Response to Referee #1:

Dear Referee, we appreciate your insightful and thorough comments and suggestions according to which we improved our revised MS carefully. Thank you for your time and critical evaluation and enclosed please kindly find our responses (written in blue) as follows.

General comments:

(1) My main concern in the manuscript is the uncertainty around the Ra concentrations. As shown by the authors, there was a great range in Ra concentrations over the tidal cycle during their time series. Using a one off survey to gather Ra data for a mass balance introduces a large amount of uncertainty into how representative the survey was. More information is needed in the methods on how the survey was conducted (ie over 1 tidal cycle? over multiple days?) and how this might affect the Ra concentrations over the survey.

RESPONSE:

Thank you for raising these important points. In this manuscript, the uncertainty of the Ra concentrations came from the errors of sampling, treatment and measurement. Actually, the dominant error was from Ra measurement. Using HPGe Gamma spectrometry (well-type, ORTEC, GWL-120-15-XLB-AWT), the error of ^{226}Ra and ^{228}Ra can be controlled below 20 % (Du et al., 2013; Wang et al., 2014, 2016), which was the similar case in other labs as well (e.g. Kim et al., 2005; Liu et al., 2012).

The time series observation was conducted by sampling at every 3 hours in a continuous 24-hour period over one complete tidal cycle. It is a very common method to evaluate the submarine groundwater discharge (SGD) by the time series observation (e.g. Peterson et al., 2008; Garcia-Orellana et al., 2010; Wang et al., 2016). During the time series observation, the tide variation can result in the change of Ra activity in the water column， because the water component is changing. At the low tide, weaker intrusion of the open seawater with low Ra concentration occurred along with the observation of higher percentage of submarine groundwater with higher Ra concentration. At the high tide, the situation was opposite, and hence the high activity of Ra was observed at low tide, whereas low Ra activity was observed at high tide.

Moreover, some information about this time series observation has been added in the Sampling strategy and Results and discussion sections in the revised manuscript as follows:

"In the KRE, we also conducted a continuous 24-hour time series observation over a complete tidal cycle by sampling the surface water at time-series (TS) station every three hours (Figure 1), which has been widely used to evaluate the SGD (e.g., Peterson et al., 2008; Garcia-Orellana et al., 2010; Wang et al., 2016)."

"Activities of ^{226}Ra and ^{228}Ra showed similar opposite trend with respect to salinity due to the tidal variation (Figures 6a and 6b). At the low tide, weaker intrusion of the open seawater with low Ra concentration occurred along with the observation of higher percentage of submarine groundwater with higher Ra concentration. At the high tide, the situation was opposite, and hence the high activity of Ra was observed at low tide, whereas low Ra activity was observed at high tide."

Du, J. Z., Moore, W. S., Hsh, H. F., Wang, G. Z., Scholten, J., Henderson, P., Men, W., Rengarajan, R., Sha, Z. J., and Jiao, J. J.: Inter-comparison of radium analysis in coastal sea water of the Asian region, Mar, Chem., 156, 138-145, doi: 10.1016/j.marchem.2013.04.008, 2013.

Garcia-Orellana, J., Cochran, J. K., Bokuniewicz, H., Yang, S., and Beck, A. J.: Time-series sampling of ^{223}Ra and ^{224}Ra at the inlet to Great South Bay (New York): a strategy for characterizing the dominant terms in the Ra budget of the bay, J. Environ. Radioact., 101(7), 582-588, doi:10.1016/j.jenvrad.2009.12.005, 2010.

Kim, G., Ryu, J. W., Yang, H. S. and Yun, S. T.: Submarine groundwater discharge (SGD) into the Yellow Sea revealed by ^{228}Ra and ^{226}Ra isotopes: implications for global silicate fluxes, Earth Planet. Sci. Lett., 237(1), 156-166, doi: 10.1016/j.epsl.2005.06.011, 2005

Liu, Q., Dai, M., Chen, W., Huh, C.A., Wang, G., Li, Q. and Charette, M.A.: How significant is submarine groundwater discharge and its associated dissolved inorganic carbon in a river-dominated shelf system?, Biogeosciences, 9(5), 1777-1795, doi: 10.5194/bg-9-1777-2012, 2012.

Peterson, R. N., Burnett, W. C., Taniguchi, M., Chen, J., Santos, I. R., and Ishitobi, T.: Radon and radium isotope assessment of submarine groundwater discharge in the Yellow River delta, China. J. Geophys. Res.: Oceans, 113(C9), doi:10.1029/2008JC004776, 2008.

Wang, X., Du, J., Ji, T., Wen, T., Liu, S. and Zhang, J.: An estimation of nutrient fluxes via submarine groundwater discharge into the Sanggou Bay-a typical multi-species culture ecosystem in China, Mar. Chem., 167, 113-122, doi:10.1016/j.marchem.2014.07.002, 2014.

Wang, X. and Du, J.: Submarine groundwater discharge into typical tropical lagoons: A case study in eastern Hainan Island, China, Geochem. Geophys. Geosyst., 17(11), 4366-4382, doi:10.1002/2016GC006502, 2016.

(2) The authors state that trends in Ra activities were low in freshwaters, highest at the mouth and low in the estuary based on Figure 4. While there is a clear relationship between salinity and the sampling sites, I do not believe this is evident in Figure 4 particularly for 226Ra with highest 228Ra concentrations corresponding to near the lowest 226Ra. I believe, the error bars refer to analytical uncertainties from instrumentation rather than replicate measurements so do not give an indication a sampling variability at each site which would have been useful. A salinity vs Ra concentration plot would also have been useful. This plot is presented in Figure 7 and is said to include sampling "between Krka River water and open seawater" however the estuary samples presented fall in a very narrow salinity range (10-20) which do not correspond to those seen during the survey. Also there are more estuary measurements than sampling sites along the estuary. As such, it is not clear where this data comes from. This same comment applies

to the author’s interpretation of time series data in figure 6 (Page 4, line 34) as I do not believe a trend is evident. Statistical analysis would help quantify any trends. Added to this is the time series took place in a location where the authors note freshwater springs are present which is suggested to be the cause of higher Ra concentrations during the survey. This would dramatically skew flux calculations based on high point source Ra concentrations using the time series.

RESPONSE:

In general, the Ra isotopes are conservative tracers, and their conservative behavior is more evident in the estuaries. In the freshwater, Ra isotopes are adsorbed on the suspended particles, then following the salinity increase in the estuary, Ra concentration increases due to the release of Ra from suspended particles or other Ra source input in low and middle range of salinity (below ~20). In higher salinity (over ~20) zone, owing to mixing with the open seawater, the Ra activity in seawater decreased with the rise of salinity, as the open seawater in general has notably lower Ra activity (Rutgers van der Loeff et al., 2003). Such case is very common in the estuarine zone, which is termed as inversed V type (e.g., Moore and Krest, 2004; Liu et al., 2012). It is shown in Figure 4, in which the ^{228}Ra variation trend is more observable than ^{226}Ra, because the ^{228}Ra (half-life 5.7 yrs) in the freshwater and open sea water is much lower than that in the estuary relative to ^{226}Ra (half-life 1600 yrs) and these result in less effects from freshwater and open sea water for ^{228}Ra, thus the inversed V type variation trend of ^{228}Ra was more evident. Our results are in agreement with earlier studies (e.g., Beck et al., 2007; Rengarajan and Sarma, 2015).

In this manuscript, the Ra error bars really refers to analytical uncertainties from instrumentation (HPGe Gamma spectrometry) rather than replicate measurements, and the measurement error bars are widely used for Ra worldwide (e.g., Liu et al., 2012; Rodellas et al., 2015).

Figure 7 shows more measurements than sampling sites in the estuary. We apologize that the presentation was not clear in the original manuscript. Actually the time series observation data are also included into the Figure 7. Besides that, only the estuarine data are plotted in Figure 7 and because of that, the salinity falls into the narrow range of 11.2-19. Since, the survey was conducted from the freshwater end-member to the open sea end-member, we have revised Figure 7 which now includes all the data from the freshwater end-member to the open sea end-member.

Figure 6 shows that the Ra activity has a negative correlation with salinity (r=-0.55, p=0.079 for ^{226}Ra and r=-0.60, p=0.057 for ^{228}Ra). This is due to the fact that open seawater has low Ra activity whilst the submarine groundwater inputs have high Ra activities.

We used only the high point source Ra concentrations of the time series observation to calculate the SGD flux. In fact, all the Ra data of the time series observation are used as shown by equation (12). That is why we can calculate the continuous variation of SGD flux at each time point during the tidal cycle, and obtain an integrated SGD flux range using the time series observation.

Finally, we corrected the concerned parts to clarity our presentation in the revised manuscript.

Beck, A.J., Rapaglia, J.P., Cochran, J.K. and Bokuniewicz, H.J.: Radium mass-balance in Jamaica Bay, NY: evidence for a substantial flux of submarine groundwater, Mar. Chem., 106(3), 419-441, doi: 10.1016/j.marchem.2007.03.008, 2007.

Liu, Q., Dai, M., Chen, W., Huh, C.A., Wang, G., Li, Q. and Charette, M.A.: How significant is submarine groundwater discharge and its associated dissolved inorganic carbon in a river-dominated shelf system?, Biogeosciences, 9(5), 1777-1795, doi: 10.5194/bg-9-1777-2012, 2012.

Moore, W.S. and Krest, J.: Distribution of ^{223}Ra and ^{224}Ra in the plumes of the Mississippi and Atchafalaya Rivers and the Gulf of Mexico. Mar. Chem., 86(3), 105-119, doi: 10.1016/j.marchem.2003.10.001, 2004.

Rengarajan, R. and Sarma, V. V. S. S.: Submarine groundwater discharge and nutrient addition to the coastal zone of the Godavari estuary, Mar. Chem., 172, 57-69, doi:10.1016/j.marchem.2015.03.008, 2015.

Rodellas, V., Garcia-Orellana, J., Masqué, P., Feldman, M., and Weinstein, Y.: Submarine groundwater discharge as a major source of nutrients to the Mediterranean Sea, Proc. Natl. Acad. Sci., 112(13), 3926-3930, doi:10.1073/pnas.1419049112, 2015.

Rutgers van der Loeff, M., Kühne, S., Wahsner, M., Höltzen, H., Frank, M., Ekwurzel, B., Mensch, M., Rachold, V.: ^{228}Ra and ^{226}Ra in the Kara and Laptev Seas, Cont. Shelf Res., 23(1), 113-124, doi:10.1016/S0278-4343(02)00169-3, 2003.

Specific comments:

(1) Overall, I found the manuscript contains numerous grammar and structural mistakes which at times made information difficult to follow. However, I believe this can be easily rectified by a thorough professional proof read and will not include those suggests below.

RESPONSE: We followed the advice of the referee, and the whole manuscript is proof read by the professor who is a native English speaker.

(2) Page 4 Line 3. The authors variability in Ra concentrations due to hysteresis but do not demonstrate this. Statistical analysis or including the hysteresis analysis in a figure is needed to show that relationship as it is not clear.

RESPONSE: We agree with the referee on this point. The Ra sources, especially SGD could not respond to the tidal variation so fast, which results in hysteresis (e.g., Sadat-Noori et al., 2015). When the hysteresis was taken into consideration, the correlation analysis showed that Ra concentrations and salinity had a considerable negative correlation (r=-0.55 for ^{226}Ra and r=-0.60 for ^{228}Ra) despite of the non-significant p-values (p=0.079 for ^{226}Ra p=0.057 for ^{228}Ra). We have added this point in the revised manuscript.

Sadat-Noori, M., Santos, I. R., Sanders, C. J., Sanders, L. M. and Maher, D. T.: Groundwater discharge into an estuary using spatially distributed radon time series and radium isotopes, J. Hydrol., 528,703-719, doi:10.1016/j.jhydrol.2015.06.056, 2015.

(3) Page 4 Line 5. As with the Ra concentrations, the nutrient trends are not clear from the figures. Correlation analysis would help clarify if such a relationship exists.

RESPONSE: We followed the advice of the referee. Similar to that of Ra activity, DIP and DSi variations had an opposite trend to salinity with a small hysteresis effect observed. There was no obvious variation correlation between DIN and salinity. Therefore, as with the Ra, with the hysteresis effect considered, we performed the correlation analysis, which showed that none of the nutrients had a significant correlation with salinity (r=-0.44, p=0.123 for DIP, r=-0.43, p=0.147 for DSi and r=0.16, p=0.341 for DIN).

(4) Page 6 line 1. As queried above, it is unclear where the estuary samples come from as they fall in a very narrow salinity range and do not come from the entire survey. Therefore, the mass balance is based on a very narrow range of Ra concentrations in potentially a portion of the estuary receiving point sources of Ra (freshwater springs).

RESPONSE: As shown by the blue dashed line box in Figure 1, the Ra data in three end-member mixing model includes only time series samples (TS-1~9) and the samples from the estuary (KR4~7). Only the middle zone of the estuary and its surface waters above the halocline are presented in this figure.

In this survey, the salinity of the KRE in surface water was below 21.7 (Table 1), similar to the salinity of the Ra samples used in the three end-member mixing model and mass balance model. Therefore, we believe it is reasonable to calculate the SGD flux using only the estuarine samples. In consideration of morphology and sediment properties, freshwater spring is assumed to be similar, because when the freshwater spring comes out it mixes with seawater immediately and usually the salinity is in the range of the KRE samples.

(5) Page 7 Line 5. The episodic breakdown of boundary layers (ie Simpson et al Estuar. Coast. 1990 and Scully et al Estuar. Coast. 2005) needs to be discussed. This break down of the boundary layer may deliver high concentrations of Ra and nutrients to surface waters both spatially and temporally.

RESPONSE: The Krka River Estuary is highly stratified and the breakdown of the boundary layer is less likely and less important than in some other estuaries. The boundary layer (i.e. halocline) is permanent in KRE, whilst the thickness and the steepness of the salinity gradient change seasonally and longitudinally from its head to mouth (Žutić and Legović, 1987; Legović, 1991; Cukrov et al., 2009). Figure 5 shows that the parameters are highly different above and below the halocline, and it is obvious that the halocline can significantly slow down the diffusion of nutrients from the underlying water to the surface layer water, in line with Legović et al. (1994). Thus, we omitted the impact of diffusion of Ra and nutrients through the halocline.

Cukrov, N., Mlakar, M., Cuculić, V., and Barišić, D.: Origin and transport of ^{238}U and ^{226}Ra in riverine, estuarine and marine sediments of the Krka River, Croatia, J. Environ. Radioact., 100(6), 497-504, doi:10.1016/j.jenvrad.2009.03.012, 2009.

Legović, T.: Exchange of water in a stratified estuary with an application to Krka (Adriatic Sea), Mar. Chem., 32(2), 121-135, doi:10.1016/0304-4203(91)90032-R, 1991.

Legović, T., Žutić, V., Gržetić, Z., Cauwet, G., Precali, R., and Viličić, D.: Eutrophication in the Krka estuary, Mar. Chem., 46(1), 203-215, doi:10.1016/0304-4203(94)90056-6, 1994.

Žutić, V. and Legovic, T.: A film of organic matter at the fresh-water/sea-water interface of an estuary. Nat., 328(6131):612-614, doi:10.1038/328612a0, 1987.

(6) Page 8 Line 20. I believe this interpretation is limited as it does not include evapotranspiration, aquifer recharge or surface storage. Further to this, I believe the fact that this analysis contains significant uncertainties and it does not add to the main scientific story of the manuscript which is the use Ra isotopes to quantify SGD and SGD nutrient fluxes, I would omit.

RESPONSE: The water balance model includes evaporation as Q_E term in Equation (13), but really neglects the net variation of water storage with time (i.e. over a tidal period) in this system, because this model is a classic method to build water balance in the system (Benduhn and Renard, 2004; Wang et al., 2015). It is a necessary step for establishing the following nutrients budgets and emphasizing the importance of the SGD-derived nutrients. For these reasons, we would like to keep these results in the revised manuscript.

Benduhn, F. and Renard, P.: A dynamic model of the Aral Sea water and salt balance. J. Mar. Syst., 47(1):35-50, doi:10.1016/j.jmarsys.2003.12.007, 2004.

Wang, X. Li, H., Jiao, J. J., Barry, D. A., Li, L., Luo, X., Wang, C., Wan, L., Wang, X., Jiang, X., Ma, Q., and Qu, W.: Submarine fresh groundwater discharge into Laizhou Bay comparable to the Yellow River flux, Sci. Rep., 5, 8814, doi:10.1038/srep08814, 2015.

(7) Page 9 Line 23. The uncertainty in combine groundwater mass balance nutrient fluxes and average wastewater treatment plant fluxes needs to be discussed. Without knowing the time specific discharge of the plant and how it affected river and estuary nutrient concentration there are large assumptions in this model.

RESPONSE: As the water balance model, the Land Ocean Interactions in the Coastal Zone (LOICZ) approach is extensively used to establish nutrients budgets in the estuaries (e.g. Gordon et al., 1996; Hung and Hung, 2003; Liu et al., 2009, 2011). This model is established under several assumptions, for example, the estuary is treated as a single box and is assumed to be at a steady state.

Hung, J.-J. and Hung, P.-Y.: Carbon and nutrient dynamics in a hypertrophic lagoon in southwestern Taiwan, J. Mar. Syst., 42, 97–114, doi:10.1016/S0924-7963(03)00069-1, 2003.

Gordon, D. C., Boudreau, P. R., Mann, K. H., Ong, J. E., Silvert, W. L., Smith, S. V., Wattayakorn, G., Wulff, F., and Yanagi, T.: LOICZ Biogeochemical Modelling Guidelines (vol 5), LOICZ Core Project, Netherlands Institute for Sea Research, 1996.

Liu, S. M., Hong, G. H., Zhang, J., Ye, X. W., and Jiang, X. L.: Nutrient budgets for large Chinese estuaries, Biogeosciences, 6(10), 2245-2263, doi:10.5194/bg-6-2245-2009, 2009.

Liu, S. M., Li, R. H., Zhang, G. L., Wang, D. R., Du, J. Z., Herbeck, L. S., Zhang, J., and Ren, J. L.: The impact of anthropogenic activities on nutrient dynamics in the tropical Wenchanghe and Wenjiaohe Estuary and Lagoon system in East Hainan, China, Mar. Chem., 125(1), 49-68, doi:10.1016/j.marchem.2011.02.003, 2011.

(8) Figure 3. Using distance on the x axis would make the plot more easily interpreted. Including the sampling points in the plots would also help show the reader how accurate the interpolation of data points was.

RESPONSE: We agree with referee and have corrected it in the revised manuscript.

(9) Figure 4. Using distance or salinity on the x axis would be more useful.

RESPONSE: We have followed the advice of referee and have revised it as distance on the x axis.

(10) Figure 6. This was difficult to interpret due to how the legend was presented. Using titles on the y axis and a legend on each plot would help with this.

RESPONSE: We have followed the advice of referee and corrected it.

(11) Figure 7. As above, unclear where the estuary samples are from as they have a narrow range and there are more of them than the survey. It could be problematic for the mass balance if the samples are from the time series due to point source Ra discharge.

RESPONSE: The samples in Figure 7 include time series samples (TS-1~9) and the samples from the estuary (KR4~7).

(12) Figure 8. It is unclear why only the middle section survey sites are included here.

<u>RESPONSE</u>: The study was focused on the Krka River Estuary that was shown in the blue dashed box in Figure 1. We displayed the data for this main part of the estuary, namely the middle section of KRE presented at Figure 8.