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 these discrepancies 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, NH₄NO₃, NH₄HCO₃, NaNO₃, NH₄Cl, (NH₄)₂CO₃, Ca₃(PO₄)₂, (NH₄)₃PO₄, fused calcium-magnesium phosphate fertilizer (Ca-Mg-P), Urea and K₂CO₃ were established in this column experiment, where limestone and dolostone tablets were buried at the bottom of each to determine the weathering amount and ratio of carbonate in soil. The result showed that the addition of urea, NH₄NO₃, NH₄HCO₃, NH₄Cl and (NH₄)₂CO₃ distinctly increased carbonate weathering, which was attributed to the nitrification of NH₄⁺, and the addition of Ca₃(PO₄)₂, Ca-Mg-P and K₂CO₃ induced carbonate precipitation due to common ion effect. Whereas the (NH₄)₃PO₄ and NaNO₃ addition did not impact significantly on carbonate weathering. The results of NaNO₃ 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 CO₂ consumption by carbonate weathering at the regional/global scale if the effect of NO₃ and NH₄ are not distinguished.

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). 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 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 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 larger 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 CO₂ uptake due to N-fertilizer addition (usually in form of NH₄NO₃) represent up to 5.7-13.4% and only 1.6-3.8% of the total CO₂ 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. (NH₄)₂SO₄, NH₄NO₃, or NH₄Cl) 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% NO₃⁻
produced after the addition (NH₄)₂SO₄ and NH₄Cl derive from the nitrification of NH₄⁺, comparatively, only 50% after the addition NH₄NO₃. The difference of NO₃⁻ source may cause the evaluated deviation of the impact of N-fertilizer addition on CO₂ 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 (NH₄ and NO₃), 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 CO₂ 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 CO₂ consumption by carbonate weathering (Chao et al., 2014; Jiang and Yuan, 1999; Jiang et al., 2013; Plan, 2005). Although Liu (2011) argue that the carbonate-rock-tablet test may lead to the deviation of estimated CO₂ consumption by carbonate weathering at the regional/global scale in the case of insufficient representative data (Liu, 2011), our results show that it is a preferred option for the condition controlled contrast or stimulated experiment (Chao et al., 2011; Chao et al., 2014), where the result from the
carbonate-rock-tablet test is consistent to the major element geochemical data of
leachates from soil column (Chao et al., 2011).

Therefore, a field column experiment embedding carbonate rock tablets 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 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 °C and annual precipitation of 1200 mm (Lang et al.,
2006). A monsoonal climate often results in high precipitation during summer and
much less during winter, although the humidity is often high during most of the year
(Han and Jin, 1996). Agriculture is a major land use in order to produce the vegetables
and foods in the suburb of Guiyang (Liu et al., 2006). The consumption of chemical
fertilizer increased from 0.8 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 a cabbage-corn or capsicum-corn rotation
plantation in Huaxi district. It was air-dried, ground to pass through a 2-mm sieve, mixed thoroughly and used for soil columns. The pH (V_soil:V_water = 1:2.5) were determined by pH meter. The chemical characteristics of soil including organic matter (OM), NH_4-N, NO_3-N, available P, available K, available Ca, available Mg, available S and available Fe were determined according to the Agro Services International (ASI) Method (Hunter, 1980), where the extracting solution used for OM contained 0.2 mol l\(^{-1}\) NaOH, 0.01 mol l\(^{-1}\) EDTA, 2% methanol and 0.005% Superfloc 127, NH_4-N, NO_3-N, available Ca and Mg were determined based on extraction by 1 mol l\(^{-1}\) KCl solution, available K, P and Fe were extracted by extracting solution containing 0.25 mol l\(^{-1}\) NaHCO_3, 0.01 mol l\(^{-1}\) EDTA, 0.01 mol l\(^{-1}\) NH_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 soil column. 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. 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$_4$NO$_3$ fertilizer (CF); (3) 85g NH$_4$HCO$_3$ fertilizer (NHC); (4) 91g NaNO$_3$ fertilizer (NN); (5) 57g NH$_4$Cl fertilizer (NCL); (6) 51g (NH$_4$)$_2$CO$_3$ fertilizer (NC); (7) 52g Ca$_3$(PO$_4$)$_2$ fertilizer (CP); (8) 15g (NH$_4$)$_3$PO$_4$ fertilizer (NP); (9) 44g fused calcium-magnesium phosphate fertilizer (Ca-Mg-P); (10) 32g Urea fertilizer (U) and (11) 10g K$_2$CO$_3$ 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: 150 kg P$_2$O$_5$·ha$^{-1}$; K fertilizer: 50 kg K·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 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 °C for 4 hours then weighed in a 1/10000 electronic balance in the laboratory, tied to a label with fishing line and buried at the bottom of each soil column. They were taken out carefully, rinsed, baked and weighed after a whole year.
The amount of carbonate weathering ($A_{cw}$), the ratio of carbonate weathering ($R_{cw}$) and the rate of carbonate weathering ($Rac_{cw}$) were calculated according to the weight difference of the tablets using the following formulas:

\[ A_{cw} = (W_i - W_f) \]  
\[ R_{cw} = (W_i - W_f)/W_i \]  
\[ Rac_{cw} = (W_i - W_f)/(S*T) \]

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 ($Rac_{cw}$) of carbonate weathering were listed in Table 2 and Fig. 3. The results 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 the $A_{cw}$, $R_{cw}$ and $Rac_{cw}$ of carbonate weathering under urea, $\text{NH}_4\text{NO}_3$, $\text{NH}_4\text{HCO}_3$, $\text{NH}_4\text{Cl}$ and $(\text{NH}_4)_2\text{CO}_3$ 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 $(\text{NH}_4)_3\text{PO}_4$ 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 $\text{NH}_4$-fertilizers as mentioned above. The $A_{cw}$, $R_{cw}$ and $Rac_{cw}$ in $\text{NaNO}_3$ treatment failed to show a remarkable difference with control treatment, implying little effect of $\text{NaNO}_3$ 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 $R_{acw}$ 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

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):

$$MeCO_3 + H^+ \rightarrow Me^{2+} + HCO_3^-$$  \hspace{1cm} (4)

$$MeCO_3 + H_2CO_3 \rightarrow Me^{2+} + 2HCO_3^-$$  \hspace{1cm} (5)

$$MeCO_3 \rightarrow Me^{2+} + CO_3^{2-}$$  \hspace{1cm} (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 other proton contributors, as mentioned in introduction section: the nitrification processes of NH$_4^+$, the sulfuric acid, organic acid secreted by microorganisms, and 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$_4$NO$_3$, NH$_4$HCO$_3$, NH$_4$Cl and (NH$_4$)$_2$CO$_3$ amendment increased (10 to 17-fold) the natural weathering rate of 2.00 g·m$^{-2}$·a$^{-1}$ from limestone tablets in control treatment (table 2). These increases may be, in the one hand, attributed to the effect of the proton released from the nitrification of NH$_4^+$. On the other hand, it may be, in theory, related to enhanced microbiogenic CO$_2$ due to nitrogenous nutrients stimulation (Eq(5)), because fertilizer application can increase soil CO$_2$ flux (Sainju et al., 2008; Bhattacharyya et al., 2013), the increased CO$_2$ can enhance carbonate dissolution rate at near neutral or alkali pH (Andrews and Schlesinger, 2001).

According to the added amount of different fertilization treatment, the molar amount of added nitrogen nutrient in NaNO$_3$ treatment is 1.07 mol, much bigger than in NH$_4$NO$_3$, equivalent to NH$_4$HCO$_3$ and NH$_4$Cl treatment. However, the $A_{cw}$ and $R_{cw}$, and $R_{acw}$ of NaNO$_3$ treatment is far less (Fig. 3 and table 2), inhibiting that the increases of carbonate weathering rate in urea, NH$_4$NO$_3$, NH$_4$HCO$_3$, NH$_4$Cl and (NH$_4$)$_2$CO$_3$ amendment have no distinct relationship with enhanced microbiogenic
4.3 The effect of nitrification of NH₄-fertilizer

In urea (CO(NH₂)₂) treatment, the enzyme urease rapidly hydrolyzes the urea-N (CO(NH₂)₂) to NH₄⁺ ions (Eq. (7)) when urea is applied to the soil (Soares et al., 2012).

\[
\text{CO(NH₂)₂} + 3\text{H₂O} \rightarrow 2\text{NH₄⁺} + 2\text{OH⁻} + \text{CO₂} \quad (7)
\]

Table 3 shows that the amount of NH₄⁺ hydrolyzed from urea is 1.06 mol, while NH₄⁺ ionized from NH₄NO₃, NH₄HCO₃, NH₄Cl, (NH₄)₂CO₃ and (NH₄)₃PO₄ 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 NH₄⁺ may be lost as ammonia (NH₃) and subsequently as nitrous oxide (N₂O) (Singh et al., 2013), yet the rest ammonium (NH₄⁺) is mainly oxidized in soil by autotrophic bacteria (like Nitrosomonas) during nitrification, resulting in nitrite NO₂⁻ and H⁺ ions. Nitrite is, in turn, oxidized by another bacterium, such as Nitrobacter, resulting in nitrate (NO₃⁻) (Eq. (8)) (Perrin et al., 2008).

\[
\text{NH₄⁺} + 2\text{O₂} \rightarrow \text{NO₃⁻} + \text{H₂O} + 2\text{H⁺} \quad (8)
\]

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))

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

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

\[
\text{Ca}_{(1-x)}\text{Mg}_x\text{CO}_3 + \text{H⁺} \rightarrow (1-x) \text{Ca}^{2⁺} + x\text{Mg}^{2⁺} + \text{HCO₃⁻} \quad (10)
\]

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).

$$2Ca(1-x)Mg_xCO_3 + NH_4^+ + 2O_2 → 2(1-x)Ca^{2+} + 2xMg^{2+} + NO_3^- + H_2O + 2HCO_3^-$$ (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 $3.72 \times 10^5$ kg C/year and account for 18.7% of this flux in the entire catchment(Yue et al., 2015). This is similar to estimates from other small agricultural carbonate basins (12–26%) in Southwest France (Semhi and Suchet, 2000; Perrin et al., 2008).

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

13
2Ca_{(1-x)}Mg_xCO_3 + NH_4NO_3 + 2O_2 \rightarrow 2(1-x) \text{Ca}^{2+} + 2x\text{Mg}^{2+} + 2\text{NO}_3^- + \text{H}_2\text{O} + 2\text{HCO}_3^- \quad (12)

2Ca_{(1-x)}Mg_xCO_3 + NH_4HCO_3 + 2O_2 \rightarrow 2(1-x) \text{Ca}^{2+} + 2x\text{Mg}^{2+} + \text{NO}_3^- + \text{H}_2\text{O} + 3\text{HCO}_3^- \quad (13)

2Ca_{(1-x)}Mg_xCO_3 + NH_4\text{Cl} + 2O_2 \rightarrow 2(1-x) \text{Ca}^{2+} + 2x\text{Mg}^{2+} + \text{NO}_3^- + \text{Cl}^- + \text{H}_2\text{O} + 2\text{HCO}_3^- \quad (14)

3Ca_{(1-x)}Mg_xCO_3 + (\text{NH}_4)_2\text{CO}_3 + 4\text{O}_2 \rightarrow 3(1-x) \text{Ca}^{2+} + 3x\text{Mg}^{2+} + 2\text{NO}_3^- + 2\text{H}_2\text{O} + 4\text{HCO}_3^- \quad (15)

3Ca_{(1-x)}Mg_xCO_3 + \text{CO(NH}_2)_2 + 4\text{O}_2 \rightarrow 3(1-x) \text{Ca}^{2+} + 3x\text{Mg}^{2+} + 2\text{NO}_3^- + 4\text{HCO}_3^- \quad (16)

The $A_{cw}$ and $R_{cw}$ 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 $\text{HCO}_3^-$ and $\text{Me}^{2+}$ in the river as an indicator is usually used to make estimations of $\text{CO}_2$ consumption by carbonate weathering at the regional/global scale (Hagedorn and Cartwright, 2009; Li et al., 2009). At agricultural areas, the relationship between $(\text{Ca}+\text{Mg})/\text{HCO}_3^-$ and NO$_3^-$ is usually employed to estimate the contribution of N-fertilizer to riverine $\text{Ca}^{2+}$, $\text{Mg}^{2+}$ and alkalinity (Etanchu and Probst, 1988; Jiang, 2013; Jiang et al., 2009; Perrin et al., 2008; Semhi and Suchet, 2000). In these studies, the nitrification described as Eq. (8) is usually considered as the unique origin of NO$_3^-$. According to the result of NaNO$_3$ treatment in this study, the contribution of protons from nitrification to carbonate weathering may be overestimated if anthropogenic NO$_3^-$ is neglected, since the anthropogenic NO$_3^-$ does not release the proton described as Eq. (8). For NH$_4$NO$_3$ fertilizer, the (Eq. (12)) show that the two moles of $\text{Ca}^{2+}+\text{Mg}^{2+}$, NO$_3^-$ and $\text{HCO}_3^-$ will be produced when one mole NH$_4$NO$_3$ react with 2 moles of carbonate, where only half of NO$_3^-$ originate from nitrification described as Eq. (8). This will result in doubled overestimation on the true contribution of the nitrification to $\text{CO}_2$ consumption by carbonate weathering.

At regional scales, If different fertilizers are added to an agricultural area, the estimation of $\text{CO}_2$ consumption by carbonate weathering might became more complicated, since the mole ratio of $\text{Ca}+\text{Mg}$, $\text{HCO}_3^-$ and/or NO$_3^-$ between different fertilization treatment is different (see Eq. (8)-(12)). Thus, the related anthropogenic inputs (e.g. $\text{Ca}+\text{Mg}$, NH$_4$, NO$_3^-$, $\text{HCO}_3^-$, etc.) need to be investigated to more accurately estimate the impact of fertilization on carbonate weathering and its $\text{CO}_2$ consumption.

5. Conclusion

The impact of the addition of different fertilizer (NH$_4$NO$_3$, NH$_4$HCO$_3$, NaNO$_3$,
NH₄Cl, (NH₄)₂CO₃, Ca₃(PO₄)₂, (NH₄)₃PO₄, Ca-Mg-P, Urea and K₂CO₃) 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, NH₄NO₃, NH₄HCO₃, NH₄Cl and (NH₄)₂CO₃ distinctly increased carbonate weathering, which was attributed to the nitrification of NH₄⁺, and the addition of Ca₃(PO₄)₂, Ca-Mg-P and K₂CO₃ induced carbonate precipitation due to common ion effect. While the (NH₄)₃PO₄ and NaNO₃ addition did not impact significantly on carbonate weathering, where the former can be attributed to low added amount of (NH4)₃PO₄, may be related to the inhibition of phosphate, and the latter seemed to be raising a new question. The little impact of nitrate on carbonate weathering may result in the overestimation of impact of N-fertilizer on CO₂ consumption by carbonate weathering at the regional/global scale if the effect of NO₃⁻ and NH₄ are not distinguished. Thus, the related anthropogenic inputs (e.g. Ca+ Mg, NH₄, NO₃⁻, HCO₃⁻, etc.) need to be investigated to more accurately estimate the impact of fertilization on carbonate weathering and its CO₂ consumption.

6. Acknowledgements

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Table 1 Chemical composition of soil

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Values</th>
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<tbody>
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<td>pH</td>
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<td>Organic matter</td>
<td>%</td>
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<tr>
<td>NH$_4^+$-N</td>
<td>mg/kg</td>
<td>339.87</td>
</tr>
<tr>
<td>NO$_3^-$-N</td>
<td>mg/kg</td>
<td>569.05</td>
</tr>
<tr>
<td>Available P</td>
<td>mg/kg</td>
<td>8.18</td>
</tr>
<tr>
<td>Available K</td>
<td>mg/kg</td>
<td>56.88</td>
</tr>
<tr>
<td>Available Ca</td>
<td>mg/kg</td>
<td>3041.06</td>
</tr>
<tr>
<td>Available Mg</td>
<td>mg/kg</td>
<td>564.83</td>
</tr>
<tr>
<td>Available S</td>
<td>mg/kg</td>
<td>100.72</td>
</tr>
<tr>
<td>Available Fe</td>
<td>mg/kg</td>
<td>24.41</td>
</tr>
</tbody>
</table>
## Table 2 Carbonate weathering under different fertilizer treatments

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Limestone</th>
<th>Dolostone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acw /g</td>
<td>Ra /g·m⁻²·a⁻¹</td>
</tr>
<tr>
<td>Control</td>
<td>0.0014±0.0004</td>
<td>2.00±0.58</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>0.0174±0.0014</td>
<td>24.86±2.01</td>
</tr>
<tr>
<td>NH₄HCO₃</td>
<td>0.0147±0.0024</td>
<td>21.00±3.45</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>0.0031±0.0012</td>
<td>4.43±1.73</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>0.0149±0.0017</td>
<td>21.29±2.45</td>
</tr>
<tr>
<td>(NH₄)₂CO₃</td>
<td>0.0144±0.0031</td>
<td>20.57±4.46</td>
</tr>
<tr>
<td>Ca₃(PO₄)₂</td>
<td>0.0003±0.0006</td>
<td>0.43±0.86</td>
</tr>
<tr>
<td>(NH₄)₃PO₄</td>
<td>0.0028±0.0008</td>
<td>4.00±1.15</td>
</tr>
<tr>
<td>Ca-Mg-P</td>
<td>-0.0013±0.0003</td>
<td>-1.86±0.43</td>
</tr>
<tr>
<td>Urea</td>
<td>0.0243±0.0030</td>
<td>34.71±4.32</td>
</tr>
<tr>
<td>K₂CO₃</td>
<td>-0.0008±0.0004</td>
<td>-1.14±0.58</td>
</tr>
</tbody>
</table>

**Acw** - the amount of carbonate weathering; **Ra** - the ratio of carbonate weathering; **Ra** - the rate of carbonate weathering; Acw = (Wi-Wf); Ra = (Wi-Wf)/(S·T), where Wi is the initial weight of the carbonate rock tablets, and Wf 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

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Relative molecular mass /g/mol</th>
<th>Amount of added fertilizer /g</th>
<th>Molar concentration /mol</th>
<th>Initial NH$_4^+$ /mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$NO$_3$</td>
<td>80</td>
<td>43</td>
<td>0.54</td>
<td>0.54</td>
</tr>
<tr>
<td>NH$_4$HCO$_3$</td>
<td>79</td>
<td>85</td>
<td>1.08</td>
<td>1.08</td>
</tr>
<tr>
<td>NaNO$_3$</td>
<td>85</td>
<td>91</td>
<td>1.07</td>
<td>0.00</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>53.5</td>
<td>57</td>
<td>1.07</td>
<td>1.07</td>
</tr>
<tr>
<td>(NH$_4$)$_2$CO$_3$</td>
<td>96</td>
<td>51</td>
<td>0.53</td>
<td>1.06</td>
</tr>
<tr>
<td>Ca$_3$(PO$_4$)$_2$</td>
<td>310</td>
<td>52</td>
<td>0.17</td>
<td>0.00</td>
</tr>
<tr>
<td>(NH$_4$)$_3$PO$_4$</td>
<td>149</td>
<td>15</td>
<td>0.10</td>
<td>0.30</td>
</tr>
<tr>
<td>Ca-Mg-P</td>
<td>/</td>
<td>44</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Urea</td>
<td>60</td>
<td>32</td>
<td>0.53</td>
<td>1.06</td>
</tr>
<tr>
<td>K$_2$CO$_3$</td>
<td>138</td>
<td>10</td>
<td>0.07</td>
<td>0.00</td>
</tr>
</tbody>
</table>
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$_4$NO$_3$; 3-NH$_4$HCO$_3$; 4-NaNO$_3$; 5-NH$_4$Cl; 6-(NH$_4$)$_2$CO$_3$; 7-Ca$_3$(PO$_4$)$_2$; 8-(NH$_4$)$_3$PO$_4$; 9-Ca-Mg-P; 10-Urea; 11-K$_2$CO$_3$. R$_{cw}$=(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.
Fig. 4 The ratio of limestone weathering and the molar amount of produced NH$_4^+$ under different fertilization treatment

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