



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
15 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
20 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
25 carbon flux was $(7\pm 1.9)\times 10^{10}$ g C year⁻¹ and dominated by DIC and POC. Total CO₂ emissions from water surface were $(3.7\pm 0.5)\times 10^{10}$ 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 $(7.8\pm 4.1)\times 10^{10}$
30 g C year⁻¹, representing 42% of the total riverine carbon export from terrestrial ecosystems on an annual basis $((18.5\pm 4.5)\times 10^{10}$ 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.

35 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
40 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 C 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 (*p*CO₂) 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 *p*CO₂ 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 *p*CO₂ 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.

135 Water samples for dissolved organic and inorganic carbon (DOC and DIC) were filtered on site
shortly after collection using Whatman filters (0.45 μm pore size). DOC was analyzed on an
Elementar Vario TOC select analyzer following procedures in Ran et al. (2017). Total alkalinity
was determined by titration in the field and DIC was calculated from total alkalinity, pH, and
140 temperature by using the program CO_2calc (Robbins et al., 2010). We also drilled sediment cores
within 4 check dams by using a soil auger (Figure 1). Sediment samples were collected at 20-cm
intervals and the drilling depth was 4–6 m depending on sedimentation history. Samples
collected from filters and sediment coring for particulate organic carbon (POC) were first dried
for 12 h and then pulverized in a mortar. The obtained fine powder was fumigated by
concentrated HCl for 24 h to remove inorganic carbon and measured using a PerkinElmer 2400
145 Series II CHNS/O elemental analyzer (analytical error: <0.3%). Isotopic signature of the eleven
 SrCO_3 samples was determined using accelerator mass spectrometry (AMS) at the Beta Analytic
Radiocarbon Dating Laboratory (Miami, USA). The $\Delta^{14}\text{C}$ values were reported as percent
modern carbon (pMC) based on modern standard and conventional radiocarbon ages were
calculated using the ^{14}C half-life (5570 years) following the procedures outlined by Stuiver and
150 Polach (1977). Meanwhile, stable carbon isotope ($\delta^{13}\text{C}$) was simultaneously reported and its
values were reported in ‰ relative to the VPDB standard at a precision of $\pm 0.3\text{‰}$ or better.

2.3 Carbon fluxes and CO_2 emissions

Using the monthly sampling results and daily flow and sediment records measured at the
155 catchment outlet Baijiachuan 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
160 by multiplying annual sediment deposition rate by POC content.

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

$$165 \quad F_{\text{CO}_2} = 1000 \times \left(\frac{dp\text{CO}_2}{dt} \right) \left(\frac{V}{RTS} \right) \quad (1)$$

where, $dp\text{CO}_2/dt$ 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).

170 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
175 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 CO₂
emissions for equally four months (i.e., spring sampling: January–April (120 d); summer
180 sampling: May–August (123 d); autumn sampling: September–December (122 d)). With this
assumption in mind, we calculated the yearly CO₂ 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
185 (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
190 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:
$$\text{NEP} = \text{NPP} - R_h \quad (2)$$

To calculate R_h , total soil respiration (S_R) was first derived from the global soil CO₂ efflux
195 database described by Raich and Potter (1995) who estimated S_R at a 0.5° 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.

200 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,
205 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 3th–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
210 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
215 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 $39.2 \pm 7.8 \text{ mg L}^{-1}$ 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 $3.3 \pm 0.4 \text{ mg L}^{-1}$ and $0.61 \pm 0.29\%$, respectively. Because the flow regime in 2017 was significantly biased due to an extreme flood in July (spontaneous discharge: $4490 \text{ m}^3 \text{ s}^{-1}$; 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 $(7 \pm 1.9) \times 10^{10} \text{ g C}$, of which the DIC, DOC, and POC fluxes were $(3 \pm 0.6) \times 10^{10}$, $(0.3 \pm 0.03) \times 10^{10}$, and $(3.7 \pm 1.8) \times 10^{10} \text{ g C}$, 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 $\text{mmol m}^{-2} \text{ d}^{-1}$, respectively. In the loess subcatchment, it was 70, 78, 80, 57, 209, 268 $\text{mmol m}^{-2} \text{ d}^{-1}$, respectively. In association with the water surface area over the three seasons (Table S1 in Supplementary), total CO₂ emissions in 2015 were $(3.7 \pm 0.5) \times 10^{10} \text{ g C}$, 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 $66.5 \text{ mmol m}^{-2} \text{ d}^{-1}$ in spring, -33.5 to $19 \text{ mmol m}^{-2} \text{ d}^{-1}$ in summer, and -17 to $42.1 \text{ mmol m}^{-2} \text{ d}^{-1}$ in autumn. The mean CO₂ efflux for these three seasons was 4.2, -16.2 , and $12.3 \text{ mmol m}^{-2} \text{ d}^{-1}$, 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 $-2.9 \text{ mmol m}^{-2} \text{ d}^{-1}$, respectively. Currently, there are 337 reservoirs in the catchment with the water surface varying from 0.01 to 10.35 km^2 (Figure S2 in Supplementary). Total water surface area is 107 km^2 , including 31.8 km^2 in the sandy subcatchment and 75.2 km^2 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



260 0.05×10^{10} 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
265 depleted $\delta^{13}\text{C}$ signature (-30.2‰). With the $\delta^{13}\text{C}$ values most depleted in spring, the mean $\delta^{13}\text{C}$ values in spring, summer, and autumn were -30.2‰, -24.5‰, and -23.2‰, respectively. The $\Delta^{14}\text{C}$ 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
270 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
275 94.3% and total sediment deposition rate is 3720×10^{10} 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
280 $0.21 \pm 0.11\%$. Total OC burial behind check dams was estimated to be $(7.8 \pm 4.1) \times 10^{10}$ 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 g C m^{-2} and the total NPP was $(668 \pm 60) \times 10^{10}$ g C. Based on the global soil
285 respiration flux database (Raich and Potter, 1995), the R_h for this catchment is about $450 \text{ g C m}^{-2} \text{ year}^{-1}$. 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 $183 \text{ g C m}^{-2} \text{ year}^{-1}$ or 554×10^{10} g C
290 year⁻¹ in total. By subtracting R_h from NPP, a first-order estimation shows a NEP of $38 \text{ g C m}^{-2} \text{ year}^{-1}$ or 114×10^{10} 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

295 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
300 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
305 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).

310 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
315 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
320 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).

325 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
330 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
335 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
340 stronger impact of groundwater input, although both sub-catchments 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
345 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).

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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 *p*CO₂ 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.

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370 **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).

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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

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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.

395 CO₂ 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
CO₂ 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
400 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
405 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
410 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
415 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
CO₂ or CH₄ along fluvial delivery. It is important to recognize that, as a top priority soil
420 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
425 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 CO₂

430 CO₂ emissions from rivers originate from decomposition of organic matter derived from
terrestrial ecosystems and/or aquatic photosynthesis. The emitted CO₂ exhibited a ¹³C-depleted
 $\delta^{13}\text{C}$ 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



435 (Zhang et al., 1995). Although we did not analyze the $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ of DIC by 3–5‰ (Doctor et al., 2008). Therefore, the emitted CO_2 is less
440 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 $\delta^{13}\text{C}$. This is
consistent with the $\delta^{13}\text{C}$ changes in soil CO_2 in sandy catchments (Gillon et al., 2012).

Instead, the $\delta^{13}\text{C}$ 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
445 in dry seasons dominated by groundwater inputs, the more depleted $\delta^{13}\text{C}$ in spring demonstrated
the contribution of CO_2 in soil water to CO_2 emissions. In comparison, the $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ end-member of -12‰ (Brunet et al.,
2009). Constrained by dry climate, major crops in the catchment are predominantly C4 plants,
450 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 $^{12}\text{CO}_2$ may have also contributed to the more depleted $\delta^{13}\text{C}$
455 values in the emitted CO_2 than that of the C4 plants. Aquatic algae with their $\delta^{13}\text{C}$ 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
460 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 $\Delta^{14}\text{C}$ exhibited a positive correlation with $\delta^{13}\text{C}$, showing an increasing
465 trend from spring through summer to autumn (Figure 9). Because DIC from carbonate
dissolution is characterized by typically enriched $\delta^{13}\text{C}$ and highly depleted $\Delta^{14}\text{C}$ (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
470 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
475 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.



480 Special efforts are therefore needed to quantify this old CO₂ outgassing and assess its
significance for global carbon cycle and climate mitigation over longer timescales than recent
sharp anthropogenic CO₂ emissions (i.e., since the 1850s).

4.4 Riverine carbon budget and NEP

485 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 Luyssaert et al., 2007) while significantly
higher than that for other ecosystems. For example, it is 63% in the tropical Nyong River
490 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 CO₂ 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,
495 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.

500 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
505 exported carbon (Figure 10). Shibata et al. (2005) did not quantify CO₂ emissions, which can be
exceptionally higher than lateral fluxes, especially in first-order streams with strong boundary
turbulence (Marx et al., 2017).

510 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
515 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
520 et al., 2017). Carbon loss through CO₂ 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.



525 From a mass balance point of view, our analysis shows that more carbon was buried in sediments
than was emitted as CO₂ from rivers and check dam-formed reservoirs in the Wuding catchment.
The 2-fold higher OC burial than CO₂ 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
530 climate, leading to a small extent of water-air interface for CO₂ emissions, though the areal CO₂
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 CO₂ emissions,
since CH₄ 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.

535 **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
540 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,
545 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.

CO₂ emissions represented an important pathway, amounting to 20% of the total riverine carbon
flux. Carbon isotopic analysis showed that the age of the emitted CO₂ ranged from 810 to 1890
550 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,
555 roughly twice the carbon loss through CO₂ 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.

560 Through a comprehensive assessment of riverine carbon in terms of downstream export, OC
burial in sediments, and CO₂ 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
565 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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Table 1. CO₂ emissions from check dam-formed reservoirs within the Wuding catchment.

Subcatchment	Spring	Summer	Autumn	Spring (120 d)	Summer (123 d)	Autumn (122 d)
	mmol m ⁻² d ⁻¹			million mol		
Sandy subcatchment	28±36.2	-12±19.3	15.3±5.6	107±138	-47±75	59±22
Loess subcatchment	-2.9±9.9	-17.4±14.8	11.5±17.6	-26±89	-161±137	106±161
Total				81±165	-208±156	165±163

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

Site	Spring			Summer			Autumn		
	pMC	Age (year)	δ ¹³ C (‰)	pMC	Age (year)	δ ¹³ C (‰)	pMC	Age (year)	δ ¹³ C (‰)
S1	82.3±0.3	1560	-32.3	88±0.3	1030	-33.9	84.2±0.3	1380	-24.4
S2	79±0.3	1890	-27.5	84±0.3	1400	-22.2	86±0.3	1220	-19.9
S3	85.1±0.3	1290	-26.5	90.4±0.3	810	-22.7	90.3±0.3	820	-25.2
S4*	80.9±0.3	1700	-34.3	89.3±0.3	910	-19.3			

745 *Sample for site S4 in October was lost during treatment.

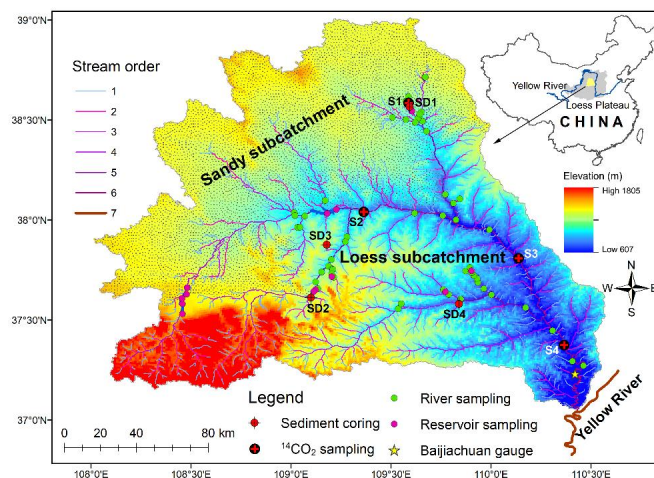


Figure 1. Map of the Wuding catchment showing the sampling sites. SD1–SD4 and S1–S4 denote the sampling location of sediment coring behind check dams and carbon isotope, respectively.

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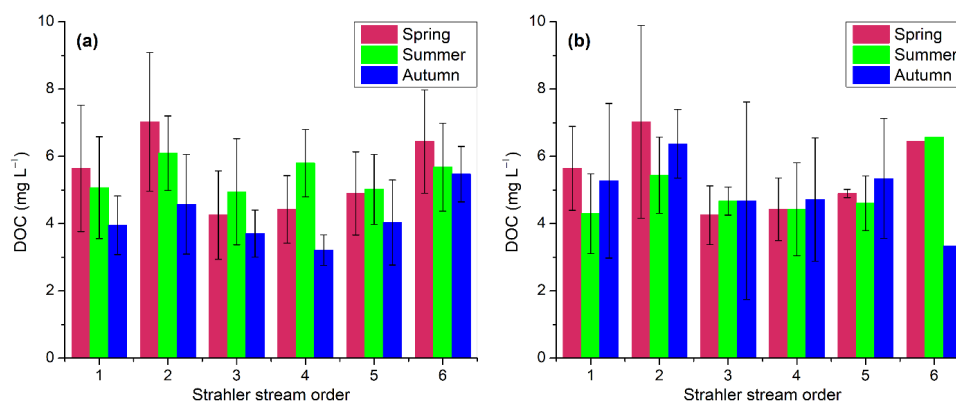
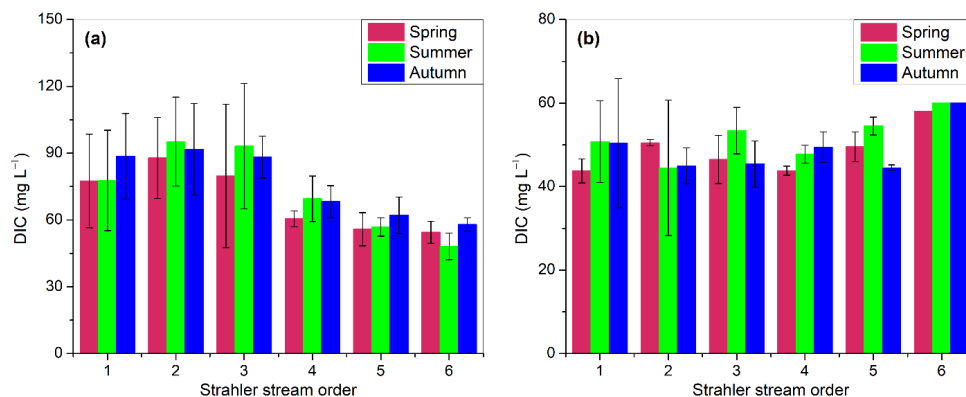
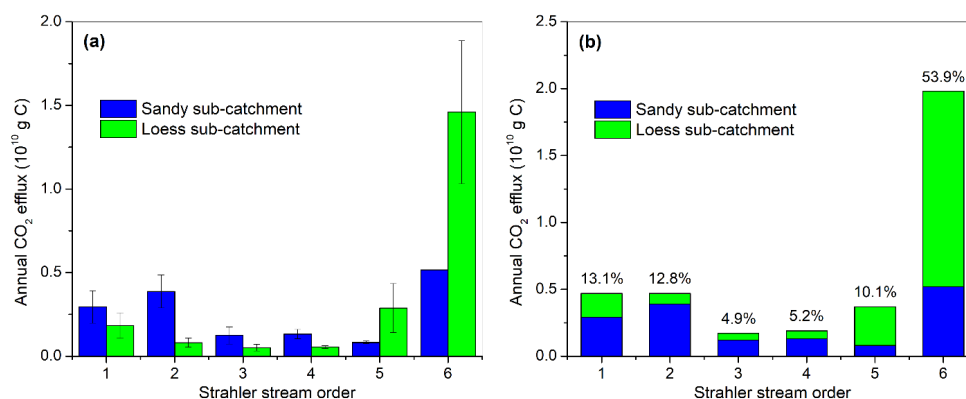


Figure 2. Spatial changes in DOC along the 6 Strahler stream orders in (a) loess subcatchment and (b) sandy subcatchment. Error bars denote the standard deviation.



755 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.



760 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.

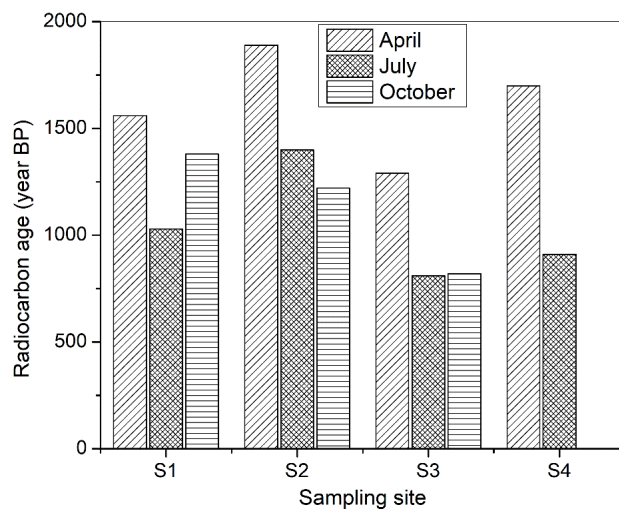
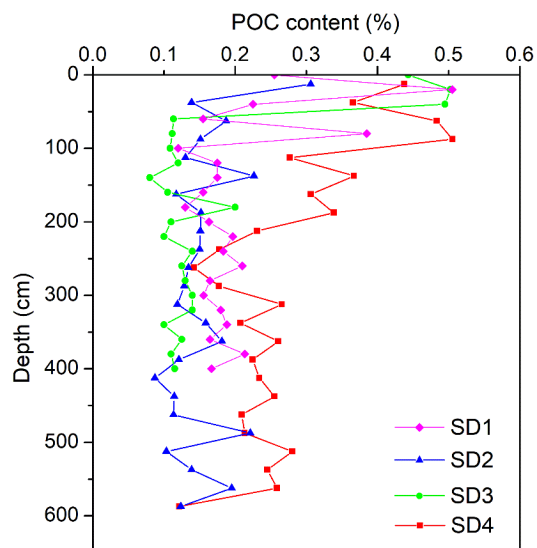


Figure 5. Seasonal variations in conventional age of the emitted CO₂ from the Wuding catchment.



765 Figure 6. Variations of POC content with depth in buried sediments behind check dams (refer to Figure 1 for their location).

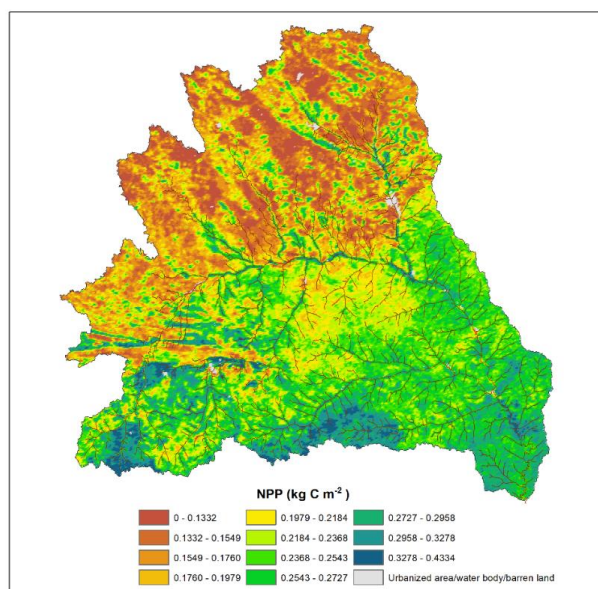


Figure 7. Spatial distribution of NPP within the Wuding catchment in 2015 showing significant differences between the sandy and loess subcatchments.

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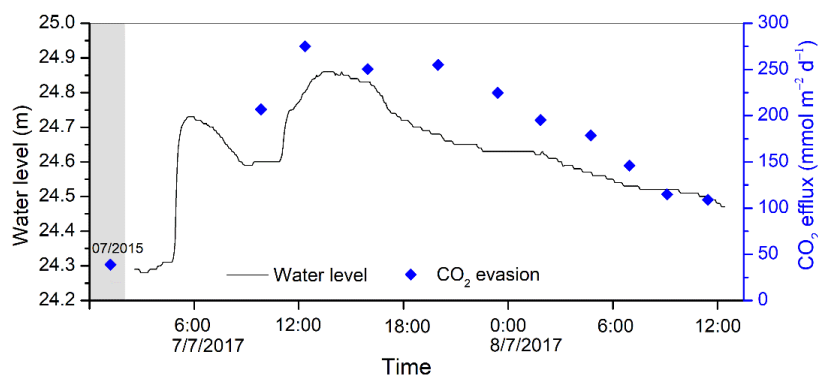


Figure 8. Temporal variation in CO₂ efflux during a high-discharge flood event in the Wuding River at Baijiachuan gauge (refer to Figure 1 for its location).

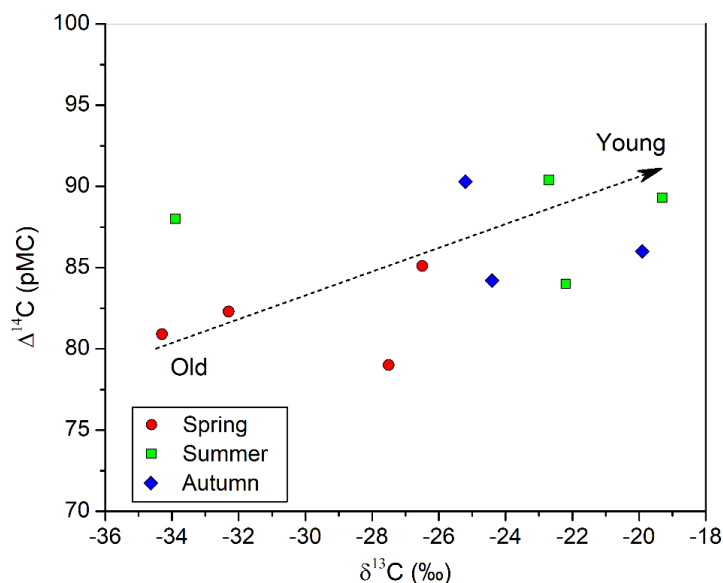


Figure 9. Relationship between $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ of the emitted CO_2 from the Wuding catchment.

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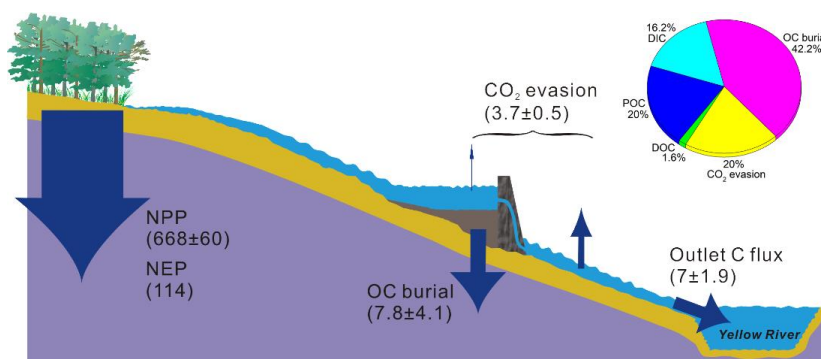


Figure 10. Fluvial carbon budget within the Wuding catchment in relation to terrestrial ecosystem production (unit: $\times 10^{10} \text{ g C yr}^{-1}$). The inserted pie chart denotes the partitioning of fluvial carbon among its five phases.

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