

“Source and flux of POC in a karstic area in the Changjiang River watershed: impacts of reservoirs and extreme drought”

Reply to referee #2

Comment 1: One objective of the paper is to study the impact of dams on the organic matter carried or settled in the Wujiang. However, it is not easy to identify how dams affect sampling parameters. Fig. 4 is important but not easy to read. I suggest a diagram comparing the quantitative variations of studied parameters along the river course (as a function of distance) for the two studied periods with the position of dams marked. The points that are considered as directly affected by reservoirs could be clearly identified on Figs. 4, 8, not only in Table 2. It might be more realistic to distinguish points that directly affected by reservoirs and those less affected, rather than “affected” and “unaffected” points. All points are probably more or less affected by the cascade of reservoirs.

Response: Thank you for your valuable comment. According to the suggestion, we tried to make a diagram with quantitative variations of studied parameters along the river course (as a function of distance). However, this diagram was not easy to read because there were many dams and sampling sites. Moreover, some sites were too close to present them clearly. In the Fig. 4, the dams were marked in order to make it easy to read. According to the comment, we have modified the description of sampling sites as “directly affected by reservoirs” and “less affected by reservoirs”.

Comment 2: The authors used combined DIC $\delta^{13}\text{C}$, C/N and $\delta^{15}\text{N}$ results to identify the source of organic matter.

①As shown by the diagram of Fig. 5, there are more than two possible sources. It is thus not clear how the authors made simple quantitative mixing models between phytoplankton and C3 plants, and between C3 and C4 plants on the basis of $\delta^{13}\text{C}$ alone (results shown on Fig. 6). Most $\delta^{13}\text{C}$ in Fig. 5 are consistent with a dominant C3 plant source (after given into account the variability of the C3 plant source). The most enriched points most possibly reflect C4 soil plant

input and the most depleted one phytoplankton input. It is however not possible to make quantitative estimations (on the basis of $\delta^{13}\text{C}$ alone) as three possible sources are mixed.

Response: Thank you for your valuable comment. In the present study, the linear relationship of TN and POC was relatively weak compared with other studies (see details in answer to comment 4). This could limit the usefulness of C/N ratios as a tracer of particulate organic matter source. The $\delta^{13}\text{C}$ of POC in the suspended matters in August averaged $-27.23 \pm 2.93\%$, indicating that the terrestrial source was a major source of POC. While the corresponding C/N averaged 8.84 ± 3.73 , indicating that phytoplankton was a dominant source of POC. The lack of power to resolve the source of organic matter using C/N ratios was also noticed in other studies (Sarma et al., 2012; Middelburg and Herman 2007). Thus, we use $\delta^{13}\text{C}$ to calculate the contribution of different sources of organic matter. Soil organic matter (including litterfall) is eventually a mixture of residues from the overlying vegetation, which is composed of C3 and C4 plants. Thus, the $\delta^{13}\text{C}$ values of soil organic matter can be used to reflect the terrestrial sources of POC. In the present study, the contribution of C3 plants and C3 plant-dominated soil together represented the C3 source; C4 plants and C4 plant-dominated soil together represented the C4 source. According to the source criteria developed from the $\delta^{13}\text{C}$, we think that the contribution of phytoplankton, C3 and C4 source can be distinguished.

Middelburg, J.J., Herman, P.M.J.: Organic matter processing in tidal estuaries, *Mar. Chem.* 106:127–147, 2007.

②The identification of the phytoplankton end-member in the text is confusing. It is stated that it can be measured on the basis of dissolved DIC $\delta^{13}\text{C}$ and fractionation factor of -21% (page 6, lines 10-11). A calculated range (?) of -32.6 to -24.4% was given although not DIC $\delta^{13}\text{C}$ have been given. They could be supplied as supplementary material if available. It is also stated that phytoplankton $\delta^{13}\text{C}$ is lower than -30% (page 6, line 5), then that it has a typical range between -42 and -24% (page 6 line 13).

Response: Thank you for your valuable comment. Measured $\delta^{13}\text{C}$ -DIC in the Wujiang River ranged from -11.55% to -3.41% , with an average value of -8.67% . These data is included in another paper, which is under review. Thus, we do not show them in Table 1. Based on the range of $\delta^{13}\text{C}$ -DIC and fractionation factor of -21% , the estimated $\delta^{13}\text{C}$ values for phytoplankton (-32.6%

~ -24.4‰) can be obtained.

In order to make it uniform, the typical $\delta^{13}\text{C}$ range of phytoplankton from Mook and Tan (1991) was corrected as Kendall et al. (2001) and references therein based on the study by Li (2009) on $\delta^{13}\text{C}$ of phytoplankton ($-29.5\pm 5.5\%$) in Maotiao River (a tributary of Wujiang River).

③ An average $\delta^{13}\text{C}$ of -13.4% is given for C4 plants in the catchment from Tao et al. (2009) (page 6, line 24), but the sigma value (with reference) is not given. The exact values and references (published in English) for the average and sigma values of C3 fresh plant and soil end-members (shown in Fig. 5) were not given. Note that the average $\delta^{13}\text{C}$ values for C3 plants (ca. -28% from Fig. 5) seem a bit more depleted than expected. If measurements exist for the main C3 plants in the catchment are available, they could be added as supplementary material.

Response: Thank you for your valuable comment. The $\delta^{13}\text{C}$ of different endmembers were taken from other studies in the Wujiang River (Tao et al., 2009 and references therein; Li 2009; Wu et al., 2007). Unfortunately, we did not collect the different endmembers of organic matter in the Wujiang River. Thus, the related data were not shown in supplementary material. The $\delta^{13}\text{C}$ of different endmembers (mean \pm standard deviation) were added in Fig. 4 (new edition).

④ Fig. 5 clearly shows a set of points with high C/N, suggesting an important contribution of fresh terrestrial plant material, essentially from C3 plants. This point is not discussed.

Response: Thank you for your valuable comment. As shown by the contribution of different organic matter, POC in the Wujiang River was mainly derived from the terrestrial source. Given the limitation of C/N in the studied basin (see details in answer to comment 4), it was difficult to distinguish the contribution of C3 plants from the C3 plant-dominated soil. In the present study, these two sources represented C3 source.

Comment 3: The discussion on sediments $\delta^{13}\text{C}$ is not easy to read. As shown by the authors (Fig 5, 8 and page 7 lines 10-19), the sediments are enriched in ^{13}C (relative to suspended sediments). The authors proposed that there is a relative increase in C4 plant debris in the sediment or preferential loss of light isotopes in the sediment (lines 13-4) and then later proposed a preferential biodegradation of the phytoplankton in the water column (lines 16-17). These three possible options are not discussed. The $\delta^{13}\text{C}$ sediment/suspended sediment plot was introduced later (page 8, lines 14-15) and can be useful in that part of the discussion.

Response: Thank you for your valuable comment. As mentioned in the comment, the enriched $\delta^{13}\text{C}$ in the sediments might be attributed to three causes. Given that POC and TN contents were higher in most sediment samples than suspended sediments, we think that the biodegradation of the phytoplankton was not significant. Thus, the higher $\delta^{13}\text{C}$ in the sediments was mainly due to the contribution of refractory allochthonous organic matter (i.e. C4 plants). The related discussion has been added in the corresponding section.

Comment 4: It is not clear why the positive relation between POC and TN (total nitrogen) suggested that a fraction of nitrogen is inorganic (page 5 line 24; page 7 line 5-6). One would expect indeed a positive relation between POC and particulate organic nitrogen, with the slope depending on organic C/N ratio. It could also be useful to specify the possible inorganic forms of nitrogen in sediments and suspended matter. $\delta^{15}\text{N}$ is considered as a tracer of POC source throughout the text (see page 5, line 19 among others). It is actually a tracer of nitrogen source and by consequence of organic matter source.

Response: Thank you for your constructive comment. Ratios of C/N have been used to distinguish sources of organic carbon in marine and coastal environments based on the assumption that all of the sedimentary TN exclusively reflects N bound to organic matter (Meyers, 1997). As mentioned in the comment, the slope of linear relationship between TN and POC content depend on organic C/N ratio and the intercept value could reflect the inorganic nitrogen. In the present study, the linear relationship of TN and POC was relatively weak (May: $\text{TN}=0.07*\text{POC}+0.09$, $R^2=0.54$, $P<0.001$; August: $\text{TN}=0.04*\text{POC}+0.23$, $R^2=0.39$, $P<0.001$) compared with other studies ($R^2=0.71$ in Hu et al., 2006; $R^2=0.9$ in Guerra et al., 2013). Thus we think that the inorganic nitrogen in the present study was relatively high in comparison with the above studies. The related discussion has been added in this part.

The related reference:

Meyers, P.A., 1997. Organic geochemical proxies of paleoceanographic, pleolimnologic, and paleoclimatic processes. *Organic Geochemistry* 27, 213-250

Comment 5: The discussion of $\delta^{15}\text{N}$ is confusing (page 8, lines 1-10).

①To explain the variation in $\delta^{15}\text{N}$ in suspended matter, the authors refer to dissolved nitrate

$\delta^{15}\text{N}$ (Fig. 8a). These data are however not given in Table 1. They used these data to assess that high $\delta^{15}\text{N}$ of N in suspended sediments indicated manure and domestic sewage (page 8, lines 1-2), but then to confirm nitrogen input from phytoplankton (line 4-10). The importance of sewage organic matter / phytoplankton N derived from sewage-nitrate is not at all discussed.

Response: Thank you for your valuable comment. The dual isotopes of dissolved nitrate are included in another paper which is under review. Thus, we do not show them in Table 1. The discussion about anthropogenic source has been rewritten.

②.... the good correlation between ^{15}N in sediment and suspended matter (Fig. 8c) is not really discussed. Relative high $\delta^{15}\text{N}$ values are observed in both the sediment and suspended sediment. This is not in agreement with previous assumptions made by the authors that high $\delta^{15}\text{N}$ is essentially tied to the phytoplankton input and that phytoplankton is mainly decomposed in the water column. This might suggest an enriched source of “recalcitrant” N or an incorporation of phytoplankton-N in recalcitrant sediment nitrogen.

Response: Thank you for your constructive comment. The discussion about the correlation of sediment and suspended matter has been rewritten in the corresponding section.

Comment 6: Figures (3, 9 and may be 7) and tables (1, 3, 5) might be supplied as supplementary materials. The information from table 2 can be given in the text. It is better to put the measurements for a given site on one given line in Table 1. For Fig. 6, see above point 2.

Response: Thank you for your valuable advice. As suggested by the reviewer, Figure 3, table (1, 3, 5) were put in the supplementary materials. Considering that the Figure 7 and Figure 9 are meaningful for comparison with the world rivers, we put them in the paper. In order to make it easy to understand the comparison of parameters between dam-affected sites and less dam-affected sites, the information in Table 2 was shown as a table.

Comment 7: I suggest a revision of the paper by native English speaker.

page 1, line 27 “characterized” instead of “charactered”

.....

Page 4 line 8 and throughout the text “cascade of reservoirs” instead of “cascade reservoirs”

Response: Thank you for careful work. We have accepted the suggestion and made corresponding corrections according to the comment.

Reply to referee #3

General overview:

The authors measured $\delta^{13}\text{C}_{\text{POC}}$, $\delta^{15}\text{N}_{\text{TN}}$ and C/N ratios in both suspended and surface sediments along the Wujiang River and attempted to identify source and flux of POC in the Wujiang River and addressed the impacts of reservoir on POC flux into the Changjiang (or finally into the East China Sea). I think the authors had lots of data sets in two different seasons, but the whole paper presentation is not very good. I am confused about the title, introduction and interpretation about the content. Overall, I think the paper need a major revision before it can be considered to be published.

Response: Thank you very much for reviewing the manuscript and for the valuable comments. We have revised the manuscript based on the comments and suggestions.

My major comments are as follows:

Comment 1. The title is not suitable because the data set of POC flux and POC sources in the Changjiang River is only from upper branch. The authors mentioned POC fluxes in different rivers in the introduction, but it did not touch real POC flux in the Changjiang River mouth or the East China Sea. The title should be modified.

Response: Thank you for the comment. The Wujiang River is the largest tributary of the upper Changjiang River in its south bank. Although there are many tributaries for Changjiang River, Wujiang River is a typical karst watershed. Thus, we think that the title can represent the major objectives of our study.

Comment 2. As addressed above, the introduction described the importance of riverine POC flux to different marginal seas and the main objective of the manuscript seems to emphasize the effect

of Three Gorge Dam on POC flux to the East China Sea. I suggest that the authors should review possible difference of POC flux in the Changjiang before and after the construction of Three Gorge Dam. For example, the authors keeping saying POC flux to marginal seas are quite important, but they said that..... “Wujiang River is still scarce after the Three Gorges Dam began impounding sediment in 2004. Based on analyses of $\delta^{13}\text{C}_{\text{POC}}$, $\delta^{15}\text{N}_{\text{TN}}$ and C/N ratios in the suspended and surface sediments, this study identified source and flux of POC in the Wujiang River and examined the impacts of reservoir and climate.” I did not see the description above associated with whole Changjiang watershed because the Wujiang River is only a part of Changjiang branches. Plus, they attempted to study the impacts of reservoir (Three Gorge Dam?) and climate based on two season data sets. I think the little data can not wholly support their perspective. Instead, the author should point out what POC flux in the Changjiang River before the construction of Three Gorge Dam are in the introduction? In the next step, they want to examine the impacts of trapped POC in Three Gorge Dam affecting the output of Changjiang River. Anyway, the introduction and abstract need to be re-worked. A useful reference should be helpful for the authors. Hung et al. (2003). Fluxes of particulate organic carbon in the East China Sea in summer. *BG*, 10, 6469-6484.

Response: Thank you for the comment. As suggested in the comment, variations of POC flux in the Changjiang River before and after the construction of Three Gorges Dam are important to identify the influence of damming on the local carbon cycle and even on the global carbon cycle to some extent. The related review has been added in the introduction. Eleven artificial dams have been constructed along the mainstream of Wujiang River (Fig. 1). However, related study on the impacts of these cascades of dams is limited. Thus, one of the objectives of our study is to estimate the impacts of the above eleven cascades of dams on the POC source and flux in a karstic watershed. The objectives of this study in the introduction have been made clearer. Two season samples were collected in the present study. These data may lead to a high level of error when estimating the impacts of reservoirs and drought of 2013. However, we think that it is helpful for understanding the variations of POC source and flux in the Wujiang River in the special drought year of 2013.

Comment 3. Source of organic carbon in suspended particles and sediments are roughly separated

to two main sources which may not be right. I can see authors discussed the percentage of each compound (C3 and phytoplankton) in equations 1~3 in the text, but they also explain possible sources such as C4 and C4-soil and include these compounds into equations. It is quite inconsistent for the data interpretation. I suggest the authors need do it based on other sources.

Response: Thank you for the comment. According to the comment, we have carefully modified the mixing model using indicators of $\delta^{13}\text{C}$ values and C/N ratios. The combination of $\delta^{13}\text{C}$ values and C/N ratios is also used in other studies (Jiang and Ji, 2013; Lu et al., 2013).

Lu, F. Y., Liu, Z. Q., Ji, H. B.: Carbon and nitrogen isotopes analysis and sources of organic matter in the upper reaches of the Chaobai River near Beijing, China. *Science China Earth Science*, 56(2), 217-227, 2013.

Jiang, Y. and Ji, H.: Isotopic indicators of source and fate of particulate organic carbon in a karstic watershed on the Yunnan-Guizhou Plateau. *Appl. Geochem.*, 36, 153–167, 2013.

Results.

Comment 3.1 line 25-26, it has been described in the method, delete it.

Response: Thank you for the comment. The mentioned description has been deleted.

Comment 3.2 Line 21-23 content should show in the method section

Line 27, how significant? Showing p and n

Response: Thank you for the comment. The mentioned content (Line 21-23) has been moved in the method section. The values of relation coefficient and p have been added in the Table S2.

Discussion

Comment 4.1 ...line 23 suggested the dominant terrestrial contribution to SPM in May and increased phytoplankton input in August. As discussed, all samples were collected in the fresh water suspended particles or sediments, it is absolutely from terrestrial source.

Response: Thank you for the comment. As mentioned in the comment, POC is generally derived from terrestrial source in the fresh water. However, aquatic source increases as more and more artificial dams are constructed. A similar study can be seen from one tributary of Wujiang River (Jiang and Ji, 2013), in which POC of SPM was mainly derived from phytoplankton.

Comment 4.2 line 27-29 showed a relatively significant positive correlation, which suggested that a fraction of TN was inorganic nitrogen in the SPM. Why? Thus, the phytoplankton inputs might be overestimated based on C/N ratios. How can you explain this? Is it related to Redfield ratio?

Response: Thank you for the valuable comment. According to Meyers (1997), ratios of C/N are used to distinguish sources of organic carbon in marine and coastal environments based on the assumption that all of the sedimentary TN exclusively reflects N bound to organic matter. As discussed in the manuscript, the slope of linear relationship between TN and POC content depend on organic C/N ratio and the intercept value could reflect the inorganic nitrogen. In the present study, the linear relationship of TN and POC was relatively weak (May: $TN=0.07*POC+0.09$, $R^2=0.54$, $P<0.001$; August: $TN=0.04*POC+0.23$, $R^2=0.39$, $P<0.001$) compared with other studies ($R^2=0.71$ in Hu et al., 2006; $R^2=0.9$ in Guerra et al., 2013). The intercept of the above regressions was more than zero, which suggested that a fraction of TN was inorganic nitrogen in the SPM (Guerra et al., 2013; Hu et al., 2006). Because contents of total nitrogen included some inorganic nitrogen in the study area, measured C/N ratios were underestimated, which led to phytoplankton inputs overestimated based on measured C/N ratios.

Guerra, R., Pistocchi, R. and Vanucci, S.: Dynamics and sources of organic carbon in suspended particulate matter and sediments in Pialassa Baiona lagoon (NW Adriatic Sea, Italy), *Estuar. Coast. Shelf S.*, 135, 24-32, 2013.

Hu, J., Peng, P. A., Jia, G., Mai, B. and Zhang, G.: Distribution and sources of organic carbon, nitrogen and their isotopes in sediments of the subtropical Pearl River estuary and adjacent shelf, Southern China, *Mar. Chem.*, 98(2), 274–285, 2006.

Meyers, P.A.: Organic geochemical proxies of paleoceanographic, pleolimnologic, and paleoclimatic processes. *Organic Geochemistry* 27, 213-250, 1997.

Comment P6, line 9-20, are C3 and phytoplankton POC only two sources? How about other sources? Do authors have other C sources like C4 etc.? If other C sources exist, the equations 2 and need to solved? There is a useful reference (Hung et al., *ECSS*, 84, 566-572) which reported that POC/Chl-a ratio in summer ranged from 50 to 70, if the authors have Chlorophyll-a data. They can estimate POC source from phytoplankton based on suspended POC data.

Response: Thank you for constructive comment. The method in the study of Huang et al. (2003) is useful to estimate POC source from phytoplankton. Unfortunately, we did not measure the values of Chlorophyll-a in our study. As mentioned in the comment, there exist C4 source in addition to C3 and phytoplankton. The mixing model of end-members was modified.

Comment Line 25-34 why the phytoplankton in affected and the unaffected areas has large difference? They are both affected by fresh water largely. Is it due to residence time or other carbon sources?

Response: Thank you for the comment. Two mechanisms could explain the elevated phytoplankton contribution in sites affected by reservoirs: (1) extended water retention time in reservoirs with low flow; (2) increasing light availability due to the low TSS concentrations in reservoirs. This related discussion was included in the section 4.4 (Impacts of reservoir and climate on riverine POC).

Comment P7, ...Compared with SPM, the elevated C/N ratios of surface sediments indicated more land-derived fraction contribution to the surface sediments. What other sources contributed to POC in sediments? Line 10-13, If C4 is partially associated with POC, then the end member mixing model should be modified.

Response: Thank you for the valuable comment. According to the comment, we have carefully modified the mixing model using indicators of $\delta^{13}\text{C}$ values and C/N ratios.

Comment 4.3 & 4.4 Flux of POC in Wujiang River, as mentioned early, the amount of POC flux is totally into Three Gorge Dam? It is quite simple to estimate POC and PIC fluxes. The important thing should be focused on how much POC are trapped in the TGD and affect the POC export flux to the East China Sea. I think this portion should need deep discussion. For example, the author should compare the POC flux at the upper and lower watershed of TGD before and after construction of TGD. Plus, the authors keep saying possible impacts of the TGD, ...the variations of suspended sediment load could reflect the POC flux variations under the condition of dam and extreme drought..." What my understanding is that the authors should provide POC flux in the lower watershed of TGD rather than upper watershed because these upper POC finally will empty

TGD, right?

Response: Thank you for the comment. The Wujiang River flows into the Three Gorges Reservoir in Chongqing Municipality. It is better to estimate the POC flux using a depth-integrated concentration (Coynel et al., 2005). However, due to the large elevation gradients with about 1500 m in its upper reach and 500 m in its lower reach, Wujiang River has high flow rates. This makes it difficult to collect samples in different water depths. The POC concentration of river mouth is used to calculate the POC flux, which is frequently used in other studies (Aucour et al., 2006; Tao et al., 2009). As mentioned in the comment, it is very important to study the influence of TGD on POC export flux to the East China Sea. For our study area, there are eleven cascades of reservoirs along the mainstream of Wujiang River. The objective of our study is to examine the impacts of these cascades of reservoirs. The impact of TGD on the POC export to East China Sea is not our goal. Because suspended sediment at the mouth of Wujiang River directly flowed into Three Gorges Reservoir (TGR), the impact of climate on TGR sediment revealed the similar impacts on the mouth of Wujiang River. Thus, in order to estimate the impacts of climate on Wujiang River, we compare sediments inputs in the upper watershed of TGR between normal and drought year.

Coynel, A., Seyler, P., Etcheber, H., Meybeck, M. and Orange, D.: Spatial and seasonal dynamics of total suspended sediment and organic carbon species in the Congo River, *Global Biogeochem. Cy.*, 19, doi:10.1029/2004GB002335, 2005.

Aucour, A.M., France-Lanord, C., Pedoja, K., Pierson-Wickmann, A.C., and Sheppard, S.M.F.: Fluxes and sources of particulate organic carbon in the Ganga-Brahmaputra river system, *Global Biogeochem. Cy.*, 20, doi:10.1029/2004GB002324, 2006.

Tao, F.X., Liu, C.Q. and Li, S.L.: Source and flux of POC in two subtropical karstic tributaries with contrasting land use practice in the Yangtze River Basin, *Appl. Geochem.*, 24 (11), 2102–2112, 2009.

Comment Figure 2, the authors should provide water discharge data in the lower watershed of Changjiang such as Datong station and compare what is the difference of water discharge and POC flux between flood and drought seasons. If the authors have those data sets, the manuscript will provide evidence if TGD has significant impact or not.

Response: Thank you for the comment. We agree with the comment that data in the Datong

station is important to estimate the impact of TGD. Unfortunately, we fail to provide POC flux in Datong station. We think that this would not influence our conclusions since our study is to examine the impact of eleven cascades of reservoirs along the mainstream of Wujiang River on the POC export flux.

Comment Figure 5, there are five carbon components in the figure showing different contributions of carbon sources to suspended and/or sediments. However, the authors only used two end-member to calculate possible contributions of phytoplankton and C3-plant. Why?

Response: Thank you for the comment. According to the comment, the mixing model has been modified by combined use of indicators of $\delta^{13}\text{C}$ values and C/N ratios.

Source and flux of POC in a karstic area in the Changjiang River watershed: impacts of reservoirs and extreme drought

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Abstract. Isotopes of carbon and nitrogen along with C/N ratios of particulate organic carbon (POC) were used to identify source and transformation of organic carbon in the suspended and surface sediments in a typical karstic watershed (Wujiang River, an important tributary of the Changjiang River). Isotopic values indicated that POC was mainly derived from phytoplankton and C3-dominated soil with increased contribution of phytoplankton in sites directly affected by reservoir. In contrast, the POC in surface sediments was mainly derived from C3- and C4-dominated soil with little reservoir influence. The positive correlations of carbon and nitrogen isotopes between suspended and surface sediments indicated that these two carbon pools were tightly coupled. On basis of the conservative estimation, POC transported 1.17×10^{10} g to the Three Gorges Reservoir in 2013. POC yield in Wujiang River ($0.13 \text{ t km}^{-2} \text{ yr}^{-1}$) was much lower than large rivers with high carbonate percentage. Based on the carbonate distribution patterns of POC yield, percentage of carbonate area might not be a significant factor of riverine POC transport. The cascade of reservoir and extreme drought had significant influence on the POC flux in Wujiang River.

批注 [L11]: Because the mixing model has been modified, the related conclusions have also been modified.

1 Introduction

20 Globally, about 0.4 Gt of riverine organic carbon is transported to the world's oceans each year, of which 0.15–0.17 Gt is POC (Hedges et al., 1997; Ludwig et al., 1996; Schlesinger and Melack, 1981). Rivers are important channels for transporting organic carbon from land to ocean. The riverine POC provides integrated information both on the natural processes and human activities within the drainage basin (Meybeck and Ragu, 1996; Kendall et al., 2001). Previous studies indicate that climate and human disturbance are two important factors of POC transport. For example, POC fluxes decrease in response to dam construction and extreme drought (Bianchi et al., 2007; Yu et al., 2011; Zhang et al., 2009) and increase in response to deforestation and flood event (Kao and Liu, 1996; Sun et al., 2007).

25 Riverine POC ultimately originates from terrestrial and aquatic organic matter. Because different sources of POC are characterized by distinguished $\delta^{13}\text{C}_{\text{POC}}$, $\delta^{15}\text{N}_{\text{TN}}$ and C/N ratios, these indicators have been widely used to constrain sources and transformation of riverine POC. However, some physical and chemical process can alter the original composition of element and isotopes, which should be carefully considered. For example, decomposition of organic matter decreases C/N ratios (Tremblay and Benner, 2006) and abundant inorganic nitrogen also limit the usefulness of C/N ratios as a tracer of

particulate organic matter source (Guerra et al., 2013; Hu et al., 2006). Therefore, researchers utilize different combinations of $\delta^{13}\text{C}_{\text{POC}}$, $\delta^{15}\text{N}_{\text{TN}}$ and C/N ratios to identify the sources and calculate associated contribution of these sources. For example, Kendall et al. (2011) use C/N ratios and $\delta^{15}\text{N}_{\text{TN}}$ as source criteria in 54% of the samples in four large river systems across the United States, while Wu et al. (2007) use $\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{N}_{\text{TN}}$ to estimate the contribution of POC sources in the Changjiang River.

The Wujiang River drains a typical karst catchment with cascade of reservoirs along the mainstream. The damming of rivers and climate may exert significant influence on source and fate of POC delivered to the oceans. Recent studies have focused on the effects of Three Gorges Dam and extreme drought in the Changjiang River (Bao et al., 2014; Wu et al., 2007; Yu et al., 2011). POC flux has decreased from $7.4 \times 10^{12} \text{ t yr}^{-1}$ during 1984–1998 to $1.52 \times 10^{12} \text{ t yr}^{-1}$ after the impoundment of Three Gorges Dam (Wu et al., 2007; Wang et al., 2012). However, little attention is paid to rivers draining karstic area, which are more subject to different geochemical processes and anthropogenic activities than non-karst rivers (Liu, 2007; Ogrinc et al., 2008; Tao et al., 2009). Eleven artificial reservoirs have been constructed along the mainstream of Wujiang River since 1970s. The related study on POC in the Wujiang River is still limited after the construction of these reservoirs. According to the Changjiang Sediment Bulletin (2013), an extreme drought occurred in most areas of Guizhou Province. Based on the analyses of $\delta^{13}\text{C}_{\text{POC}}$, $\delta^{15}\text{N}_{\text{TN}}$ and C/N ratios in the suspended and surface sediments in the Wujiang River, this study identified source and flux of POC in the Wujiang River and examined the impacts of reservoir and climate.

批注 [Li2]: According to the comment, the related introduction has been rewritten.

2 Materials and Methods

2.1 Study sites description

The Wujiang River is the largest tributary of the upper Changjiang River in its south bank. It originates from the eastern Wumeng Ranges in Yunnan-Guizhou Plateau and flows through Yunnan Province, Guizhou Province, Sichuan Province and Hubei Province. It flows into the Three Gorges Reservoir in Fuling District, Chongqing Municipality. The drainage area of Wujiang River is 87920 km^2 , of which 76% drains in Guizhou Province. Its average annual discharge is $534 \times 10^8 \text{ m}^3 \text{ yr}^{-1}$. The watershed belongs to a warm subtropical climate. The mean annual air temperature varies from 10°C to 18°C with mean annual precipitation from 800 mm to 1400 mm. The altitudes of Wujiang River range from 500 m to 2400 m with a decreasing trend from west to east. Plant species are diverse with the upper reach dominated by broadleaf evergreen forest and dryland crop, the middle reach dominated by evergreen broadleaf forest and deciduous broadleaf mixed forest, and the lower reach dominated by subtropical evergreen Castanopsis forest. Yellow soil and limestone soil are dominant in the watershed (Zhang et al., 1995). The land use is dominated by forest land, cultivated land and grass land, which account for 50%, 31% and 18%, respectively. The soil erosion rate decreased from $2678 \text{ t km}^{-2} \text{ yr}^{-1}$ in 1980s to $2313 \text{ t km}^{-2} \text{ yr}^{-1}$ in 1990s due to sustainable soil conservation measures (Wang, 2011).

The Wujiang River is a typical karst watershed. In the upper reaches, Permian and Triassic carbonate rocks and basalt are dominant with coal-bearing formations outcropping in the western area. In the midstream area, Permian and Triassic

limestones, dolomitic limestones, and dolomites are dominant whereas the lower reaches are dominated by carbonate rocks intercalated with shales, sandy shales, and siltstones (Zhang et al., 1995).

2.2 Sampling and analyses

Twenty-five samples of suspended particulate matter (SPM) were collected from the mainstream and major tributaries of the Wujiang River (Fig. 1) in May and August 2013, respectively. Eighteen surface sediments were sampled in August 2013. An extreme drought occurred in most Guizhou Province during June and August. Fig. 2 showed the monthly water discharge and suspended sediment load in 2013 at the Wulong Hydrological Station, located in Wujiang River mouth. The data were taken from Changjiang Sediment Bulletin (2013). As plotted in the Fig. 2, water discharge and suspended sediment load decreased abruptly from June and August due to the drought event.

Sampling of SPM were conducted by filtration through precombusted (450°C for 6h) and preweighted 47mm glass fiber filters for SPM weight concentrations and stable isotopic analyses of carbon and nitrogen. Surface sediments were collected using a 0.05 m² Van Veen grab (Jiang and Ji, 2013). All samples were stored in a freezer (<-20°C) prior to laboratory analyses.

The filter samples were freeze-dried before the particulate substance was scraped from the filter. The freeze-dried suspended matter and sediment were sieved to 200 mesh, treated with 1 M HCl to remove inorganic carbon, while nitrogen isotopes of particulate matter were measured on the bulk samples without acidification. Organic carbon (OC) and total nitrogen (TN) contents as well as isotopes of carbon and nitrogen were determined by using an elemental analyzer (Flash EA 1112HT, Thermo Fisher Scientific, Inc., USA) coupled with an isotope-ratio mass spectrometer (Finnigan Delta V Advantage, Thermo Fisher Scientific, Inc.) in the Laboratory of Stable Isotope Ratio Mass Spectrometry, Chinese Academy of Forestry (Beijing 100091, China). Stable isotope ratios are reported in δ-unit notation as follows:

$$\delta X(\text{‰}) = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000 \quad (1)$$

where R_{sample} is the $\delta^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$ ratios of the sample, and R_{standard} is the corresponding ratios of sample standard. $\delta^{13}\text{C}$ values are reported relative to Pee Dee Belemnite (PDB) and $\delta^{15}\text{N}$ values are reported relative to N_2 in atmospheric air (AIR). Precision for $\delta^{13}\text{C}$ is 0.2‰ and for $\delta^{15}\text{N}$ is 0.2‰.

The minerals of suspended particulate and surface sediment were analyzed in State Key Laboratory for Advanced Metals and Materials, University of Science and Technology, Beijing. To test the relationships between TSS concentrations, elemental compositions (POC%, TN% and C/N ratios) and isotopic compositions, Person's correlation coefficient (Table S2) was calculated using SPSS software (version 16.0 for Windows).

3 Results

3.1 The mineral properties of suspended particulate and surface sediments

As presented in the Fig. S1, the major minerals of SPM in the Wujiang River included detrital minerals (quartz, calcite and dolomite), clay minerals (illite, kaolinite and smectite), magnetite and ilmenite. In contrast, the surface sediments contained little clay minerals, reflecting the preferential enrichment of clay minerals in SPM. The enrichment of clastic carbonate minerals in surface sediment indicated the preferential sedimentation of clastic carbonate relative to clay minerals. This was similar to the study in the Changjiang River by Ding et al. (2014). The dolomite in the SPM and surface sediment was observed in the middle and lower reaches, which was in agreement with the catchment lithology. The mineral composition of SPM and surface sediment reflected the process of physical and chemical weathering.

批注 [L13]: The method description has been deleted.

3.2 Elemental and isotope composition (carbon and nitrogen) in SPM

The ratios of carbon to nitrogen showed a wide range of 2.8–29.3, with a mean value of 13.6 in May and 8.8 in August (Table S1), indicating the source with high C/N ratios in May and low C/N ratios in August. Fig. 3 showed the spatial and seasonal variations of C/N ratios, $\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{N}_{\text{TN}}$ in the Wujiang River. Compared with August, more samples in May had C/N ratios higher than 15. While more samples had C/N ratios <8 in August, which were distributed in sites near or in reservoirs, for example sites 1, 2 and 19 (Fig. 3). Considering the cascade of reservoirs in along the Wujiang River, the impact of reservoir should be examined. The sampling sites were divided into two kinds based on the relation with reservoirs: sites directly affected by reservoirs and less affected by reservoirs. Table 1 showed the comparison of elemental and isotopic parameters in these two kinds of sites. As shown in the Table 1, C/N ratios were lower in sites directly affected by reservoir than those in sites less affected by reservoir.

$\delta^{13}\text{C}_{\text{POC}}$ of SPM in May ranged from -30.18 to -21.09% and averaged -26.30% . Differently, $\delta^{13}\text{C}_{\text{POC}}$ in August displayed relatively depleted values with an average value of -27.23% . $\delta^{15}\text{N}_{\text{TN}}$ of SPM ranged from 1.88‰ to 12.93‰ and averaged 6.82‰, with higher values in August (7.58‰) than those in May (6.05‰). Spatially, $\delta^{13}\text{C}_{\text{POC}}$ values, especially in August, were more depleted in reservoirs and sites downstream of the reservoirs ($-28.65 \pm 1.22\%$, Table 1 and Fig. 3) than those less affected by reservoirs ($-26.68 \pm 3.23\%$, Table 1 and Fig. 3). In contrast, $\delta^{15}\text{N}_{\text{TN}}$ values were more enriched in sites directly affected by reservoirs than other sites. Chen and Jia (2009) obtained the similar trend of $\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{N}_{\text{TN}}$ in a dam-controlled subtropical river. As presented by Fig. 3, the heavier $\delta^{15}\text{N}_{\text{TN}}$ values ($>10\%$) in August corresponded to lighter $\delta^{13}\text{C}_{\text{POC}}$ values and lower C/N ratios (Fig. 3).

As shown in Table S2, POC%, TN% and $\delta^{15}\text{N}_{\text{TN}}$ were significantly negatively correlated with TSS concentrations in May, i.e., POC%, TN% and $\delta^{15}\text{N}_{\text{TN}}$ decreased when TSS concentrations increased. In contrast, $\delta^{13}\text{C}_{\text{POC}}$ was significantly positively correlated with TSS concentrations, i.e., $\delta^{13}\text{C}_{\text{POC}}$ increased when TSS concentrations increased. Similar results are obtained in the freshwater part of the Scheldt Estuary (Hellings et al., 1999). However, the relationships between isotopic parameters and TSS concentrations in August were not significant. This might be due to the low concentrations of TSS in

August, when extreme drought occurred in most Guizhou Province. No significant correlation of $\delta^{15}\text{N}_{\text{TN}}$ and $\delta^{13}\text{C}_{\text{POC}}$ was observed, which could be related to the inorganic nitrogen in samples (Guerra et al., 2013; Hu et al., 2006).

3.3 Compositions of element and isotopes (carbon and nitrogen) in surface sediments

Carbon to nitrogen ratios in the surface sediments presented higher values ranging from 7.7 to 41.1 compared with those of SPM. Like the SPM, POC% and TN% in surface sediments displayed a relatively significant positive correlation ($R=0.595$, $P<0.01$), which indicated that some nitrogen in the sediments was inorganic nitrogen. Compared with the C/N ratios in SPM, surface sediments had higher C/N ratios, indicating different sources of POC in surface sediments.

$\delta^{13}\text{C}_{\text{POC}}$ of surface sediments showed a relatively narrow range of -26.40‰ to -22.73‰ with an average value of -24.76‰ . The enriched $\delta^{13}\text{C}_{\text{POC}}$ of surface sediments in contrast with SPM indicated a source with elevated $\delta^{13}\text{C}_{\text{POC}}$ values.

10 The variation trend of $\delta^{13}\text{C}_{\text{POC}}$ in surface sediments was similar to that in SPM, which indicated these two carbon pools might be coupled. $\delta^{15}\text{N}_{\text{TN}}$ of surface sediments ranged from 2.88‰ to 9.39‰ with a mean value of 6.01‰. Spatially, the mean values of $\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{N}_{\text{TN}}$ in sites directly affected by reservoir and sites less affected by reservoir were $-24.85\pm 0.91\text{‰}$ vs. $-24.73\pm 1.04\text{‰}$ and $6.23\pm 2.22\text{‰}$ vs. $5.93\pm 1.55\text{‰}$ (Table 1), respectively. Compared with the SPM, the difference of isotopic values were smaller in surface sediment between sites directly by reservoir and sites less affected by
15 reservoir.

4 Discussion

4.1 Sources and variations of POC in the Wujiang River

4.1.1 Sources of POC in SPM

Potential sources of POC in the river contain allochthonous sources (C3 and C4 plants, soil organic matter) and autochthonous sources (macrophytes and phytoplankton). C/N ratios and isotopic values of POC are an effective method for constraining the sources of riverine POC. Generally, aquatic phytoplankton is characterized with low C/N ratios (5–8) and terrestrial organic matter with high C/N ratios (higher than 8, Kendall et al., 2001). Soil organic matter reflects carbon isotopic compositions of residues from the overlying vegetation with an average $\delta^{13}\text{C}$ value of -27.0‰ for C3 plants and -14‰ for C4 plants (Smith and Epstein, 1971). The typical $\delta^{15}\text{N}$ values for soil organic nitrogen are 2–5‰ (Kendall et al.,
25 2001).

C/N ratios as well as isotopic compositions of carbon are plotted in Fig. 4 together with typical values of potential end members of POC. As shown in the Fig. 4, C/N ratios of SPM in the Wujiang River showed temporal variations with higher C/N ratios in May (13.6 ± 7.6) than those in August (8.8 ± 3.7), which suggested the increased phytoplankton input in August. Of note, the precondition of C/N ratios for identifying organic matter sources was that all of TN in POC exclusively reflected
30 nitrogen bound to organic matter (Meyers, 1997). Therefore, contents of organic carbon (POC%) and total nitrogen (TN%)

was expected to show a significant linear correlation. The linear relationship of TN and POC was relatively weak (May: $TN=0.07*POC+0.09$, $R^2=0.54$, $P<0.001$; August: $TN=0.04*POC+0.23$, $R^2=0.39$, $P<0.001$) compared with other studies ($R^2=0.71$ in Hu et al., 2006; $R^2=0.9$ in Guerra et al., 2013). The intercept of the above regressions was more than zero, which suggested that a fraction of TN was inorganic nitrogen in the SPM (Guerra et al., 2013; Hu et al., 2006). Thus, the phytoplankton inputs might be overestimated based on C/N ratios.

$\delta^{13}C_{POC}$ of SPM in May and August averaged -26.30% and -27.23% , respectively. The depleted $\delta^{13}C_{POC}$ in August indicated decreased terrestrial contribution and increased phytoplankton contribution. This was in accordance with the conclusion deduced from the C/N ratios. The Wujiang River had high flow rates and rocky river beds and banks, which limited the macrophytes growth. Thus, phytoplankton was the main aquatic plants in the catchment (Tao et al., 2009). Phytoplankton was reported to have depleted $\delta^{13}C$ values with a typical range of -42% to -24% (Kendall et al., 2001 and references therein). The $\delta^{13}C_{POC}$ values of SPM were more negative in reservoir-affected sites than those less affected by reservoir (Table 1). This could be due to long water retention time of the reservoir, which was in favor of phytoplankton enhancement. The aquatic source increase in the reservoir was reported in other rivers (Chen and Jia, 2009; Zhang et al., 2009).

The contribution proportions were calculated by a mixing model based on the C/N ratios and $\delta^{13}C_{POC}$ values. The C/N of terrestrial source is assigned as 19.4, which is the average C/N value of soil and plants in the Wujiang watershed (Tao et al., 2009). Therefore, if $C/N > 19.4$, the proportion of terrestrial source is 100%. Other end-members of POC are shown in Fig. 4. The $\delta^{13}C$ of phytoplankton end member can be estimated based on the measured $\delta^{13}C$ values of dissolve inorganic carbon ($\delta^{13}C_{DIC}$) and an uptake fractionation of 21‰ (i.e. $\delta^{13}C$ of phytoplankton= $\delta^{13}C_{DIC}-21\%$, Mook and Tan, 1991). Measured $\delta^{13}C$ -DIC in the Wujiang River ranged from -11.55% to -3.41% , with an average value of -8.67% (unpublished data). Thus, the estimated $\delta^{13}C$ values for phytoplankton ranged from -32.55% to -24.41% with an average value of -29.67% . This results fell in the typical $\delta^{13}C$ range (-42% to -24%) of freshwater plankton (Kendall et al., 2001 and references therein). This was also in accordance with the study by Li (2009) in Maotiao River (a tributary of Wujiang River), where the average of $\delta^{13}C_{POC}$ of phytoplankton was $-29.6\pm 5.5\%$. The Wujiang River is the largest tributary of the upper Changjiang River in its south bank. Wu et al. (2007) reported the average $\delta^{13}C$ value of soil end-member ($-26.1\pm 0.3\%$) within the southern tributaries of the upper Changjiang River, which was taken as the upper limit of C3 plant-dominated soil end-member. The average $\delta^{13}C$ of C4 plants in the catchment was -13.4% (Tao et al., 2009), which was taken as the upper limit of C4 plant sources. The corresponding equations of mixing model are as follows:

If $C/N < 7$, the proportion of phytoplankton was 100%.

If $7 < C/N < 19.4$, the POC was derived from the mixing of phytoplankton, C3 plant-dominated soil and C4 plant-dominated soil. The corresponding mixing model is:

$$\delta^{13}C_{POC} = \delta^{13}C_{phyto} \times f_{phyto} + \delta^{13}C_{C3} \times f_{C3} + \delta^{13}C_{C4} \times f_{C4} \quad (2)$$

$$C/N_{POC} = C/N_{phyto} \times f_{phyto} + C/N_{C3} \times f_{C3} + C/N_{C4} \times f_{C4} \quad (3)$$

$$f_{phyto} + f_{C3} + f_{C4} = 1 \quad (4)$$

批注 [Li4]: The mixing model has been modified.

The subscripts phyto, C3 and C4 represent the end-member of phytoplankton, C3 plant-dominated soil and C4 plant-dominated soil, respectively. The subscript POC denotes $\delta^{13}\text{C}$ or C/N values of samples measured in this study. The calculated results are presented in Fig. 5. POC of SPM was mainly derived from phytoplankton (67%) and C3 plant-dominated soil (22%) with increasing contribution of phytoplankton in August. The average phytoplankton contribution in sites directly affected by reservoir was higher than sites less affected by reservoirs.

批注 [L15]: The mixing model and the related discussion have been modified.

4.1.2 Sources of POC in sediments

C/N ratios and the $\delta^{13}\text{C}_{\text{POC}}$ values of surface sediments reflected the compositions of organic matter in recent decades (Krull et al., 2009). C/N ratios of surface sediments ranged from 7.7 to 41.1 with an average value of 18.0, which verified the dominant terrestrial sources. Compared with SPM, the elevated C/N ratios of surface sediments indicated more land-derived fraction contribution to the surface sediments. The POC% and TN% in surface sediments exhibited relatively strong correlation ($\text{TN}=0.02*\text{POC}+0.13$, $R^2=0.33$, $P=0.008$). The intercept of the regression equation suggested that there was some inorganic nitrogen in the surface sediments. From June to August 2013, drought hit most parts of Guizhou Province. Soil organic matter and plant debris might be deposited and mineralized on the ground before they were transported into the rivers. Consequently, contents of organic components decreased and inorganic components increased, which might result in the weak correlation between POC% and TN%.

批注 [L16]: The related discussion has been modified to make it clearer.

The relation of $\delta^{13}\text{C}_{\text{POC}}$ and C/N in surface sediments (Fig. 4b) indicated that POC was mainly derived from terrestrial origin. In contrast with the SPM, the enriched $\delta^{13}\text{C}_{\text{POC}}$ values of surface sediments (averaging -24.76%) suggested that there was an increased source of C4 plants to sediments, and/or depleted carbon isotope in surface sediment were not retained in the sediment (Guerra et al., 2013). Given that POC and TN contents were higher in most sediment samples than suspended sediments, the biodegradation of the phytoplankton was not the major cause of enrichment of $\delta^{13}\text{C}_{\text{POC}}$ values in surface sediments.

The contributions of different POC sources in surface sediments were calculated based on the similar equations in section 4.1.1. Contribution of C3 plant-dominated soil and C4 plant-dominated soil averaged 64% and 13%, respectively. The proportions of phytoplankton were lower than that in SPM. Spatial variation of source contribution was not significant in the surface sediment (Fig. 5), indicating that reservoir influence was relatively weak in surface sediment compared with those in SPM.

批注 [L17]: Because the mixing model has been modified, the related result has also been corrected.

4.2 Transformation of POC in the Wujiang River

Knowledge of the POC transformation is useful to get a better understanding of the riverine carbon cycle. In-stream processes, such as assimilation and respiration of phytoplankton, affect the isotopic compositions and element contents of carbon and nitrogen. Hence, $\delta^{13}\text{C}_{\text{POC}}$, $\delta^{15}\text{N}_{\text{TN}}$ and C/N can be utilized to trace transformation processes of organic matter. The trend of increasing TSS concentrations with decreasing POC contents (%), Fig. 6 indicated that POC contents (%) of SPM were diluted with the inorganic constituents derived from soil erosion. This was similar to other rivers (Ludwig et al.,

1996; Jiang and Ji, 2013; Zhang et al., 2009). The positive correlation between TSS concentrations and POC contents ($\mu\text{mol L}^{-1}$, Table S2) indicated that terrestrial organic matter was an important source of POC in SPM, which confirmed the erosion process. Although the erosion rate catchment decreased significantly in the Wujiang River (Wang, 2011), soil erosion had remarkable influence on the riverine carbon cycles.

5 $\delta^{15}\text{N}$ is a potential tracer to identify aquatic biogeochemical processes. High $\delta^{15}\text{N}$ may be caused by anthropogenic activities and transformation processes, such as denitrification and assimilation. Denitrification was excluded due to the weak correlation between $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ (unpublished data). Kendall et al. (2007) reported that animal waste and domestic effluents had typical values of $\delta^{15}\text{N-NO}_3^- > 10\%$. Some samples had high $\delta^{15}\text{N}_{\text{TN}}$ values with elevated $\delta^{15}\text{N-NO}_3^-$ values ($> 8\%$), indicating the inputs of manure and domestic sewage. Particulate organic carbon could be influenced by
10 sewage water through the uptake of NH_4^+ and NO_3^- by phytoplankton. Uptake of NO_3^- with high $\delta^{15}\text{N}$ by phytoplankton might result in elevated $\delta^{15}\text{N}_{\text{TN}}$ values (Kendall et al., 2001; Jiang and Ji, 2013). This process was confirmed by the significant positive correlation of $\delta^{15}\text{N}_{\text{TN-SPM}}$ vs. $\delta^{15}\text{N-NO}_3^-$ and $\delta^{15}\text{N}_{\text{TN-SPM}}$ vs. NO_3^- in May (Fig. 7a). However, some samples with $\delta^{15}\text{N}_{\text{TN-SPM}} > 10\%$ ($\delta^{15}\text{N-NO}_3^- < 8\%$) (Fig. 7a) deviated from other data in August, indicating other influencing factors. One mechanism might be related to uptake of other forms of dissolved inorganic nitrogen. The drought
15 event during June to August created longer time for mineralization of soil organic matter, favourable to the production of ammonia with heavy $\delta^{15}\text{N}$ values. The elevated $\delta^{15}\text{N}_{\text{TN-SPM}}$ might be caused by the uptake of nitrification-derived NH_4^+ , as nitrifiers preferentially consumed ^{14}N , leading to increase in $\delta^{15}\text{N-NH}_4^+$ of the remaining ammonia. Consumption of such enriched $^{15}\text{N-NH}_4^+$ by phytoplankton resulted in the scattered trend of $\delta^{15}\text{N}_{\text{TN-SPM}}$ in August. The similar result was observed in the study by Sarma et al. (2012).

20 Positive correlations of $\delta^{13}\text{C}_{\text{POC}}$ (Fig. 7b) and $\delta^{15}\text{N}_{\text{TN}}$ (Fig. 7c) between suspended and surface sediments indicated that intense exchange might exist in these two carbon pools (Jiang and Ji, 2013; Sarma et al., 2012). The resuspension/deposition of suspended matter with mixing of different organic matter sources might result in the significant correlation of $\delta^{13}\text{C}_{\text{POC}}$ (Fig. 7b) and $\delta^{15}\text{N}_{\text{TN}}$ (Fig. 7c). Compared with suspended matter, the heavier $\delta^{13}\text{C}_{\text{POC}}$ and lighter $\delta^{15}\text{N}_{\text{TN}}$ in sediments indicated enriched source of refractory allochthonous organic matter. The good correlations between river water and SPM as well as
25 surface sediment indicated that these carbon pools were tightly connected.

4.3 Flux of POC in Wujiang River and comparison with world rivers

Flux of POC (F_{POC}) was estimated based on a simple method from Tao et al. (2009):

$$F_{\text{POC}} = [\text{POC}]_{\text{H}} \times \text{Discharge} \times 66\% + [\text{POC}]_{\text{L}} \times \text{Discharge} \times 34\% \quad (5)$$

where $[\text{POC}]_{\text{H}}$ and $[\text{POC}]_{\text{L}}$ is the average POC concentration of SPM in high-water season and low-water season,
30 respectively. The POC concentration of river mouth (sample 18 in Fig. 1) was used to calculate the POC flux. Water discharge of the Wujiang River in 2013 (website: www.cjw.gov.cn) was taken from the Wulong hydrologic station, which was close to the river mouth. Discharge in high-flow and low-flow season account for 66% and 34% of the annual discharge in 2013, respectively (Changjiang Sediment Bulletin 2013). Since the water discharge in May was the almost highest

compared with other months (Fig. 2), the POC concentration in May collected at river mouth (site 18 in Fig. 1) was used to calculate the POC flux in high-water season. Similarly, POC concentration in August was used to calculate the POC flux in low-water season since water discharge in August was close to that in low-water season (Fig. 2). The estimated POC flux was 1.17×10^{10} g in 2013, lower than that in the Wujiang River determined by Tao et al. (2009) in 2002. The decrease in POC flux might be due to measures of soil and water conservation, dam construction (Wu et al., 2007) as well as decreased discharge due to extreme drought in 2013 in Guizhou Province.

In Table 2 water discharge, TSS concentration, POC%, POC flux and yield were compared with 15 world rivers. The total drainage area of the 15 rivers amounted to 30.3×10^6 km² (Table 2), accounting for 55% of the 60 world rivers' area from the study of Gaillardet et al. (1999). As shown in Table 2, the very low POC yield in Wujiang River was the fourth lowest observed in the documented rivers before Yenisey, Ob and St. Lawrence. In comparison, the first two rivers in terms of POC yield were Zhujiang and Ganges-Brahmaputra with POC yield higher than $3 \text{ t km}^{-2} \text{ yr}^{-1}$. Both Zhujiang and Ganges-Brahmaputra were located in the mid latitude, subject to tropical and subtropical climate. The latitudinal distribution patterns of POC yield were examined for the 15 world rivers and Wujiang River (Fig. 8a). As shown in the Fig. 8a, POC yields were higher in the mid-latitude rivers and tended toward the subtropical rivers. This was similar to the distribution feature of HCO₃⁻ yield for the world rivers in the study of Cai et al. (2008). According to Amiotte Suchet et al. (2003), carbonate rocks were mainly distributed between 20°N and 50°N. The carbonate area in the documented 15 world rivers accounted for 8% of the 60 world rivers' area, while POC flux accounted for 13% of the global POC flux of 0.17 Gt (10^{15} g) estimated by Ludwig et al. (1996). It appeared that more carbonate would result in elevated POC export. Unfortunately, no clear correlation was found between carbonate percentage and POC yields (Fig. 8b), which indicated that percentage of carbonate area was not a significant factor of riverine POC transport. This was not similar to Mackenzie River, where organic-rich sedimentary rocks contributed a significant particulate organic matter (Carrie et al., 2009). However, the influence of carbonate might be underestimated as discussed by Cai et al. (2008) since carbonate rocks were defined as those that contained up to 50% of carbonate minerals (Amiotte Suchet et al., 2003).

Compared with the previous study in Wujiang River, the POC yield decreased from $0.47 \text{ t km}^{-2} \text{ yr}^{-1}$ (Tao et al., 2009) to $0.13 \text{ t km}^{-2} \text{ yr}^{-1}$ (Table 2). It was noted that five dams were constructed in the lower reach of Wujiang River after the study of Tao et al. (2009). Moreover, POC yield in the Wujiang River were much lower than those in Xijiang and Zhujiang with high carbonate percentage. This could be related to the smaller watershed area and extensive water reservoirs in the Wujiang River (Zhang et al., 2006). The impacts of reservoirs will be discussed below.

4.4 Impacts of reservoir and climate on riverine POC

There are eleven artificial dams along the mainstream of Wujiang River (Fig. 1). The cascade of reservoirs created by dams may exert significant impacts on source and transport of riverine POC. In addition, extreme drought must be noted when considering the meteorological characteristics of the Wujiang River in 2013.

$\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ proved to be potentially useful indicators for qualitatively estimation of reservoir and climatic impact on POC in dam-affected rivers (Chen and Jia, 2009; Zhang et al., 2009). In order to analyze the reservoir impact on riverine POC, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values were compared in sites directly affected by dams with those less affected in the Wujiang River (Table 1). As shown in Table 1, $\delta^{13}\text{C}$ were more depleted in sites affected by dam than those less affected by dam. This was similar to the study by Chen and Jia (2009) in a dam-controlled river. Compared with sites far from the dam, the more depleted values of $\delta^{13}\text{C}$ in sites close to dam were attributed to increasing phytoplankton contribution. This was confirmed by the higher phytoplankton contribution to POC of SPM in sites directly affected by dam with an average of 47% relative to those less affected with an average of 27%. Two mechanisms could explain this elevated phytoplankton contribution: (1) extended water retention time in reservoirs with low flow; (2) increasing light availability due to the low TSS concentrations (Table 1) in reservoirs. In contrast with $\delta^{13}\text{C}$ values, $\delta^{15}\text{N}$ values were heavier in sites close to reservoir than those far from reservoir. Delong and Thorp (2006) reported that $\delta^{15}\text{N}$ values in aquatic algal were more enriched than detrital fraction. Thus, the heavier $\delta^{15}\text{N}$ values in sites directly affected by dam might result from the aquatic algal and plankton. This hypothesis was verified by the concurrent lighter $\delta^{13}\text{C}$ values and lower C/N ratios in the sites directly influenced by reservoirs (Table 1). Besides, denitrification could be another cause for the heavier $\delta^{15}\text{N}$ values in the reservoirs since hypoxic environments might occur in the deep water. Further study of $\delta^{15}\text{N}$ variations in different water depths could help to trace the denitrification process. Seasonally, the average $\delta^{13}\text{C}$ values in August at sites directly affected by reservoir (-28.65%) were much higher than other sites (-26.68%). This large difference could be related to the higher temperature and extreme drought during June to August, which was favourable to in-situ phytoplankton production. According to Chen and Jia (2009), accumulated terrestrial organic matters in winter were flushed during the first heavy rain, which resulted in increasing terrestrial input in the onset of the wet season. This could also be the reason for the Wujiang River in May, when the water discharge increased abruptly.

It is difficult to quantitatively evaluate the impact of dams and extreme drought. The method described in the study of Yu et al. (2011) made it possible to distinguish the impact of dams and climate. This method was based on the significant correlation between POC flux and suspended sediment load. Thus, the variations of suspended sediment load could reflect the POC flux variations under the condition of dam and extreme drought. The comparison of suspended sediment loads was made between normal years and the drought year 2013 in the Wulong hydrologic station, the Wujiang River mouth (Table S3). As shown in Table S3, the suspended sediment loads in 2013 at Wulong station reduced by 80% compared with normal years, which could be due to the combined impacts of cascade of dams and extreme drought. Because suspended sediment at Wulong station directly flowed into Three Gorges Dam (TGD), the impact of climate on TGD sediment revealed the similar impacts on Wulong station. The impacts of extreme drought can be estimated based on the comparison of sediments inputs to TGD between normal and drought year. The reduction 41% of sediment inputs to TGD was obtained in 2013 compared with normal years, which was attributed to the climate impact. Thus, the impact of cascade of dams was 39%. The normalized impacts of cascade of dams and extreme drought were 49% and 51%, respectively. This result was similar to the impacts of extreme drought in 2006 on TGD determined by Yu et al. (2011). This result indicated that extreme drought and

dams were important factors of suspended sediment load. Considering the significant correlation between TSS concentrations and POC concentrations (Table S2), the reservoir and extreme drought had similar impact on the POC transport. However, this estimation based on the Wujiang River mouth was limited relative to the whole basin.

5 Conclusions

5 The carbon to nitrogen ratios and its isotopic compositions of POC were determined in suspended and surface sediments in Wujiang River. The results indicated that POC in SPM was mainly derived from phytoplankton and C3-dominated soil with increased phytoplankton input in sites affected by reservoirs. In comparison, POC in surface sediments was mainly derived from C3- and C4-dominated soil. The relationships of carbon and nitrogen isotopes between suspended and surface sediments indicated that these two carbon pools are closely coupled. In-stream process, such as microbiological
10 decomposition in water column and surface sediments, might result in the difference in terms of POC sources between suspended and surface sediments. POC transported 1.17×10^{10} g to the Three Gorges Reservoir in 2013. POC yield in Wujiang River ($0.13 \text{ t km}^{-2} \text{ yr}^{-1}$) was much lower than large rivers with high carbonate percentage. The carbonate distribution patterns of POC yield indicated that percentage of carbonate area was not a significant factor of riverine POC transport. The cascade of reservoir and extreme drought had significant influence on the POC flux in Wujiang River.

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Author contributions

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References

- Amiotte Suchet, P., Probst, J. L. and Ludwig, W.: Worldwide distribution of continental rock lithology: implications for the atmospheric/soil CO₂ uptake by continental weathering and alkalinity river transport to the oceans, *Global Biogeochem. Cy.*, 17(2), 7-1, 2003.
- 5 Aucour, A.M., France-Lanord, C., Pedoja, K., Pierson-Wickmann, A.C., and Sheppard, S.M.F.: Fluxes and sources of particulate organic carbon in the Ganga-Brahmaputra river system, *Global Biogeochem. Cy.*, 20, doi:10.1029/2004GB002324, 2006.
- Bao, H.Y., Wu, Y., Zhang, J., Deng, B. and He, Q.: Composition and flux of suspended organic matter in the middle and lower reaches of the Changjiang (Yangtze River)-impact of the Three Gorges Dam and the role of tributaries and channel erosion, *Hydrol. Process.*, 28(3), 2877-2877, 2014.
- 10 Bianchi, T.S., Wysocki, L.A., Stewart, M., Filley, T.R. and Mckee B.A.: Temporal variability in terrestrially-derived sources of particulate organic carbon in the lower Mississippi River and its upper tributaries, *Geochim. Cosmochim. Ac.*, 71(18), 4425-4437, 2007.
- Cai, W.J., Guo, X., Chen, C.T.A., Dai, M., Zhang, L., Zhai, W., Lohrena, S. E., Yin, K., Harrison, P.J. and Wang, Y.: A comparative overview of weathering intensity and HCO₃⁻ flux in the world's major rivers with emphasis on the Changjiang, Huanghe, Zhujiang (Pearl) and Mississippi Rivers, *Cont. Shelf Res.*, 28, 1538-1549, 2008.
- 15 Carrie, J., Sanei, H., Goodarzi, F., Stern, G. and Wang, F.: Characterization of organic matter in surface sediments of the Mackenzie River basin, Canada. *Int. J. Coal Geol.*, 77(3), 416-423, 2009.
- Chen, F. and Jia, G.: Spatial and seasonal variations in δ¹³C and δ¹⁵N of particulate organic matter in a dam-controlled subtropical river, *River Res. Appl.*, 25(9), 1169-1176, 2009.
- 20 Coyne, A., Seyler, P., Etcheber, H., Meybeck, M. and Orange, D.: Spatial and seasonal dynamics of total suspended sediment and organic carbon species in the Congo River, *Global Biogeochem. Cy.*, 19, doi:10.1029/2004GB002335, 2005.
- Delong, M.D. and Thorp, J.H.: Significance of instream autotrophs in trophic dynamics of the Upper Mississippi River, *Oecologia*, 147: 76-85, 2006.
- 25 Ding, T., Gao, J., Tian, S., Shi, G., Feng, C., Wang, C., Luo, X. and Han, D.: Chemical and isotopic characteristics of the water and suspended particulate materials in the Yangtze river and their geological and environmental implications, *Acta Geol. Sin-Engl.*, 88(1), 276-360, 2014.
- Guerra, R., Pistocchi, R. and Vanucci, S.: Dynamics and sources of organic carbon in suspended particulate matter and sediments in Pialassa Baiona lagoon (NW Adriatic Sea, Italy), *Estuar. Coast. Shelf S.*, 135, 24-32, 2013.
- 30 Hedges J. I., Keil R. G. and Benner R.: What happens to terrestrial organic matter in the ocean? *Org. Geochem.*, 27(5), 195-212, 1997.

- Hélie, J.F. Geochemistry and fluxes of organic and inorganic carbon in aquatic systems of eastern Canada: examples of the St. Lawrence River and Robert-Bourassa Reservoir: isotopic approach, Research Gate, 2005.
- Hellings, L., Dehairs, F., Tackx, M., Keppens, E. and Baeyens, W.: Origin and fate of organic carbon in the freshwater part of the Scheldt Estuary as traced by stable carbon isotope composition, *Biogeochemistry*, 47, 167–186, 1999.
- 5 Hu, J., Peng, P. A., Jia, G., Mai, B. and Zhang, G.: Distribution and sources of organic carbon, nitrogen and their isotopes in sediments of the subtropical Pearl River estuary and adjacent shelf, Southern China, *Mar. Chem.*, 98(2), 274–285, 2006.
- Jiang, Y. and Ji, H.: Isotopic indicators of source and fate of particulate organic carbon in a karstic watershed on the Yunnan-Guizhou Plateau. *Appl. Geochem.*, 36, 153–167, 2013.
- KanduĀ, T., Ogrinc, N. and Mrak, T.: Characteristics of suspended matter in the river sava watershed, slovenia.. *Isot. Environ. Healt. S.*, 43(4), 369-86, 2007.
- 10 Kao, S.J. and Liu, K.K.: Particulate organic carbon export from a subtropical mountainous river (Lanyang Hsi) in Taiwan, *Limnol. Oceanogr.*, 41, 1749–1757, 1996.
- Kendall, C., Silva, S.R. and Kelly, V.J.: Carbon and nitrogen isotopic compositions of particulate organic matter in four large river systems across the United States, *Hydrol. Process.*, 15, 1301–1346, 2001.
- 15 Köhler, H., Meon, B., Gordeev, V.V., Spitzzy, A., Amon, R.M.W. and Shirshov, P.P.: Dissolved organic matter (DOM) in the estuaries of Ob and Yenisei and the adjacent Kara Sea, Russia, *P. Mar. Sci.*, 6, 281–308, 2003.
- Krull, E., Haynes, D., Lamontagne, S., Gell, P., Mckirdy, D., Hancock, G., Mcgowan, J. and Smernik, R.: Changes in the chemistry of sedimentary organic matter within the Coorong over space and time, *Biogeochemistry*, 92, 9–25, 2009.
- Li, G.R.: Cascade Damming of the River and its Phytoplankton Evolution Carbon Isotope Compositions–A Case Study of Maotiao River drainage area in Guizhou Province, PhD Dissertation, Guizhou Normal Univ., China, 2009 (in Chinese with English abstract).
- 20 Liu, C.Q.: The Process of Biogeochemistry and the Cycle of Surface MassRiverine Erosion and Elemental cycle in Southwest China, Science Press, Beijing, 2007 (in Chinese).
- Ludwig, W., Probst, J.L. and Kempe, S.: Predicting the oceanic input of organic carbon by continental erosion, *Glob. Biogeochem Cy.*, 10(1): 23–41, 1996.
- 25 Lyons, W.B., Nezat, C.A., Carey, A.E. and Hicks, D.M.: Organic carbon fluxes to the ocean from high-standing islands, *Geology* 30:443–446, 2002.
- Moreira-Turcq, P., Seyler, P., Guyot, J.L. and Etcheber, H.: Exportation of organic carbon from the Amazon River and its main tributaries, *Hydrol. Process.*, 17(7), 1329-1344, 2003.
- 30 Meybeck, M., and Ragu, A.: River discharges to the oceans: An assessment of suspended solids, major ions, and nutrients, environment information and assessment report, 250 pp., U.N. Environ. Programme, Nairobi, 1996.
- Meyers, P.A.: Organic geochemical proxies of paleoceanographic, pleolimnologic, and paleoclimatic processes, *Org. Geochem.*, 27, 213–250, 1997.

- Mook, W.G. and Tan, F.C.: Stable carbon isotopes in rivers and estuaries, in: Degens, E.T., Kempe, S., Richey, J.E. (Eds.), *Biogeochemistry of Major World Rivers*, Wiley, New York, 245–264 pp., 1991.
- Ogrinc, N., Markovics, R., Kanduc, T., Walter, L.M. and Hamilton, S.: Sources and transport of carbon and nitrogen in the River Sava watershed, a major tributary of the River Danube, *Appl. Geochem.*, 23, 3685–3698, 2008.
- 5 Reschke, S., Ittekkot, V. and Panin, N.: The nature of organic matter in the Danube river particles and north-western black sea sediments, *Estuar. Coast. Shelf S.*, 54(3), 563–574, 2002.
- Sarma, V.V.S.S., Arya, J., Subbaiah, C.V., Naidu, S.A., Gawade, L., Kumar, P.P. and Reddy, N.P.C.: Stable isotopes of carbon and nitrogen in suspended matter and sediments from the Godavari estuary, *J. Oceanogr.*, 68(2), 307–319, 2012.
- Semiletov, I.P., Pipko, I.I., Shakhova, N.E., Dudarev, O.V., Pugach, S.P., Charkin, A.N., McRoy, C. P., Kosmach, D., and Gustafsson, O.: Carbon transport by the Lena River from its headwaters to the Arctic Ocean, with emphasis on fluvial input of terrestrial particulate organic carbon vs. carbon transport by coastal erosion, *Biogeosciences*, 8(9), 2407–2426, 2011.
- 10 Schlesinger, W.H. and Melack, J.M.: Transport of organic carbon in the world's rivers, *Tellus.*, 33, 172–187, 1981.
- Smith, B.N. and Epstein, S.: Categories of $^{13}\text{C}/^{12}\text{C}$ ratios for higher plants, *Plant Physiol.*, 47, 380–384, 1971.
- 15 Tremblay, L. and Benner, R.: Microbial contributions to N-immobilization and organic matter preservation in decaying plant detritus, *Geochim. Cosmochim. Ac.*, 70, 133–146, 2006.
- Sun, H.G., Han, J.T., Zhang, S.R. and Lu, X.X.: The impacts of '05.6' extreme flood event on riverine carbon fluxes in Xijiang River, *Chinese Sci. Bull.*, 52(6), 805–812, 2007.
- Tao, F.X., Liu, C.Q. and Li, S.L.: Source and flux of POC in two subtropical karstic tributaries with contrasting land use practice in the Yangtze River Basin, *Appl. Geochem.*, 24(11), 2102–2112, 2009.
- 20 Wan, G.J.: *Carbonates and Environment (Vol. I)*. Beijing: Seismological Press, 1995.
- Wang, Y.: Simulation study on soil erosion in karst area—a case study of Wujiang River in Guizhou Province. Ph.D. Dissertation, Peking University, 2011 (in Chinese).
- Wang, X., Ma, H., Li, R., Song, Z. and Wu, J.: Seasonal fluxes and source variation of organic carbon transported by two major Chinese Rivers: The Yellow River and Changjiang (Yangtze) River, *Global Biogeochem. Cy.*, 26, doi:10.1029/2011GB004130, 2012.
- 25 Wu, Y., Zhang, J., Liu, S.M., Zhang, Z.F., Yao, Q.Z., Hong, G.H. and Cooper, L.: Sources and distribution of carbon within the Yangtze River system, *Estuar. Coast. Shelf S.*, 71(1), 13–25, 2007.
- Yu, H., Wu, Y., Zhang, J., Deng, B. and Zhu, Z.: Impact of extreme drought and the Three Gorges Dam on transport of particulate terrestrial organic carbon in the Changjiang (Yangtze) River, *J. Geophys. Res.*, 116, doi:10.1029/2011JF002012, 2011.
- 30 Zhang, L.C., Yu, Z.S. and Zhang, S.: *Chemical elements in Changjiang River system monograph series (2): study on chemical elements in water environment*, China Environmental Science Press, Beijing, 1995 (in Chinese).

Zhang, L.K., Qin, X.Q., Yang, H., Huang, Q.B. and Liu, P.Y.: Transported fluxes of the riverine carbon and seasonal variation in Pearl River Basin, *Environ. Sci.*, 34(8), 3025-3034, 2013 (in Chinese).

Zhang, S., Lu, X.X., Sun, H., Han, J. and Higgitt, D.L.: Geochemical characteristics and fluxes of organic carbon in a human-disturbed mountainous river (the Luodingjiang River) of the Zhujiang (Pearl River), China. *Sci. Total Environ.*, 407(2), 815–825, 2009.

Zhang, Q., Xu, C.Y., Becker, S. and Jiang, T.: Sediment and runoff changes in the Yangtze River basin during past 50 years, *J. Hydrol.*, 331, 511–523, doi:10.1016/j.jhydrol.2006.05.036, 2006.

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Table captions

Table 1 Comparison of TSS concentrations, C/N ratios and isotopic values (mean \pm standard deviation) in sites affected by reservoirs with those unaffected by reservoirs in the Wujiang River

Table 2 Particulate organic carbon fluxes (FPOC) and yields (YPOC) in some World Rivers and Wujiang River

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Figure captions

Fig. 1 Location of sampling sites in the Wujiang River. Zones of W I, W II and W III are the upper reaches, middle reaches and lower reach, respectively. W I is dominated by Permian and Triassic carbonate rocks and basalt with coal-bearing formations outcrop in west. W II is dominated by Permian and Triassic limestones, dolomitic limestones, and dolomites. W III is distributed carbonate rocks intercalated with detrital rocks (shales, sandy shales, and siltstones).

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Fig. 2 Monthly water discharge and suspended sediment load in 2013 at Wulong Hydrological Station. The data were taken from Changjiang Sediment Bulletin 2013 (website: www.cjw.gov.cn).

Fig. 3 The spatial variations of C/N ratios, $\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{C}_{\text{TN}}$ of suspended particulate matter in the Wujiang River.

Fig. 4 $\delta^{13}\text{C}_{\text{POC}}$ and C/N ratios of suspended and surface sediments in the Wujiang River. The isotopic and elemental compositions of different end-members are taken from Li (2009), Wu et al. (2007) and Tao et al. (2009) and references therein.

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Fig. 5 Contribution proportions of different sources to POC in suspended matters and surface sediments.

Fig. 6 Correlations between TSS concentrations (mg L^{-1}) and POC (%). The related data were summarized in Table 2. Amazon, Changjiang, Congo, Danube, Ganges-Brahmaputra, Huanghe, Indus, Lena, Mackenzie, Mississippi, St.

Lawrence, Wujiang, Xijiang, Yenisey, Zhujiang are abbreviated to Amaz, Chang, Cong, Danu, Gabr, Hua, Inds, Lena, Mack, Mis, StL, Wu, Xi, Yens, Zhu, respectively.

Fig. 7 (a) Correlations of $\delta^{15}\text{N}_{\text{TN}}$ values in suspended matters and $\delta^{15}\text{N}\text{-NO}_3^-$ (a1) as well as NO_3^- concentrations (a2) in corresponding river water in the Wujiang River; (b) Correlations of $\delta^{13}\text{C}$ values between suspended matters (sus) and surface sediments (sed); (c) Correlations of $\delta^{15}\text{N}$ values between suspended matters and surface sediments.

Fig. 8 (a) Relationship between POC yield and latitude; (b) Relationship between POC yield and percentage of carbonate area (carbonate%). Latitude and percentage of carbonate area were taken from Cat et al. (2008) and Amiotte Suchet et al. (2003), respectively.

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