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ORIGINAL ARTICLE

Effects of mineral-organic fertilizer on the biomass of green Chinese cabbage and potential carbon sequestration ability in karst areas of Southwest China

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Abstract The karst mountain areas of Southwest China contain barren farmland soils and suffer from nutritional and water deficiencies that affect crop productivity. Hence, it is imperative to apply suitable fertilizers to restore soil fertility and maintain crop yield. The aim of this study is to investigate the effects of mineral-organic fertilizer (MOF) made of potassic rock and organic waste on the growth of crops. For this purpose, green Chinese cabbage grown using three different fertilization methods including MOF, inorganic fertilizer (IF), and a control was evaluated. We determined soil water content, agronomic characteristics, and biomass of green Chinese cabbage in different treatments. Furthermore, surface runoff from the pot experiments and soil leachate from pot experiments were collected to determine water temperature, pH, and cation and anion concentrations. The results demonstrate that MOF can improve the soil water-holding capacity of soil, and the basic agronomic characteristics of the cabbage treated with MOF were superior to those with IF. Using MOF can promote the increase in cabbage biomass. Additionally, the concentration of inorganic carbon (largely in the form of HCO_3^-) in surface runoff water treated by MOF was higher than the other treatments, establishing carbon sequestration potential. This work provides a novel and environmentally friendly fertilization pattern in karst areas, which will improve crop yield and also increase the carbon sequestration potential of crops.

Keywords Potassic rock · Carbonate · Karst · Ion chromatograph · Carbon sequestration

1 Introduction

China has 3.44 million km^2 of karst areas, mainly in southwest China and on the Yunnan–Guizhou Plateau (Peng et al. 2008). Due to the general geological structures of karst areas (Ruan et al. 2013), lack of soil parent materials, serious water deficiency, and soil erosion, the soil contains low nutrients and thereby yields low agricultural productivity (Feng et al. 2016). Therefore, increasing the available and slowly available nutrient contents in the karst mountain soils is regarded as one of the most important ways to improve agricultural production in such areas (Lian et al. 2010). Silicates, a key component of rock-forming minerals and soil, contain rich nutrient elements (K, P, Fe, Ca, Mg, etc.) essential to plants. China, as the largest importer of potash fertilizers in the world, has one quarter to one-third of her farmland soil by area suffering from a severe lack of potassium, especially in the southern parts of the country (Xie 1998; Ma

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Qibiao Sun and Yulong Ruan have equal contribution to this work.

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et al. 2010). Such natural conditions greatly limit the development of the agricultural economy in karst areas. However, the reserves of low-grade potassic silicate rocks (such as K-feldspar and illite, < 10% K_2O) is extremely abundant in China, which are potential sources of mineral nutrients for potassium (Ma et al. 2010). Based on the study of soil evolution in karst mountain areas and bioconversion technology of potassium-containing silicate minerals, Lian et al. (2008, 2010) proposed the production of organic fertilizers through fermentation by using locally abundant K-bearing minerals, such as K-feldspar, as substrates. The organic fertilizers are suggested to be used in plant production in farmlands of karst areas to supplement soil-forming materials and thereby promote soil evolution in these areas and effectively improve soil fertility.

Nishanth and Biswas (2008) used straw, waste mica, and phosphate rock powder to ferment composts with a strain of *Aspergillus awamori*. After fermentation, the contents of water-soluble P and K greatly increased and good effects were obtained in field fertilization experiments on *Triticum aestivum*. By planting *Amaranthus tricolor* and applying organic fertilizers fermented in the presence of potassic rocks and organic waste, Yu and Lian (2011) found that above ground biomass of *A. tricolor* was equal to that when treated with inorganic fertilizers. Moreover, *A. tricolor* fertilized by the fermented organic fertilizer showed a significant increase in its capability to accumulate potassium. The results indicate that this fermented organic fertilizer can replace inorganic compound fertilizer under these experimental conditions, which promote the growth of *A. tricolor* and are conducive to accumulation of potassium in *A. tricolor*. Yang et al. (2012) found that nitrogen losses in chicken manure fermentation greatly decreased (from 26.02 to 7.48 mg/kg) after adding K-bearing rocks. Moreover, compared with the control group, the amounts of total nitrogen and available K increased by 15.8% and 76.0%, respectively and the amount of available P is 16.8% higher than that of before composting. Xiao et al. (2016) reported that the addition of dolomite and K-feldspar is likely to accelerate organic and inorganic carbon accumulation and increase the available K content in the soil. These reports provide an important basis for producing organic compound biological potassium fertilizers by fermenting and treating potassic rocks using microorganisms (Yu and Lian 2011; Yang et al. 2012; Xiao et al. 2016).

In recent years, the weathering and regulation of microorganisms on silicate minerals has enriched the understanding of mutual action processes and interactive mechanisms between microorganisms and minerals. Xiao et al. (2012a, b) discovered that microorganisms can synthesize certain proteins involved in the weathering of potassic rocks under potassium deficiency which accelerate weathering and release potassium from such minerals. Moreover, Sun et al. (2013) showed that potassic silicate mineral (K-feldspar) can increase expression levels of fungal carbonic anhydrase (CA). CA, as a group of ubiquitous microbial enzymes, can catalyze the hydration reaction of CO_2 to generate H^+ and HCO_3^- (Tripp et al. 2001). Microorganisms capable of producing CA can catalyze CO_2 hydration through CA and accelerate the weathering of potassium-containing minerals under potassium deficient conditions (Xiao et al. 2015). Hence, the weathering by microorganisms on silicate minerals can consume CO_2 (to some extent) and contribute to carbon sequestration. For example, the weathering of olivine can remove billions of tons of CO_2 from the atmosphere (Schuiling 2014). Furthermore, adding CA to karst systems can catalyse CO_2 conversion, increase the dissolution rate of limestone by one order of magnitude (Liu and Dreybrodt 1997; Li et al. 2005; Favre et al. 2009) and promote the removal of CO_2 from the atmosphere (Smith et al. 1999; Liu 2001; Zhang et al. 2011). However, the application of fermented organic fertilizers on plant growth and carbon sequestration in karst soils is still poorly understood. The capture and storage of atmospheric CO_2 through rock weathering (mainly carbonate and silicate rock weathering) on land is an important part of the global carbon cycle (Meybeck 1987; Berner 1995; Liu et al. 2010; Zeng et al. 2017). Therefore, this study is of great significance under the backdrop of global change.

Green Chinese cabbage (*Brassica chinensis*) is a common vegetable in China, growing rapidly with strong adaptability. Based on the properties of this cabbage, it is used as a model plant material in this study. The aim is to determine the effects of mineral-organic fertilizer (MOF) on the growth of the cabbage and carbon sequestration in the soil of karst areas of Southwest China by analyzing the parameters of cabbage biomass, soil liquid inorganic carbon, etc. This study provides a new idea for improving soil fertility of farmlands in karst areas coupled with mitigating atmospheric CO_2 concentration by beneficial long-term agricultural practice.

2 Materials and methods

2.1 Study area and materials used in this study

The study was conducted in the Karst Ecosystem Observation and Research Station of Puding, Chinese Academy of Science. The inorganic fertilizers used in this study consisted of chemical compound fertilizer (having N, P_2O_5, and K_2O individually accounted for 15%), carbamide (46.4% N) and calcium superphosphate (12.0% P_2O_5), purchased from Sichuan Yingfeng Industrial Co., Ltd, Bijie

Jinhe Chemical Co., Ltd, and Yunnan Xinzhengda Phosphorus Chemical Industry Co., Ltd, China, respectively. The MOF was fermented from potassic rock powder and organic matter. The organic matter for fermentation consisted of corn, sorghum stalks, and chicken manure (1/1/4, by weight). Furthermore, potassic rock powder having ~ 76% K-feldspar (X-ray powder diffraction assay), and chemical compositions being: Al_2O_3 17.11%, SiO_2 54.06%, K_2O 9.09%, CaO 1.9%, total Fe_2O_3 6.15%, and MgO 3.41% (X-ray fluorescence analysis) was mixed with the organic matter to a mass ratio of 1:3 and then microbial fermenting agent (1 kg of microbial fermenting agent per 10 t of substrate) were added. Then, the raw materials were thoroughly mixed and fermented for 30 days with periodic stirring. Nutrient indices were as follows: 2.3% of available N, 2.3% of available P_2O_5, 2.7% of available K_2O, 34% of organic matter, and a pH of 8.48. The whole fermentation process was carried out in Puding Heye Biological Organic Fertilizer Co., Ltd. Guizhou, China (Xiao et al. 2017). Besides, seeds of green Chinese cabbage were bought from Degao Vegetable Seed and Seedling Research Institute (Shandong, China).

2.2 Layout of the experiment

Three groups of experiments including flat and sloping field experiments (reclaimed wasteland on which no plants had been planted before) and pot experiments were laid out. Nine small experimental fields (each with an area of 6 m^2) separated by cement-soil retaining walls were set for each flat and sloping land experiment, respectively. To prevent the release of calcium of the cement into leachate through rainwater infiltration, a layer of epoxy resin was painted onto the surfaces of the retaining walls. Additionally, drainage tubes were installed in appropriate positions through the retaining walls, so as to drain the surface water into buckets with lids for subsequent analysis. The pot experiment area was 0.21 m^2 and leachate was collected through drilling holes in the bottom of pots. The experiential design is illustrated in Fig. 1.

The detailed fertilization of each treatment was as follows: in the control, neither inorganic fertilizer (IF) nor MOF was applied; in the IF treatment, the dose of IF (chemical compound fertilizer, pH 7.35) was 900 kg/ha; for the MOF treatment, the dose of MOF was 500 kg/ha with an addition of urea (43.05 kg/ha) and calcium superphosphate (166.20 kg/ha), maintaining the same amounts of N/P/K applied in the IF treatment. The application quantity of fertilizer used in this study was N 9.0 kg/ha, P_2O_5 9.0 kg/ha and K_2O 9.0 kg/ha, according to the local fertilization habit. Each treatment was carried out in triplicate. The cabbage seedlings that grew well were transplanted to the experimental fields or pots with unified management. Base fertilizers were applied while planting cabbage seedlings (half of the total dose) and the remaining fertilizer was applied in two batches with a 14-day interval after seedlings were planted.

2.3 Determination of soil and plant parameters

2.3.1 Monitoring of soil water content

The ML2x soil moisture tachymeter (Delta-T Devices Cambridge, UK) was used to determine the water content of the soil in pot experiments treated with different fertilizers. To ensure accuracy of the data, four monitoring points were set per pot. 500 ml of distilled water was poured every 2 days for each pot experiment until the end of the experiment, and the water content was measured on the second day after irrigation.

2.3.2 Growth characteristics of plant samples

After culture, the samples were collected and 10 fresh plants were randomly collected from each treatment group to measure their height and fresh mass. Furthermore, the plants were dried in an oven at 65 °C to a constant mass so as to measure their dry mass.

2.3.3 Water quality

Surface water and leachate from the trial pots were immediately collected after rainfall. The following methods were used for measuring relevant chemical indices of the water. A WTW Multi 3420 hand-held digital multiparameter meter (WTW Company, Germany) and the alkalinity test box Aquamerck® (MERCK Company, Germany) were used to determine water temperature (*T*), pH value, and HCO_3^- content on site. Water samples were collected for cation and anion determination using the AA900F atomic absorption spectrophotometer (PE Company, USA) and the ICS-90 type ion chromatograph (Dionex Company, USA), respectively. Additionally, the saturation indices of the calcites were calculated using Visual MINTEQ Version 3.0 (http://vminteq.lwr.kth.se/).

2.4 Statistical analyses

MS-Excel® was used to process the experimental data and the standard deviation was calculated therewith. ANOVA analysis by Tukey's HSD post hoc test was performed in SPSS 24.0 (IBM SPSS Statistics, USA).

Fig. 1 Overview of the experiment design. **A** Pot experiment; **B** Flat and sloping field experiments

3 Results and discussion

3.1 Influence of different fertilization treatments on soil physicochemical properties

The soil water contents of each treatment applied by different fertilization practices in the pot experiment were measured at fixed points every 2 days (Fig. 2). As shown in Fig. 2, due to the influences of temperature, sunlight, and precipitation, the soil water contents of different treatments all varied. The soil water content increased during precipitation while it decreased in sunlight. However, the soil water content in the MOF treatment was significantly higher than that in the IF and control treatments, which may be due to the clay minerals formed by biological transformation of potassium—containing silicate mineral powders in MOF being able to combine and absorb water.

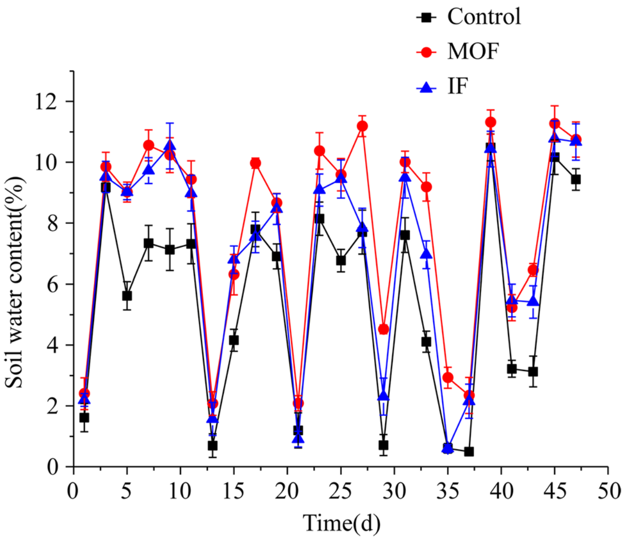


Fig. 2 Comparison of soil water contents of different treatment groups in the pot experiment. *MOF* mineral-organic fertilizer, *IF* inorganic fertilizer

The roots of green Chinese cabbage treated by the MOF were more developed and could retain a certain amount of water. The plants treated with MOF, with a large leaf area, can provide a measure of shelter from the sun and reduce evaporation of soil water. In addition, the roots and aboveground parts of plants treated by the IF were more developed than those in the control treatment. Therefore, the water content of treatments applied with MOF and IF were higher than control.

In this experiment, plants in the MOF treatment notably can resist the hot sun, while plants in the IF treatment lost water seriously (Fig. 3A, B). Moreover, the soil was dry and lacked water; however, those of green Chinese cabbage treated by MOF were upright and had sufficient water. Due to dry weather, on the fortieth day, the leaves of those green Chinese cabbage treated by IF became yellow and the plants gradually wilted, while those treated by the MOF remained dark green (Fig. 3C, D). Therefore, fertilizing with MOF enables the soil to hold more water, contributing to a high soil water content, which is conducive to the growth of green Chinese cabbage. The use of organic fertilizer is favorable to forming mineral-associated organic water-stable aggregates (Aoyama et al. 1999), which contributes to the retention of soil moisture.

The concentration of soil-soluble cations applied by MOF and IF was increased by more than that in the control group (Supplemental Material *S1.docx*): at most sampling points the amount of soil soluble cations (Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}) in MOF-applied treatments was significantly higher than that under IF treatments. The concentration of soil soluble cations increased later in the culture process with MOF: however, the concentration of soil soluble cations was increased after IF application, which indicated IF has a short duration effect on fertility. Interestingly, the concentrations of K^{+} and Ca^{2+} on 25 April, 29 April and 4 May increased significantly (Supplementary Material *S1.docx*), which may be mainly responsible for the

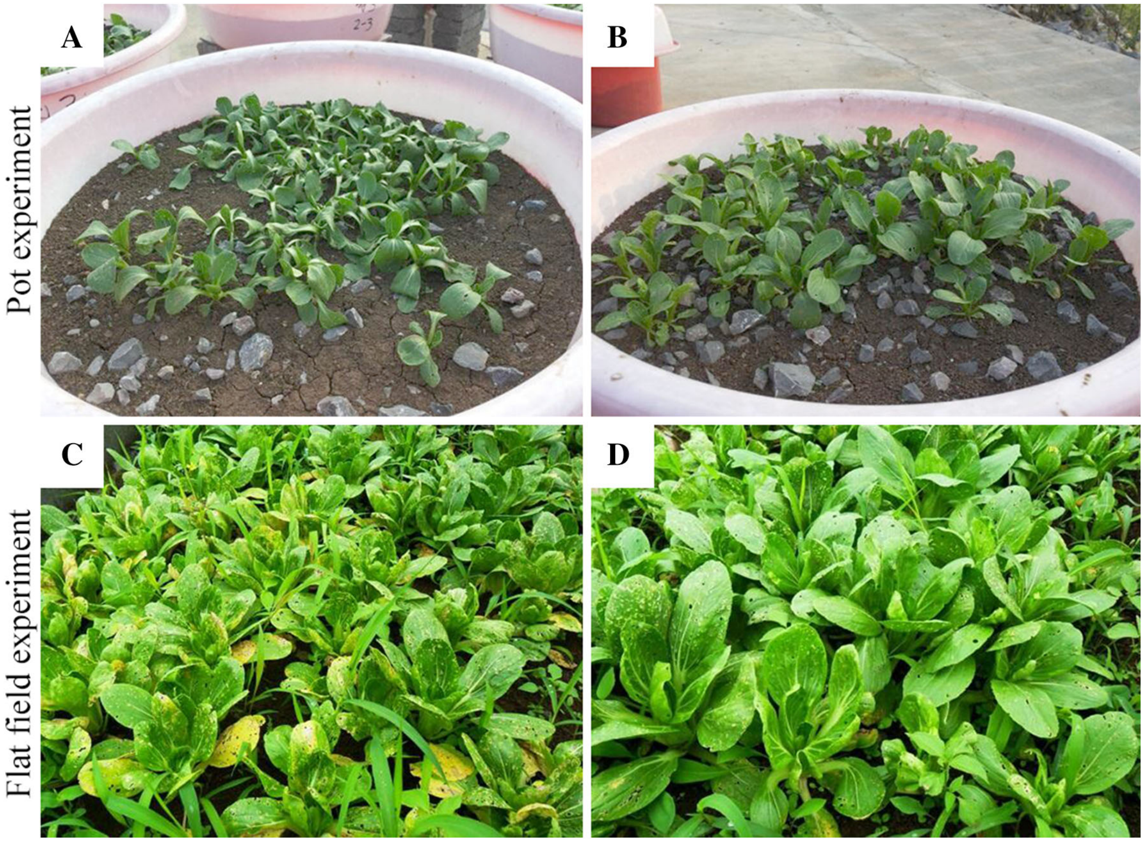


Fig. 3 The growth profiles of green Chinese cabbage in pot and flat field experiments added by IF (**A**, **C**) and MOF (**C**, **D**)

decomposition of organic matter and the further bioweathering of potassic rocks by soil microbes that released large amounts of K^+ and Ca^{2+} immobilized in organic matter. The result suggests that fermented mineral-organic matter used can maintain soil fertility in the longer-term. Bhattacharyya et al. (2007) showed the application of compost made of municipal solid waste contributes to improving the sustainable supply of exchangeable potassium in lowland rice. The application of organic fertilizer not only improves available macronutrient content but may also increase soil micronutrient availability (Li et al. 2007). The IF is widely used in karst region due to extremely poor land conditions, largely contributing to the deterioration of the environment. Therefore, the application of MOF, aimed at the characteristics of karstic land, shows potential practical value.

3.2 Effects of different fertilization treatments on the growth characteristics of green Chinese cabbage

Samples of green Chinese cabbage were collected and the height of plants and their biomass were measured (Table 1). Different fertilizer applications significantly affected the growth of green Chinese cabbage. As listed in Table 1, in flat land, sloping land, and pot experiments, the plant heights of green Chinese cabbage treated by IF and MOF were higher than those in the control and the plants treated by MOF were higher than those treated by IF. Furthermore, the aboveground and underground biomasses (fresh and dry masses) of green Chinese cabbage treated by MOF and IF were higher than those of the control, suggesting the application of MOF or IF is important for vegetable growth in a karst region. The aboveground fresh mass of green Chinese cabbage treated by MOF on sloping land was slightly lower than that under IF treatment (no significant difference). Except for this, the biomass of others treated by MOF was larger than, or equal to, that of the IF treatment. The results showed that fermented MOF is able to replace IF and provide nutrients for the growth of green Chinese cabbage in the long term. Billah and Bano (2015) showed that rock phosphate-enriched compost contributes to the nutrient uptake and growth of plants, indicating MOF can be used as a novel environment-friendly fertilizer in karst areas to improve soil properties and crop yield. Furthermore, MOF promotes the development of basic agronomic characteristics and accumulation of biomass with superior effects compared with traditional IFs. The underground biomass (fresh and dry mass) of green Chinese cabbage treated by MOF was greater than,

Table 1 Influences of different fertilisation practices on the growth of green Chinese cabbage

	Treatment	Plant height (cm)	Biomass (g/plant)				Root/shoot ratio	
			Aboveground fresh mass	Underground fresh mass	Above ground dry mass	Underground dry mass	Fresh mass ratio	Dry mass ratio
Flat land	Control	6.82 ± 0.41^{d}	3.41 ± 0.44^{d}	0.25 ± 0.02^{e}	0.45 ± 0.03^{e}	0.08 ± 0.01^{e}	0.073	0.178
	MOF	15.40 ± 0.57^{a}	44.63 ± 1.64^{a}	1.86 ± 0.13^{aB}	3.29 ± 0.16^{aA}	0.55 ± 0.04^{a}	0.042	0.167
	IF	13.12 ± 0.62^{b}	32.34 ± 2.01^{b}	1.79 ± 0.08^{a}	2.90 ± 0.07^{b}	0.55 ± 0.02^{a}	0.055	0.190
Slope land	Control	5.92 ± 0.26^{d}	2.19 ± 0.19^{d}	0.15 ± 0.02^{e}	0.27 ± 0.05^{e}	0.05 ± 0.01^{e}	0.068	0.185
	MOF	12.65 ± 0.85^{b}	17.53 ± 1.38^{b}	1.37 ± 0.09^{b}	1.65 ± 0.08^{c}	0.30 ± 0.04^{b}	0.078	0.182
	IF	12.54 ± 0.92^{b}	17.57 ± 1.27^{b}	1.19 ± 0.09^{bc}	1.57 ± 0.06^{c}	0.25 ± 0.04^{bc}	0.068	0.159
Pot	Control	3.99 ± 0.21^{e}	1.87 ± 0.15^{d}	0.10 ± 0.02^{e}	0.23 ± 0.04^{e}	0.03 ± 0.01^{e}	0.053	0.130
	MOF	8.68 ± 0.61^{c}	8.51 ± 0.83^{c}	0.96 ± 0.12^{cd}	0.85 ± 0.10^{d}	0.20 ± 0.03^{c}	0.113	0.235
	IF	8.44 ± 0.47^{c}	8.49 ± 0.79^{c}	0.93 ± 0.10^{d}	0.80 ± 0.08^{d}	0.19 ± 0.02^{c}	0.110	0.238

Root/shoot ratio is calculated by average data

Values followed by the same letter within each column have not significantly difference according Tukey's HSD post hoc test at $p < 0.05$, respectively

or equal to, that under IF treatments. This indicated that MOF significantly promoted root development in green Chinese cabbage. Such well-developed roots could provide favorable conditions for green Chinese cabbage with regard to their nutrient and water absorption, paving a foundation for the development of aboveground parts and accumulation of biomass. Gomes et al. (2005) showed that silicon can induce plant resistance to insects, indicating that, adding silicate minerals/rocks to organic fertilizer can contribute to the increased vigor of plant defense mechanisms (Correa et al. 2005; Gomes et al. 2005) as the bio-weathering of minerals/rocks can release silicon.

3.3 Carbon sequestration effects of using MOF

MOF can facilitate the development of green Chinese cabbage and the accumulation of plant biomass (Table 1), which fixes more atmospheric CO_2 through photosynthesis, and increases organic carbon sequestration. Furthermore, the inorganic carbon contents (mainly in the form of HCO_3^-) of surface runoff from sloping land and leachate from pots were significantly increased after fertilizing with MOF compared with the control and the IF treatment (Table 2). In the pot experiments, the HCO_3^- concentration in the MOF treatment collected on 29 April and 4 May (the seventh and eighth time of collection) was less than that in the IF treatment but higher than that of the control (Table 2). Except for this, HCO_3^- concentrations in the MOF treatment collected on the other seven occasions were the highest. HCO_3^- concentrations in water samples treated by IF were sometimes lower and sometimes higher than those of the control. In flat land experiments, the surface runoff was collected only once. Taken together, the HCO_3^- concentrations in MOF treatment were the highest, which suggested that the application of MOF is beneficial to the increase of soil HCO_3^-. The reasons can be analyzed from three aspects. Firstly, abundant organic acids existing in the MOF provided H^+ to generate HCO_3^- by reacting with $CaCO_3$, namely $CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$. All the carbon in this part of the HCO_3^- came from the rocks (carbonate mineral particles in soil and bedrock), so there was no carbon sequestration effect. However, due to the alkalinity (finished fertilizer pH = 8.48) of MOF, this should be negligible. Secondly, a larger number of microorganisms in the MOF were able to secrete CA (Tripp et al. 2001; Smith and Ferry 2000) so as to promote the hydration of CO_2 to produce H^+ which was then reacted with $CaCO_3$ to generate HCO_3^-. That is, $CO_2 + H_2O \leftrightarrow H^+ + HCO_3^-$, $CaCO_3 + H^+$ $Ca^{2+} + HCO_3^-$ and the total reaction was $CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^-$. In the part represented by HCO_3^-, half of the carbon came from rocks and the other half came from atmospheric CO_2, so there was a carbon sequestration effect. Thirdly, the MOF contains silicate mineral powders which underwent weathering in the progress of microbial metabolisms to produce HCO_3^- (Xiao et al. 2012b, 2015; Sun et al. 2013). This part of HCO_3^- comes from soil and atmospheric CO_2, causing a net carbon sequestration effect. The HCO_3^- generated can be cycled in four ways: it can flow into rivers or oceans and can be fixed by algal or microbial photosynthesis (Liu et al. 2010), be transferred into CO_2 to return to atmosphere, be transferred and utilized by microorganisms, or be absorbed and used by plants and transferred into organic carbon. While being transferred and utilized by microorganisms, HCO_3^- is involved in bacterial metabolism and is fixed as organic carbon to participate in the biological cycle and enter any sediment present, thus generating carbon sequestration effects (Lian et al. 2011; Liu 2001).

Table 2 The concentration of HCO_3^- in different treatments

	Sampling time	HCO_3^- (mmol/L)		
		Control	MOF	IF
Pot	2015/3/12	1.01 ± 0.10^{aB}	1.33 ± 0.12^{cdA}	$0.98 \pm 0.08\ ^{dB}$
	2015/3/24	1.03 ± 0.06^{aA}	1.13 ± 0.06^{deA}	0.87 ± 0.08^{deB}
	2015/3/26	0.63 ± 0.06^{cdB}	0.97 ± 0.10^{efA}	0.63 ± 0.07^{efB}
	2015/4/2	1.05 ± 0.05^{a}	1.23 ± 0.06^{cd}	$1.08 \pm 0.13\ ^{cd}$
	2015/4/9	1.13 ± 0.15^{aB}	2.10 ± 0.10^{bA}	1.25 ± 0.10^{bcB}
	2015/4/25	1.00 ± 0.09^{aB}	2.60 ± 0.15^{aA}	0.92 ± 0.08^{dB}
	2015/4/29	0.90 ± 0.08^{abB}	0.95 ± 0.09^{efB}	1.80 ± 0.13^{aA}
	2015/5/4	0.75 ± 0.09^{bcB}	0.76 ± 0.06^{fgB}	1.10 ± 0.09^{cdA}
	2015/5/9	1.03 ± 0.10^{aB}	1.47 ± 0.07^{cA}	1.47 ± 0.12^{bA}
Sloping land	2015/3/26	$0.71 \pm 0.08b^{cdB}$	0.92 ± 0.03^{efA}	0.88 ± 0.03^{deA}
	2015/4/2	$0.68 \pm 0.05b^{cdB}$	0.82 ± 0.06^{fgA}	0.45 ± 0.05^{fB}
	2015/5/4	$0.47 \pm 0.04\ ^{dB}$	0.74 ± 0.05^{fgA}	0.54 ± 0.05^{fB}
	2015/5/9	$1.11 \pm 0.08\ ^{dB}$	1.34 ± 0.07^{cdA}	1.12 ± 0.07^{cdB}
Flat land	2015/3.26	$0.59 \pm 0.04c^{dB}$	0.68 ± 0.03^{gA}	0.46 ± 0.04^{fC}

Values followed by the same lowercase letter within each column have not significantly difference according to Tukey's HSD post hoc test at $p < 0.05$

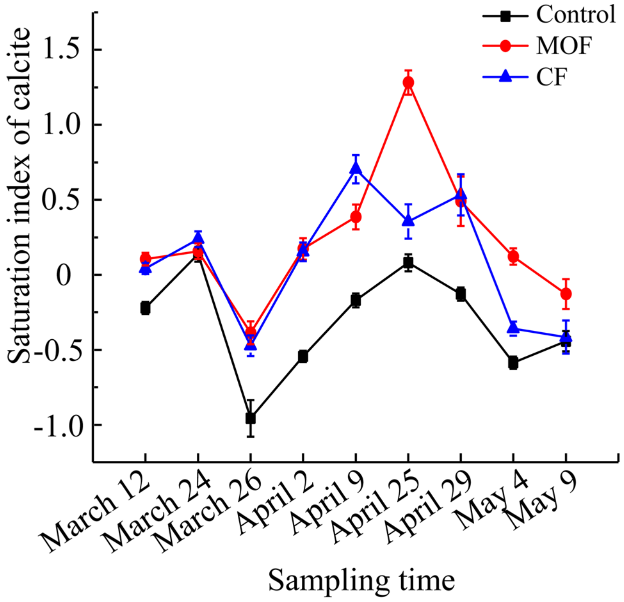
Values followed by the same uppercase letter within each row have not significantly difference according to Tukey's HSD post hoc test at $p < 0.05$

In this study, the application of MOF rather than IF increased the content of soil HCO_3^- compared to the control, when the fluctuation of HCO_3^- in solution was taken into account (Table 2). It suggests that the application of MOF is able to increase carbon sequestration according to the reaction: ($CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3 + x(CO_2 + H_2O) + (1 - x)(CH_2O + O_2)$), proposed by Liu et al. (2010, 2011). Some reports conclude that not all the carbon involved in plant photosynthesis comes from atmospheric CO_2, but also comes from soil inorganic carbons through the absorption of roots (Overstreet et al. 1940; Wu et al. 2011; Zhu et al. 2013). When CO_2 utilization is limited due to reduced or closed leaf stomatal conductance, HCO_3^- absorbed and stored in plants is used as a carbon source for photosynthesis under the effects of CA. This process is more prominent in plants suited to cultivation in karst regions where water is in short supply (Wu et al. 2005; Hu et al. 2010; Wu 2011), which further indicates that soil HCO_3^- is able to be absorbed and utilized by plants to increase sequestration capacity for inorganic carbons.

As shown in Fig. 4A, in pot experiments, the saturation index of calcites in leachate from the control treatment was mostly negative, while in groups treated with MOF and IF the same were positive and negative. Overall, the saturation index of calcites in the treatment group with MOF was the highest. Figure 4B shows that the saturation indices of calcite in sloping land experiments were negative, while the saturation indices of leachates treated by MOF were higher than those of the control treatment (on the whole). Surface runoff was collected only once in flat land experiments and the saturation indices of calcites in the control, MOF, and IF groups were -1.457 ± 0.071, -1.031 ± 0.081, and -1.548 ± 0.122, respectively. It can be seen that the saturation index of calcite in the MOF treatment group was more positive. Calcite ($CaCO_3$) experienced a weathering reaction, as follows:

$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^-$ where the carbon in the HCO_3^- came from rocks and the other half came from CO_2 in the atmosphere. When the saturation index of calcite (SI_c) was 0, this reversible reaction was at its critical equilibrium state. When $SI_c < 0$, calcite was in an unsaturated state and the reversible reaction still moved forward, and Ca^{2+} and HCO_3^- ions mainly existed in water. When $SI_c > 0$, the calcite was over-saturated, which indicated that $CaCO_3$ was separated from the water. If $SI_c < 0$, the larger the value, that is, the closer the value to a saturation critical value of zero, the more saturated the calcite and the larger the forward progression of the reversible reaction and the higher the concentrations of Ca^{2+} and HCO_3^- in water. For $SI_c > 0$, the larger the value, the more saturated the calcite and the more $CaCO_3$ was separated out. To meet the conditions for separation, the amounts of Ca^{2+} and HCO_3^- in water were bound to be the largest, so as to turn the reversible reaction to the separation of $CaCO_3$. In conclusion, SI_c was at its maximum in the water collected from the group treated by MOF, which demonstrated that the water therein contained the most HCO_3^-. This suggests that fertilizing the MOF is

A pot experiment



B slope experiment

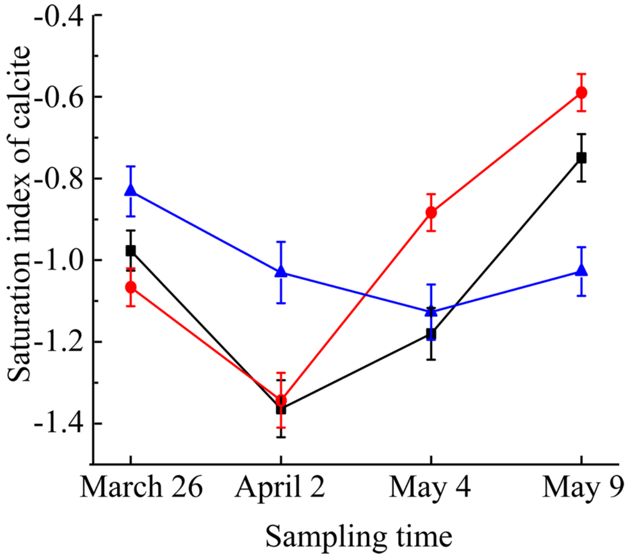


Fig. 4 Saturation index of calcite. **A** Pot experiment; **B** Sloping land experiment

beneficial when seeking to increase the inorganic carbon content (as HCO_3^-) in a soil.

After harvesting green Chinese cabbage, soil samples treated by different fertilization methods were collected and pH values were measured and compared with those before the experiment. It can be seen from Table 3 that the initial soil pH in the experimental fields was 7.10, indicating that the soil was practically neutral. The pH of the soil varied after different treatments, but remained basically unchanged in the control group, at ~ 7.10. Apart from few samples on flat lands, the pH values of soil treated by MOF increased slightly, while the pH value of soil treated by IF was significantly reduced. The soil pH in pot experiments was lower than those of flat land and sloping land, which indicates that the use of IF can readily lead to soil acidification. The soil treated by MOF showed the highest alkalinity, which coincided with the comparative results of HCO_3^- concentration in different treatments as shown in Table 2, indicating that the MOF facilitated the generation of HCO_3^- in the soil. The soil treated by IF was acidic, which demonstrates that the IF led to soil acidification causing carbonate rock dissolution in karst areas to release CO_2, and thus increasing soil erosion. Further, soil acidification increased the activity of heavy metals in the soil and which could be easily absorbed by crops via roots, thus increasing the risk of heavy metal pollution.

4 Conclusion

1. The MOF applied can increase the absorption and storage capacity of the soil for water and promote mineral nutrient absorption in green Chinese cabbage, showing superior effects to IF. Furthermore, it can promote the development of agronomic characteristics of green Chinese cabbage. The MOF also promotes the accumulation of biomass in crops and enhance their photosynthetic capacity to allow them to absorb more atmospheric CO_2, showing certain carbon sequestration effects.

Table 3 pH profiles of soil treated by different fertilisation practices

Time	Experimental field	Control	MOF	IF
Pre-trial	Natural soil	7.10 ± 0.01		
Post-trial	Flat land	7.11 ± 0.02^{a}	7.06 ± 0.02^{bA}	6.98 ± 0.04^{cB}
	Sloping land	7.07 ± 0.02^{a}	7.16 ± 0.05^{bB}	6.97 ± 0.02^{cB}
	Pot	7.06 ± 0.03^{a}	7.18 ± 0.03^{bB}	6.43 ± 0.07^{cA}

Values followed by the same lowercase letter within each column have not significantly difference according to Tukey's HSD post hoc test at $p < 0.05$. Values followed by the same uppercase letter within each row have not significantly difference according to Tukey's HSD post hoc test at $p < 0.05$

2. The application of MOF can also promote microbial CA activities, which increased the dissolution of carbonate rocks, driven by microbial CAs and consumption of atmospheric CO_2.

As the soil parent material in karst areas in Southwest China mainly consist of carbonate rocks, the soil nutrient levels are poor. The technology of microbial fermentation engineering, combined with organic waste, and the locally abundant potassic rocks will contribute to improvements in the properties of farmland soils and the growth of crops in karst areas. Moreover, carbon sequestration functions in karst areas can be enhanced. Therefore, this study provides a new way of studying agricultural fertilization practice, carbon cycling, and climate regulation in karst areas.

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