# Variation Characteristics of CO2 Exchange Flux at the Water-Air Interface of the Kuye River and Analysis of Controlling Factors (Postprint)

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## Abstract

In recent years, CO2 emissions from inland water bodies have received widespread attention. To reveal the emission characteristics of CO2 from inland water bodies in the Loess Plateau region, high-frequency observations of water CO2 partial pressure (pCO2) and water-air interface CO2 exchange flux (FCO2) were conducted on the Kuye River and representative reservoirs using a LI-7000 CO2 analyzer in July and October 2018 and March and June 2019, and their spatiotemporal variation patterns were analyzed. The results showed that the pCO2 and FCO2 of the Kuye River water body (996 atm and 94.5 mmol · m-2 · d-1, respectively) were both higher than those of the reservoirs (752 atm and 10.3 mmol · m-2 · d-1, respectively). FCO2 exhibited significant seasonal differences: for rivers, it was highest in autumn (165.7 mmol · m-2 · d-1) and lowest in spring (42.9 mmol · m-2 · d-1); for reservoirs, the trend was completely opposite, being highest in spring (16.6 mmol · m-2 · d-1) and lowest in autumn (-5.4 mmol · m-2 · d-1). The FCO2 of tributaries with stronger biogeochemical activity (107.4 mmol · m-2 · d-1) was approximately 50% higher than that of the main stream (66.5 mmol · m-2 · d-1); meanwhile, the FCO2 of reservoirs located in the middle-lower reaches of the Loess Hilly Region (16.4 mmol · m-2 · d-1) was significantly higher than that of reservoirs in the upper reaches of the Huer Hilly Region (1.2 mmol · m-2 · d-1). Overall, the pCO2 of water bodies in the basin was most influenced by the carbonate system, followed by organic carbon decomposition; flow velocity was the key factor controlling the gas exchange rate at the water-air interface. On an annual scale, both river and reservoir water bodies of the Kuye River were continuous carbon sources to the atmosphere. The average CO2 emission from the Kuye River was similar to that of China's Yangtze River and foreign temperate rivers, but lower than other tributaries in the middle reaches of the Yellow River.

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# Full Text

## Variations of CO Exchange Flux Across the Water–Air Interface in the Kuye River and Their Influencing Factors

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### Abstract

This study aimed to examine riverine CO emissions on the Loess Plateau. The partial pressure of CO ($p\text{CO}_2$) and CO outgassing flux across the water–air interface ($F\text{CO}_2$) in the Kuye River basin, situated in the northern Loess Plateau, were investigated through high-frequency sampling in July and October 2018 and March and June 2019 using a LI-7000 CO analyzer. Both $p\text{CO}_2$ and $F\text{CO}_2$ were higher in rivers (996 $\mu$atm and 94.5 mmol $\cdot$ m$^{-2}$ $\cdot$ d$^{-1}$, respectively) than in reservoirs (752 $\mu$atm and 10.3 mmol$\cdot$m$^{-2}\cdot$d$^{-1}$, respectively). The $F\text{CO}_2$ exhibited pronounced seasonal variations: for river waters, the highest flux of 165.7 mmol$\cdot$m$^{-2}\cdot$d$^{-1}$ occurred in autumn and the lowest of 42.9 mmol$\cdot$m$^{-2}\cdot$d$^{-1}$ in spring; for reservoir waters, the opposite pattern was observed, with the highest flux of 16.6 mmol $\cdot$ m$^{-2}$ $\cdot$ d$^{-1}$ in spring and the lowest of $-5.4$ mmol $\cdot$ m$^{-2}$ $\cdot$ d$^{-1}$ in autumn. Spatially, tributary rivers with stronger biogeochemical activity showed significantly higher $F\text{CO}_2$ (107.4 mmol$\cdot$m$^{-2}\cdot$d$^{-1}$) than the Kuye mainstream (66.5 mmol$\cdot$m$^{-2}\cdot$d$^{-1}$). For reservoirs, the $F\text{CO}_2$ in the upper sandy hilly area (1.2 mmol $\cdot$ m$^{-2}$ $\cdot$ d$^{-1}$) was lower than that in the middle and lower loess hilly area (16.4 mmol $\cdot$ m$^{-2}$ $\cdot$ d$^{-1}$). Overall, $p\text{CO}_2$ was primarily controlled by the carbonate system, followed by dissolved organic carbon decomposition. Flow velocity was the key factor controlling gas transfer velocity ($k$), whereas wind speed showed no significant correlation with $k$. On an annual scale, both rivers and reservoirs acted as persistent carbon sources to the atmosphere, with average effluxes comparable to the Yangtze River but substantially lower than other tributaries in the middle Yellow River basin.

**Keywords:** carbon dioxide outgassing; partial pressure of carbon dioxide;

spatio-temporal variation; reservoir; Kuye River

# 1. Introduction

Rivers serve as critical linkages between terrestrial and oceanic carbon pools. Recent research indicates that carbon fluxes entering rivers from terrestrial ecosystems significantly exceed those delivered to the ocean, demonstrating that rivers function not merely as passive carbon conduits but actively "retain" carbon through burial in sediments or transformation and subsequent release as greenhouse gases. Raymond et al. [5] estimated global inland water CO emissions at 2.6 Pg $C \cdot a^{-1}$, equivalent to the annual net carbon uptake by terrestrial ecosystems. Numerous studies have shown that $p\mathrm{CO}_2$ and $F\mathrm{CO}_2$ in inland waters result from combined effects of watershed physiochemical properties and human activities. For instance, Abril et al. [3] found that $p\mathrm{CO}_2$ in the Amazon River was primarily controlled by groundwater inputs and in-stream respiration, whereas Davidson et al. [4] reported that $p\mathrm{CO}_2$ dynamics in the Yukon River basin were mainly influenced by groundwater, surface runoff, and latitude, with respiration playing a minor role. Consequently, $F\mathrm{CO}_2$ exhibits significant spatio-temporal variability. For the Yellow River, Song [6] observed $F\mathrm{CO}_2$ ranging from 56.4 to 344.1 $\mathrm{mmol} \cdot \mathrm{m}^{-2} \cdot \mathrm{d}^{-1}$ in the delta region, while Yang [7] reported an average $F\mathrm{CO}_2$ of 118.1 $\mathrm{mmol} \cdot \mathrm{m}^{-2} \cdot \mathrm{d}^{-1}$ in the middle reaches. These variations underscore the importance of studying CO exchange fluxes in representative rivers to properly understand global carbon cycling.

The middle Yellow River flows through the Loess Plateau, where intense physical erosion and chemical weathering transport substantial carbon loads into aquatic systems. The Kuye River basin, a major source of coarse sediment in the middle Yellow River, provides an ideal setting for investigating carbon transport and budget dynamics across the Loess Plateau. This study examines the spatio-temporal patterns of $F\mathrm{CO}_2$ and associated controlling factors throughout the Kuye River basin and its representative reservoirs, aiming to enhance understanding of CO emission dynamics in severely eroded regions and provide data support for regional carbon budget assessments.

# 2. Methods

## 2.1 Study Area

The Kuye River basin (109°30 –110°50 E, 38°22 –39°30 N) originates in Badinggou, Dongsheng City, Inner Mongolia, and flows through Yijinhuoluo Banner and Fugu County in Shaanxi Province before joining the Yellow River at Shamatou Village, Shenmu County. The mainstem extends 242 km with a drainage area of 8,706 $\mathrm{km}^2$. Major tributaries include the Wulanmulun and Benniuchuan rivers. The upper reaches (from source to Shenmu) traverse the sandy hilly region of Inner Mongolia–Ordos, characterized by sandy soils, while the middle and lower reaches pass through loess hilly areas with carbonate-rich loess soils. The basin lies within a coarse sediment source area of 4,001 $\mathrm{km}^2$, accounting for a significant portion of the Yellow River's coarse sediment supply. With pronounced seasonal flow variations, the basin experiences concentrated rainfall events during July–September, which constitute approximately 70% of annual precipitation. Recent vegetation restoration has alleviated soil erosion, though the basin still experiences a two-month ice cover period from mid-December to mid-February.

Field sampling was conducted during four periods: late March 2019 (spring ice-melt), July 2018 (summer wet season), October 2018 (autumn), and June 2019 (summer dry season). A total of 20 river sites and 4 reservoir sites were selected upstream of urban areas and pollution sources [Figure 1: see original paper]. River sites included mainstem (R0), first-order tributaries (R1), and second-order tributaries (R2). Reservoirs were small-type (capacity $< 100 \times 10^4$ $m^3$): an upstream reservoir (age 3 years, area 3.3 $km^2$) in the sandy hilly region and a downstream reservoir (age 20 years, area 0.05 $km^2$) in the loess hilly region with severe upstream erosion.

### 2.2 Field CO Measurements

Water samples were collected 20 cm below the surface after triple-rinsing bottles. The partial pressure of CO ($p\mathrm{CO_2}$) was measured using the headspace equilibrium method. A 630 mL bottle was filled with sample water, sealed, and shaken vigorously for 2 minutes to achieve equilibrium between water and headspace gas. The headspace gas was then connected to a LI-7000 CO analyzer (LI-COR, USA) via a filter to prevent contamination, with gases passing through soda lime and magnesium perchlorate for drying. Measurements were repeated three times with errors within ±5%, and final $p\mathrm{CO_2}$ values were calculated using Henry's law constants, headspace ratios, and equilibrium concentrations [7].

The CO flux ($F\mathrm{CO_2}$) was measured using a floating chamber (volume 10.77 L, contact area 0.10 $m^2$) wrapped in aluminum foil to minimize solar radiation effects and equipped with a thermometer. The chamber was connected to the LI-7000 analyzer in a closed loop. After pressure equilibration, the chamber was placed on the water surface and CO accumulation was recorded for approximately 10 minutes. $F\mathrm{CO_2}$ was calculated as:

$$F\mathrm{CO_2} = \frac{dp\mathrm{CO_2}}{dt} \cdot \frac{V}{RTS}$$

where $dp\mathrm{CO_2}/dt$ is the rate of $p\mathrm{CO_2}$ change ($\mu\mathrm{atm} \cdot \mathrm{s}^{-1}$), $V$ is chamber volume (L), $R$ is the gas constant, $T$ is temperature (K), and $S$ is the water contact area ($m^2$).

The gas transfer velocity ($k$) was calculated using the model:

$$F\mathrm{CO_2} = k(c_{aq} - c_{eq})$$

where $c_{aq}$ is the measured aqueous CO concentration and $c_{eq}$ is the atmospheric equilibrium concentration. The $k$ values were standardized to a Schmidt number of 600 ($k_{600}$) using:

$$k = k_{600}\left(\frac{600}{Sc}\right)^{1/2}$$

For river water, the temperature-dependent Schmidt number was calculated as [10]:

$$Sc = 1911.1 - 118.11 \times T + 3.4527 \times T^2 - 0.041320 \times T^3$$

### 2.3 Water Environment Measurements

Water temperature, pH, and salinity were measured using a Multi-3630 IDS multi-parameter probe (WTW, Germany) calibrated with standard solutions. Alkalinity was determined by titration with 0.1 $\text{mol} \cdot \text{L}^{-1}$ HCl to pH $\approx$ 4.4 using methyl orange indicator, with errors within $\pm 5\%$. Dissolved organic carbon (DOC) was measured in 40 mL samples filtered through 0.7 $\mu$m Whatman GF/F filters, acidified with phosphoric acid, and analyzed using a vario TOC analyzer (Elementar, Germany) with errors within $\pm 3\%$. Chlorophyll-a (Chl a) was extracted from 10 mL water samples treated with magnesium carbonate suspension, filtered, and measured using a UV-2600 spectrophotometer (Shimadzu, Japan) with precision of $\pm 0.01$ $\mu\text{g} \cdot \text{L}^{-1}$. Wind speed and air temperature were recorded using a Kestrel 5500 weather meter.

## 3. Results

### 3.1 River pCO and FCO Variations

The Kuye River's $p\text{CO}_2$ ranged from 716 to 2,604 $\mu$atm, showing clear seasonal patterns: spring (2,355 $\mu$atm) > summer wet season (2,162 $\mu$atm) > summer dry season (1,104 $\mu$atm) > autumn (1,089 $\mu$atm) [Figure 2: see original paper]. Tributaries exhibited significantly higher $p\text{CO}_2$ than the mainstem, particularly during summer wet season (2,604 vs. 1,124 $\mu$atm). The $F\text{CO}_2$ ranged from 42.9 to 369 $\text{mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, with contrasting seasonal patterns: autumn (165.7 $\text{mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$) > summer wet season (103.1 $\text{mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$) > summer dry season (66.1 $\text{mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$) > spring (42.9 $\text{mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$) [Figure 3: see original paper]. Tributary $F\text{CO}_2$ (107.4 $\text{mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$) exceeded mainstem values (66.5 $\text{mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$) by 61%, reflecting stronger biogeochemical activity and higher gas transfer velocities in tributaries [Figure 4: see original paper].

### 3.2 Reservoir pCO and FCO Variations

Reservoir $p\text{CO}_2$ showed opposite seasonal trends to rivers, ranging from 371 to 1,511 $\mu$atm: spring (1,056 $\mu$atm) > summer dry season (837 $\mu$atm) > summer wet season (785 $\mu$atm) > autumn (460 $\mu$atm) [Figure 5: see original paper]. The upstream sandy hilly reservoir (460 $\mu$atm) had lower $pCO_2$ than the downstream loess hilly reservoir (1,105 $\mu$atm). Reservoir $FCO_2$ ranged from $-5.4$ to 60.3 $mmol \cdot m^{-2} \cdot d^{-1}$, with spring showing the highest flux (16.6 $mmol \cdot m^{-2} \cdot d^{-1}$) and autumn the lowest ($-5.4$ $mmol \cdot m^{-2} \cdot d^{-1}$), indicating a carbon sink in autumn. The loess hilly reservoir (16.4 $mmol \cdot m^{-2} \cdot d^{-1}$) exhibited higher $FCO_2$ than the sandy hilly reservoir (1.2 $mmol \cdot m^{-2} \cdot d^{-1}$), particularly during summer wet season when the downstream reservoir reached 60.3 $mmol \cdot m^{-2} \cdot d^{-1}$ .

# 4. Discussion

## 4.1 pCO  and the Carbonate System

The carbonate system, formed through intense chemical weathering on the Loess Plateau, is the primary control on $pCO_2$. Dissolved CO  exists in three forms ($CO_2$(aq), $H_2CO_3$, and $HCO_3^-$), with their concentrations governed by pH through the equilibrium:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow 2H^+ + CO_3^{2-}$$

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca^{2+} + 2HCO_3^-$$

In the Kuye River, $pCO_2$ showed strong negative correlations with pH across all seasons ($p < 0.001$) , indicating carbonate buffering as the dominant control mechanism. The carbonate buffering effect was particularly pronounced in loess hilly areas where carbonate-rich soils enhance $HCO_3^-$ concentrations (mean 118.1 $mg \cdot L^{-1}$) compared to the Yellow River average (57.8 $mg \cdot L^{-1}$). In reservoirs, $pCO_2$ correlated positively with $HCO_3^-$ ($p < 0.01$) , reflecting groundwater inputs as the primary dissolved carbon source in these relatively stagnant systems.

## 4.2 pCO  Relationships with Chlorophyll-a and Water Temperature

Chl a concentration serves as a proxy for phytoplankton biomass. Riverine $pCO_2$ showed significant negative correlation with Chl a only during summer dry season ($R = -0.61$, $p < 0.001$) , when low flow conditions favored phytoplankton growth and CO  uptake. In contrast, reservoir $pCO_2$ exhibited year-round negative correlations with Chl a ($p < 0.05$) , attributed to longer water residence times, enhanced sedimentation that increases water clarity, and favorable conditions for photosynthetic CO  consumption [17, 16].

Water temperature influences both carbonate equilibrium thermodynamics and biological activity. While temperature typically correlates positively with $pCO_2$ through decreased CO  solubility [22], it also promotes phytoplankton growth. In the Kuye River basin, these opposing effects resulted in no significant overall correlation between temperature and $pCO_2$, consistent with findings from other temperate systems [16].

### 4.3 pCO and DOC Concentrations

DOC represents a major carbon pool in aquatic systems, derived from both autochthonous (in-situ production) and allochthonous (terrestrial) sources [23]. Riverine $pCO_2$ correlated significantly with DOC during summer wet season ($p < 0.001$) , when high runoff transported substantial terrestrial organic matter into the channel. Microbial respiration and photochemical oxidation of this allochthonous DOC generated CO , making terrestrial carbon inputs a critical source of riverine CO [11, 15]. Reservoir $pCO_2$, however, showed no significant DOC correlation, indicating that internal carbon cycling dominates in these lentic environments.

### 4.4 Hydrodynamic Controls on Gas Transfer Velocity (k)

**4.4.1 Flow Velocity Effects** Flow velocity emerged as the dominant control on $k_{600}$ in the Kuye River ($R^2 = 0.72$, $p < 0.001$) [Figure 7: see original paper], with $k_{600}$ values closely tracking $FCO_2$ seasonal patterns. Higher velocities increase surface turbulence and water–air contact area while resuspending bed sediments, thereby enhancing carbon supply and gas exchange [10, 11]. The relationship was particularly strong during summer wet season when velocities reached $1.0\ \mathrm{m \cdot s^{-1}}$, generating $k_{600}$ values of $15.2\ \mathrm{cm \cdot h^{-1}}$. In contrast, summer dry season velocities of $0.3\ \mathrm{m \cdot s^{-1}}$ produced minimal $k_{600}$ values ($2.1\ \mathrm{cm \cdot h^{-1}}$), limiting CO efflux despite high $pCO_2$.

**4.4.2 Wind Speed Effects** Wind speed is a primary driver of gas exchange in large water bodies [13]. However, during our sampling period, wind speeds averaged only $0.76\ \mathrm{m \cdot s^{-1}}$, well below the $3.5\ \mathrm{m \cdot s^{-1}}$ threshold where wind significantly affects $k$ [28]. Consequently, no significant correlation was observed between wind speed and $k_{600}$ for either rivers or reservoirs [Figure 8: see original paper]. The floating chamber method itself may have further dampened wind effects, suggesting that flow velocity, not wind, controlled gas exchange in this system.

### 4.5 Regional Comparisons and Carbon Budget Implications

Compared to other global rivers, the Kuye River's $FCO_2$ ($94.5\ \mathrm{mmol \cdot m^{-2} \cdot d^{-1}}$) aligns with temperate rivers like the Colorado River ($70–120\ \mathrm{mmol \cdot m^{-2} \cdot d^{-1}}$) and the Yangtze River ($85\ \mathrm{mmol \cdot m^{-2} \cdot d^{-1}}$), but remains substantially lower than tropical rivers ($200–400\ \mathrm{mmol \cdot m^{-2} \cdot d^{-1}}$) . The lower efflux reflects temperate climate conditions, lower water temperatures, and reduced terrestrial carbon inputs relative to tropical systems [26, 27]. Notably, while the Kuye River's $pCO_2$ is similar to the neighboring Wuding River, its $FCO_2$ is lower due to reduced flow velocity and weaker water–air turbulence, despite comparable $pCO_2$ levels [17].

Reservoirs fundamentally alter riverine carbon cycling by modifying hydrological regimes and water chemistry. The Kuye River reservoirs showed lower average $FCO_2$ (10.3 $mmol \cdot m^{-2} \cdot d^{-1}$) than the river network, with some sites acting as carbon sinks in autumn. This demonstrates that dam impoundment reduces gas exchange velocities and promotes carbon burial, altering the basin's carbon budget [18, 19]. Regional carbon assessments must therefore integrate both river and reservoir processes to accurately quantify water–air CO  exchange and avoid underestimating carbon retention in regulated systems.

## 5. Conclusions

High-frequency measurements of $pCO_2$ and $FCO_2$ across seasons and geomorphological zones in the Kuye River basin reveal four key findings:

1. **Riverine CO  dynamics**: Surface water $pCO_2$ ranged from 716 to 2,604 $\mu$atm, with $FCO_2$ varying from 42.9 to 165.7 $mmol \cdot m^{-2} \cdot d^{-1}$. Seasonal patterns showed autumn maxima and spring minima, while spatially, tributary $FCO_2$ exceeded mainstem values by 61% due to stronger biogeochemical activity.
2. **Reservoir CO  dynamics**: Reservoir $pCO_2$ (371–1,511 $\mu$atm) and $FCO_2$ ($-5.4$ to 60.3 $mmol \cdot m^{-2} \cdot d^{-1}$) exhibited inverse seasonal patterns to rivers, with spring maxima and autumn minima. The downstream loess hilly reservoir showed higher $FCO_2$ than the upstream sandy hilly reservoir.
3. **Controlling factors**: The carbonate system was the primary control on $pCO_2$, followed by DOC decomposition. Flow velocity was the key factor regulating gas transfer velocity ($k$), while wind speed showed no significant effect. Chlorophyll-a influenced $pCO_2$ only in reservoirs and during low-flow river conditions.
4. **Regional context**: The Kuye River's average CO  efflux aligns with other temperate rivers but is lower than tropical rivers and other Yellow River tributaries. Integrating river and reservoir processes is essential for accurate regional carbon budget assessments, as reservoirs can shift systems toward carbon sinks.

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*Note: Figure translations are in progress. See original paper for figures.*