



Original scientific paper

UDC: 556.3:551.44:550.4

<https://doi.org/10.2298/IJGI251010007A>




Received: October 10, 2025

Reviewed: February 4, 2026

Accepted: March 28, 2026



CO₂ DYNAMICS AND HYDROGEOCHEMICAL CONTROLS IN KARST GROUNDWATER SYSTEMS: A REVIEW

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Abstract: Karst landscapes play a significant role in the global carbon cycle by regulating carbon dioxide (CO₂) through carbonate weathering and groundwater processes. This structured literature review revisits carbon cycling in karst landscapes, integrating perspectives on the roles of CO₂ dynamics and hydrogeochemical processes in carbonate reactions. It synthesizes studies examining the relationships among partial pressure of CO₂ ($p\text{CO}_2$), dissolved CO₂, and key chemical processes such as limestone dissolution and calcite precipitation. The review synthesizes findings from laboratory experiments, field measurements, and numerical simulations conducted across diverse karst environments worldwide. The reviewed studies consistently report strong correlations between soil-derived CO₂ and aqueous CO₂, influenced by biogenic inputs, cave degassing, hydrodynamics, and lithological variation. The literature further indicates that anthropogenic factors and sulfur-induced acidification alter carbonate equilibria and carbon fluxes. However, the existing body of research also highlights notable gaps, particularly in understanding how land-use differences shape carbon cycling within karst landscapes. Many published studies still do not integrate aboveground, belowground, and aquatic carbon fluxes across land-use types. Addressing these gaps is essential for developing comprehensive carbon budgets and improving model predictions under environmental change. This review emphasizes the importance of interdisciplinary approaches that link hydrogeochemistry with land-use analysis to better characterize carbon pathways in both tropical and temperate karst landscapes.

Keywords: structured literature review; CO₂ flux; carbonate weathering; land use impact; carbon cycle

1. Introduction

Research on the relationship between the partial pressure of CO₂ ($p\text{CO}_2$) and dissolved CO₂ in karst waters has become increasingly important because of its central role in karstification and the global carbon cycle. Karst systems cover about 10–15% of the Earth's continental surface and develop through chemical reactions between carbonate rocks and CO₂-enriched water (Chen et al., 2017; Milanolo, 2016b; Pu et al., 2014). Over the past few decades, advances in karst geochemistry have clarified the thermodynamic and kinetic controls governing carbonate dissolution and precipitation (De Waele & Gutiérrez, 2022; Ford & Williams, 2007;

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White, 2016). These processes directly affect hydrochemical parameters, including pH, saturation index, and $p\text{CO}_2$. Such parameters are essential for understanding the characteristics and long-term evolution of karst aquifers (Guo et al., 2020; Pu et al., 2018). Research on CO₂ dynamics in karst aquifers is not only of academic value but also of considerable practical relevance. A deeper understanding of these processes supports sustainable water resource management, improves geochemical modeling, and contributes to climate change mitigation. Karst aquifers are very important because they provide drinking water for a large portion of the world's population (Li Vigni et al., 2023; Milanolo, 2016b).

Although much progress has been made, the mechanisms linking $p\text{CO}_2$ to dissolved CO₂ in karst water remain poorly understood. Knowledge gaps remain, particularly in how limestone dissolution and calcite precipitation affect this relationship (Cao et al., 2020; Pu et al., 2014). Soil respiration and microbial activity in the vadose zone are well known as major CO₂ sources. However, the effects of density-driven dissolution at the water table and subsurface redox reactions have only recently been explored in detail (Class et al., 2021, 2023b; Oberhelman et al., 2024). There is ongoing debate about whether mixing-induced dissolution or heterogeneous CO₂ distribution plays the dominant role in driving karstification (Gulley et al., 2015, 2016). These uncertainties make it difficult to quantify karst carbon sinks accurately and to predict hydrogeochemical responses under changing environmental conditions (Mo et al., 2023). Addressing these gaps is essential to refine conceptual models and improve strategies for karst system management (J. Liu et al., 2020; Sládek et al., 2023).

The conceptual framework of this review integrates carbonate system equilibria, $p\text{CO}_2$, dissolved inorganic carbon species in the aqueous phase, and the hydrogeochemical processes of dissolution and precipitation. Figure 1 shows the coupling between atmospheric and aqueous $p\text{CO}_2$, dissolved inorganic carbon (DIC) species, and carbonate mineral dissolution–precipitation reactions. The $p\text{CO}_2$ regulates carbonic acid formation, which controls limestone dissolution and calcite saturation (Milanolo, 2016a; Wallin & Bjerle, 1990). Interactions among CO₂ derived from soil, cave-atmosphere CO₂, and water chemistry create a dynamic equilibrium that determines the composition of karst waters (Faimon et al., 2012; Pracný et al., 2016). This conceptual model serves as a basis for examining how chemical processes modulate the relationship between $p\text{CO}_2$ and dissolved CO₂ concentration in karst waters.

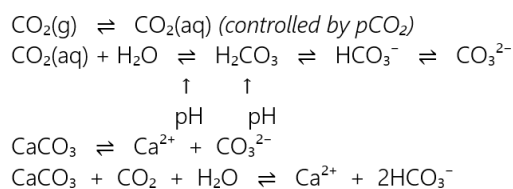


Figure 1. Conceptual representation of carbonate system equilibria in karst groundwater.

This review is based on a comprehensive literature survey encompassing high-resolution monitoring data, geochemical modeling, and laboratory-based investigations. The selected studies encompass various karst settings and methodological approaches to capture a wide range of relevant processes. The analytical framework focuses on the relationships among

*p*CO₂, hydrochemical parameters, and mineral saturation indices. The results are structured into three sections: empirical observations, mechanistic interpretations, and modeling analyses, followed by an integrated discussion on their implications for carbon dynamics in karst environments.

Although previous studies have investigated CO₂ dynamics and hydrogeochemical processes in karst waters, research has rarely examined how different land-use types shape the connections between aboveground, belowground, and aqueous carbon fluxes. This review highlights the need to integrate these components in order to achieve a more comprehensive understanding of carbon cycling in karst landscapes.

This review consolidates current understanding of the relationship between *p*CO₂ and dissolved CO₂ in karst waters, with particular focus on the governing chemical processes of limestone dissolution and calcite precipitation. By integrating insights from laboratory experiments, field observations, and modeling studies, it elucidates the key mechanisms controlling CO₂ dynamics and the hydrochemical variability of karst systems. The synthesis provides a conceptual framework that enhances predictive models of karst hydrogeochemistry and informs more effective management of karst water resources and carbon cycling under changing environmental conditions. Ultimately, this synthesis aims to advance theoretical understanding and inform practical applications in karst hydrogeology and global carbon cycling. The specific objectives are as follows: 1) to evaluate current understanding of CO₂ dynamics and its controlling processes in karst groundwater systems; 2) to assess hydrochemical models and dissolution–precipitation mechanisms in response to CO₂ fluctuations in karst environments; 3) to examine the influence of external factors such as soil CO₂ production, cave ventilation, and anthropogenic impacts on karst CO₂ dynamics.

2. Methodology

This structured literature review follows established methodological guidance for evidence synthesis. In addition to applying the PRISMA (Preferred Reporting Items for Systematic Reviews and Meta-Analyses) framework to ensure transparency in the study selection process, the search strategy was conceptually structured using the PCC framework (Principle–Concept–Context), which is commonly applied in structured and scoping literature reviews to define the scope of evidence retrieval.

The PCC framework has been widely used in health sciences to define eligibility criteria and guide evidence synthesis. More recently, its application has extended to interdisciplinary, environmental, and earth system-related studies, where it supports the systematic organization of heterogeneous datasets and complex process-based research (e.g., environmental risk assessments and climate-related reviews). This makes the PCC framework particularly suitable for synthesizing hydrogeochemical and carbon cycle processes in karst groundwater systems (Arksey & O'Malley, 2005; Rouhi et al., 2024; Strachan & Markwick, 2025).

This structured literature review employed a structured search strategy organized around three core components: guiding principles (carbon cycling and CO₂ dynamics), key concepts (dissolved CO₂, soil CO₂ production, and carbonate mineral reactions), and contextual settings (karst hydrological systems, particularly groundwater and spring environments). This structure was used to ensure transparency and consistency in defining the scope of literature retrieval. Relevant studies on carbon cycling in karst aquatic ecosystems were identified through the Scopus database.

Boolean search formula was used: ("carbon cycling" OR "carbon budget" OR "CO₂ dynamics" OR "carbon sequestration") AND ("dissolved CO₂" OR "pCO₂" OR "carbonate dissolution" OR "calcite precipitation" OR "soil CO₂ production") AND ("karst aquifer" OR "karst groundwater" OR "karst spring" OR "karst ecosystem" OR "tropical karst").

The initial dataset comprised 198 papers, including 139 retrieved from search queries and 59 identified through citation chaining. A relevance ranking was then applied to refine the analytical focus and prioritize studies most consistent with the review objectives. From this process, 193 papers were deemed relevant, with 50 classified as highly relevant and selected for detailed analysis. Research priority was determined based on the strength of justification, potential impact, and urgency as evaluated by the author (Scells et al., 2020).

To enhance transparency and reproducibility in the literature selection process, the screening and eligibility stages were further organized following the PRISMA framework. The PRISMA flow structure was adopted to clearly document the identification, screening, inclusion, and exclusion steps applied to the retrieved records. This approach enables transparent documentation of how the initial pool of 198 studies was progressively refined to the final set of 50 highly relevant articles analyzed in depth. The detailed selection pathway is illustrated in Figure 2.

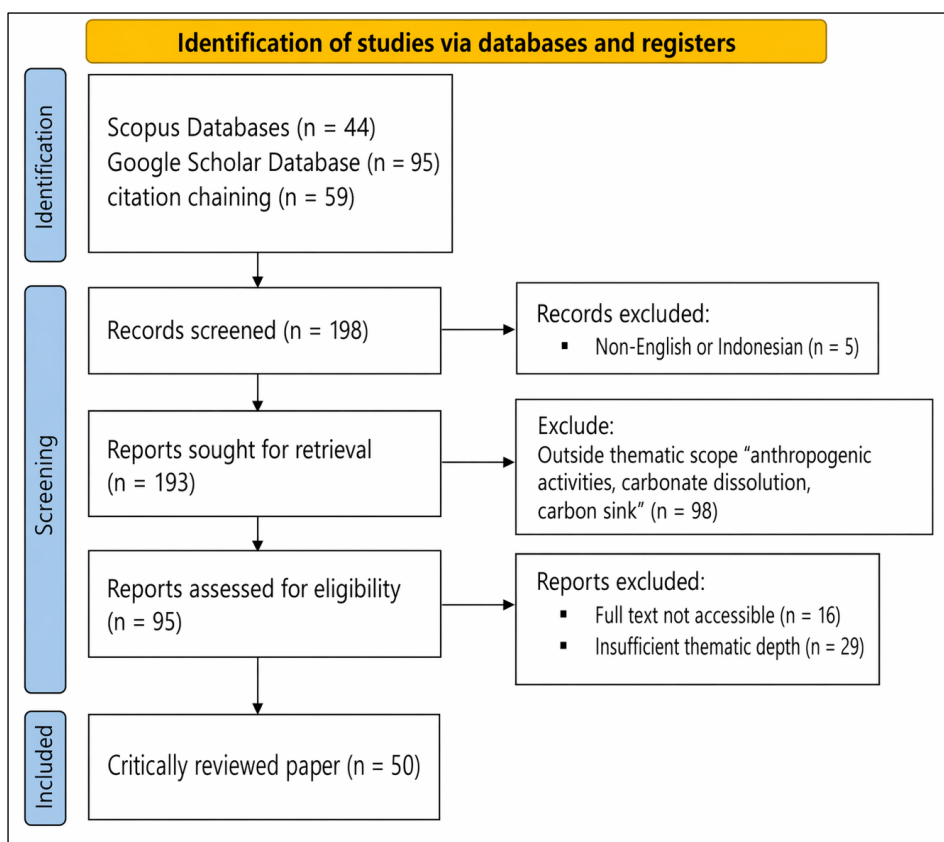


Figure 2. PRISMA workflow for paper selection.

To synthesize the reported findings, each of the 50 highly relevant studies was systematically examined to extract information on (i) reported relationships between $p\text{CO}_2$ and dissolved CO_2 , (ii) identified controlling processes, and (iii) methodological approaches and hydrological contexts. Recurring patterns were identified through cross-comparison of study results, enabling the consolidation of consistent findings and the identification of areas of uncertainty. The synthesis does not involve quantitative meta-analysis but instead relies on qualitative comparison and thematic interpretation of reported outcomes.

This approach is particularly important given the high heterogeneity among the reviewed studies in terms of methodological designs, spatial scales, hydrogeochemical settings, and reported variables. Such variability limits the comparability of datasets and reduces the suitability of statistical aggregation. Therefore, a qualitative synthesis allows for a more comprehensive interpretation of complex hydrogeochemical processes and facilitates the identification of conceptual patterns and research gaps in karst CO_2 dynamics.

3. Results and discussion

This synthesis underscores methodological diversity and identifies the limitations of existing models in representing spatial and temporal variations in karst CO_2 dynamics. These findings highlight the challenges in developing universally applicable frameworks due to differences in hydrogeochemical settings, monitoring approaches, and data resolution across studies. Consequently, the following discussion integrates key results from the reviewed literature to better understand the controlling processes and improve the conceptualization of CO_2 dynamics in karst groundwater systems.

3.1. Agreement and divergence across studies

Numerous studies report a strong correlation between $p\text{CO}_2$ and dissolved CO_2 in karst waters, mainly driven by soil respiration and vadose-zone biological activity. Geochemical processes, particularly limestone dissolution and calcite precipitation, govern this relationship and produce marked spatial and seasonal variations in CO_2 dynamics. However, uncertainties remain regarding the influence of density-driven dissolution, anthropogenic impacts, and cave ventilation. These differences reflect variations in methodological approaches, observation periods, and hydrological conditions.

These synthesized statements are derived from a structured comparative analysis of the 50 highly relevant studies selected through the PRISMA-guided process. For each article, key variables were extracted, including reported relationships between $p\text{CO}_2$ and dissolved CO_2 , identified controlling mechanisms, environmental drivers, and methodological approaches. The studies were then systematically compared to identify recurring patterns of agreement as well as areas of divergence. Rather than applying statistical meta-analysis, this review employs qualitative thematic consolidation to highlight consistent findings and sources of variability across different karst settings. The main areas of convergence and divergence identified through this process are summarized in Table 1.

Table 1. Summary of agreement and divergence in karst CO₂ studies

Criteria	Studies in agreement	Studies in divergence	Potential explanations
Correlation strength	Multiple studies confirm a positive correlation between <i>p</i> CO ₂ and dissolved CO ₂ concentration in karst water, linked to soil CO ₂ production and carbonate dissolution processes (Cao et al., 2020; Faimon et al., 2012; J. Liu et al., 2020; Pu et al., 2014, 2018).	Some studies note weaker or more complex correlations due to other influencing factors like degassing or closed system effects, e.g., limited influence of cave air CO ₂ on drip water <i>p</i> CO ₂ in closed cavities (Benavente et al., 2015; Cao et al., 2020; Pracný et al., 2016; Wang et al., 2021; Xiong et al., 2023).	Differences in hydrological settings (open vs. closed systems), measurement frequency (high-resolution vs monthly), and local cave ventilation conditions explain varying correlation strengths.
Process representation	Agreement on key chemical processes governing CO ₂ dynamics: dissolution of limestone and calcite precipitation driven by aqueous CO ₂ , with reaction kinetics and equilibrium chemistry well characterized (Gombert, 2002; Renard et al., 2005; Wallin & Bjerle, 1990; White, 2016).	Divergence in recognizing additional processes such as redox-induced acid generation enhancing dissolution (Oberhelman et al., 2024), sulfuric acid involvement modifying CO ₂ sinks, and density-driven dissolution at the water table (Class et al., 2023b).	Variability in study focus (Field data vs. lab experiments vs. modeling), geographic and geological context (e.g., presence of sulfides, organic carbon oxidation), and temporal scale (short term vs. long-term) cause differences in process emphasis.
Temporal variability	Consensus that <i>p</i> CO ₂ and aqueous CO ₂ concentrations exhibit pronounced seasonal and diurnal fluctuations controlled by soil microbial activity, temperature, rainfall, and ventilation (Cao et al., 2020, 2024; Pu et al., 2014, 2018; Troester & White, 1984).	Some studies find limited diurnal variation due to buffering by vadose zone and cave voids (Pu et al., 2014), or steady <i>p</i> CO ₂ in deep drip waters indicating stable deep sources (Benavente et al., 2015; Pracný et al., 2016).	Variation in karst system type (active cave streams vs. stagnant pools), hydrodynamic conditions, and measurement intervals explain differences in observed temporal variability.
Spatial heterogeneity	Spatial variability in CO ₂ parameters are widely observed, influenced by factors such as flow path length, recharge altitude, vegetation cover, and lithology (Mo et al., 2023; Özler, 2010; Pu et al., 2018; Yanes & Moral, 2024).	Some studies report homogeneous <i>p</i> CO ₂ within certain cave zones or seasonal uniformity in closed systems (Benavente et al., 2015; Pracný et al., 2016; Xiong et al., 2023), while others note sharp spatial gradients driven by cave ventilation or gas migration (Kukuljan et al., 2021; Wróblewski et al., 2024).	Geographic setting, karst type (epikarst, phreatic, vadose), cave morphology, and external inputs (e.g., soil CO ₂ , anthropogenic effects) drive variability in spatial patterns; measurement density and resolution also impact observed heterogeneity.
External influences	Agreement that soil CO ₂ production and temperature are primary external drivers controlling karst CO ₂ chemistry, with cave ventilation and biogenic activity modulating CO ₂ fluxes and concentrations (Cao et al., 2020; Houillon et al., 2020; Lai et al., 2024; Pu et al., 2014, 2018).	Divergent views on the role of anthropogenic influences and cave ventilation: some studies document significant urban impact altering <i>p</i> CO ₂ and emissions, while others report minor influence from cave air CO ₂ on drip waters (Xiong et al., 2023).	Differences in land use, urbanization levels, and cave openness, as well as methodological differences in quantifying anthropogenic effects, explain disagreement; also, some focus on pristine environments versus disturbed areas.

Table 1. Summary of agreement and divergence in karst CO₂ studies (*continued*)

Criteria	Studies in agreement	Studies in divergence	Potential explanations
Role of density driven dissolution	Emerging consensus on the importance of density driven CO ₂ dissolution at the karst water table enhancing CO ₂ concentrations and dissolution deep in the water column (Class et al., 2021, 2023a, 2023b).	Earlier literature and many field studies do not consider or find evidence for the significance of density driven dissolution processes in karst hydrochemistry (Mo et al., 2023; Pu et al., 2014, 2018).	Recent methodological advances integrating numerical modeling with high-resolution monitoring have successfully revealed this mechanism, an aspect that may have been overlooked or underestimated in earlier research due to the absence of such combined methodologies.

3.2. Theoretical and practical implications

This section discusses the theoretical and practical implications derived from the findings of this review. Although such discussions are often incorporated within concluding remarks, they are presented here as a separate section in order to more clearly highlight the conceptual contributions and practical relevance of the synthesized findings regarding CO₂ dynamics and hydrogeochemical processes in karst groundwater systems.

3.2.1. Theoretical implications

The reviewed studies emphasize that $p\text{CO}_2$ plays a key role in controlling carbonate dissolution and calcite precipitation in karst systems. These results support classical geochemical equilibrium concepts but also reveal the influence of dynamic environmental factors, including soil-derived CO₂, cave ventilation, and hydrological variability (Milanolo, 2016b; Pu et al., 2014; White, 2016). Evidence shows that CO₂ behavior in karst environments is highly variable in both space and time, directly affecting mineral saturation and solubility.

Recent studies using high-resolution monitoring and modeling have identified density-driven CO₂ dissolution near the karst water table as an important but previously overlooked process influencing dissolved CO₂ concentrations and karstification potential (Class et al., 2021, 2023a, 2023b). These findings challenge the traditional emphasis on percolation-driven CO₂ transport and highlight the need to include convective and diffusive mechanisms in hydrogeochemical models of karst systems.

The interaction between biogenic CO₂ sources, such as soil respiration and microbial activity, and abiotic processes, including carbonate dissolution and redox-driven generation of noncarbonic acids, introduces additional complexity to the carbon cycle in karst aquifers. This suggests that carbonate weathering is not exclusively controlled by carbonic acid but is also affected by sulfuric and nitric acids produced through subsurface redox reactions. (Oberhelman et al., 2024; Ye et al., 2024). These insights broaden the theoretical framework of karst geochemistry, moving beyond the traditional carbonic acid-dominated perspective.

Moreover, spatial variability in $p\text{CO}_2$ across different zones of karst aquifers, such as the epikarst and phreatic regions and the occurrence of semi-closed to closed system conditions significantly affect the extent and spatial distribution of carbonate dissolution and precipitation processes (Benavente et al., 2015; Faimon et al., 2012; Prachý et al., 2016). This

lends support to the view of karst systems as spatially heterogeneous and compartmentalized environments characterized by diverse and dynamic geochemical conditions.

The integration of isotopic analyses ($\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{18}\text{O}$, $\delta^2\text{H}$) with hydrochemical data provides detailed insights into the sources and transformations of dissolved inorganic carbon. This approach enables clear differentiation among soil-respired CO₂, atmospheric inputs, and deeper endogenous sources (Huang et al., 2015; Lai et al., 2024; J. Liu et al., 2020; Zhang et al., 2017). This integrative approach significantly advances the theoretical understanding of carbon cycling pathways in karst groundwater systems.

Recent advances in experimental and modeling approaches, such as reactive percolation experiments and coupled hydrodynamic and geochemical simulations have improved the mechanistic understanding of limestone dissolution kinetics under varying $p\text{CO}_2$ and hydrological conditions. These developments also enhance the ability to predict karst landscape evolution and related carbon fluxes (Renard et al., 2005; Vialle et al., 2014; Wallin & Bjerle, 1990).

3.2.2. Practical implications

A thorough understanding of $p\text{CO}_2$ dynamics and their effects on carbonate dissolution and precipitation is essential for managing karst water resources. Such knowledge helps anticipate changes in water quality and supports the long-term sustainability of aquifers under both climatic and anthropogenic pressures (Guo et al., 2020; D. Liu et al., 2023; Sládek et al., 2023). Understanding these mechanisms also plays a crucial role in protecting drinking water sources and minimizing contamination risks.

The identification of density-driven CO₂ dissolution and its strong influence on karst hydrochemistry underscores the need to incorporate these processes into monitoring and modeling frameworks. Doing so would improve predictions of karst aquifer behavior in response to environmental changes an essential aspect for infrastructure planning and hazard risk assessment in karst terrains (Class et al., 2021, 2023a, 2023b).

The identification of sulfuric acid and other non-carbonic acids as additional drivers of carbonate dissolution has notable implications for estimating karst carbon sinks and for climate modeling. Omitting these acid-driven processes from analysis can lead to substantial errors in estimating karst carbon sinks, resulting in either overestimation or underestimation. Therefore, incorporating these processes is crucial to improve the accuracy of global carbon budgets and to strengthen climate change mitigation strategies (Oberhelman et al., 2024).

The documented seasonal and spatial variability in CO₂-related parameters, driven by soil CO₂ production, vegetation dynamics, and urbanization, underscores the importance of high-resolution and spatially explicit monitoring programs. Such programs are essential for accurately assessing karst carbon cycling and CO₂ emissions, and for supporting evidence-based land use planning and environmental policy in karst regions (Pu et al., 2014; Yanes & Moral, 2024). Furthermore, the observed effects of biological processes including microbial activity and photosynthesis by submerged plants on CO₂ fluxes at the water–air interface in karst rivers and caves highlight opportunities to enhance carbon sequestration through ecosystem-based management. These insights also have potential applications in carbon offset programs and biodiversity conservation (Lai et al., 2024).

Advances in understanding the interaction between hydrochemical processes and the physical properties of karst rocks, particularly permeability and porosity changes driven by

CO₂-induced dissolution have supported the development of geophysical monitoring tools and predictive models of karstification. These tools are vital for applications such as engineering design, groundwater management, and the mitigation of natural hazards in karst environments (Z. Li et al., 2023; Rembert et al., 2023; Vialle et al., 2014).

3.3. Limitations in reviewed literature

The main limitations identified in the reviewed literature were summarized in Table 2. The most prominent issues include strong geographic and temporal biases, which restrict the general applicability of existing findings. Methodological simplifications and limited consideration of non-carbonic acids further constrain the accuracy of current hydrochemical models. Additionally, insufficient integration of biological processes and limited analysis of spatial variability reduce the comprehensiveness of our understanding of karst CO₂ dynamics. The lack of detailed assessment of anthropogenic impacts also highlights a critical research gap. Collectively, these limitations underscore the need for multi-scale, interdisciplinary approaches that combine field observations, modeling, and experimental studies to better capture the complexity of karst carbon processes.

The limitations presented in this section were identified through systematic content analysis of the selected studies. For each article, reported methodological constraints, acknowledged uncertainties, data limitations, and modeling assumptions were extracted and documented. Particular attention was given to recurring concerns explicitly stated by the authors, as well as implicit limitations inferred from restricted spatial coverage, short monitoring duration, or simplified process representation. These limitations were then grouped into thematic categories based on similarity of methodological or conceptual constraints. The frequency and consistency with which these issues appeared across independent studies were considered when determining their relative prominence. The synthesized limitations derived from this comparative evaluation are summarized in Table 2.

Table 2. Literature limitations

Area of limitation	Description of limitation	Articles
Geographic bias	Numerous investigations have focused on specific karst regions, particularly in subtropical China and southern Europe, thereby limiting the external validity of their findings. This geographic concentration constrains the generalizability of conclusions to karst systems in differing climatic and geological settings.	(Benavente et al., 2015; Guo et al., 2020; D. Liu et al., 2023; Pu et al., 2014, 2018; Yanes & Moral, 2024; Zhang et al., 2017)
Temporal resolution	Numerous studies are based on short-term or seasonally restricted datasets, which may fail to adequately reflect long-term hydrochemical patterns or interannual variability. Such temporal limitations weaken the reliability of conclusions concerning CO ₂ behavior and karst-related processes over extended timescales.	(Cao et al., 2020; Pu et al., 2014, 2018; Troester & White, 1984; Zeng et al., 2012)
Methodological constraints	Constraints in experimental design (such as simplifying assumptions like the absence of surface resistance in dissolution models, or difficulties arising from the computational intensity of numerical simulations) undermine the precision and practical utility of hydrochemical and reactive transport models in karst environments.	(Class et al., 2021, 2023a, 2023b; Renard et al., 2005; Vialle et al., 2014; Wallin & Bjeler, 1990)

Table 2. Literature limitations (*continued*)

Area of Limitation	Description of Limitation	Articles
Limited consideration of non-carbonic acids	A large proportion of research emphasizes carbonic acid as the dominant agent of dissolution, frequently overlooking contributions from sulfuric, nitric, and other acids. This omission may result in a partial or skewed interpretation of dissolution dynamics and carbon cycling within karst aquifers.	(Oberhelman et al., 2024; Ye et al., 2024)
Insufficient integration of biological factors	Biological influences such as microbial activity, soil respiration, and aquatic plant metabolism are often underexplored in studies of CO ₂ dynamics. This underrepresentation limits the development of a comprehensive understanding of the biogeochemical interactions governing karst water chemistry.	(Class et al., 2023a; Houillon et al., 2020; Lai et al., 2024; J. Liu et al., 2020)
Anthropogenic impact understudied	Although certain studies recognize anthropogenic influences like urban development and agricultural practices, the specific pathways and magnitude by which these activities affect pCO ₂ levels and karst water chemistry remain poorly quantified. This knowledge gap hinders the applicability of findings to human impacted karst systems.	(Guo et al., 2020; K. Li et al., 2023; Ye et al., 2024)
Limited spatial variability analysis	Spatial heterogeneity in karst aquifers especially variations in pCO ₂ and saturation indices has received limited systematic investigation, restricting understanding of site specific dissolution and precipitation processes.	(Gulley et al., 2015; D. Liu et al., 2023; Pracný et al., 2016; Yanes & Moral, 2024)

3.4. Gaps and future research directions

The research gaps identified in this review were derived from a structured qualitative synthesis of the selected literature. The identification process was guided by the PCC framework to define the scope of the reviewed studies, while the study selection and screening procedures followed the PRISMA-guided review process. Through this combined approach, the reviewed studies were systematically analyzed to identify recurring limitations, underexplored hydrogeochemical mechanisms, and emerging research needs related to CO₂ dynamics in karst groundwater systems (Table 3).

Each article was critically evaluated to identify recurring methodological limitations, conceptual inconsistencies, underexplored variables, and emerging research needs. These issues were then grouped into thematic categories representing major knowledge gaps in karst carbon cycling research. The prioritization was based on the frequency of occurrence, scientific significance, and implications for improving carbon budget assessments.

Bibliometric mapping tools such as VOSviewer are widely used to visualize structural and temporal patterns of scientific production. Danese and Gioia (2021) applied VOSviewer to construct keyword co-occurrence networks, identify thematic clusters, and generate overlay visualizations illustrating the temporal evolution of research topics. These approaches are particularly effective for quantitatively mapping citation structures, keyword relationships, and research trends within a field.

The present study employs a structured literature review methodology aimed at conceptual and process-based synthesis rather than bibliometric network analysis. The objective is to critically integrate hydrogeochemical mechanisms, methodological constraints, and research gaps in karst carbon cycling. Accordingly, the analysis focuses on

thematic interpretation and qualitative synthesis of content rather than on quantitative clustering or citation network visualization.

Table 3. Thematic research gaps and future research directions in karst CO₂ dynamics

Gap area	Description	Future research	Justification	Research priority
Influence of anthropogenic activities on karst CO ₂ dynamics	The influence of urban development, mining operations, and agricultural practices on pCO ₂ and carbonate system dynamics in karst water bodies remains insufficiently studied and is frequently constrained to localized case studies.	There is a need to conduct cross-regional comparative analyses within karst landscapes subject to varying intensities of anthropogenic disturbance, incorporating land-use information, hydrochemical profiles, and CO ₂ flux observations to derive more general insights into human-induced impacts.	Human activities modify the sources of CO ₂ and the associated degassing fluxes, thereby influencing both the natural carbon cycle and water quality in karst systems (Gu et al., 2022; K. Li et al., 2023; Ye et al., 2024).	High
Long-term monitoring and climate change effects	Long-term variations in pCO ₂ and carbonate dissolution processes under evolving climate conditions remain poorly characterized and inadequately documented.	Developing long-term monitoring networks across a range of karst settings is essential for evaluating climate-induced shifts in CO ₂ behavior, carbonate dissolution rates, and the capacity of karst systems to function as carbon sinks.	Fluctuations in climate parameters influence soil CO ₂ generation, hydrological regimes, and temperature patterns, collectively shaping carbon dynamics and sequestration potential within karst landscapes (Pu et al., 2018; Yanes & Moral, 2024; Zeng et al., 2012).	High
Temporal resolution of episodic events impacting CO ₂ dynamics	The effects of episodic phenomena such as storms, floods, and diurnal biological activity on pCO ₂ and carbonate chemistry remain incompletely understood.	Implement continuous, high-frequency monitoring during episodic events at multiple karst locations to capture transient CO ₂ and hydro-chemical responses and enhance predictive modeling.	Episodic events trigger rapid hydrochemical shifts that influence CO ₂ behavior and carbonate saturation levels (Cao et al., 2020; L. Li et al., 2016; Mo et al., 2023; Pu et al., 2014).	High
Integration of density-driven CO ₂ dissolution in karst model	While density-driven CO ₂ dissolution at the water table is acknowledged, it is rarely incorporated into karst hydrogeochemical modeling.	Numerical models should be expanded to incorporate density-driven CO ₂ dissolution, supported by high-resolution field observations, to evaluate its role in karstification and CO ₂ transport.	Density-driven dissolution promotes CO ₂ replenishment in stagnant zones, affecting deep karst hydrochemistry (Belfar et al., 2017; Class et al., 2021, 2023a, 2023b).	High
Quantification of non-carbonic acid contributions	The relative contributions of sulfuric, nitric, and other non-carbonic acids to carbonate dissolution and CO ₂ dynamics in karst systems remain poorly quantified	Conduct integrated geochemical and isotopic studies to quantify the spatial and temporal variability of non carbonic acid inputs and their effects on carbonate dissolution and CO ₂ fluxes in diverse karst settings.	Non-carbonic acids significantly alter carbonate dissolution rates and CO ₂ consumption, impacting carbon sink estimates and karst evolution (Oberhelman et al., 2024; Vargas-Sánchez et al., 2024; Ye et al., 2024).	High

Table 3. Thematic research gaps and future research directions in karst CO₂ dynamics (*continued*)

Gap Area	Description	Future Research	Justification	Research Priority
Multi-Scale Spatial Variability and Scaling	Spatial heterogeneity of pCO ₂ and aqueous concentrations is documented but scaling point measurements to regional karst systems remain challenging.	Implement multiscale monitoring campaigns combining cave air, soil, epikarst, and groundwater CO ₂ measurements with spatially explicit modeling to upscale findings.	Spatial variability controls localized dissolution and precipitation patterns, critical for regional carbon cycling (Gulley et al., 2015; Pu et al., 2018; Yanes & Moral, 2024).	Medium
Comprehensive Multidisciplinary Data Integration	Integration of hydrochemical, isotopic, geophysical, and modeling data remains fragmented, limiting holistic understanding of CO ₂ -driven karst processes.	Develop standardized protocols and data frameworks to integrate multidisciplinary datasets across temporal and spatial scales, enhancing model validation and process interpretation.	Multidisciplinary approaches provide complementary insights but require better integration for robust karst system characterization (J. Liu et al., 2020; Vialle et al., 2014; Zhang et al., 2017).	Medium

Based on the systematic evaluation of the selected studies, the thematic synthesis indicates that research on karst CO₂ dynamics remains fragmented and often focused on isolated processes. Key gaps include limited assessment of anthropogenic impacts, insufficient long-term monitoring, and inadequate consideration of episodic hydrological events such as storms and rapid recharge. Although carbonate dissolution and precipitation are widely studied, fewer investigations evaluate how land-use change, climate variability, and human activities influence CO₂ dynamics at broader spatial and temporal scales.

Methodological limitations remain evident in the existing literature. Important processes such as density-driven dissolution and the role of non-carbonic acids are not consistently incorporated into hydrogeochemical models, potentially affecting estimates of carbon sink capacity. In addition, the integration of hydrochemical, isotopic, and modeling approaches remains limited, restricting comprehensive system-level understanding. Addressing these limitations requires improved coordination across disciplines and more consistent methodological frameworks that can link localized hydrogeochemical processes to regional carbon dynamics.

4. Conclusion

This review confirms a strong and dynamic relationship between the pCO₂ and dissolved CO₂ in karst waters. The relationship is primarily governed by soil respiration and cave degassing, which drive carbonate dissolution and influence the saturation state of calcite and dolomite. Environmental factors such as microbial activity, temperature, precipitation, and gas exchange regulate CO₂ variability across spatial and temporal scales. Non-carbonic acids also contribute to carbonate weathering, adding complexity to estimates of net CO₂ consumption. Although thermodynamic and kinetic models effectively represent CO₂-driven dissolution and precipitation, they remain limited in addressing spatial heterogeneity, reaction kinetics under low-flow conditions, and the influence of deep-seated CO₂ sources. Anthropogenic activities further alter natural CO₂ regimes, potentially reducing the carbon sink capacity of karst systems.

This review is subject to several limitations. The synthesis relies primarily on peer-reviewed publications indexed in a single database, which may introduce publication bias and limit the inclusion of regional or non-English studies. In addition, differences in measurement techniques, monitoring durations, and model parameterization across studies create inherent heterogeneity, limiting direct comparability.

This synthesis highlights the need to integrate environmental and human-induced drivers into future models of karst carbon cycling. Future research should emphasize long-term, multi-scale observations and develop coupled biogeochemical and hydrological models to predict CO₂ dynamics and improve the reliability of global carbon assessments in karst environments.

Acknowledgements

The authors would like to thank the Indonesian Education Scholarship (BPI), the Center for Higher Education Funding and Assessment (PPAPT), Ministry of Higher Education, Science, and Technology of the Republic of Indonesia, and the Indonesia Endowment Fund for Education (LPDP) for supporting this research.

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