Riverine carbon export in the arid-semiarid Wuding River catchment on the Chinese Loess Plateau

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Abstract: Riverine export of terrestrially-derived carbon represent a key component of the global carbon cycle. In this study we quantify the redistribution of riverine carbon within the Wuding catchment on the Chinese Loess Plateau. Export of dissolved organic and inorganic carbon (DOC and DIC) exhibited pronounced spatial and temporal variability. While the DOC concentration was spatially comparable within the catchment, it was generally higher in spring and summer than in autumn, especially in the loess subcatchment. This reflects the enhanced organic matter inputs from agricultural tillage in spring and from terrestrial ecosystems in summer. DIC concentration in the loess subcatchment is significantly higher than that in the sandy subcatchment, due largely to dissolution of carbonates that are abundant in loess. In addition, content of particulate organic carbon (POC) shown strong seasonal variability with low values in the wet season owing to input of subsurface soils by gully erosion. The downstream carbon flux was (7±1.9)×10¹⁰ g C year⁻¹ and dominated by DIC and POC. Total CO₂ emissions from water surface were (3.7±0.5)×10¹⁰ g C year⁻¹. Radiocarbon analysis revealed that the degassed CO₂ was 810–1890 years old, indicating the release of old carbon previously stored in soil horizons. Riverine carbon export in the Wuding catchment has been greatly modified by check dams. Our estimate shows that carbon burial through sediment storage was (7.8±4.1)×10¹⁰ g C year⁻¹, representing 42% of the total riverine carbon export from terrestrial ecosystems on an annual basis ((18.5±4.5)×10¹⁰ g C year⁻¹). Moreover, the riverine carbon export accounted for 16% of the catchment NEP. It appears that the magnitude of carbon sink of terrestrial ecosystems in this arid-semiarid catchment has been significantly offset by riverine carbon export.

1. Introduction

Inland waters (e.g., rivers, lakes, and dam-formed reservoirs) are a key component of the global carbon cycle (Cole et al., 2007;Regnier et al., 2013). Of these water bodies, rivers play an exceptionally significant role by directly linking terrestrial ecosystems and the oceans. Prior studies indicate that the amount of terrestrially-derived carbon entering inland waters was substantially larger than that discharged into the oceans mainly through fluvial transport of global rivers (Mendonça et al., 2017;Battin et al., 2009). With respect to river systems, this carbon imbalance suggests that rivers are not passive pipes simply transporting terrestrial carbon,
but are biogeochemically active in processing massive quantities of carbon along river course. Riverine carbon is subject to a number of physical and biogeochemical processes, such as burial, evasion, in-situ production, and decomposition. The CO₂ emissions from water surface of global rivers and streams combined are conservatively estimated at 1.8 Pg year⁻¹ (Raymond et al., 2013). In addition, carbon loss due to long-term sediment storage in reservoirs through burial is also substantial (Battin et al., 2009; Cole et al., 2007; Mendonça et al., 2017; Clow et al., 2015). Inclusion of CO₂ emissions and carbon burial in sediments is thus critical for a holistic understanding of carbon cycling in river systems at different spatial scales.

Although studies on riverine fluxes of carbon have been exponentially increasing over the recent 20 years, great uncertainties remain to be properly resolved even for catchment-scale assessments, not to mention the larger regional and global estimates (Marx et al., 2017). An important source for these uncertainties is the underrepresentation of current carbon flux measurements, which are mostly confined to tropical and boreal rivers that are sensitive to climate change. In contrast, few studies have investigated the terrestrial and fluvial fluxes of carbon in arid and semiarid rivers though they are globally abundant (Tranvik et al., 2009). Increased concerns over global riverine carbon export and emissions necessitate an improved understanding of carbon cycling in these underexplored rivers. Studying their riverine carbon cycling on the basis of individual catchments will shed light on refining global riverine carbon flux estimates and thereby assessing their biogeochemical importance, as has been done for tropical and temperate rivers (e.g., Butman and Raymond, 2011; Richey et al., 2002).

With the role of arid-semiarid rivers in global riverine carbon cycle in mind, we investigated the transport and fate of carbon from terrestrial ecosystems through drainage network to catchment outlet in the medium-sized Wuding catchment on the arid-semiarid Loess Plateau (in northern China). The overall aim of this study was to quantify the redistribution of riverine carbon among its three pathways, including downstream export to catchment outlet, CO₂ evasion from water surface, and organic carbon (OC) burial through sediment storage, within the arid-semiarid Wuding catchment. To achieve this aim, a catchment-scale carbon balance was constructed. The major objectives are to: 1) explore the spatial and temporal variability of riverine carbon export, 2) trace the sources and age of the emitted CO₂ using carbon isotope techniques, and 3) evaluate the riverine carbon cycle in relation to the catchment’s terrestrial ecosystem production. This study is built upon our earlier work of Ran et al. (2017) in which we analyzed environmental controls and dam impacts on riverine CO₂ emissions. These results will provide insights into riverine carbon studies for rivers in arid-semiarid climates and improve the accuracy of extrapolation from watershed-based carbon studies to global-scale estimates.

2. Study area and methods
2.1 Study area
The Wuding River (37°–39° N; 108°–110.5° E) is one of the largest tributaries of the Yellow River and located on the central Chinese Loess Plateau (Figure 1). Its drainage area is 30,261 km² and multi-annual mean water discharge is 35 m³ s⁻¹. Based on geomorphological landscape, the catchment can be further divided into the southeastern loess subcatchment covered with 50–100 m deep loess and the northwestern sandy subcatchment composed mainly of aeolian sand (Figure
1). While barren terrain is extensive in the sandy subcatchment, agriculture is the primary land use type in the loess subcatchment with traditional ploughing tillage as the dominant land management practice. Annual precipitation decreases from 500 mm in the southeast to 300 mm in the northwest, of which 75% falls in the wet season from June until September (Li et al., 2007). Several heavy storms in summer can account for half of the annual precipitation. Except the periods of heavy storms, hydrological regime is controlled by groundwater input, especially in the sandy subcatchment. Due to highly erodible loess and sparse vegetation, the Wuding catchment once suffered severe soil erosion of a rate of 7000 t km⁻² per year (Ran et al., 2017).

Check dams have long been proposed as an effective soil conservation strategy. By 2011, more than 11,000 check dams have been constructed (Ran et al., 2017). Because their primary purpose is for reducing sediment loss, these structures are generally designed without sluice gates. Consequently, most of the sediment from upstream hillslopes and gullies can be effectively trapped (Ran et al., 2013), resulting in a short life time for these dams because of rapid sediment accumulation, generally less than 20 years (Xu et al., 2013). The resulting organic carbon (OC) burial is likely substantial, but remains to be quantified (Zhang et al., 2016), as does the altered CO₂ exchange at the formed standing water surface. Because of widespread presence of calcite in loess (up to 20%; Zhang et al., 1995) and carbonate dissolution and precipitation under dry climate, this catchment shows hard-water attributes in rivers and check dam-formed reservoirs featuring high dissolved solids. Its mean alkalinity was 3850 μmol L⁻¹ and long-term river water CO₂ partial pressure (pCO₂) ranged between 1000 and 2500 μatm (Ran et al., 2015a).

2.2 Field sampling and laboratory analysis

While detailed information has been provided in Ran et al. (2017), a brief description was provided here. Three sampling campaigns were conducted in the Wuding catchment in 2015: before the wet season (March–April; denoted as spring), during the wet season (July–August; summer), and after the wet season (September–October; autumn). Sampling was not performed in winter due to ice coverage. The sampling was performed at 74 sites, including 60 river sites in six Strahler order rivers (Strahler, 1957) and 14 reservoir sites in 8 check dam-formed reservoirs (Figure 1). Moreover, monthly samples were collected at the catchment outlet Baijiachuan gauge (Figure 1) in 2017 and daily hydrological records for 2015 and 2017 were also retrieved from the gauge. The sampling frequency was intensified (i.e., 2-h intervals) during typical flood events.

We employed the drifting floating chamber technique to measure in situ CO₂ emissions (Ran et al., 2017). Briefly, an infrared Li-7000 gas analyzer (Li-Cor, Inc, USA) was connected to a rectangular chamber (volume: 17.8 L) via rubber-polymer tubes to measure CO₂ concentration changes inside the chamber over time. We also measured in situ surface water pCO₂ using the headspace equilibrium method by means of the Li-7000 gas analyzer (Müller et al., 2015). Triple measurements at each site showed a high consistency with 3% variability only. Finally, surface water pCO₂ was calculated and calibrated with the solubility constants for CO₂ from Weiss (1974). To determine the age of the emitted CO₂, we collected radiocarbon (Δ¹⁴C) samples by using the precipitation method widely used in groundwater dating studies (Vita-Finzi and Leaney, 2006). After the CO₂ emissions measurement, the accumulated CO₂ in the chamber was directly injected into 50 mL SrCl₂ solution in a closed recirculating loop using an external pump.
Reaction of chamber CO$_2$ with SrCl$_2$ results in the precipitation of SrCO$_3$. The precipitated SrCO$_3$ was then filtered, dried, and stored in a cool and dark environment until analysis. Eleven SrCO$_3$ samples were collected at four sites during the three campaigns.

**2.3 Carbon fluxes and CO$_2$ emissions**

Using the monthly sampling results and daily flow and sediment records measured at the catchment outlet Bajiaochuan gauge, we calculated the yearly dissolved (DOC and DIC) and particulate (POC) carbon export from the Wuding catchment. This was achieved by multiplying daily flow rates or sediment concentrations averaged over sampling intervals by measured DOC and DIC concentrations in water or POC content in sediments. The yearly total carbon flux was calculated as the sum of the monthly fluxes. Total OC burial behind check dams was estimated by multiplying annual sediment deposition rate by POC content.

Areal fluxes of CO$_2$ emissions across water-air interface ($F_{CO_2}$, mmol m$^-2$ d$^{-1}$) was determined from the slope of the linear regression of $p$CO$_2$ against time (coefficient of determination $r^2$ ≥0.97):

$$F_{CO_2} = 1000 \times \left( \frac{dpCO_2}{dt} \right) \left( \frac{V}{RTS} \right)$$

(1)

where, $dpCO_2/dt$ is the slope of CO$_2$ change within the chamber (Pa d$^{-1}$; converted from μatm min$^{-1}$), $V$ is the chamber volume, $R$ is the gas constant, $T$ is chamber temperature (K), and $S$ is the area of the chamber covering the water surface (0.09 m$^2$).

To calculate CO$_2$ efflux from the entire catchment, we estimated the areal extent of river water surface by means of the 90-m resolution Shuttle Radar Topography Mission (SRTM) DEM data set (Ran et al., 2015b). The delineated drainage network was then classified using the Strahler ordering system (Strahler, 1957). The measured widths of all sampled rivers during fieldwork...
were aggregated based on stream order to calculate the water surface area. For reservoirs, our earlier work (Ran and Lu, 2012) has identified their location and areal extent. Both the delineated drainage network and reservoir were calibrated through ground truthing during fieldwork. We further assumed that each round of field sampling was representative of CO\(_2\) emissions for equally four months (i.e., spring sampling: January–April (120 d); summer sampling: May–August (123 d); autumn sampling: September–December (122 d)). With this assumption in mind, we calculated the yearly CO\(_2\) efflux from both rivers and reservoirs.

### 2.4 Estimation of terrestrial ecosystem production

To evaluate the magnitude of riverine carbon flux, we compared the total carbon entering the drainage network with the Wuding catchment’s net ecosystem production (NEP). MOD17A3H (MODIS/Terra Net Primary Production) produced by USGS (https://lpdaac.usgs.gov/) was used to first estimate net primary productivity (NPP). The MOD17A3H Version 6 provides global NPP estimates at 500-m pixel resolution and in units of kg C m\(^{-2}\). While NPP is an important indicator of carbon uptake by terrestrial ecosystems, it does not account for carbon losses through heterotrophic soil respiration \((R_h)\). Heterotrophic soil respiration due to bacterial activities tends to release a significant fraction of the sequestered carbon into the atmosphere, depending on soil temperature, moisture, and substrate availability (Wei et al., 2015). Therefore, the NEP was used for the assessment and it can be estimated by subtracting \(R_h\) from NPP: \(\text{NEP} = \text{NPP} - R_h\) \(\text{(2)}\).

To calculated \(R_h\), total soil respiration \((S_R)\) was first derived from the global soil CO\(_2\) efflux database described by Raich and Potter (1995) who estimated \(S_R\) at a 0.5\(^\circ\) latitude by longitude spatial scale. \(S_R\) was then divided into its two components of autotrophic and heterotrophic soil respiration. \(R_h\) was finally estimated according to the assumption by Hanson et al. (2000) that \(R_h\) accounts for 54\% and 40\% of \(S_R\) in forested and non-forested areas, respectively.

### 3. Results

#### 3.1 Lateral riverine carbon fluxes

DOC concentrations ranged from 1.4 to 9.5 mg L\(^{-1}\) throughout the three sampling periods with both the lowest and highest DOC concentrations occurred in spring. The DOC averaged 5, 5.2, and 4.5 mg L\(^{-1}\) in spring, summer, and autumn, respectively. DOC first exhibited a downward trend along the river course from headwater downstream and then increased in the 6th order mainstem river in both the sandy and loess subcatchments (Figure 2). While the DOC in the low-order streams (i.e., 1st–2nd) was on average 9.4–20.6\% higher than in the 3rd–5th order streams, it increased to 5.7 mg L\(^{-1}\) in the 6th mainstem. The POC in sediments varied from 0.28\% to 1.72\% (dry weight) and shown pronounced seasonal variations. The averaged POC content in spring, summer, and autumn was 0.91\%, 0.44\%, and 0.69\%, respectively.

With the pH in range of 7.68–9.29, the calculated DIC was approximately equal to alkalinity. The Wuding waters presented significantly higher DIC than DOC concentrations. DIC in spring, summer, and autumn varied in the range of 39–119, 32–132, and 34–143 mg L\(^{-1}\) with the average at 62.1, 66.7, and 67.7 mg L\(^{-1}\), respectively. In the loess subcatchment, the DIC declined remarkably from headwater streams towards the mainstem channel (Figure 3a); but it remained
constant in the sandy subcatchment from the 1st order through the 5th order streams (Figure 3b). The high DIC values in the 6th order mainstem channel in the sandy subcatchment (Figure 3b) is reflective of the confluence of the two subcatchments. If only the 1st–5th order streams were considered, DIC in the sandy subcatchment was 38% lower than that in the loess subcatchment.

At Baijiachuan gauge, the DIC remained highly stable at 39.2±7.8 mg L⁻¹ over time. In comparison, the DOC concentration was 16% higher in the wet season than in the dry season while the POC content (range: 0.15–1.16%) in the former was less than half of that in the latter.

The mean DOC and POC were 3.3±0.4 mg L⁻¹ and 0.61±0.29%, respectively. Because the flow regime in 2017 was significantly biased due to an extreme flood in July (spontaneous discharge: 4490 m³ s⁻¹; Figure S1 in Supplementary), we used the hydrological data for 2015 to calculate downstream carbon export assuming that carbon content was comparable in 2015 and 2017. The annual downstream carbon export at Baijiachuan gauge was estimated to be (7±1.9)×10¹⁰ g C, of which the DIC, DOC, and POC fluxes were (3±0.6)×10¹⁰, (0.3±0.03)×10¹⁰, and (3.7±1.8)×10¹⁰ g C, respectively. DOC flux was around 10% of the DIC and POC fluxes, comprising only 4% of the total flux. DIC and POC fluxes were comparable, accounting for 53% and 43%, respectively, of the total flux.

### 3.2 CO₂ emissions from rivers and check dam-formed reservoirs

In our earlier work, we calculated the areal CO₂ emissions from rivers (Ran et al., 2017). In the sandy subcatchment, the mean CO₂ efflux from the 1st order headwater streams to the 6th order mainstem was 280, 422, 155, 216, 256, and 238 mmol m⁻² d⁻¹, respectively. In the loess subcatchment, it was 70, 78, 80, 57, 209, 268 mmol m⁻² d⁻¹, respectively. In association with the water surface area over the three seasons (Table S1 in Supplementary), total CO₂ emissions in 2015 were (3.7±0.5)×10¹⁰ g C, of which 42% was degassed from the sandy subcatchment rivers and 58% from the loess subcatchment rivers. At the catchment scale, CO₂ outgassing along fluvial transport first decreased from upland headwater rivers until the 4th order rivers, and then increased remarkably in the 5th and 6th order rivers in both subcatchments (Figure 4a). The headwater 1st and 2nd order rivers accounted for 26% of the total CO₂ efflux (Figure 4b). With the biggest areal extent of water-air interface (43% of the total; Table S1 in Supplementary), the 6th order mainstem contributed 54% of the total CO₂ efflux (Figure 4b).

CO₂ effluxes from check dam-formed reservoirs varied from -23.5 to 66.5 mmol m⁻² d⁻¹ in spring, -33.5 to 19 mmol m⁻² d⁻¹ in summer, and -17 to 42.1 mmol m⁻² d⁻¹ in autumn. The mean CO₂ efflux for these three seasons was 4.2, -16.2, and 12.3 mmol m⁻² d⁻¹, respectively (Ran et al., 2017). Of the 8 reservoirs, 2 reservoirs are located in the sandy subcatchment and 6 in the loess subcatchment (Figure 1). Reservoir CO₂ effluxes in the sandy subcatchment were constantly higher or less negative than that in the loess subcatchment with the mean efflux at 10.4 and -2.9 mmol m⁻² d⁻¹, respectively. Currently, there are 337 reservoirs in the catchment with the water surface varying from 0.01 to 10.35 km² (Figure S2 in Supplementary). Total water surface area is 107 km², including 31.8 km² in the sandy subcatchment and 75.2 km² in the loess subcatchment. Assuming the water surface remained constant (i.e., no significant seasonal fluctuations), the annual CO₂ emissions were conservatively estimated at 38 million mol (or
0.05×10^{10} \text{ g C}; Table 1). CO$_2$ outgassing in spring and autumn was offset by CO$_2$ uptake in summer by 85%.

The isotopic composition of the emitted CO$_2$ varied significantly between sampling sites and between seasons (Table 2). The sandy subcatchment (site S1; Figure 1) showed the most depleted $\delta^{13}$C signature (-30.2‰). With the $\delta^{13}$C values most depleted in spring, the mean $\delta^{13}$C values in spring, summer, and autumn were -30.2‰, -24.5‰, and -23.2‰, respectively. The $\Delta^{14}$C values also displayed seasonal variations and the conventional age ranged from 810 to 1890 years (Table 2; Figure 5). The emitted CO$_2$ exhibited the oldest age in spring at all the 4 sites with the age in summer and autumn 36% and 29% younger, respectively. The average $^{14}$C age in the three seasons was 1610, 1038, and 1140 years, respectively. There was no discernible correlation between DIC and DOC concentrations and the isotopic composition.

### 3.3 OC burial behind check dams

Based on our earlier estimate of sediment trapping, the trapping efficiency in this catchment is 94.3% and total sediment deposition rate is 3720×10^{10} \text{ g year}^{-1} (Ran et al., 2013). Analysis of sediment profiles from the four check dams (Figure 1) shows the POC content varied from 0.1% to 0.5% with high POC contents in the surface soils (0–60 cm) and it declined rapidly with depth and remained constant thereafter at around 0.2% (Figure 6). The mean POC content was 0.21±0.11%. Total OC burial behind check dams was estimated to be (7.8±4.1)×10^{10} \text{ g C year}^{-1}.

### 3.4 Terrestrial NPP and NEP fluxes

The NPP in the Wuding catchment in 2015 was spatially heterogeneous (Figure 7). The mean areal NPP was 221 \text{ g C m}^{-2} and the total NPP was (668±60)×10^{10} \text{ g C}. Based on the global soil respiration flux database (Raich and Potter, 1995), the $R_h$ for this catchment is about 450 \text{ g C m}^{-2} year$^{-1}$. Recent land use studies show that forest cover in this catchment occupies only 5% of the total area (Wang et al., 2014), while the remaining is dominated by cropland or barren terrain. Using the ratios of autotrophic to heterotrophic soil respiration for forested and non-forested land suggested by Hanson et al. (2000), $R_h$ was estimated to be 183 \text{ g C m}^{-2} year$^{-1}$ or 554×10^{10} \text{ g C year}^{-1} in total. By subtracting $R_h$ from NPP, a first-order estimation shows a NEP of 38 \text{ g C m}^{-2} year$^{-1}$ or 114×10^{10} \text{ g C year}^{-1} for the entire catchment. The NEP represented only 17% of the NPP, and heterotrophic soil respiration consumed 83% of the sequestered carbon.

### 4. Discussion

#### 4.1 Carbon export dynamics within the catchment

Carbon export from terrestrial ecosystems into drainage networks is controlled by hydrological regime, geomorphological landscape, biogeochemical processes, and human impact within the catchment of concern (Noacco et al., 2017; Stimson et al., 2017). Affected by sparse vegetation coverage, both DOC and POC contents in the Wuding catchment were relatively low compared with most rivers in the world. Stream water OC is susceptible to degradation by microbial or photochemical reactions during transit (Raymond et al., 2016). The downstream DOC decline along the 1st–5th order streams suggests that the labile fraction of DOC was decomposed in the river course (Figure 2). This decomposition is generally associated with increasing water
residence time for bacterial respiration in downstream streams due to decreasing flow velocities. In contrast, the deeply incised headwater streams in the Wuding catchment exhibit an opposite landscape with the flow velocities increasing from headwater streams to the mainstem channel (Ran et al., 2017). Thus, the decreasing water residence time cannot fully explain the decreasing DOC concentration. Instead, the gradually increasing temperature with declining elevation might have enhanced bacterial respiration (Peierls and Paerl, 2010). The water temperature in the lowland streams was on average 2–5 °C higher than in the headwater streams (Ran et al., 2017).

The high DOC values in the 6th mainstem channel reflect direct DOC influxes from low-order streams (Figure 1) and the mixture of carbon export from the two subcatchments. There was no discernible seasonal difference in DOC concentrations in both subcatchments, although the hydrograph varied significantly among the three seasons. Consequently, there was no significant correlation between DOC and flow based on the spatial sampling results (p>0.05). Although the extensive implementation of agricultural tillage practices in April and May tends to mobilize vast amounts of OC, OC export through surface runoff into the drainage network is limited to episodic high-discharge events in June to September. The timing inconsistency suggests that the mobilized soil OC in this dry catchment was either leached into deep soil layers or released into the atmosphere after mineralization. Lateral export into the drainage network caused by surface runoff is negligible. The predominance of groundwater input over the entire year and its highly stable DOC illustrates the insensitivity of DOC concentration to flow dynamics. In contrast, the spatial heterogeneity of DIC with higher values in the loess subcatchment was likely caused by dissolution of carbonates which are abundant in loess (Zhang et al., 1995).

The POC content in sediments is at the lower end of global rivers (range: 0.3–10.1%), which reflects the ancient sedimentary OC origin of about 0.5% for fluvial sediments worldwide (Ludwig et al., 1996). This can also be seen from the isotopic signature of the Yellow River sediment that is primarily derived from the Loess Plateau. Wang et al. (2012) found that the exported POC is quite old (4110–8040 years) and biogeochemically refractory. The substantially lower POC contents in summer than in spring and autumn reflected the impact of gully erosion, which is quite common on the Loess Plateau during periods of heavy storms in summer (Wang et al., 2017). Gully erosion is usually associated with the mobilization of subsurface soils that have a substantially lower OC content (i.e., 0.2–0.3%; Ran et al., 2015a) than the surface soils. As a result, input of subsurface soils into rivers caused the lower POC content in summer, thereby generating a negative correlation between POC and suspended solids concentration.

With respect to CO₂ outgassing, the higher effluxes in the drier sandy subcatchment reflect the stronger impact of groundwater input, although both subcatchments are heavily controlled by groundwater inflow. While several heavy rainstorms in summer are responsible for a large share of the annual precipitation (i.e., >70%; Wang et al., 2017), our field measurements in 2015 did not capture the storm-caused CO₂ outgassing. Thus, the CO₂ emissions results reveal largely the groundwater-derived CO₂ degassing. This may have caused considerable uncertainty in the annual CO₂ outgassing estimation (see discussion below). Although the sandy subcatchment rivers exhibited higher areal CO₂ effluxes than that in the loess subcatchment in all the 1st–5th order rivers except the 6th mainstem, the lower contribution of CO₂ emissions from the former
(42%) is because its water surface accounts for 32% only of the total water surface. In comparison, the larger contribution of the loess subcatchment rivers (58%) reflects their higher drainage density and larger water surface area (68% of the total; Table S1 in Supplementary).

Unlike natural rivers showing strong CO2 outgassing, the measured reservoirs presented considerably lower and even negative CO2 effluxes. The contrasting magnitude and direction of CO2 exchange suggest the physical and biogeochemical differences between lotic and lentic waters. Compared with rivers with fast moving water and high sediment concentrations, reservoirs display greatly reduced flow turbulence and enhanced algal production resulting from increased light penetration after the settling of suspended sediment (Cole et al., 2007). Analysis of chlorophyll-a also shows that it is 100% higher in reservoirs than in rivers in summer and autumn (Ran et al., 2017), indicative of carbon uptake by aquatic plants through photosynthesis. In the sandy subcatchment, the predominance of groundwater with high pCO2 has probably maintained its relatively higher reservoir CO2 effluxes (mean: 10.4 mmol m⁻² d⁻¹). For the loess subcatchment reservoirs, intensive nutrient loading from agricultural fields may have facilitated the growth of aquatic plants like phytoplankton, causing the net carbon uptake (mean: -2.9 mmol m⁻² d⁻¹). Overall, these reservoirs differ from their tropical counterparts that typically act as strong CO2 source hot spots (Barros et al., 2011;Deemer et al., 2016), yet they are consistent with other temperate reservoirs with similar landscape attributes (Knoll et al., 2013). Given the global abundance of hard-water reservoirs and their unique carbon processing mechanisms (Tranvik et al., 2009), estimating global CO2 emissions from reservoirs must pay comparable attention to these currently underrepresented reservoirs as to their tropical counterparts.

### 4.2 Downstream carbon export at catchment outlet and OC burial

The monthly carbon export at Baijiachuan gauge illustrates diverse responses of different carbon species to hydrological regime. Hydrologic storm events in wet seasons play a disproportionately important role in transporting terrestrially-derived carbon. Our high-frequency sampling during flooding periods at Baijiachuan gauge indicates that DOC concentrations were ~20% higher in the flooding periods than that in normal flow conditions. The positive correlation between DOC export and hydrography demonstrates the enhanced leaching of organic matter from surface vegetation and organic-rich top soil layers (Hernes et al., 2008). Moreover, increased stream velocities in the flooding periods have reduced water residence time and consequently, even the labile fraction of DOC could be quickly transported downstream, resulting in a greater export of DOC (Raymond et al., 2016). In comparison, the DIC concentration displayed a weak sensitivity to flow dynamics. Widespread presence of calcite in loess and intensive carbonate dissolution tend to provide sufficient DIC input, which have probably prevented the dilution effect observed in many other rivers (Ran et al., 2015a;Raymond and Cole, 2003).

The substantially lower POC content in the wet season largely reflects the impact of gully erosion as discussed earlier. With respect to sediment sources on the Loess Plateau, it has been widely realized that more than 50% of the sediment in wet seasons, especially during heavy storm periods, is derived from subsurface soils through gully erosion (Wang et al., 2017;Ran et al., 2015a). Mobilization of subsurface soils with a low OC content (i.e., 0.2–0.3%) and subsequent fluvial transport resulted in the observed low POC contents in the wet season. Our
results of 0.15–0.26% for samples collected during floods agreed well with the low carbon content in subsurface soils. Despite the low POC content, however, the POC flux in the wet season is considerable on an annual basis because of the high sediment loading.

CO$_2$ outgassing during flooding periods have also been significantly enhanced due largely to stronger near-surface turbulence and thus a higher gas transfer velocity (Figure 8). The average CO$_2$ efflux for the monitored flooding period was 5 times that in normal flow conditions (196 vs. 39 mmol m$^{-2}$ d$^{-1}$). When looking at the annual total fluxes, episodic high-discharge events were responsible for a significant percentage of annual carbon export though the duration of high-discharge events made up 4% only of the sampling year 2017. A conservative calculation using the sampling results at Baijiachuan gauge indicates that 85% of the annual downstream carbon export occurred during the three extreme floods (Figure S1 in Supplementary). Therefore, any sampling strategies missing episodic high-discharge events would create great uncertainties for annual-scale carbon export estimates (Lee et al., 2017; Jung et al., 2014). This is particularly true for arid-semiarid catchments, such as the Wuding River studied here, where episodic rainfall events make an exceptionally large share of annual water and sediment export.

The decreasing POC content in the deposited sediments with depth demonstrates the OC burial efficiency. Soil OC within the Wuding catchment is spatially homogeneous. The content in hillslope soils varies from 0.4–0.7% and it is less than 0.2% in the gully soils due to strong mineralization in the Quaternary loess (Wang et al., 2017), which is approximately equal to the POC content in the trapped sediments. The negligible OC loss after erosion reflects the spatial location and the high sediment trapping efficiency of check dams. Most check dams are located at the bottom of highly erodible loess gullies. This spatial closeness to erosional sites suggests that the eroded soils can be rapidly deposited after a short delivery distance (Wang et al., 2011). In view of the huge sediment deposition by check dams, the resulting OC burial represents an important carbon sink for the atmosphere that would have otherwise been mineralized to form CO$_2$ or CH$_4$ along fluvial delivery. It is important to recognize that, as a top priority soil conservation strategy, numerous check dams have been constructed on Loess Plateau over the past 60 years and more are under construction to replace the filled ones (Zhang et al., 2016; Wang et al., 2017). Assessing the potential OC burial efficiency and amount may have important implications for regional and even global carbon budgets. Regional estimates of OC burial in lakes have recently been made (Zhang et al., 2017; Kastowski et al., 2011). Considering the larger number of check dams and reservoirs of China, quantifying their OC burial will be critical for a more robust OC burial assessment in global lakes and reservoirs (Mendonça et al., 2017). Clow et al. (2015) provide a novel attempt to estimate large-scale OC burial by using regression models to extrapolate from limited measurements.

### 4.3 Carbon isotopic signature in the emitted CO$_2$

CO$_2$ emissions from rivers originate from decomposition of organic matter derived from terrestrial ecosystems and/or aquatic photosynthesis. The emitted CO$_2$ exhibited a $\delta^{13}$C-depleted signature significantly different from that from carbonate-dominant river basins (i.e., 0‰, Brunet et al., 2009). As stated earlier, the Wuding catchment is characterized by extensive presence of carbonates, and carbonate dissolution is the primary source of DIC to groundwater
(Zhang et al., 1995). Although we did not analyze the $\delta^{13}C$ of DIC, prior studies indicate that it generally ranges from -6.7 to -12.9‰ in Loess Plateau rivers (Liu and Xing, 2012). For natural rivers with the DIC dominated by HCO$_3^-$, kinetic isotope fractionation due to CO$_2$ outgassing tends to enrich the $\delta^{13}C$ of DIC by 3–5‰ (Doctor et al., 2008). Therefore, the emitted CO$_2$ is less likely to be derived from the interactions between water and carbonates, because the kinetic isotope fractionation process is not able to compensate the great discrepancy in $\delta^{13}C$. This is consistent with the $\delta^{13}C$ changes in soil CO$_2$ in sandy catchments (Gillon et al., 2012).

Instead, the $\delta^{13}C$ values of the emitted CO$_2$ are close to the isotopic composition of soil organic matter that varies between -24 and -34‰ (Brunet et al., 2009). For the catchment with its runoff in dry seasons dominated by groundwater inputs, the more depleted $\delta^{13}C$ in spring demonstrated the contribution of CO$_2$ in soil water to CO$_2$ emissions. In comparison, the $\delta^{13}C$ values were comparatively enriched in summer and autumn (Table 2; Figure 9), which probably suggests the impact of decomposition of C4 plants that have a $\delta^{13}C$ end-member of -12‰ (Brunet et al., 2009). Constrained by dry climate, major crops in the catchment are predominantly C4 plants, such as corn and millet, and their growing season from May until October overlaps well with the summer and autumn samplings. Thus, decomposition of these $^{13}C$-enriched organic matter in summer and autumn resulted in more positive $^{13}C$ than that in spring. In addition, CO$_2$ diffusion process itself can induce isotopic fractionation (Deirmendjian and Abril, 2018; Geldern et al., 2015). Preferential outgassing of $^{12}CO_2$ may have also contributed to the more depleted $\delta^{13}C$ values in the emitted CO$_2$ than that of the C4 plants. Aquatic algae with their $\delta^{13}C$ value ranging from -40 to -26‰ (Alin et al., 2008) is likely another contributor, as suggested by the 2-fold higher Chl a contents in summer and autumn than in spring at some sites (Ran et al., 2017). Deeply incised stream channels provide favorable stagnant water, albeit highly site-specific, for algae growth during non-flooding periods. However, this process seems to be of minor importance given the low light penetration due to extremely high turbidity.

As a useful tracer, natural radiocarbon has been widely used in terrestrial, aquatic, and marine carbon studies to trace the nature (i.e., age and source) and processing of carbon during transit (Gillon et al., 2012). The $\Delta^{14}C$ exhibited a positive correlation with $\delta^{13}C$, showing an increasing trend from spring through summer to autumn (Figure 9). Because DIC from carbonate dissolution is characterized by typically enriched $\delta^{13}C$ and highly depleted $\Delta^{14}C$ (Mayorga et al., 2005; Brunet et al., 2009), distribution of the sampled CO$_2$ in this dual-isotope plot also suggests the negligible contribution of carbonate dissolution to CO$_2$ emissions. Instead, in spring dominated by groundwater influx, aged soil-respired CO$_2$ and decomposition of old OC leached from deep soil horizons have likely led to the older CO$_2$ age (Figure 5), which suggests the outgassing of ancient terrestrial OC after entering aquatic systems (McCallister and del Giorgio, 2012). Addition of recently-fixed organic matter in summer and autumn through surface water inputs and decomposition of the labile fraction have played a ‘dilution’ effect, causing the younger age of the emitted CO$_2$ and thus the seasonal distinctions. Notably, the emitted CO$_2$ is inconsistent with that from the tropical Amazon rivers where respiration of contemporary young organic matter is the primary source of CO$_2$ outgassing (Abril et al., 2014; Mayorga et al., 2005). The evasion of old carbon from the Wuding catchment is likely to be widespread in arid-semiarid catchments worldwide with similar hydrological regime and terrestrial ecosystems.
Special efforts are therefore needed to quantify this old CO$_2$ outgassing and assess its significance for global carbon cycle and climate mitigation over longer timescales than recent sharp anthropogenic CO$_2$ emissions (i.e., since the 1850s).

4.4 Riverine carbon budget and NEP

Our first-order estimate of NEP for the Wuding catchment indicates that its terrestrial ecosystems sequester only small quantities of carbon on an annual basis. Approximately 83% of the NPP was consumed by microbial activities. This ratio is comparable to the estimate for global temperate semiarid ecosystems (i.e., 84% from Luysaert et al., 2007) while significantly higher than that for other ecosystems. For example, it is 63% in the tropical Nyong River catchment in western Africa (Brunet et al., 2009) and 42% in the temperate Schwabach River catchment in Germany (Lee et al., 2017). Furthermore, the total carbon export from the Wuding catchment accounted for 16% of its catchment NEP (Figure 10). This percentage of NEP as fluvial export is also substantially higher than recent studies in other regions which found that the sum of DOC, DIC, and CO$_2$ emissions generally represented <3% of the NEP (e.g., Brunet et al., 2009; Lee et al., 2017). Although POC flux and OC burial are not quantified in these studies, the missing amounts are small due to weak soil erosion and absence of dams in their catchments. Similarly, Shibata et al. (2005) found that the annual export of dissolved and particulate carbon from a first-order catchment in northern Japan made up only 2% of its NEP.

These discrepancies between Wuding and these catchments likely reveal the internal differences in soil property and erosion. Erosion-induced mobilization of heavily weathered soils with high calcite content into the Wuding drainage network exhibit a high DIC concentration and percentage flux (Figure 10). Compared with these catchments with weak soil erosion, the strong soil erosion intensity in the Wuding catchment mobilized huge quantities of carbon into the river network. OC burial through sediment storage plays a significant role in re-distributing the exported carbon (Figure 10). Shibata et al. (2005) did not quantify CO$_2$ emissions, which can be exceptionally higher than lateral fluxes, especially in first-order streams with strong boundary turbulence (Marx et al., 2017).

While the proportion of total fluvial carbon export to catchment NEP is significantly higher than other catchment-based estimates, this percentage (i.e., 16%) falls into the range of global-scale estimate of 50–70% by Cole et al. (2007). Compared with other ecosystems, the arid-semiarid Wuding catchment has a lower terrestrial NEP but a higher carbon export rate because of severe soil erosion. The resulting 16% likely represents the upper limit of the proportion of fluvial carbon export to terrestrial NEP. Thus, the conservative estimate by Cole et al. (2007) may have overestimated the importance of fluvial export in modulating terrestrial carbon uptake (Lee et al., 2017). Although 16% of the annual NEP was exported into the Wuding drainage network, it is worth noting that ~42% of it was buried behind check dams and sequestered thereafter. Given the rapid sedimentation and subsequent land management (i.e., cropland reclamation), this OC burial could be regarded as a long-term carbon sink (Zhang et al., 2016; Wang et al., 2011; Wang et al., 2017). Carbon loss through CO$_2$ outgassing can offset only 3% of the catchment NEP (Figure 10). However, this first-order calculation may have underestimated carbon loss because the exported carbon exiting the river mouth is subject to further processing and emission.
From a mass balance point of view, our analysis shows that more carbon was buried in sediments than was emitted as CO$_2$ from rivers and check dam-formed reservoirs in the Wuding catchment. The 2-fold higher OC burial than CO$_2$ emissions is partially due to the strong soil erosion and high sediment trapping efficiency of check dams, resulting in high OC burial rates (Mendonça et al., 2017). Another reason is the low drainage density of the river network governed by dry climate, leading to a small extent of water-air interface for CO$_2$ emissions, though the areal CO$_2$ emission fluxes are similar in magnitude to rivers in other climate zones (Ran et al., 2017; Wallin et al., 2013). However, it should be noted that this comparison was based only on CO$_2$ emissions, since CH$_4$ emissions were not accounted for in the budget, although its contribution is likely negligible owing to high sedimentation rates, low water temperature, and low OC content.

5. Conclusion
The Wuding catchment serves as a typical arid-semiarid study area for assessing the fate of terrestrially-derived riverine carbon. Export of riverine carbon was predominantly composed of DIC due to widespread carbonate dissolution and groundwater input. Export of DOC and DIC displayed pronounced spatial and temporal variability. Continuous mineralization of the labile fraction of DOC has probably caused the spatially downstream decline in DOC concentration in low order streams. Enhanced organic matter inputs from agricultural tillage in spring and from terrestrial ecosystems in summer resulted in higher DOC concentrations. POC content was characterized by strong seasonal variability throughout the catchment or at the catchment outlet, indicating the control of gully erosion in wet seasons in mobilizing subsurface soils with low carbon content. The POC flux is comparable to the DIC flux on an annual basis, both of which are an order of magnitude larger than the DOC flux.

CO$_2$ emissions represented an important pathway, amounting to 20% of the total riverine carbon flux. Carbon isotopic analysis showed that the age of the emitted CO$_2$ ranged from 810 to 1890 years. Outgassing of this old carbon previously stored in soils has important biogeochemical implications for carbon budget studies. Our first-order estimate suggests that the riverine carbon export from terrestrial ecosystems was significant when compared with NEP, representing 16% of the latter. Riverine carbon cycle in the Wuding catchment has been greatly modified by check dams through sediment storage. Approximately 42% of the total riverine carbon was buried, roughly twice the carbon loss through CO$_2$ emissions. With more new check dams under construction, OC burial will be a more vital component in reshaping the carbon balance. In addition, episodic storms play a disproportionate role in annual carbon export and future sampling strategy should attempt to capture these short-duration, high-discharge events to better constrain uncertainty.

Through a comprehensive assessment of riverine carbon in terms of downstream export, OC burial in sediments, and CO$_2$ emissions in a complete catchment, the present research can be treated as an exploratory study integrating river carbon cycle with terrestrial carbon uptake by ecosystems. A better understanding of linkages between terrestrial ecosystems and fluvial carbon export, and of interactions between environmental controls and human impacts, is essential for providing additional constraints on the accuracy of carbon budget estimates. Moreover, for future
studies of riverine CO₂ emissions, it is critical to trace its isotopic composition and age to more holistically explore its biogeochemical significance.

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References


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### Table 1. CO₂ emissions from check dam-formed reservoirs within the Wuding catchment.

<table>
<thead>
<tr>
<th>Subcatchment</th>
<th>Spring (120 d)</th>
<th>Summer (123 d)</th>
<th>Autumn (122 d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandy subcatchment</td>
<td>28±36.2</td>
<td>-12±19.3</td>
<td>15.3±5.6</td>
</tr>
<tr>
<td>Loess subcatchment</td>
<td>-2.9±9.9</td>
<td>-17.4±14.8</td>
<td>11.5±17.6</td>
</tr>
<tr>
<td>Total</td>
<td>81±165</td>
<td>-208±156</td>
<td>165±163</td>
</tr>
</tbody>
</table>

### Table 2. Carbon isotope signature of the emitted CO₂ from the Wuding catchment.

<table>
<thead>
<tr>
<th>Site</th>
<th>pMC (year)</th>
<th>δ¹³C (%)</th>
<th>Age (year)</th>
<th>pMC</th>
<th>δ¹³C (%)</th>
<th>Age (year)</th>
<th>δ¹³C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>82.3±0.3</td>
<td>-32.3</td>
<td>1560</td>
<td>88±0.3</td>
<td>-33.9</td>
<td>1030</td>
<td>84.2±0.3</td>
</tr>
<tr>
<td>S2</td>
<td>79±0.3</td>
<td>-27.5</td>
<td>1890</td>
<td>84±0.3</td>
<td>-22.2</td>
<td>1400</td>
<td>86±0.3</td>
</tr>
<tr>
<td>S3</td>
<td>85.1±0.3</td>
<td>-26.5</td>
<td>1290</td>
<td>90.4±0.3</td>
<td>-22.7</td>
<td>810</td>
<td>90.3±0.3</td>
</tr>
<tr>
<td>S4*</td>
<td>80.9±0.3</td>
<td>-34.3</td>
<td>1700</td>
<td>89.3±0.3</td>
<td>-19.3</td>
<td>910</td>
<td></td>
</tr>
</tbody>
</table>

*Sample for site S4 in October was lost during treatment.
Figure 1. Map of the Wuding catchment showing the sampling sites. SD1–SD4 and S1–S4 denote the sampling location of sediment coring behind check dams and carbon isotope, respectively.

Figure 2. Spatial changes in DOC along the 6 Strahler stream orders in (a) loess subcatchment and (b) sandy subcatchment. Error bars denote the standard deviation.
Figure 3. Spatial changes in DIC along the 6 Strahler order streams in (a) loess subcatchment and (b) sandy subcatchment. Error bars denote the standard deviation.

Figure 4. Longitudinal changes in CO₂ emissions along stream order in (a) the sandy subcatchment and the loess subcatchment and (b) the entire Wuding catchment (b). Error bars denote the standard deviation.
Figure 5. Seasonal variations in conventional age of the emitted CO$_2$ from the Wuding catchment.

Figure 6. Variations of POC content with depth in buried sediments behind check dams (refer to Figure 1 for their location).
Figure 7. Spatial distribution of NPP within the Wuding catchment in 2015 showing significant differences between the sandy and loess subcatchments.

Figure 8. Temporal variation in CO$_2$ efflux during a high-discharge flood event in the Wuding River at Baijiachuan gauge (refer to Figure 1 for its location).
Figure 9. Relationship between $\delta^{13}C$ and $\Delta^{14}C$ of the emitted CO$_2$ from the Wuding catchment.

Figure 10. Fluvial carbon budget within the Wuding catchment in relation to terrestrial ecosystem production (unit: $\times 10^{10}$ g C yr$^{-1}$). The inserted pie chart denotes the partitioning of fluvial carbon among its five phases.