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Effects of agricultural activities coupled with karst structures on riverine biogeochemical cycles and environmental quality in the karst region

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ABSTRACT

The karst region in southwestern China is a typical region with fragile ecological environments, and the coordination of regional agricultural development and environmental protection faces enormous challenges. Based on the soil and hydrological characteristics of karst in southwestern China, this study summarized water-related environmental issues caused by agricultural activities in this karst region. Agriculture in the karst hills is more likely to cause soil and nutrient losses due to the fast hydrological flow through special karst structures with high permeability. Thus, this review emphasized the impacts of agricultural development on the riverine biogeochemical cycles of elements based on previous studies. Meanwhile, the carbon cycle is also strongly impacted by agricultural activities in this karst region due to enhanced carbonate weathering by nitric acid from the nitrification of ammonium. This weathering mechanism represents a net source of atmospheric CO_2 and might impact regional and global carbon cycling in the Anthropocene. Based on the results summarized in this study, we advocate that in the future, better management of agricultural land, improvement of fertilizer use efficiency, and boosting of nutrient recycling rate should be taken into account for reducing nutrient losses and water quality deterioration. Targeted management of local agricultural practices along with guidance from scientific research results is needed to be devoted to sustainable development of agriculture and economies while protecting water environment.

1. Introduction

Karst can be defined as a terrain comprised of distinctive landforms and hydrology with well-developed secondary (fracture) porosity, which results from highly soluble rocks (e.g., limestone, marble, and gypsum) (Fig. 1) (Ford and Williams, 2013). Karst landscapes developed on carbonate rocks occupy roughly 20 % of the Earth's ice-free continental surface and provide sources of drinking water for about 20–25 % of the world's population (Ford and Williams, 2013; Hartmann and Moosdorf, 2012). In many karst regions, karst landscapes (e.g., caverns, springs, towers, and sinkhole plains) are also natural tourist attractions, but their complex and unique geographic features pose challenges for local agricultural and economic developments (Fenton et al., 2017; Hartmann et al., 2014; Liu, 2007; Jiang et al., 2014; Ulloa-Cedamanos et al., 2020; Wang et al., 2019; Wang, 2004). The increase in population and the decline in land productivity have triggered the expansion of agriculture to marginal farmland on slopes and ridges, which has caused many agriculture-related ecological deteriorations in karst terrains (Wang et al., 2019; Yue et al., 2019). It is thus crucial to carefully coordinate agricultural development and environmental protection in karst regions, especially in southwestern China where the economy is still underdeveloped and the majority of the population relies largely on agricultural production.

Karst soils are typically thin, patchy, and fragile to disturbances, easily causing losses of nitrogen (N) and phosphorus (P) leached from those soils (Fenton et al., 2017). Karst systems (e.g., epikarst) are also highly permeable due to the widely spread formation of fissures, fractures, and conduits in karst systems (Hartmann et al., 2014). It leads to the rapid infiltration of rainwater that carries pollutants (e.g., from livestock, domestic and industrial discharge), which can easily pollute both groundwater and surface water in karst regions (Li et al., 2019; Xu et al., 2020a; Wang et al., 2020; Yue et al., 2019). The availability of

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arable lands in karst regions is mostly constrained by the distribution and thickness of overlying soils of epikarst, as well as soil nutrients and quantity (Cao et al., 2004; Green et al., 2019). Ensuring food security is an important foundation for the sustainable development of national economy and society (Yu, 2019; Yu et al., 2019). With the increasing demand for food, the application of chemical fertilizers in agriculture has increased considerably, rendering that nitrogen use efficiency has dramatically decreased over recent years in China for agricultural production; combined with the highly permeable characteristics of karst soils and subsurface hydrological systems, karst regions are more than ever prone to nitrate pollution under the influences of anthropogenic activities (Yu et al., 2019; Yue et al., 2015, 2019; Zhang et al., 2015).

The increased fertilizer application and decreased nitrogen use efficiency impact not only water quality, but also chemical weathering processes of crustal rocks, which has been evidenced in previous studies (Li and Ji, 2016; Perrin et al., 2008; Yue et al., 2015). Carbonate rocks can weather quickly (e.g., carbonates weather 10 times faster than granites) and are therefore very sensitive to anthropogenic perturbation, including the increasing levels of sulfuric (H_2SO_4) and nitric (HNO_3) acids in the environment due to anthropogenic emissions (Fig. 1) (Goudie and Viles, 2012; Li and Ji, 2016; Li et al., 2008, 2010; Liu and Han, 2020; Perrin et al., 2008; Spence and Telmer, 2005; Yue et al., 2015). The H_2SO_4 derived from anthropogenic origin and oxidative weathering of sulfide minerals has been found to extensively involve in rock weathering (Li et al., 2008; Spence and Telmer, 2005; Torres et al., 2014). The protons liberated by the nitrification process of nitrogen fertilizers will increase with the increasing use of nitrogen fertilizers, and thus, it is more likely to dissolve carbonate rocks in the karst areas (Perrin et al., 2008; Yue et al., 2015). Carbonate weathering by H_2SO_4 and HNO_3 can increase the release of CO_2 to the ocean-atmosphere system and might notably impact the carbon cycle in the Anthropocene (Barnes and Raymond, 2009; Perrin et al., 2008; Torres et al., 2014; Yu et al., 2019; Zhang et al., 2015). Due to the high susceptibility of karst systems to the increasing use of nitrogen fertilizers, the HNO_3 weathering of both carbonate and silicate rocks in karst areas need to be further studied to identify and quantify their impacts on the regional and global carbon cycles and budgets.

In southwestern China, soil erosion and rocky desertification pose another great environmental concern to the agricultural sustainability and ecosystem stability. This concern is the combined result of the extremely low formation and high erosion rates of karst soils, primarily due to the characteristics of thin soil layer, steep slope, loss of vegetation cover, irrational land use, and high overland flow induced by precipitation, among others, in this region (Cao et al., 2020; Green et al., 2019; Jiang et al., 2014; Liu, 2007; Wang, 2004). The karst region in southwestern China is one of China's major areas for ethnic minorities and one of the most underdeveloped regions in China. This region currently has a population of 117 million with a population density of 1.6 times the national average, and its gross domestic product (GDP) per capita is less than 50 % of the national average (Green et al., 2019; Wang et al., 2019). Extensive human activities engaged in agriculture in this ecologically fragile karst region exacerbated the ecological and environmental problems. There exist complicated interlinks between the karst ecosystem and agricultural development. As shown in the conceptual diagram of Fig.1, with the high vulnerability of karst ecosystems, the mounting pressures from human activities in karst areas are not conducive to local agricultural development and food production, which in turn puts an enormous pressure on the local ecological environment. Thus, understanding the interplays among agricultural activities, biogeochemical cycling, and environmental quality, along with unique features of karst systems, is crucial for the sustainable development of agriculture and environmental protection in this karst region.

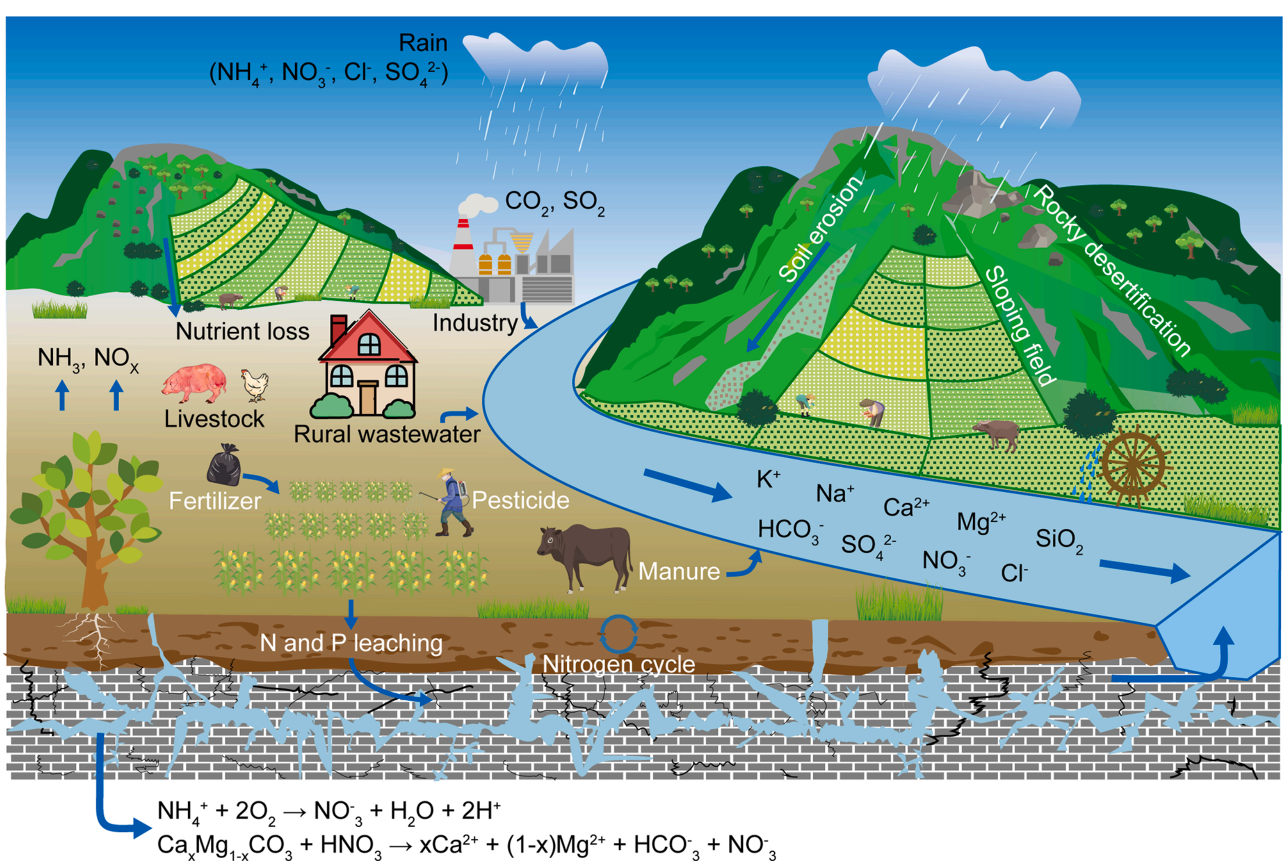

Fig. 1. The conceptual diagram showing the effects of agricultural activities coupled with karst structures on riverine biogeochemical cycles and environmental quality in the karst region.

2. Characteristics of the karst region in southwestern China

The total karst area (buried, covered, and exposed carbonate rock areas) in China is approximately 3.44×10^6 km^2, which is about 36 % of China's total land area and 15.6 % of world's karst area (Jiang et al., 2014). The karst region in southwestern China is one of the most extensive karst areas in the world, which is distributed across eight provinces and one municipality with an area of ~1.95×10^6 km^2 (Fig. 2). The exposed carbonate rocks in this karst region have a total area of ~5.1×10^5 km^2, which are mainly situated in Yunnan (~6.1×10^4 km^2), Guizhou (~1.3×10^5 km^2), and Guangxi (~8.9×10^4 km^2) provinces (Liu, 2007, 2009; Jiang et al., 2014). This

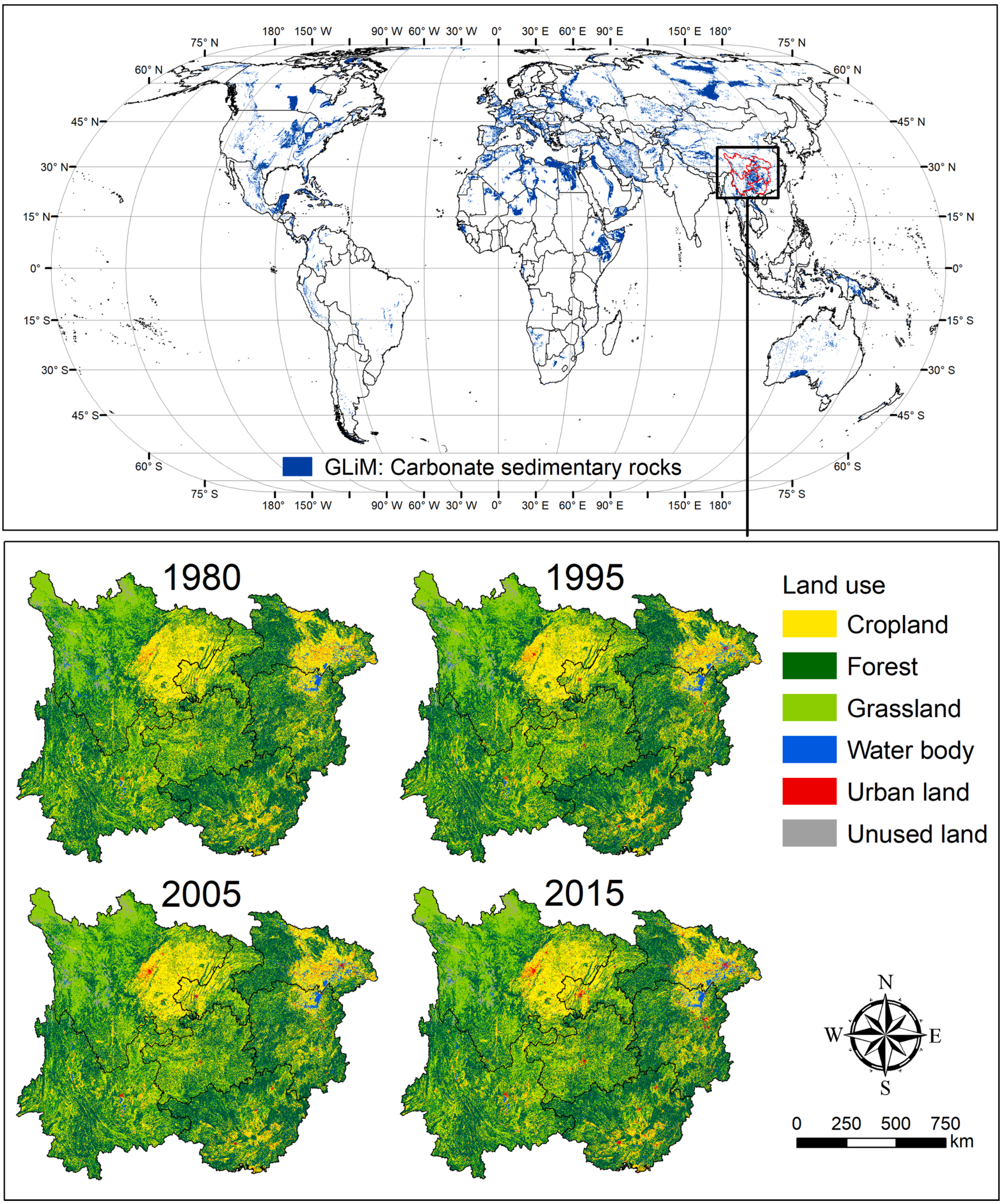

Fig. 2. Land use changes in the karst region in southwestern China (eight provinces and one municipality) during 1980–2015. The distribution of carbonate sedimentary rocks was referenced from Hartmann and Moosdorf (2012). Land use datasets with a spatial resolution of 1 km were accessed from http://www.resdc.cn.

karst region has 292 counties with an exposed carbonate rock area accounting for more than 30 % of their land area (Cao et al., 2004). A variety of landforms (e.g., mountains, hills, valleys, basins and plains) and special karst landscapes (e.g., towers (fenglin), pinnacles (shilin), cones (fengcong), giant collapse depressions (tiankeng), gorges, and caverns) are developed in this region (Wang et al., 2019). Land use in this karst region has changed significantly in the past four decades, especially urban land (Fig. 2). Cropland has always been the main land use type in this region.

2.1. Karst soil and hydrological structure

Karst soil can be defined as a calcareous soil formed from carbonate rocks (Liu, 2009). The formation of karst soils predominantly depends on the silicate minerals occurring in the bedrock, which provide both a structural matrix and additional elements (Green et al., 2019). Carbonate rocks are more prone to post depositional alteration than other sediments and their accumulation is highly dependent upon organic activity, resulting in their distinctive characteristics (Ford and Williams, 2013). As a major parent material for soil formation in southwestern China, carbonate rocks also significantly affect the biogeochemical characteristics of karst soils. The formation of karst soils is not only positively related to the dissolution rate of carbonate rocks, but also to the level of insoluble contents in the carbonate rocks (Cao et al., 2003). The soil-forming materials in carbonate rocks are inherently insufficient, resulting in a shortage of soil resources in karst areas.

Highly heterogeneous distributions of soils in karst regions are determined by a range of factors, such as elevation, terrain (slope and aspect), and anthropogenic disturbances (Wang et al., 2019). The basic geological conditions in karst areas lead to the slow formation of soil, and the runoff from steeply sloping karst terrains can significantly accelerate soil erosion processes, leading to widespread soil losses due to the thin soil layer and less vegetation cover in karst regions (Liu, 2009; Xu and Liu, 2017). For instance, the soil erosion rate estimated using the riverine suspended load method (56−129 g m^{-2} a^{-1}) was tens to hundreds of times higher than the soil formation rate (0.21–6.8 g m^{-2} a^{-1}) in the karst region of Guizhou and Guangxi provinces (Cao et al., 2003). Recent research conducted in the Chenqi catchment in southwestern China showed that the distribution of soil erosion was controlled by agricultural activities, and that rainfall-induced surface runoff was a crucial impacting factor of soil erosion, especially in the farming season in summer (June to August) (Cao et al., 2020). Additionally, a few large erosive events were predominantly responsible for the annual soil loss in the Wujiang River and Xijiang River catchments in southwestern China, and the high flow variability generally resulted in high sediment yield (Li et al., 2020). Rock desertification refers to the processes of transforming karst areas covered by vegetation and soil into rocky landscapes, which is mainly caused by soil erosion (Jiang et al., 2014). Therefore, soil erosion is a serious environmental problem affecting agricultural development, which in turn is affected by agricultural activities in the karst region of southwestern China (Cao et al., 2003, 2004; Jiang et al., 2014). In the karst ecosystem, maintaining the balance or growth of the total amount of soil is crucial to reduce its vulnerability to environmental and anthropogenic disturbances.

Karst subsurface systems developed from carbonate rocks contain extensive underground water systems, which are composed of fractures, conduits, and caves etc., and are important for water resources management. Particularly, karst landscapes and aquifers are the result of dynamic and complex water-rock interactions. The formation of karst aquifers is a selective process, which is primarily controlled by the dissolution kinetics of carbonate rocks. Specifically, the wider fractures generally lead to fast flow and high calcite dissolution rates, and thus tend to grow faster than the narrower fractures, leading to the hierarchy structure of pores and fractures in karst subsurface geological materials (Ford and Williams, 2013; Hartmann et al., 2014). As a result, there are three types of porosities in karst subsurface systems (Hartmann et al., 2014): (1) micropores, (2) small fissures and fractures, and (3) large fractures and conduits. The first two porosities are usually referred to as the matrix, while the latter is called (karst) conduits (Hartmann et al., 2014). These structures form complicated water flow systems in karst areas, which might lead to the rapid flow of water and dissolved loads in the underground water systems.

2.2. Development of agriculture in southwestern China

China is a large agricultural country, and the rural population engaged in agricultural production and operation accounts for more than 40 % of the national population (China Statistical Yearbook, 2019). In addition, arable land represents around 20 % of the China's land surface area (China Statistical Yearbook, 2019). More importantly, agricultural production of China need feed around 18 % of the world's population with only 8% of the world's arable land (China Statistical Yearbook, 2019). In the context of China's agricultural development, the karst region in southwestern China is also facing the same development problems brought by agriculture. Here, China's agricultural development in the past seventy years is introduced to understand anthropogenic pressure posed by agriculture in the karst region in southwestern China.

After the late 1970s, China's grain crop outputs have increased significantly (Fig. 3). In addition to the adjustment of rural policies, the renewal of crop varieties, and the construction of agricultural water conservancy, the continuous increase in chemical fertilizer inputs (Fig. 3), especially nitrogen fertilizer inputs, are the key factors for the dramatical increase of grain outputs in China over the past four decades (Wang et al., 2016). Over the past century, the use of nitrogen fertilizers in agriculture has supported additionally ∼27 % of the world's population that is equivalent to approximately 4 billion people born since 1908 (Erisman et al., 2008). In China, the consumption of nitrogen fertilizers began in 1920s, but the consumption was only 0.006 Mt a^{-1} by 1949 (Wang et al., 2016). With the development of the social economy since 1978, the consumption of total chemical fertilizers increased from 8.8 Mt in 1978 to 60.2 Mt in 2015, and decreased to 54.0 Mt in 2019 (Fig. 3). The agricultural application of nitrogen fertilizers in the world increased from 12 Mt in 1961 to 110 Mt in 2014, with about one third of the consumption in China (FAOSTAT, 2014).

Food production in China has also increased significantly in the past four decades, but the sown areas have not changed much (Fig. 3). The outputs of grain crops increased from 113.2 Mt in 1949 to 663.8 Mt in 2019, of which the corn, wheat, and rice outputs increased from 12.4 to 260.8 Mt, from 13.8 to 133.6 Mt, and from 48.6 to 209.6 Mt, respectively. The output of grain crops per unit area also increased significantly, from 102.9 t km^{-2} in 1949 to 562.1 t km^{-2} in 2018, indicating a significantly increased efficiency of agricultural production. According to the modeling results of grain yields reported by Yu et al. (2019), 45 ± 3 % of current grain yields can be attributed to the use of synthetic nitrogen fertilizers. In addition, irrigation reduced the risk of agricultural drought in China by 31 ± 2 % (Yu, 2019). The irrigated agricultural areas in China increased from 4.5×10^5 km^2 in 1978 to 6.76×10^5 km^2 in 2019, which was supported by the construction of water conservancy facilities. With the increase in food production, the excessive application of nitrogen fertilizers in China's croplands has also caused serious environmental pollution, and the nitrogen use efficiency has been steadily decreasing since the 1960s (Yu et al., 2019; Zhang et al., 2015). Since 2015, the consumption of total chemical fertilizers has decreased, but the output of grain crops per unit area has continued to rise, indicating that the improvement of China's agricultural policies has achieved initial results.

Due to the unique features of karst systems, mountain agriculture in the karst region of southwestern China is more likely to cause fertilizer losses, reduce the nitrogen use efficiency, and cause severe nitrate pollution under the existence of the karst aquifers (Liu, 2007). In order to maintain the balance between food security, regional development,

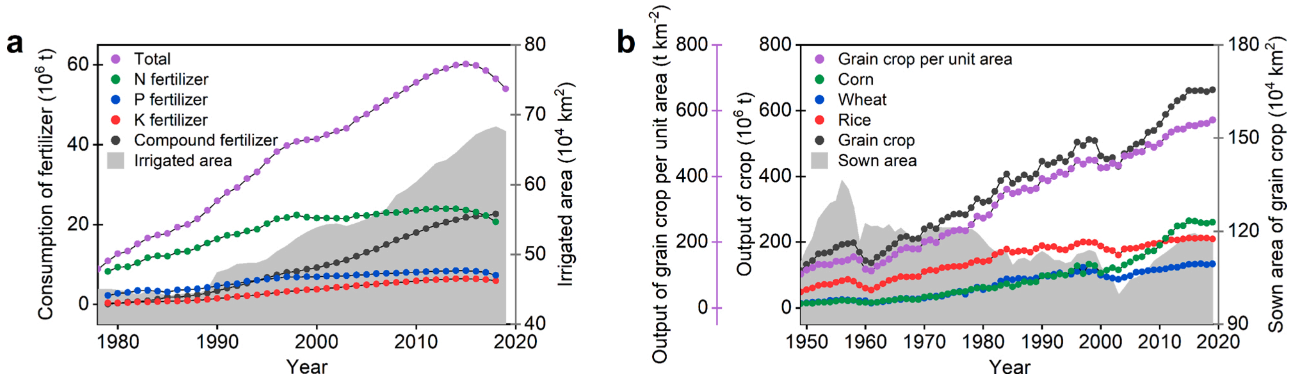

Fig. 3. **a**. The changes in consumption of chemical fertilizers and in irrigated area in China during 1980–2019. **b**. The changes in food production and in sown area in China during 1949–2019. The data were collected from the National Bureau of Statistics of the People's Republic of China (http://www.stats.gov.cn).

and environmental protection, it is necessary to explore the coupled impacts of agricultural development and karst system on regional environmental quality.

3. Impact of agriculture on water quality

Since the national economic reforms in 1978, China's rapid economic development has caused many ecological and environmental problems (Liu and Diamond, 2005; Ma et al., 2020; Tong et al., 2020). The widespread degradation of surface water quality in China is one of the most serious environmental problems, owing to industrial, municipal, and rural wastewater discharges, applications of agricultural fertilizers and pesticides, aquaculture, and livestock farming etc (Ma et al., 2020; Tong et al., 2020). Agriculture has increased the efficiency of producing grain and protein to meet the world's growing population by the increasing use of fertilizers, while the frequency and severity of water quality impairment associated with nonpoint pollutions of nutrients transported from agriculture to surface and underground waters have become greater (Galloway et al., 2008; Sharpley, 2013).

Karst aquifers provide an important water supply for the population in agricultural karst regions, while its highly conductive surface soils and subsurface hydrological systems make pollutants to easily enter the water body and be transmitted rapidly (Zhang et al., 2017; Yue et al., 2015, 2019). The impacts of agriculture on water quality in the karst region of southwestern China have received wide attention (Buckerfield et al., 2019; Xu et al., 2020b; Yue et al., 2015). In addition to the soil and pesticide losses caused by agricultural activities, most of the environmental problems center on the nonpoint transport of nitrogen (N) (Liu, 2007; Wang et al., 2020; Yue et al., 2019; Zeng et al., 2020), which is an essential input for optimum crop and animal production, and microbial water pollution (e.g., *E. coli*) (Buckerfield et al., 2019).

The Houzhai River catchment, a typical agricultural karst catchment in southwestern China, has a drainage area of 73.4 km^2 with an agricultural land coverage of 41 % (Yue et al., 2019). Hach nitrate ion-selective electrodes (NISE) sensors and isotopic technologies had been used in combination to study the high-frequency time dynamics of nitrate export at five sites in this catchment (Yue et al., 2019). The authors showed that nitrate concentrations changed by several orders of magnitude with changes in rainfall-induced discharge. During the wet season, up to 94 % of the nitrate was exported from headwater catchments within two months, but on a relative large catchment scale, only 61 % of total exports occurred during six months (Yue et al., 2019). This study pointed out that this karst catchment had chronic aquifer nitrate pollution, suggesting that the timing of nitrate loss was dependent on the interactions among land use, hydrology and karst architecture.

Rainfall can cause nutrients to be transported quickly in the karst aquifer systems. Water samples were collected at high frequency (hourly) during rainfall events from a small karst watershed (Dengzhan River) with a catchment area of 11.0 km^2 (Wang et al., 2020). This study found that during rainfall events, chemical fertilizer, soil organic nitrogen, manure and sewage varied with discharge, and were the major sources of nitrate in river waters. Meanwhile, the results suggested that the high proportion of nitrate was derived from chemical fertilizers and soil organic nitrogen, especially in the agricultural dry land on the hillside. Thus, nutrient losses from peak clusters and dry farmland with high slopes during heavy rainfall events should be paid more attention in karst areas.

Nitrogen deposition is a major nitrogen source for natural vegetation. Two sampling sites with different land uses were selected to assess wet and dry deposition for one year in the Houzhai River catchment (Zeng et al., 2020). This study found that agriculture-derived NH_4^+ was the major contributor of annual total wet nitrogen deposition (>55 %), and agricultural soil emission was a major contributor to wet nitrogen deposition during the summer growing season (Zeng et al., 2020). *E. coli*-discharge dynamics at increasing spatial scales in the Houzhai River catchment were analyzed (Buckerfield et al., 2019). This study found that rainfall characteristics, land use and karstic hydrology were the main controls on *E. coli*-discharge dynamics and export. Urban and agricultural land can contribute high *E. coli* loadings to receiving waters, and the distribution of hydrological pathways is also important in determining maximum *E. coli* concentration and subsequent recession rates.

The Wujiang River is the largest river in Guizhou Province with a drainage area of approximately 87,920 km^2, of which 70 % are covered by exposed carbonate rocks (Han and Liu, 2004; Li and Ji, 2016). As shown in Fig. 4, hydrochemistry in the Wujiang River basin had changed significantly in 2013 compared with that in 1999. The mean concentrations of Na^+, NO_3^-, and Cl^- increased from 178 ± 109, 115 ± 93, and 111 ± 66 μmol L^{-1} in 1999 to 371 ± 284, 205 ± 78, and 181 ± 124 μmol L^{-1} in 2013, respectively. At the same time, land use had also changed significantly in the Wujiang River basin, especially urban land that had increased from 288 km^2 in 1999 to 984 km^2 in 2013 (Table 1). Although the cropland areas in the Wujiang River basin have not changed much in the past ten years, the total use of chemical fertilizers has increased considerably as the result of the increasing demand for food. The increase in ion concentration in the past ten years, especially the increase in the concentration of NO_3^- in riverine waters, should be most closely related to this change.

4. Impact of agriculture on chemical weathering

Chemical weathering affects the global carbon cycle at both short (years to millennia) and long (million years) timescales, and plays a significant role in the chemical composition of the ocean and climatic evolution of the Earth's surface (Berner et al., 1983; Spence and Telmer, 2005; Torres et al., 2014). The riverine hydrochemistry in karst regions

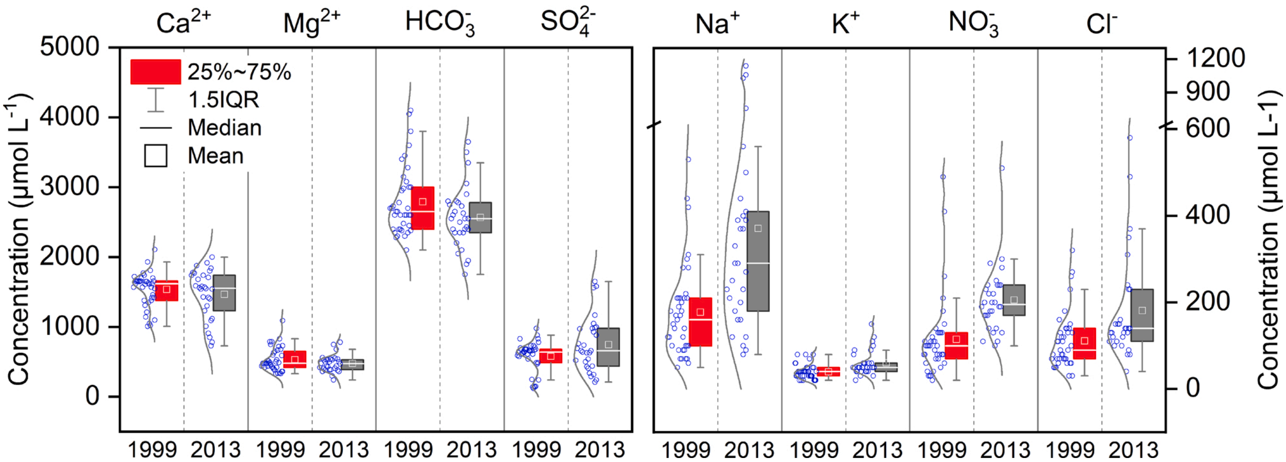

Fig. 4. Comparison of hydrochemical data in the Wujiang River basin in January and February 1999 with that in May 2013 (Represent data during the dry season). The data from 1999 and 2013 were referenced from Han and Liu (2004) and Li and Ji (2016), respectively.

Table 1
Areas of cropland, forest, and urban land in the Wujiang River basin from 1980 to 2015.

Year	Cropland km^2	Forest km^2	Urban land km^2
1980	26480	45352	288
1995	26036	45591	343
2005	26696	45368	353
2015	26221	45272	984

Note: the data was obtained from land use datasets using ArcGIS version 10.2.

is mainly controlled by the weathering of carbonate rocks, which react with atmospheric and/or soil CO_2 to produce Ca^{2+}, Mg^{2+}, and HCO_3^- that are transported into rivers and oceans (Han and Liu, 2004; Li et al., 2010). Silicate weathering can impact the carbon cycle and regulate climate change because weathering reactions involve only atmospheric CO_2; however, carbonate weathering is generally not considered to have affected the long-term global climate because the oceanic carbonate mineral precipitation equals the continental carbonate weathering flux (Berner, 2003; Berner et al., 1983; Han and Liu, 2004). The relevant equations of weathering reactions are shown below:

$$Ca_xMg_{1\text{-}x}CO_3 + CO_2 + H_2O \rightarrow xCa^{2+} + (1\text{-}x)Mg^{2+} + 2HCO_3^- \quad (1)$$

$$CaSiO_3 + 2CO_2 + 3H_2O \rightarrow Ca^{2+} + 2HCO_3^- + H_4SiO_4 \quad (2)$$

The equations of oceanic carbonate precipitation are shown below (Berner et al., 1983):

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + H_2O + CO_{2(g)} \quad (3)$$

$$Mg^{2+} + 2HCO_3^- \rightarrow MgCO_3 + H_2O + CO_{2(g)} \quad (4)$$

However, as indicators of chemical weathering products, Ca^{2+}, Mg^{2+}, and HCO_3^- may also be derived from rock weathering by strong acids, such as H_2SO_4 resulted from acid deposition and pyrite oxidation, and HNO_3 originated from the nitrification of nitrogen fertilizers (Barnes and Raymond, 2009; Li et al., 2008; Liu and Han, 2020; Perrin et al., 2008; Spence and Telmer, 2005; Ulloa-Cedamanos et al., 2020; Yue et al., 2015; Zhang et al., 2020). Given that carbonic acid is not the only weathering agent and nitrogen fertilizers are now widely applied for agricultural activities, assessing the impact of nitrogen fertilizers on chemical weathering is important for the estimation of regional and/or global carbon budgets.

For carbonate weathering by HNO_3, the protons can be produced during the nitrification process of NH_4^+ from nitrogen fertilizers. In agricultural practice, various nitrogen fertilizers (e.g., $(NH_4)_2SO_4$, NH_4NO_3, NH_4Cl, $NaNO_3$ or urea) used for crops have different production efficiencies of protons, which may result in different contributions of HNO_3 to carbonate weathering (Galloway et al., 2008; Perrin et al., 2008; Yue et al., 2015; Zhang et al., 2020). For oxidation of NH_4^+, the production of HNO_3 and its weathering reactions with carbonate and silicate minerals can be illustrated by the following equations:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \quad (5)$$

$$Ca_xMg_{1\text{-}x}CO_3 + HNO_3 \rightarrow xCa^{2+} + (1\text{-}x)Mg^{2+} + HCO_3^- + NO_3^- \quad (6)$$

$$CaSiO_3 + 2HNO_3 + H_2O \rightarrow Ca^{2+} + 2NO_3^- + H_4SiO_4 \quad (7)$$

Similar to sulfuric acid weathering carbonate minerals, reaction (6) represents a net source of CO_2 to the atmosphere. This is in contrast to the traditional paradigm that the carbonate weathering is an important CO_2 sink.

Large consumption of chemical fertilizers in karst areas may be a disturbance factor for the carbonate weathering and carbon cycle. Previous studies have documented that nitrogen fertilizer additionally increased the carbonate weathering rates and the total export of dissolved inorganic carbon (DIC) from agricultural watersheds (Barnes and Raymond, 2009; Perrin et al., 2008). However, the relationships of agricultural activities with carbonate weathering and DIC fluxes in the karst region of southwestern China are as yet not well known. The Houzhai River catchment contains primarily middle Triassic carbonates (limestone and dolomite) that account for nearly 90 % of the catchment area (Li et al., 2010), and has been studied since 1976 for monitoring hydrology and hydrochemistry (Yan et al., 2011). In this karst catchment, the amounts of Ca^{2+}, Mg^{2+} and HCO_3^- originating from silicate weathering were negligible (Li et al., 2010). If there was only carbonate weathering by carbonic acid (Eq. 1) to convert atmospheric CO_2 to HCO_3^-, the theoretical $(Ca^{2+}+ Mg^{2+})/HCO_3^-$ molar ratio should be 0.5. As shown in Fig. 5, in the past two decades, the $(Ca^{2+}+ Mg^{2+})/HCO_3^-$ molar ratios of river waters from surface and underground rivers in the Houzhai river catchment were mostly greater than 0.5, indicating that besides being weathered by carbonic acid, carbonates in this catchment might also be weathered by strong acids.

Yue et al. (2015) showed the long-term variations in the use of synthetic nitrogen fertilizers in Guizhou Province and the changes in hydrochemistry of river waters at the outlet of the Houzhai catchment since 1987–2006. The results showed that the average concentration of Ca^{2+}+Mg^{2+} in the Houzhai River catchment had the same yearly trend as the one for the use of nitrogenous fertilizer. This yearly trend could be attributed to the enhanced carbonate weathering by HNO_3 as a result of nitrification of NH_4^+. The coverage of land use types of the Houzhai River catchment in 2007 and 2016 is shown in Table 2. It can be seen that the

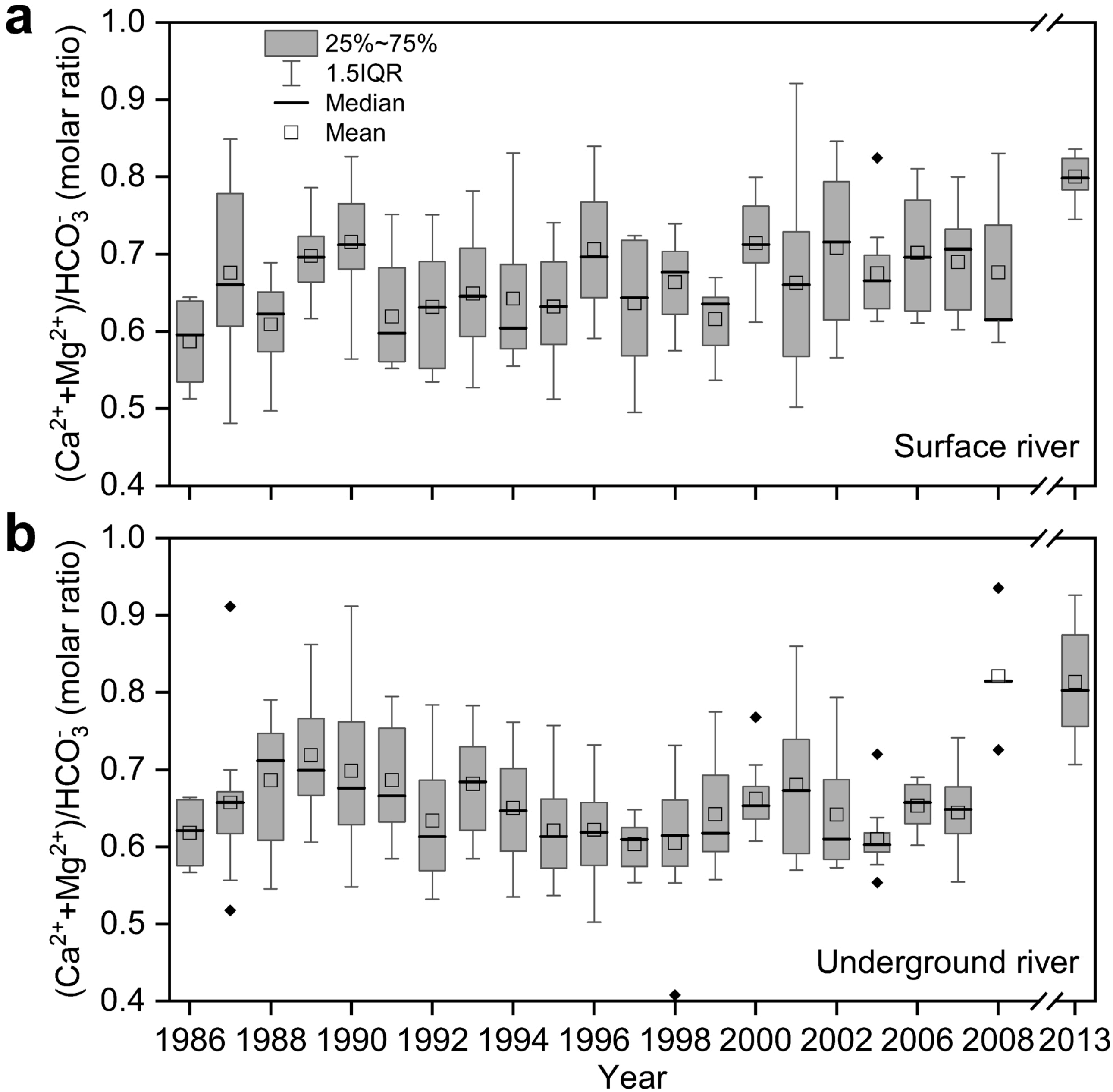

Fig. 5. Variations in $(Ca^{2+} + Mg^{2+})/HCO_3^-$ ratio of the surface (**a**) and underground (**b**) river waters in the Houzhai River catchment. The data from 1986 to 2007 were referenced from Yan et al. (2011); the data in 2008 and 2013 were referenced from Li et al. (2010) and Qin et al. (2019), respectively.

areas of dry land had increased significantly while the areas of bare rock had decreased significantly, which might be attributed to the management of rocky desertification in the past decade (Wang et al., 2019). According to the monitoring results of hydrochemistry in the Houzhai River catchment in 2013 (Qin et al., 2019), the $(Ca^{2+}+ Mg^{2+})/HCO_3^-$ molar ratios of river waters, especially surface river waters, are significantly higher than that in the past ten years (Fig. 5). This might be related to the increased weathering of carbonate rocks by HNO_3, which in turn was increased due to the increased fertilizer use and agriculture related to dry land in mountains. High concentration and large flux of NO_3^-–N were observed in karst rivers in southwestern China (Table 3), suggesting that HNO_3-driven carbonate weathering may have extensively presented in this karst region. The smaller karst catchment has a higher concentration and a larger flux of NO_3^-–N than the larger karst catchment (Table 3), indicating that the agricultural activities might have more nitrogen losses than that observed in the downstream and the NO_3^-–N might be buffered by the karst aquifers (Yue et al., 2019). Given that the cropland of the karst region in southwestern China is mainly distributed in mountainous areas, the accelerated dissolution of carbonate rocks caused by agriculture and the accompanying release of CO_2 to atmosphere cannot be underestimated.

Table 2
Land use composition of the Houzhai River catchment in 2007 and 2016.

Land use	2007[a]	2016[b]
Paddy field (%)	13.8	11.1
Dry land (%)	6.7	29.9
Natural vegetation (forest, shrub & grass, %)	48.9	45.1
Water area (river & reservoir, %)	1.0	1.4
Developed area (road & build area, %)	1.8	11.1
Bare Rock (%)	27.8	1.4

Note: [a] was referenced from Meng and Wang (2007); [b] was referenced from Yue et al. (2019).

Table 3
Comparison of the concentration and flux of NO_3^-–N form different karst catchments in southwestern China.

Catchment	Country & studied year	Catchment size km^2	Average concentration of NO_3^-–N µmol L^{-1}	Normalised NO_3^-–N export kg hm^{-2} y^{-1}	Reference
Houzhai	China (2016–2017)	73.4	268	22.2	Yue et al. (2019)
Wujiang	China (2013–2014)	87,920	150	12.8	Zhong et al. (2017)
Chishui	China (2017–2018)	18,852	218	15.7	Xu et al. (2020b)
Xijiang	China (2013–2014)	353,120	90	5.89	Li et al. (2019)
Beipan	China (2013–2014)	56,880	163	11.3	Liu et al. (2017)
Nanpan	China (2013–2014)	26,590	168	11.3	Liu et al. (2017)

5. Beneficial management practices and water environment protection

As the world's largest producer of active nitrogen and the largest consumer of nitrogen fertilizers, the nitrogen balance of China's agricultural ecosystem has received widespread attention, both domestically and internationally (Wang et al., 2016; Yu et al., 2019). It is generally believed that excessive nitrogen is applied to agriculture in China, which has resulted in serious environmental pollution. To solve the current China's nitrogen pollution problem, transformational changes in urban and rural nutrient recycling are needed; to limit nitrogen losses within safety thresholds, it is necessary to improve the nitrogen use efficiency, and increase the current returning rate of organic manure to the field from below 40 % to above 86 % (Yu, 2019; Yu et al., 2019).

Nitrogen fertilizers are applied in a variety of ways, including injection, seeding, banding and with irrigation water, which generally depend on the machinery, fertilizer types and compatibility with overall crop management practices of farmers (Sharpley, 2013). In the karst region of southwestern China, the scattered mountain agriculture is prone to nitrogen losses and can significantly impact the water environment of the catchment. For example, research from the Houzhai River catchment found that the highest contents of NO_3^-–N and normalized annual fluvial export occurred in a headwater catchment with a developed karst aquifer system (Yue et al., 2019). The methods and timing of fertilizer application can affect the concentration of nitrogen in runoff. Improvement of nitrogen use efficiency and adjustment of structure and layout of agricultural industry are key measures to reduce nitrogen pollution in the karst region of southwestern China (Xu et al., 2020b; Yu et al., 2019; Yue et al., 2015, 2019). The intensity and duration of rainfall, and when it occurs (relative to the timing of fertilization), are also important factors affecting the concentration of nitrogen in runoff and the overall loss of nitrogen from nitrogen fertilizers. By studying the dynamics of nutrient transport in a typical karst catchment in southwestern China during rainfall events, it was found that applied fertilizers would be flushed directly into surface rivers and nitrate from chemical fertilizers would be leached, resulting in the high concentrations of nitrate in karst rivers (Wang et al., 2020).

More efficient use and management of water are critical to addressing the growing demand for water resources as one of important sustainable development goals (https://sdgs.un.org/goals). Meanwhile, rational land use planning and highly efficient fertilizer using policy would reduce nutrient loss and water pollution. To achieve sustainable development of agriculture while protecting water environment, a long-term coordinated plans among government departments should be formulated under a unified scientific framework. Scientific research and practical application should be combined, aiming at the development of karst areas and local environmental protection (Yue et al., 2019; Oliver et al., 2020). The management of local agricultural practices in the karst areas is particularly important, and the scientific and reasonable agricultural development orientation according to local conditions will build a good coordinating relationships between agriculture and environmental protection in the future.

6. Conclusions and outlook

The karst region in southwestern China underlies a quarter of southwestern China's total land, and provides water for extensive agricultural activities and a large number of population. By selecting an agricultural karst catchment in southwestern China as an example, it was found that agricultural activities had greater impacts on the concentration and export of solutes in rivers, chronic aquifer nitrate pollution, wet nitrogen deposition, and microbial water pollution. The nitrate concentration of water in the large karst river in southwestern China has increased significantly in the past decade or so, which is also related to the increase in nitrogen fertilizer use brought by agricultural development. Additionally, the use of nitrogen fertilizers will promote the production of HNO_3 (e.g., oxidation of NH_4^+), which weathering carbonate rocks is a net source of CO_2 to the atmosphere. Therefore, to decrease the impacts of agricultural development on riverine biogeochemical cycles of elements and environmental quality, this review summarized the development of agriculture and its significant impacts on the water environment in the fragile karst ecosystem based on the previous research results. It hints some measures should be adopted to provide scientific decision for the realization of sustainable agricultural development and environmental protection in the karst region.

Declaration of Competing Interest

The authors report no declarations of interest.

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