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CALCIUM-ENRICHED IRRIGATION DRIVES PLANT-MEDIATED CARBON SEQUESTRATION DYNAMICS IN KARST SOILS

S KALCIJEM OBOGATENO NAMAKANJE V KRAŠKIH TLEH POSPEŠUJE DINAMIKO SEKVESTRACIJE OGLJIKA Z RASTLINAMI

Yang MA[1], Hui YANG[2,*], Mitja PRELOVŠEK[3], Jianhua CAO[1,4,5] & Tongbin ZHU[1,4,5]

Abstract

Yang Ma, Hui Yang, Mitja Prelovšek, Jianhua Cao & Tongbin Zhu: Calcium-Enriched Irrigation Drives Plant-Mediated Carbon Sequestration Dynamics in Karst Soils

Mineral-organic complexes are key regulators of soil organic carbon (SOC) sequestration in agricultural ecosystems. As a dominant soil mineral, calcium (Ca) plays a particularly important role in SOC stabilization. Although numerous studies have indicated that Ca can enhance SOC storage, particularly in the karst regions of Southwest China, the specific mechanisms underlying Ca-SOC interactions and their associated biological processes remain poorly understood. In this study, we used a controlled pot experiment with maize (*Zea mays L.*) irrigated for 112 days with allogenic waters containing different Ca^{2+} concentrations (2, 54, and 108 mg L^{-1}). Soil respiration, in situ soil CO_2 concentrations, and leachate carbon fractions were monitored at 7-day intervals, and leachate carbon fractions including total organic carbon (TOC), dissolved organic carbon (DOC), and dissolved inorganic carbon (DIC). The results showed that: (1) soil respiration rates and CO_2 concentrations were progressively higher in maize rhizosphere soils than in unvegetated controls and displayed pronounced temporal dynamics; (2) TOC, DOC, and DIC concentrations in leachates were significantly elevated in vegetated systems compared with bare soils, indicating enhanced carbon mobilization and transformation driven by plant activity; (3) DIC sources differed between treatments, with carbonate-derived carbon being the predominant contributor to DIC in maize-cultivated soils, while soil/atmospheric CO_2 was the main source in bare

Izvleček

Yang Ma, Hui Yang, Mitja Prelovšek, Jianhua Cao & Tongbin Zhu: S kalcijem obogateno namakanje v kraških tleh pospešuje dinamiko sekvestracije ogljika z rastlinami

Mineralno-organski kompleksi so ključni regulatorji sekvestracije organskega ogljika v tleh v kmetijskih ekosistemih. Kalcij (Ca) kot prevladujoči mineral v tleh ima posebej pomembno vlogo pri stabilizaciji organskega ogljika v tleh. Iz številnih študij je razvidno, da lahko kalcij poveča zaloge organskega ogljika v tleh, zlasti na kraških območjih jugozahodne Kitajske, specifični mehanizmi, ki povezujejo medsebojno delovanje kalcija in organskega ogljika v tleh s povezanimi biološkimi procesi, pa so še vedno slabo razumljeni. V tej študiji smo izvedli kontrolirani poskus v lončkih s koruzo (*Zea mays L.*), ki smo jo 112 dni namakali z alogeno vodo z različnimi koncentracijami Ca^{2+} (2, 54 in 108 mg L^{-1}), pri čemer smo podatke spremljali v 7-dnevnih intervalih ter vključili respiracijo tal, *in situ* koncentracije CO_2 v tleh ter frakcije ogljika v izcedni vodi, vključno s skupnim organskim ogljikom, raztopljenim organskim ogljikom in raztopljenim anorganskim ogljikom. Iz rezultatov je razvidno, da: (1) so bile ravni respiracije tal in koncentracije CO_2 v rizosferi koruze postopno višje kot v kontrolnih tleh brez rastlinja in je bila razvidna izrazita časovna dinamika, (2) so bile koncentracije skupnega organskega ogljika, raztopljenega organskega ogljika in raztopljenega anorganskega ogljika v izcedni vodi v sistemih z rastlinjem precej višje v primerjavi z golimi tlemi, kar kaže na povečana zbiranje in preoblikovanje ogljika zaradi vpliva rastlin, (3) so se viri raztopljenega anorganskega ogljika med posameznimi obdelavami razlikovali, pri čemer je bila karbonatna kamnina prevladujoč vir

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soils. These findings highlight that Ca-rich irrigation, in combination with plant and microbial activity, can substantially modify C fluxes and carbonate weathering pathways in calcareous soils, providing mechanistic insights into biologically mediated carbon sequestration processes in Southwest China's karst agroecosystems.
Keywords: karst area, calcium content, allogenic water, soil carbon transfer, biological processes.

v tleh, na katerih se je gojila koruza, v tleh brez rastlinja pa je bil glavni vir CO_2 iz tal oziroma ozračja. Ti rezultati kažejo, da lahko namakanje z vodo, bogato s kalcijem, v kombinaciji z rastlinsko in mikrobno aktivnostjo pomembno spremeni tokove ogljika ter poteke razpadanja karbonatnih kamnin v apnenčastih tleh zaradi vremenskih vplivov, kar omogoča mehanistični vpogled v biološko posredovane procese sekvestracije ogljika v kraških kmetijskih ekosistemih jugozahodne Kitajske.
Ključne besede: kraško območje, vsebnost kalcija, alogena voda, prenos ogljika v tleh, biološki procesi.

1. INTRODUCTION

As the second largest terrestrial carbon pool after the lithosphere, soils store roughly twice as much carbon as the atmospheric (Malik et al., 2018). This critical pool comprises both SOC and soil inorganic carbon (SIC) components (Guo et al., 2021; Raheb et al., 2023), with SOC widely recognized as a key indicator of soil quality that governs agricultural productivity, carbon sequestration potential, and ecosystem services (Gomez et al., 2024; Wu et al., 2015; Lal et al., 2004). The biogeochemical cycling of soil carbon (Figure 1) is driven by three principal processes: (1) photosynthetic CO_2 fixation by plants, followed by microbial decomposition and transformation of organic residues into more stable SOC forms (Cao et al., 2011); (2) respiratory CO_2 efflux from soils to the atmosphere; (3) carbonate dissolution that consumes soil CO_2, generating DIC that can subsequently fuel aquatic photosynthesis (Zhao et al., 2015; Zhou et al., 2020). Together, these interconnected pathways position SOC as a pivotal regulator of the global carbon cycle and highlight the need for a mechanistic understanding of how SOC is formed, stabilized, and lost (Wu et al., 2015).

Calcium (Ca), an essential macronutrient for plant physiology and photosynthetic function (Cui et al., 2019; Lian et al., 2022), exerts a dual influence on soil systems

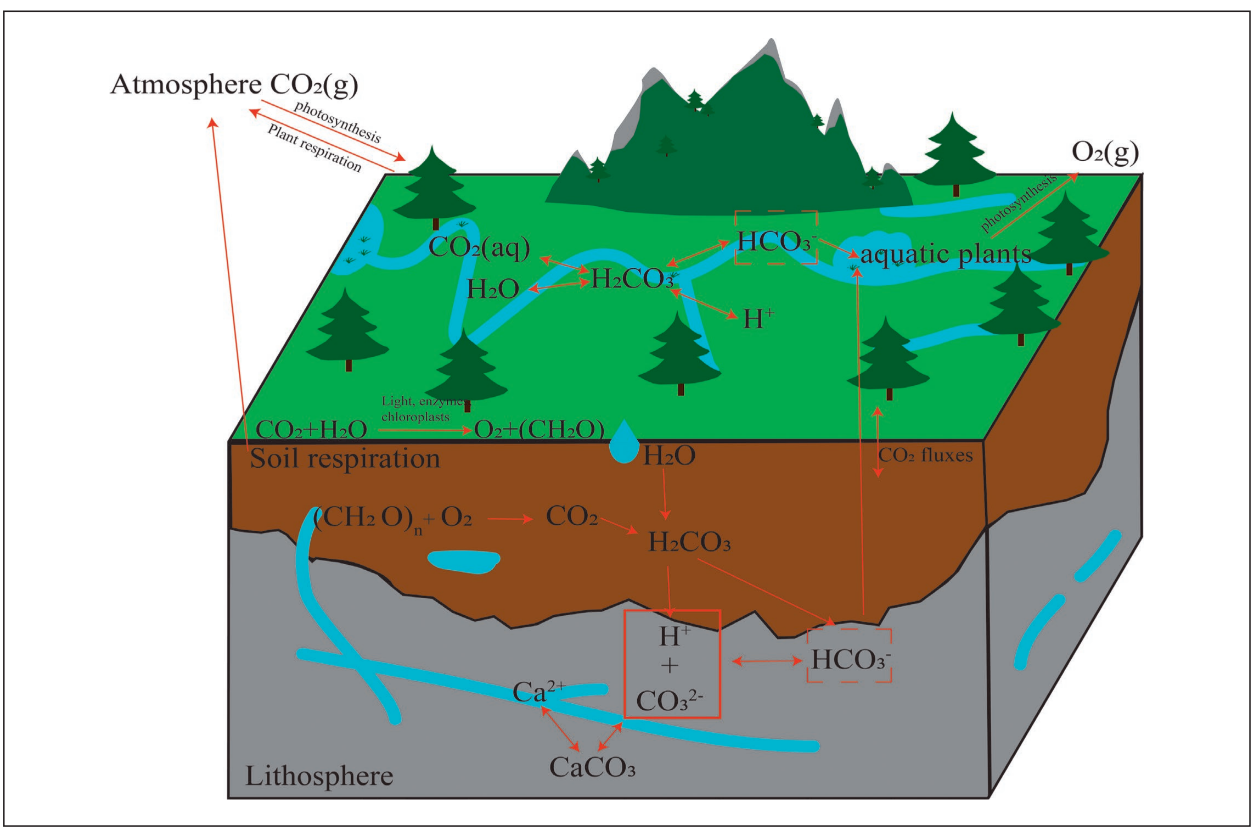

Figure 1: Soil carbon transport and transformation processes.

by modulating nutrient bioavailability and SOC stabilization (Liu et al., 2005; Yang et al., 2018). Through cation bridging, Ca^{2+} promotes organic-mineral associations between clay surfaces and organic matter, particularly in neutral to alkaline soils where Ca availability plays a critical role in SOC protection mechanisms (Oades, 1984; Rasmussen et al., 2018). Although these physicochemical roles are well documented, the biologically mediated interactions among Ca, SOC dynamics, and carbonate dissolution remain poorly understood.

This investigation therefore addresses two primary objectives: (i) to quantify the relative contributions of plant inputs, microbial activity, and Ca dynamics to SOC variations; and (ii) to characterize biologically mediated carbonate dissolution processes in karst soils. Employing karst soils subjected to controlled irrigation regimes with exogenous calcium chloride solutions (varying Ca^{2+} concentrations) and allochthonous water inputs, we systematically monitored CO_2 efflux dynamics and carbon speciation. Through comparative analysis of organic/inorganic carbon partitioning and translocation patterns, this study elucidates the biogeochemical mechanisms through which Ca-enriched irrigation waters modulate carbon cycling in karst ecosystems. The findings provide theoretical insights for managing carbonate-rich agricultural systems under varying hydrological regimes and for enhancing carbon sequestration in karst landscapes.

2. MATERIALS AND METHODS

2.1 EXPERIMENTAL MATERIALS

The experimental soil was collected from a typical karst region in Guilin, Guangxi Zhuang Autonomous Region, China. The soil is classified as a brown calcareous soil (*calcic cambisol*), with an initial pH of 7.85, SOC content of 8.36 g kg^{-1}, and soil microbial biomass carbon (MBC) content of 33.59 mg kg^{-1}. Incubations were conducted in cylindrical fiberglass vessels (30 cm diameter × 50 cm height), each containing a 20 cm-thick basal layer of marine sedimentary carbonate rock. A drainage tap was installed at the base of each vessel to collect leachate.

Allogenic irrigation water was sourced from springs discharges in a clastic rock-dominated area nearby. The key physicochemical parameters of the irrigation water are summarized in Table 1.

2.2 EXPERIMENTAL DESIGN

The experiment was conducted in a climate-controlled ventilated shed. Each fiberglass vessel was filled with a 20 cm basal layer of marine sedimentary carbonate rock with a grain size of 1 to 3 cm^3, overlain by 30 cm of homogenized karst soil. A dual layer of 2 mm mesh gauze was placed at the soil-rock interface to modulate infiltration and prevent soil loss. Six treatments were established based on allogenic Ca supplementation (Figure 2): T1 and CK1: allogenic water irrigation (baseline $Ca^{2+} \approx$ 2 mg L^{-1}) with maize (*Zea mays L. Jinguan 218*) cultivation and bare soil controls; T2 and CK2: allogenic water supplemented with 54 mg L^{-1} Ca^{2+} (as $CaCl_2$); T3 and CK3: Exogenous water supplemented with 108 mg L^{-1} Ca^{2+} (as $CaCl_2$). The Ca^{2+} concentration gradients were designed to approximate the range observed in regional karst groundwater (Wei, 2023). Each treatment included three replicate vessels, totaling 18 experimental units. Maize seedlings were transplanted on 25th August 2023. A staged fertilization regime was applied: 10 g compound fertilizer at 21, 35 and 56 days after transplantation, corresponding to seedling, jointing and heading stages, and 8 g of organic fertilizer (≥40% organic matter) was applied.

Table 1: Physico-chemical characteristics of allogenic irrigation water. Ion concentrations are in mg L^{-1}, electrical conductivity (EC) is in $\mu S \cdot cm^{-1}$, and coefficients of variation are in %.

Parameter \ Testing index	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	NO_3^-	TOC	DOC	pH	EC
Minimum value	0.02	0.24	0.67	0.31	0.45	1.62	2.04	0.27	0.35	0.30	5.45	4.59
Maximum value	0.50	0.91	4.64	1.04	3.49	5.47	16.34	5.32	1.57	1.53	6.93	13.63
Mean value	0.12	0.38	2.08	0.46	1.64	3.41	7.85	1.97	1.02	0.94	6.33	7.98
Standard deviation	0.13	0.11	1.11	0.17	1.07	1.41	3.40	1.57	0.26	0.25	0.44	2.20
Coefficient of variation	1.08	0.29	0.53	0.37	0.65	0.41	0.43	0.80	0.25	0.27	0.07	0.28

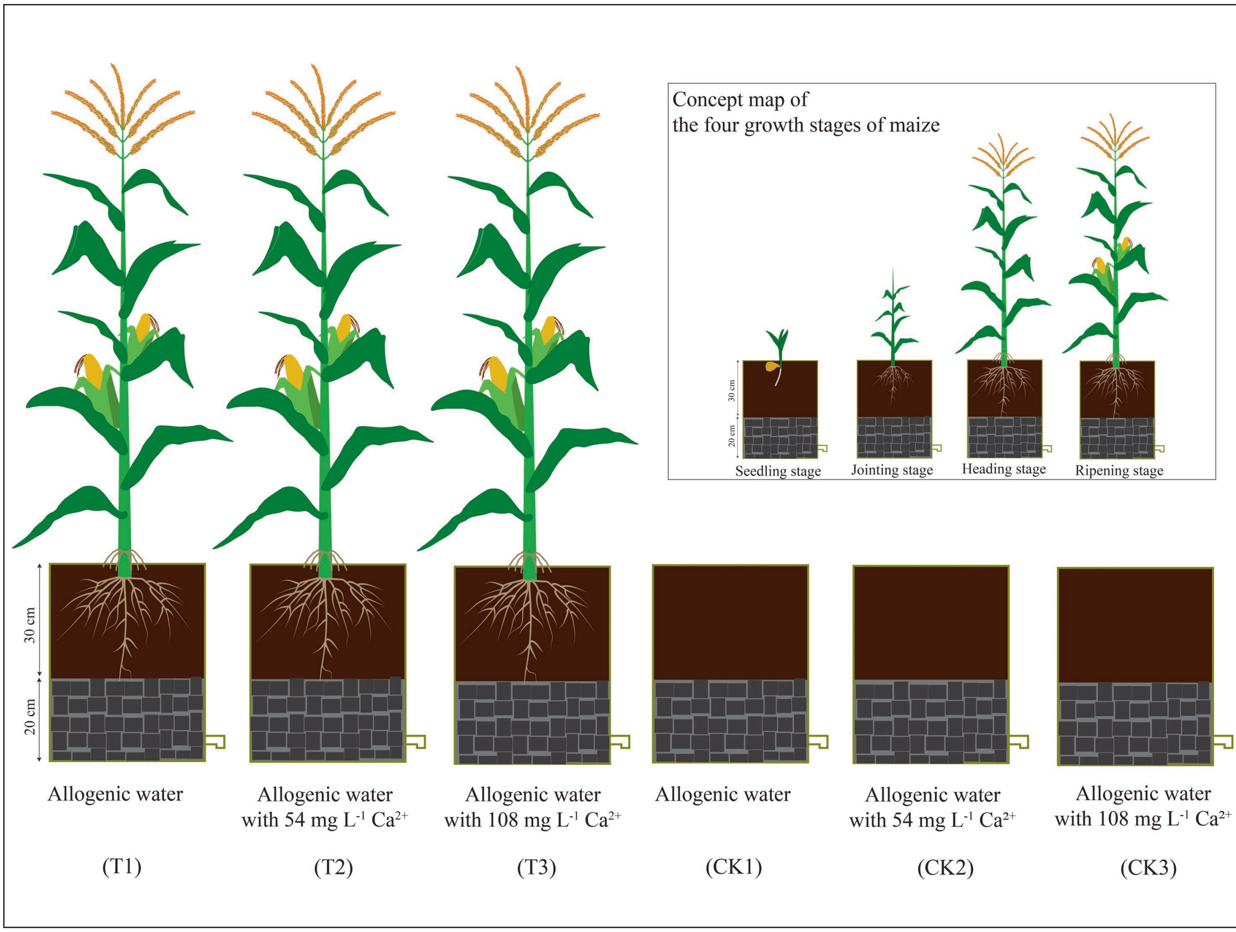

Figure 2: Design of the potted plant experiment.

All treatments received identical irrigation volumes and fertilization schedules at 7-day intervals. Bare soil controls were subjected to the same hydrological and nutrient regimes as the corresponding maize treatments to isolate the effects of vegetation.

2.3 SOIL GAS SAMPLING AND LEACHATE COLLECTION

2.3.1 Soil respiration monitoring

Soil CO_2 efflux was measured using the static dark chamber method, Measurements began 7 days after transplantation and were conducted at 7-day intervals between 09:00-11:00 am China Standard Time (CST) to minimize diurnal variability (Huang et al., 2020). During each sampling, ambient CO_2 concentration was recorded and surface soil temperature was measured using a soil multi-parameter meter (COMECAUSE).

2.3.2 Soil-rock interface CO_2 sampling

A custom soil gas sampling system (Figure 3) was used to collect CO_2 at the soil-carbonate rock interface. Preirrigation gas samples were extracted into pre-evacuated borosilicate vials and transported to the laboratory for analysis. CO_2 concentration and $\delta^{13}C$-CO_2 was determined using a PICARRO G2131-I instrument analyzer.

2.3.3 Soil leachate collection and preservation

Leachate was collected from the drainage tap at the base of each vessel immediately after irrigation events. For geochemical analysis, 600 ml aliquots were transferred into pre-acid-washed high-density polyethylene (HDPE) bottles. To minimize particulate contamination, particularly for TOC and DOC determination samples were first filtered in the field through precombusted glass fiber filters (Whatman GF/F, 0.7μm) and then passed through 0.45 μm cellulose acetate membrane to remove remaining fine particulates. Filtrates for anion/cation quantification and dissolved carbon speciation (TOC, DOC, DIC) were stored at 4°C until analysis. A separate 30 mL subsample was collected after glass fiber filtration and preserved in amber polyethylene (PE) bottles for $\delta^{13}C$-DIC

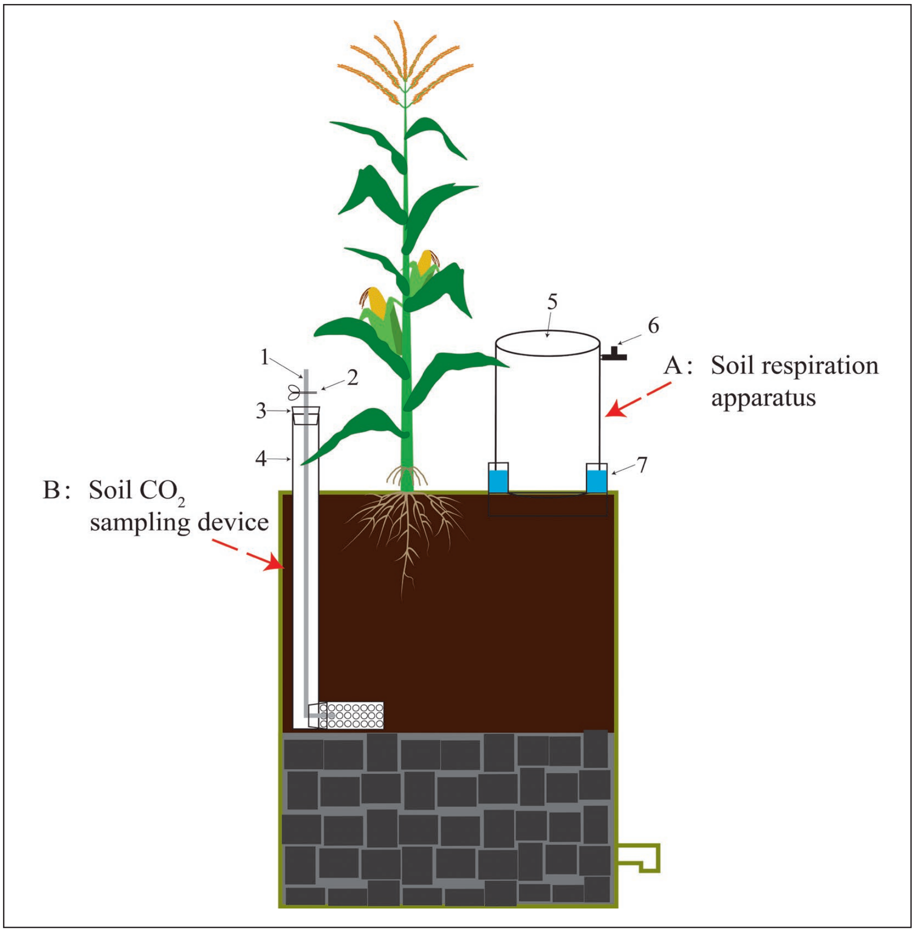

Figure 3: Soil gas collection device. 1. Flexible conduit; 2. Water stop clips; 3. Rubber plugs; 4. PVC pipe; 5. Gas collecting tank; 6. Three-way valve; 7. Base.

analysis, with microbial activity inhibited by addition of 0.1% saturated $HgCl_2$ solution.

2.3.4 Stratified soil sampling

At the end of the experiment, soil profiles were sectioned into two depth intervals (0-15 cm and 15-30 cm) using a stainless-steel corer. Fresh soils were passed through a 2 mm nylon sieve to remove roots, stones, and other debris. Each sieved sample was split into two portions: one was air-dried in the shade for the determination of soil physicochemical properties, and the other was stored at 4°C for the determination of MBC and soil microbial biomass nitrogen (MBN).

2.4 SAMPLE DETERMINATION AND ANALYSIS

CO_2 concentrations and $\delta^{13}C$-CO_2 values were analyzed with a PICARRO G2131-I analyzer, calibrated against NOAA-certified reference gases. Soil pH was determined in a 2.5:1 water-to-soil ratio suspension with a DMP-2mV/pH meter. SOC content was determined by $K_2Cr_2O_7$-H_2SO_4 oxidation. Total nitrogen (TN) content was determined by semi-micro Kjeldahl method. MBC and MBN were determined by chloroform fumigation. SOC was classified into particulate organic carbon (POC) and mineral-associated organic carbon (MAOC) for determination according to Cotrufo et al. following the physical classification method (Cotrufo et al., 2019). Briefly, soils were dispersed and wet-sieved through a 53 μm mesh to separate the coarse (> 53 μm, POC-rich) and fine (< 53 μm, MAOC-rich) fractions, which were then dried and analyzed for organic carbon content. All measurements were performed in triplicate for each treatment.

2.5 DATA PROCESSING

Prior to parametric analysis, all datasets were tested for normality using the Shapiro-Wilk test and for homogeneity of variance via Levene's test. Significant differences among treatments were evaluated by one-way analysis of variance (ANOVA) using SPSS 19.0, followed by Duncan's multiple range test for mean comparisons. Statistical significance was set at $P < 0.05$. All figures were generated using the 'ggplot2' package in R software.

3. RESULTS

3.1 DYNAMICS OF SOIL RESPIRATION

All treatments showed positive soil CO_2 efflux, ranging from 1 to 17 mg C m^{-2} h^{-1}. Maximum fluxes in the maize-cultivated treatments (T1-T3) were on average 2.8 times higher than those in the bare soil controls (CK1-CK3). Maize phenological development was divided into four stages: seedling (0-28 days), jointing (28-49 days), heading (50-77 days), and ripening (78-112 days) (Figure 4). During the seedling stage, CO_2 efflux did not differ significantly among treatments ($P > 0.05$). A marked divergence emerged at jointing onset, with vegetated systems exhibiting 184 % higher efflux rates ($P < 0.05$) that peaked during late tasseling (T1-T3: 14.3-17.1 mg C m^{-2} h^{-1}). This enhancement correlated with rhizosphere activation-root elongation increased substrate availability through exudation, stimulating microbial mineralization. No significant calcium gradient effects ($P > 0.05$) were observed among T1-T3 treatments. Contrastingly, bare soil efflux declined progressively from 3 to 1 mg C m^{-2} h^{-1}, reflecting substrate depletion in unplanted systems. Post-senescence (ripening phase), vegetated systems returned to baseline efflux levels, though a temperature-associated anomaly was observed at 105 days post-sowing. Bare soils maintained stable, low-level emissions throughout ($P > 0.05$ for temporal variation).

3.2 SOIL-ROCK INTERFACE CO_2 DYNAMICS

Consistent with soil respiration patterns, there was no significant inter-treatment differences ($P > 0.05$) in soil-rock interface CO_2 concentration were observed at the soil-rock interface across treatments during the maize seedling stage (Figure 5). However, there was a significant difference ($P < 0.05$) emerged in soil profile CO_2 concentration between the maize cultivation group and bare ground group from the jointing to ripening stage. The maize planting group exhibited a progressive increase in soil-rock interface CO_2 concentration corresponding to crop growth progression. Within the maize cultivation group, interface CO_2 concentrations were highest in T2 and lowest in T3, with T1 consistently intermediate. This pattern suggests a concentration-dependent regulatory effect of Ca^{2+}, with moderate Ca^{2+} addition (54 mg L^{-1}, T2) enhancing CO_2 accumulation at the interface, whereas higher Ca^{2+} addition (108 mg L^{-1}, T3) suppressed it. The bare ground group maintained consistent CO_2 patterns across treatments ($P > 0.05$), with post-seedling interface concentrations remaining significantly lower than vegetated systems ($P < 0.01$). Notably, unvegetated soils sustained stable CO_2 levels persistently exceeding atmospheric baselines (~400×10^{-6}), suggesting sustained heterotrophic respiration despite the absence of plant-mediated processes.

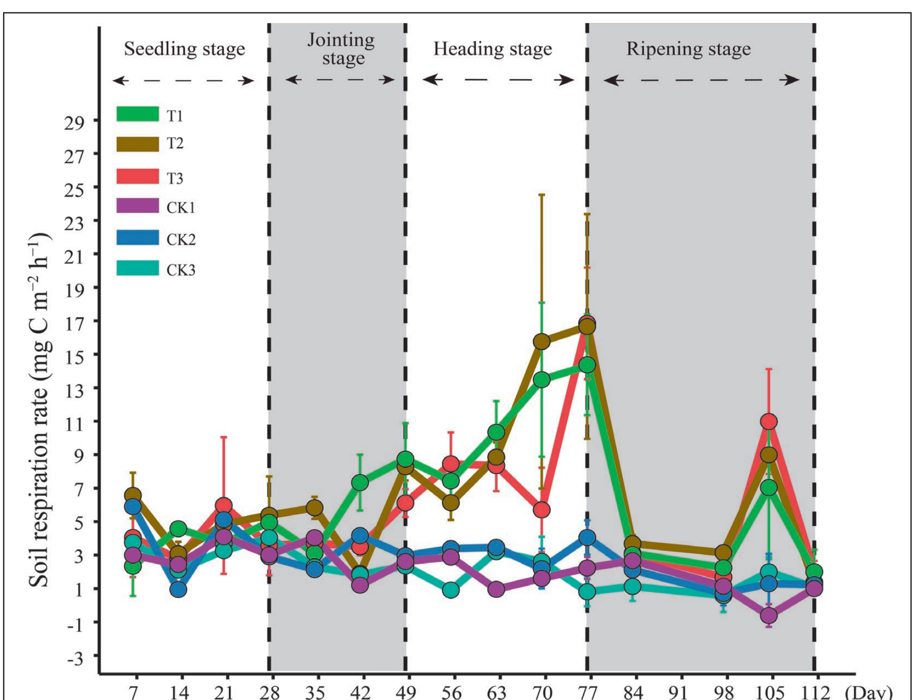

Figure 4: CO_2 emission dynamics from soil respiration at different growth stages of maize.

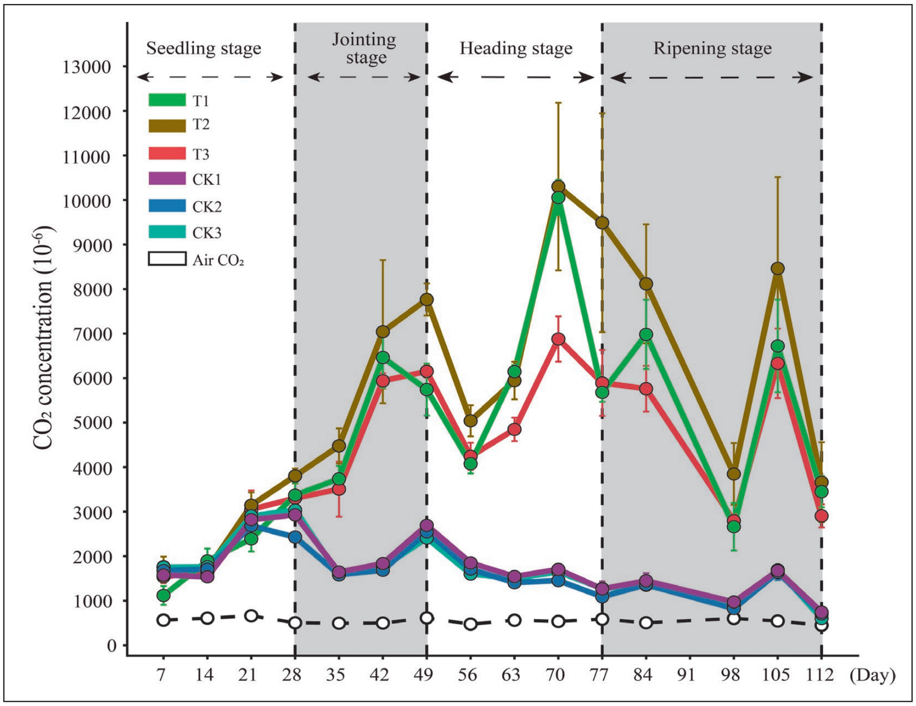

Figure 5: Changes in CO_2 concentration at the soil-rock interface corresponding to each growth stage of maize.

3.3 EFFECT OF CA-ENRICHED ALLOGENIC WATER IRRIGATION ON SOIL CARBON FRACTIONS

In maize cultivation systems, SOC and MAOC exhibited significant decreases with increasing Ca concentrations. POC demonstrated concentration-dependent responses, with T2 (baseline Ca) showing 7.75-6.25 % greater POC content than T1 (54 mg L^{-1} Ca^{2+}) and T3 (108 mg L^{-1} Ca^{2+}) respectively ($P < 0.05$). The contents of MBC displayed an optimal calcium threshold, peaking at T2

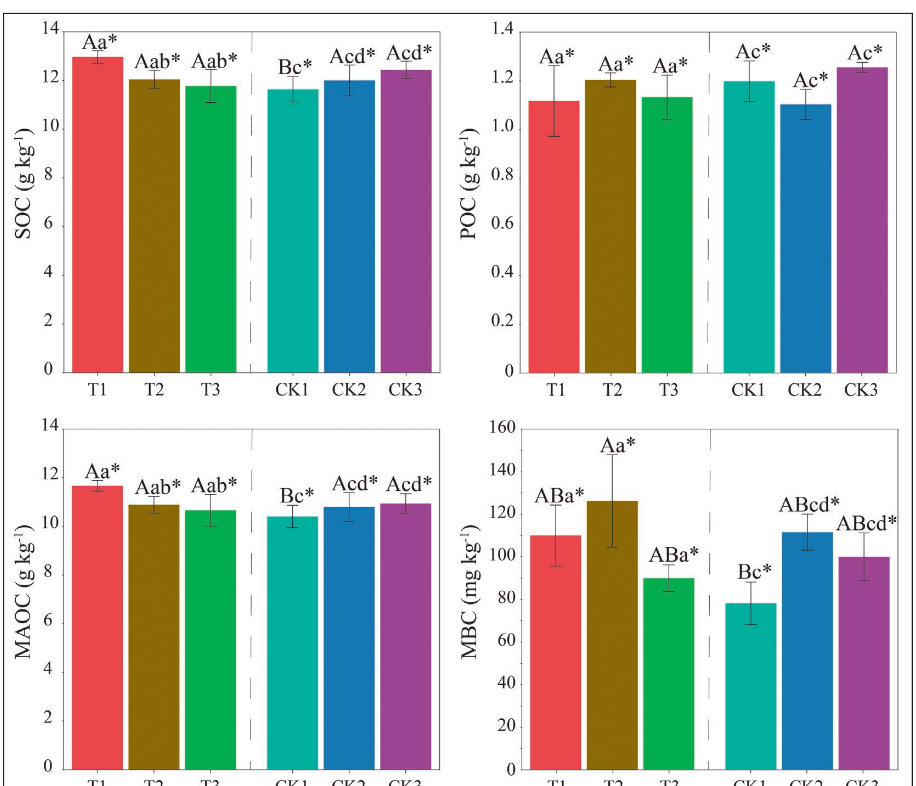

*Figure 6: Content of different forms of carbon in soil 0-15 cm. Letters a and b indicate significant differences at the $P < 0.05$ level for the maize planting group, letter d indicates no significant difference at the $P < 0.05$ level for the bare ground group, letters A and B indicate significant differences between the maize planting group and the bare ground group at the $P < 0.05$ level, and * indicates the variability between soils from 0-15 cm and 15-30 cm of the same treatment.*

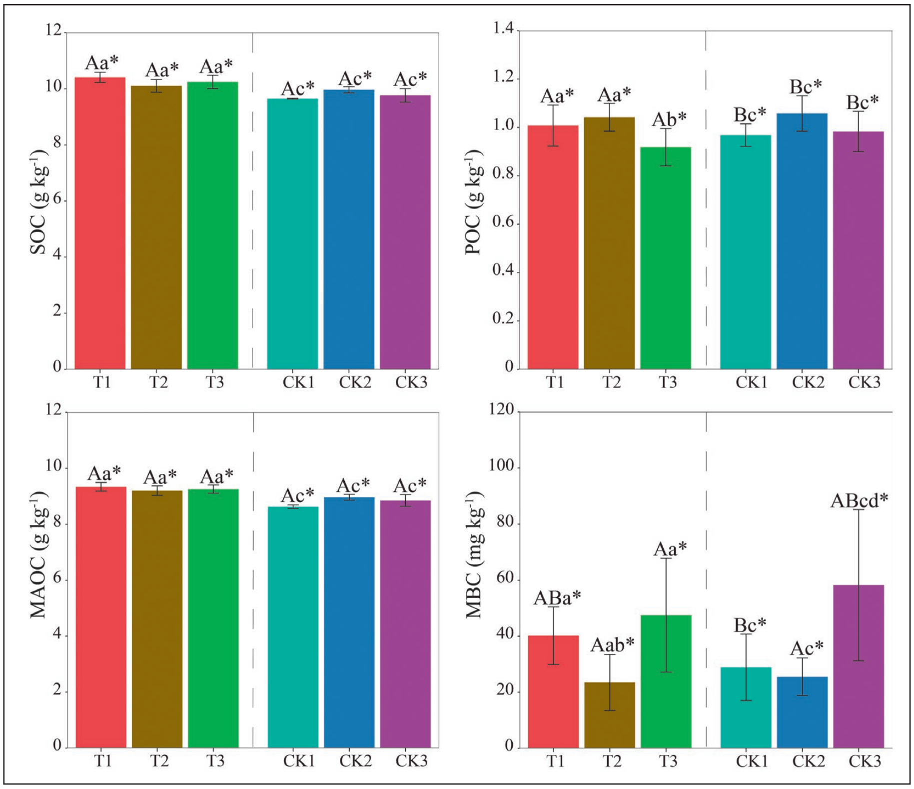

*Figure 7: Content of different forms of carbon in soil 15-30 cm. Letters a and b indicate significant differences at the P < 0.05 level for the maize planting group, letter d indicates no significant difference at the P < 0.05 level for the bare ground group, letters A and B indicate significant differences between the maize planting group and the bare ground group at the P < 0.05 level, and * indicates variability between soils of the same treatment of 0-15 cm and 15-30 cm.*

with values 14.77-40.38 % higher than both T1 and T3. Contrastingly, bare ground systems revealed divergent trends: SOC and MAOC increased progressively with Ca addition; Minimum POC accumulation occurred in CK2 control soils; Maximum MBC accumulation occurred in CK2 control soils.

Comparative analysis revealed distinct Ca-mediated carbon dynamics between maize cultivation and unvegetated systems. In the maize planting group, the SOC and MAOC contents in the T1 treatment were significantly higher than those in the CK1 treatment. However, SOC exhibited opposite trends along the Ca concentration gradient between the maize planting group and the bare soil group: in the maize planting system, SOC content was negatively correlated with Ca^{2+} concentration (decreasing by 10.11 % from T1 to T3), whereas in the bare soil, SOC content increased by 6.86 %. Notably, the MBC content in the T1 treatment was 40.70 % higher than that in the CK3 treatment ($P < 0.05$), and the MBC content in the T2 treatment was 13.16 % higher than that in the CK2 treatment ($P < 0.05$), highlighting calcium's selective enhancement of mineral-associated carbon pools in rhizosphere environments.

In the 15-30 cm soil layer (Figure 7), no significant differences in SOC and MAOC were observed between the maize planting groups (T1-T3) and the bare soil control groups (CK1-CK3). For POC, the lowest value was found in the T3 treatment within the maize planting groups, while no significant differences were detected among the bare soil groups. Regarding MBC, within the maize planting groups, the T2 treatment exhibited significantly lower MBC than T1 and T3; within the bare soil groups, CK3 showed significantly higher MBC than CK1 and CK2. Additionally, MBC in T1 was significantly higher than that in CK1, whereas MBC in T3 was significantly lower than that in CK3.

Across both depth intervals, SOC, POC, MAOC and MBC in both maize cultivation and bare soils declined significantly active surface layer.

3.4 SOIL LEACHATE CHEMISTRY

3.4.1 Bicarbonate dynamics in soil leachate

Leachate HCO_3^- concentrations showed clear temporal and treatment-specific patterns (Figure 8). Maize-cultivated plots exhibited significantly higher HCO_3^- concentrations than bare soil controls throughout the growing season ($P < 0.05$). Bare soils showed no statistically significant HCO_3^- variation across sampling intervals ($P > 0.05$). In maize treatments, HCO_3^- increased with plant developmental and peaked around 77 days in T2 (54 mg L^{-1} Ca^{2+}) and T3 (108 mg L^{-1} Ca^{2+}) treatments, coinciding with elevated CO_2 concentrations at 30 cm depth. This co-occurrence suggests that rhizosphere activity enhanced carbonate dissolution. Across treatments, HCO_3^- yields followed the order T2 > T1 > T3, implying that intermediate Ca^{2+} levels (54 mg L^{-1}) maximize carbonate dissolution, whereas higher Ca^{2+} (108 mg L^{-1}) may introduce ionic stress and/or reduce dissolution efficiency. This hierarchical pattern aligns with established thresholds for ionic stress in karst agroecosystems, where excessive Ca^{2+} (> 80 mg L^{-1}) disrupts soil biogeochemical equilibria through cation competition and osmotic imbalance mechanisms.

3.4.2 Temporal dynamics of TOC and DOC in soil leachate

The temporal evolution of TOC and DOC in leachate exhibited congruent exponential decay patterns across all treatments (Figure 9). Maize-cultivated systems consistently generated 32-48 % higher TOC/DOC fluxes than bare soil controls ($P<0.01$), attributable to rhizodeposition and root turnover fueling colloidal organic matter production. Increasing allogenic Ca^{2+} concentrations progressively reduced leachate carbon loads, with TOC declining by 19 % (54 mg L^{-1} Ca) and 37 % (108 mg L^{-1} Ca) versus controls ($P < 0.05$). This inverse relationship between DOC/TOC and Ca^{2+} suggests Ca^{2+} promotes organo-mineral complexation and flocculation, thereby immobilizing organic carbon in the soil matrix. These results highlight Ca's dual role as both a geochemical regulator of carbon mobility and a determinant of soil organic matter turnover kinetics in karst agricultural systems.

3.5 ISOTOPIC CONSTRAINTS ON CARBON SOURCE PARTITIONING

Stable carbon isotopes ($\delta^{13}C$) provided critical insights into carbon provenance and transformation pathways. Maize, a C_4 plant, has $\delta^{13}C$ values between -17 ‰ to -9 ‰, with an average of -13 ‰ (Yang et al., 2020), and

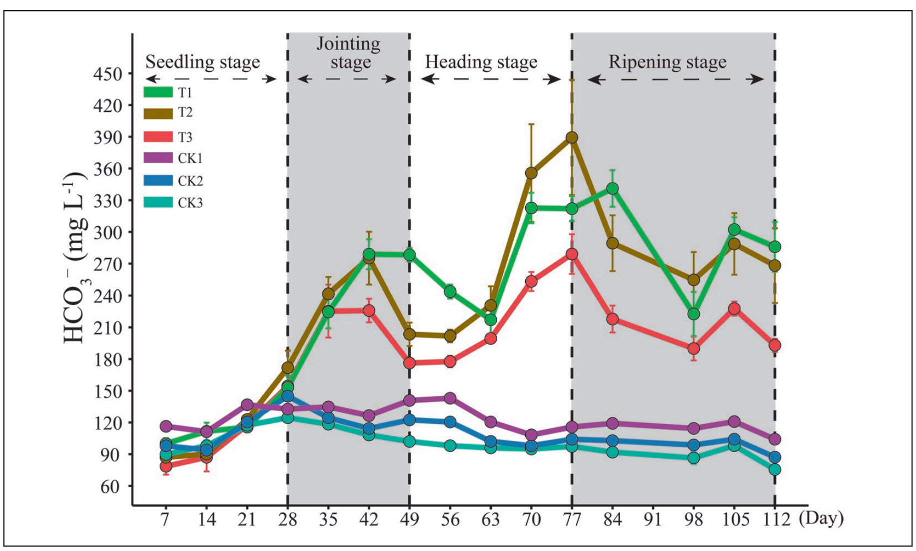

Figure 8: Changes of HCO_3^- in leachate under irrigation with allogenic water with different Ca concentration.

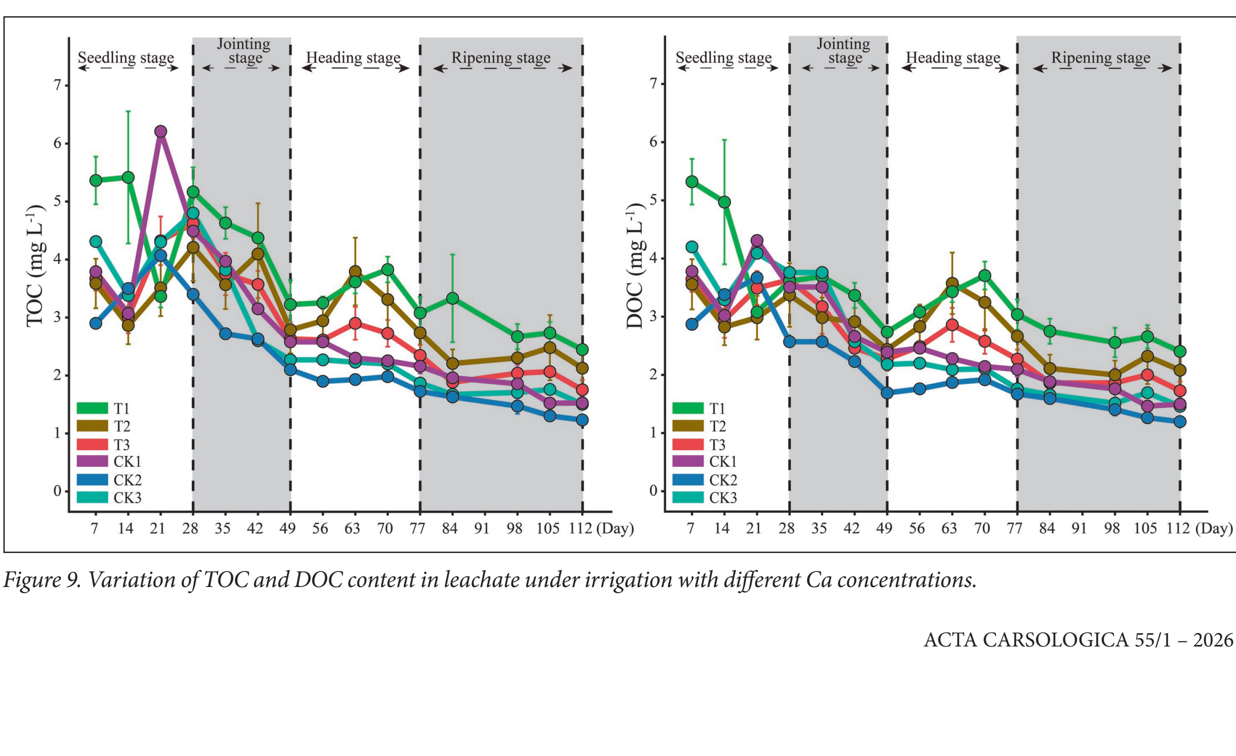

Figure 9. Variation of TOC and DOC content in leachate under irrigation with different Ca concentrations.

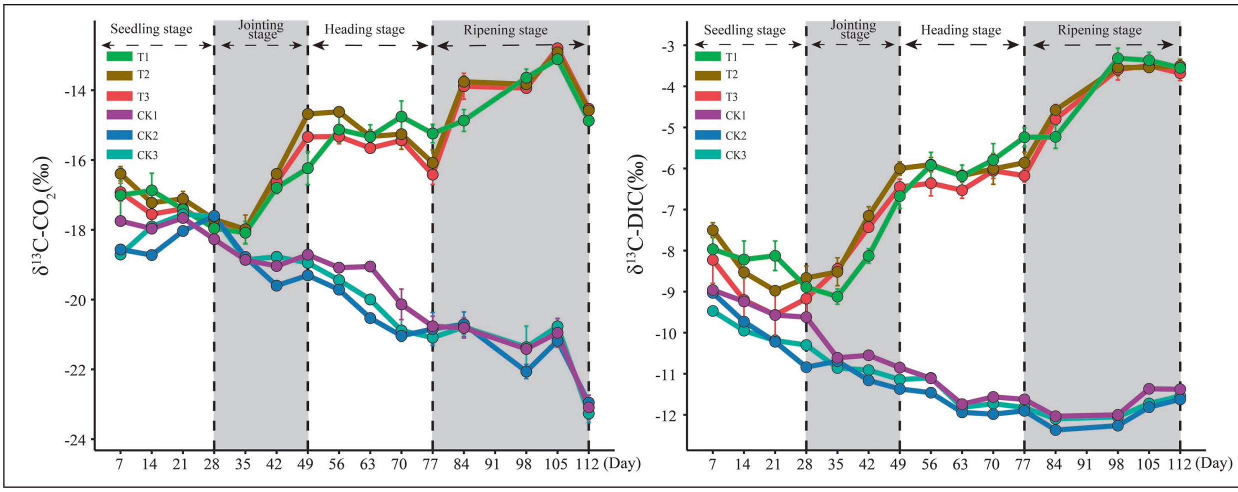

Figure 10: Changes in $\delta^{13}C$-CO_2 and $\delta^{13}C$-DIC at the soil-rock interface under days of maize growth, T1-T3: plants, CK1-CK3: soil CO_2 blank control.

its root system's $\delta^{13}C$ was -13.15 ‰. The soil used in the experiment was collected from karst scrub soils dominated by C_3 plants and has a mean $\delta^{13}C$ value of -22.80 ‰ (Yang et al., 2020), which is much lower than the $\delta^{13}C$ value of -0.85 ‰ for marine carbonate rocks. Fractionation of CO_2 occurs in the soil, with a soil carbon isotope value of -22.80 ‰ while the initial average carbon isotope value for soil CO_2 is -17.17 ‰. Soil microorgan-

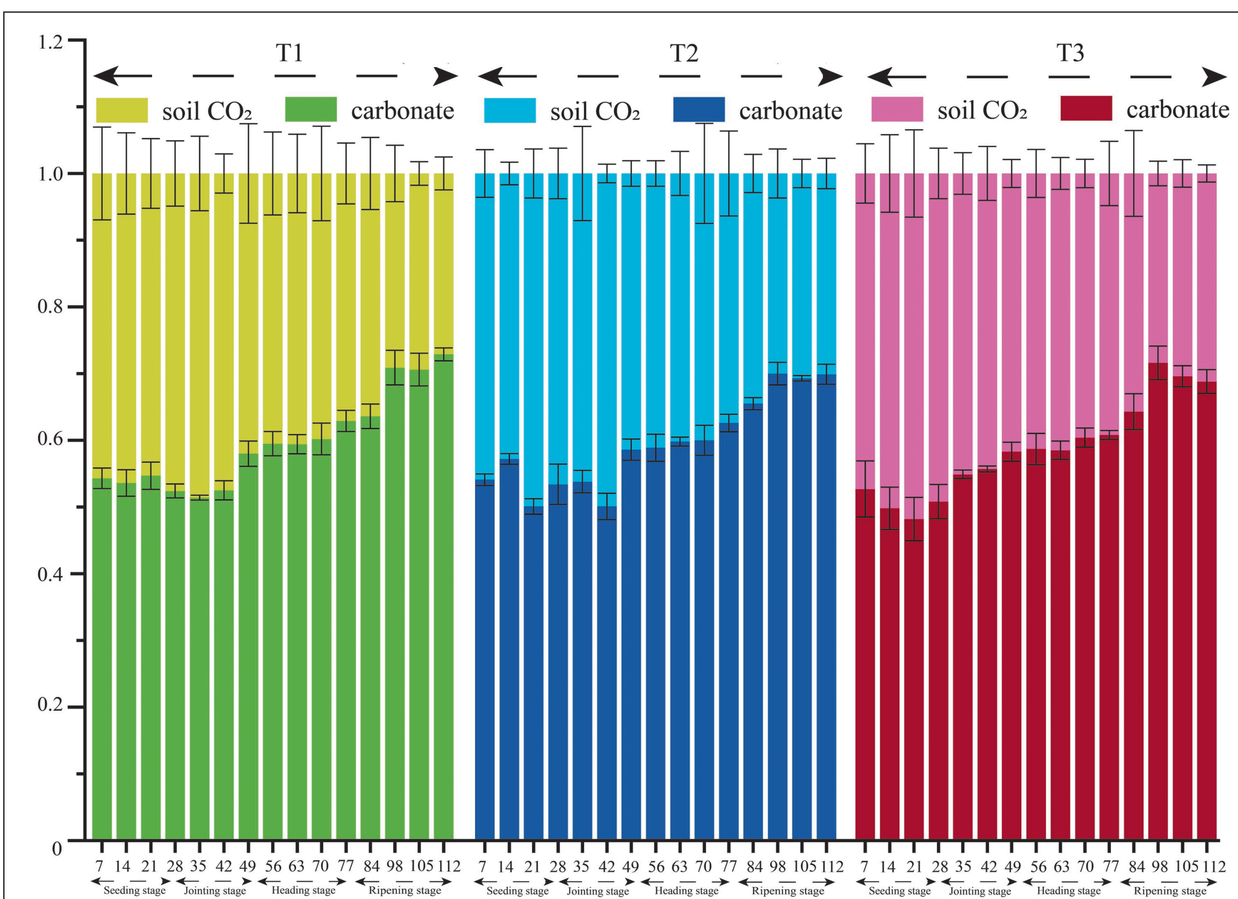

Figure 11: Carbon sources of DIC in leachate from maize cultivation group.

isms have slightly higher $\delta^{13}C$ values than soil organic matter, and are mainly concentrated in the topsoil. This study also showed that soil microbial biomass carbon decreased with soil depth in both maize-cultivated and bare soils. The $\delta^{13}C$ value of CO_2 at the soil-rock interface in the maize cultivated soil can be seen in Figure 10. Overall, there's an enrichment trend as maize growth days increase, indicating that soil CO_2 mainly originates from the maize root system respiration. The $\delta^{13}C$-CO_2 values of the bare soil (CK1-CK3 sites) showed a general linear ^{13}C-depletion during the experiment.

The $\delta^{13}C$ of DIC in leachate from the maize-cultivated and bare soils followed a similar trend to soil CO_2. The maize-cultivated group showed a constant $\delta^{13}C$ enrichment, while the bare soil group showed $\delta^{13}C$ depletion. However, $\delta^{13}C$-DIC values are significantly lower when compared to CO_2 reaching value of -3.5 ‰ in maize-cultivated group and -12 ‰ in the bare soil group by the end of the experiment.

The carbon source of DIC in leachate was determined using the end-member mixing model. Figure 11 illustrates that as the number of maize growth days increased, the contribution of carbonate rock-derived carbon to DIC in leachate also increased. From the heading stage to the maturity stage of maize, carbonate rock became the primary carbon source for DIC in leachate, while the contribution of soil CO_2-derived carbon decreased continuously. The results indicate that there were no significant differences ($P > 0.05$) in the carbon sources of DIC in leachate from three different Ca concentrations of allogenic water, and no similar trends were observed.

During the experiment, the C source from soil CO_2 for HCO_3^- in soil leachate at the bare soil showed a continuous increasing trend. As for the carbon source from carbonate rock, it first decreased, and then increased again after the 56 day of maize planting. This pattern suggests a shift in the balance between abiotic dissolution and residual SOC mineralization in the absence of plants.

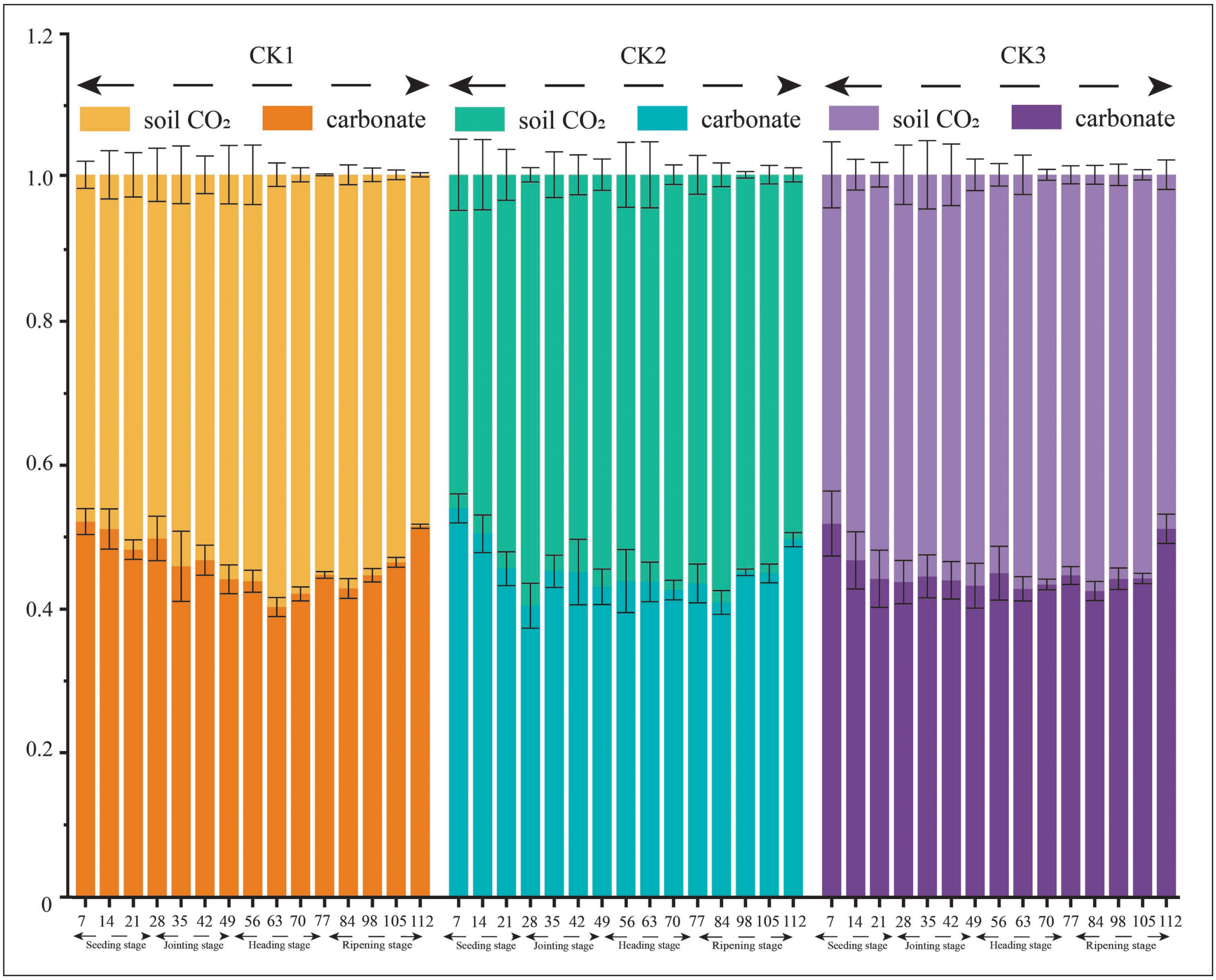

Figure 12: Carbon sources of DIC in leachate from the Bare Earth Formation.

3.6 INFLUENCE OF SOIL PHYSICO-CHEMICAL PROPERTIES ON CARBON TRANSPORT AND TRANSFORMATION

To investigate how Ca content, pH and TN affect SOC, POC, MAOC and MBC, correlation analyses were performed. Results showed that there was a significant positive correlation between MAOC and SOC and TN in the range of 0-15 cm, while there was a significant positive correlation between total Ca and POC and SOC in the range of 15-30 cm. In the bare soil group, Ca showed a significant positive correlation with TN in the 0-15 cm layer, while MAOC and POC also exhibited a significant positive correlation. In the 15-30 cm layer, Ca demonstrated a significant positive correlation with MAOC.

At the soil-rock interface, correlation analyses were conducted between Ca^{2+}, pH and key leachate parameters including EC, TDS, TOC and DOC, HCO_3^-, SO_4^{2-}, NO_3^-, and CO_2 concentrations. In maize-cultivated soils, Ca^{2+} concentrations were significantly positively correlated with HCO_3^-, indicating that higher Ca^{2+} levels were associated with enhanced carbonate dissolution. In bare soils, however, Ca^{2+} and HCO_3^- showed a strong negative correlation, possibly reflecting different dissolution-precipitation equilibria in the absence of rhizosphere processes. In both maize and bare soil groups, SO_4^{2-} and NO_3^- were positively correlated with Ca^{2+}, suggesting co-transport or shared sources (e.g. fertilizer inputs). Interestingly, in maize plots SO_4^{2-} and HCO_3^- were positively correlated, whereas in bare soils the relationship was negative (Fig-

Figure 13: Correlation between physico-chemical properties and different forms of soil carbon in maize-cultivated and bare soil groups. (A) represents the maize planting group and (B) represents the bare soil group.

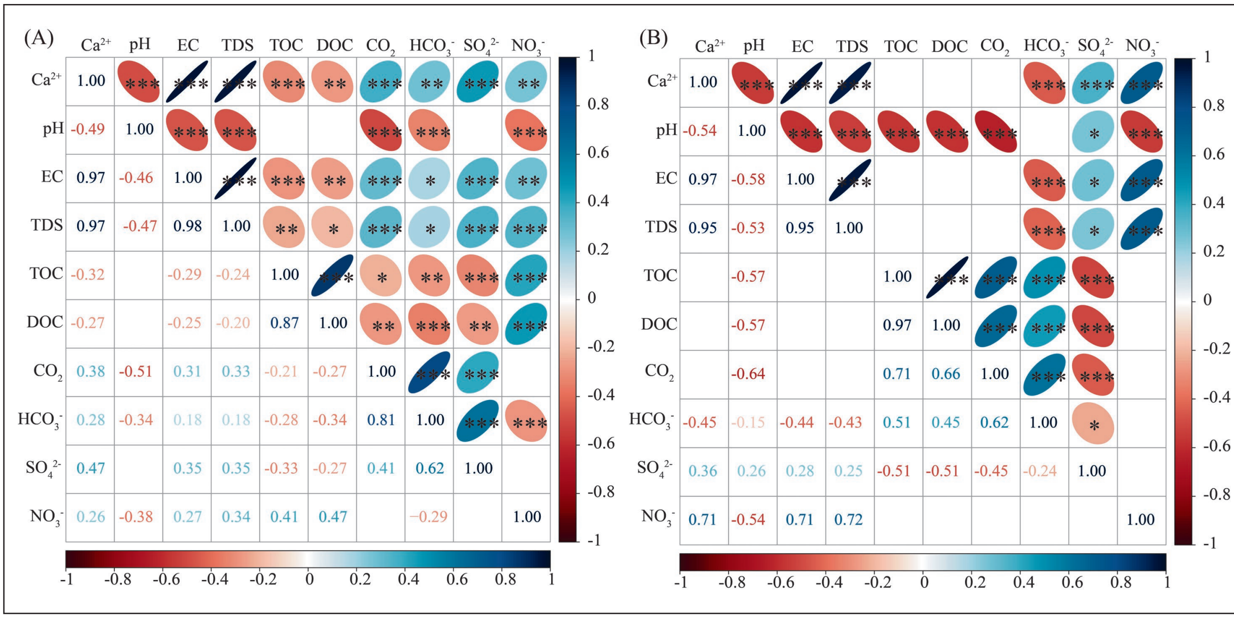

Figure 14: Correlation between physico-chemical properties and different forms of carbon in leachate from maize cultivation (A) and bare ground groups (B).

ure 14), underscoring that vegetation fundamentally alters the coupling between sulfur, nitrogen and carbonate cycling in the leachate. In the maize-cultivated group, Ca^{2+} concentration was significantly positively correlated with HCO_3^-, indicating that higher Ca^{2+} levels were associated with enhanced carbonate dissolution.

4. DISCUSSION

4.1 IMPACTS OF ALLOGENIC CA-ENRICHED IRRIGATION ON INORGANIC CARBON DYNAMICS

Soil respiration is a composite flux that integrates root respiration (autotrophic), microbial metabolism, and soil fauna activity (Liu and Fang, 1997), and represents a major pathway of terrestrial carbon efflux to the atmosphere (Li et al., 2002). In this study, cumulative soil CO_2 emissions were highest under allogenic water irrigation with an intermediate Ca^{2+} concentration of 54 mg L^{-1}, compared with both the baseline (≈2 mg L^{-1}) and the high-Ca^{2+} treatment (108 mg L^{-1}). This suggests that excessive Ca^{2+} may suppress soil respiration, whereas moderate Ca^{2+} levels are stimulatory. As expected, soil respiration rates were significantly higher in the maize-cultivated treatments than in the bare soil controls, reflecting the strong enhancement of biological activity (root respiration and rhizosphere microbial processes) by crops (Jiang and Song, 1993). The highest CO_2 concentration at the soil-rock interface occurred at 54 mg L^{-1} Ca, where moderate Ca promoted plant and microbial growth. However, 108 mg L^{-1} Ca irrigation hindered maize growth, possibly as high Ca^{2+} disrupts cell membranes (Li et al., 2013). Furthermore, adding allogenic Ca to alkaline karst soils with high native Ca exposes plant roots at the soil-rock interface to high salinity ions (Yang et al., 2018). During the tassel stage, maize's peak growth phase (Hu et al., 2004), respiration and CO_2 production in the soil are elevated. This CO_2 mainly comes from root system and microbial activity. In addition to Ca, soil temperature significantly impacts soil respiration and CO_2 concentration. Pearson's correlation analysis (Table 2) showed a strong positive link between them. Specifically, in the bare ground treatment, soil CO_2 concentration strongly positively correlated with temperature.

The HCO_3^- concentration in leachate reflects both CO_2 concentration at the soil-rock interface and the intensity of carbonate dissolution. Approximately half of the carbon in HCO_3^- originates from soil CO_2, and the other half from carbonate rocks. The CO_2 from plant root respiration and soil microbial respiration not only enters the soil air but also interacts with carbonate rocks

*Table 2: Correlation between soil respiration, soil CO_2 concentration and temperature. Note: *Significantly correlated at the 0.05 level (two-sided), **Significantly correlated at the 0.01 level (two-sided).*

	Soil temperature	Soil respiration in corn plantation group	Soil respiration in bare ground group	Soil CO_2 concentration in corn planting group	Soil CO_2 concentration in bare ground group
Soil temperature	1				
Soil respiration in corn plantation group	-0.203*	1			
Soil respiration in bare ground group	-0.031	0.546**	1		
Soil CO_2 concentration in corn planting group	0.202*	0.148	0.211	1	
Soil CO_2 concentration in bare ground group	0.583**	0.049	0.234*	0.056	1

through dissolution (Entry et al., 2004). When comparing the carbon sources of DIC in the leachate between maize cultivated and bare ground treatment, it was found that, although the maize cultivated group produced more CO_2, this gas readily reacts with carbonate rock in moist soil, causing continuous erosion. In addition, root activities and the microbial decomposition of plant material can produce acidifying substances (Finlay et al., 2020). Fertilizer application further lowers the soil pH, as the sulfur, phosphorus, and nitrogen in fertilizers can be converted into acids that also erode carbonate rocks (Zhang et al., 2012). This study showed that applying moderate Ca concentration to irrigated karst soils increased soil CO_2 concentration, promoting the dissolution of carbonate rock. Notably, on the 49th day of maize growth after fertilizer application (Figure 14), there was a significant increase in sulphate and nitrate levels in the leachate. At this point, the proportion of carbon from carbonate rock in the DIC of leachate also increased. This indicated that fertilizer application caused some carbonate rock dissolution, which may lead to errors in calculating the carbon source of DIC in leachate using the end-element mixing approach. Therefore, fertilizer application has facilitated carbonate rocks dissolution, resulting in inaccu-

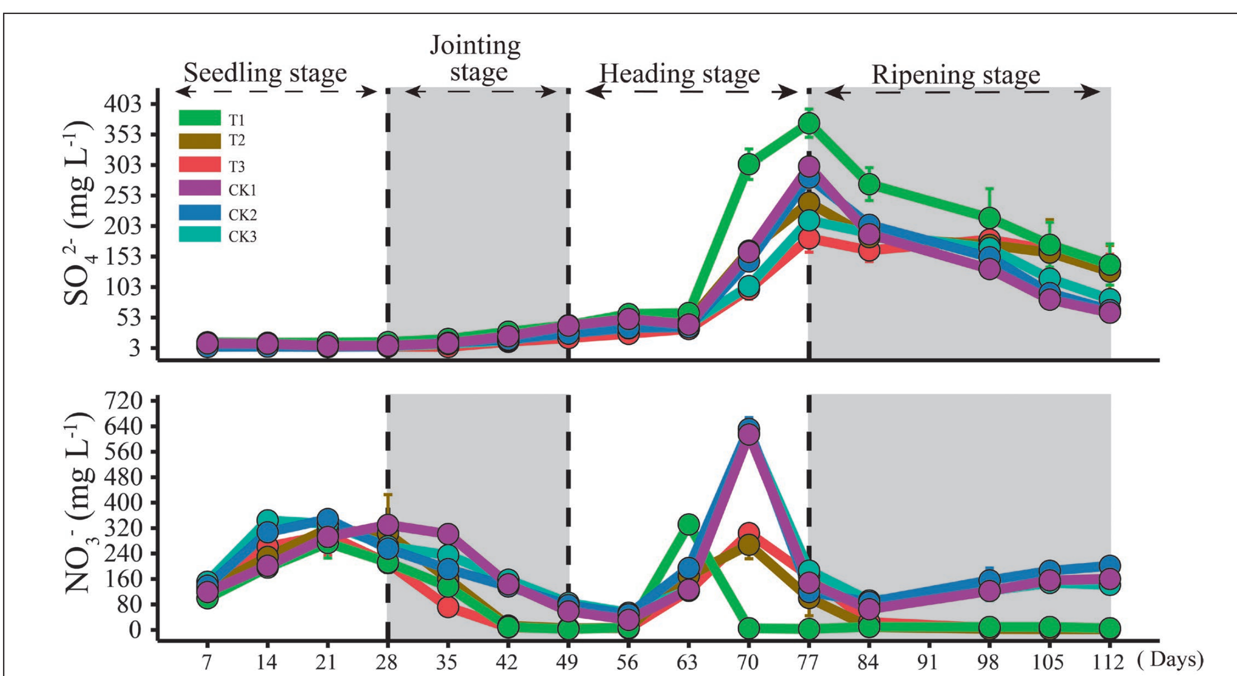

Figure 15: Variation of SO_4^{2-} and NO_3^- content in leachate.

racies in estimating DIC carbon sources. Previous studies have demonstrated that different types of fertilizers profoundly influence carbonate rock weathering through distinct mechanisms. Farmyard manure inhibits dissolution through complex biogeochemical processes (Zhang et al., 2012; Liu et al., 2009), whereas chemical fertilizers promote dissolution by generating strong acids (Li et al., 2025).

In summary, in maize-cultivated treatment, atmospheric CO_2 is first fixed into plant via photosynthesis. Root and soil microbial respiration then release CO_2 back into the atmosphere and into the soil. As irrigation water infiltrates, soil CO_2 dissolves and becomes reactive; when this CO_2-charged water percolates through the carbonate layer (≈10 cm), it enhances rock dissolution and generates HCO_3^-, increasing the $\delta^{13}C$ of leachate HCO_3^-. In bare soils, the initial photosynthetic fixation step is absent. However, the subsequent steps are consistent with those observed in the maize cultivated treatment.

When irrigation occurs, water continuously infiltrates from the soil surface. In calcareous and alkaline soils with high CO_2 partial pressure, this infiltration, guided by Henry's law, leads to ongoing dissolution of soil air CO_2 (Sánchez-Cañete et al., 2018). The infiltrating water possesses erosive properties (Kang and He, 2011), and flows through 10 cm of carbonate rock. This interaction triggers a reaction producing HCO_3^-, resulting in an overall positive influence on the carbon isotope value of HCO_3^- in the leachate.

4.2 EFFECT OF CA-ENRICHED ALLOGENIC IRRIGATION ON SOIL ORGANIC CARBON FRACTIONS

Soil organic carbon is a key soil quality indicator that directly impacts soil fertility and crop yield. As illustrated in Figures 6 and 7, the addition of allogenic Ca chloride has increased the total organic carbon content in the soil. Research showed that Ca interacts with soil organic matter to form Ca humate, a more decomposition resistant compound (Dong et al., 2020; Cao et al., 2001), which can lower organic carbon content in potting soil compared to initial levels. On the one hand, Ca^{2+}, a high-valency cation, acts as an inorganic binder, enhancing soil aggregate stability and improving overall soil structure (Rowley et al., 2018). On the other hand, the Ca^{2+} bridge mechanism plays a vital role in SOC stabilization (Boiteau et al., 2020). The content of organic carbon in the top 0-15 cm of soil gradually decreased as allogenic Ca concentration increased under maize cultivation, while the content of organic carbon in the soil in bare soil increased gradually. Some studies indicated that fertilizer application can raise SOC content (Xie et al., 2024). However, excessive Ca^{2+} may occupy binding sites with organic matter, leading to the formation of microaggregates composed of sticky or powdery particles (Dou et al., 2024; Shabtai et al., 2023; Guo et al., 2004). This interaction can negatively affect the stabilization and accumulation of organic carbon (Shabtai et al., 2023; Shi et al., 2017), leading to a negative correlation between microaggregates Ca carbonate content and organic carbon levels (Tao et al., 2021). In the maize-cultivated group, the lowest SOC content was observed in the 15-30 cm soil layer when the Ca concentration reached 54mg L^{-1} through allogenic water irrigation. At this concentration, conditions favor organic carbon mineralization, while higher Ca levels inhibited SOC mineralization. Ca is not easily translocated within plants and tends to accumulate in roots (Li et al., 2013). Elevated Ca concentration can inhibit root system growth (Wang et al., 2024), and the low root density at deeper soil layers may contribute to organic carbon retention in these subsurface layers (Henneron et al., 2022).

Recent studies suggest that partitioning SOC into POC and MAOC provides better insight into SOC accumulation and persistence (Cotrufo et al., 2019, 2015; Yu et al., 2022). POC mainly comes from partially decomposed plant material but is prone to decomposition under suitable conditions (Angst et al., 2023). In contrast, MAOC, bound to minerals via ligand exchange or encapsulated in small microaggregates (< 50 μm) (Totsche et al., 2018; Chen et al., 2015), is more resistant to decomposition, and its content is usually much higher than that of POC. In this study, POC declined with increasing Ca^{2+} concentration with depth. Also, since POC is lighter than minerals (Chen et al., 2015), it is more susceptible to physical export and mineralization. The maize-cultivated soils contained more MAOC than bare soils, likely due to additional root-derived inputs and enhanced MAOC storage (Angst et al., 2023). We found that MAOC content decreased with higher concentrations of Ca ion in the 0-15 cm soil layer. It has been shown that in limestone soils, Ca primarily exists in an exchangeable form where it is highly reactive and susceptible to leaching (Cao et al., 2003). A near-neutral or alkaline soil pH strengthens the competitive ability of Ca^{2+} against organic ligands of cations like iron, aluminum, and magnesium thus affecting MAOC content.

Soil MBC and DOC are key parts of the active SOC pool and indicate changes in pre-existing SOC (Ge et al., 2012). This study found that irrigating with allogenic water containing a 54mg L^{-1} Ca led to higher MBC levels in the 0-15 cm soil layer than in soil without Ca additions. Yet, MBC decreased when Ca concentrations were too high. Specifically, 54mg L^{-1} Ca increased microbial turnover relative to no allogenic Ca addition, and microbial activity was further boosted by plant cultivation, accelerating organic carbon cycling. Conversely, high Ca2+ levels tend to form stable Ca-humic complexes (Li, 2022), reducing carbon source availability to soil microorganisms. This reduction lowers microbial activity and MBC (Li et al., 2019; Li et al., 2022). Moreover, the results of this study showed that even without crops, applying gypsum and lime can alter soil microbiota and boost organic carbon content (Shabtai et al., 2023).

TOC and DOC in leachate stem from organic carbon transported by irrigation water during soil infiltration. In the maize-cultivated group, TOC and DOC levels in the leachate gradually decreased as irrigation water Ca concentration increased. In the bare soil group, the lowest TOC and DOC levels occurred at 54mg L^{-1} Ca. Previous research has shown that Ca ions can significantly reduce SOC loss from leaching (Minick et al., 2017), which aligns with this study's findings. In particular, the addition of Ca lowers DOC concentration (Minick et al., 2017). The soils in those studies had lower pH, higher organic carbon levels, and lower cation exchange capacity (Minick et al., 2017; Marinos and Bernhardt 2018). Our findings therefore suggest that the impact of Ca^{2+} on TOC (DOC) in karst soils is context-dependent and controlled by the interplay among pH, mineralogy, and SOC status.

4.3 INTERPLAY BETWEEN KARST DYNAMICS AND BIOLOGICAL PROCESSES

Karstification is fundamentally driven by the dissolution of carbonate rocks through carbonic acid (H_2CO_3) generated from atmospheric and soil CO_2 dissolution in water. Previous studies demonstrate that biological agents substantially amplify this geochemical process. Lower plants, such as lichens and mosses, enhance carbonate dissolution rates by 1.5-3 times compared to abiotic controls, attributable to their localized CO_2 enrichment and extracellular organic acid secretion (Cao et al., 2011; "Reform of Carbonate Rock Subsurface by Crustose Lichens and Its Environmental Significance" 1998). Higher plants further intensify weathering through rhizospheric activities: root respiration elevates soil CO_2 partial pressure (pCO_2), while root exudates (e.g., oxalic and citric acids) directly chelate Ca^{2+} ions from carbonate matrices (Finlay et al., 2020; Kang and He, 2011). This synergistic mechanism establishes vegetation as a biogeochemical bridge linking atmospheric CO_2 sequestration with lithospheric carbon cycling (Figure 16).

Within the karst critical zone, vegetation mediates interactions among the atmosphere, pedosphere, and lithosphere through three main pathways: (i) rhizosphere modulation, root networks reconfigure soil microenvironments by altering porosity, moisture retention, and

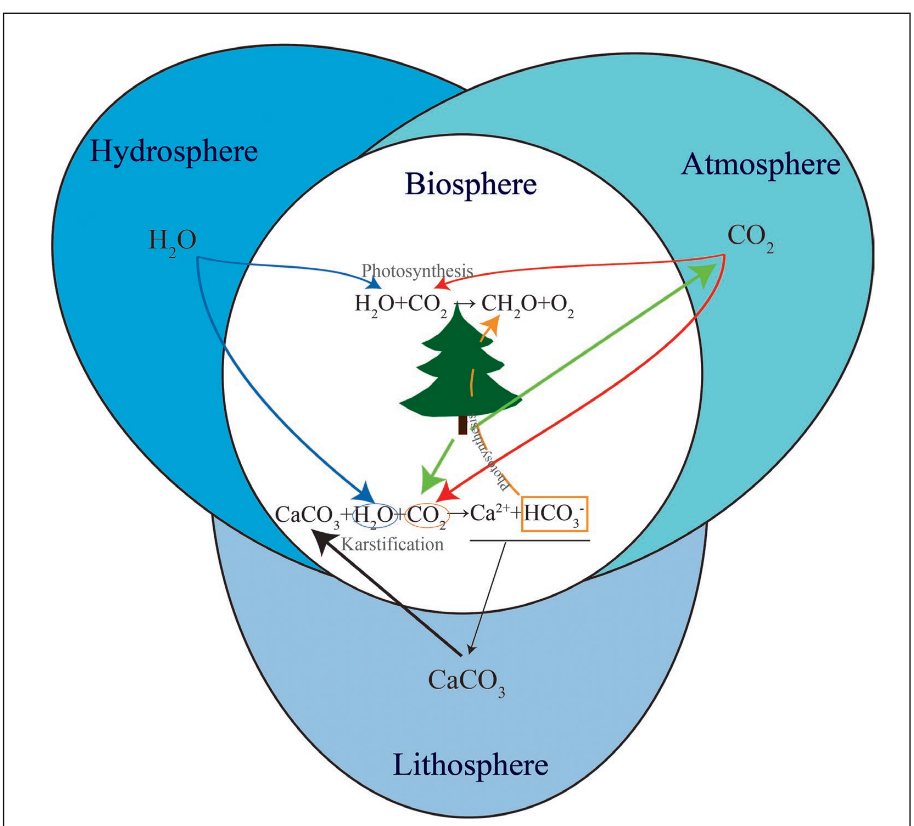

Figure 16: Coupled biogeochemical pathways of karstification and photosynthetic systems.

microbial consortia, thereby amplifying soil respiration rates and CO_2 concentrations. Field measurements revealed maize-cultivated soils exhibit 40 % higher pCO_2 and 25 % greater HCO_3^- leaching than bare soils (Entry et al., 2004; Finlay et al., 2020). (ii) Successional feedbacks: vegetation succession (e.g., grassland to shrubland to forest) progressively enhances weathering capacity. Deeper root systems in forests, relative to shrubs and grasses, deliver organic acid to deeper carbonate layers, while increasing biomass is associated with higher pCO_2 production (Li et al., 2024; Kang et al., 2020). (iii) Spatiotemporal heterogeneity: shallow grass roots generate transient CO_2 hotspots near the surface, whereas woody plants induce sustained deep weathering through lignified root channels (Yu et al., 2023). This hierarchy explains why grassland soils exhibit maximum pCO_2 at 0-20 cm depth, while forests are more effective at driving carbonate dissolution below 50 cm (Li et al., 2024; Yu et al., 2023; Wen et al., 2021).

5. CONCLUSIONS

Compared with the bare soil (non-vegetation) treatments, the maize-planted treatments showed a pronounced increase in both soil respiration and CO_2 concentration at the soil-rock interface as the days of maize growth progressed, showing a multi-peak temporal pattern ($P < 0.05$). In contrast, the bare soil group variations in soil respiration ($P > 0.05$) in soil respiration and CO_2 concentration at the soil-rock interface throughout the incubation cycle, even under irrigation with three different concentrations of Ca^{2+} in the allogenic water.

(1) Consistent with the patterns of CO_2 concentration and soil respiration, the concentration of DIC in soil leachate from the maize-planted group showed a multi-peak pattern during maize growth, whereas leachate DIC in the bare soil group remained relatively stable. Overall, DIC concentrations were significantly higher in maize-planted soils than in bare soils. In the bare soil treatments, TOC, DOC, and DIC concentrations in leachate did not differ significantly among the three Ca^{2+} levels. irrigated with allogenic water showed no significant variation across the three Ca concentrations. For both maize-planted and bare soils, TOC and DOC concentrations in leachate showed a gradual decline as the experiment progressed, indicating a progressive reduction in leachable organic carbon with time.

(2) Based on $\delta^{13}C$ stable isotope analyses, the DIC in leachate from the maize-cultivated soils was dominated by carbonate-derived carbon, and the relative contribution from carbonate rocks increased with maize growth duration. In contrast, in bare soils, DIC in leachate was derived mainly from soil-CO_2 sources, with little change over time. This contrast demonstrates that biological processes—particularly plant growth and rhizosphere activity substantially enhance carbonate dissolution and thus play a key role in karstification and carbon cycling in carbonate-rich agroecosystems.

CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Yang Ma: Writing-original draft, Methodology, Formal analysis, Data curation. **Hui Yang**: Writing-review & editing, Funding acquisition, Conceptualization. **Mitja Prelovšek**: Writing-review & editing, Investigation. **Jianhua Cao**: Supervision, Conceptualization. **Tongbin Zhu**: Writing-review & editing, Conceptualization.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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DATA AVAILABILITY

Data will be made available on request.

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