Dear reviewer,

We thank you very much for your comments on our manuscript.

This manuscript detailing long-term patterns of pCO2 and alkalinity in the Yangtze River is generally well-written and includes strong methodology and data. The work will be of general interest as the authors have clearly shown the relevance of this carbon component in the framework of the larger carbon cycle. My main concern with this manuscript is the overly broad interpretations of underlying processes. The very simple correlations between water chemistry and discharge with alkalinity and pCO2 certainly point towards specific processes, but the authors do not dig too deeply into these relationships. Therefore, many of the conclusions, and a fair bit of the discussion is overly speculative. I would like to see a more formal set of questions and hypotheses that could be evaluated with the data available. I believe further evaluations and rationale will be needed to sort out the interesting pattern of stable pCO2 across a range of discharges in the mainstem (Figure 5b). The discussion of in-stream processes vs. tributary dilution and terrestrial CO2 sources is at present too speculative (lines 295-316).

Reply: Based on your comments, we have further analyzed the underlying processes controlling riverine $p\mathrm{CO_2}$ changes in the Yangtze River watershed. In addition to the discussion based on the three typical sub-catchments with contrasting lithologic features (i.e., Wujiang, Jialingjiang, and Ganjiang catchments), we have also examined the relationships between $p\mathrm{CO_2}$ and representative water chemistry variables (e.g., $\mathrm{Ca^{2+}}$ and $\mathrm{SiO_2}$) at the entire watershed scale (Fig. S1 in the Supplement). The indiscernible $p\mathrm{CO_2}$-$\mathrm{Ca^{2+}}$ and $p\mathrm{CO_2}$-$\mathrm{SiO_2}$ relationship for the entire watershed may be attributed to the spatial heterogeneity in lithology that has obscured the signature. While both positive and negative relationships existed in sub-catchments with predominant carbonate or siliciclastic sediment rocks (Figs. 6 and S3), these relationships may have counteracted each other when all data points were plotted together. For the $p\mathrm{CO_2}$ changes in the mainstem channel (Fig. 5b), it is likely because the increased dissolved $\mathrm{CO_2}$ inputs by soil organic matter decomposition from one region has been counteracted by low $p\mathrm{CO_2}$ waters derived from other regions. This is highly possible given its heterogeneous catchment settings in terms of vegetation cover, soil type, and rainfall intensity. Furthermore, the large catchment implies a long travel time of land-derived organic carbon during fluvial delivery (3-5 months). Coupled with limited floodplains along the mainstem channel (please refer to lines 407-407), direct inputs of $\mathrm{CO_2}$ from soil respiration would be relatively low whereas strong $\mathrm{CO_2}$ evasion in lower-order turbulent tributaries might have already exhausted dissolved $\mathrm{CO_2}$. Moreover, the mainstem rivers are generally characterized by comparatively low gas transfer velocities due to weakened turbulence and mixing with benthic substrates (Butman and Raymond, 2011; Borges et al., 2015), which can effectively inhibit $\mathrm{CO_2}$ degassing and therefore maintain the balance. An example is the Yangtze estuary that presents considerably low $\mathrm{CO_2}$ evasion fluxes of 16-34 mol $\mathrm{m^{-2}}$ $\mathrm{yr^{-1}}$, despite its significantly higher riverine $p\mathrm{CO_2}$ than the overlying atmosphere (Zhai et al., 2007. Marine Chemistry,107, 342-356). Thus, its $p\mathrm{CO_2}$ dynamics appeared to be independent of hydrograph. Clearly, this stable $p\mathrm{CO_2}$ regardless of water discharge changes is different from that in tributaries. (please refer to lines 328-337)

Moreover, we further conducted a comparative analysis regarding the differences in $p\mathrm{CO_2}$ among sub-catchments by relating to their hydrological connectivity, flow regime and $\mathrm{CO_2}$ sources, including in-stream processing, terrestrial CO_2 sources, and dilution in wet seasons. In addition to the Hanjiang (Figs. 5c and 5d), we plotted the relationship between water discharge and $p\mathrm{CO}_2$ at Wusheng (Jialingjiang catchment) and Xiajiang (Ganjiang catchment) stations (please see Figure A below) to analyze the underlying processes controlling $p\mathrm{CO}_2$. Because there is only 1-year long record of discharge at Wusheng station (18 measurements in 1983), the relationship between discharge and $p\mathrm{CO}_2$ is not as significant as that at Xiajiang station. However, the significant negative correlation between water discharge and concomitant alkalinity clearly indicates a dilution effect of surface runoff in the wet season. For the Ganjiang catchment (Xiajiang station) with dominant lithology being siliciclastic sedimentary rocks (Table 3 in the manuscript), there is a significant negative correlation between discharge and $p\mathrm{CO}_2$ (please refer to Figure A_b below, also included in the Supplement (Fig. S3)). This relationship is different from that observed at Yunxian station in Hanjiang catchment (Fig. 5d), suggesting that SiO_2 in the Ganjiang catchment is a tracer for baseflow contribution to $p\mathrm{CO}_2$. The deceasing $p\mathrm{CO}_2$ at Xiajiang station with discharge is indicative of the impact of groundwater input on riverine carbon dynamics (Figs. S2 and 6f). We have added these discussion and justifications into the revised manuscript and Supplement files. (lines 324-328; 359-366)

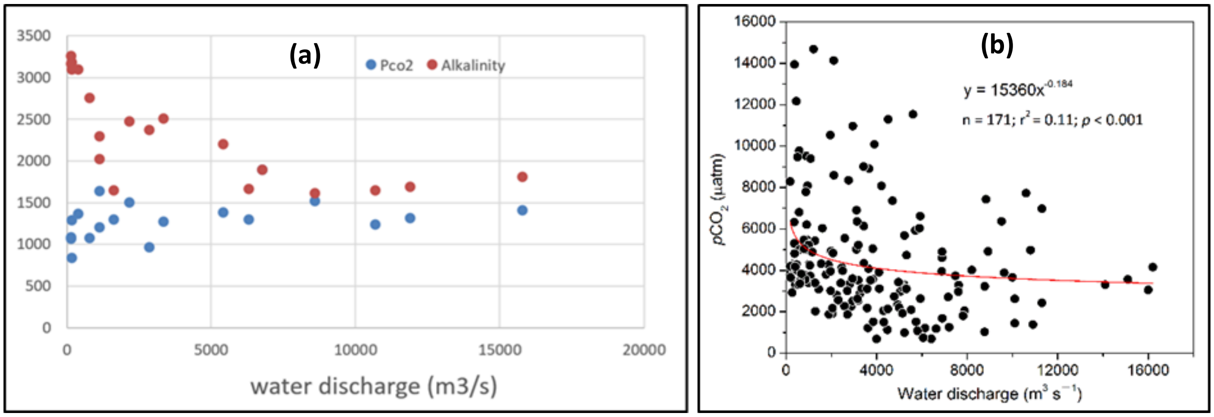

Figure A: Relationship between $p\mathrm{CO}_2$ and water discharge at (a) Wusheng (Jialingjiang catchment) and (b) Xiajiang (Ganjiang catchment) stations.

With respect to the impact of hydrologic connectivity, presence of wetlands and floodplains affects river biogeochemistry (Teodoru et al., 2015. Biogeosciences, 12, 2431-2453). For example, because of the impoundment of Danjiangkou Reservoir and other smaller reservoirs, there are plenty of newly-formed floodplains and wetlands along the river and within the Hanjiang catchment (*Liu et al*., 2011. Soil, Air, Water, 39, 109-115). The observed positive response of $p\mathrm{CO}_2$ to discharge at Yunxian station indicates the importance of enhanced connectivity between river and wetlands/floodplains on river biogeochemistry, especially during wet seasons (Fig. 5d). That is, the enhanced connectivity between river and wetlands/floodplains along aquatic continuum, especially during wet seasons, has maintained the high $p\mathrm{CO}_2$ levels (Fig. 5d), as has been observed by Abril et al. (2014. Nature, 505, 395-398) in the Amazon River. A comparative analysis between Hanjiang and Ganjiang catchments suggests the differences in underlying processes influencing riverine $p\mathrm{CO}_2$. Particularly, in dry seasons with groundwater dominating the runoff, SiO_2 serves as a good tracer of groundwater inputs and can explain ~25% of the $p\mathrm{CO}_2$ variability in sub-catchments covered mainly with siliciclastic sediment rocks, such as the Ganjiang catchment (see Figure B below). This is comparable to the results by Humborg et al. (2010) in Sweden. (lines 359-366).

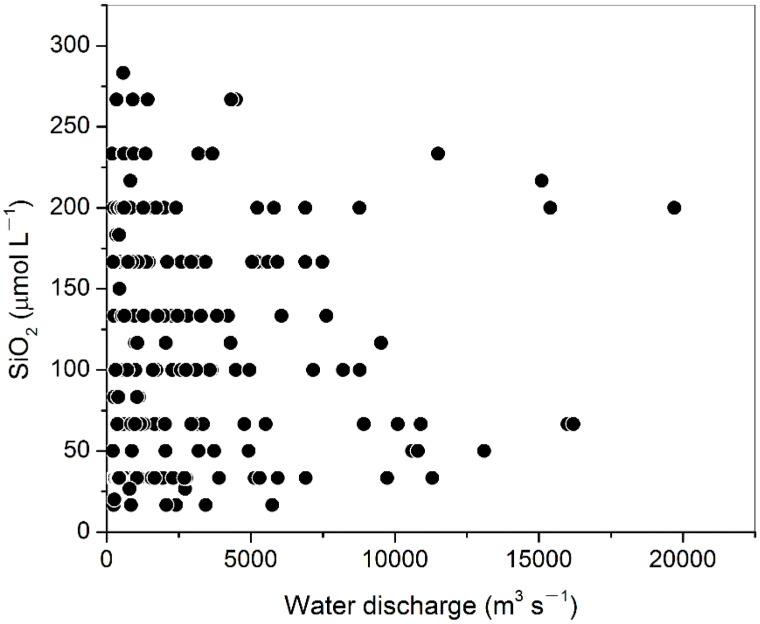

Figure B: Correlation between water discharge and dissolved SiO_2 at Xiajiang station (Ganjiang catchment) with high SiO_2 concentrations (e.g., >200 µmol L^{-1}) primarily observed in low flow periods (dry seasons).

Overall, we have further investigated the underlying processes affecting riverine pCO_2 within the Yangtze River basin by more systematically exploring the relationships between pCO_2 and various environmental variables. These discussions have been added into the revised manuscript or supplement, and related references have also been added to justify our arguments. In addition, to make the computed pCO_2 data be accessible to the public for global-scale CO_2 evasion estimate, we have also summarized the 339 station-based pCO_2 in the Supplement (Table S1). Major changes and additions have been highlighted in the revised version of the manuscript. Thanks again for your constructive comments.