A neglected anthropogenic source of carbon triggered by the combustion of coal: evidence from riverine sulfate

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Abstract

To effectively reduce CO_2 emissions, it's vital to identify and quantify their sources. While the focus has been on CO_2 from fossil fuel combustion, especially coal, the CO_2 produced from coal's other elements, such as sulfur, through chemical reaction, remains an 'invisible' carbon source. Using river sulfate fluxes, we analyzed the invisible carbon flux due to coal burning in the Xijiang River Basin, a highly industrialized region in China. Dissolved sulfate concentration in the Xijiang River rose by over 300% from 1985 to 2011, largely due to coal combustion. In 2011, this resulted in 3.14 Mt of invisible carbon dioxide. We evaluated the impact of two flue gas desulfurization (FGD) methods on carbon emissions with a predictive model. By enhancing SO_2 removal efficiency through these methods, China could cut invisible carbon emissions by 27.8 Mt CO_2 annually, paving the way for a sustainable future.

Keywords: Climate Change, Carbon Emission, Coal Burning, Sulfur Dioxide

Introduction

Climate change is a global issue that has garnered significant attention in recent years [*Berrang-Ford et al.*, 2019; *Fuhrman et al.*, 2023]. The increasing concentration of greenhouse gases (GHG), especially carbon dioxide (CO_2), in the atmosphere is one of the primary drivers of climate change [*Andrews and Forster*, 2008; *Charney et al.*, 1979]. According to the Paris Agreement (2015), governments across the globe are making efforts to avoid a 1.5°C increase before 2025 [*Christoff*, 2016; *Fuhrman et al.*, 2023; *Rogelj et al.*, 2018]. To achieve this objective, efforts are being made to mitigate further increases in atmospheric CO_2 by increasing carbon sinks and decreasing carbon emissions. Increasing carbon sinks typically include carbon capture, mineral carbon sequestration, and enhanced silicate mineral weathering [*Beerling et al.*, 2018; *Fuhrman et al.*, 2023; *Hartmann and Kempe*, 2008; *Kealy*, 2019; *Zhu et al.*, 2017]. Carbon emissions can be decreased by adopting renewable energy sources and improving energy efficiency [*Guan et al.*, 2018; *Orsini and Marrone*, 2019].

While green energy is increasingly replacing the traditional burning of fossil fuels to reduce carbon emissions, more still needs to be done to explore ways to reduce 'invisible' carbon sources associated with indirect CO_2-production pathways. For example, the burning of coal is a complex process that not only oxidizes fossil carbon into CO_2 but also releases elements such as sulfur into the environment [*Ding et al.*, 2013; *Kato and Akimoto*, 1992; *Zhao and Sun*, 1986]. Sulfur, when involved in subsequent chemical reactions, such as the chemical weathering of carbonates, releases CO_2 into the atmosphere (Eqs 1-3), which is widely recognized as a significant carbon source in the geological carbon cycle [*Burke et al.*, 2018; *Calmels et al.*, 2007; *M Torres et al.*, 2016; *M Torres et al.*, 2014; *M A Torres et al.*, 2015]. Therefore, this study focuses on the invisible carbon source from sulfur (or sulfide) oxidative weathering from the coal-burning process (Kato and Akimoto, 1992; Wu et al., 2006; Zhao and Sun, 1986). Sulfide oxidative weathering can be described by the generalized equation [*Calmels et al.*, 2007; *M Torres et al.*, 2014], which results in the release of sulfuric acid:

$$\frac{1}{2}FeS_2 + \frac{15}{8}O_2 + \frac{7}{4}H_2O \rightarrow \frac{1}{2}Fe(OH)_3 + H_2SO_4 \ (Eq. 1)$$

The released sulfuric acid typically dissolves surrounding carbonate minerals:

$$H_2SO_4 + CaCO_3 \rightarrow Ca^{2+} + SO_4^{2-} + CO_2 + H_2O \ (Eq. 2)$$

Sulfuric acid can also react with bicarbonate in river water:

$$H_2SO_4 + 2HCO_3^- \rightarrow SO_4^{2-} + 2CO_2 + 2H_2O \ (Eq. 3)$$

Both reactions lead to the release of CO_2 into the atmosphere [*Calmels et al.*, 2007; *M Torres et al.*, 2014].

Therefore, the burning of coal not only releases CO_2 directly but also results in the production of SO_2, which can contribute to the formation of an "invisible" CO_2 source through Eqs. 2-3. This process is expected to result in a significantly higher CO_2 flux, especially given the massive amounts of sulfur released by coal combustion [*Dai et al.*, 2018; *Ding et al.*, 2013; *Kato and Akimoto*, 1992; *Lu et al.*, 2010; *D Wu et al.*, 2006; *Zhao and Sun*, 1986], which still accounts for more than half of China's energy consumption [*Tang et al.*, 2019]. In fact, there has been a noticeable increase in sulfate flux in coal-burning regions, with sulfate concentrations in the Yangtze River increasing from 147 μM in 1978 to 285 μM in 2006 and 483 μM in 2011 [*Chetelat et al.*, 2008; *Xiaoqian Li et al.*, 2015; *Ming-hui et al.*, 1982]. Similarly, the sulfate concentration in the Mississippi River has increased from about 154 μM before industrialization to 611 μM in the 2010s [*Killingsworth and Bao*, 2015]. A large amount of CO_2 has been released into the atmosphere through Equations 1, 2, and 3. However, the flux of this anthropogenic-produced source of invisible CO_2 emissions and its disturbance to the geological carbon cycle in catchments are still poorly understood.

To fill this knowledge gap, we examined the Xijiang River basin in China, a system that allowed us to evaluate the influence of invisible carbon from coal burning at continental scales. This region was chosen due to its rapid industrialization and significant coal consumption, making it an ideal place to conduct the study [*Xia Li and Yeh*, 2004; *H-b Wang et al.*, 2019a; *S Wang et al.*, 2019b]. We mainly focused on evaluating the changes in sulfate concentrations in the Xijiang River basin during the period of rapid industrialization from the 1980s to 2010s to determine the contribution of coal combustion to the sulfate flux. Additionally, this work calculated the invisible carbon flux introduced by coal combustion based on riverine sulfate flux. Then we propose a plan to reduce this source of atmospheric carbon and assess its expected effectiveness in the Xijiang River basin and throughout China. Finally, we design a prediction model based on coal consumption rates to estimate the flux of anthropogenically-produced invisible carbon under different strategies in China from 1990 to 2050 to inform policy. Overall, this study aims to contribute to the global effort to combat climate change by identifying invisible sources of carbon, evaluating their impact on the carbon cycle, and proposing effective mitigation strategies to reduce carbon emissions.

Materials and Methods

Study Area

This study focuses on the Xijiang River basin (Figure 1A, B), which was chosen for its high degree of human activity, industrialization, fossil fuel consumption, and significant occurrence of sulfuric acid rain [*Aas et al.*, 2007; *Ding et al.*, 2013]. The Xijiang River basin is located in southern China, extending from eastern Yunnan Province to southern Guangdong Province. The river, which originates from the eastern foot of the Maxiong Mountain in Yunnan, flows east through Guangdong, entering the Pearl River Delta east of Zhaoqing and exiting into the South China Sea west of Macau. The basin has a drainage area of 3.53×10^5 km^2, an average annual temperature ranging from 14°C to 22°C, and mean annual precipitation ranging from 1000 mm to 2200 mm, with precipitation concentrated from April to September. The basin's abundance of carbonate rocks, particularly limestone, is another crucial reason for its selection, allowing for the observation of sulfuric acid weathering of carbonate rocks. The basin has undergone extensive karst geomorphological processes at the surface and underground due to approximately 44% of its composition being carbonate rocks [*Gao et al.*, 2009; *Wei et al.*, 2013] (Figure 1).

The Xijiang River basin is one of China's most developed regions, with a population of over 120 million. Coal accounts for 70% of China's energy budget [*Tang et al.*, 2019], and the basin's industrialization has accelerated since the 1980s with the implementation of China's reform and opening-up policy [*P Wang et al.*, 2013a; *X Wang et al.*, 2013b], resulting in the increased combustion of fossil fuels and the release of substantial amounts of sulfur. The region is home to a variety of industries, including coal-fired power plants, which have significantly increased in number and size since the 2000s. This makes the Xijiang River basin an ideal case for our study.

Data Collection and Preprocessing

Water chemistry data of the Xijiang River between 1980s~2000s was selected from the United Nations Global Environmental Monitoring System (GEMS) Water Program (http://www.gemstat.org/), which has collated and recorded high-quality data sets of the most important rivers globally over the past few decades. These include pH, temperature, electric conductivity (EC), and major ions (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, alkalinity, Cl^{-}, SO_4^{2-}). The corresponding water temperature and discharge at the time of sampling were also recorded. Sampling areas are shown in Figure 1. Based on other previous works, we obtained the water chemistry data from 2000 to 2011 [*Gao et al.*, 2009; *Han et al.*, 2019; *Sun et al.*, 2010; *B Wang et al.*, 2012; *Wei et al.*, 2013; *Xu and Liu*, 2007; 2010]. The sampling areas of these works are also shown in Figure 1B.

Model Design

This study developed a comprehensive invisible carbon prediction model (ICPM) based on coal combustion rates to estimate the flux of anthropogenically-produced invisible carbon sources under different strategies in China from 1990 to 2050 to estimate the invisible carbon emissions resulting from coal burning. The model takes into account several factors, such as the reaction of acid rain with carbonate rocks, SO_2 emissions from coal combustion, riverine sulfate flux, and potential CO_2 emissions (SI S1, 2, 3).

Results

Sulfate Concentration Trends and Comparison

The concentration of dissolved sulfate in the Xijiang River has been increasing steadily over the three decades from the 1980s to the 2010s (Figure 2). Specifically, the concentration of dissolved sulfate increased from 87 μM in 1985 to 358 μM in 2011, representing a more than 300% increase in 26 years. The rate of increase has been particularly significant since the 2000s (Figure 2).

The sulfate concentration in the Xijiang River basin was compared to other major rivers around the world using data from the year 2011. The results reveal that the concentration of dissolved sulfate in the Xijiang River (358 μM) was significantly higher than the volume-weighted average sulfate concentration (108 μM) of rivers representing over 46% of the global water discharge [*Burke et al.*, 2018]. The Yamuna and Ganges rivers, similar to the Xijiang, have also experienced significant increases in sulfate concentrations, with concentrations of 360 μM and 370 μM, respectively. These increases are likely due to intensive expansion of human and industrial activities in those basins [*Burke et al.*, 2018; *Rahaman et al.*, 2012].

Discussion

Coal Combustion & Sulfate Flux

The sulfate concentration in the Xijiang River has increased by over 300% from the 1980s to the 2010s (Figure 2), and due to its relatively high levels compared to other major rivers worldwide, further investigation of the possible impact of anthropogenic sulfate on the environment in this region is necessary. Firstly, it is essential to distinguish the sources of sulfate, which is crucial for subsequent evaluation and estimation of invisible carbon flux. Possible sources of sulfate in the Xijiang River include natural sulfide weathering, evaporate dissolution within the basin, as well as anthropogenic activities [*Meybeck*, 2003]. However, the sparsely distributed evaporates in the upstream basin and the limited sulfides in the basin are unlikely to cause such a significant change in sulfate concentration downstream, ruling out the possibility of natural sources [*Jiang et al.*, 2018; *Xiaoqian Li et al.*, 2015] (Figure 1A). Rather anthropogenic activities, such as coal burning for industrial or power generation purposes, have been shown in previous studies to significantly contribute to the riverine sulfate flux in this area in recent years [*Han and Liu*, 2006; *Han et al.*, 2019; *Han et al.*, 2011; *J Liu et al.*, 2022a; *Q Wu et al.*, 2012]. Moreover, the growth trend of the sulfate concentration in the Xijiang River from 1985 to 2011 corresponds to the trend of coal burning in China (Figure 3A), which also implies the contribution of coal burning to sulfate.

To investigate whether the rapid increase in sulfate in the Xijiang River between the 1980s and 2010s is indeed mainly due to coal combustion, a correlation analysis was conducted between the combustion of coal and sulfate concentration. Results from Figure 3B demonstrate a robust positive correlation between the combustion of coal in the Guangdong Province, mostly located in the study area, and dissolved sulfate in the Xijiang River from 1995 to 2012, which provides further evidence that the increase in sulfate concentration over the past three decades has come mainly from coal combustion[*Kuang*, 2015]. Besides, the intercept of the fitted regression equation indicates that the concentration of dissolved sulfate in the Xijiang River was around 48.9 μM in the absence of coal combustion, which is consistent with previous research that estimated the concentration of sulfate in the Xijiang River to be around 56.25 μM before the 1990s [*S-R Zhang et al.*, 2007].

Sulfur-Driven CO_2 Emissions

The previous section has shown that coal burning has significantly contributed and elevated sulfate concentration in Xijiang River Basin. Notably, coal burning does not only impact the sulfate flux in the river basin; it also leads to invisible carbon emissions. Previous studies have shown that there is a large proportion of high-sulfur coal in the Xijiang River basin, where over 95% of sulfur is present in the forms of organic sulfur and pyrite, while the sulfate form of sulfur is only a small fraction [*Dai et al.*, 2018; *Dai et al.*, 2017; *Jiang et al.*, 2018]. During high-temperature combustion, organic sulfur and pyrite are released into the atmosphere as SO_2, forming acid rain. This is supported by the recent occurrences of intense acid rain in the middle reaches of the Xijiang River [*Aas et al.*, 2007; *Ding et al.*, 2013; *Hao et al.*, 2001].

Before or after entering the river, the sulfur from coal combustion reacts with carbonates and/or bicarbonates in the form of sulfuric acid, releasing significant amounts of CO_2 into the atmosphere (Eqs. 1-3), contributing to the "invisible carbon." This phenomenon is particularly apparent in carbonate-rich river basins like the Xijiang. We calculated the invisible CO_2 emission rate in the Xijiang River basin from 1995-2011 based on sulfate concentrations (Detailed calculation is in SI S4). Specifically, the invisible CO_2 emission rates at Zhaoqing (Gaoyao) Station were 4.18×10^4 mol km^{-2}a^{-1} and 20.2×10^4 mol km^{-2}a^{-1} in 1995 and 2011, respectively, which offset all of the silicate weathering carbon sink (5.49×10^4 mol km^{-2}a^{-1}) in 2011 (Figure 1B, 4A, Table S2) [*Gaillardet et al.*, 1999]. In other words, the invisible CO_2 flux to the atmosphere in the Xijiang River basin was 3.14 Mt in 2011 [*Xu and Liu*, 2010], indicating a significant carbon source that was previously overlooked. This highlights the importance of considering not only direct emissions from fossil carbon burning but also indirect emissions from secondary processes that are triggered by human activities.

The increasing trend of invisible CO_2 rate from 1995-2011 (Figure 4A) shows that the impact of this process, triggered by coal burning, is becoming more and more significant. Importantly, this not only contributes to the overall sulfate flux in the basin but also release CO_2 into the atmosphere, affecting the carbon cycle. This observation corroborates previous studies that note that carbonate dissolution can occur through sulfuric acid and carbonic acid [*M Torres et al.*, 2016] and the proportion of carbonate dissolution from sulfuric acid is increasing in recent years [*Han et al.*, 2019; *S-L Li et al.*, 2008; *Xu and Liu*, 2007]. The identified continuous rise in anthropogenic invisible CO_2 emissions, resulting from the dissolution of carbonate rocks and/or bicarbonates by sulfuric acid in the Xijiang River basin, highlights the need to adopt more comprehensive and integrated approaches to addressing carbon emissions and their impact on the environment.

Mitigation Strategies

The important yet often overlooked source of CO_2 emissions in the Xijiang River has been linked to the presence of sulfuric acid. This source of carbon has shown a steady increase, with a recorded value of 3.14 million tons in 2011, equal to the carbon reduction achieved by more than 1000 fully-loaded 1.5 MW wind turbines operating for one year [*Chen et al.*, 2011; *Kealy*, 2019]. To address this issue, one potential solution is to implement flue gas desulfurization (FGD) (SI S1) [*Cordoba*, 2015; *van Ewijk and McDowall*, 2020; *B Wu et al.*, 2020]. Sulfur in coal mainly exists in the form of organic sulfur and sulfides, with an average mass fraction of about 2% [*Chou*, 2012]. Preventing sulfur from entering the terrestrial environment and participating in subsequent chemical reactions could reduce the carbon emissions from sulfuric acid dissolution of carbonate rocks. This can be achieved through FGD [*Cordoba*, 2015].

It is important to note that many countries, including China, have implemented measures to reduce SO_2 emissions. Under China's "Eleventh Five-Year Plan" since around 2006, specific measures were introduced to reduce nitrogen and sulfur oxide emissions, primarily aiming to protect the environment [*X Wang et al.*, 2013b; *Q*

Zhang et al., 2012]. As evidenced by the case of the Xijiang River basin, these measures have successfully reduced the flux of anthropogenic sulfur to the atmosphere and consequently the anthropogenic invisible carbon source (Figure S2).

However, the reality is more complex. More than simply reducing SO_2 emissions is needed to fully address the problem, as CO_2 may also be produced during desulfurization, depending on the method used. Different flue gas desulfurization (FGD) methods have varying carbon emissions patterns [*Cordoba*, 2015]. For example, the limestone-gypsum method, also known as "wet limestone FGD," releases a large amount of CO_2 (SI S1, Eq. S1) [*Cordoba*, 2015]. In contrast, spray-dry FGD systems do not have this issue (SI S1, Eq. S1) [*Cordoba*, 2015; *Zheng et al.*, 2002].

Thus, while FGD methods can effectively reduce SO_2 emissions, their implementation may also lead to carbon emissions. Therefore, it is crucial to consider the carbon emissions generated by various FGD methods when selecting the appropriate technology. Here, the impact of two typical FGD methods (wet limestone FGD and spray-dry FGD) on carbon emissions was examined to show their effects on coal burning-invisible carbon emissions in 2030 and 2050 in China through our invisible carbon prediction model (ICPM) (SI S3).

Model Application and Policy Implication

Based on the invisible carbon prediction model (ICPM), we calculated the invisible carbon flux generated by different desulfurization methods and SO_2 removal efficiency during coal burning in China from 1990 to 2050 (SI S1, 2). China's coal consumption rate from 1990 to 2019 comes from the China Statistical Yearbook, and the projected consumption of coal from 2030 to 2050 is sourced from the International Energy Agency (IEA). Figure 4B shows the variation of carbon emission flux caused by different desulfurization methods and SO_2 removal efficiency.

Firstly, 'Wet limestone desulfurization,' where the flue gas produced by coal burning directly reacts with calcium carbonate, and the sulfur dioxide (SO_2) in the flue gas is absorbed by calcium carbonate, can effectively prevent SO_2 from entering the atmosphere (SI S1). However, when SO_2 reacts with calcium carbonate, it produces large amounts of CO_2 (as shown in Equation S1), which is also considered part of the invisible carbon emissions. Therefore, this FGD method does not reduce invisible carbon emissions. If this method is applied, China's maximum invisible carbon emission would equate to approximately 40 Mt in 2019 (Figure 4B).

The other desulfurization method we selected for model calculation is ‘spray-dry FGD systems’ (SI S1) [*Cordoba*, 2015; *X Liu et al.*, 2022b; *Zheng et al.*, 2002]. The invisible carbon emission introduced by coal burning under this desulfurization method is significantly lower than that of ‘wet limestone FGD’. Moreover, with the increase of the SO_2 removal efficiency, the invisible carbon emission is significantly reduced (Figure 4B). If the SO_2 removal efficiency reaches 75%, China’s invisible carbon emissions will decrease by 27.8 Mt of CO_2 in 2019, reducing to 4.9 Mt by the year 2050 (Figure 4B).

The estimated invisible carbon emissions under the two different desulfurization methods and SO_2 removal efficiency in China from 1990 to 2050 highlight the importance of selecting appropriate desulfurization methods. This demonstrates the potential benefits of implementing desulfurization methods, such as spray-dry FGD systems, that do not generate additional ‘invisible’ CO_2, thereby contributing to global efforts to mitigate climate change. By adopting the most suitable desulfurization methods and increasing the SO_2 removal efficiency, China can significantly reduce its invisible carbon emissions during coal burning, moving towards a more sustainable future by addressing two of the Sustainable Development Goals of the United Nations (namely 7 – Affordable and Clean Energy and 13 – Climate Action).

Conclusion

This work has revealed the significant contribution of coal combustion to the sharp increase in riverine sulfate concentration over time in the Xijiang River basin, as well as the invisible carbon emission originating from the reaction of sulfuric acid with carbonates and/or bicarbonates. An upward trend in the invisible carbon flux is evident from 1995-2011, underscoring the growing significance of this process. This rising trend in anthropogenic invisible CO_2 emissions has profound implications for our understanding of carbon emissions and their environmental impacts.

Moreover, the implementation of Flue Gas Desulfurization (FGD) technologies emerges as a potential solution to mitigate this issue. Our invisible carbon prediction model (ICPM) reveals that the choice of desulfurization method and the SO_2 removal efficiency significantly impact the carbon emission flux. For example, using a desulfurization method that does not produce additional CO_2, such as spray dry FGD systems, and increasing the SO_2 removal efficiency could substantially reduce China's invisible carbon emissions by 2050.

In conclusion, the study of the Xijiang River basin has underscored the pressing need to address not only direct emissions from fossil fuel combustion but also indirect emissions arising from secondary processes triggered by human activities. The selection of appropriate desulfurization methods and optimization of SO_2 removal efficiency can help to reduce invisible carbon emissions, thereby contributing to the global effort to mitigate climate change. As we continue to refine our understanding of these complex processes, we are better equipped to design and implement strategies to reduce carbon emissions and foster a more sustainable future.

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Data Availability Statement

Data used in this study can be accessed through this link: https://figshare.com/s/fef51a91d60cfda01a78

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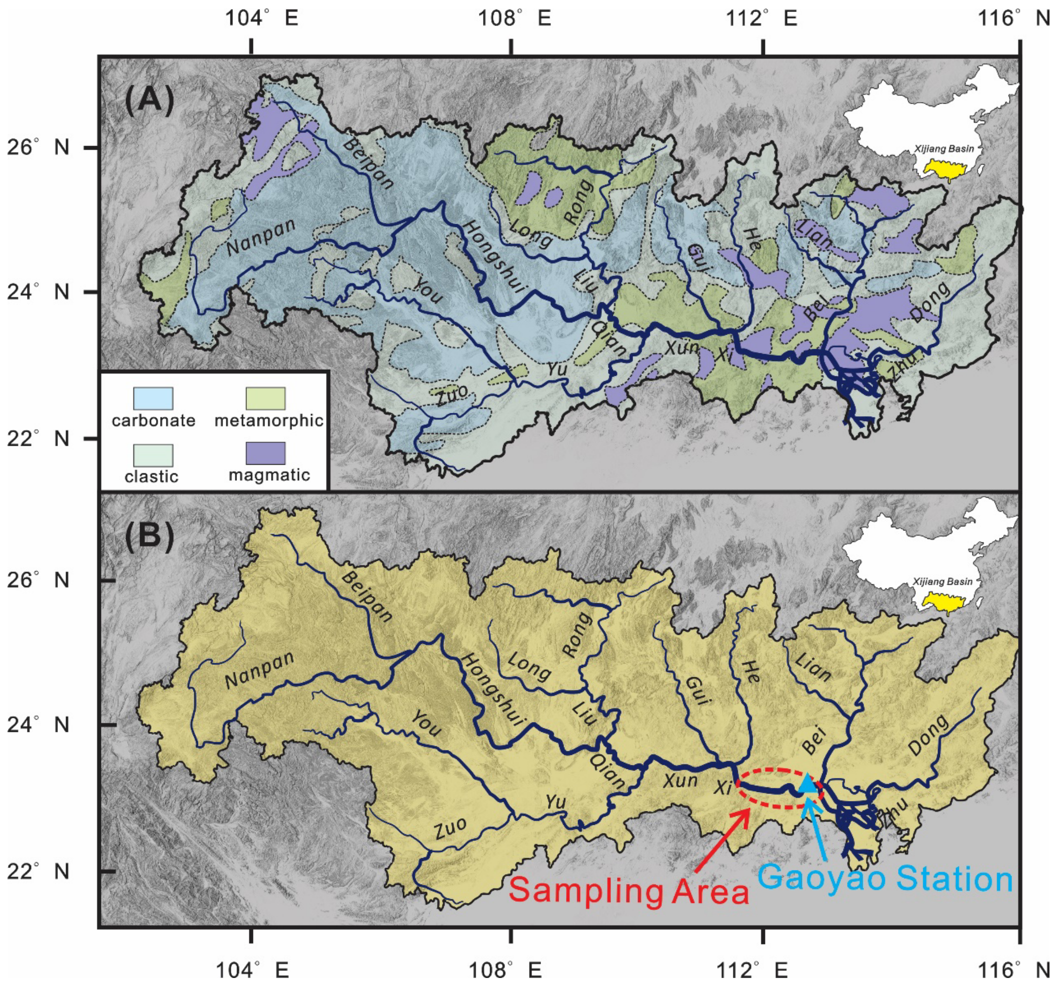

Figure 1. (A) Geological settings and (B) Sampling areas in Xijiang River Basin. The sampling positions of all data are located in the red ellipse area. The blue triangle represents the position of Gaoyao Station.

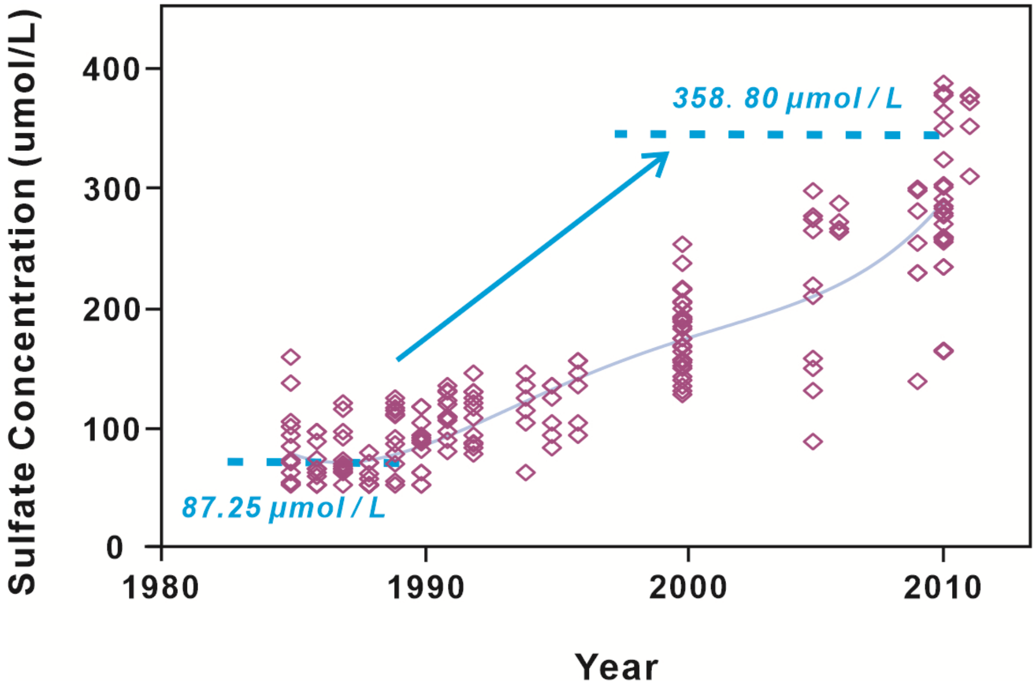

Figure 2. Interannual variation of sulfate concentration in the Xijiang River basin from the 1980s to 2010s. The "purple diamonds" are sulfate concentrations of the lower reaches of the Xijiang River from the 1980s to the 2010s. The "blue dotted lines" are the average sulfate concentrations in 1985 and 2011, which are 87.25 uM and 358.80 uM, respectively. The "blue arrows" represent the trend of change.

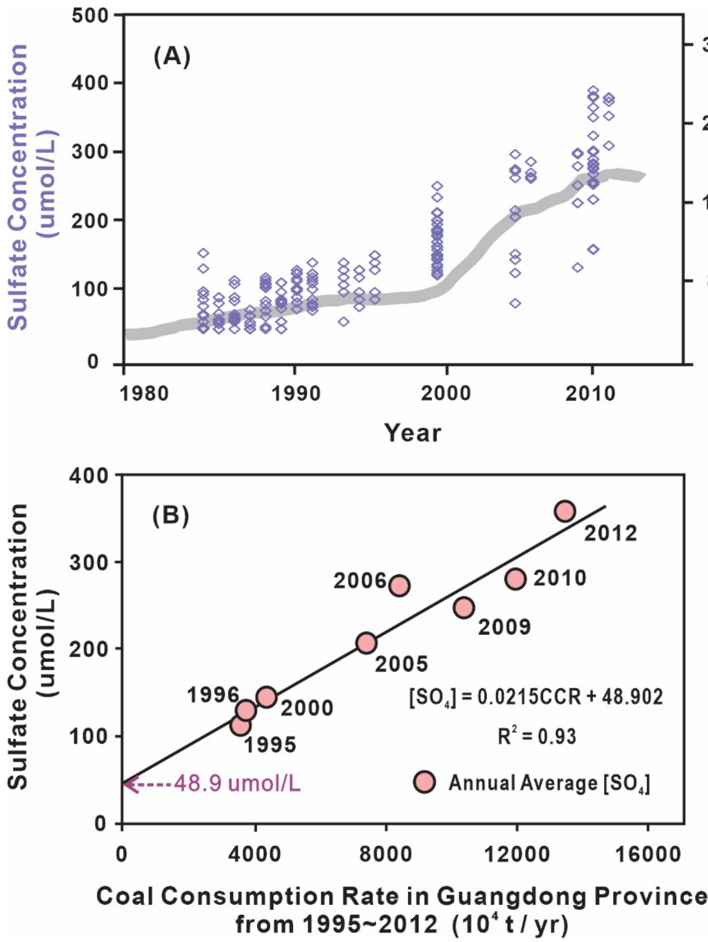

Figure 3. (A) Interannual variation of sulfate concentration in the Xijiang River basin (purple diamonds) and interannual variation of coal consumption in China (gray curve). Data for interannual variation of coal consumption in China were collected from the China Statistical Yearbook. (B) Positive correlation between coal consumption Rate (CCR) in the Guangdong Province from 1995 to 2012 and dissolved sulfate in the Xijiang River. The purple dotted arrow indicates the longitudinal intercept of the fitted linear equation, representing the sulfate concentration in the lower reaches of the Xijiang River without coal burning.

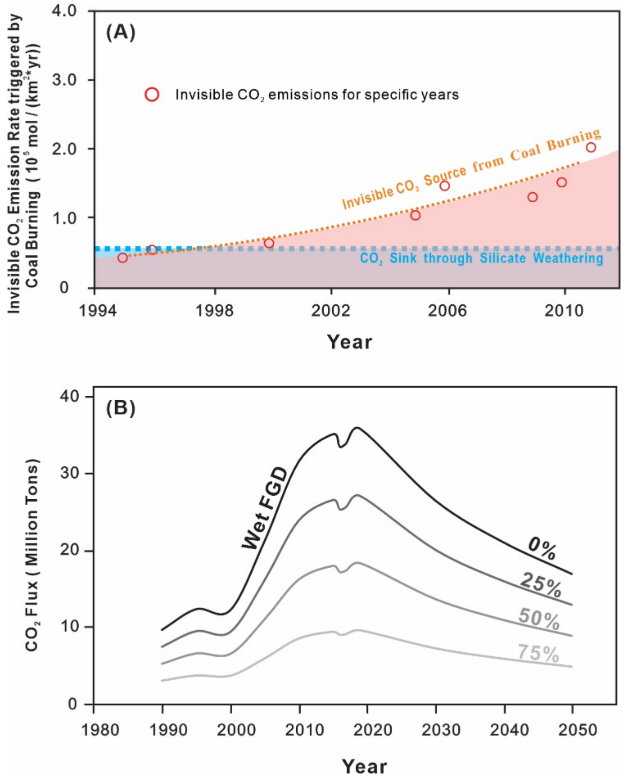

Figure 4. (A) Comparison of invisible carbon source induced by coal burning with natural silicate chemical weathering carbon sink in the Xijiang River basin. The blue area represents the silicate chemical weathering carbon sink, and light orange area represents the invisible carbon source caused by coal burning. (B) The annual flux of invisible carbon emissions induced by coal burning in China from 1990 to 2050 with different desulfurization methods and SO_2 removal efficiency. The top black line represents the invisible carbon emissions after wet limestone FGD application. 0, 25%, 50%, and 75%, respectively, represent the invisible carbon emissions caused by coal burning after the application of "non-carbon emission FGD" with an SO_2 removal efficiency of 0, 25%, 50%, and 75%.