

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 #1:

The submarine groundwater discharge (SGD) may be an important source of nutrients to the South China Sea but it has never been quantified rigorously. The only known reference to my knowledge is that of Chen et al. (2001, Marine Chemistry). In that paper the SGD nutrient flux was assumed to be 10% of the riverine flux. This manuscript gave a much higher ratio of 49-96% for nitrate and 50-99% for phosphate. I have trouble accepting such high values because there is no indication of such wide-spread nutrient-rich waters near the Guangdong coast.

[Response]: We thank the reviewer for bringing Chen et al. (2001) to our attention while pointing out the potential importance of the submarine groundwater discharge (SGD) in contributing nutrients to the South China Sea. As pointed out by the reviewer, the 10% SGD's nutrient contribution was assumed in Chen et al. (2001), while the actual SGD and the SGD associated flux were not determined. In this study, Ra-derived SGD flux was determined to be 13-25% of the Pearl River flow, which was an average flux in the week prior to our sampling campaign on the shelf. In the previous version of the MS, we estimated higher percentages of 49-96% for nitrate and 50-99% for phosphate, which were based on the SGD-delivered nutrient flux of the present study and the riverine nutrient flux in the wet season of 2000 reported in Cai et al. (2004). Now, by comparing the nutrient fluxes from SGD and the Pearl River in the same sampling period of the present study, these percentages became 10-40% for dissolved inorganic nitrogen (DIN) and 4-79% for phosphate. This has been corrected in the revised MS.

The reviewer raised a very good question, i.e., how significantly can the SGD contribute to the enhancement in nutrient concentrations on the shelf, in this case, near the Guangdong coast? To answer the question, we did the following calculation. The nutrient inputs to the northern South China Sea (NSCS) from SGD were $8-31 \times 10^9 \text{ mol yr}^{-1}$ for DIN and $3-70 \times 10^7 \text{ mol yr}^{-1}$ for PO_4^{3-} . These nutrient fluxes can be converted to the inventory in the shelf water of $3-12 \times 10^8 \text{ mol}$ for DIN and $1-28 \times 10^6 \text{ mol}$ for PO_4^{3-} , which could at most support increases in DIN and PO_4^{3-} concentrations of $1.0-3.8 \mu\text{mol L}^{-1}$ and $0.004-0.088 \mu\text{mol L}^{-1}$, respectively, on the NSCS shelf. These slight increases in nutrient concentrations would as a matter of fact further be reduced by biological consumption. As such, it would be hard to see wide-spread nutrient-rich waters near the Guangdong coast although SGD did deliver high nutrients to the shelf water.

Besides, Peng et al. (2008, JO) have pointed out that SGD outflow from Taiwan may be dominated by a few fault lines. Since there is little karst and probably few fault lines in the Guangdong coast it is difficult to imagine high SGD outflows there. Note Taiwan and the Pearl River Basin are all traversed by the Tropic of Cancer with high rainfalls.

[Response]: Groundwater can be classified into different types based on the aquifer properties, karstic water, fracture water, and interstitial water (loose Quaternary deposits). High SGD fluxes have been reported in all these types of groundwater (Taniguchi et al., 2002; Kim et al., 2005; Burnett et al., 2006). The reviewer is right that highest SGD rates can occur in permeable or deformed regions (Peng et al., 2008 and references therein).

Karst areas facilitate groundwater transport with conduit flows in subsurface due to the dissolution of CaCO_3 . Faults provide important groundwater outflow passages especially in fractured rock. Peng et al. (2008) reported significant fracture-delivered fresh SGD via fault passages in Taiwan. It should be pointed out that SGD includes both fresh groundwater and recirculated seawater. Many published SGD studies have in fact been associated with the groundwater component with a high proportion of recirculated seawater especially in areas with wide distribution of sandy sediments and high tidal ranges (Kim et al., 2005). This is also the case in our study area, northern South China Sea (NSCS), where the aquifer is mainly composed of highly permeable sandy sediments of loose Quaternary deposits (Chen, 2008).

This leads to my concern about the methodology although I have no question about the quality of the data. To start with, upwelling was ignored in the model which is a nono. The authors should measure more samples or get literature data to obtain the end member for the source of the upwelled water.

[Response]: For the overall NSCS region, upwelling brings up subsurface water contributing to the mass balance of nutrients and other elements (if enriched in the subsurface) in the surface. This is particularly true in the near shore areas of the NSCS where upwelling is prominent in summer. In our mass balance calculation however, we have excluded these nearshore zones. Also note that our calculation concerned the mass balance in the upper mixed layer which is ~10 m. In this context, we have excluded the contribution from upwelling. This is further explained as of below.

First of all, the upwelled water end-member is defined as the offshore subsurface water sourced from ~150 m with a high salinity of 34.5, a potential temperature of 17°C (Cao et al., 2011). Here we took the long-lived Ra (^{228}Ra and ^{226}Ra) activity at 150 m depth from a cruise conducted in April, 2009 as the offshore subsurface end-member. This water mass has end-member values of ^{228}Ra , ^{226}Ra and TALK very similar to the offshore surface water, as illustrated in Fig. 7a and b. This suggests that we can neglect the contribution of long-lived Ra and TALK to surface water from upward diffusion and advection. Hence, our three end-member mixing model should be in order when excluding the nearshore upwelling zone and when the surface layer is concerned.

Secondly, in our focused zone (mixed layer) excluding the nearshore upwelling area, the offshore surface water contributed 77% of the mass while the offshore subsurface water only contributed 1.5% to the shelf water based on the conservation of potential temperature and salinity (Cao et al., 2011; Han et al., 2012). This suggests once again that the subsurface water contribution is insignificant as compared to the offshore surface water.

Finally, it is clear that from the TALK versus long-lived Ra plots (Fig.7), only very few data points fall onto the two end-member mixing line between river plume and the offshore surface water. Instead, most of the surface water samples are influenced by a third source characterized by high ^{228}Ra , ^{226}Ra , and TALK, which we inferred to be SGD.

In the revised MS, we have rewritten Section 4.2.1 according to the above reasoning.

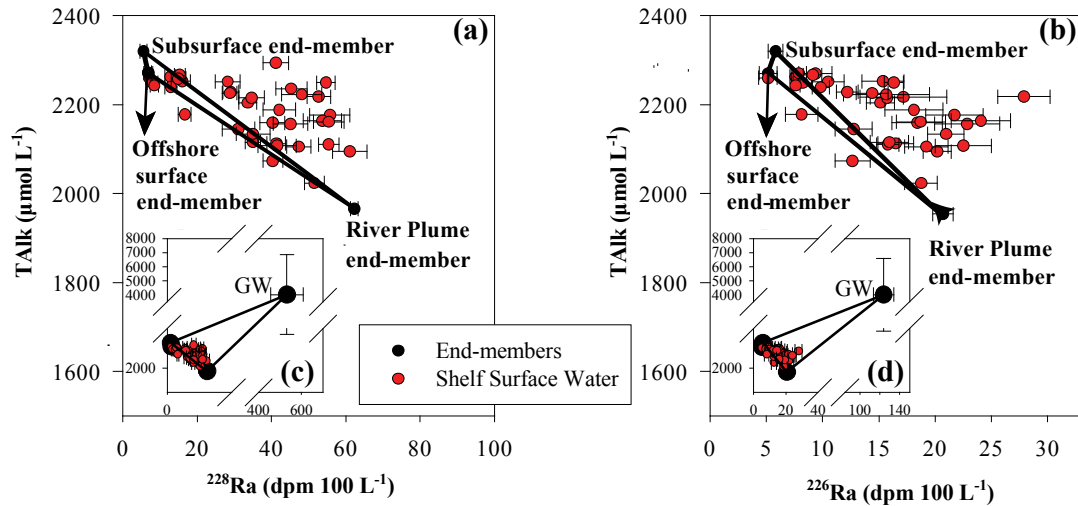


Fig 1A1 (Fig. 7 in the revised MS). Total alkalinity (TALK) versus ^{228}Ra (a) and ^{226}Ra (b) in the surface water of the northern South China Sea excluding the nearshore upwelling zone. Surface water samples were taken from 30 June - 8 July, 2008. Subsurface end-member values for ^{228}Ra and ^{226}Ra 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 ($\pm 1\sigma$).

My second concern is the widespread end members for well water and river water. The authors should make a plot of the 3 end member mixing so that it is clear whether their assumption of the end member values are valid. This must be done as the result is very sensitive to the choice of end members. Of course, the fourth end member MUST be included.

[Response]: We have redrawn Fig. 7 to better present the 3 end-member mixing scheme showing the individual end-member values. As discussed in the text on sensitivity analysis with regards to the choice of end-members, the three end-member mixing model is very sensitive to the end-member of plume and surface seawater values. For example, a 5% decrease in TALK can change the SGD flux by 59.5-75.2%. We have reported in Cao et al. (2011) that TALK of these two end-members was relatively constant with only a 0.95-1.75% variation. The most variable end-members were indeed TALK and Ra in coastal groundwater. However, our model is much less sensitive to the changes in this term (6.0-7.5% SGD change with 5% end-member variation). The higher the TALK/Ra end-member for groundwater, the lower the SGD flux will be obtained. TALK in groundwater had a large spatial variation, ranging from 381 to 9009 $\mu\text{mol L}^{-1}$. However, the SGD rate would change by 61% with the usage of the maximum TALK compared with the average, a change that is within the bounds of the error estimation of the model. Notably, the re-estimated SGD would not change within uncertainties even if the groundwater Ra end-member was increased by 300%, which already covered the spatial variation of Ra end-member used in the three end-member mixing model.

Lastly, what does it mean "the age of water"? It should be clearly defined.

[Response]: We added the definition of water age as "Water age is defined as the time a water

parcel has spent since entering the estuary/ continental shelf through one of its boundaries (Charette et al., 2008).”

References:

Burnett, W. C., Aggarwal, P. K. A., Aureli, Bokuniewicz, H., Cable, J. E., Charette, M. A., Kontar, E., Krupa, S., Kulkarni, K. M., Loveless, A., Morre, W. S., Oberdorfer, J. A., Oliveria, J., Ozyurt, N., Povinec, P., Privitera, A. M., Rajar, G. R., Ramessur, R. T., Scholten, J., Stieglitz, T., Taniguchi M., and Turner, J. V.: Quantifying submarine groundwater discharge in the coastal zone via multiple methods. *Sci. Total Environ.*, 367, 498–543, 2006.

Cai, W.-J., Dai, M.H., Wang, Y.C., Zhai, W.D., Huang, T., Chen, S.T., Zhang, F., Chen, Z.Z., Wang, Z.H.: The biogeochemistry of inorganic carbon and nutrients in the Pearl River estuary and the adjacent Northern South China Sea, *Cont. Shelf Res.*, 24, 1301–1319, 2004.

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.

Charette, M. A., Moore, W. S., and Burnett, W. C.: Uranium-and thorium-series nuclides as tracers of submarine groundwater discharge, in: U-Th series Nuclides in Aquatic systems eds. S. Krishnaswami, J.K. Cochran, 13, Amsterdam: Elsevier, 155–191, 2008.

Chen, C-T A., Wang, S-L., Wang, B-J., and Pai, S-C.: Nutrient budgets for the South China Sea basin, *Mar. Chem.*, 75, 281–300, 2001.

Chen, Y.: Groundwater analysis in the watershed downstream of Hanjiang along the coast of Yue Dong, *Guangdong water resources and hydropower*, 31-32, 2008 (in Chinese).

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.

Kim, G., Ryu, J. W., Yang, H. S., and Yun, S. T.: Submarine groundwater discharge (SGD) into the Yellow Sea revealed by Ra-228 and Ra-226 isotopes: Implications for global silicate fluxes, *Earth Planet. Sci. Lett.*, 237, 156–166, 2005.

Peng, T.R., Chen, C.T.A., Wang, C.H., Zhang, J., and Lin, Y.J.: Assessment of terrestrial factors controlling the submarine groundwater discharge in water shortage and highly deformed island of Taiwan, Western Pacific Ocean; *J. Oceanogr.*, 64, 323–337, 2008.

Taniguchi, M., Burnett, W. C., Cable, J. E. and Turner, J. V.: Investigation of submarine groundwater discharge. *Hydrol. Process.*, 16, 2115–2129, 2002.