that the amount of NH_4^+ hydrolyzed from urea is 1.06 mol, while NH_4^+ ionized from NH_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).

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

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

(i) either by exchange process with base cations in the soil exchange complex (Eq. (9)) $$Soil - Ca + 2H^+ \rightarrow Soil - 2H^+ + Ca^{2+} \quad (9)$$

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

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

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

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

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 A*cw* and R*cw* in $(NH_4)_3PO_4$ treatment, unlike in other NH_4-fertlizer treatments, had not a significant increase comparing with control treatment, which is not only owing to the low amount of added NH_4^+ in $(NH_4)_3PO_4$ treatment (0.3 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.

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Table 1 Chemical composition of soil

Parameter	Unit	Values
pH	-	6.94
Organic matter	%	0.99
NH_4^+-N	mg/kg	339.87
NO_3^--N	mg/kg	569.05
Available P	mg/kg	8.18
Available K	mg/kg	56.88
Available Ca	mg/kg	3041.06
Available Mg	mg/kg	564.83
Available S	mg/kg	100.72
Available Fe	mg/kg	24.41

Table 2 Carbonate weathering under different fertilizer treatments

Treatment	Limestone		Dolostone	
	Acw /g	Racw / g m^{-2} a^{-1} ~~Rcw /‰~~	Acw /g	Racw /g m^{-2} a^{-1} ~~Rcw /‰~~
Control	0.0014±0.0004	2.00±0.58 ~~0.48~~	-0.0011±0.0006	-1.57±0.86 ~~-0.31~~
NH_4NO_3	0.0174±0.0014	24.86±2.01 ~~6.42~~	0.0144±0.0008	20.57±1.15 ~~5.30~~
NH_4HCO_3	0.0147±0.0024	21.00±3.45 ~~4.44~~	0.0096±0.0027	13.71±3.88 ~~3.22~~
$NaNO_3$	0.0031±0.0012	4.43±1.73 ~~0.86~~	0.0022±0.0012	3.14±1.73 ~~0.53~~
NH_4Cl	0.0149±0.0017	21.29±2.45 ~~5.54~~	0.0131±0.0006	18.71±0.86 ~~4.77~~
$(NH_4)_2CO_3$	0.0144±0.0031	20.57±4.46 ~~4.84~~	0.0186±0.0053	26.57±7.62 ~~4.94~~
$Ca_3(PO_4)_2$	0.0003±0.0006	0.43±0.86 ~~0.01~~	-0.0013±0.0009	-1.86±1.29 ~~-0.55~~
$(NH_4)_3PO_4$	0.0028±0.0008	4.00±1.15 ~~1.08~~	0.0007±0.0007	1.00±1.01 ~~0.75~~
Ca-Mg-P	-0.0013±0.0003	-1.86±0.43 ~~-0.31~~	-0.0022±0.0005	-3.14±0.72 ~~-0.97~~
Urea	0.0243±0.0030	34.71±4.32 ~~8.48~~	0.0185±0.0019	26.43±2.73 ~~6.59~~
K_2CO_3	-0.0008±0.0004	-1.14±0.58 ~~-0.26~~	-0.0018±0.0003	-2.57±0.43 ~~-0.59~~

A*cw* - the amount of carbonate weathering; R*cw* - the ratio of carbonate weathering; Ra*cw* - the rate of carbonate weathering; A*cw* = (W*i*-W*f*); ~~R*cw* = (W*i*-W*f*)/W*i*,~~ Ra*cw* = (W*i*-W*f*)/(S*T), where W*i* is the initial weight of the carbonate rock tablets, and W*f* is their final weight. S is the surface area of carbonate weathering tablets, and T is the experiment period.

带格式表格

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Table 3: The amount of generated NH_4^+ at the initial phase of the experiment

Treatment	Relative molecular mass /g/mol	Amount of added fertilizer /g	Molar concentration /mol	Initial NH_4^+ /mol
NH_4NO_3	80	43	0.54	0.54
NH_4HCO_3	79	85	1.08	1.08
$NaNO_3$	85	91	1.07	0.00
NH_4Cl	53.5	57	1.07	1.07
$(NH_4)_2CO_3$	96	51	0.53	1.06
$Ca_3(PO_4)_2$	310	52	0.17	0.00
$(NH_4)_3PO_4$	149	15	0.10	0.30
Ca-Mg-P	/	44	0.00	0.00
Urea	60	32	0.53	1.06
K_2CO_3	138	10	0.07	0.00

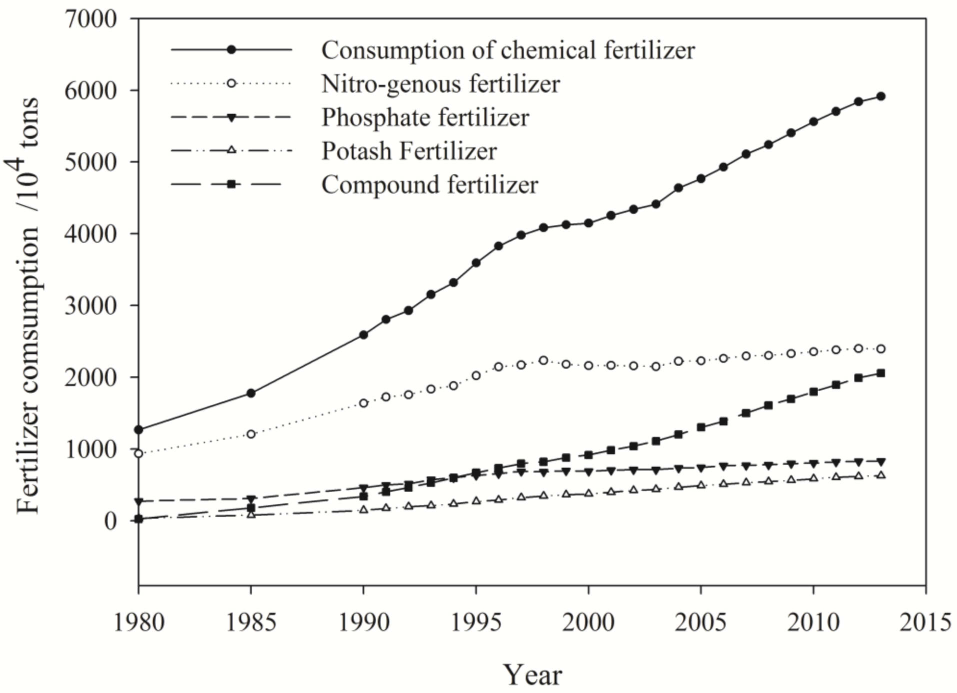

Fig. 1 The change of chemical fertilizer consumption in China during 1980-2013

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

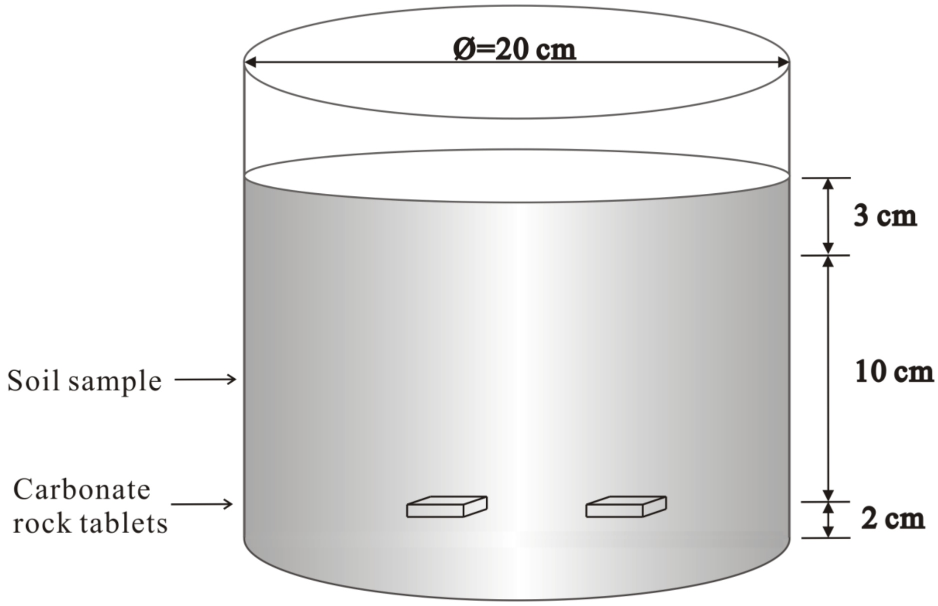

Fig. 2 Sketch map of the soil column

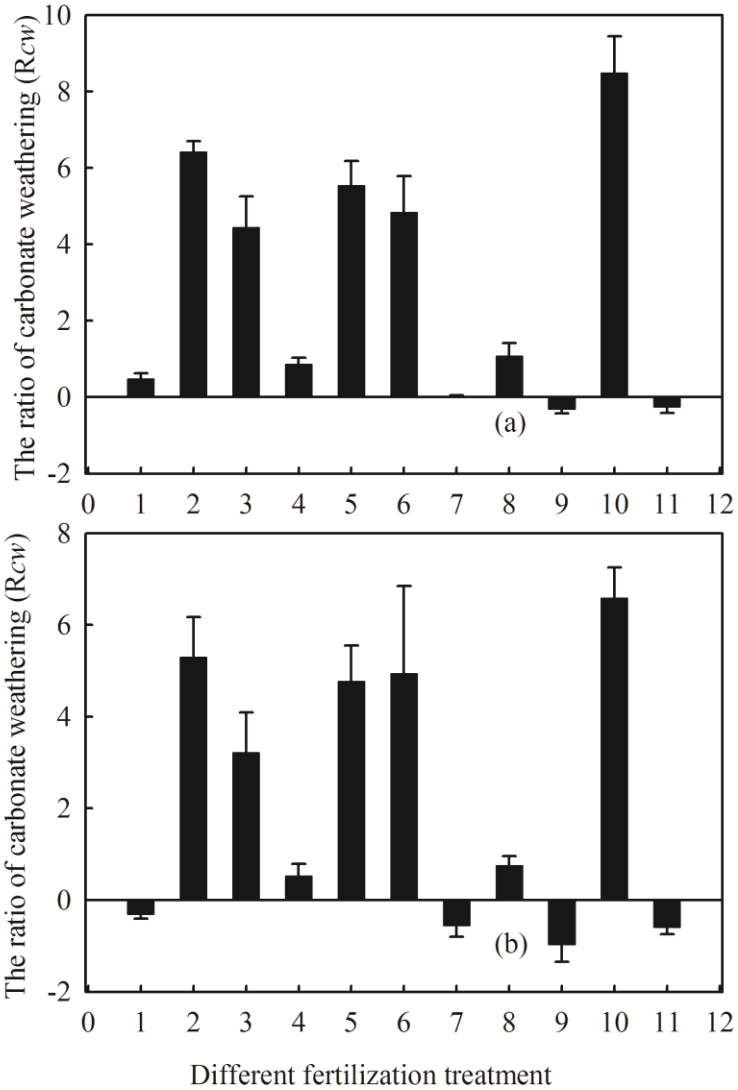

Fig. 3 The ratio of carbonate weathering under different fertilization treatment

(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. $Rcw = (Wi - Wf)/Wi$, where Wi is the initial weight of the carbonate rock tablets, and Wf is their final weight.

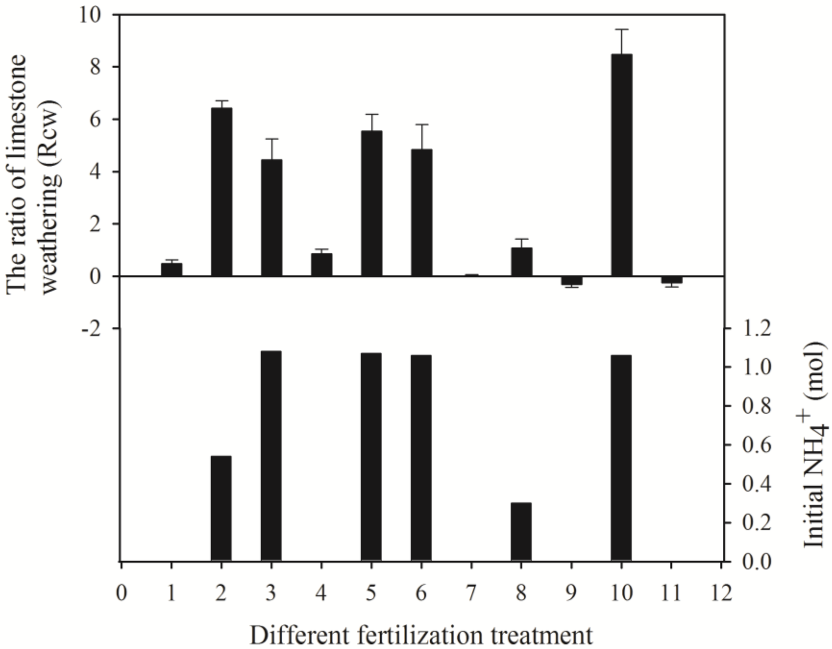

Fig. 4 The ratio of limestone weathering and the molar amount of produced NH_4^+ under different fertilization treatment

Treatment 1-Control; 2-NH_4NO_3; 3-NH_4HCO_3; 4-$NaNO_3$; 5-NH_4Cl; 6-$(NH_4)_2CO_3$; 7-$Ca_3(PO_4)_2$; 8-$(NH_4)_3PO_4$; 9-Ca-Mg-P; 10-Urea; 11-K_2CO_3. R*cw* =(W*i*-W*f*)/W*i*, where W*i* is the initial weight of limsestone tablets, and W*f* is their final weight.