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 represents a key component of the global carbon cycle. In this study we quantify the fate of riverine carbon within the Wuding River catchment on the Chinese Loess Plateau. Export of dissolved organic and inorganic carbon (DOC and DIC) exhibited pronounced spatial and temporal variability. While DOC concentration first presented a downward trend along the river course and then increased in the mainstem river, it showed no significant seasonal differences and was not sensitive to flow dynamics. This likely reflects the predominance of groundwater input over the entire year and its highly stable DOC. 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%) showed strong seasonal variability with low values in the wet season owing to input of deeper soils by gully erosion. The downstream carbon flux was $(7\pm1.9)\times10^{10}$ g C year^{-1} and dominated by DIC and POC. Total CO_2 emissions from water surface were $(3.7\pm0.5)\times10^{10}$ g C year^{-1}. Radiocarbon analysis revealed that the degassed CO_2 was 810–1890 years old, indicating the release of old carbon previously stored in soil horizons. Riverine carbon export in the Wuding River catchment has been greatly modified by check dams. Our estimate shows that carbon burial through sediment storage was $(7.8\pm4.1)\times10^{10}$ g C year^{-1}, representing 42% of the total riverine carbon export from terrestrial ecosystems on an annual basis ($(18.5\pm4.5)\times10^{10}$ g C year^{-1}). Moreover, the riverine carbon export accounted for 16% of the catchment's net ecosystem production (NEP). It appears that the estimate of terrestrial NEP in this arid-semiarid catchment has been significantly offset by lateral transport of carbon from the terrestrial biosphere to the drainage network.

1. Introduction

Rivers play an exceptionally significant role in the global carbon cycle by directly linking terrestrial ecosystems and the oceans (Cole et al., 2007;Regnier et al., 2013;Drake et al., 2017). 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 the river course. Riverine carbon is subject to a number of physical and biogeochemical processes such as burial, evasion, *in situ* production, and decomposition. The CO_2 emissions from water surface of global rivers and streams combined are conservatively estimated at 1.8–3.2 Pg C $year^{-1}$ (Raymond et al., 2013;Drake et al., 2017). In addition, carbon loss due to long-term sediment storage through burial is also substantial, ranging from 0.15 to 0.6 Pg C $year^{-1}$ (Battin et al., 2009;Cole et al., 2007;Mendonça et al., 2017;Clow et al., 2015). Inclusion of CO_2 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 considerably increasing over the last 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 the drainage network to the catchment outlet in the medium-sized Wuding River catchment on the arid-semiarid Loess Plateau (northern China). The overall aim of this study was to quantify the fate of riverine carbon among its three pathways, including downstream export to catchment outlet, CO_2 evasion from water surface, and organic carbon (OC) burial through sediment storage, within the arid-semiarid Wuding River 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 CO_2 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 CO_2 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 is located on the central Chinese Loess Plateau (Fig. 1). Its drainage area is 30,261 km^2 and mean water discharge during the period 1956–2017 is 35 m^3 s^{-1} or 11.2×10^8 m^3 $year^{-1}$. Based on geomorphological landscape, the catchment can be further divided into the southeastern loess

subcatchment generally covered with 50–100 m deep loess soils and the northwestern sandy subcatchment composed mainly of aeolian sand (Fig. 1). While grassland is extensive in the sandy subcatchment, agriculture and grassland are the primary land use types in the loess subcatchment with traditional ploughing tillage as the dominant land management practice. Annual precipitation during the period 1956–2004 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 (Li et al., 2007). Due to highly erodible loess and sparse vegetation, the Wuding River catchment once suffered severe soil erosion of a rate of 7000 t km^{-2} per year during the period 1956–1969 (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). 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 CO_2 partial pressure (pCO_2) 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 is provided here. Three sampling campaigns were conducted in the Wuding River 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 (Fig. 1). Moreover, monthly samples were collected at the catchment outlet Baijiachuan gauge (Fig. 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* CO_2 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 CO_2 concentration changes inside the chamber over time. We also measured *in situ* surface water pCO_2 using the headspace equilibrium method by means of the Li-7000 gas analyzer (Müller et al., 2015). Triplicate measurements at each site showed a high consistency with 3% variability only. Finally, surface water pCO_2 was calculated and calibrated with the solubility constants for CO_2

from Weiss (1974). To determine the age of the emitted CO_2, we collected samples for ^{14}C analysis by using the precipitation method widely used in groundwater dating studies (Vita-Finzi and Leaney, 2006). After the CO_2 emissions measurement, the accumulated CO_2 in the chamber was directly injected into 50 mL $SrCl_2$ 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.

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). Triplicate injections indicated an analytical precision of less than 3%, and the average of the three injection results was calculated to represent the DOC concentration. Total alkalinity was determined by triplicate titrations in the field with 0.1 M HCl and methyl orange indicator. DIC was calculated from total alkalinity, pH, and temperature by using the program CO_2calc (Robbins et al., 2010). Both DOC and DIC data have been presented in Ran et al. (2017). We also drilled sediment cores within 4 check dams by using a soil auger (Fig. 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 at 65 °C for 24 h to remove inorganic carbon and measured using a PerkinElmer 2400 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 ^{14}C results were reported as percent modern carbon (pMC) based on modern standard and conventional radiocarbon ages (year before present, BP) were calculated using the ^{14}C half-life (5568 years) following the procedures outlined by Stuiver and Polach (1977). Meanwhile, stable carbon isotope ($\delta^{13}C$) was simultaneously analyzed by the AMS and its values were reported in ‰ relative to the VPDB standard at a precision of ±0.3‰ or better.

2.3 Carbon fluxes and CO_2 emissions

Using the monthly sampling results of DOC and DIC concentrations in water and POC concentration (POC%) in the total suspended sediments (dry weight) measured at the catchment outlet Baijiachuan gauge, we calculated the yearly DOC, DIC, and POC fluxes from the Wuding River catchment. Because daily flow and sediment records are available, the yearly carbon flux was calculated by using the Beale's stratified ratio estimator which generally exhibits greater estimation accuracy and lower bias than other flux estimation techniques (Lee et al., 2016). The estimator can be expressed as follows:

$$\mu_y = \mu_x \frac{m_y}{m_x} \left(\frac{1+\frac{1}{n}\frac{S_{xy}}{m_x m_y}}{1+\frac{1}{n}\frac{S_x^2}{m_x^2}} \right) \quad (1)$$

where, μ_y is the estimated flux, μ_x is the mean daily water discharge for the year measured, m_y is the mean daily carbon flux for the days on which the dissolved and particulate carbon concentrations were determined, m_x is the mean daily water discharge for the days on which the

carbon concentrations were determined, and n is the number of days on which the carbon concentrations were determined. Furthermore,

$$S_{xy} = \frac{1}{(n-1)}\sum_{i=1}^{n} x_i y_i - n m_x m_y \quad (2)$$

$$S_x^2 = \frac{1}{(n-1)}\sum_{i=1}^{n} x_i^2 - n m_x^2 \quad (3)$$

where, x_i is the individual measured discharge, y_i is the daily carbon flux for each day on which the dissolved and particulate carbon concentrations were measured. Clearly, the yearly DOC, DIC, and POC fluxes are derived from m_y/m_x, which is defined as the ratio of the mean of measured fluxes to the mean of water discharge of the days when fluxes were quantified. This ratio is used with the overall mean water discharge (μ_x) to estimate the annual carbon flux. The calculated annual fluxes of DOC, DIC, and POC were then added up to determine the total downstream carbon export from the Wuding River catchment.

Areal fluxes of CO_2 emissions across water-air interface (F_{CO_2}, mmol m^{-2} d^{-1}) were determined from the slope of the linear regression of pCO_2 against time ($r^2 \geq 0.97$):

$$F_{CO_2} = 1000 \times \left(\frac{dpCO_2}{dt}\right)\left(\frac{V}{RTS}\right) \quad (4)$$

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). Particularly, results of the areal CO_2 emissions have been presented in our earlier work (Ran et al., 2017).

Total OC burial behind check dams was estimated by multiplying annual sediment deposition rate by POC% in sediments. Our earlier work (Ran et al., 2013) has estimated the average annual sediment deposition rate behind all check dams in the study catchment by considering sediment input into each check dam and its sediment trapping efficiency. To calculate CO_2 efflux from the entire catchment, we estimated the areal extent of river water surface by using the 90-m resolution Shuttle Radar Topography Mission (SRTM) DEM data set (Ran et al., 2015b). A threshold value of 100 cells was first set to delineate the drainage network on the assumption that a stream initiates within the cells. The delineated network was then classified using the Strahler ordering system (Strahler, 1957). Because the width of all rivers is less than the resolution and it fluctuates between dry and wet seasons, we measured widths of all sampled rivers and aggregated them 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 and reservoirs were calibrated through ground truthing. We further assumed that each round of field sampling is 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 first-order estimate of yearly CO_2 efflux from both rivers and reservoirs.

2.4 Estimation of terrestrial ecosystem production

To further evaluate the riverine carbon export, we compared the total carbon entering the drainage network with the 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 heterotrophs 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:

$$\mathrm{NEP} = \mathrm{NPP} - R_h \quad (5)$$

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° 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} in the three sampling seasons with both the lowest and highest values observed in spring. The DOC averaged 5±1.6, 5.2±1.3, and 4.5±1.6 mg L^{-1} in spring, summer, and autumn, respectively, without discernible seasonal variation in both the loess and sandy subcatchments. Although statistically insignificant, DOC first exhibited a downward trend along the river course and then increased in the 6th order mainstem river in both subcatchments (Fig. 2). While the DOC in the headwater 1st–2nd order streams (4.7–5.4 mg L^{-1}) was on average 9–21% higher than in the 3th–5th order streams (4.2–4.9 mg L^{-1}), it increased to 5.2–6.1 mg L^{-1} in the 6th order mainstem river, representing an increase of 18–36% relative to the 3th–5th order streams. The POC% varied from 0.28% to 1.72% and spatially remained largely constant from the headwater stream to the mainstem (Table S1 in Supplement). However, it showed pronounced seasonal variations. The averaged POC% in spring, summer, and autumn was 0.91±0.32%, 0.44±0.1%, and 0.69±0.21%, respectively.

With the pH in the 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±21.4, 66.7±23.8, and 67.7±21.9 mg L^{-1}, respectively. In the loess subcatchment, the DIC declined remarkably from headwater streams towards the mainstem river (one-way ANOVA test, $p \leq 0.05$; Fig. 3a); but it remained constant in the sandy subcatchment from the 1st order through the 5th order streams (Fig. 3b). The high DIC values in the 6th order mainstem river in the sandy subcatchment (Fig. 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±4.7 mg L^{-1}. The DOC concentrations were 16% higher in the wet season than in the dry season while the POC% (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±0.23%, respectively (Table S2 in Supplement). The flow regime in 2017 was significantly biased by an extreme flood in July (rainfall of 203 mm and spontaneous discharge of 4490 m^3 s^{-1}; see He et al. (2018) and Fig. S1 in Supplement) with the precipitation ~26% higher than the long-term average. Hence, we used the hydrological data for 2015, which is 4% lower than the long-term average, to calculate downstream carbon export by assuming that carbon concentration was comparable in 2015 and 2017. The annual downstream carbon export at this gauge was estimated to be (7±1.8)×10^{10} g C, of which the DIC, DOC, and POC fluxes were (3 ±0.4)×10^{10}, (0.3±0.03)×10^{10}, and (3.7±1.8)×10^{10} 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 CO_2 emissions from rivers and check dam-formed reservoirs

In our earlier work, we calculated the areal CO_2 emissions from rivers (Ran et al., 2017). In the sandy subcatchment, the mean CO_2 efflux from the 1st order headwater streams to the 6th order mainstem river 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 S4 in Supplement), total CO_2 emissions in 2015 were (3.65±0.5)×10^{10} g C, of which 42% was degassed from the sandy subcatchment rivers and 58% from the loess subcatchment rivers. At the catchment scale, CO_2 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 (Fig. 4a). The headwater 1st and 2nd order rivers accounted for 26% of the total CO_2 efflux (Fig. 4b). With the biggest areal extent of water-air interface (43% of the total; Table S4 in Supplement), the 6th order mainstem river contributed 54% of the total CO_2 efflux (Fig. 4b).

CO_2 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 CO_2 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 (Fig. 1). Reservoir CO_2 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 with the water surface varying from 0.01 to 10.35 km^2 (Fig. S2 in Supplement). 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 area remained constant (i.e., no significant seasonal fluctuations), the annual CO_2 emissions were conservatively estimated at 38 million mol (or 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%. Thus, the total CO_2 outgassing from rivers and reservoirs was (3.7±0.5)×10^{10} g C in 2015.

The isotopic composition of the emitted CO_2 varied significantly between sampling sites and between seasons (Table 2). The sandy subcatchment (site S1; Fig. 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; Fig. 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 BP, 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} g year^{-1} (Ran et al., 2013). Analysis of sediment profiles from the four check dams (Fig. 1) shows the POC% varied from 0.1% to 0.5% with high POC% values in the surface sediments (0–60 cm) and it declined rapidly with depth and remained constant thereafter at around 0.2% (Fig. 6; Table S3 in Supplement). The mean POC% was 0.21±0.11%. Total OC burial behind check dams was estimated to be $(7.8\pm4.1)\times10^{10}$ g C year^{-1}.

3.4 Terrestrial NPP and NEP fluxes

The NPP in the Wuding River catchment in 2015 was spatially heterogeneous (Fig. 7). The mean areal NPP was 221 g C m^{-2} and the total NPP was $(668\pm60)\times10^{10}$ g C. Based on the global soil respiration flux database (Raich and Potter, 1995), the S_R for this catchment is the range of 400–500 g C m^{-2} year^{-1}. Hence, we used 450±50 g C m^{-2} year^{-1} to represent its soil respiration. This rate is consistent with recent measurements under different vegetation types in this arid-semiarid region (e.g., Fu et al., 2013; Jia et al., 2013). 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 dry grassland (Li et al., 2007). 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±20 g C m^{-2} year^{-1}. By subtracting R_h from NPP, a first-order estimation shows a NEP of 38±28 g C m^{-2} year^{-1} or $(114\pm85)\times10^{10}$ 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

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). For the Wuding River catchment, its DOC concentrations are comparable to the global average DOC of 5.4 mg L^{-1} while its POC% is lower than most rivers in the world (mean: 0.95%; Ludwig et al., 1996). Stream water OC is susceptible to degradation by microbial reactions during transit (Raymond et al., 2016). The downstream DOC decline in the 1st–5th order streams likely suggests the mineralization of the bioavailable fraction of DOC along the river course (Fig. 2), especially in spring and autumn. This can also be seen from the 9–21% higher DOC concentrations in the headwater 1st–2nd order streams than in the 3rd–5th order streams. This mineralization is generally associated with increasing water residence time for bacterial respiration in downstream

streams due to longer travel times which increase the potential for in-stream processes on DOC. In contrast, the deeply incised headwater streams in the Wuding River catchment exhibit an opposite landscape with the flow velocities increasing from headwater streams to the mainstem river (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 river reflect direct DOC influxes from low-order streams (Fig. 1) and the mixture of carbon from the two subcatchments. Owing to the insignificant seasonal difference in DOC concentration measured across the catchment, there was no discernible relationship 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, carbon 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 deeper soils or released into the atmosphere after mineralization. Lateral export into the drainage network by surface runoff is negligible. The predominance of groundwater input over the entire year and its highly stable DOC illustrate 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% in suspended sediments in the Wuding River catchment is at the lower end of global rivers (range: 0.3%–10.1%; Ludwig et al., 1996), which likely reflects the contribution of ancient sedimentary OC of ~0.5% to POC in fluvial sediments (Meybeck, 1993). This can also be seen from the isotopic signature of the Yellow River sediment that is primarily derived from the Loess Plateau, especially the studied Wuding River and other nearby rivers. By using carbon isotope techniques, Wang et al. (2012) discovered that the exported POC is quite old (4110–8040 years BP) and is largely derived from highly weathered loess soils and ancient kerogen. The much lower POC% in summer than in spring and autumn reflected the impact of gully erosion, which is quite common on the Loess Plateau during heavy rainstorm periods (Wang et al., 2017). Gully erosion is usually associated with the mobilization of sedimentary rocks that generally have a substantially lower POC% (i.e., 0.2–0.3%; Zhang et al., 1995; Ran et al., 2015a) than the surface soils. As a result, input of sedimentary rocks into rivers caused the lower POC% in summer, thereby generating a negative correlation between POC% and sediment concentration.

With respect to CO_2 outgassing, the higher effluxes in the drier sandy subcatchment reflect the 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 CO_2 outgassing. Thus, the CO_2 emissions results reveal largely the groundwater-derived CO_2 degassing. This may have caused considerable uncertainty in the

annual CO_2 outgassing estimation (see discussion below). Although the sandy subcatchment rivers exhibited higher areal CO_2 effluxes than that in the loess subcatchment in all the 1st–5th order rivers except the 6th order mainstem river, the lower contribution of CO_2 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 S4 in Supplement).

Unlike natural rivers showing strong CO_2 outgassing, the measured reservoirs presented considerably lower and even negative CO_2 effluxes. The contrasting magnitude and direction of CO_2 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 phytoplankton through photosynthesis. In the sandy subcatchment, the predominance of groundwater with high pCO_2 has probably maintained its relatively higher reservoir CO_2 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 phytoplankton like algae, 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 CO_2 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 CO_2 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 26% 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 bioavailable fraction of DOC could be quickly transported downstream, resulting in a greater export of DOC (Raymond et al., 2016). Clearly, this positive response contradicts the indiscernible relationship between DOC and flow discharge within the catchment. This is probably because the three intensive seasonal samplings did not capture the carbon export in high-flow conditions. The flow discharge during the three sampling periods varied in the range of 0.002–105 m^3 s^{-1}, which largely reflects the carbon export processes during low flow to, at most, medium flow conditions. In comparison, the high-frequency sampling at Baijiachuan gauge captured the carbon export during extremely high flows (200–1760 m^3 s^{-1}, Table S2 in

Supplement). In addition, 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% values in the wet season may have reflected the hydrodynamic sorting of terrestrially derived organic carbon. Recent studies on size distribution of POC% in the Yellow River (the Loess Plateau) suggest that 85% of its POC is concentrated in sediments with grain size smaller than 32 μm (Zhang et al., 2013;Wang et al., 2012). Coarser sediments transported by high discharges in the wet season thus have a lower POC%. In addition, the lower POC% is likely associated with the erosion processes 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 rainstorm periods, is derived from gully erosion (Wang et al., 2017;Ran et al., 2015a). Mobilization of deeper soils with a low POC% (i.e., 0.2–0.3%) and subsequent fluvial transport resulted in the observed low POC% values in the wet season. Our results of 0.15–0.26% for samples collected during floods agreed well with the low carbon content in deeper soils. Despite the low POC%, however, the POC flux in the wet season is considerable on an annual basis because of the high sediment loading, accounting for 65% of the annual total POC flux.

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 (Fig. 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 (Fig. S1 in Supplement). 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% in the deposited sediments with depth demonstrates the OC burial efficiency. Soil OC within the Wuding River 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 roughly equal to the POC% in the trapped sediments. The negligible POC% difference likely 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 addition, the distinctive behaviour of soil erosion in the study catchment can partially explain the small POC% difference. Recent studies indicate that, if the rainstorm intensity is sufficiently strong, all grain-size fractions of loess soils on hillslopes can be eroded without sorting (Zheng et al., 2008).

Based on combined use of ^{137}Cs and $\delta^{13}C$ techniques, Wang et al. (2017) discovered that approximately 70% of the eroded soil OC can be buried by check dams in the Wuding River catchment. However, it is worth noting that the POC% showed significant variations with depth (Fig. 6). The estimated total OC burial rate is associated with uncertainty and warrants further investigation by taking POC% changes with depth into account.

In view of the huge sediment deposition behind check dams, the resulting OC burial represents an important carbon sink for the atmosphere that would have otherwise been partially mineralized to form CO_2 or CH_4 in the water column and outgassed along fluvial delivery (Drake et al., 2017;Battin et al., 2009). 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).

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 ^{13}C-depleted $\delta^{13}C$ signature significantly different from that originated from carbonate-dominant rivers (i.e., 0‰, Brunet et al., 2009). As stated earlier, widespread carbonate dissolution in the Wuding River catchment is the primary source of DIC in its groundwater (Zhang et al., 1995;Chen et al., 2005). Although we did not analyze the $\delta^{13}C$ signature of DIC, prior studies suggest that it generally ranges from -6.7‰ to -12.9‰ in Loess Plateau rivers, indicative of strong dominance of carbonate dissolution (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; Fig. 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;Hemingway et al., 2017). The ^{14}C exhibited a weak positive correlation with $\delta^{13}C$, showing an increasing trend from spring through summer to autumn (Fig. 9). Because DIC from carbonate dissolution is characterized by typically enriched $\delta^{13}C$ and highly depleted ^{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 ^{14}C age (Fig. 5). This suggests that the emitted CO_2 is derived from ancient terrestrial OC which is mineralized either in soils and then transported into rivers or in aquatic systems during transit (McCallister and del Giorgio, 2012). Addition of recently-fixed organic matter in summer and autumn through surface water inputs and decomposition of the bioavailable fraction have likely played a 'dilution' effect, causing the younger ^{14}C age and thus the seasonal distinctions. Notably, the emitted CO_2 is inconsistent with that from the tropical Amazon rivers where respiration of contemporary organic matter is the primary source of excess CO_2 (Abril et al., 2014;Mayorga et al., 2005). Therefore, special efforts are 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 River 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 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 into the Wuding river network is $(18.5\pm4.5)\times10^{10}$ g C year^{-1}, amounting to 16% of its catchment NEP (Fig. 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. However, the estimated NEP in this study is likely associated with large uncertainty.

While a ratio of 40% of S_R was used to calculate R_h in non-forested areas, it can vary from 10% to 90% depending on land cover type (Hanson et al., 2000). Further research involving field experiments and remote sensing technique is needed to constrain this estimate.

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 river network exhibit a high DIC concentration and percentage flux (Fig. 10). Compared with these catchments with weak soil erosion, the strong soil erosion intensity in the Wuding River 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 (Fig. 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 in this catchment (i.e., 16%) is higher than other catchment-based estimates, it is substantially lower than the global-scale estimate of 50–70% by Cole et al. (2007). Compared with other ecosystems, the arid-semiarid Wuding River 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 river network, approximately 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 (Fig. 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 River 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, 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 River 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. DOC export was characterized by spatial variability. Continuous mineralization of the bioavailable fraction of DOC has probably caused the spatially downstream decline in DOC concentration in low order streams. In addition, the predominance of groundwater input over the entire year may has likely explained the seasonal insensitivity of DOC concentration to flow dynamics. POC% displayed strong seasonal variability throughout the catchment or at the catchment outlet, indicating the control of gully erosion in wet seasons in mobilizing deeper 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 are quantitatively important, 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 River 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 CO_2 emissions, it is critical to trace its isotopic composition and age to more holistically explore its biogeochemical significance.

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Table 1. CO_2 emissions from 337 check dam-formed reservoirs within the Wuding River catchment (±1SD).

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 CO_2 from the Wuding River catchment (±1SD).

Site	Spring			Summer			Autumn		
	pMC	Age (year BP)	$\delta^{13}C$ (‰, VPDB)	pMC	Age (year BP)	$\delta^{13}C$ (‰, VPDB)	pMC	Age (year BP)	$\delta^{13}C$ (‰, VPDB)
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			

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

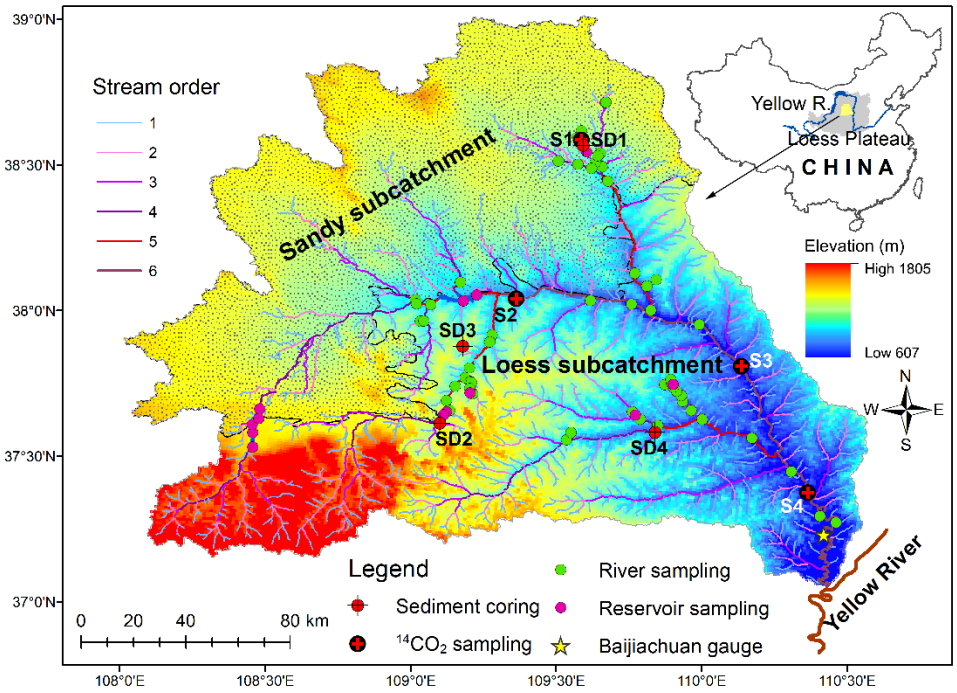

Figure 1. Map of the Wuding River catchment showing the sampling sites. SD1–SD4 and S1–S4 denote the sampling location of sediment coring behind check dams and carbon isotope, respectively. The inserted map shows its location on the Loess Plateau.

850

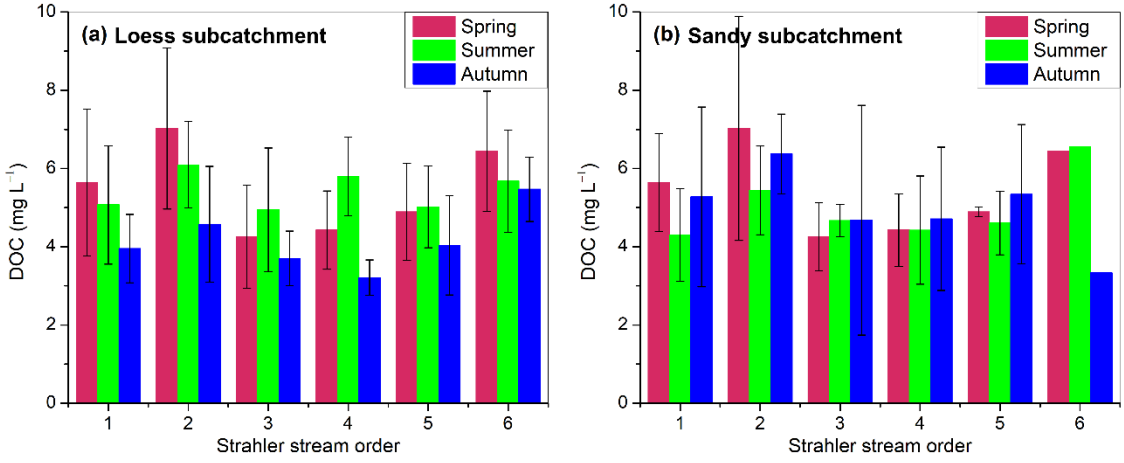

Figure 2. Spatial changes in DOC along the 6 Strahler stream orders in (a) the loess subcatchment and (b) the sandy subcatchment. Error bars denote the standard deviation (±1SD).

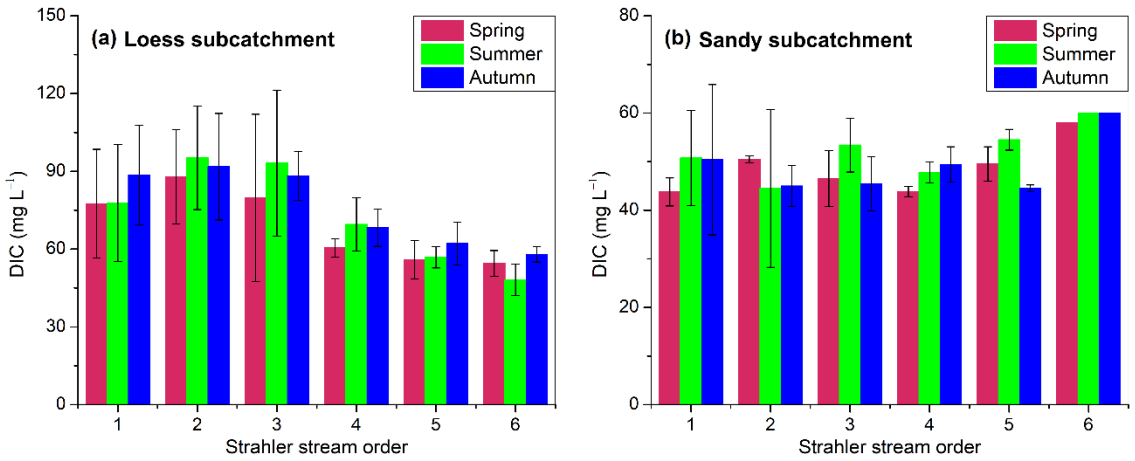

Figure 3. Spatial changes in DIC along the 6 Strahler order streams in (a) the loess subcatchment and (b) the sandy subcatchment. Error bars denote the standard deviation (±1SD).

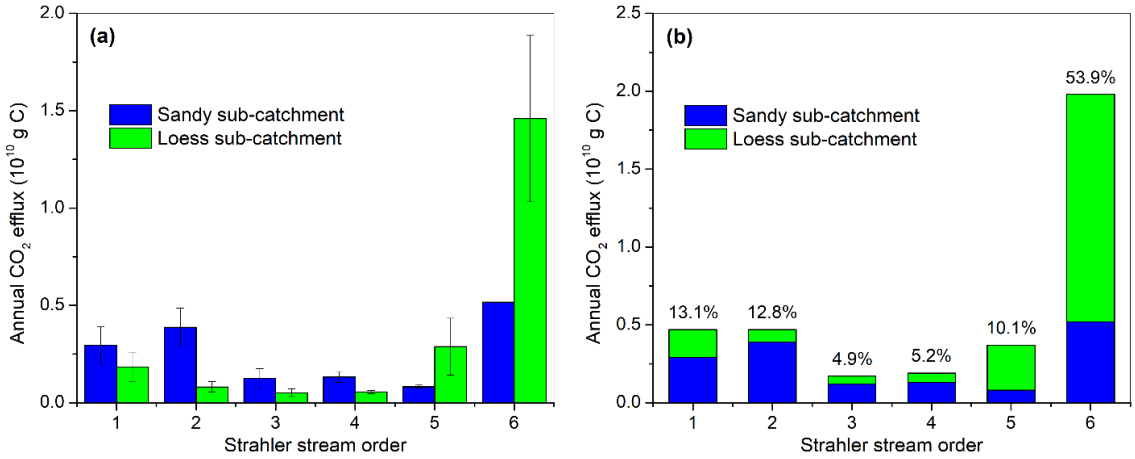

Figure 4. Longitudinal changes in CO_2 emissions along stream order in (a) the sandy subcatchment and the loess subcatchment and (b) the entire Wuding River catchment. The percentage above each order in (b) represents the proportion of CO_2 emissions from that order streams to the total CO_2 emissions. Error bars denote the standard deviation (±1SD).

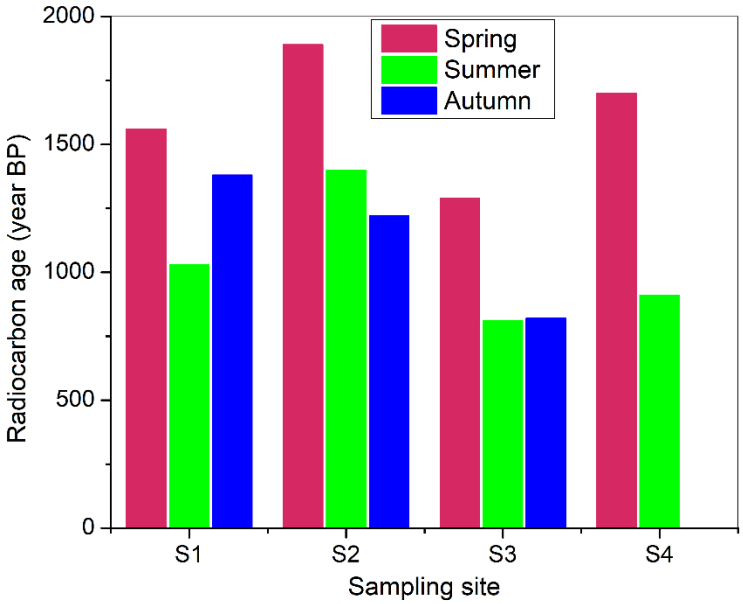

Figure 5. Seasonal variations in radiocarbon ages (year BP) for the emitted CO_2 from the Wuding River catchment.

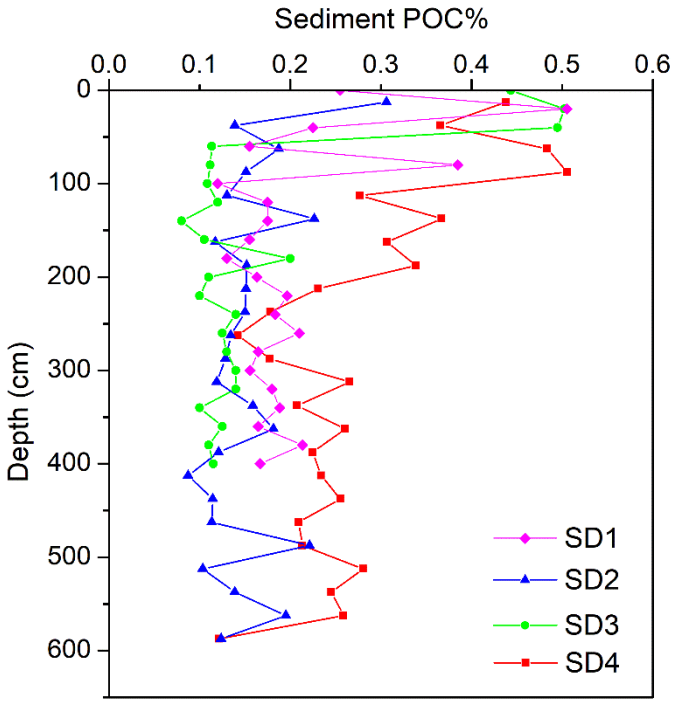

Figure 6. Variations of POC% with depth in buried sediments behind check dams (refer to Figure 1 for their location).

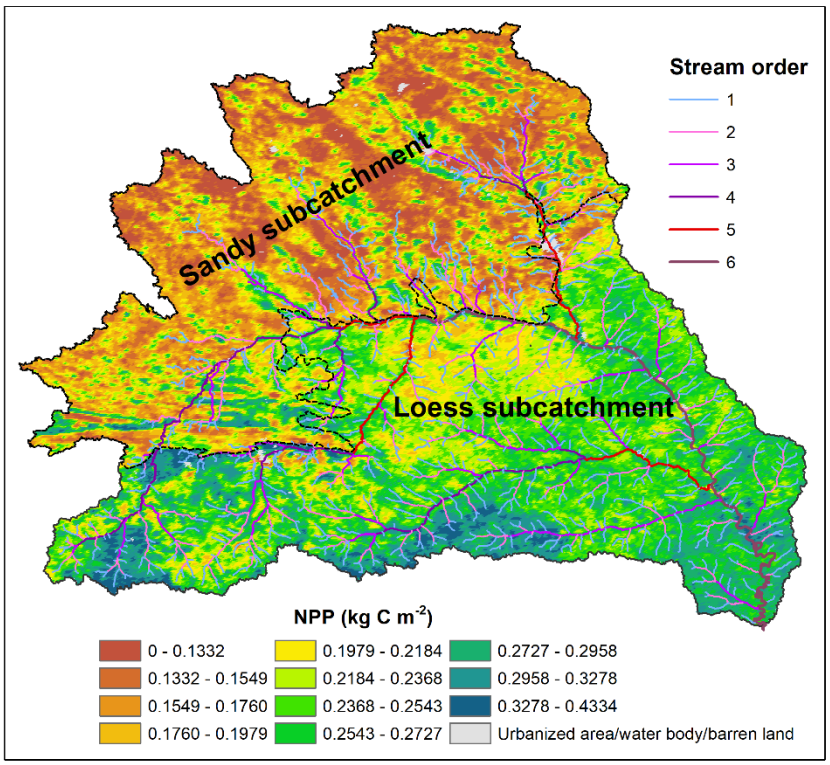

Figure 7. Spatial distribution of NPP within the Wuding River catchment in 2015 showing significant differences between the northwestern sandy and southeastern loess subcatchments.

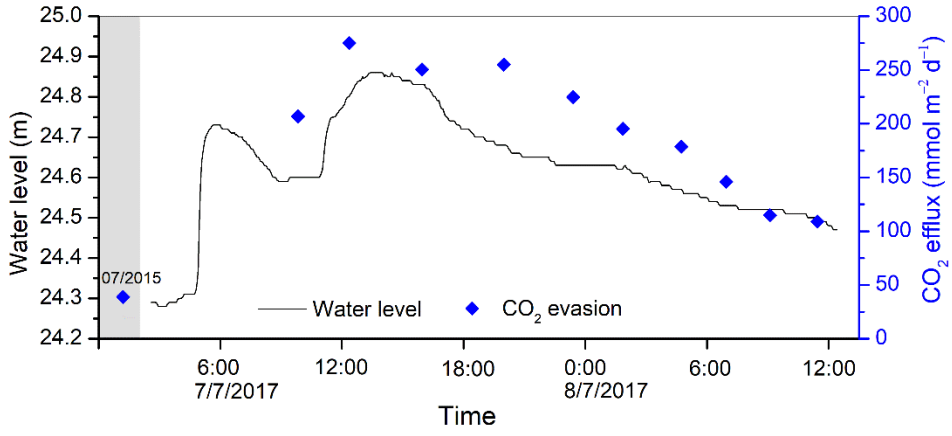

Figure 8. Temporal variation in CO_2 efflux during a high-discharge flood event in the Wuding River at Baijiachuan gauge (refer to Figure 1 for its location).

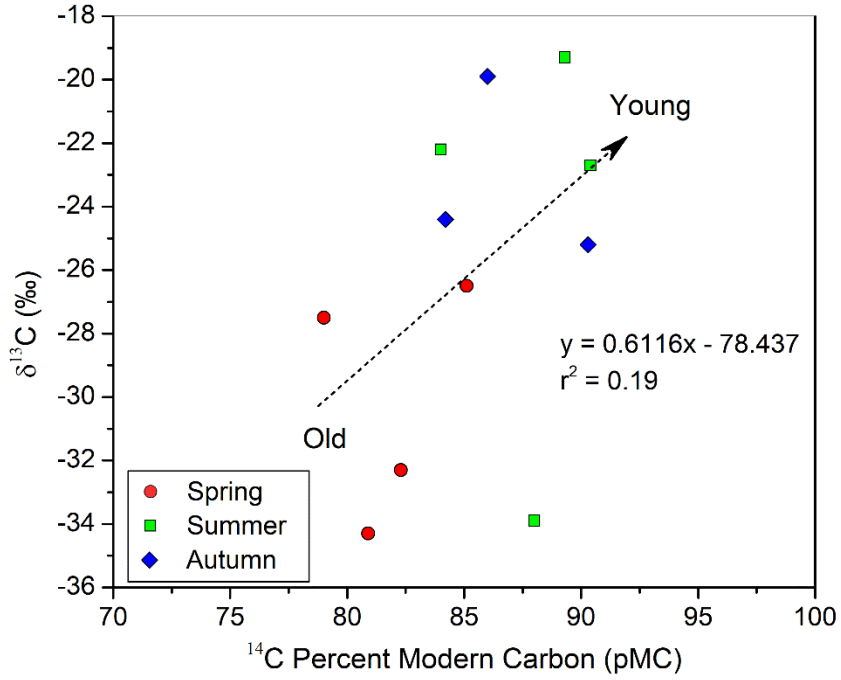

Figure 9. Relationship between $\delta^{13}C$ and ^{14}C of the emitted CO_2 from the Wuding River catchment.

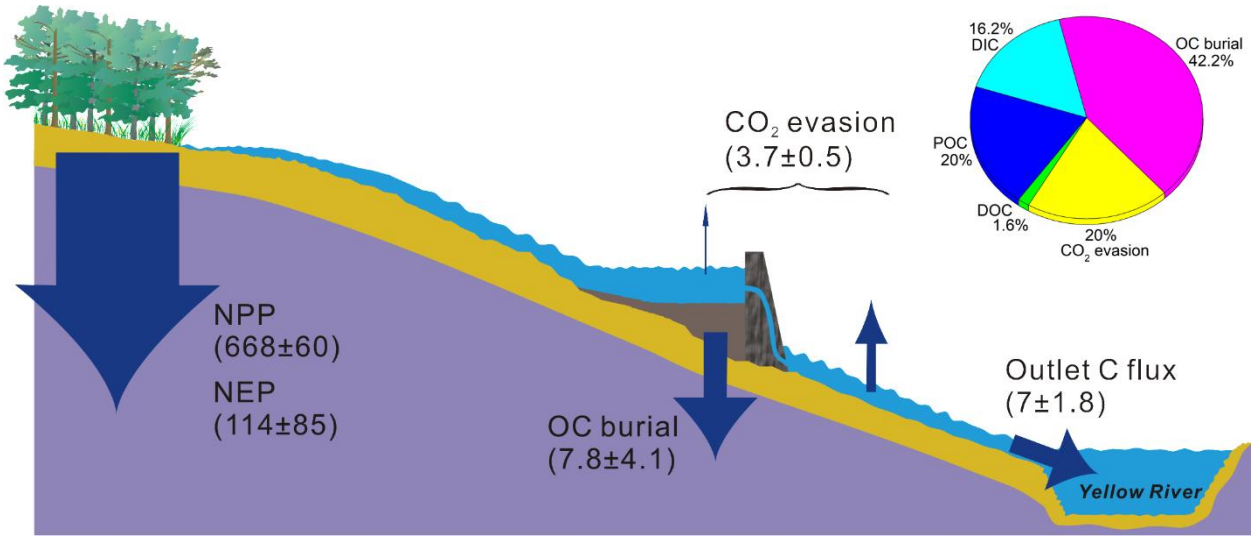

Figure 10. Fluvial carbon budget within the Wuding River catchment in relation to terrestrial ecosystem production (unit: $\times 10^{10}$ g C yr^{-1}). The inserted pie chart denotes the partitioning of riverine carbon among its five phases with the sum (100%) representing all the carbon entering the river network.

Dear reviewer,

Many thanks for your comments on our manuscript. Based on your very constructive comments, we have thoroughly revised the manuscript. Additional discussion and justifications have been added into the manuscript or into the Supplement. Please see below the detailed responses. Major changes have also been highlighted in the revised manuscript.

With best regards
Lishan Ran, on behalf of the coauthors

General comments:
Ran et al. reported new data on riverine carbon export in the arid-semiarid Wuding River watershed on the Chinese Loess Plateau. Considering that river systems in the East Asia, especially those in the arid-semiarid climates are under-represented in the global budget of riverine carbon fluxes, this study could provide valuable datasets. However, the paper can be improved further by explaining in detail how the errors were calculated in load estimates and CO2 evasion, offering detailed explanation in the methods (e.g. the river surface area), and providing discussion on the observed patterns with statistical significance testing results. Specific comments are below, which the authors may consider when revising the manuscript.
Reply: Thanks a lot for your constructive comments. Please find below our responses to your comments.

Specific comments:
Lines 48-: "substantial" is a relative term. Please provide a value or a range just like 1.8 Pg C year-1 in the previous sentence.
Reply: The annual OC burial due to sediment storage in global reservoirs and lakes ranges from 0.15 to 0.6 Pg C $year^{-1}$. This range has been added into the revised manuscript. (lines 47-48)

Lines 84-: "multi-annual" is an unspecific term. Please provide more information on how the mean of water discharge was calculated. For example, you can provide the period (e.g. 1980-2010?) Also, year-1 as a time unit would be appropriate for annual discharge. Is it 11.2 * 10^8 m3 yr-1 (Ran et al., 2017)?
Reply: The calculated mean water discharge of 35 m^3 s^{-1} is based on the period 1956–2017. The mean annual water discharge during this period is 11.2×10^8 m^3 $year^{-1}$. These changes have been added into the text. (lines 84-85)

Lines 149-: Isn't the 14C half-life 5,730 years?
Reply: The half-life used in carbon dating calculations by the Beta Analytic Inc. is 5568 years, the value worked out by chemist Willard Libby, and not the more accurate value of 5730 years, which is known as the Cambridge half-life. Although it is less accurate, the Libby half-life was retained to avoid inconsistencies or errors when comparing carbon-14 test results that were produced before and after the Cambridge half-life was derived. Detailed description on the 14C half-life can be found at the Beta Analytic website: https://www.radiocarbon.com/PDF/AMS-Methodology.pdf.

Lines 156-158: Detailed explanation is needed on the validity of the methods on how the riverine carbon exports were calculated considering that the major findings of this paper are the new estimates of the riverine carbon loads. Detailed explanation is needed on how river flow was measured. The method of load estimation appears to be too simple and with many assumptions, not specifying errors associated with each step. There are several methods for load estimation (e.g. Sickman, J.O. et al., 2007, Water Resources Research, Effects of urbanization on ...) you may try these and compare the results because load calculation is crucial to draw conclusions. One way to calculate daily load of stream ions is to use the LOADEST software developed by USGS if daily water discharge data are available. The software also provides confidence intervals.

Reply: Many thanks for your comment. Estimating riverine carbon flux is a very important part of this study in which we attempt to investigate the fate of carbon after entering the drainage network from terrestrial ecosystems. Just as you have pointed out, there are a number of methods to estimate the annual fluxes of dissolved and particulate matter transported by rivers. Major methods currently used include linear interpolation and ratio estimators, regression-based methods historically employed by the USGS, and recent flexible techniques such as Weighted Regressions on Time, Discharge, and Season (WRTDS), etc. As you have also suggested, the most commonly used USGS software package for estimating constituent load using regression is known as LOADEST (Runkel et al., 2004. Load Estimator (LOADEST): A FORTRAN Program for Estimating Constituent Loads in Streams and Rivers. U. S. Geological Survey Techniques and Methods Book 4, Chapter A5). Lee et al. (2016) recently reviewed the potential for flux estimation bias across a broader range of estimation methods and concluded that the Beale's ratio estimator and WRTDS generally exhibit greater estimation accuracy and lower bias (Lee et al., 2016. An evaluation of methods for estimating decadal stream loads. *Journal of Hydrology*, 542, 185-203). Our annual carbon flux estimation in this study was based on the Beale's stratified ratio estimator. Since the riverine carbon concentrations were measured with "sparse" sampling frequency while flow and suspended sediment had a continuous daily measurement, this method could greatly reduce the bias introduced by relatively low sampling frequency, in particular the high flow events that are often under-sampled (Parks and Baker. 1997. Sources and transport of organic carbon in an Arizona river-reservoir system. *Water Research*, 31, 1751-1759). Indeed, we have already used the Beale's ratio estimator in our earlier estimation of carbon flux in the Yellow River with success (i.e., Ran et al., 2013. Spatial and seasonal variability of organic carbon transport in the Yellow River, China. *Journal of Hydrology*, 498, 76-88). And the Beale's ratio estimator has proven to be highly reliable and is recommended if the relationship between discharge and concentration is weak (e.g., Fulweiler and Nixon, 2005. *Biogeochemistry*, 74, 115-130; Awad et al., 2017. *Environmental Pollution*, 220, 788–796; Chen et al., 2014. *Journal of Geophysical Research: Biogeosciences*, 119, 95-109; Sun et al., 2017. *Hydrological Processes*, 31, 2062-2075). In comparison, we have also estimated the carbon flux by using the suggested LOADEST software package. The flux results show high consistency with each other, with a difference of less than 4.5%. We have added a detailed description of the estimate method (i.e., the Beale's ratio estimator) in the revised manuscript. Please refer to the highlighted changes in the text. (lines 161-180)

Lines 160-: Do you mean the POC concentration not "content"? It appears the term "content" is misused throughout the manuscript.

Reply: Based on your and other reviewers' comments, we have re-defined the concentration of POC throughout the manuscript. It should be the POC concentration (POC%) in the total suspended solids (dry weight). (lines 161-163)

Lines 170-: How large is the river width? If it is near or lower than 90 meters, how can you estimate river surface areas using the DEM data of 90-m resolution? In other words, aren't you using too coarse data to estimate river water surface areas?
More detailed explanation is required on how the water surface area is calculated since this is a critical term for CO2 evasion estimates.
Reply: Because the Wuding River catchment is located in an arid-semiarid climate zone, the rivers and streams of drainage network is generally narrower than their counterparts in tropical rivers due to lower water discharge. The widths of the rivers and streams vary from 1.8 (first order streams) to ~61 m (the mainstem channel) (see Table 1 in our earlier wor: Ran et al., 2017. *JGR-Biogeosciences*, 122, 1439-1455), significantly lower than the DEM resolution of 90 m. Therefore, we only used the DEM data to delineate the drainage network in terms of stream length (usually >2.5 km) and stream number. The delineated drainage network was also calibrated through ground truthing during our fieldwork. Because the width of all rivers is less than the resolution and it fluctuates between dry and wet seasons, we measured widths of all sampled rivers during our fieldwork and aggregated them based on stream order to calculate the water surface area. We have revised the description of the water surface area calculation in the revised manuscript. (lines 198-203)

Lines 183-198: The method is better than nothing for sure. However, it appears the used references are relatively old (1995 and 2000). Do you have newer references on heterotrophic respiration than those? How the errors associated with the approach are calculated?
Reply: To estimate the Wuding River catchment's net ecosystem production (NEP), we used the global soil CO_2 efflux database described by Raich and Potter (1995) and the heterotrophic soil respiration (*Rh*) estimated by Hanson et al. (2000). Based on the global soil respiration flux database (Raich and Potter, 1995), the S_R for this catchment is the range of 400-500 g C m^{-2} $year^{-1}$. Hence, we used 450±50 g C m^{-2} $year^{-1}$ to represent its soil respiration. This rate is consistent with recent measurements under different vegetation types in this arid-semiarid region (e.g., Fu et al., 2013). Fu et al. (2013. Soil respiration as affected by vegetation types in a semiarid region of China. *Soil Science and Plant Nutrition*, 59, 715-726) measured total soil respiration in this arid-semiarid region. Their mean soil respiration rates under 4 different vegetation types are in the range of 1-1.4 µmol m^{-2} s^{-1}, which are equivalent to 380-530 g C m^{-2} $year^{-1}$. Thus, our estimate is reliable. Although the references are relatively old, using the ratios derived from Hanson et al. (2000) has been widely used to assess heterotrophic soil respiration in river catchments under different land cover types (e.g., Brunet et al., 2009. Terrestrial and fluvial carbon fluxes in a tropical watershed: Nyong basin, Cameroon. *Chemical Geology*, 3, 563-572; Lee et al., 2017. A high-resolution carbon balance in a small temperate catchment: Insights from the Schwabach River, Germany. *Applied Geochemistry*, 85, 86-96). In addition, the propagated errors are calculated and presented in the revised manuscript. We have also added new references to justify our arguments. (lines 316-326)

Lines 208-: Does the 'sediment' mean 'suspended sediment'? If so, please clarify it to prevent confusion. Do you mean the POC concentration not "content"?

Reply: Yes, here it means the POC concentration in suspended sediment. We have clarified this in the revised manuscript 'The POC% in suspended solids…'. (lines 161-163)

Lines 222- and throughout the manuscript: What is the "+/-"? Standard deviation? Or standard error?
Reply: The '±' denotes standard deviation (SD) throughout the manuscript. We have explicitly indicated this when it is used for the first time in the revised manuscript (i.e., in Figure 2). Many thanks.

Lines 225-: While [DOC] (3.3 mg/L) is larger than [POC] (0.61 mg/L), the DOC export is much lower (0.3*10^10 g (yr-1?)) than POC export (3.7*10^10 g (yr-1?)). Why is that so?
Reply: Here the DOC concentration (mg/L) is expressed as the DOC content per unit volume of water, and the POC is expressed as POC% in total suspended solids (TSS, dry weight). Although the DOC concentration is larger than the POC%, the annual water discharge (7.71×10^8 m^3/yr) at the catchment outlet Baijiachuan gauge is relatively low due to low precipitation and the concomitant annual TSS flux (610×10^{10} g/yr) is quite high owing to severe soil erosion. As a result, the annual DOC flux (g C/yr) is much lower than the POC flux.

Lines 228-233: The river water discharge and carbon loads can be highly dependent on precipitation. Was the year of field campaign categorized as wet, dry, or normal year compared to the long term mean (e.g. 1980-2017 precipitation)?
Reply: The multiannual precipitation for the Wuding River catchment is in the range of 300-500 mm during the period 1956-2010 with a mean precipitation of 430 mm/yr (available at http://www.yellowriver.gov.cn/; Li et al., 2007. *Hydrological Processes*, 21, 3485-3491). The precipitation in 2015 is about 410 mm, indicative of a normal year relative to the long-term mean precipitation. In comparison, the precipitation in 2017 is larger than 540 mm, significantly higher than the long-term mean precipitation (i.e., 26% higher). That is why we used the 2015 hydrological data to calculate the carbon flux. Another reason is because the three seasonal samplings were also performed in 2015. We have revised the hydrological information in the manuscript. (lines 256-261)

Lines 258–261: As the authors mentioned, the precipitation is high during summer. Thus, this assumption of no significant seasonal fluctuations may not be valid. Can you provide a range of stream surface area and CO2 evasion depending on season?
Reply: For CO_2 evasion from river waters, we separately estimated the total water surface of rivers in spring, summer, and autumn (please refer to Table S4 in Supplement for the estimated water surface area in the three seasons) and calculated the CO_2 evasion in these three seasons. The annual total CO_2 evasion was obtained by summing up the three seasonal CO_2 estimates. But for CO_2 evasion from reservoir waters, because these check dam-formed reservoirs are mostly constructed in steep gully channels and operated primarily for the purpose of sediment trapping and water storage, variation of the water surface area is much less significant than that of the rivers. Although there are also seasonal fluctuations, the magnitude should be quite minor compared with rivers. Thus, we assumed that there was no significant seasonal variation. (lines 289-293)

Lines 300–: Is the decreasing trend of DOC (Fig. 2) statistically significant? It appears the error bars are large. If this is not statistically significant, the following argument is vague. The decrease of DOC can be microbial- or photo-degradation to CO2, sorption to particulate matter, and dilution from increased water discharge of low [DOC]. The following discussion is speculative and could be strengthened by checking each factor.
Reply: Based on your comment, we have performed the significance test for DOC concentrations along the stream order. Because of the large error bars as shown in the figure, the decreasing trend of DOC is not statistically significant at the 95% confidence level. To reflect the downstream DOC concentration change, we aggregated the 1st-5th streams into 2 groups, including the headwater 1st-2nd streams and the higher order 3rd-5th streams, because it is usually believed that headwater low-order streams process organic carbon more rapidly and emit CO_2 at faster rates than downstream high-order streams (e.g., Butman and Raymond, *Nature Geoscience*, 4, 839-842; Crawford et al. 2013. *Journal of Geophysical Research: Biogeosciences*, 118, 482-494). Our results indicated that the DOC concentrations in the headwater 1st-2nd streams were on average 16-39% higher than that in the downstream 3rd-5th streams. Thus, the downstream DOC decline in the 1st-5th order streams likely suggests the mineralization of the bioavailable fraction of DOC along the river course (Figure 2), especially in spring and autumn. In addition, sorption and input of increased water with low DOC may partially dilute the DOC concentration as you commented. However, in view of the spatial homogeneity in terms of soil erosion rate, SOC content in soils, and hydrologic regime within each subcatchment and the spatially constant POC% from the headwater to the mainstem channel, the sorption and 'dilution effect' are expected to be minimal. Accordingly, we have revised the claims in the manuscript. (lines 230-245; 333-349)

Line 325–336 (and lines 385–394, and Fig. 6): I am confused. Do you mean the POC concentration not "content"? Why the "content" has the unit of concentration, %, not just grams? I think heavy rain during summer could generate high POC content but low POC concentration. Please clarify.
Reply: Many thanks for your comment. It should have been POC concentration in the text. We have clarified the POC concentration in the total suspended solids (TSS, dry weight) in the units of POC% throughout the manuscript. By multiplying the annual TSS flux, we can calculate the annual POC flux.

Line 351–368: The pCO2 is a function of pH and alkalinity. The pCO2 is high when the water pH is low. The ground water of the area has the pH of >~8. Then, the calculated pCO2 is very low which is well described in the line 211. Then, how CO2 evasion can be high when pCO2 is low? Please clarify.
Reply: Just as you have pointed out, pCO_2 is a function of pH and alkalinity, and it can be calculated from the latter two variables. The observed pH in the study catchment ranged from 7.68 to 9.29 and the pH in groundwater is generally slightly higher than 8.0. Even so, for the sandy subcatchment reservoirs, the pH of the groundwater is still lower than that of the river water into the reservoirs (e.g., 8.7-9.3). With extremely high alkalinity (DIC) concentrations, despite the relatively high pH of around 8.0, the calculated pCO_2 is well above the atmospheric equilibrium (i.e., ~390 µatm), and facilitates the observed CO_2 evasion. We have revised the manuscript to make the claim more clear and accurate. (lines 398-405)

Lines 400: Which part of the Figure S1 supports this sentence?
Reply: We have added the information on carbon export during typical floods in the Supplement (Figure S1).

Lines 430-481: Very interesting findings.
Reply: Many thanks for your comments. We collected carbon isotope samples of the emitted CO_2 from river waters and attempted to explore its potential sources in association with carbonate dissolution and respiration of recent organic matter.

Tables: What is the "+/-"? Standard deviation? Or standard error?
Reply: The '±' denotes standard deviation (SD) and the description has been added in the revised manuscript.

Table 1: Please provide information on how many reservoirs were used to draw the table.
Reply: There are currently 337 reservoirs in operation within the Wuding River catchment (please see the figure below). This information has been added into the caption, and this map has also been included in the Supplement (Figure S2).

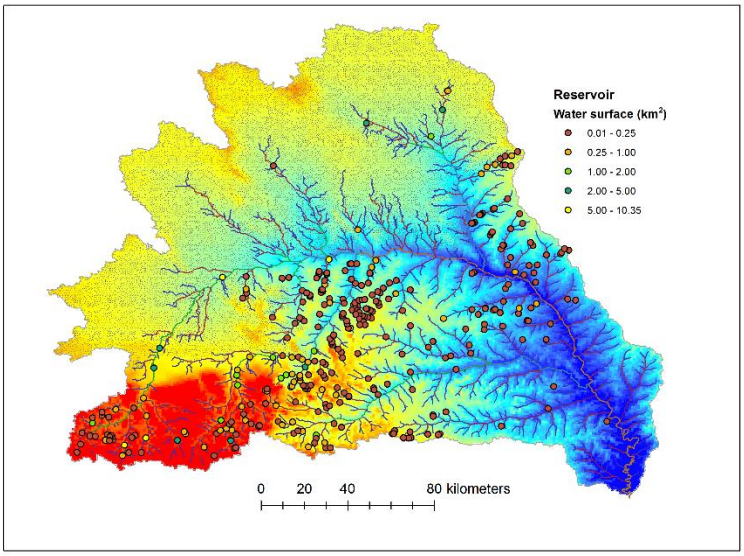

Figure: Spatial location of the 337 reservoirs within the Wuding River catchment.

Figure captions need to provide more detailed description of the figures including explanation on legends.
Reply: We have significantly improved the figure captions based on your comments and detailed information has been added. Please refer to highlighted changes in the revised manuscript.

Figure 1: It is hard to differentiate the colors of the stream order, especially with the background altitude colors. Please revise the figure so that each symbol can be seen clearly.
Reply: We have carefully adjusted this figure in terms of color scheme, marker size, label size, etc., and have added the subcatchment boundaries to make the figure much easier to read.

Dear Dr Hemingway,

We thank you very much for your comments on our manuscript. Based on your very constructive comments, we have thoroughly revised the manuscript. Additional discussion and justifications have been added into the manuscript or into the Supplement. Please see below the detailed responses. Major changes have also been highlighted in the revised manuscript.

With best regards
Lishan Ran, on behalf of the coauthors

Synopsis

The central focus of this manuscript is to investigate carbon cycling in the arid-semiarid Wuding River catchment using both campaign-style and time-series sampling approaches. The authors quantify dissolved carbon concentrations, both organic (DOC) and inorganic (DIC), as well as particulate organic carbon (POC) concentrations and CO2 outgassing fluxes throughout the catchment over multiple seasons. In particular, the authors compare and contrast signals across a range of Strahler stream orders (1 to 6) from subcatchments underlain by sand and by loess and quantify differences in their respective carbon budgets.

As the authors point out, arid-semiarid river catchments are severely underrepresented in global riverine carbon-cycle budgets. By presenting a large dataset for the Wuding River catchment, this study begins to ameliorate this issue. I therefore find the goals and targets of the present study to be impactful, as they attempt to advance our collective understanding riverine carbon cycling. However, I do have some issues with the interpretation of these data, particularly related to a number of claims that seem unsubstantiated or somewhat contradictory. Additionally, I feel that there are some areas that warrant further clarification and detail. Overall, I feel that the authors should remove some of the weaker and highly speculative text that attempts to prescribe carbon sources and should instead focus on the strengths of this dataset – namely, carbon fluxes and budgets. If the authors can address these issues, which I think they can, then I believe that this manuscript could provide a valuable contribution to Biogeosciences.

I outline my larger concerns in detail below, followed by a list of smaller concerns and questions. Please do not hesitate to contact me for further discussion regarding this review.

Sincerely,

Jordon Hemingway
jordon_hemingway@fas.harvard.edu

Reply: Many thanks for your very constructive comments. Please find below our responses to each of your comments.

Larger Comments

<u>Methods details and measurement uncertainty</u>

In general, I feel that more detail is required in describing the methodology and presenting data uncertainty. In particular, the paragraph beginning on L135 should be expanded considerably. For example, I would like to see more details related to:

Reply: Many thanks for your very constructive comments.

i) Field titration methods. How was this done? Were any standards measured? Field titrations generally have quite high uncertainty associated with them (~5 – 10%), yet there is no uncertainty assessment presented here. What is the resulting propagated uncertainty for calculated DIC concentration values?

Reply: Total alkalinity was determined by triplicate titrations in the field with 0.1 M HCl, and methyl orange was used as the indicator, following the standards as suggested by APHA (1999, *Standard Methods for the Examination of Water and Wastewater*). For the Wuding River with widespread presence of carbonates, its river water alkalinity is quite high (62.1–67.7 mg L^{-1}). Our field triplicate titration results are highly consistent with the difference between the three results generally less than 3%. Thus, we expected the obtained alkalinity results are reliable with high confidence. Finally, DIC was calculated from total alkalinity, pH, and temperature by using the program CO2calc. Because the measured pH varied from 7.68 to 9.29, the calculated DIC was approximately equal to alkalinity, with >96% of the alkalinity composed of HCO_3^-, consistent with the relative speciation (%) of CO_2, HCO_3^-, and CO_3^{--} in water as a function of pH (please refer to the figure below). The revised descriptions have been added into the manuscript. (lines 142-145)

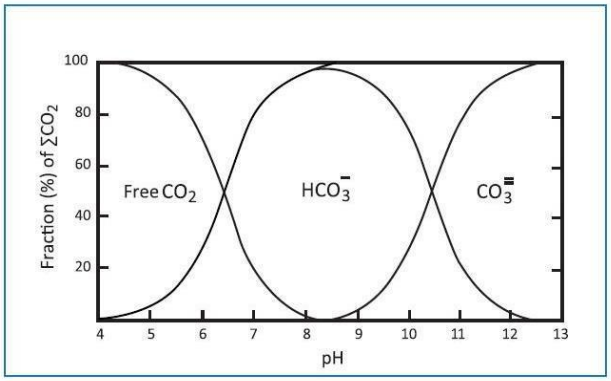

Figure: Relative concentrations of the different inorganic carbon compounds against pH.

ii) DOC uncertainty. How was DOC uncertainty estimated? Was a standard calibration curve used? If so, how often was the calibration curve analyzed? Was each sample injected in triplicate? Duplicate? Single injection?

Reply: DOC was determined by the high-temperature combustion method (850 ºC) by using an Elementar Vario TOC Select Analyzer. A standard calibration curve was used for every round of field samples. Generally, the standard calibration curve was analyzed and re-determined for each 60-80 samples, depending on the variability of the DOC concentration. Triple injections indicated an analytical precision of <3%, and the average of the three injection results was calculated to represent the sample's DOC concentration. These descriptions have been added into the revised manuscript. (lines 140-142)

iii) Were solid samples fumigated with HCl at room temperature or at ≥60°C? I ask because dolomite will not be removed at temperatures below 60°C. If these samples are expected to contain dolomite, and if they were fumigated at room temperature, then I would expect resulting POC estimates to be biased upward.

Reply: To measure the POC concentration, the solid soil and sediment samples were fumigated at 65 °C for 24 h. For the Chinese Loess Plateau, carbonates in its loess–paleosols consist mostly

of calcite and dolomite, and the latter is the primary detrital material (please see Yang et al., 2000. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 157, 151-159). Therefore, we carefully removed the dolomite with concentrated HCl at a higher temperature than the room temperature. We have added the description into the revised manuscript. (lines 149-151)

iv) CO2 d13C values. Were these analyzed by Beta Analytic using an IRMS on a separate gas split, or are these values generated by the AMS? I would expect these to be IRMS values, but this should be stated clearly.
Reply: The CO_2 $\delta^{13}C$ results are generated by the AMS at the Beta Analytic Radiocarbon Dating Laboratory (Miami, USA). This has been clearly stated in the revised manuscript. (lines 156-158)

v) Radiocarbon notation. Throughout the manuscript, the authors conflate 14C age, Δ14C (which is always reported in units of per mille!) and percent modern, or pMC. I would strongly suggest that the authors choose one notation and stick with it (my personal choice would be to use pMC). Still, if the authors choose to use 14C age, this be reported in units of "14C yr BP" rather than simply "years", as the latter is ambiguous and could refer to a calibrated age, which would not be appropriate here.
Reply: Thanks a lot for your suggestion on how to describe the ^{14}C analysis results. We have chosen to use the percent modern (pMC) to describe the results throughout the manuscript, mainly in Sections 3.2 and 4.3. But, to compare our results with Wang et al (2012. *Global Biogeochemical Cycles*, 10, 26, GB2025, doi:10.1029/2011GB004130) that investigated the ^{14}C age of DOC and POC in the Yellow River, we have kept '^{14}C age' results in Table 2 and Figure 5, and the simple notations 'years' have been replaced by '^{14}C yr BP'. (lines 153-156; 533-540)

vi) Sediment accumulation rates. In Figure 10, a burial flux is presented in units of g C yr-1, yet I find no reference to calculations for sediment accumulation rates (SAR). How was SAR calculated for each of these cores? This information is necessary in order to convert the measured %OC numbers into burial fluxes…
Reply: The sediment accumulation rate behind check dams in the Wuding River catchment was based on our earlier estimate (i.e., Ran et al., 2013. *Global and Planetary Change*, 10, 308-319; please also refer to Section 3.3 of the manuscript). Our earlier work shows that the annual sediment accumulation rate in this study catchment is 3720×10^{10} g $year^{-1}$. In addition, based on the POC concentration (POC%) of the four sediment cores distributed in both the sandy and loess subcatchments (Figure 1), we calculated the arithmetic mean of the POC% (0.21±0.11%). With the sediment accumulation rate and the POC% in deposited sediment we estimated the total OC burial rate ($(7.8\pm4.1)\times10^{10}$ g C $year^{-1}$). Because the POC content in the top 0-60 cm soils is considerably higher that that in the deeper soil layers, our simple estimate is associated with great uncertainty. Future efforts are therefore needed for a more accurate assessment. In addition to Section 3.3, we have also added these justifications into the manuscript. (lines 469-477)

Additionally, all of the numbers reported in the "Results" section should include corresponding uncertainty, either analytical uncertainty (when reporting single values) or sample population uncertainty (when presenting averages). For averages, please be clear if reporting standard errors or standard deviations. Similarly, significant figures should be consistent throughout the manuscript!

Reply: Many thanks for your suggestion. We have provided the uncertainty, mainly standard deviation, for all of the numbers in the 'Results' section. In addition, we have also double checked the consistency of significant figures throughout the manuscript. Please refer to highlighted changes in the revised manuscript. (lines 230-245; 261-265; 289-298; 316-326)

Net Ecosystem Production

I am left somewhat confused by the assumptions and uncertainties related to NEP calculations. To convert SR to Rh, the authors apply a "forested" and "non-forested" fraction heterotrophic derived from Hanson et al. (2000). However, the "non-forested" estimates from this reference are for pasture and grassland, not barren landscapes such as those presented in the current study. Presumably nearly 100% of soil respiration on barren landscapes is heterotrophic, no? Additionally, while the "non-forested" fraction heterotrophic in Hanson et al. averages 40%, they observe values ranging from 10% to 90% -- nearly the entire possible range!

I wonder if the authors have any way to estimate the uncertainty on NEP estimates presented here – if so, these should be discussed in detail. I would expect these uncertainties to be quite large, yet this is not mentioned or discussed in the manuscript. For example, how do the values here compare to those calculated by subtracting SR from MODIS-derived GPP values? To me, this seems like a more straightforward method to estimate NEP that isn't subject to the uncertainties associated with converting SR to Rh.

Reply: We divided the study catchment into two subcatchments, including the sandy subcathment and the loess subcatchment. While forest cover in the Wuding River catchment is quite low (less than 5%) as a result of low precipitation, grassland is the major land cover in the sandy subcatchment and agriculture and grassland predominate the loess subcatchment (Wang et al., 2014. Spatial-temporal changes of land use in Wuding River Basin under ecological restoration, *Bulletin of Soil and Water Conservation*, 34, 237-243 (in Chinese with English abstract). This is largely the result of the implementation of the Grain-for-Green Project which was initiated by the Chinese government in 1999. After more than 10 years of implementation of this vegetation restoration program, the vegetation cover (forest and grassland) has greatly increased. Please also refer to two photos below showing the landscape of the sandy subcatchment (left) and of the loess subcatchment (right). Both photos were taken by me in 2015 when doing the fieldwork. To better describe the landscape of the catchment, we have revised the description in Section 2.1 'Study area' (lines 88-90). Therefore, the landscape and land cover of the Wuding River catchment are generally consistent with the distinction of "forested" and "non-forested" by Hanson et al. (2000). With respect to the huge range of the "non-forested" fraction heterotrophic (i.e.,10-90% as you have noticed), we have discussed the potential uncertainty in the revised manuscript. (lines 560-563).

Figure: Landscape characteristics of the sandy (left) and loess (right) subcatchments.

Our rate is consistent with recent measurements under different vegetation types in this arid-semiarid region (e.g., Fu et al., 2013). Fu et al. (2013. Soil respiration as affected by vegetation types in a semiarid region of China. *Soil Science and Plant Nutrition*, 59, 715-726) measured total soil respiration in this arid-semiarid region. Their mean soil respiration rates under 4 different vegetation types are in the range of 1-1.4 μmol m^{-2} s^{-1}, which are equivalent to 380-530 g C m^{-2} $year^{-1}$. Thus, our estimate is reliable. We have carefully revised the manuscript with new references to justify our arguments (lines 316-326). Using the ratios derived from Hanson et al. (2000) has been widely used in the world to assess heterotrophic soil respiration in river catchments under different land cover types (e.g., Brunet et al., 2009. Terrestrial and fluvial carbon fluxes in a tropical watershed: Nyong basin, Cameroon. *Chemical Geology*, 3, 563-572; Lee et al., 2017. A high-resolution carbon balance in a small temperate catchment: Insights from the Schwabach River, Germany. *Applied Geochemistry*, 85, 86-96). Just as you have commented, this portioning is associated with potential uncertainty. Our ongoing research assessing NEP storage dynamics on the entire Loess Plateau is using the MODIS-derived GPP products. A preliminary estimate for the Wuding River catchment suggests that the results of the two methods are generally equal with a difference of ~11%. We greatly appreciate your suggestion and we will adopt the more straightforward method. Many thanks.

Interpretation of DIC, CO2 d13C, and Δ14C

In general, I am confused by the discussion on DIC sources, especially as they relate to measured CO2 d13C and Δ14C values – there seem to be a number claims that are either contradictory or are not explained in significant detail. Beginning in the abstract (L21) and repeated throughout the manuscript, the authors state that DIC is largely sourced from carbonate dissolution, especially in the loess subcatchment. Intuitively, this makes sense to me since loess contains a significant amount of carbonate, as the authors rightly state. However, this is incompatible with the d13C and Δ14C values presented in this study, which suggest that remineralization of terrestrially derived OC is the main source of outgassed CO2 behind check dams. What mechanisms could explain this discrepancy? I feel that there needs to be significantly more discussion and clarification here.

Furthermore, I find some of the claims related to CO2 outgassing to be overstated. For example, the statement: "The evasion of old carbon [derived from pre-aged OC respiration as is seen here] is likely to be widespread in arid-semiarid catchments worldwide with similar hydrological regime and terrestrial ecosystems" (L477). This seems to be quite a stretch, especially given my confusion related to the lack of carbonate dissolution signature as stated above.

Reply: We collected CO_2 emission samples in the Wuding River catchment for carbon isotope analysis by using the $SrCl_2$ solution. Thus, the measured $\delta^{13}C$ and $\Delta^{14}C$ results are for the emitted CO_2 from river water. Unfortunately, we did not collect water samples for $\delta^{13}C$ and $\Delta^{14}C$ analysis of the DIC. But prior studies indicate that the $\delta^{13}C$ of DIC generally ranges from -6.7‰ to -12.9‰ in Loess Plateau rivers (Liu and Xing, 2012. *Chemical Geology*, 296, 66-72). For the arid-semiarid Wuding River catchment and the whole Yellow River basin in which the Wuding River is located, carbonate dissolution has been found to be the primary source of DIC (mainly HCO_3^-) due to its high carbonate content in loess soils (up to 20%; please see Chen et al., 1995. Major element chemistry of the Huanghe (Yellow River), China: Weathering processes and

chemical fluxes. *Journal of Hydrology*, 168, 173-203; Chen et al., 2005. Spatial and temporal analysis of water chemistry records (1958–2000) in the Huanghe (Yellow River) basin. *Global Biogeochemical Cycles*, GB3016, doi: 10.1029/2004gb002325). Therefore, we conclude that DIC is largely sourced from carbonate dissolution, especially in the loess subcatchment. With respect to CO_2 emissions, however, the emitted CO_2 is characterized by much depleted $\delta^{13}C$ values (-19.3‰ – -33.9%), which is significantly different from the $\delta^{13}C$ signature of DIC carbonates (i.e., 0‰ for DIC derived from carbonates by proton attack and -8.5‰ for DIC derived from carbonate dissolution; Barth et al., 2003. *Chemical Geology*, 200, 203-216; Brunet et al., 2009. *Chemical Geology*, 265, 563-572). In comparison, the $\delta^{13}C$ values of the emitted CO_2 largely reflect the contribution of C3 and C4 plants which have a $\delta^{13}C$ values signature of -27‰ and -15‰, respectively. Mineralization of terrestrially derived OC has been widely found to be the primary source of river water CO_2 emissions. For example, Mayoga et al. (2005) found that respiration of contemporary organic matter (less than 5 years old) originating on land and near rivers is the dominant source of excess CO_2 that drives outgassing in the Amazon rivers (Mayorga et al., 2005. *Nature*, 436, 538-541). Similarly, Borges et al. (2015) discovered that lateral transport of soil or wetland DOC and POC that is mineralized to CO_2 within the rivers maintains CO_2 outgassing in African rivers (Borges et al., 2015. *Nature Geoscience*, 8, 637-642). Therefore, in combination with the measured $\delta^{13}C$ and $\Delta^{14}C$ results of the emitted CO_2, we conclude that decomposition of the terrestrially derived OC drives CO_2 outgassing in the Wuding River catchment although DIC is largely originated from carbonate dissolution. We have added more justifications with relevant references in the revised version of the manuscript to support our arguments. Based on your comments, we have removed the overstated comments, including the one you mentioned here, from the revised manuscript to make sure all the arguments are supported by our results and figures. Major changes have been highlighted in the manuscript. (lines 495-504; 525-528; 533-540)

DOC sources and trends

Beginning on L204 and continuing throughout the manuscript, the authors refer to a "significant downward trend along the river course from headwater downstream… in both subcatchments." However, when I look at Figure 2, I am left puzzled and wondering if these trends are, in fact, significant. Given the large error bars for each stream order, my guess is that they are not. In my opinion, any subsequent discussion related to DOC sources and trends (e.g. L300-313; L306-309; L318-324) is highly speculative at best.

Additionally, I find some of these claims to be contradictory. For example, on L314, the authors state that "…there was no significant correlation between DOC and flow based on the spatial sampling results". However, for the high-frequency sampling the authors observe a "positive correlation between DOC export and hydrography [that] demonstrates the enhanced leaching of organic matter from surface vegetation and organic-rich top soil layers". Why would a positive correlation be expected during storm events yet not on a seasonal basis? What mechanism could explain this? This discrepancy is not addressed.

Reply: Many thanks for your comment on DOC sources and trends. To detect the DOC concentration changes along the river course from headwater downstream, we plotted the average DOC concentration with standard deviation (error bars) based on stream order (Figure 2). The '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)'. Because the downward trend does not pass the significance test at the

significance level of 0.05, we did not use the word '*significant'* in the description. If we categorize the first 5 stream orders (1–5) into 2 groups (1st–2nd and 3rd–5th), we can easily detect that DOC in the headwater 1st–2nd order streams (4.7–5.4 mg L^{-1}) was on average 9 21% higher than in the 3th–5th order streams (4.2–4.9 mg L^{-1}), it increased to 5.2–6.1 mg L^{-1} in the 6th order mainstem, representing an increase of 18–36% relative to the 3th–5th order streams. This is particularly true for the loess subcatchment (Figure 2a). When combining the two subcatchments together, the DOC in the 6th mainstem was 5.7 mg L^{-1}, which was 27% higher than the average of the 3rd–5th order streams (4.5 g L^{-1}). To more accurately describe the DOC trend, we have revised the statement: 'Although statistically insignificant, DOC first exhibited a downward trend along the river course…', and also the description of the results (lines 230-237).

When plotting the DOC measured across the whole catchment over three seasons against the concomitant flow, there was no significant correlation between DOC and flow based on the spatial sampling results ($p>0.05$; please refer to the graph below). In comparison, our high-frequency sampling at the catchment outlet Baijiachuan gauge indicates that DOC concentrations were 26% 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. *Geochimica et Cosmochimica Acta*, 72, 5266-5277). Clearly, this positive response contradicts the indiscernible relationship between DOC and flow discharge within the catchment. This is probably because the three intensive seasonal samplings did not capture the carbon export in high-flow conditions. The flow discharge during the three sampling periods varied in the range of 0.002–105 $m^3 s^{-1}$ (please see this range in the figure below), which largely reflects the carbon export processes during low flow to, at most, medium flow conditions. In comparison, the high-frequency sampling at Baijiachuan gauge captured the carbon export during extremely high flows (200–1760 $m^3 s^{-1}$). We have also presented the raw data of monthly flow discharge and DOC concentrations in the Supplement (Table S2), so they are now available for free use. Please refer to the explanation of this discrepancy in the revised manuscript (lines 417-429).

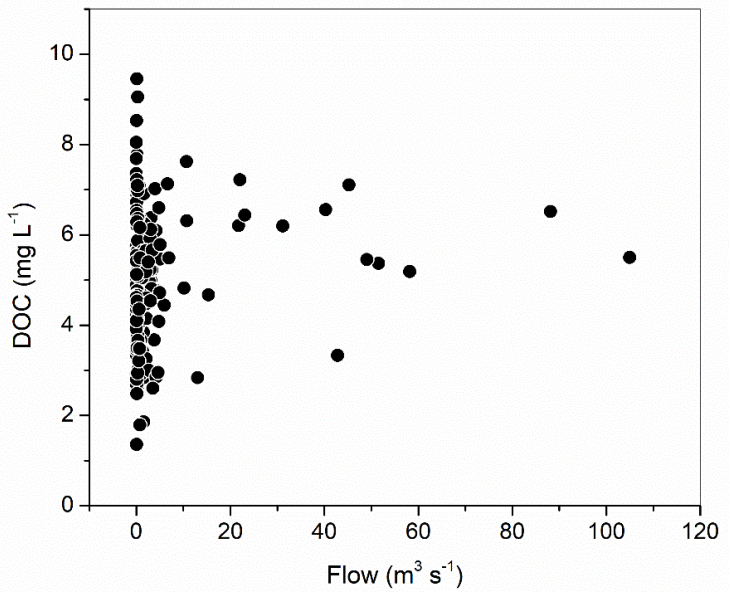

Figure: Relationship between flow discharge and DOC based on the three sampling results.

POC sources and trends

I find that a significant amount of discussion related to POC sources and sinks needs to be substantiated with more evidence or, at a minimum, alternate explanations need to be addressed. First, beginning on L326, the authors claim that low POC content (by which they mean % of suspended solids, a point that I address below) "reflects the ancient sedimentary OC origin of about 0.5% for fluvial sediments worldwide… [and is also] seen from the isotopic signature of the Yellow River sediment…" The authors go on to state that low %OC reflects "mobilization of subsurface soils that have a substantially lower OC content than surface soils" (L334). However, "ancient sedimentary OC" presumably refers to sedimentary rock derived material, which is certainly not the same as "subsurface soils". I'm left confused as to what the authors expect to be the major source of POC – sedimentary rocks or subsurface soils? I think that, with concentration measurements alone, one cannot make strong claims either way.

The well-known relationship between grain size and %OC is also not addressed. The observed POC concentration trends could easily be explained by variable hydrologic sorting – i.e. coarser, OC-poor sediments that are transported during high discharge periods – which would mask any POC source signal. In the absence of isotopic (d13C, Δ14C) or grain-size-dependent measurements (e.g. %OC as a function of Al/Si ratios), I find it hard to believe that POC sources can be prescribed as is done here (also repeated beginning on L385).

Reply: Thanks a lot for your comment. Just as you mentioned, in this manuscript we expressed the POC content in the total suspended solids (TSS). Therefore, it is a percentage of the TSS (dry weight). To make it more clear and consistent throughout the manuscript, we have replaced this term with 'POC%' throughout the manuscript, including all figures and tables. This has been explicitly introduced in manuscript (lines 161-163). As for the sources of POC, it is closely related to the soil erosion and sediment yielding characteristics of the Wuding River catchment, or generally, the whole Chinese Loess Plateau. The Chinese Loess Plateau (area: ~440,000 km^2) is covered with 100-300 m thick highly weathered loess soils (Zhao et al., 2013. *Land Degradation & Development*, 24, 499–510; Nie et al., 2015. *Nature Communications*, 6:8511, doi: 10.1038/ncomms9511). As a result of the very fine soil particles, soils in the Loess Plateau are extremely susceptible to erosion. And gully erosion is the major erosion type and is responsible for >70% of the total erosion rate for most parts of the Loess Plateau (Xu, 1999. *Catena*, 36, 1-19; Li et al., 2015. *Geomorphology*, 248, 264-272). Actually, gully erosion of tens of meters is quite common (please also see the photo below for a visual experience).

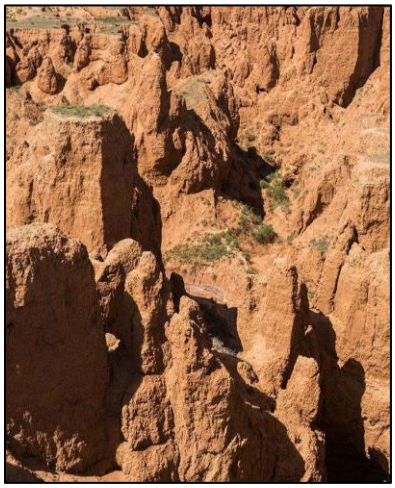

Figure: Gully erosion on the Loess Plateau.

The low POC% in the sampled sediments is quite close to the organic carbon content of sedimentary rocks (i.e., 0.5%; Ludwig et al., 1996. *Global Biogeochemical Cycles*, 10, 23-41). Recent studies investigating POC of the Yellow River sediment by means of $\delta^{13}C$ and $\Delta^{14}C$ analysis also suggest that its POC is not from the recently fixed terrestrial plant materials and freshwater plankton, but from the highly decomposed loess soils and weathering of sedimentary rocks and ancient kerogen (Wang et al., 2012. *Global Biogeochemical Cycles*, 10, 26, GB2025, doi:10.1029/2011GB004130). As the primary source of the Yellow River sediment, we can expect that the sediment in the Wuding River catchment carries similar carbon isotopic signatures as that in the Yellow River sediment. Therefore, in association with the high contribution of gully erosion to annual TSS transport and the low organic carbon content of the sampled TSS, we concluded that the lower POC% in suspended solids in summer likely reflects the origin of sedimentary rocks mobilized by gully erosion. Based on your comment, we have carefully revised the manuscript and corrected the misuse of 'subsurface soils' and 'ancient sedimentary rocks'. In addition, necessary references have been added to justify the arguments. Please refer the highlighted changes in the manuscript (lines 369-378).

With respect to the relationship between grain size and POC%, prior studies have investigated the POC% changes in relation to the grain size of sediment in the Loess Plateau and the Yellow River. For example, Zhang et al. (2013. *Biogeosciences*, 10, 2513–2524) divided TSS into five categories (i.e., <8 µm, 8–16 µm, 16–32 µm, 32–63 µm, and >63 µm) and determined the POC% of each category. Their results show that more than 75 % of the POC was concentrated in sediment particles with grain size smaller than 16 µm, which suggests that the TSS grain size was the dominant factor controlling POC transport in the Loess Plateau and the Yellow River. Same results of a higher POC% in smaller particles are also discovered by Wang et al. (2012. *Global Biogeochemical Cycles*, 10, 26, GB2025, doi:10.1029/2011GB004130). We have added these justifications into the revised manuscript, and references have been used to justify our arguments (lines 434-446). In addition, our ongoing (biweekly) sampling at the catchment outlet Baijiachuan gauge is aimed to explore the relationship between grain size and POC%, and hopefully the sources of POC could be better prescribed. Many thanks for your comments and inspirational suggestions.

Similarly, beginning on L408, %OC content behind check dams is compared to that on hillslopes and is used as evidence for burial efficiency. However, this "negligible OC loss after erosion" (L412) could be explained by alternative hypotheses. For example, deposited material could (likely does?) contain a different grain size distribution than that of hillslope soils, and thus a different %OC content. Also, any remineralization of terrestrially derived POC could be masked due to replacement by aquatic sources (as is discussed). Again, I find it hard to prescribe POC sources and burial efficiencies without additional measurements such as d13C and Δ14C. I also find the claim that this material "would have otherwise been mineralized to form CO2 or CH4 along fluvial delivery" (L418) to be somewhat speculative. Presumably some of this material would have been transported and buried in coastal marine sediments. Heuristically, it makes sense that burial efficiencies behind check dams are higher than for coastal marine sediments, as the authors imply, but I find a general lack of evidence supporting this claim.
Reply: The hilly areas of the Loess Plateau is dominated by gully erosion which can mobilize both the surface soils and the deeper soils as shown in the figure above. And numerous studies on soil erosion in the Loess Plateau have also confirmed the dominant role of gully erosion in

annual total soil erosion rate as mentioned above. For example, in the Wuding River catchment, Zheng et al. (2008. *Geomorphology*, 93, 288-301) concluded that '*when rainstorm intensity is sufficiently strong (> 0.3 mm min^{-1}), all grain-size fractions of loess on a hillslope are eroded without sorting*'. Because most of the check dams are constructed on gully channels and very close to the eroding sites, the eroded soils from hillslopes and gullies can be quickly trapped by check dams after a short delivery distance (usually less than 5 km based on our field surveys). The sediment trapping efficiency is surprisingly high (e.g., >90%) as most dams only have a small intake for irrigation and don't have spillway gates (please see a typical check dam shown below, taken by Lishan Ran during the fieldwork). Thus, the loss during fluvial transport is likely small as suggested by the comparison between POC% in sediments and soil OC in hillslopes. Moreover, just as you commented, any remineralization of terrestrially derived POC may have been masked due to replacement by aquatic sources. However, based on the combined use of ^{137}Cs and δ^{13}C techniques as well as C/N ratios, our earlier work (Wang et al., 2017. *Agriculture, Ecosystems and Environment*, 247, 290-297. Nufang Fang, a co-author of this manuscript, conceived the cited paper) discovered that most of the buried POC is derived from soil erosion from the catchment. In addition, approximately 70% of the eroded soil OC can be buried by check dams in the study catchment. Finally, eroded soil OC is subject to a number of biogeochemical processes, such as burial by impoundments, mineralization in the water column, outgassing, and export to the ocean depending on a suite of physicochemical conditions (e.g., Battin et al., 2009. *Nature Geoscience*, 2, 598-600; Drake et al., 2017. *Limnology and Oceanography Letters*, doi: 10.1002/lol2.10055). For the statement 'would have otherwise been mineralized to form CO_2 or CH_4 along fluvial delivery', we have reworded this sentence to make it more clear and accurate and added references to justify the claim. Please refer to the highlighted changes in the revised manuscript (lines 469-482).

Figure: A typical check dam in the Wuding River catchment.

Finally, I find that reporting "OC content" as %OC rather than a concentration (e.g. mg OC L-1) or a flux (e.g. t OC km-2 d-1) is ineffective and is somewhat misleading. For example, the authors state that "the substantially lower POC content in the wet season largely reflects the impact of gully erosion" (L385). However, one would expect that POC concentration and flux are actually significantly higher during the wet season! As described above, changes in %OC could reflect hydrologic sorting and are not necessarily indicative of source. I would strongly

recommend discussing POC trends in the context of concentration and flux, rather than %OC. This would allow the authors to shift the focus away from attempting to prescribe POC sources (which I find to be a weakness overall) and toward OC flux and budget estimates, which I think is a strength of this manuscript.

Reply: First of all, many thanks for your comment and suggestion. Because the POC sampling is conducted at 74 nested sites across the whole catchment (Figure 1), we did not delineate the boundary of the sub-catchment that each sampling site controls and calculate the POC yield (in units of t OC km^{-2} d^{-1}) by normalizing to the size of each sub-catchment. Also, it is not feasible to calculate the annual POC flux at these sampling sites based only on the 3 sampling campaigns in spring, summer, and autumn. Instead, we only calculated the annual flux of C (g C yr^{-1}), including DOC, DIC, and POC, at the catchment outlet Baijiachuan gauge for which we have monthly C results and daily flow and sediment export data. And this gauge-based fluxes were used in the C budget to evaluate riverine carbon export in relation to NEP. To better present the POC results, we have now used POC% (i.e., the percentage of POC in total suspended solids (dry weight)) to express the POC content in suspended solids. The term 'POC%' has now been used throughout the manuscript to avoid unnecessary misunderstandings. Just as you have expected, although the POC% in the wet season is lower than that in the dry season, the POC flux in the wet season is considerable on an annual basis because of the high sediment loading, accounting for 65% of the annual total POC flux. Also, with respect to the potential sources of POC, we have thoroughly revised the manuscript based your earlier comments. Please refer to the highlighted changes in the revised manuscript (lines 434-447; 469-477).

Data availability

In my opinion, a major strength of data-rich manuscripts such as this is the ability for readers to incorporate these data into future studies – whether those be review articles or comparisons to other, similar catchments. Along those lines, I am left wondering why the authors do not make all of their raw data available as supplemental tables? I would strongly suggest do so or, at a minimum, including a "Data Availability" statement pointing the reader to a repository that includes these data.

Reply: Many thanks for your comment. We strongly agree with your suggestion. This study is an extension of our earlier work (Ran et al., 2017. *JGR-Biogeosciences*, 122, 1439-1455). In the Supplementary Information of the Ran et al. (2017) paper, we have already made most of our raw data used in this study available. These data include the physiochemical parameters (e.g., location, elevation, channel slope, flow velocity, wind speed, pH, water temperature, dissolved oxygen, Chl *a*, etc.), CO_2 emissions (pCO_2 and areal flux), and dissolved carbon concentration (DOC and DIC) in both river and reservoir waters. To facilitate future review studies and/or comparison analyses, we have made the leftover data available by presenting them in the Supplement of this study. Specifically, these data include POC of sediment samples (2015 and 2017) and of drilled sediment from check dams, monthly DOC and DIC concentrations at the catchment outlet (Baijiachuan gauge) as well as the concomitant flow information. Please refer to the Supplement for these data (Tables S1-S3).

Smaller Comments

L14: Remove dash between "terrestrially derived", change "represent" to "represents".

Reply: Changed.

L15 (also L68): What is meant by "redistribution"? Do the authors mean "partitioning between DIC, DOC, and POC"? I would change this wording for clarity.
Reply: Here we meant the fate of riverine carbon during its transport from headwater streams to the catchment outlet, including downstream export to catchment outlet, CO_2 evasion from water surface, and organic carbon (OC) burial through sediment storage. We have replaced the word 'redistribution' with 'fate' for clarity in both sentences. (Lines 15 and 69)

LL17: Change to "While DOC…"
Reply: Changed.

L18: What is meant by "DOC concentration is spatially comparable within the catchment"? I'm confused by this statement. Don't you argue that DOC concentrations decrease with increasing stream order? (although I question this trend, as stated above).
Reply: Based on your comment, we have removed this ambiguous claim and rephrased the abstract. We have also discussed the spatial variation of DOC concentration from the headwater streams to the mainstem channel. (lines 17-19; 231-236). Many thanks.

L19: "This reflects the enhanced…" seems overly confident. I would say "This likely reflects…"
Reply: Changed.

L21-22: I'm still confused by the DIC sources – carbonate dissolution seems incompatible with the measured CO2 d13C and Δ14C values.
Reply: The measured $\delta^{13}C$ and $\Delta^{14}C$ values of the emitted CO_2 are different from that in the DIC of the Loess Plateau rivers (i.e., -6.7 to -12.9‰; Liu and Xing, 2012. Isotopic indicators of carbon and nitrogen cycles in river catchments during soil erosion in the arid Loess Plateau of China, *Chemical Geology*, 296, 66-72). Also, based on the $\delta^{13}C$ values of the DIC, Liu and Xing, (2012) discovered that it is largely derived from carbonate dissolution (48.1-94.6%,). The observed differences in this study reveal that the emitted CO_2 is not likely from carbonate dissolution-derived DIC. We have also revised the claim in the manuscript. (lines 495-504)

L23: Please be clear that you mean %OC in sediments when stating that "[POC content] shows low values in the wet season." As stated, this implies that POC concentration or flux are lower in the wet season, which I presume is not true.
Reply: Thanks a lot for your comment. We have clearly stated the 'POC%' in the abstract and throughout the manuscript.

L27 (and throughout): Please update the 14C notation, as described above. "Indicating the release of old carbon previously stored in soil horizons." Couldn't this also be described as a mixture of 14C-free carbonate dissolution and respired young OC? I'm not sure that this claim is supported.
Reply: Based on your major comment above, we have updated the ^{14}C notation throughout the manuscript. If looking at the ^{14}C results only, it could also a mixture of 14C-free carbonate dissolution and respired young OC as you suggested. But if we take the $\delta^{13}C$ results into account, it seems the contribution of carbonate dissolution is quite small, because the $\delta^{13}C$ signature of carbonate-derived DIC is 0‰ for DIC derived from carbonates by proton attack and -8.5‰ for DIC derived from carbonate dissolution (Barth et al., 2003. *Chemical Geology*, 200, 203-216;

Brunet et al., 2009. *Chemical Geology*, 265, 563-572). This $\delta^{13}C$ signature is significantly different from the observed $\delta^{13}C$ values of the emitted CO_2. Please also refer to our detailed responses to your major comment above. (lines 495-504; 525-528; 533-540)

L32: Define "NEP". I don't follow the last sentence of the abstract. What is meant by "…has been significantly offset by riverine carbon export"?
Reply: The definition of NEP 'net ecosystem production' has been inserted into the abstract. Because the lateral C export into the Wuding river network can be considered a loss of carbon from its terrestrial ecosystems, whether it is related to lateral transport of soil CO_2 (i.e., respiration taking place in soils) or lateral transport of SOC that is processed within the aquatic column. Therefore, the lateral transport of C from the upland terrestrial biosphere to the Wuding river network and its subsequent outgassing to the atmosphere offsets the estimates of terrestrial NEP. Similarly, Borges et al. (2015) discovered that riverine CO_2 evasion in African rivers offsets the terrestrial NEP of the Arica (Borges et al., 2015. *Nature Geoscience*, 8, 637-642). We have rephrased this claim in the revised text. (lines 32-34)

L38: "Rivers play an exceptionally significant role by directly linking…" Role in what? The global carbon cycle?
Reply: 'The global carbon cycle' has been added into the text.

L39: Remove dash between "terrestrially" and "derived".
Reply: Removed

L43: add "the" between "along" and "river".
Reply: Added.

L44: Remove comma after "processes".
Reply: Removed.

L45: Change "in-situ" to "in situ" for consistency.
Reply: Changed throughout the manuscript.

L46: How up-to-date is this 1.8 Pg C yr-1 number? See Drake et al. (2017) L&O Letters for an updated number.
Reply: Many thanks for your information. We have checked the updated C outgassing from global rivers and streams in Drake et al. (2017), which is now 3.2 Pg C $year^{-1}$, excluding the outgassing from non-running inland waters. This has been inserted into the revised manuscript. (lines 45-47)

L51: Has the number of studies on riverine carbon really been increasing exponentially? Change "recent" to "last".
Reply: To better describe the increasing studies on riverine carbon, we have reworded the statement: 'Although studies on riverine fluxes of carbon have been considerably increasing over the recent last 20 years…'. (lines 53-54)

L66: this should read "…through the drainage network to the catchment outlet…"

Reply: Revised. Many thanks.

L67: Remove “in” before “northern”.
Reply: Removed.

L83: This should read “…and is located”
Reply: Added.

L85: Consider defining “loess” here.
Reply: Because we divided the river catchment into two subcatchments based on the geomorphological landscape. For the loess subcatchment (Figure 1), it is generally covered with 50–100 m deep loess soils. (lines 88-89)

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L92: Citation for hydrologic regime description?
Reply: A reference (Li et al., 2007. Assessing the impact of climate variability and human activities on streamflow from the Wuding River basin in China. *Hydrological Processes*, 21, 3485-3491) has been inserted to support the statement. (lines 94-95)

L94: I’m confused – is this sentence saying that one particular extreme event led to an erosion rate of 7000 t km-2 yr-1 for a particular year? If so, what is the average erosion rate? I feel like this would be more informative.
Reply: The Wuding River catchment suffered severe soil erosion during the period 1956-1969, prior to the implementation of large-scale soil conservation programmes which were initiated from the early 1970s. The average soil erosion rate is about 7000 t km^{-2} yr^{-1} during this period. Since then, the soil erosion rate has been significantly reduced due to soil conservation, and current soil erosion is only 1500 t km^{-2} yr^{-1}. We have reworded the description in the revised manuscript. (lines 95-97)

L102-103: “[The altered CO2 exchange] remains to be quantified”. Didn’t you quantify this in Ran et al. (2017)? If so, how does this “remain to be quantified”?
Reply: We have quantified the CO_2 exchange in our earlier work (i.e., Ran et al., 2017. *Journal of Geophysical Research: Biogeosciences*, 122, 1439-1455) and have removed this statement from the revised manuscript.

L110: Change “was” to “is”.
Reply: Changed.

L124: Change “triple” to “triplicate”.
Reply: Changed.

L127: “radiocarbon Δ14C samples” is somewhat redundant. Change to “collected samples for 14C analysis” or similar.
Reply: Changed. Many thanks.

L147 (and throughout): “The Δ14C values were reported as percent modern carbon (pMC)”. These are two separate units! (see above discussion).

Reply: We have clarified the descript in the revised manuscript 'The ^{14}C results were reported as percent modern carbon (pMC)'. (lines 153-156)

L156: How reliable is this method for calculating carbon loads? This seems too simple. Why was something like LoadEst not used?
Reply: Estimating riverine carbon flux is a very important part of this study in which we attempt to investigate the fate of carbon after entering the drainage network from terrestrial ecosystems. Just as you have pointed out, there are a number of methods to estimate the annual fluxes of dissolved and particulate matter transported by rivers. Major methods currently used include linear interpolation and ratio estimators, regression-based methods historically employed by the USGS, and recent flexible techniques such as Weighted Regressions on Time, Discharge, and Season (WRTDS), etc. As you have also suggested, the most commonly used USGS software package for estimating constituent load using regression is known as LOADEST (Runkel et al., 2004. Load Estimator (LOADEST): A FORTRAN Program for Estimating Constituent Loads in Streams and Rivers. U. S. Geological Survey Techniques and Methods Book 4, Chapter A5). Lee et al. (2016) recently reviewed the potential for flux estimation bias across a broader range of estimation methods and concluded that the Beale's ratio estimator and WRTDS generally exhibit greater estimation accuracy and lower bias (Lee et al., 2016. An evaluation of methods for estimating decadal stream loads. *Journal of Hydrology*, 542, 185-203). Our annual carbon flux estimation in this study was based on the Beale's stratified ratio estimator. Since the riverine carbon concentrations were measured with "sparse" sampling frequency while flow and suspended sediment had a continuous daily measurement, this method could greatly reduce the bias introduced by relatively low sampling frequency, in particular the high flow events that are often under-sampled (Parks and Baker. 1997. Sources and transport of organic carbon in an Arizona river-reservoir system. *Water Research*, 31, 1751-1759). Indeed, we have already used the Beale's ratio estimator in our earlier estimation of carbon flux in the Yellow River with success (i.e., Ran et al., 2013. Spatial and seasonal variability of organic carbon transport in the Yellow River, China. *Journal of Hydrology*, 498, 76-88). And the Beale's ratio estimator has proven to be highly reliable and is recommended if the relationship between discharge and concentration is weak (e.g., Fulweiler and Nixon, 2005. *Biogeochemistry*, 74, 115-130; Awad et al., 2017. *Environmental Pollution*, 220, 788–796; Chen et al., 2014. *Journal of Geophysical Research: Biogeosciences*, 119, 95-109; Sun et al., 2017. *Hydrological Processes*, 31, 2062-2075). In comparison, we have also estimated the carbon flux by using the suggested LOADEST software package. The flux results show high consistency with each other, with a difference of less than 4.5%. We have added a detailed description of the estimate method (i.e., the Beale's ratio estimator) in the revised manuscript. Please refer to the highlighted changes in the text. (lines 161-180)

L160: "by multiplying annual sediment deposition rate…" How was deposition rate calculated? This is not described at all in the text.
Reply: Our earlier work (Ran et al., 2013. *Global and Planetary Change*, 100, 308-319) has estimated the average annual sediment deposition rate behind all check dams in the study catchment by considering sediment input into each check dam and its sediment trapping efficiency. This has been added into the revised manuscript. (lines 191-193)

L162: Change "was" to "were". Were these CO2 flux data taken directly from Ran et al. (2017),

or are these new data originally presented in this study? Overall, I would clearly state which data are new and which data are taken from previous studies (as these authors appear to have published multiple papers on this dataset…)
Reply: Changed. The CO_2 efflux data are taken from our earlier work (Ran et al., 2017). This study is built upon our earlier work (i.e., Ran et al., 2017). But in Ran et al. (2017), we only explored the environmental controls and dam impoundment impact on areal CO_2 emissions (mmol m^{-2} d^{-1}). In this study, we aim to evaluate the riverine C budget by considering lateral C export, OC burial, and CO_2 emissions from the whole drainage network. We have clearly stated which data are new (thus presented in the manuscript or in Supplement) and which data have been presented in our earlier work (i.e., Ran et al., 2017) in the revised manuscript. (lines 146; 187-188; 23-238; 271-272; 309-310)

L172: Please provide the minimum catchment threshold area, as this will affect calculated Strahler stream order.
Reply: To delineate the stream network, a threshold value of 100 cells (90-m resolution) was set on the assumption that a stream initiates within the cells. The delineated stream network was then classified using the Strahler ordering system. We have applied this minimum catchment threshold to delineate the whole Yellow River catchment and the result was validated with ground-truthing (Ran et al., 2015. *JGR-Biogeosciences*, 120, 1334-1347). This description has been added into the manuscript. (lines 195-200)

L177: How valid is the assumption that "each round of field sampling [is] representative of CO2 emissions" for these four-month periods? What about for DIC, DOC, and POC concentrations – presumably you assume these are representative too?
Reply: Located in the arid-semiarid climate zone, the surface water pCO_2 in the Wuding River catchment shows temporal variations between the dry and wet seasons (please see Ran et al., 2017. *JGR-Biogeosciences*, 122, 1439-1455). However, the *p*CO2 is generally consistent within the dry (or wet) season, which is probably because of the dominance of groundwater inflow. Our fieldwork in each campaign lasted ~25 days, and repeated pCO_2 measurements at some sites over 20-day intervals show high consistency (e.g., <6% difference). Thus, in view of the hydrologic regime (mainly groundwater input), we assumed that the three sampling campaign results in different seasons are representative of CO_2 emissions in the three four-month periods. To make it clearer, we have added 'a first-order estimate' into the statement. As for the DIC, DOC, and POC concentrations, we instead used the monthly sampling results at the catchment outlet (i.e., Baijiachuan gauge in Fig. 1) for the yearly flux calculation. (lines 205-206)

L189: Heterotrophic soil respiration need not be due to bacteria – this could also be fungal or archaeal respiration. I would simply stick with "heterotrophs".
Reply: Many thanks. We have revised the statement and 'heterotrophs' was used instead.

L216: Is this decline (insofar as it is statistically significant) really "remarkable"?
Reply: We performed a one-way ANOVA test for the DIC in the loess subcatchment. The p value in spring, summer, and autumn is 0.02, 0.05, and 0.01. Thus, we concluded that this decline is remarkable (statistically significant). We have added the 'one-way ANOVA test, $p \leq 0.05$' into the manuscript to justify the claim. (lines 245-247)

L225: I'm confused by the sentence beginning with "Because the flow regime in 2017 was significantly biased…" What is this saying? You applied the 2015 hydrological regime to the 2017 data?
Reply: The flow regime in 2017 was significantly biased due to an extreme flood on 25-26 July caused by heavy rainstorms (maximum daily rainfall: 203 mm; spontaneous discharge: 4490 m^3/s with a return period of 200 years. Figure S1 in Supplement). In comparison, the multi-annual mean water discharge is 35 m^3/s. As a result, the annual water flux in 2017 is 1.5-fold the recent mean annual water flux (2000-2015). Because both CO_2 emissions and NPP were measured in 2015, we used the hydrological data for 2015 to calculate downstream carbon export by assuming that carbon concentration was comparable in 2015 and 2017 and evaluated the carbon budget. We realized that this may have caused errors to the flux estimation. We also calculated the carbon flux based on the 2017 flow data. The results show that, if the extreme flood on 25-26 July was excluded, the carbon flux in 2017 is close to that in 2015 (7.3×10^{10} vs. $(7\pm1.9)\times10^{10}$ g). We have revised the statement in the manuscript for clarity and a new reference has been added to justify the impact of this extreme flood (He et al., 2018. *Geomatics, Natural Hazards and Risk*, 9, 70-18) (lines 256-261). In addition, we have also added a detailed description of the extreme flood event on 25-26 July in the Supplement (Figure S1).

L230: Fluxes should be in units of "g C yr-1" (I'm assuming the "yr-1" got dropped by accident).
Reply: Because we have already mentioned the 'annual' in the statement (The *annual* downstream carbon export…), adding 'yr-1' is redundant.

L257: This should read "Assuming the water surface area remained constant…"
Reply: Changed.

L265 (and throughout) Please add "VPDB" after "‰" when reporting d13C values.
Reply: Added throughout the manuscript. Thanks a lot.

L277: Should "soils" instead read "sediments"? How can sediment cores contain "soils"?
Reply: Revised.

L300: How turbid are these rivers? If they are quite turbid, then I would expect that photochemical degradation is probably insignificant.
Reply: The Wuding River catchment is one of the major sediment sources of the Yellow River as a result of severe soil erosion. The average suspended sediment concentration in recent years is in the range of 7900-11,000 mg/L, and it can reach 120,000 mg/L during floods. The extreme of in 2017 is recorded on 26 July at 488,000 mg/L. Thus, we have removed the claim of photochemical degradation from the text. (lines 340-342)

L301 (and throughout): Please change "labile" to "bioavailable" as this language is more consistent with our current understanding of OC decay dynamics.
Reply: Changed throughout the manuscript.

L312: I'm confused by the statement "…and the mixture of carbon export from the two subcatchments." I thought the "6th mainstem channels" are the two subcatchments, which combine to form the 7th order Wuding River? Or have I misinterpreted this? (It is hard to see on

Figure 1).
Reply: We have double checked the drainage network in Figure 1. The mainstem channel of the northwestern sandy subcatchment is in the 5th order and the mainstem channel of the southwestern loess subcatchment is in the 6th order. Thus, when the two subcatchment mainstem channels confluence, it is still a 6th order river. We have carefully adjusted this figure in terms of color scheme, marker size, label size, etc., and have added the subcatchment boundaries to make the figure much easier to read. Please refer to the revised Figure 1 for the changes.

L330: Similarly, please change "biogeochemically refractory" to "persistent" in order to be consistent with our current understanding of OC decay dynamics.
Reply: Many thanks for your suggestion. We have replaced this statement in the text.

L358 & 362: Phytoplankton are not aquatic plants. Please clarify this language.
Reply: Thanks a lot for your comment. While phytoplankton are plant-like in their ability to use sunlight to convert CO_2 and water into energy, they are not plants. We have reworded the claim in the revised manuscript '…intensive nutrient loading from agricultural fields may have facilitated the growth of phytoplankton like algae, …'. (lines 402-405)

L426: I'm confused by the inclusion of this sentence – what does it add to the discussion?
Reply: It seems this sentence is irrelevant to the discussion as you commented. It has thus been removed.

L464: Is the correlation between d13C and Δ14C statistically significant? Figure 9 does not report the regression slope equation nor any statistics, so I have no way of gauging the strength of this relationship (I'm not even sure if the line drawn in Figure 9 is a regression line…) Please clarify.
Reply: Based on your comment, we have performed the regression analysis by using the results of all the three sampling campaigns and have added the regression equation (slope and r^2) into the revised figure. Accordingly, we have clarified the argument in the revised text. Thanks a lot for your comment. (lines 525-528)

L470: "…which suggests the outgassing of ancient terrestrial OC after entering aquatic systems". I'm confused here – OC itself cannot be outgassed. Does this refer to CO2 generated from remineralization of old OC? If so, how do the authors know that this was remineralized after entering the aquatic system and not simply remineralized in soils and transported with soil pore waters?
Reply: As you have commented, the OC itself cannot be directly outgassed from the water-air interface. Here it refers to the CO_2 generated from remineralization of old OC, which is mineralized either in soils and then transported into rivers or in aquatic systems during transit. We have reworded the claim in the revised manuscript 'This suggests that the emitted CO_2 is derived from ancient terrestrial OC which is mineralized either in soils and then transported into rivers or in aquatic systems during transit…'. (lines 533-536)

L472: This claim (and others throughout the manuscript) isn't necessarily supported – I would urge caution when making concrete statements such as this. Rather, I would phrase this along the lines of "These results are consistent with…"

Reply: Thanks a lot for your comment. We have rephrased the wording of these claims, including this one and also others throughout the manuscript, to make them more accurate and appropriate. Thanks again. (lines 469-482; 495-504; 525-528; 533-540, etc.)

L510: I'm confused by the statement "…this percentage (16%) falls into the range of global-scale estimates of 50-70%..." 16% is not in the range of 50-70%... am I missing something?
Reply: Many thanks for pointing out this misinterpretation. The percentage of 16% in this study is lower than the global-scale estimate of 50-70% by Cole et al. (2007). We have revised this in the manuscript '… this percentage (i.e., 16%) is much lower than the global-scale estimate of 50 70% by Cole et al. (2007)'. (lines 575-577)

L514: In what way is the estimate of Cole et al. (2007) "conservative"?
Reply: Based on published estimates of gas exchange, sediment accumulation, and carbon transport, Cole et al. (2007) constructed a carbon budget for the role of inland waters (particularly lakes, rivers, and reservoirs) in the global carbon cycle. However, constrained by data availability, they were not able to characterize carbon transport in each inland water body and in most cases, they used mid-range values for the estimation. This can be seen from their paper, they repeatedly mentioned that their carbon flux estimates are conservative and associated with considerable uncertainties. The full citation is: Cole et al., 2007. Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. *Ecosystems*, 10, 171-184.

L516-517 (and 531): Please remove "… it is worth noting that".
Reply: Both have been removed based on your suggestions.

L537: Remove the dash between "terrestrially" and "derived".
Reply: Changed.

L548: "CO2 emissions represented an important pathway…" An important pathway for what? Carbon loss from the landscape? I would change this to "CO2 emissions are quantitatively important…" or similar.
Reply: We have rephrased the claim based on your suggestion. Thanks a lot.

Figure 1: This figure is hard to read given the current color scheme and marker sizes. I would consider changing the color scheme for clarity and making the markers significantly larger. Also, please provide a catchment outline for the "sandy" and "loess" subcatchments, as this delineation is currently unclear.
Reply: Thanks a lot for your suggestion. We have carefully adjusted this figure in terms of color scheme, marker size, label size, etc., and have added the subcatchment boundaries to make the figure much easier to read.

Figures 2-3: I would consider writing "Loess Subcatchment" and "Sandy Subcatchment" above panels (a) and (b) so that the reader does not have to dig through the caption to understand what is presented.
Reply: The names of the two subcatchments have been added into the two panels in both figures. Many thanks for your suggestion.

Figure 4: I'm confused by what the percentage numbers represent. This should be clarified in the figure caption.
Reply: The percentage above each order in (b) represents the proportion of CO_2 emissions from that order streams to the total CO_2 emissions. This has been clarified in the figure caption.

Figure 5: Why has the nomenclature and color scheme changed for this figure? Why not use the colored bars from Figures 2-3 and the "spring", "summer", "autumn" notation that is used throughout the text? Also, what is meant by "conventional age"? Is this equivalent to 14C yr BP?
Reply: The nomenclature and color scheme for this figure have been adjusted for consistency by using the same notation in the text. In addition, the caption has been revised to 'Seasonal variations in radiocarbon ages (year before present, BP) for the emitted CO_2 from the Wuding River catchment'.

Figure 7: Why is this figure showing NPP when the authors are interested in NEP? Why not show NEP directly? Also, please include the river network, subcatchment outlines, labels, etc. as in Figure 1.
Reply: Because NEP is calculated from NPP by subtracting the heterotrophic soil respiration (R_h) and the R_h is just a single numerical figure, we presented the spatial variation of the NPP within the catchment. The river network, subcatchment outlines, labels, etc. have now been included in the revised figure.

Figure 9: Why are units of pMC (which is not the same as Δ14C!) used in this Figure but 14C years used in Figure 5? Is this dashed line a regression line? If so, please include the regression equation and statistics. Technically, "young" and "old" only correspond to the y-axis and should point vertically, as the x-axis of this figure says nothing about age.
Reply: Based on your earlier comment, we chosen to use the percent modern (pMC) to describe the ^{14}C results throughout the manuscript. To compare our results with Wang et al (2012. *Global Biogeochemical Cycles*, 10, 26, doi:10.1029/2011GB004130) that investigated the ^{14}C age of DOC and POC in the Yellow River, we kept the '^{14}C yr BP' results in Figure 5. In addition, we have included the regression equation and statistics (r^2) in the figure.

Figure 10: I'm confused by the inset pie chart – what does 100% represent? Is this all of the carbon in the river network? If so, at what time points, or does this represent the relative annual fluxes? Again, more detail in the caption would be very much appreciated.
Reply: The inserted pie chart denotes the partitioning of riverine carbon among its five phases with the sum (100%) representing all the carbon entering the river network (i.e., $(18.5\pm4.5)\times10^{10}$ g C $year^{-1}$). We have added more details into the figure caption.

Figure captions: In general, I would like to see significantly more description in this figure captions.
Reply: We have significantly improved the figure captions on the basis of your comments and detailed information has been added. Please refer to the highlighted changes in the revised manuscript.

Dear Dr Lee,

Many thanks for your comments on our manuscript. Based on your very constructive comments, we have thoroughly revised the manuscript. Additional discussion and justifications have been added into the manuscript or into the Supplement. Please see below the detailed responses. Major changes have also been highlighted in the revised manuscript.

With best regards
Lishan Ran, on behalf of the coauthors

This study provides rich river carbon data from a watershed influenced by arid-semiarid climate. The data, including river carbon concentrations, exports, contents, and emissions in different carbon species, are very informative. I believe that more careful analyses of these comprehensive data can enhance our understanding of river carbon cycling and its role in linking terrestrial and marine biogeochemistry. I found some small and large problems which I think should be addressed for publication of this manuscript in Biogeosciences.

Estimation method of river carbon exports P4L156-160: River carbon exports are one of key results of this study, and thus should be estimated very carefully. However, I found that the estimate method of the exports is not clear. There are various estimation methods that could be applied. Aulenbach, B.T., Buxton, H.T., Battaglin, W.A., and Coupe, R.H., 2007, Streamflow and nutrient fluxes of the Mississippi-Atchafalaya River Basin and subbasins for the period of record through 2005: U.S. Geological Survey Open-File Report 2007-1080, https://toxics.usgs.gov/pubs/of-2007-1080/index.html Cohn, T.A., Caulder, D.L., Gilroy, E.J., Zynjuk, L.D., Summers, R.M., 1992, The validity of a simple statistical model for estimating fluvial constituent load-sâAˇTˇAn empirical study involving nutrient loads entering Chesapeake Bay: Water Resources Research, v. 28, no. 9, p. 2353–2363. Runkel, R.L., Crawford, C.G., and Cohn, T.A., 2004, Load estimator (LOADEST)âAˇTˇA FORTRAN program for estimating constituent loads in streams and rivers: U.S. Geological Survey Techniques and Methods, book 4, chap. A5, 69 p.
Reply: Estimating riverine carbon flux is a very important part of this study in which we attempt to investigate the fate of carbon after entering the drainage network from terrestrial ecosystems. Just as you have pointed out, there are a number of methods to estimate the annual fluxes of dissolved and particulate matter transported by rivers. Major methods currently used include linear interpolation and ratio estimators, regression-based methods historically employed by the USGS, and recent flexible techniques such as Weighted Regressions on Time, Discharge, and Season (WRTDS), etc. As you have also suggested, the most commonly used USGS software package for estimating constituent load using regression is known as LOADEST (Runkel et al., 2004. Load Estimator (LOADEST): A FORTRAN Program for Estimating Constituent Loads in Streams and Rivers. U. S. Geological Survey Techniques and Methods Book 4, Chapter A5). Lee et al. (2016) recently reviewed the potential for flux estimation bias across a broader range of estimation methods and concluded that the Beale's ratio estimator and WRTDS generally exhibit greater estimation accuracy and lower bias (Lee et al., 2016. An evaluation of methods for estimating decadal stream loads. *Journal of Hydrology*, 542, 185-203). Our annual carbon flux estimation in this study was based on the Beale's stratified ratio estimator. Since the riverine carbon concentrations were measured with "sparse" sampling frequency while flow and

suspended sediment had a continuous daily measurement, this method could greatly reduce the bias introduced by relatively low sampling frequency, in particular the high flow events that are often undersampled (Parks and Baker. 1997. Sources and transport of organic carbon in an Arizona river-reservoir system. *Water Research*, 31, 1751-1759). Indeed, we have already used the Beale's ratio estimator in our earlier estimation of carbon flux in the Yellow River with success (i.e., Ran et al., 2013. Spatial and seasonal variability of organic carbon transport in the Yellow River, China. *Journal of Hydrology*, 498, 76-88). And the Beale's ratio estimator has proven to be highly reliable and is recommended if the relationship between discharge and concentration is weak (e.g., Fulweiler and Nixon, 2005. *Biogeochemistry*, 74, 115-130; Awad et al., 2017. *Environmental Pollution*, 220, 788–796; Chen et al., 2014. *Journal of Geophysical Research: Biogeosciences*, 119, 95-109; Sun et al., 2017. *Hydrological Processes*, 31, 2062-2075). In comparison, we have also estimated the carbon flux by using the LOADEST software package. The flux results show high consistency with each other, with a difference of less than 4.5%. We have added a detailed description of the estimate method (i.e., the Beale's ratio estimator) in the revised manuscript. Please refer to the highlighted changes in the text. (lines 161-180)

Estimation method and uncertainty of NEP P5L182-199 and P7281-291: For river carbon budget analysis, the NEP result is critical to drive the conclusion. However, I am a bit skeptical about the approach to calculate NEP. The authors are using different independent data sources for NPP and SR, and then, to calculate Rh, adapting another study's assumption "Rh accounts for 54% and 40% of SR in forested and non-forested areas,". This methodology probably led to large uncertainty in the final NEP estimate, which should be at least discussed.
Reply: Thanks a lot for your comment. Estimating NEP is quite important for the carbon budget analysis of this study. We divided the study catchment into two subcatchments, including the sandy subcathment and the loess subcatchment. While forest cover in the Wuding River catchment is quite low (less than 5%) as a result of low precipitation, grassland is the major land cover in the sandy subcatchment and agriculture and grassland predominate the loess subcatchment (Wang et al., 2014. Spatial-temporal changes of land use in Wuding River Basin under ecological restoration, *Bulletin of Soil and Water Conservation*, 34, 237-243 (in Chinese with English abstract). This is largely the result of the implementation of the Grain-for-Green Project which was initiated by the Chinese government in 1999. After more than 10 years of implementation of this vegetation restoration program, the vegetation cover (forest and grassland) has greatly increased. Please also refer to two photos below showing the landscape of the sandy subcatchment (left) and of the loess subcatchment (right). Both photos were taken by me in 2015 during the fieldwork). To better describe the landscape of the catchment, we have revised the description in Section 2.1 'Study area' (lines 88-90). Therefore, the landscape and land cover of the Wuding River catchment are generally consistent with the distinction of "forested" and "non-forested" by Hanson et al. (2000). With respect to the huge range of the "non-forested" fraction heterotrophic (i.e.,10-90%), we have discussed the potential uncertainty in the revised manuscript. (lines 560-563).

Our rate is consistent with recent measurements under different vegetation types in this arid-semiarid region (e.g., Fu et al., 2013). Fu et al. (2013. Soil respiration as affected by vegetation types in a semiarid region of China. *Soil Science and Plant Nutrition*, 59, 715-726) measured total soil respiration in this arid-semiarid region. Their mean soil respiration rates under 4

different vegetation types are in the range of 1-1.4 µmol m^{-2} s^{-1}, which are equivalent to 380-530 g C m^{-2} $year^{-1}$. Thus, our estimate is reliable. We have carefully revised the manuscript with new references to justify our arguments (lines 316-326). Using the ratios derived from Hanson et al. (2000) has been widely used in the world to assess heterotrophic soil respiration in river catchments under different land cover types (e.g., Brunet et al., 2009. Terrestrial and fluvial carbon fluxes in a tropical watershed: Nyong basin, Cameroon. *Chemical Geology*, 3, 563-572; Lee et al., 2017. A high-resolution carbon balance in a small temperate catchment: Insights from the Schwabach River, Germany. *Applied Geochemistry*, 85, 86-96). Just as you have commented, this portioning is associated with potential uncertainty. We have further discussed this in the revised manuscript. (lines 320-326; 560-563)

Figure: Landscape characteristics of the sandy (left) and loess (right) subcatchments.

Data availability and clarification A strength of this study is that it provides and interpret the very comprehensive river carbon data. Biogeosciences readers would be interested to see the data/results in more detail. There are many results which are described in texts, yet cannot be directly read by figures or tables. Also, the authors might want to have a simple table that lists the data with time (which year, season,...), units (concentration, contents, exports...), and brief estimation methods. This study covers a lot of interesting data, but I am confused by how they were presented. Also, I am confused by the use of "concentrations" and "contents".
Reply: Based on your and other reviewers' comments, we have compiled all the data that are not included in our earlier work (i.e., Ran et al., 2017. *Journal of Geophysical Research: Biogeosciences*, 122, 1439-1455) in the Supplementary Information. In the Supplementary Information of the Ran et al. (2017) paper, we have already made most of our raw data used in this study available. These data include the physiochemical parameters (e.g., sampling time/season, location, elevation, channel slope, flow velocity, wind speed, pH, water temperature, dissolved oxygen, Chl *a*, etc.), CO_2 emissions (pCO_2 and areal flux), and dissolved carbon concentration (DOC and DIC) in both river and reservoir waters. To facilitate future review studies and/or comparison analyses, we have made the leftover data available by presenting them in the Supplementary of this study. Specifically, these data include POC of sediment samples (2015 and 2017) and of drilled sediment from check dams (2015), monthly DOC and DIC concentrations at the catchment outlet (Baijiachuan gauge, 2017) as well as the concomitant flow information. Please refer to the Supplement for these data (Tables S1-S3).

P1L15: What do you mean by "redistribution"?
Reply: Here we meant the fate of riverine carbon during its transport from headwater streams to the catchment outlet, including downstream export to catchment outlet, CO_2 evasion from water

surface, and organic carbon (OC) burial through sediment storage. We have replaced the word 'redistribution' with 'fate' for clarity in the text. (lines 15 and 69)

P1L17-18: I am not sure what you meant with this "While the DOC concentration was spatially comparable within the catchment," I would remove this.
Reply: Based on your comment, we have removed this ambiguous claim and rephrased the abstract. (lines 17-20). Many thanks.

P1L18-19 vs. P8L312-314: Is this sentence consistent with your claims in P8L312-314? I am confused. "it was generally higher in spring and summer than in autumn, especially in the loess subcatchment." vs. "There was no discernible seasonal difference in DOC concentrations in both subcatchments, although the hydrograph varied significantly among the three seasons."
Reply: Many thanks for your comment. We have reworded these inconsistent arguments in the text. The DOC concentration showed no significant seasonal differences among the three sampling campaigns and was not sensitive to flow dynamics, although the flow discharge changed by a factor of 3. This likely reflects the predominance of groundwater input over the entire year and its highly stable DOC, which may have masked the 'dilution effect' with lower DOC concentrations usually observed in high-flow periods. Please refer to the highlighted changes in the manuscript. (lines 17-20; 351-355; 605-609)

P1L19-21 vs P8314-321 vs P9L375-377: I am also confused that these discussions appear to contradict each other. High soil carbon leaching due to high rainfalls in many cases leads to high river carbon exports (massC/time), but not high river carbon concentrations (massC/volume H2O). High rainfalls increase river flows as well, so concentrations can increase or decrease.
Reply: We completely agreed with your comments. High soil organic carbon leaching due to high rainfalls tends to result in high riverine carbon export (mass C), but not high DOC or POC concentrations (mg/L or POC% in suspended solids). This largely reflects the 'dilution effect' during high-flow periods, especially in (sub)tropical and temperate catchments with continuous surface runoff contribution in the wet season. In the arid-semiarid Wuding River catchment, although there were no significant seasonal differences in the riverine carbon concentrations (massC/water volume) between the three sampling campaigns, the carbon fluxes in the wet season (high-flow periods) were much higher than that in the dry season. This can also be discovered from the annual carbon flux at the catchment outlet estimated from monthly sampling. Based on your comments, we have carefully revised these claims in the manuscript. (lines 17-21; 417-429; 434-438; 442-447)

P1L23 and P5L209: Did you mean "showed" by "shown"?
Reply: Changed.

P2L84, P2L89, P2L94: An exact time period or years should be provided.
Reply: The time periods of mean water discharge (1956–2007), annual precipitation (1956–2004), and soil erosion (1956–1969) have been added into the revised manuscript. (lines)

P6L225-228: The assumption should be justified better. Why did you particularly use hydrological data for 2015?

Reply: The flow regime in 2017 was significantly biased due to an extreme flood on 25-26 July caused by heavy rainstorms (maximum daily rainfall: 203 mm; spontaneous discharge: 4490 m3/s with a return period of 200 years. Figure S1 in Supplement). In comparison, the multi-annual mean water discharge is 35 m^3/s. As a result, the annual water flux in 2017 is 1.5-fold the recent mean annual water flux (2000-2015). Because both CO_2 emissions and NPP were measured in 2015, we used the hydrological data for 2015 to calculate downstream carbon export by assuming that carbon concentration was comparable in 2015 and 2017 and evaluated the carbon budget. We realized that this may have caused errors to the flux estimation. We also calculated the carbon flux based on the 2017 flow data. The results show that, if the extreme flood on 25-26 July was excluded, the carbon flux in 2017 is close to that in 2015 (7.3×10^{10} vs. 7×10^{10} g). We have revised the statement in the manuscript for clarity and a new reference has been added to justify the impact of this extreme flood (He et al., 2018. G*eomatics, Natural Hazards and Risk*, 9, 70-18) (lines 256-261). In addition, we have also added a detailed description of the extreme flood event on 25-26 July 2017 in the Supplement (Figure S1).

P7L298: Did you mean "concentrations" by "contents"?
Reply: To make it clearer, we have revised the term and now use the 'POC content (POC%) in sediments' throughout the manuscript. Please also refer to our response to your comment below P8L326-328.

P7L299: Specify by providing values to support "both DOC and POC contents in the Wuding catchment were relatively low compared with most rivers in the world."
Reply: For the Wuding catchment, its DOC concentrations are comparable to the global average DOC of 5.4 mg/L while its POC% is lower than most rivers in the world (mean: 0.95%; Ludwig et al., 1996. *Global Biogeochemical Cycles*, 10, 23-41). These global averages have been inserted into the text. (lines 333-335)

P8L303: I am not sure if this statement is valid. "This decomposition is generally associated with increasing water residence time for bacterial respiration in downstream streams due to decreasing flow velocities." I don't think that flow velocity generally decreases toward downstream. I think that travel time generally increases toward downstream and longer travel times provide more opportunity for decomposition.
Reply: Thanks a lot for the comment. We completely agree with your explanation on the downstream decrease in organic carbon concentrations after checking the flow velocity changes along the stream order. Thus, we have revised this claim: 'This mineralization is generally associated with increasing water residence time for bacterial respiration in downstream streams due to longer travel times which increase the potential for in-stream processes on DOC'. (lines 340-342).

P8L326-328: I don't understand what you mean here.
Reply: For POC, we used the POC content (POC%) in the total suspended solids (TSS) to present the results. This is because we tried to compare our results in the Wuding River catchment with the POC% values of the global rivers. Ludwig et al. (1996. *Global Biogeochemical Cycles*, 10, 23-41) synthesized global POC export into the oceans by continental erosion via major rivers. The average POC% values of the global rivers vary from 0.3% to 10.1%, although values above 1.5% are only observed in rivers with very low suspended

sediment concentrations (i.e., <300 mg/L). In addition, Meybeck (1993) assumed that riverine suspended loads have an ancient sedimentary OC origin of about 0.5% on average (Meybeck, 1993. C, N, P and S in rivers: from sources to global inputs, in: Interactions of C, N, P and S Biogeochemical Cycles and Global Change, Edited by: Wollast, R., Mackenzie, F. T., and Chou, L., Springer-Verlag, Berlin, 163-193). Comparing the POC% in the Wuding River basin with that of the global rivers shows the POC% in the Wuding River is at the lower end of the global rivers, which reflects the ancient sedimentary OC origin of about 0.5% for fluvial sediments. We have revised our justifications with new references in the revised version. (lines 333-335; 366-368)

Dear Authors,

After reading the very comprehensive and detailed comments by the two referees, as well as those from Dr Lee, it appears that your MS will need important revisions and probably a second round of review before it can be considered for final publication in BG. These three scientists well specialized in the field of your MS have raised very important points that must be carefully addressed in your revised MS. In particular, methodological aspects of carbon fluxes calculation deserve a detailed attention. I was in general satisfied with your answers to most of theses comments, and I strongly recommend you deeply re-work and re-organize your MS in consequence. I will be happy to read soon a revised version of your paper.

With best Regards
Gwenaël Abril, Biogeosciences Associate Editor

Dear Dr Gwenaël Abril,

Many thanks for your comments on our manuscript.

We have thoroughly reworked the manuscript based on your and the three reviewers' constructive comments. In particular, we have added a detailed description of the methodologies of carbon fluxes calculation into the revised manuscript. To calculate the annual flux of riverine carbon (DIC, DOC, and POC) at the catchment outlet Baijiachuan gauge, we used the Beale's stratified ratio estimator (Dolan, D.M. et al., 1981. Evaluation of river load estimation for total phosphorus. *J. Great Lakes Res.* 7, 207-214). As mentioned by the reviewers, the LOADEST method calculates fluxes by using statistical approaches like maximum likelihood estimation and least absolute deviation, and is better designed to estimate water-quality constituent flux in streams and rivers (Runkel et al., 2004. Load Estimator (LOADEST): A FORTRAN Program for Estimating Constituent Loads in Streams and Rivers. U.S. Geological Survey Techniques and Methods Book 4, Chapter A5). In addition, Lee et al. (2016) evaluated the accuracy of several commonly-used load estimation methods, including linear interpolation and ratio estimators (e.g., the Beale's stratified ratio estimator), regression-based methods (e.g., the LOADEST and FLUXMASTER software packages developed by the USGS), the Weighted Regressions on Time, Discharge, and Season (WRTDS)(please see: Lee et al., 2016. An evaluation of methods for estimating decadal stream loads. *Journal of Hydrology*, 542, 185-203). Lee et al. (2016) concluded that "*the Beale's ratio estimator and WRTDS generally exhibit greater estimation accuracy and lower bias*" than other load estimation methods. This is especially true for suspended-sediment load and POC flux estimations. Indeed, we have used the Beale's stratified ratio estimator in our earlier estimation of carbon flux in the Yellow River with success (Ran et al., 2013. Spatial and seasonal variability of organic carbon transport in the Yellow River, China. *Journal of Hydrology*, 498, 76-88).

Because our riverine carbon concentrations were measured with "sparse" sampling frequency while flow and suspended sediment had a continuous daily measurement, this method (i.e., the

Beale's stratified ratio estimator) could greatly reduce the bias introduced by relatively low sampling frequency, in particular the high flow events that are often under-sampled (Parks and Baker. 1997. Sources and transport of organic carbon in an Arizona river-reservoir system. *Water Research*, 31, 1751-1759). Thus, we use this method to calculate the annual carbon fluxes. For comparison, we have also calculated the carbon fluxes using the LOADEST software package downloaded from the USGS website. The flux results from the two methods are consistent and the difference is less than 5%. A detailed description of the Beale's stratified ratio estimator is shown below (please also refer to the lines 161-182 in the revised manuscript).

"Using the monthly sampling results of DOC and DIC concentrations in water and POC concentration (POC%) in the total suspended sediments (dry weight) measured at the catchment outlet Baijiachuan gauge, we calculated the yearly DOC, DIC, and POC fluxes from the Wuding River catchment. Because daily flow and sediment records are available, the yearly carbon flux was calculated by using the Beale's stratified ratio estimator which generally exhibits greater estimation accuracy and lower bias than other flux estimation techniques (Lee et al., 2016). The estimator can be expressed as follows:

$$\mu_y = \mu_x \frac{m_y}{m_x} \left(\frac{1+\frac{1}{n}\frac{S_{xy}}{m_x m_y}}{1+\frac{1}{n}\frac{S_x^2}{m_x^2}} \right) \quad (1)$$

where, μ_y is the estimated flux, μ_x is the mean daily water discharge for the year measured, m_y is the mean daily carbon flux for the days on which the dissolved and particulate carbon concentrations were determined, m_x is the mean daily water discharge for the days on which the carbon concentrations were determined, and n is the number of days on which the carbon concentrations were determined. Furthermore,

$$S_{xy} = \frac{1}{(n-1)} \sum_{i=1}^{n} x_i y_i - n m_x m_y \quad (2)$$

$$S_x^2 = \frac{1}{(n-1)} \sum_{i=1}^{n} x_i^2 - n m_x^2 \quad (3)$$

where, x_i is the individual measured discharge, y_i is the daily carbon flux for each day on which the dissolved and particulate carbon concentrations were measured. Clearly, the yearly DOC, DIC, and POC fluxes are derived from m_y/m_x, which is defined as the ratio of the mean of measured fluxes to the mean of water discharge of the days when fluxes were quantified. This ratio is used with the overall mean water discharge (μ_x) to estimate the annual carbon flux. The calculated annual fluxes of DOC, DIC, and POC were then added up to determine the total downstream carbon export from the Wuding River catchment."

When the annual DOC, DIC, and POC fluxes were separately calculated by using the Beale's stratified ratio estimator, the total downstream carbon export from the Wuding River catchment was determined as the sum of the fluxes of DOC, DIC, and POC at the catchment outlet. In addition, we have also significantly re-organized the manuscript to make it clearer and logically more consistent throughout the manuscript. Because there are several major changes and it is difficult to present all of them here, we have highlighted these major changes in yellow in the text, mainly in Sections 2.2, 2.3, 3.1, 3.4, 4.1, 4.2, and 4.3.

Furthermore, the data used in this study have been tabulated in the Supplement to make them available to other researchers for future comparative analyses and syntheses. We greatly appreciate the constructive comments made by the three scientists, which have improved the

manuscript. Based on their comments and suggestions, we have carefully revised the manuscript, as also shown in our point-by-point responses. However, please note that, because we have further revised the manuscript based on your comments, the line numbers in our earlier responses to the three reviewers may not necessarily match the changes in the latest manuscript version.