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 agricultural fertilization since the addition of fertilizers tends to change the chemical characteristics of soil such as pH value. Different fertilizers may exert a different impact on carbonate weathering, but these discrepancies are not still well-known so far. In this study, a field column experiment was conducted to explore the responses of carbonate weathering to the addition of different fertilizers. We compared 11 different treatments including a control treatment using 3 replicates per treatment. Carbonate weathering was assessed by measuring the weight loss of carbonate and dolomite tablets buried at the bottom of the columns. The result showed that the addition of urea, NH₄NO₃, NH₄HCO₃, NH₄Cl and (NH₄)₂CO₃ distinctly increased carbonate weathering, which was attributed to the nitrification of NH₄⁺. The addition of Ca₃(PO₄)₂, Ca-Mg-P and K₂CO₃ induced carbonate precipitation due to common ion effect. The addition of (NH₄)₃PO₄ and NaNO₃ did not significantly impact carbonate weathering. The results of NaNO₃ treatment raise a new question: the negligible impact of nitrate on carbonate weathering may result in the overestimation of impact of N-fertilizer on CO₂ consumption by carbonate weathering at the regional/global scale if the effects of NO₃ and NH₄ are not distinguished.

Keywords: Carbonate weathering; Column experiment; Nitrogenous fertilizer; Phosphate fertilizer; Southwest China
1. **Introduction**

Carbonate weathering plays a significant role in consumption of atmospheric CO$_2$ (Kump et al., 2000; Liu et al., 2010; 2011). The riverine hydro-chemical composition such as the ratio of HCO$_3^-$ to Ca$^{2+}$+Mg$^{2+}$ is usually employed as an indicator to estimate the CO$_2$ consumption by natural carbonate weathering at the regional/global scale (Hagedorn and Cartwright, 2009; Li et al., 2009). However, fluvial alkalinity may also be produced by other processes including the reaction between carbonates and the protons derived (i) from the nitrification of N-fertilizer (Barnes and Raymond, 2009; Chao et al., 2011; Gandois et al., 2011; Hamilton et al., 2007; Oh and Raymond, 2006; Perrin et al., 2008; Pierson-wickmann et al., 2009; Semhi and Suchet, 2000; West and McBride, 2005), (ii) from the sulfuric acid (Lerman and Wu, 2006; Lerman et al., 2007; Li et al., 2008; Li et al., 2009), (iii) from organic acid secreted by microorganisms (Lian et al., 2008) as well as (iv) from acidic soil (Chao et al., 2014). Given that atmospheric CO$_2$ is not the unique weathering agent, differentiating the agent of carbonate weathering is important for the accurate budgeting of the net CO$_2$ consumption by carbonate weathering, especially in agricultural areas where mineral fertilizers are used.

The world average annual increase in mineral fertilizer consumption was 3.3% from 1961 to 1997, and FAO’s study predicts a 1% increase per year until 2030 (FAO, 2000). For China, the consumption of chemical fertilizer increased from 12.7 Mt in 1980 to 59.1 Mt in 2013 (Fig. 1). The Increasing consumption of mineral fertilizer is a significant disturbance factor of carbonate weathering and carbon cycle. Several
studies showed that nitrogen fertilizer additions increased weathering rates and increased the total export of DIC from agricultural watersheds (Barnes and Raymond, 2009; Gandois et al., 2011; Hamilton et al., 2007; Oh and Raymond, 2006; Perrin et al., 2008; Pierson-wickmann et al., 2009; Probst, 1986; Semhi and Suchet, 2000; West and McBride, 2005). According to estimates by Probst (1988) and Semhi et al. (2000), the contribution of N-fertilizers to carbonate dissolution was 30% and 12-26% in two small agricultural carbonate basins in south-western France, the Girou and the Gers respectively (subtributary and tributary of the Garonne river, respectively). For the Garonne river basin, which is larger basin (52,000 km²), this contribution was estimated at 6% by Semhi et al. (2000). Perrin et al. (2008) estimated that the contribution of N-fertilizer (usually in form of NH₄NO₃) represent up to 5.7-13.4% and 1.6-3.8% to carbonate dissolution for France and on a global scale, respectively. The estimates described above were usually based on calculations assuming that a single type of fertilizer (e.g. (NH₄)₂SO₄, NH₄NO₃, or NH₄Cl) was used throughout the whole basin that was considered. However, 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. Because the addition of different N-fertilizers (e.g. (NH₄)₂SO₄, NH₄NO₃, NH₄Cl, NaNO₃ or urea) may result in different contributions to carbonate weathering and relative products such as HCO₃⁻, Ca²⁺ and Mg²⁺. For phosphate fertilizer, the
coprecipitation of phosphate ions with calcium carbonate may inhibit carbonate weathering (Kitano et al., 1978). We suppose that the response of carbonate weathering to the addition of different fertilizer such as N-fertilizer (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), yet it is a preferred option for the condition controlled contrast or stimulated experiment (Chao et al., 2011; Chao et al., 2014).

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 (about 8,000 km²), 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 150 kg/ha in 1980 to 190 kg/ha 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 (\(V_{\text{soil}}:V_{\text{water}} = 1:2.5\)) 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 1\(^{-1}\) NaOH, 0.01 mol 1\(^{-1}\) 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 1\(^{-1}\) KCl solution, available K, P and Fe were extracted by extracting solution containing 0.25 mol 1\(^{-1}\) NaHCO\(_3\), 0.01 mol 1\(^{-1}\) EDTA, 0.01 mol 1\(^{-1}\) NH\(_4\)F, and 0.005% Superfloc 127, and available S was extracted by 0.1 mol 1\(^{-1}\) Ca(H\(_2\)PO\(_4\))\(_2\) and 0.005% Superfloc 127. The results are shown in Table 1.

### 2.3 Soil column and different fertilization treatments

In order to test the hypothesis that the responses of the impact of different chemical fertilizer on carbonate weathering may be different, columns (Ø=20 cm, H=15 cm) 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) 43 g NH\(_4\)NO\(_3\) fertilizer (CF); (3) 85 g NH\(_4\)HCO\(_3\) fertilizer (NHC); (4) 91 g NaNO\(_3\) fertilizer (NN); (5) 57 g NH\(_4\)Cl fertilizer (NCL); (6) 51 g (NH\(_4\))\(_2\)CO\(_3\) fertilizer (NC); (7) 52 g Ca\(_3\)(PO\(_4\))\(_2\) fertilizer (CP); (8) 15 g (NH\(_4\))\(_3\)PO\(_4\) fertilizer (NP); (9) 44 g fused calcium-magnesium phosphate fertilizer (Ca-Mg-P); (10)
32 g Urea fertilizer (U) and (11) 10 g K₂CO₃ fertilizer (PP). The 6 kg soil was weighed (bulk density=1.3 g/cm³), mixed perfectly with above fertilizer, respectively, and filled in its own column. These soil columns were placed at the field experiment site in Guiyang of Southwestern China for a whole year.

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

The amount of weathering (Aw), the ratio of weathering (Rw) and the rate of weathering (Raw) for limestone and dolomite were calculated according to the weight difference of the tablets using the following formulas:

\[ Aw = (Wi-Wf) \]  \hspace{1cm} (1)

\[ Rw = (Wi-Wf)/ Wi \]  \hspace{1cm} (2)

\[ Raw = (Wi-Wf)/(S*T) \]  \hspace{1cm} (3)

where Wi is the initial weight of the carbonate rock tablets, Wf is their final weights, S is the surface area of carbonate weathering tablets, and T is the length of the
2.4 Statistical analysis

Statistical analysis was performed using IBM SPSS 20.0 (Statistical Graphics Crop, Princeton, USA). All results of carbonate weathering were reported as the means±standard deviations (SD) for the three replications. One-way analysis of variance (ANOVA) was used to determine the differences of weathering rate between limestone and dolostone.

3. Results

3.1 The weathering rate of carbonate under different fertilized treatments

The Rw and Raw of limestone and dolostone were listed in Table 2. The results showed that the Rw of limestone under urea, NH₄NO₃, NH₄Cl, (NH₄)₂CO₃ and NH₄HCO₃ treatments were 8.48±0.96, 6.42±0.28, 5.54±0.64, 4.44±0.81 and 4.48±0.95‰ (mean±SD, p<0.05), much bigger than that under the control treatment 0.48±0.14‰ (see Fig. 3) as observed in dolomite (6.59±0.67, 5.30±0.87, 4.77±0.78, 4.94±1.91 and 3.22±0.87‰ under these five fertilization treatments vs. -0.31±0.09‰ in control treatment). This manifested that the addition of these five fertilizers increased the rate of carbonate weathering.

According to the results of ANOVA analysis, the rest treatments had no significant differences (p>0.05) in the Rw and Rcw of limestone and dolomite in comparison with control treatment (Table 2). In (NH₄)₃PO₄ treatment, the Rw, and Raw were only 1.08±0.34‰ and 0.75±0.21‰ for limestone and dolomite, 4.00±1.15 g·m⁻²·a⁻¹ and 1.00±1.01 g·m⁻²·a⁻¹ for limestone and dolomite, respectively, less than
those under other four NH₄-fertilizers as mentioned above. The Rw and Raw in NaNO₃ treatment failed to show a remarkable difference with the control treatment, exhibiting little effect of NaNO₃ fertilizer addition on carbonate weathering (Fig. 3). Except the Rw of limestone in Ca₃(PO₄)₂ treatment approaching zero, all the values of Rw and Raw in Ca-Mg-P, K₂CO₃ and Ca₃(PO₄)₂ treatments showed a negative value, indicating that the addition of Ca-Mg-P, K₂CO₃ and Ca₃(PO₄)₂ fertilizers can lead to the precipitation at the surface of carbonate mineral, which can be explained by common ion effect.

3.2 The comparison of limestone of dolomite

The statistical significance of the Rw between limestone and dolomite using one-way analysis of variance (ANOVA) was 0.320 (>0.05), suggesting that the results between limestone and dolostone weathering under different treatments were similar. We will explain the results with carbonates instead of individual dolostone and limestone.

4. Discussion

4.1 The kinetics of carbonate dissolution/precipitation: controlling factors

Experimental studies of carbonate dissolution kinetics have shown metal carbonate weathering usually depends upon three parallel reactions occurring at the carbonate interface (Chou et al., 1989; Plummer et al., 1978; Pokrovsky et al., 2009):

\begin{align*}
\text{MeCO}_3 + \text{H}^+ & \leftrightarrow \text{Me}^{2+} + \text{HCO}_3^- \quad (4) \\
\text{MeCO}_3 + \text{H}_2\text{CO}_3 & \leftrightarrow \text{Me}^{2+} + 2\text{HCO}_3^- \quad (5) \\
\text{MeCO}_3 & \leftrightarrow \text{Me}^{2+} + \text{CO}_3^{2-} \quad (6)
\end{align*}
where Me=Ca, Mg. As Eq. (5) describes, atmospheric/soil CO$_2$ is usually regard as the natural weathering agent of carbonate. In watersheds with calcite- and dolomite-containing bedrock, H$_2$CO$_3$ formed in the soil zone usually reacts with carbonate minerals, resulting in dissolved Ca, Mg, and HCO$_3^-$ as described in Eq. (5) (Shin et al., 2014; Andrews and Schlesinger, 2001). Although it has been proven that the reaction of carbonate dissolution is mainly controlled by the amount of rainfall (Amiotte Suchet et al., 2003; Egli and Fitze, 2001; Kiefer, 1994), we consider that the effect of rainfall is equal in each soil column and hence unconsidered as a controlling factor in this study. The Eq. (4) suggests that the proton from other origins such as the nitrification processes of NH$_4^+$, as mentioned in introduction section, can play the role of weathering agent in agricultural areas. 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). Thus these increases are strongly relative to the effect of the proton released from the nitrification of NH$_4^+$. On the contrary, the carbonate precipitation will occur as due to the backward reaction of the Eq. (5) in following cases: (1) the degassing of dissolved CO$_2$, (2) soil evapotranspiration or (3) common ion effect: the increase of Ca$^{2+}$, Mg$^{2+}$ or CO$_3^{2-}$ in a weathering-system with equilibrium between water and calcite (Calmels et al., 2014; Dreybrodt, 1988).

4.2 The main reactions and effects in different treatments

The main reactions and effects of every treatment in this study were listed in Table 3.
(1) The nitrification in \( \text{NH}_4 \)-fertilizer: \( \text{NH}_4\text{NO}_3, \text{NH}_4\text{HCO}_3, \text{NH}_4\text{Cl}, (\text{NH}_4)_2\text{CO}_3 \) and urea

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

\[
\text{CO}(\text{NH}_2)_2 + 3\text{H}_2\text{O} \rightarrow 2\text{NH}_4^+ + 2\text{OH}^- + \text{CO}_2
\]  

(7)

Although the study from Singh et al showed that a part of \( \text{NH}_4^+ \) may be lost as ammonia (\( \text{NH}_3 \)) and subsequently as nitrous oxide (\( \text{N}_2\text{O} \)) (Singh et al., 2013), yet the rest ammonium (\( \text{NH}_4^+ \)) is mainly oxidized in soil by autotrophic bacteria (like Nitrosomonas) during nitrification, resulting in nitrite \( \text{NO}_2^- \) and \( \text{H}^+ \) ions. Nitrite is, in turn, oxidized by another bacterium, such as Nitrobacter, resulting in nitrate (\( \text{NO}_3^- \)) (Eq. (8)) (Perrin et al., 2008).

\[
\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + 2\text{H}^+
\]  

(8)

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

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

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

(9)

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

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

(10)

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

\[
2\text{Ca}_{(1-x)}\text{Mg}_x\text{CO}_3 + \text{NH}_4^+ + 2\text{O}_2 \rightarrow 2(1-x) \text{Ca}^{2+} + 2x\text{Mg}^{2+} + \text{NO}_3^- + \text{H}_2\text{O} + 2\text{HCO}_3^-
\]  

(11)
As discussed above, provided that the loss as ammonia (NH$_3$) and nitrous oxide (N$_2$O) after hydrolyzation is unconsidered in this study, the final equation of carbonate weathering in NH$_4$NO$_3$, NH$_4$HCO$_3$, NH$_4$Cl, (NH$_4$)$_2$CO$_3$ and urea treatments will be followed as, respectively:

\[
2\text{Ca}_{(1-x)}\text{Mg}_x\text{CO}_3 + \text{NH}_4\text{NO}_3 + 2\text{O}_2 \rightarrow 2(1-x) \text{Ca}^{2+} + 2x\text{Mg}^{2+} + 2\text{NO}_3^- + \text{H}_2\text{O} + 2\text{HCO}_3^- \quad (12)
\]

\[
2\text{Ca}_{(1-x)}\text{Mg}_x\text{CO}_3 + \text{NH}_4\text{HCO}_3 + 2\text{O}_2 \rightarrow 2(1-x) \text{Ca}^{2+} + 2x\text{Mg}^{2+} + \text{NO}_3^- + \text{H}_2\text{O} + 3\text{HCO}_3^- \quad (13)
\]

\[
2\text{Ca}_{(1-x)}\text{Mg}_x\text{CO}_3 + \text{NH}_4\text{Cl} + 2\text{O}_2 \rightarrow 2(1-x) \text{Ca}^{2+} + 2x\text{Mg}^{2+} + \text{NO}_3^- + \text{Cl}^- + \text{H}_2\text{O} + 2\text{HCO}_3^- \quad (14)
\]

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

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

(2) No effect of NO$_3$-fertilizer treatment: NaNO$_3$ treatment

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

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

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

In K$_2$CO$_3$ treatment, CO$_3^{2-}$ and HCO$_3^-$ will produce according to Eq. (18) after adding K$_2$CO$_3$, hence resulting in carbonate precipitation described in Eq. (19) due to the common ion effect.
For $(\text{NH}_4)_3\text{PO}_4$ treatment, the reaction of carbonate weathering will occur according to Eq. (11) due to the nitrification of $\text{NH}_4^+$ ionized from $(\text{NH}_4)_3\text{PO}_4$ fertilizer will occur the nitrification. Whilst the $\text{PO}_4^{3-}$ anion will exert an inhibition to calcite dissolution: calcium orthophosphate (Ca-P) precipitation produces on the surface of calcite after the addition of $\text{PO}_4^{3-}$ in soil, resulting in inhibiting the dissolution of calcite.

(5) Complex effects: Common ion effect versus Inhibition effect of $\text{PO}_4$ in $\text{Ca}_3(\text{PO}_4)_2$ and Ca-Mg-P treatments

In $\text{Ca}_3(\text{PO}_4)_2$ and Ca-Mg-P treatments, on the one hand, the $\text{Ca}_{(1-x)}\text{Mg}_x\text{CO}_3$ produces when the concentrations of $\text{Ca}^{2+}$ (or/and $\text{Mg}^{2+}$) increases as following Eq. (19). On the other hand, the inhibition effect of phosphate will cause that calcium phosphate precipitation produces on the surface of carbonate mineral after the addition of $\text{P}$ in soil, correspondingly resulting in inhibiting the carbonate precipitation.

4.3 The difference between $\text{NH}_4^+$ and $\text{NO}_3^-$ in impacts on carbonate weathering and the implication on the estimation of $\text{CO}_2$ consumption

In order to further compare the difference between $\text{NH}_4^+$ and $\text{NO}_3^-$ effects on carbonate weathering, the initial molar amount of fertilizer-derived $\text{NH}_4$ per unit in every treatment were calculated and listed in Table 4. The results show that the
amount of NH$_4^+$ hydrolyzed from urea is 1.06 mole, while NH$_4^+$ ionized from
NH$_4$NO$_3$, NH$_4$HCO$_3$, NH$_4$Cl, (NH$_4$)$_2$CO$_3$ and (NH$_4$)$_3$PO$_4$ is 0.54 mole, 1.08 mole,
1.07 mole, 1.06 mole and 0.03 mole, respectively (Table 3). The $R_w$ of limestone
tablets and the initial amount of NH$_4^+$ are plotted in Fig. 4. A distinct relationship
between them is observed: the $R_w$ in NH$_4$NO$_3$, NH$_4$HCO$_3$, NH$_4$Cl, (NH$_4$)$_2$CO$_3$ and
urea treatments are bigger than in control treatment, where the initial amount of NH$_4^+$
displays similar results (Fig. 4). This suggests that carbonate weathering in NH$_4$NO$_3$,
NH$_4$HCO$_3$, NH$_4$Cl, (NH$_4$)$_2$CO$_3$ and urea treatments are mainly attributed to the
dissolution reaction described as Eq. (11). This process of carbonate weathering by
protons from nitrification has been proven by many studies, from laboratory to field
(Semhi and Suchet, 2000; Bertrand et al., 2007; Oh and Raymond, 2006; Errin et al.,
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).
We have noted that the $R_w$ values in NH$_4$HCO$_3$ and (NH$_4$)$_2$CO$_3$ treatment are lower
than even half of those in urea treatment in spite of adding the same amount of
fertilizer-derived NH$_4$ (about 1.07 mole). This is probably because the two fertilizers,
NH$_4$HCO$_3$ and (NH$_4$)$_2$CO$_3$, are easier to decompose and produce the NH$_3$ and CO$_2$
gases as following Eq. (20) and (21), resulting in the amount of fertilizer-derived NH$_4$
of lower than 1.07 moles.

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

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

The $A_w$ and $R_w$ in (NH$_4$)$_3$PO$_4$ treatment, unlike in other NH$_4$-fertilizer treatments,
had not a significant increase comparing with control treatment, which is not only
owing to the low amount of added NH$_4^+$ in (NH$_4$)$_3$PO$_4$ treatment (0.3 mole, see Table
but also more or less relative to the inhibition of phosphate (Chien et al., 2011; Wang et al., 2012). After the addition of (NH₄)₃PO₄ in soil, calcium orthophosphate (Ca-P) precipitation will form on calcite surface which is initiated with the aggregation of clusters leading to the nucleation and subsequent growth of Ca-P phases, at various pH values and ionic strengths relevant to soil solution conditions (Chien et al., 2011; Wang et al., 2012).

However, in Fig. 3, the Rw without significant difference with control treatment in NaNO₃ treatment indicates that the addition of NO₃-fertilizer does not significantly influence carbonate weathering.

A notable issue herein is that the NaNO₃ treatment produces the same amount of NO₃⁻ (1.07 mole) as other NH₄ fertilizer (NH₄NO₃, NH₄HCO₃, NH₄Cl, (NH₄)₂CO₃ and urea), but it fails to impact on carbonate weathering, which is raising a new problem. Eq. (5), usually as an expression for the natural weathering process of carbonate, is an important reaction for understanding the kinetics process of carbonate dissolution in carbonate-dominated areas, where the molar ratio of HCO₃⁻ and Me²⁺ in the river as an indicator is usually used to make estimations of CO₂ consumption by carbonate weathering at the regional/global scale (Hagedorn and Cartwright, 2009; Li et al., 2009). At agricultural areas, the relationship between (Ca+Mg)/HCO₃⁻ and NO₃⁻ is usually employed to estimate the contribution of N-fertilizer to riverine Ca²⁺, Mg²⁺ and alkalinity (Etchanchu and Probst, 1988; Jiang, 2013; Jiang et al., 2009; Perrin et al., 2008; Semhi and Suchet, 2000). In these studies, the nitrification described as Eq. (8) is usually considered as the unique origin of NO₃⁻. According to the result of NaNO₃ treatment in this study, the contribution of protons from nitrification to carbonate weathering may be overestimated if anthropogenic NO₃ is neglected, since the anthropogenic NO₃⁻ does not release the proton described as Eq. (8). For NH₄NO₃
fertilizer, the (Eq. (12)) show that the two moles of Ca\(^{2+}\)+Mg\(^{2+}\), NO\(_3^-\) and HCO\(_3^-\) will be produced when one mole NH\(_4\)NO\(_3\) react with 2 moles of carbonate, where only half of NO\(_3^-\) originate from nitrification described as Eq. (8). This will result in a double overestimation on the contribution of the nitrification to carbonate weathering and thus mislead the estimation of CO\(_2\) consumption therein.

At regional scales, if different fertilizers are added simultaneously to an agricultural area, the estimation of CO\(_2\) consumption by carbonate weathering might became more complicated, since the mole ratio of Ca+Mg, HCO\(_3^-\) and/or NO\(_3^-\) between different fertilization treatment is different (see Table 3). Thus, the related anthropogenic inputs (e.g. Ca+Mg, NH\(_4^+\), NO\(_3^-\), HCO\(_3^-\), etc.) need to be investigated to more accurately estimate the impact of fertilization on carbonate weathering and its CO\(_2\) consumption.

4.4 The comparison with other studied results

The Rw and Raw of limestone in control treatment in this study is 0.48‰ and 2.00 g·m\(^{-2}\)·a\(^{-1}\), which is consistent with the observations of 0.51-32.97 g·m\(^{-2}\)·a\(^{-1}\) (for Raw) in Nongla, Guangxi, a karst area of Southwestern China (Zhang, 2011) and the results of 0.05-5.06‰ (for Rw) and 1.08-136.90 g·m\(^{-2}\)·a\(^{-1}\) (for Raw) from the north slope of the Hochschwab massif in Australia (Plan, 2005) using limestone tablet method. But the Raw of 2.00 g·m\(^{-2}\)·a\(^{-1}\) is lower than the results (7.0-63.5 g·m\(^{-2}\)·a\(^{-1}\) for Raw) from Jinfo Mountian in Chongqing of China (Zhang, 2011). These differences in carbonate weathering are mainly attributed to the different type of carbonate rock tablet, climate, micro-environment of soil, etc. The Raw of limestone in N-fertilizers treatment is 20.57-34.71 g·m\(^{-2}\)·a\(^{-1}\), similar to the weathering rate of carbonate in Orchard (32.97 g·m\(^{-2}\)·a\(^{-1}\)) at Nongla, Manshan, Guangxi of China where usually involves in fertilization activities.
At larger scales like watershed, the weathering rate is usually estimated by using the riverine hydro-chemical method, which is inconsistent with the results from carbonate-rock-tablet test. The estimation of Zeng, et al. (2014) views that the carbon sink intensity calculated by carbonate rock tablet test is only one sixth of that estimated by using the riverine hydro-chemical method due to its own limits in methodology (Zeng et al., 2014). The results from Semhi, et al. (2000) shows the weathering rates of carbonate rock by using riverine hydro-chemical method are about 77.5 g·m⁻²·a⁻¹ and 50.4 g·m⁻²·a⁻¹ in upstream and downstream of the Garonne river, France, respectively, which are about 25-35 and 2-3 times than that in control treatment (2.00 g·m⁻²·a⁻¹ for natural weathering rate ) and the N-fertilizer treatment (20.57-34.71 g·m⁻²·a⁻¹ for anthropic weathering rate) in this study. The global natural weathering rate of carbonate reported by Amiotte Suchet, et al. (2003) is 47.8 g·m⁻²·a⁻¹, is much higher than that we observed. Thus, we conclude that it is difficult to compare between the results from the carbonate-rock-tablet test and the riverine hydro-chemical method. The carbonate-rock-tablet test is suitable for the research on the condition controlled contrast or stimulated experiment, while the riverine hydro-chemical method is appropriate for the regional investigation and estimation. According to the estimation from Yue et al. (2015), The enhanced HCO₃⁻ flux due to nitrification of NH₄⁺ at Houzhai catchment of Guizhou province would be 3.72 × 10⁵ 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).

5. Conclusion

The impact of the addition of different fertilizer (NH₄NO₃, NH₄HCO₃, NaNO₃, 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, NH$_4$NO$_3$, NH$_4$HCO$_3$, NH$_4$Cl and (NH$_4$)$_2$CO$_3$ distinctly increased carbonate weathering, which was attributed to the nitrification of NH$_4^+$, and the addition of Ca$_3$(PO$_4$)$_2$, Ca-Mg-P and K$_2$CO$_3$ induced carbonate precipitation due to common ion effect. While the (NH$_4$)$_3$PO$_4$ and NaNO$_3$ addition did not impact significantly on carbonate weathering, where the former can be attributed to low added amount of (NH$_4$)$_3$PO$_4$, may be related to the inhibition of phosphate, and the latter seemed to be raising a new question. The little impact of nitrate on carbonate weathering may result in the overestimation of impact of N-fertilizer on CO$_2$ consumption by carbonate weathering at the regional/global scale if the effect of NO$_3^-$ and NH$_4^+$ 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.

6. Acknowledgements

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References:


Dreybrodt, W., Lauckner, J., Zaihua, L., Svensson, U. and Buhmann, D., 1996. The kinetics of the reaction CO$_2$+ H$_2$O→ H$^+$+ HCO$_3^-$ as one of the rate limiting steps for the dissolution of calcite in the system H$_2$O-CO$_2$-CaCO$_3$. Geochimica et Cosmochimica Acta, 60(18): 3375-3381.


Liu, Z. et al., 2010. Wet-dry seasonal variations of hydrochemistry and carbonate precipitation rates in
a travertine-depositing canal at Baishuitai, Yunnan, SW China: Implications for the formation of biannual laminae in travertine and for climatic reconstruction. Chemical Geology, 273(3-4): 258-266.


Table 1 Chemical composition of soil

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

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Limestone</th>
<th>Dolostone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rw /‰</td>
<td>Raw / g·m⁻²·a⁻¹</td>
</tr>
<tr>
<td>Control</td>
<td>0.48 ± 0.14a</td>
<td>2.00±0.58a</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>6.42 ± 0.28c</td>
<td>24.86±2.01b</td>
</tr>
<tr>
<td>NH₄HCO₃</td>
<td>4.44 ± 0.81b</td>
<td>21.00±3.45b</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>0.86 ± 0.17a</td>
<td>4.43±1.73a</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>5.54 ± 0.64bc</td>
<td>21.29±2.45b</td>
</tr>
<tr>
<td>(NH₄)₂CO₃</td>
<td>4.48 ± 0.95bc</td>
<td>20.57±4.46b</td>
</tr>
<tr>
<td>Ca₃(PO₄)₂</td>
<td>0.01 ± 0.04a</td>
<td>0.43±0.86a</td>
</tr>
<tr>
<td>(NH₄)₃PO₄</td>
<td>1.08 ± 0.34a</td>
<td>4.00±1.15a</td>
</tr>
<tr>
<td>Ca-Mg-P</td>
<td>-0.31 ± 0.12a</td>
<td>-1.86±0.43a</td>
</tr>
<tr>
<td>Urea</td>
<td>8.48 ± 0.96d</td>
<td>34.71±4.32c</td>
</tr>
<tr>
<td>K₂CO₃</td>
<td>-0.26 ± 0.15a</td>
<td>-1.14±0.58a</td>
</tr>
</tbody>
</table>

Rw - the ratio of carbonate weathering; Raw - the rate of carbonate weathering; Rw =1000 (Wi-Wf)/Wi; Raw = (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. Values are reported as means ± standard deviations, n=3. Values in each column followed by different letters are significantly (p <0.05) different based on one-way ANOVA.
<table>
<thead>
<tr>
<th>Treatment</th>
<th>Main reactions and effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Control</td>
<td>$\text{Ca}<em>{1.4}\text{Mg}</em>{0.6}\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow (1-x) \text{Ca}^{2+} + x\text{Mg}^{2+} + 2\text{HCO}_3^-$</td>
</tr>
<tr>
<td>2. NH$_4$NO$_3$</td>
<td>$2\text{Ca}<em>{1.4}\text{Mg}</em>{0.6}\text{CO}_3 + \text{NH}_4\text{NO}_3 + 2\text{O}_2 \rightarrow 2(1-x) \text{Ca}^{2+} + 2x\text{Mg}^{2+} + 2\text{NO}_3^- + \text{H}_2\text{O} + 2\text{HCO}_3^-$</td>
</tr>
<tr>
<td>3. NH$_4$HCO$_3$</td>
<td>$\text{NH}_4\text{HCO}_3 \rightarrow \text{NH}_3 \uparrow + \text{H}_2\text{O} + \text{CO}_2 \uparrow$</td>
</tr>
<tr>
<td>4. NaNO$_3$</td>
<td>$\text{Ca}<em>{1.4}\text{Mg}</em>{0.6}\text{CO}_3 + \text{NaNO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow (1-x) \text{Ca}^{2+} + x\text{Mg}^{2+} + \text{Na}^+ + \text{NO}_3^- + 2\text{HCO}_3^-$</td>
</tr>
<tr>
<td>5. NH$_4$Cl</td>
<td>$2\text{Ca}<em>{1.4}\text{Mg}</em>{0.6}\text{CO}_3 + \text{NH}_4\text{Cl} + 2\text{O}_2 \rightarrow 2(1-x) \text{Ca}^{2+} + 2x\text{Mg}^{2+} + \text{NO}_3^- + \text{Cl}^- + \text{H}_2\text{O} + 2\text{HCO}_3^-$</td>
</tr>
<tr>
<td>6. (NH$_4$)$_2$CO$_3$</td>
<td>(NH$_4$)$_2$CO$_3 \rightarrow 2\text{NH}_3 \uparrow + \text{H}_2\text{O} + \text{CO}_2 \uparrow$</td>
</tr>
<tr>
<td>7. Ca$_3$(PO$_4$)$_2$</td>
<td>(1-x) $\text{Ca}^{2+} + x\text{Mg}^{2+} + 2\text{HCO}<em>3^-$ $\rightarrow \text{Ca}</em>{1.4}\text{Mg}_{0.6}\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td></td>
<td>(2) Inhibition of phosphate to calcite precipitation: calcium phosphate precipitation produces on the surface of calcite after the addition of PO$_4^{3-}$ in soil, resulting in inhibiting the precipitation of calcite</td>
</tr>
<tr>
<td>8. (NH$_4$)$_3$PO$_4$</td>
<td>(1) $2\text{Ca}<em>{1.4}\text{Mg}</em>{0.6}\text{CO}_3 + \text{NH}_4^+ + 2\text{O}_2 \rightarrow 2(1-x) \text{Ca}^{2+} + 2x\text{Mg}^{2+} + \text{NO}_3^- + \text{H}_2\text{O} + 2\text{HCO}_3^-$</td>
</tr>
<tr>
<td></td>
<td>(2) Inhibition of phosphate to calcite dissolution: calcium orthophosphate (Ca-P) precipitation produces on the surface of calcite after the addition of PO$_4^{3-}$ in soil, resulting in inhibiting the dissolution of calcite</td>
</tr>
<tr>
<td>9. Ca-Mg-P</td>
<td>(1) Common ion effect: The Ca$<em>{1.4}$Mg$</em>{0.6}$CO$_3$ produces when the concentrations of Ca$^{2+}$ and Mg$^{2+}$ increases</td>
</tr>
<tr>
<td></td>
<td>(1-x) $\text{Ca}^{2+} + x\text{Mg}^{2+} + 2\text{HCO}<em>3^-$ $\rightarrow \text{Ca}</em>{1.4}\text{Mg}_{0.6}\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td></td>
<td>(2) Inhibition of phosphate to calcite precipitation: calcium phosphate precipitation produces on the surface of calcite after the addition of P in soil, resulting in inhibiting the precipitation of calcite</td>
</tr>
<tr>
<td>10. Urea</td>
<td>$3\text{Ca}<em>{1.4}\text{Mg}</em>{0.6}\text{CO}_3 + \text{CO(NH}_2)_2 + 4\text{O}_2 \rightarrow 3(1-x) \text{Ca}^{2+} + 3x\text{Mg}^{2+} + 2\text{NO}_3^- + 4\text{HCO}_3^-$</td>
</tr>
<tr>
<td>11. K$_2$CO$_3$</td>
<td>Common ion effect: The Ca$<em>{1.4}$Mg$</em>{0.6}$CO$_3$ produces when the concentration of HCO$_3^-$ increases</td>
</tr>
<tr>
<td></td>
<td>(i) (1-x) $\text{Ca}^{2+} + x\text{Mg}^{2+} + 2\text{HCO}<em>3^-$ $\rightarrow \text{Ca}</em>{1.4}\text{Mg}_{0.6}\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td></td>
<td>(ii) $\text{K}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 2\text{K}^+ + \text{HCO}_3^- + \text{OH}^-$</td>
</tr>
</tbody>
</table>
Table 4: The amount of fertilizer-derived NH$_4^+$ at the initial phase of the experiment and the potential nitrogenous transformation (NH$_4^+$-NO$_3^-$)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Molecular mass g/mol</th>
<th>Amount of added fertilizer /g</th>
<th>Molar amount /mole</th>
<th>amount of fertilizer-derived NH$_4^+$ /mole</th>
<th>The maximum of N products /mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$NO$_3$</td>
<td>80</td>
<td>43</td>
<td>0.54</td>
<td>0.54</td>
<td>1.08</td>
</tr>
<tr>
<td>NH$_4$HCO$_3$</td>
<td>79</td>
<td>85</td>
<td>1.08</td>
<td>1.08</td>
<td>1.08</td>
</tr>
<tr>
<td>NaNO$_3$</td>
<td>85</td>
<td>91</td>
<td>1.07</td>
<td>0.00</td>
<td>1.07</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>53.5</td>
<td>57</td>
<td>1.07</td>
<td>1.07</td>
<td>1.07</td>
</tr>
<tr>
<td>(NH$_4$)$_2$CO$_3$</td>
<td>96</td>
<td>51</td>
<td>0.53</td>
<td>1.06</td>
<td>1.06</td>
</tr>
<tr>
<td>Ca$_3$(PO$_4$)$_2$</td>
<td>310</td>
<td>52</td>
<td>0.17</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>(NH$_4$)$_3$PO$_4$</td>
<td>149</td>
<td>15</td>
<td>0.10</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Ca-Mg-P</td>
<td>/</td>
<td>44</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Urea</td>
<td>60</td>
<td>32</td>
<td>0.53</td>
<td>1.06</td>
<td>1.06</td>
</tr>
<tr>
<td>K$_2$CO$_3$</td>
<td>138</td>
<td>10</td>
<td>0.07</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
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 $R_w$ (‰) of limestone and dolostone 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$_3$(PO$_4$)$_2$; 8-(NH$_4$)$_3$PO$_4$; 9-Ca-Mg-P; 10-Urea; 11-K$_2$CO$_3$. $R_w = 1000(W_i-W_f)/W_i$, where $W_i$ is the initial weight of the carbonate rock tablets, and $W_f$ is their final weight. Different letters on each column are significantly ($p < 0.05$) different based on one-way ANOVA.
Fig. 4 The Rw (%) of limestone 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$_3$(PO$_4$)$_2$;
- 8-(NH$_4$)$_3$PO$_4$; 9-Ca-Mg-P; 10-Urea; 11-K$_2$CO$_3$. Rw =1000(W$_i$-W$_f$)/W$_i$, where W$_i$ is the initial weight of limestone tablets, and W$_f$ is their final weight. Different letters on each column are significantly (p <0.05) different based on one-way ANOVA.