Earth Surf. Dynam. Discuss., doi:10.5194/esurf-2016-50, 2016
Manuscript under review for journal Earth Surf. Dynam.
Published: 4 October 2016

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

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Earth Surf. Dynam. Discuss., doi:10.5194/esurf-2016-50, 2016
Manuscript under review for journal Earth Surf. Dynam.
Published: 4 October 2016

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 differences 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 (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 significant to enable the accurate

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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 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

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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. Thus, in order to observe their difference between the impacts of different fertilizer addition on carbonate weathering in soil, a field column experiment with eleven different treatments was carried out in a typical karst area of southwest China.

2. Materials and Methods

2.1 The study site

This study was carried out in a typical karst area, the HuaXi district of Guiyang city, Guizhou province, SW China (26°23′N, 106°40′E, 1094 m asl). Guiyang, the capital city of Guizhou Province, is located in the central part of The Province, covering an area from 26°11′00″ to 26°54′20″N and 106°27′20″ to 107°03′00″E, with elevations ranging from 875 to 1655 m above mean sea level. Guiyang has a

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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 dug from a cabbage-corn or capsicum-corn rotation plantation, 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 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 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 mesh (Ø 0.5 mm) was placed in the bottom of the columns to prevent the loss of the filter material. Two different carbonate rock tablets were buried in the bottom of each 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. 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 column to explore the rate of carbonate weathering in soil. The two different kinds of carbonate rock were (1) limestone with 60-65%

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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:

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

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

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

where W*i* is the initial weight of the carbonate rock tablets, W*f* is their final weights, S is the surface area of carbonate weathering tablets, and T is the 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 R*cw* were plotted in Fig. 3. The results in Table 2 and Fig. 3 showed that A*cw*，Rcw 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 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

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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 protons which can originate from the nitrification processes of N-fertilizer (Semhi

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and Suchet, 2000; West and McBride, 2005; Oh and Raymond, 2006; Hamilton et al., 2007; Perrin et al., 2008; Barnes and Raymond, 2009; Pierson-wickmann et al., 2009; Chao et al., 2011; Gandois et al., 2011), from the sulfuric acid (Lerman and Wu, 2006; Lerman et al., 2007; Li et al., 2008; Li et al., 2009), from organic acid secreted by microorganisms (Lian et al., 2008), as well as from acidic soil (Chao et al., 2014).

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 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 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

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$(NH_4)_2CO_3$ 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).

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

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).

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

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))

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

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

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

Consequently, after Eq. (8) and Eq. (10) are combined, carbonate weathering by

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protons produced by nitrification is supposed to becomes (Eq. 11) (See details in Perrin et al., 2008 and Gandois et al., 2011).

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

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

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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

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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

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This study is supported jointly by the Basic Science Research Fund from the Institute of Hydrogeology and Environmental Geology (Grant No. SK201208), the Chinese National Natural Science Foundation (No. 41403104 and No. 41325010), and the China Geological Survey Projects (No. 12120113005900).

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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

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Table 2 Carbonate weathering under different fertilizer treatments

Treatment	Limestone			Dolostone		
	A*cw* /g	R*cw* /‰	Ra*cw* / g m^{-2} a^{-1}	A*cw* /g	R*cw* /‰	Ra*cw* /g m^{-2} a^{-1}
Control	0.0014	0.48	2.00	-0.0011	-0.31	-1.57
NH_4NO_3	0.0174	6.42	24.86	0.0144	5.30	20.57
NH_4HCO_3	0.0147	4.44	21.00	0.0096	3.22	13.71
$NaNO_3$	0.0031	0.86	4.43	0.0022	0.53	3.14
NH_4Cl	0.0149	5.54	21.29	0.0131	4.77	18.71
$(NH_4)_2CO_3$	0.0144	4.84	20.57	0.0186	4.94	26.57
$Ca_3(PO_4)_2$	0.0003	0.01	0.43	-0.0013	-0.55	-1.86
$(NH_4)_3PO_4$	0.0028	1.08	4.00	0.0007	0.75	1.00
Ca-Mg-P	-0.0013	-0.31	-1.86	-0.0022	-0.97	-3.14
Urea	0.0243	8.48	34.71	0.0185	6.59	26.43
K_2CO_3	-0.0008	-0.26	-1.14	-0.0018	-0.59	-2.57

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.

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

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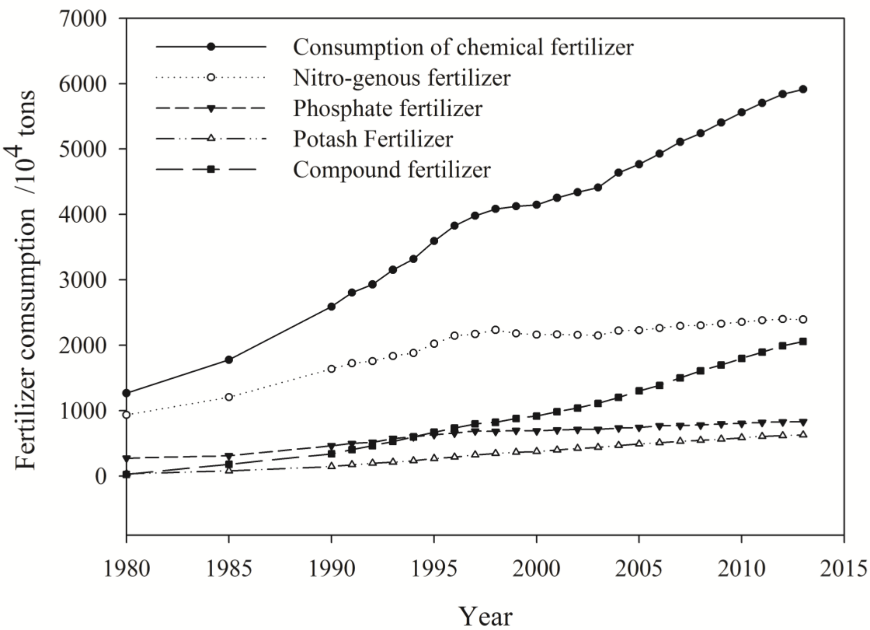

Fig. 1 The change of chemical fertilizer consumption in China during 1980-2013

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/)

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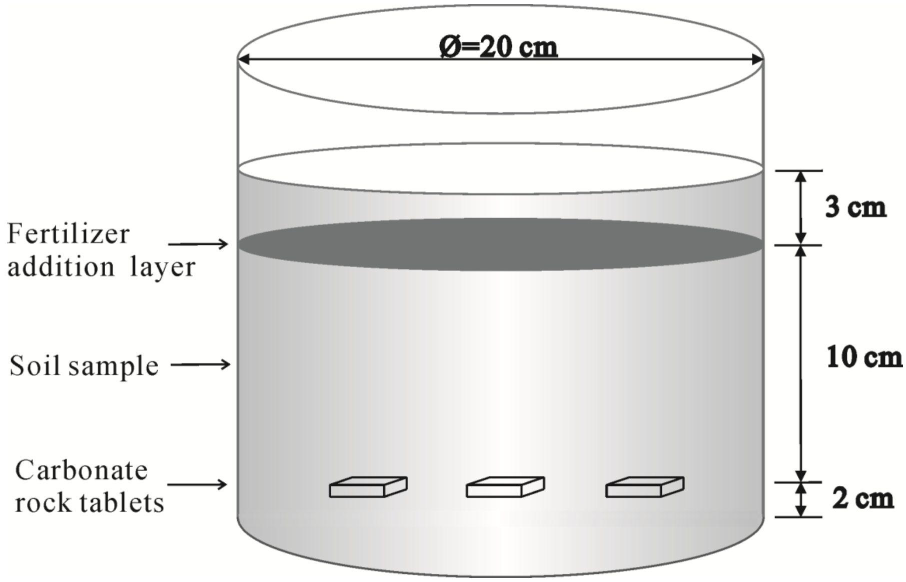

Fig. 2 Sketch map of the soil column

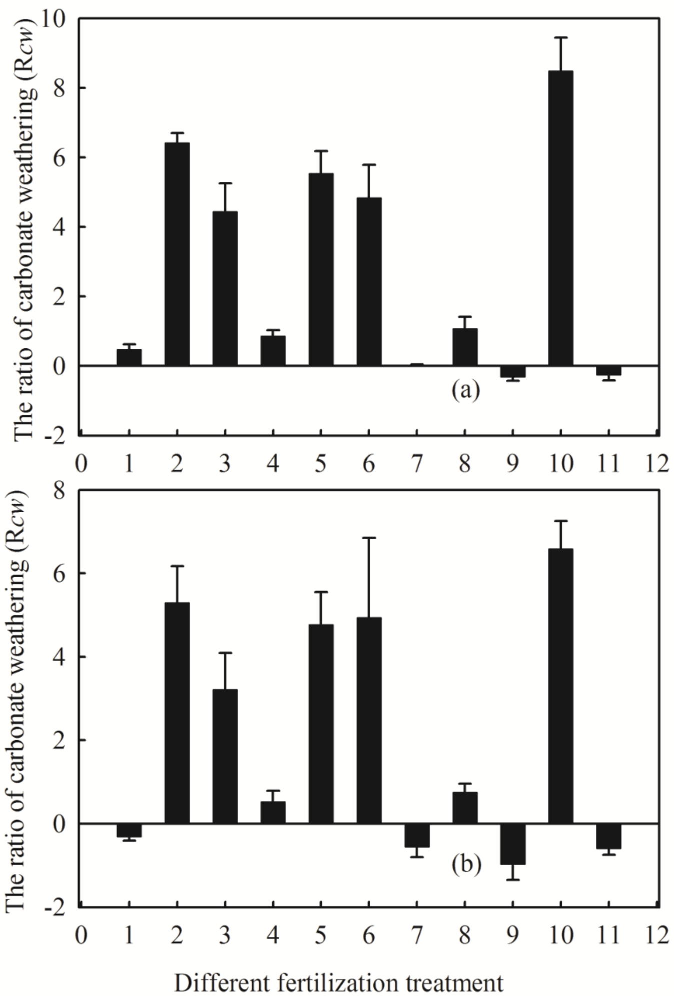

Fig. 3 The ratio of carbonate weathering under different fertilization treatment (a)-limestone; (b)-dolostone. Treatment 1-Control; 2-NH_4NO_3; 3-NH_4HCO_3; 4-$NaNO_3$; 5-NH_4Cl; 6-$(NH_4)_2CO_3$; 7-$Ca_3(PO_4)_2$; 8-$(NH_4)_3PO_4$; 9-Ca-Mg-P; 10-Urea; 11-K_2CO_3. R*cw* =(W*i*-W*f*)/W*i*, where W*i* is the initial weight of the carbonate rock tablets, and W*f* is their final weight.

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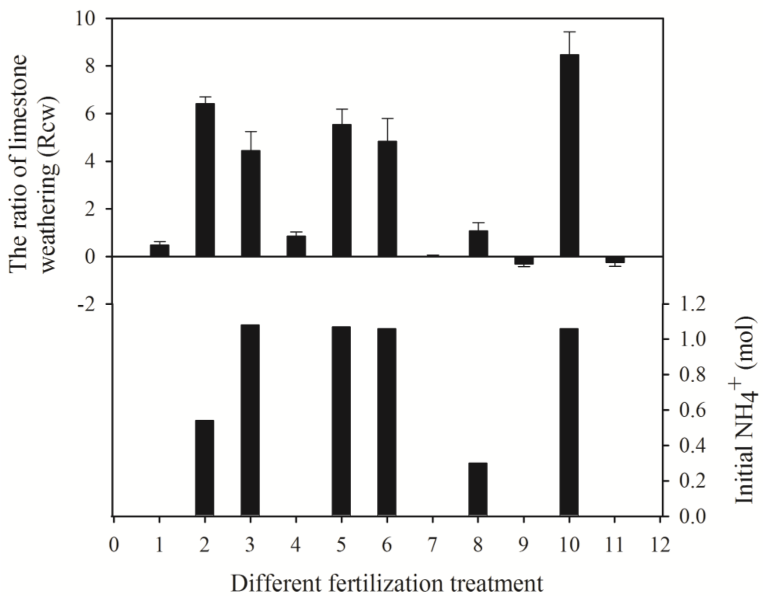

Fig. 4 The ratio of limestone weathering and the molar amount of produced NH_4^+ under different fertilization treatment

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. $Rcw = (Wi - Wf)/Wi$, where W*i* is the initial weight of limsestone tablets, and W*f* is their final weight.