Interactive comment on "How significant is submarine groundwater discharge and its associated dissolved inorganic carbon in a river-dominated shelf system-the northern South China Sea?" by Q. Liu et al.

Response to Reviewer #2:

This is an interesting paper suggesting that groundwater may play a major role on the carbon cycle off the Pearl River. I welcome this contribution since the last (and perhaps the only one!) major paper on SGD/DIC was Cai's 03 GCA paper. The sampling strategy was appropriate and the conclusions are overall sound. While I believe this paper should be ultimately published. I have a series of concerns/suggestions roughly in this order of importance:

[Response]: We appreciate the positive and constructive comments from this reviewer.

1) The three endmember mixing model relies heavily on alkalinity under the assumption that alkalinity is conservative. However, SGD is suggested to be a source of alkalinity and many other processes may drive non-conservative alkalinity behaviour both in the estuary and on the shelf. This assumption needs to be clearly stated and discussed in the manuscript. The authors briefly state in page 12394 that alkalinity was conservative, but later claim that SGD is a source of alkalinity – this contradiction needs to be reconciled. I feel that a simple alkalinity versus salinity plot would better support their model and allow the reader to judge this assumption.

[Response]: Being conservative here refers to the absence of biogeochemical modification of alkalinity along the salinity gradient rather than that alkalinity is controlled solely by the mixing between seawater and river water. Our parallel study (Cao et al., 2011) have indicated that regional salinity normalized alkalinity (NTAlk) is constant both in the river plume and the coastal upwelling zone, suggesting that alkalinity in the shelf water is conservative and is mainly controlled by physical mixing.

Possible biogeochemical processes to change alkalinity in seawater include inorganic carbon metabolism and nitrification/denitrification, etc. Constant salinity normalized Ca^{2+} and strong liner relationship between Ca^{2+} and salinity (Cao et al., 2011) have all revealed that there is no significant biogenic $CaCO_3$ dissolution /precipitation in the river plume and the upwelling zone in this study. The slope of the linear regression line showing the relationship between NTAlk and normalized dissolved inorganic carbon (NDIC) is close to the theoretical value of -0.16 deduced from organic carbon metabolism (Cao et al., 2011), indicating photosynthesis/respiration is the main biological process, which has negligible effect on alkalinity. All these strongly support that alkalinity is conservative in the shelf water. We have added a statement in the revised MS to further clarify this point.

As addressed in our response to Reviewer 1, we see from revised Fig. 7 a clear SGD signal with high Ra and high alkalinity. Thus, in our focused study area excluding nearshore upwelling zone, alkalinity is conservative but has multi-sources: Pearl River plume, offshore surface seawater, and

SGD.

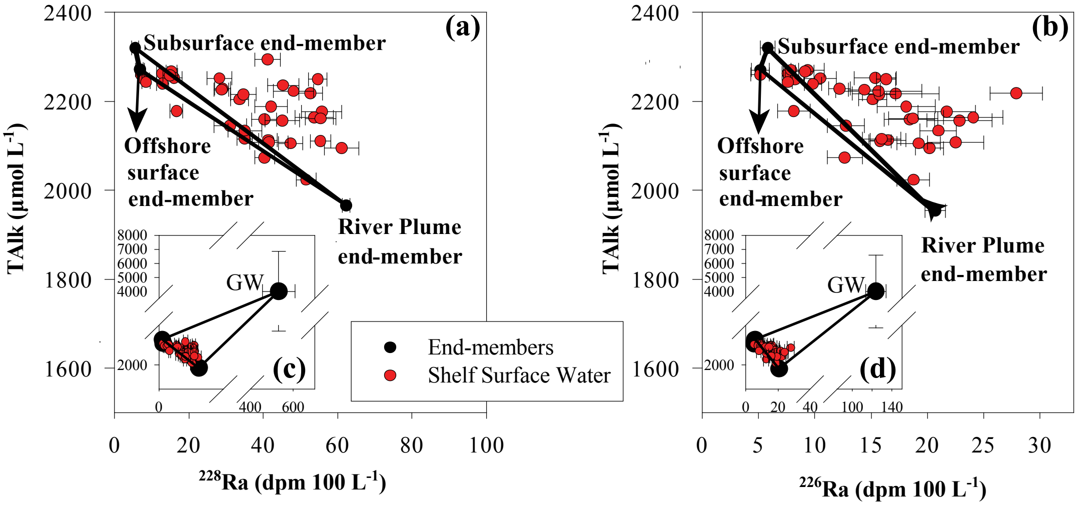

Fig. 2A1 (Fig. 7 in the revised MS). Total alkalinity (TAlk) versus ^{228}Ra (a) and ^{226}Ra (b) in the surface water of the northern South China Sea excluding the nearshore upwelling zone. Surface water samples were taken from 30 June - 8 July, 2008. Subsurface end-member values for ^{228}Ra and ^{226}Ra activity were based on the measurements at 150 m depth in the same region from a cruise conducted in April, 2009. Also shown are the individual end-member values for the three end-member mixing model (c and d).The average GW end-member values for ^{228}Ra and ^{226}Ra were sampled in December 2008 and October 2010, respectively. Red circles represent the surface data, and the error bars are associated analytical errors. Black circles represent end-member values for river plume, offshore subsurface water, offshore surface water, and average groundwater (GW), where the error bars reflect the spatial variation ($\pm 1\sigma$).

Following the suggestion by the reviewer, we plotted TAlk against salinity (figure not shown) showing an apparent two end-member mixing process in the Pear River estuary between river and offshore surface seawater in the low salinity zone (26-34.5) on the shelf. However, based on the distribution of alkalinity along the salinity gradient in the subterranean estuary, we found that alkalinity in the subterranean estuary was not conservative. Note that such nonconservative behavior of TAlk disappeared beyond the subterranean estuary, which was eventually converged into the river-seawater mixing line in the surface water beyond the discharge point, ie., upon being discharged to the shelf, TAlk behaved conservatively in the shelf water. Taken together, TAlk was conservative in the shelf waters but influenced by SGD.

2) The groundwater endmember is a major problem in the paper (as in most SGD investigations). In this case, the authors are relying only on nearshore samples. I would be surprised if their nearshore groundwater samples have the same composition of offshore groundwater that is presumably discharging to the shelf. At least some comments on that would be helpful. My guess is that their nearshore deep groundwaters would be much more enriched in radium isotopes than offshore groundwaters discharging on the shelf; if this is the case, their SGD estimates may be very conservative.

[Response]: We do appreciate the reviewer's comments regarding the offshore groundwater. We must point out that this study was primarily focused on the nearshore SGD. We calculated the SGD flux using our three end-member mixing model and a box model of mass balance, with the bottom boundary being the mixed layer rather than the whole water column. During our cruise, the surface water was well stratified from the underlying water due to the influence of strong river plume. This stratification would limit the impact of the offshore groundwater (if any) on the surface seawater. We have added a statement in the revised MS that this study only examined the coastal SGD.

We however emphasize that we agree with the reviewer that the offshore groundwater Ra could be substantial, leading to a conservative estimate of the SGD to the whole water column of the northern South China Sea, which however clearly warrants more study.

3) I missed reference to Burnett's FSU group Yellow River work – another Chinese riverdominated margin. Peterson has used radium isotopes to estimate SGD nutrient fluxes and mixing rates off the Yellow River. As there are very few studies in Chinese systems and river dominated margins in general, I feel that Peterson's study could be used to put the Pearl River in a broader regional/global perspective. Peterson, R.N. et al. 2008. Radon and radium isotope assessment of submarine groundwater discharge in the Yellow River Delta, China. Journal of Geophysical Research 113, C09021. Peterson, R.N. et al. 2008. Determination of transport rates in the Yellow River-Bohai Sea mixing zone via natural geochemical tracers. Continental Shelf Research 28, 2700-2707.

[Response]: We have added these two references in the revised MS.

4) Abstract, line 5: I suggest replacing "carbon dioxide parameters" with "carbonate system parameters".

[Response]: Accepted.

5) Page 12388, line 22: I find hard to digest that the increase in radium with distance offshore could be simply related to the dispersal of river plume. Can you provide stronger/clearer support for that?

[Response]: Radium increased with distance offshore, and correlated with low alkalinity and high dissolved inorganic nitrogen (DIN), which is a prominent feature of the Pearl River plume. Both alkalinity/salinity and DIN/salinity plots (Fig. 6, Han et al., 2012) suggest that the low alkalinity and high DIN shelf water are originated from the Pearl River. Therefore, the high radium in the offshore low salinity zone was related to the dispersal of river plume.

6) Page 12391, line 6-7: I believe this belongs to discussion.

[Response]: We deleted this part.

7) Page 12392: How have you obtained uncertainties for the radium-derived water ages? Please be clear.

[Response]: We have added a statement "The quoted age uncertainties represent one standard deviation due to the spatial variation of the concerned area"

8) Equation 1: I suggest the addition of a note on why the ratios between other isotopes (such as 224/228 or 224/223) were not attempted. Larger analytical uncertainties? Do they compare well?

[Response]: Radium-223, ^{228}Ra, and ^{226}Ra were elevated both in the nearshore and offshore river plume. However, ^{224}Ra was enriched in the nearshore river plume but depleted in the offshore river plume, likely because the half-life of ^{224}Ra ($T_{1/2}$ = 3.7 days) is too short to trace the Pearl River plume farther off the estuary mouth. Therefore, ^{224}Ra is not appropriate to estimate the water age in the river plume. Instead, we used ^{223}Ra/^{228}Ra ratio to estimate water age in the river plume zone. With respect to the nearshore upwelling area, we also adopted the ^{223}Ra/^{228}Ra ratio to calculate water age in order to avoid the analytical uncertainties caused by different Ra ratios. Note that comparable upwelling water age can be achieved using both ^{224}Ra/^{228}Ra and ^{223}Ra/^{228}Ra. We have added a note in the text to explain it.

9) Page 12395: I suggest omitting most of the text about endmembers (lines 5-15) and show these values in a table.

[Response]: Accepted. We added a table (Table 2) to show these end-member values.

10) Page 12397, Line 7: More detail on Moore 07 approach would be useful.

[Response]: Accepted. We have included in the revised MS more details about the Moore's approach.

11) Page 12400, Line 10: "Fresh SGD". As far as I understand, the authors claim to be quantifying saline SGD. How was fresh SGD estimated?

[Response]: In our original MS, we assigned that 10% of SGD flux is from fresh SGD on the basis that the average net annual groundwater recharge rate takes account 4-9% of our estimated SGD flux, which could however be subject to large uncertainties. Therefore, we deleted the estimation of fresh SGD in the revised MS.

12) Page 12400, Line 20: When comparing the Pearl River to other systems, avoid vague terms such as "similar" and "higher". I suggest spelling out the values from the literature. In addition, Cai and Moore's estimates are for tidal creeks and estuaries – any comparison between shelf waters and creeks needs to be qualified.

[Response]: Suggestions well taken. We agreed with the reviewer that comparison between shelf water and creek needs to be qualified, and thus in the revised MS, we point out the different spatial scale and only listed the DIC concentration in the groundwater and SGD-derived DIC flux at other smaller-scale sites.

13) Page 12401, Line 23: ": : :contributions from the river plume and coastal upwelling". The contribution of upwelling has not been quantified in this paper, so it is hard to follow how it can be compared to SGD. Please revise.

[Response]: We did a first order estimate of upwelling-derived DIC based on the DIC end-member value in the subsurface water and the upwelling rate. However, given that DIC is not conservative during the upwelling circulation (Cao et al., 2011) and there exists a large uncertainty with upwelling rate, we dropped off the estimation of the DIC contribution from coastal upwelling in the revised MS.

References:

Cao, Z., Dai, M., Zheng, N., Wang, D., Li, Q., Meng, F., and Gan, J.: Dynamics of the carbonate system in a large continental shelf system under the influence of both a river plume and coastal upwelling, J. Geophys. Res., 116, G02010, doi:02010.01029/02010JG001596, 2011.

Han, A., Dai, M., Gan, J., Kao, S.-J., Li, Q., Wang, L., Zhai, W., Cai, P., and Huang, B.: Nutrient dynamics in a large continental shelf system under the influence of both a river plume and coastal upwelling, Limnol. Oceanogr., 57, 486–502, 2012.