Response to the comments on “Tidal variability of nutrients in a coastal coral reef system influenced by groundwater”

Responses are in blue with page and line numbers provided where changes were made in the revision. The manuscript submitted to Journal of Marine Systems, which presents SGD-associated nutrients fluxes into Sanya Bay traced by distributions of radium isotopes, is cited in the revision (Page 3, Line 25) and enclosed.

Anonymous Referee #1

Received and published: 1 June 2017

General Comments

Apart from river and surface water runoff subsurface discharge of groundwater plays a key role in coastal water and nutrient budgets. In this study, the authors discuss about nutrients and 228Ra measurements made during ebb and flood phases of spring and neap tides. Although most of the stations are in close proximity to the coastline, the authors have not reported any data from groundwater or river/stream waters for nutrients and Ra isotopes to substantiate the submarine groundwater input. Ra isotopes are also released by shelf sediments at mid-salinities. If it was measured, this will help in understanding the exchange from land to coastal bay. Some of the results are already published in the papers quoted by the authors.

Response: Nutrients and Ra Data from groundwater close to the time-series station and the Sanya River estuary are available and are presented in a manuscript focused on the contribution of submarine groundwater discharge (SGD) to the nutrients budget in Sanya Bay, which was submitted to Journal of Marine Systems (JMS). The JMS manuscript is referred to in the revision (Page 3, Line 25) and provided for the review process to substantiate the SGD input.

It is true that desorption of radium isotopes occurs when fresh water encounters seawater and Ra desorption reaches the maximum at mid-salinities. In the case of Sanya Bay the salinity in the bay is over 33, so desorption is negligible. Diffusion from sediments is one source of radium, but it is much smaller for ^{228}Ra than submarine groundwater discharge based on our calculation as shown in our JMS manuscript.

This manuscript is a sister paper of the one published in Environmental Science &Technology (Wang et al., 2014, ES&T, p. 13069-13075). Both papers are based on the time-series observations at the coral reef station. However, the ES&T paper is focused on the carbonate system in the reef system and this manuscript is focused on the nutrients. To give a context of this manuscript, especially the hydrological conditions in the bay and the reef system, it is necessary to cite results presented in the ES&T paper in this manuscript.

Page 1:

Line 14: The authors claim that the diurnal variability in nutrients is due to the mixing of groundwater and offshore water and biological uptake and release. This manuscript does not show any results of biological measurements then how did the authors confirm that it is biological uptake and release during neap tide and groundwater input during spring tide?

Response: this claim is based on deviations from the conservative mixing of nutrients as presented in Section 4.2 (Page 8, Line 1-27). The rationale is that nutrient concentrations are determined by physical processes, such as mixing and advection, and biological processes. Advection is negligible at the reef station. Mixing results in conservative mixing of dissolved materials. The difference between the measured concentrations and those from mixing is what is contributed by biological processes. In the revision for clarity "under the combined influence…release" is removed, "deviations from" is added between "based on" and "mixing lines of these nutrients" (Page 1, Line 21), and at the end of the paragraph a summary sentence is added "Thus, the variability of nutrients in the coral reef system was regulated mainly by biological uptake and release in a spring-neap tide and impacted by mixing of tidally-driven groundwater and offshore seawater during spring tide." (Page 1, Line 26). As summarized on Page 1 Line 25, "the biological influence appeared to be less as inferred from the less significant correlations during the spring tide." As stated on Page 6 Line 26, " Greater groundwater discharge appeared during the ebb flow in the spring tide than in the neap tide as indicated by the higher activity of ^{228}Ra, bringing more groundwater into the reef system." On Page 7 Line 1, "the groundwater discharge was characterized by higher nitrate and phosphate and lower nitrite than the offshore water. The daily maximum concentration of NO_x, phosphate, and silicate appeared in the day time at relatively low tides, while the minimum showed up mostly at night at high tides, indicating the dominance of tidally-driven groundwater discharge." As discussed in Sections 4.1 & 4.2, the composition of nutrients during the neap tide is almost the same as that contributed by biological processes (shown in Figs. 7&10), suggesting a main role played by biological processes during the neap tide.

Line 17: It is mentioned that nitrite was positively correlated with water depth in the spring and neap tides. This sentence does not convey the authors' message clearly. In general, during spring tide, seawater level (tidal height) in the bay will be high whereas during neap tide, it will be low. How can nitrite be high in both spring and neap tides in order to show positive correlation with water depth? If so, what is the mechanism for this to happen?

Response: one correction has to be made to the reviewer's statement of high seawater level (tidal height) during spring tide and low level during neap tide: the tidal range is greater during spring tide than during neap tide, not the tidal height (seawater level). As mentioned in the earlier response, the groundwater discharge was characterized by lower nitrite than the offshore seawater and was greater at low tide than at high tide. Thus, at low water depth, tidally-driven groundwater discharge is greater, so that nitrite gets lower due to more groundwater in the system. At high water depth, groundwater discharge is smaller, so that nitrite gets higher due to more offshore seawater. Therefore, the mixing of nitrite-lower tidally-driven groundwater and nitrite-higher offshore seawater results in the positive correlation of nitrite with water depth. An explanation is added here in the revision (Page 1 Line 17).

Line 18: The ebb flow of the spring tide would have decreased salinity and indicates the receding seawater. What is the significant correlation between nutrients and salinity? Is it is positive or negative? This should be explained here briefly and elaborated in the discussion section.

Response: the correlation between nutrients and salinity was shown in Fig. 8, all with R^2 of >=0.9 and P<0.05. Nitrite is positively correlated with salinity, while nitrate and phosphate are negatively correlated with salinity. In the revision brief explanation is provided here (Page 1 Line 17) and elaborated in the discussion (Page 8 Line 6) as suggested.

Line 19: "by biological processes based on mixing lines of these nutrients". The deviation from the mixing line need not necessarily represent biological process alone and it may be through any other addition or removal processes in the Bay.

Response: as stated in the earlier response that nutrient concentrations are determined by physical processes, such as mixing and advection, and biological processes. Advection is negligible at the reef station. Mixing results in conservative mixing of dissolved materials. The difference between the measured concentrations and those from mixing is what is contributed by biological processes. This statement is based on what we know about the reef system. There is no influence of river, surface runoff, or wet precipitation at the reef station during the two weeks before the sampling period and during the sampling period, which is further clarified in the revision (Page 6 Line 20). Adsorption/desorption from particles might be a factor influencing the phosphate concentration, as proposed for estuaries (e.g., Froelich et al., 1982, American Journal of Science, 282, p474-511; van der Zee et al., 2007, Marine Chemistry, 106, p76-91). At the reef station the salinity is close to the seawater (>33) and the water is clear (i.e., the total suspended matter is quite low, about 15 mg/L), which makes adsorption/desorption negligible. This statement is added in the discussion in the revision (Page 7 Line 8). Benthic release due to remineralization of organic matter is included in the biological processes. This clarification is also added in the discussion in the revision (Page 8, Line 29).

Line 24: "less significant correlations". Quantify them.

Response: the suggestion is taken (Page 1, Line 22).

Page 2:
Site Description:
This section lacks basic information about the study area viz. (1) the peak rainfall and runoff period of the river and what is the annual river discharge and how it affects the salinity (2) The samples were collected during which season (although it is mentioned as a dry season, in introduction section, more details should be presented in this section) and what are the river and bay conditions during the sampling season (3) Is the river regulated by a dam in the upstream (4) Is the river fed by summer or winter monsoon (4) what is the tidal pattern and

amplitude in the bay (5) Is there any tide gauge station near the study area (if so, give the location on the map) and give the tidal variations during the study period? (6) At the end of the manuscript it is explained that the region experiences upwelling (Section 3.5; page 9) but not mentioned in this section.

Response: there is no tide gauge station near the study area. But tidal information from the literature was provided in the revision (Page 3 Line 4). Tidal variations based on our observations at the time-series station are demonstrated in the manuscript (Page 3 Line 32 & Page 4 Line 28). All the other information suggested is provided in the revision (Page 2 Line 28-31 to Page 3 Line 6 & Page 3 Line 19-21).

Line 16: (: : :with the maximum tidal range). Provide the tidal range with a reference.

Response: the suggestion is taken in the revision (Page 3 Line 32).

Line 14: It is mentioned that in this reef system, groundwater play a predominant role but there is no measurement of groundwater sample. Any measurement from lake/well/river/water pump will help us to understand the concentration in the groundwater and the exchange with the bay provided with their earlier work. The diurnal variations in nutrients observed during spring and neap tides may relate to mixing reactions like release/adsorption of nutrients as well. The mixing of high saline seawater and less saline freshwater may create mixing zones with different chemical and physical properties that create changes in nutrient concentrations. This is not addressed in the paper.

Response: as stated in the earlier response, groundwater data and river data are presented in the manuscript submitted to JMS, which is cited in the revision (Page 3 Line 25) to demonstrate the influence of groundwater-carried nutrients on the bay. The adsorption/desorption may be important for phosphate in estuaries. At the reef station the salinity is high (>33) and TSM is quite low, which makes adsorption/desorption negligible. This is clarified in the revision (Page 7 Line 8). The physical mixing of seawater and groundwater results in conservative behavior in nutrients as we demonstrated in the main text (Page 8 Line 5) and deviations from the mixing lines are changes due to chemical reactions, mainly caused by biological processes as we stated in our main text (Page 8 Line 10-11, 20-29).

Page 4:
Line 1: Statistical and Interpolation method. The sentence is not clear. Rewrite this.

Response: the suggestion is taken in the revision (Page 4 Line 16).

Line 7: Why particularly kriging interpolation was done? Give specific reason to use this algorithm.

Response: Kringing is widely used in spatial analysis and gives the best linear unbiased prediction of the intermediate values. This reason is provided in the revision (Page 4 Line 23).

Results and Discussion:

This section mostly presents the results of the study without much discussion. The first 2 paragraphs explain the results and at the end of the third paragraph, there are a few references cited to just compare these results with other. Not much scientific discussion has been done to explain the reasons for such variations and for identifying processes regulating these changes. The authors should discuss Results and Discussion separately, so that readers can understand the implications of the results. Section 3.1 describes nutrients and 228Ra at a time-series station followed by Section 3.2 explaining the nutrients in Sanya Bay and Section 3.3 again on the tidal variations in nutrient at reef station CT. The authors could have explained the results from the time-series station CT, the influence of tides on nutrient variability and then described on Sanya Bay.

Response: in the revision Results and Discussion are separated. In Results two sections are included: Section 3.1 describes variations in nutrients and ^{228}Ra at the time-series station CT and Section 3.2 describes distributions of nutrients in Sanya Bay. In Discussion two sections are included: in Section 4.1 processes regulating these variations are identified and in Section 4.2 seasonal and regional extrapolations are discussed. (see Results and Discussion).

Line 13: It is that "in the middle of the lunar month: : :.expected". If this is based on the tidal gauge data, reference to that should be made.

Response: the reference with the tidal data is added in the revision (Page 4 Line 29).

Page 5:

Line 29: How the authors are claiming that freshwater is more during ebb flow of spring tide? Please give supporting information and include reference.

Response: details supporting this claim from the cited reference here are provided in the revision (Page 6 Line 19).

Line 31: "The only source of freshwater at this site in February would be groundwater discharge". If so, provide reference. If there are earlier studies on turbidity maxima in the bay or the coastal/estuary of the study region, then it would help in discussing the role of suspended sediments in nutrient peaks or groundwater discharge.

Response: the suggestion is taken (Page 6 Line 21). The concentration of total suspended matter in the area is provided in the revision to help in discussing the role of sorption/desorption (Page 7 Line 10).

Page 6

Line 2: P values mentioned in the manuscript varies from <0.0001 to >0.2. These are looking unrealistic from the plots. How these values are calculated, by using standard software or by using online calculations? If so, please give reference or web-link.

Response: these are calculated using SigmaPlot. Reference is provided in the revision (Page 4 Line 21).

Line 13: The authors repeatedly mention about biological processes but no biological data has been included. It will be more appropriate to discuss the biological observations and then using mixing or dilution line calculations to identify nutrient removal/addition process. It should also be noted that in the absence of biological information, the differences (addition/removal) observed in nitrite, nitrate and phosphate could be due to sediment re-suspension and mixing. Enough scientific evidence from literature should be provided to support the arguments.

Response: as stated in earlier responses we infer biological processes from deviations from the mixing lines. We took advantage of dissolved inorganic nutrients and radium data to infer processes affecting nutrients concentrations. We can infer biological processes by eliminating other potential source/sink terms, such as sorption/desorption and re-suspension of sediments, without biological observations. This sort of information is provided with references to support our discussion in the revision (Page 7 Line 8-13). Benthic release due to remineralization of organic matter is included in the biological processes as we clarify in the revision (Page 8 Line 29).

Page 7:
Line 12: The equations NO2mix, NO3mix, Pmix, _NO2bio, _NO3bio, _Pbio – there are no references cited for these calculations. If this is presented first time, mention about the assumptions involved in this type of equations.

Response: assumptions are provided in the revision (Page 8 Line 18).

Page 11: In the references, Kelly and Moran, 2002 is mentioned while on page 8, this year is mentioned as 2012. This requires correction.

Response: 2002 is the correct year. Correction is made in the revision (Page 10 Line 6).

Page 14:
Figure 1 (a) and (b). Can these two be combined as one? The figure caption has repetition. Study area, sampling stations and salinity distribution are repeated.

Response: these two are combined into one figure (see Figure 1 on Page 16).

Page16:
Figure 4-The R2 values shown for nitrate (0.14) and nitrite (0.18) does not imply any significant relation. Is there any particular reason for the authors to show this trend line and R2 values?

Response: The reason that the two correlations are shown is that their P values are less than 0.05, the significance level. A small R^2 just implies that the correlation is not as good as that with a greater R^2. The value of R^2 alone can't be used to judge whether or not a correlation is significant.

Page 16:
Figure 5-The figure caption has repetition. Rewrite it.

Response: the suggestion is taken in the revision (see Figure 5 on Page 18).

Page 17:
Figure 6-The information like Hainan Island, Sanya river and Sanya Bay, is given in all the images (a-d). Giving these information in anyone figure will be more appropriate.

Response: the suggestion is taken in the revision (see Figure 6 on Page 19).

Figure 7-Rewrite the figure caption as, Concentrations of (a) NOx against phosphate and (b) silicate against NOx during : : :..

Response: the suggestion is taken in the revision (see Figure 7 on Page 19).

Page 19:
Figure10-What is the significance to show a trend line with R2=0.16?

Response: The P value for the linear regression is less than 0.05, so the correlation is regarded as significant and shown here. A small R^2 just implies that the correlation is not as good as that with a greater R^2. The value of R^2 alone can't be used to judge whether or not a correlation is significant.

Page 20:
Table 1-Give units for latitude, longitude, temperature.

Response: the suggestion is taken in the revision (see Table 1 on Page 22).

Anonymous Referee #2 Received and published: 26 July 2017
The manuscript provides winter observations of dissolved nitrite, nitrate, phosphate, silicate, 228Ra, salinity, and water depth in the Luhuitou fringing reef at Sanya Bay in the South China Sea. The authors introduced that in their another paper for the same cruise (Wang et al., 2014), they concluded that: tidally-driven groundwater discharge affected the carbonate system in the Luhuitou fringing reef. In this reef system, groundwater discharge played a predominant role during the spring tide and biological activities (including photosynthesis/respiration and calcification/dissolution) dominated during the neap tide in regulating diurnal variations of the carbonate parameters. Then in this study, the authors use

228Ra as a tracer of groundwater discharge to address tidal variability of nutrients in the coral reef system influenced by groundwater. It is an interesting topic. The key point supporting this manuscript is from the previous paper: The time-series observation of salinity at Station CT suggests that more freshwater input into the reef system occurred during the ebb flow of the spring tide than during that of the neap tide, and the only source of freshwater at this site would be groundwater discharge (Wang et al., 2014). I have to say that I don't read such an important paper. However, based on the present presentation, the arguments provided throughout the discussion were speculative in nature. This manuscript needs major revision. The key point to support this manuscript is that groundwater discharge played a predominant role during the spring tide in the fringing reef. The time-series observation was carried out at station CT, which is close to the coast, all the horizontal distribution plots do not cover the site, where water may source from terrigenous surface runoff, rainfall, water exchange with adjacent water, and groundwater discharge. Do the authors indicate that the groundwater discharge comes from the seabed or the coast? In general, nutrients at station CT were vertically mixed well. Is there any relation between nutrients distribution and groundwater discharge? The authors propose that biological processes predominantly controlled the composition of nutrients in the reef system, but the impact was less due to groundwater discharge.

Response: this manuscript is a sister of the paper published in Environmental Science &Technology (2014, p. 13069-13075). The hydrological conditions in the bay and the reef system were presented in the ES&T paper, which was cited in this manuscript to give the context. The ES&T paper is focused on the carbonate system in the reef system and this manuscript is focused on the nutrients. There is no surface runoff or river influence around Station CT in winter. No rainfall was observed two weeks before our sampling. In the revision information of rainfall, surface runoff, and river influence are provided (Page 2 Line 28-31 to Page 3 Line 6 & Page 3 Line 19-21). So the only possible source of fresh water at this station is groundwater. This is confirmed by the significant negative correlation between ^{228}Ra (the groundwater tracer) and salinity as presented in Fig. 5b (Page 18). Water exchange with the adjacent ocean water was already considered in the manuscript. At Station CT, which is about 30 m away from the coast with water depth of 0.7-2.1 m, the groundwater discharge is from both the seabed and the coast. Although nutrients peaks appeared around the highest ^{228}Ra activity (the greatest groundwater discharge), the correlation between nutrients and ^{228}Ra is not significant. This further supports the predominance of biological processes on the nutrient composition. During the spring tide, the groundwater discharge was greater than during the neap tide, and there was less significant correlation between nutrients than during the neap tide or no correlation (Figure 7, Page 19). So we propose that the impact of biological processes on the nutrient composition was less due to groundwater discharge. This is stated in the Abstract (Page 1 Line 25-29) and elaborated in Discussion (Page 7 Line 15-30 & Page 9 Line 14-28).

To quantify the contribution of biological processes to the variations in the NOx and phosphate at Station CT, they took a closer look at the behaviors of nitrite, nitrate and phosphate with salinity during the falling and rising phases in the spring tide, in which only several data points were selected for the ebb flow and flood tide of the spring tide, the difference between nitrite and nitrate (or phosphate) during the flood tide was mainly due to the two points with higher salinity, the other sources or processes may affect nutrients distribution, such as nitrate and phosphate show unusual values at salinity between 33.60-33.65. Further, the authors used the relationship derived from the several data sets to estimate the consumption and then uptake rate of NOx and phosphate. In addition, what faster or slow speed of the tide means? I don't see any data support. The statements lack logic and evidence.

Response: Data during the ebb flow and the flood tide on Feb. 7, when the greatest tidal range occurred during the spring tide period, was selected as shown in Figure 8 (Page 20) in order to examine how mixing played a role in regulating the concentrations of nutrients. Tidal-driven SGD is most prominent during the lowest tide, which occurred at the time-series station on Feb. 7, 2012 as shown in Wang et al. (2014, ES&T). Mixing of SGD and offshore seawater would be most obvious from data on this day. These are the reasons why only data on this day was selected. There are 5 data points for the ebb flow of the spring tide on Feb. 7, 2012. As Figure 8 showed, these 5 points gave a reasonable and good linear fit (i.e., there is no unusual data), which indicates mixing dominance during this period on the concentrations of nutrients and is a good representation of the mixing relationship at this site. During the flood tide on Feb. 7, 2012, as shown by dark triangles in Figure 8, and at all other time from the spring to neap tide deviations from the mixing line for any data point represent contributions from biological processes when other sources were eliminated such as adsorption/desorption and sediment re-suspension at this site (Page 7 Line 8-13). The logic is clear here. Two assumptions were made before setting up the mixing equations, (a) there was no other water mass into the reef system besides offshore seawater and groundwater, and (b) mixing of offshore seawater and groundwater from spring to neap tide follows the same relation derived from data on the day with the greatest tidal range. The assumptions are added in the revision (Page 8 Line 18). In the two weeks before our sampling and during our sampling period there were no rainfall and consequent surface runoff in this area, so there is no other water source with less salinity into the reef system. The only source of freshwater at this site is groundwater. This argument is also added in the revision (Page 6 Line 19-23). From the water depth vs. date plot (Figure 3, Page 17), the tidal speed can be estimated from the difference in water depth divided by the difference in time (i.e., $\Delta h/\Delta t$), the slope of the curve. This is added in the revision when mentioning fast or slow speed of the tide (Page 8 Line 5 & 9).

As for parameter measurements, the authors used 1-2% chloroform to store nutrient samples, and gave the detection limit of 0.04 μM for nitrate and nitrite, 0.08 μM for phosphate, and 0.16 μM for silicate. I guess these values do not include water sample pretreatment and sample storage processes. As the concentrations of nutrients were low in the investigation and the variability was also low, the authors should also provide the blanks covering filtering, storage, and measurement processes.

Response: the blanks were directly set up as the baselines during the measurement process and subtracted. This is added here in the revision (Page 4 Line 11). Our lab participated in the international inter-comparison of seawater nutrients analysis in 2006 and 2008 for samples collected in the North Pacific Ocean, which concentration ranged from 0.1-42.4 μmol kg^{-1} for nitrate, 0.0-0.6 μmol kg^{-1} for nitrite, 0.0-3.0 μmol kg^{-1} for phosphate, and 1.7-156.1 μmol kg^{-1} for silicate, organized by the Geochemical Research Department of the Meteorological Research Institute (MRI) of Japan with labs from more than 15 countries, including U.S.A, Japan, U.K., Germany, France, China, and Canada. Our data compared well with the consensus mean of these samples. So we have confidence in data.

The authors used the daily variance of water depth and salinity to separate neap tide from spring tide days (Fig. 2). In fact, the variations of water depth and salinity were not consistent. Salinity was low on Feb 6, increased on Feb 9, but dropped down on Feb 10. In addition, daily variance of water depth was shown to have unit of m2, what daily variance of water depth means? Why the authors do not use tidal level data? Water depth observations have large uncertainties. The authors used concentrations of nutrients against water depth to see the tidal effects.

Response: There is no tidal gauge station around this area. Data of water depth collected on a mooring buoy is good enough to resemble tidal level data. It is easy to tell the days with the greatest tidal range and the smallest tidal range in a spring-neap tide. But it is kind of subjective to separate the spring tide period from the neap tide period for these continuous days. So we thought about doing this separation quantitatively and came up with this variance idea. Variance is the expectation of the squared deviation of a random variable from its mean and represents how far a set of numbers are spread out from their average value (Wikipedia or any text book of statistics). Daily variance is the daily average squared deviation from the mean. So it has a unit of m^2 for daily variance of water depth. To cut a line between the spring tide and neap tide, the criteria is to look for a distinct difference in the pattern of the daily variances of water depth and salinity between adjacent days during the observation period, Feb. 6, 2012 to Feb. 13, 2012. That is how we cut the line between Feb. 9 and Feb. 10, 2012. In the revision the formula of variance is provided for clarity (Page 5 Line 2-4).

Why silicate disappeared in Fig 4? Why the concentration of silicate was not significantly correlated with the concentration of NOx during the spring tide, while the concentration of silicate showed significant correlation with the concentration of NOx during the neap tide?

Response: Silicate was accidently left out in Figure 4. In the revision silicate is added in Figure 4 (see Figure 4, Page 18). Silicate was not significantly correlated with NOx during the spring tide, while was significantly correlated with NOx during the neap tide because SGD was more prominent during the spring tide so that biological signals were compressed by mixing and silicate and NOx were not significantly correlated. During the neap tide SGD was less and the impact of biological processes was greater in regulating the composition of nutrients and consequently a significant correlation showed up. This is consistent with our conclusions.

The authors should pay much attention to the use of significant digit. Fig. 1b is not clear enough.

Response: Significant digits are checked and corrected in Tables 1 (Page 22) and s1. Figures 1a and 1b are combined into one Figure (see Figure 1, Page 16).

Tidal variability of nutrients in a coastal coral reef system influenced by groundwater

Guizhi Wang[1,2], Shuling Wang[1], Zhangyong Wang[1], Wenping Jing[1], Yi Xu[1], Zhouling Zhang[1], Ehui Tan[1], Minhan Dai[1,2]

[1]State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen, 361102, China
[2]College of Ocean and Earth Sciences, Xiamen University, Xiamen, 361102, China

Correspondence to: Guizhi Wang (gzhwang@xmu.edu.cn)

Abstract. To investigate variations in nitrite, nitrate, phosphate and silicate in a spring-neap tide in a coral reef system influenced by groundwater discharge, we carried out a time-series observation of these nutrients and ^{228}Ra, a tracer of groundwater discharge, in the Luhuitou fringing reef at Sanya Bay in the South China Sea. The maximum ^{228}Ra, 45.28 dpm 100 L^{-1}, appeared at a low tide and the minimum, 13.98 dpm 100 L^{-1}, showed up during a flood tide in the spring tide. The activity of ^{228}Ra was significantly correlated with water depth and salinity in the spring-neap tide, reflecting the tidal-pumping feature of groundwater discharge. Concentrations of all nutrients exhibited strong diurnal variations~~ under the combined influence of mixing of groundwater and offshore water and biological uptake and release~~ with a maximum~~.~~ in ~~T~~the amplitude of the diel change ~~reached a maximum~~ for nitrite, nitrate, phosphate and silicate in the spring tide~~,~~ of 0.46 μM, 1.54 μM, 0.12 μM, and 2.68 μM, respectively. Nitrate and phosphate were negatively correlated with water depth during the spring tide, but showed no correlation during the neap tide. Nitrite was positively correlated with water depth in the spring and neap tide due to mixing of nitrite-deplete groundwater and nitrite-rich offshore seawater. They were also significantly correlated with salinity (R^2>=0.9 and P<0.05) at the ebb flow of the spring tide, negative for nitrate and phosphate and positive for nitrite, indicating the mixing of nitrite-deplete, nitrate and phosphate-rich less saline groundwater and nitrite-rich, nitrate and phosphate-deplete saline offshore seawater. We quantified variations in oxidized nitrogen (NO_x) and phosphate contributed by biological processes based on deviations from mixing lines of these nutrients. During both the spring and neap tide biologically contributed NO_x and phosphate were significantly correlated with regression slopes of 4.60 (R^2=0.16) in the spring tide and 13.37 (R^2=0.75) in the neap tide, similar to the composition of these nutrients in the water column, 5.43 (R^2=0.27) and 14.18 (R^2=0.76), respectively. This similarity indicates that the composition of nutrients in the water column of the reef system was closely related with biological processes during both tidal periods, but the biological influence appeared to be less as inferred from the less significant correlations~~ ~~ during the spring tide when groundwater discharge was more prominent. Thus, the variability of nutrients in the coral reef system was regulated mainly by biological uptake and release in a spring-neap tide and impacted by mixing of tidally-driven groundwater and offshore seawater during spring tide.

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1 Introduction

Coral reefs are considered to be one of the most sensitive and stressed ecosystems occupying the coastal zone (Ban et al., 2014). Groundwater input to coral reefs was shown to be globally important and carry a significant amount of terrestrially derived nutrients to the reef systems (D'Elia et al., 1981; Paytan et al., 2006; Houk et al., 2013). Groundwater discharge is usually enriched in N relative to P with an N:P ratio higher than the Redfield ratio, 16:1 (Redfield, 1960), because of more efficient immobilization of P than N in coastal aquifers (Slomp and Van Cappellen, 2004). Such groundwater characterized by a high N:P ratio thus could have significant impacts on coastal reef ecosystems considering that benthic marine plants are much more depleted in P with an N:P ratio of about 30:1 (Atkinson and Smith, 1983). Cuet et al. (2011) have found that the net community production in a coral-dominated fringing reef at La Réunion, France is sustained by net uptake of new nitrogen from groundwater and net uptake of phosphate from the ocean.

Groundwater flux onto coral reefs was found to fluctuate with the tidal cycle (Lewis, 1987; Santos et al., 2010). The contribution of groundwater discharge to the nutrient budget of adjacent marine waters of coral reefs varies greatly from one site to another around the globe and at each site varies from one tidal state to another (Paytan et al., 2006). However, there is no study to reveal variations in the composition of nutrients from spring to neap tide in reef systems influenced by groundwater. Then, questions are posed: a) in coral reef systems influenced by groundwater how do the abundance and composition of nutrients vary from spring to neap tide? b) what contributes to the tidal variation of nutrients in such a system?

To address these questions, this study examined the nutrient variability in a spring-neap tidal cycle in the Luhuitou fringing reef in Sanya Bay, China during a dry season. Our previous study showed that tidally-driven groundwater discharge affected the carbonate system in the Luhuitou fringing reef (Wang et al., 2014). In this reef system, groundwater discharge played a predominant role during the spring tide and biological activities (including photosynthesis/respiration and calcification/dissolution) dominated during the neap tide in regulating diurnal variations of the carbonate parameters. Time-series observations of nutrients carried out at the same time as for the carbonate parameters in this reef system made this study possible. The naturally occurring radioactive radium isotope, ^{228}Ra, was utilized as a tracer of groundwater discharge in this study.

2 Materials and Methods

2.1 Site description

Sanya Bay is a tropical bay situated at the southern tip of Hainan Island, China in the northern South China Sea under the influence of the Southeast Asian monsoon (Fig. 1~~a~~). Seasonal monsoons dominate Hainan Island with northeast winds in November to March and southwest winds in May to September. Rainfall ranges from 961 to 2439 mm yr^{-1} in 1994-2011 with about 80 % precipitation occurring during May to October (Zhang et al., 2013). The coastal reef time-series station CT is located at the Luhuitou fringing reef in the southeast of Sanya Bay. There was no rain in the two weeks before our

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sampling starting on Feb. 2, 2012 and during our 11-day long sampling period based on data from the nearby meteological station in the Hainan Tropical Marine Biology Research Station, Chinese Academy of Science. No surface runoff was present during these periods in this area. Surface salinity in Sanya Bay in our sampling period ranged 33.60-33.89 (Wang et al., 2014). Irregular diurnal tides prevail in Sanya Bay, with a mean tidal range of 0.90 m and the largest of 2.14 m (Zhang, 2001). The Luhuitou fringing reef is a leeward coast with low wave energy in winter (Zhang, 2001). In summer coastal upwelling off eastern Hainan Island mainly induced by the southeast monsoon may extend to this area (Wang et al., 2016). The Holocene deposits of coral debris and biogenic carbonate sands (secondary reef) form the surfacial unconfined aquifer around the fringing reef (Zhao et al., 1983), making groundwater a diffuse source of nutrients for the reef system. Macroalgae cover about 60 %, on average, of the bottom hard substrates in the Luhuitou fringing reef (Titlyanov and Titlyanova, 2013). Living scleractinian corals were observed in the lower intertidal zone and subtidal zone with coverage of 5-40 % (Titlyanov and Titlyanova, 2013; Titlyanov et al., 2014; 2015). Cyanobacteria and Rhodophyta prevailed in the upper intertidal zone, while Rhodophyta and Chlorophyta were the most abundant in the mid and lower intertidal zones (Titlyanov et al., 2014). Rhodophyta dominated the benthic macroalgal community, 54 % in the upper subtidal zone (Titlyanov and Titlyanova, 2013). The number of species in the marine flora has increased by 28 % from 1990 to 2010 with a displacement of slow-growing species likely due to anthropogenic influences and coral bleaching (Titlyanov et al., 2015). The mean coral cover has decreased in the Luhuitou fringing reef from 90% in the 1960s to 12 % in 2009 (Zhao et al., 2012), likely owing to a combination of regional anthropogenic impacts and climate change (Li et al., 2012).

To the north of the Luhuitou fringing reef, the Sanya River flows into Sanya Bay with an annual average discharge of 5.86 m^3 s^{-1} (Wang et al., 2005). The river is fed mainly by southwest monsoons from May to October. There is no dam in the upstream to regulate the river. During our sampling period the Sanya River plume was confined in the northern part of the bay and the coastal reef station CT was outside the influence of the Sanya River plume (Fig. 1) (Wang et al., 2014). Investigations of nutrients, Chl *a* and phytoplankton in the bay have been conducted seasonally for several years (Dong et al., 2010; Wu et al., 2011; Wu et al., 2012a; 2012b) and demonstrate that the inner bay is influenced by the discharge of the Sanya River with its relatively high nutrient levels, and the central and outer bay are dominated by oceanic exchange with the South China Sea (Wu et al., 2012c). Nutrients carried by submarine groundwater discharge into Sanya Bay traced by radium isotopes account for at least 38 % phosphate, 90 % inorganic nitrogen, and 83 % silicate of the nutrients into the bay in our sampling period (Wang et al., submitted). ~~The distribution of salinity in Sanya Bay indicates that the coastal reef station CT is outside the influence of the Sanya River plume in February (Fig. 1b) (Wang et al., 2014).~~

2.~~1~~2 Sampling and measurements

The setup of the sampling platform at the time-series station CT is provided in detail in Wang et al. (2014). Briefly, water was collected using a submersible pump and depth and salinity were measured with a conductivity-temperature-depth system (Citadel, RDI Co., USA) attached on a mooring buoy. Discrete nutrient and radium samples were taken every 3 hours during

February 6-13, 2012, except on February 7-8 when~~(with~~ the maximum tidal range of 1.4 m occurred (Wang et al., 2014) ~~when~~ and the samples were collected every 2 hours. A mapping cruise was conducted in Sanya Bay during February 2-3, 2012 (Fig. 1) to evaluate the influence of the Sanya River and to constrain the end-member of the offshore water. Nutrient samples for nitrate, nitrite, phosphate and silicate were collected in Sanya Bay at surface and bottom depths using 5 L Niskin bottles. Temperature and salinity were measured using a multi-parameter sonde YSI 6600. The salinity was reported using the Practical Salinity Scale.

Nutrient samples were filtered with 0.45 μm cellulose acetate membranes and poisoned with 1-2 ‰ chloroform. One filtrate was preserved at 4 °C for dissolved silicate determination, and one was frozen and kept at -20 °C for nitrate, nitrite, and phosphate measurements. In the laboratory, nutrients were measured with an AA3 Auto-Analyzer (Bran-Luebbe, GmbH) following the same methods in Han et al. (2012). The analytical precision was better than 1 % for nitrate and nitrite, 2 % for phosphate, and 2.8 % for silicate. The detection limit was 0.04 μM for nitrate and nitrite, 0.08 μM for phosphate, and 0.16 μM for silicate. Blanks were directly set up as baselines during the measurements and subtracted. Radium samples were passed through a 1 μm cartridge filter before through a MnO_2-impregnated acrylic fiber (Mn-fiber) column to extract dissolved radium (Rama and Moore, 1996). The Mn-fibers were leached with 1 M solutions of hydroxylamine hydrochloride and HCl to release ^{226}Ra and ^{228}Ra, which were then co-precipitated with $BaSO_4$ and measured in a germanium gamma detector (GCW4022, Canberra) (Moore, 1984) with an error less than 7 %.

2.3 ~~Statistical and interpolation method~~Linear regression and contour plotting

To gain insight into factors affecting nutrients from spring to neap tide, linear regressions were conducted between water depth, salinity, and ^{228}Ra activity, between water depth, salinity, and nutrients concentration, and between biologically contributed nutrients during the spring and neap tide. A linear curve-fitting, $y=ax+b$, was applied using least-square minimization algorithm to find the coefficients (a, b) of the independent variable that gave the best fit between the linear equation and the data (e.g., Press et al., 1986). A significance level of 0.05 was taken. The data was fit using SigmaPlot (Systat Software, San Jose California USA, www.systatsoftware.com). In plotting contours in Sanya Bay, Surfer 11 was utilized with kriging interpolation due to its good linear unbiased prediction of the intermediate values in spatial analysis (Papritz and Stein, 2002).

3 Results~~ and discussion~~

3.1 Time-series observations of nutrients and radium at the coastal coral reef station

Time-series observations of salinity, ^{226}Ra, and water depth at Station CT were reported in Wang et al. (2014), which demonstrated that the water depth at Station CT varied from 0.7 to 2.1 m and the salinity ranged from 33.43 to 33.67 during

February 6-13, 2012. The greatest tidal range occurred on February 7~~6~~, 2012 (Wang et al., 2014)~~, is in~~ the ~~middle of~~16th of the lunar month~~, around which spring tides are expected~~. To separate neap tide from spring tide days, the daily variance of water depth and salinity were plotted (Fig. 2). The daily variance of a variable was calculated using Microsoft Excel (2007) as

$$\sigma^2 = \frac{n\sum x^2 - \left(\sum x\right)^2}{n(n-1)} \qquad (1)$$

where x is the average of the variable in a day and n is the number of samples of the variable in that day. A sharp decrease in the variance of salinity occurred on February 10, 2012 and the variance remained low (<0.001) afterwards. Thus, two distinctive groups stood out, with one group in the period of February 6-9, 2012 having greater variance of water depth and salinity and the other in the period of February 10-13, 2012 having less variance. Therefore, we took February 6-9, 2012 as the spring tide period and February 10-13, 2012 as the neap tide period in this work.

The concentration of nutrients varied with different patterns from spring to neap tide (Fig. 3). Nitrite varied from 0.11 to 0.71 μM during the spring tide and from 0.12 to 0.74 μM in the neap tide with the maximum diel variation of 0.46 μM present during the spring tide (Fig. 3a). The diurnal variation was 0.24-0.46 μM during the spring tide and 0.34-0.45 μM in the neap tide. Daily peaks of nitrite usually appeared at high tides from the spring to neap tide. The concentration was positively correlated with water depth ($P<0.05$) during both the spring and neap tide, but the correlation was less significant during the neap tide (Fig. 4a). Nitrate and phosphate, however, showed an opposite pattern. During the spring tide, nitrate and phosphate were negatively correlated with water depth ($P<0.05$)(Fig. 4b,c). They reached their peak concentrations of 1.91 μM and 0.22 μM, respectively in the late afternoon and their minima of 0.37 μM and 0.10 μM, respectively at night on February 7, 2012 (Fig. 3b,c). The diurnal variation fell in the range of 0.44-1.54 μM for nitrate and 0.04-0.12 μM for phosphate. During the neap tide, the concentrations of nitrate and phosphate varied from 0.27 to 1.32 μM for nitrate and 0.084 to 0.18 μM for phosphate with less diurnal variation in the range of 0.35-0.52 μM for nitrate and 0.04-0.05 μM for phosphate. The correlation with water depth was not significant for both nutrients ($P>0.15$). Nitrate is the dominant species (>50 %) of oxidized nitrogen (NO_x) during the spring-neap tidal period except at 2 O'clock on February 12, 2012 when the concentrations of nitrite and nitrate were almost equal. The NO_x:P ratio varied from 4.78 to 12.94 in the spring-neap tide (Fig. 3c). Silicate showed a trend different from either nitrite or nitrate and phosphate (Fig. 3d). It was not significantly correlated with water depth during either~~both~~ spring ~~and~~ or neap tide ($P>0.2$). The concentration of silicate, in general, decreased from spring to neap tide. During the spring tide, the concentration of silicate fell in the range of 4.57-7.25 μM. The daily peak concentration of silicate appeared almost at the daily lowest salinity. The diurnal variation in silicate was 1.91-2.68 μM. During~~Around~~ the neap tide, however, silicate ranged from 2.89 to 5.59 μM and showed less diurnal variability, 1.44-2.09 μM.

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The diurnal variation in the activity of ^{228}Ra at Station CT was 16.5-27.37 dpm 100 L^{-1} (i.e., 2.75-4.56 Bq m^{-3}) during the spring tide, the maximum of which appeared on February 7, and 5.31-10.55 dpm 100 L^{-1} around the neap tide (Fig. 3e). The maximum ^{228}Ra, 45.28 dpm 100 L^{-1}, appeared at the lowest tide on February 8 during the spring tide and the minimum, 13.98 dpm 100 L^{-1}, showed up during the flood tide of the spring tide on February 7. The activity of ^{228}Ra was significantly correlated with water depth in the spring-neap tidal period (P=0.002)(Fig. 5a). This pattern reflected the variation in the groundwater discharge induced by tidal pumping in this coral reef system (Wang et al., 2014), which is also observed in other coastal regions (Burnett and Dulaiova, 2003; Santos et al., 2010).

3.2 Distributions of nutrients in Sanya Bay

In Sanya Bay the highest concentration of nutrients appeared near the Sanya River estuary and the concentration, in general, decreased from the northeast coast, where the influence of the Sanya River plume is apparent in winter (Wang et al., 2014), to the south and west, where the South China Sea water intrudes (Fig. 6). At stations far offshore (Stations J4-5 and W3-4), the concentrations of nitrite, nitrate and phosphate were all below the detection limit and the concentration of silicate was about 4.00 μM. At other stations, the concentration of all the nutrients remained low, but was nonetheless detectable. For example, the maximum concentration of only 0.43 μM for nitrite, 0.70 μM for nitrate, 0.18 μM for phosphate and 7.92 μM for silicate were recorded at Station P1, the station closest to the Sanya River estuary. The small islands in Sanya Bay did not show apparent influence on the nutrients in the bay since nutrients were below their detection limits or remained low around these islands (Fig. 6). The water depth at these mapping stations was no less than 5 m and the concentration of nutrients at the bottom depth differed little from that at the surface at most of these offshore stations (Table 1). This vertical distribution confirms that the water in Sanya Bay is relatively homogenous in February (Wang et al., 2014). The NO_x:P ratio was less than 7 in Sanya Bay, except at Stations P2 and L6 where the NO_x:P ratio was around 9.

4 Discussion

4.1~~3.3~~ What affects tidal variations in nutrients at the reef station CT?

The time-series observation of salinity at Station CT suggests that more freshwater input into the reef system occurred during the ebb flow of the spring tide as inferred from lower salinity than during that of the neap tide (Wang et al., 2014). The distribution of salinity in Sanya Bay (Fig. 1~~b~~) demonstrated that the Sanya River plume affected the northeast of the bay with little impact on Station CT ~~(Wang et al., 2014).~~ and ~~T~~ the only source of freshwater at this site in February would be groundwater discharge (Wang et al., 2014) since in the two weeks before our sampling and during our sampling period there were no rainfall and consequent surface runoff in this area. The coincidence of the daily minimum salinity with the highest activity of ^{228}Ra during the ebb flow of the spring tide (Fig. 3e) and the significant correlation between the activity of ^{228}Ra and salinity during the spring-neap tidal period ($P<0.0001$)(Fig. 5b) confirms that the tidally-driven groundwater discharge occurred at the coral reef station CT. Greater groundwater discharge appeared during the ebb flow in the spring tide than in the neap tide as indicated by the higher activity of ^{228}Ra, bringing more groundwater into the reef system.

Under the influence of tidally-driven groundwater discharge, variations in nitrite, nitrate, phosphate and silicate during the spring tide followed a tidal pattern. Inferred from the significant correlation between nutrients and water depth during the spring tide (Fig. 4), the groundwater discharge was characterized by higher nitrate and phosphate and lower nitrite than the offshore water. The daily maximum concentration of NO_x, phosphate, and silicate appeared in the day time at relatively low tides, while the minimum showed up mostly at night at high tides, indicating the mixing of tidally-driven groundwater and offshore water. During the neap tide, however, NO_x and phosphate showed less diurnal variations. The daily maximum concentration of NO_x and phosphate appeared around the mid-night, when a flood tide appeared. This pattern reflected dominance of biological processes, consistent with the time-series observation of dissolved oxygen at this site (Wang et al., 2014). The daily minimum showed up for NO_x and phosphate in the afternoon or between mid-night and dawn at high tides, reflecting the dominance of nutrient-deplete offshore seawater. -Adsorption/desorption from particles might be a factor influencing the phosphate concentration, as proposed for estuaries (e.g., Froelich et al., 1982; van der Zee et al., 2007). At the reef station the salinity was close to the seawater (>33) and the water was clear (the total suspended matter was low, about 15 mg L^{-1}), which makes adsorption/desorption negligible. The clear water, as well as low wave energy in the reef in winter (Zhang, 2001), also limits the possibility of sediment re-suspension as a source of radium and nutrients.

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Under the controls of tidally-driven groundwater discharge and biological processes, the composition of nutrients in the reef system also differed from the spring tide to the neap tide. During the spring tide when groundwater discharge played a predominant role on regulating the concentration of nutrients in the reef system, the concentration of NO_x was positively correlated with the concentration of phosphate, with a regression slope of 5.43 and R^2 of 0.27 (Fig. 7a). The concentration of silicate was not significantly correlated with the concentration of NO_x (Fig. 7b). During the neap tide when groundwater discharge was less prominent, the correlation between the concentrations of NO_x and phosphate was more significant, with a regression slope of 14.18 and R^2 of 0.76. The NO_x:P ratio was closer to the Redfield ratio than during the spring tide. The concentration of silicate showed significant correlation with the concentration of NO_x in the water column, with a regression slope of 1.24 and R^2 of 0.58. Diatoms dominate the phytoplankton community in Sanya Bay (Zhou et al., 2009). The elemental ratio of Si:N is 0.80±0.35 for nanoplankton and 1.20±0.37 for netplankton (Brzezinski, 1985). The similarity of the composition of silicate and NO_x in the water column to the elemental ratio of diatoms implies a biological control. Unfortunately, no information is available on particular reef primary producers and sponges that may take up/release silicate in this reef system to further the discussion. The activity of ^{228}Ra, however, was not significantly correlated with the NO_x:P ratio in the water column from spring to neap tide ($P>0.05$)(Fig. 5c), indicating that the composition of nutrients in the water column was not predominantly controlled by groundwater discharge. Therefore, we propose that biological processes predominantly ~~controled~~controlled the composition of nutrients in the reef system, but the impact was less due to groundwater discharge.

~~3.4~~4.2 The generation and consumption of NO_x and phosphate at the reef station CT

N and P are the general limiting nutrients for the abundance of phytoplankton in coastal ecosystems (Jickells et al., 1998). To quantify the contribution of biological processes to the variations in the NO_x and phosphate at Station CT, a closer look was taken at the behaviors of nitrite, nitrate and phosphate with salinity during the falling and rising phases on Feb. 7, the day with the greatest tidal range in the spring tide period. Fig. 8 shows that these nutrients behaved differently during the two phases. During the ebb flow, with a fast~~er~~ falling speed as indicated by the sharp slope of water depth (Fig. 3), nitrite, nitrate and phosphate behaved conservatively, i.e., their concentrations were significantly correlated with salinity (~~R^2≥0.90,~~ $P<0.05$). Nitrite was positively correlated with salinity (R^2=0.94), while nitrate and phosphate were negatively correlated with salinity (R^2=0.91 and 0.90, respectively) (Fig. 8). These conservative behaviors indicated mixing between the groundwater discharge and the offshore seawater. During the flood tide, with a relatively slow speed as indicated by a less sharp slope of water depth (Fig. 3), however, nitrite showed an apparent removal signal relative to the conservative mixing line while additions of nitrate and phosphate showed up. This consumption of nitrite and generation of nitrate and phosphate were due to biological processes in this period. Based on the conservative mixing lines shown in Fig. 8, we could estimate nitrite, nitrate and phosphate owing to mixing of the offshore seawater and groundwater discharge using the salinity measured at Station CT (S_{CT}), designated as NO_{2mix}, NO_{3mix} and P_{mix}.

$$NO_{2mix} = 1.3696 \times S_{CT} - 45.7520$$ (2~~1~~),

$$NO_{3mix} = -1.7797 \times S_{CT} + 60.5024$$ (3~~2~~),

$$P_{mix} = -0.3565 \times S_{CT} + 12.1176$$ (4~~3~~).

Two assumptions were made before setting up these equations: (a) there was no other water mass into the reef system besides offshore seawater and groundwater, and (b) mixing of offshore seawater and groundwater from spring to neap tide followed the relation derived from data on the day with the greatest tidal range. The differences between the measured concentrations of nutrients and the nutrient concentrations resulting from mixing represented nutrients contributed by biological processes, designated as ΔNO_{2bio}, ΔNO_{3bio} and ΔP_{bio},

$$\Delta NO_{2bio} = NO_{2CT} - NO_{2mix}$$ (5~~4~~),

$$\Delta NO_{3bio} = NO_{3CT} - NO_{3mix}$$ (6~~5~~),

$$\Delta P_{bio} = P_{CT} - P_{mix}$$ (7~~6~~).

where the subscripts 'CT' represents the measured value at Station CT. The oxidized nitrogen contributed by biological processes, $\Delta NO_{x\mathrm{bio}}$, is the sum of $\Delta NO_{2\mathrm{bio}}$ and $\Delta NO_{3\mathrm{bio}}$. Positive values represent regeneration and release of nutrients in the water column and negative values reflect uptake of nutrients by marine flora (including phytoplankton and benthic flora in this system). Benthic release due to remineralization of organic matter contributes to the positive values.

The nutrients contributed by biological processes showed the greatest diurnal variation in nitrate and phosphate on February 7, 2012, which is in the spring tide, while the maximum of biologically contributed ~~greatest in~~ nitrite appeared on February 12, 2012, which is in the neap tide (Fig. 9). Nitrite contributed by biological processes ranged from -0.15 to 0.39 μM during the spring tide and from -0.20 to 0.40 μM during the neap tide (Fig. 9a). From 6 pm on February 8 to 6 pm on February 11, 2012, biologically contributed nitrite was positive throughout the period, indicating production of nitrite. For nitrate it was produced throughout the period from 4 am on February 8 to the midnight on February 11, 2012. During the spring tide biologically contributed nitrate varied from -0.24 to 1.25 μM and during the neap tide it fell in the range of -0.38 to 0.70 μM. Net NO_x production occurred from 6 pm on February 8 to 8 am on February 12, 2012 and $\Delta NO_{x\mathrm{bio}}$ was negative afterwards on February 12-13, 2012, indicating net consumption (Fig. 9b). The biological contribution of phosphate had greater diurnal variations during the spring tide than during the neap tide (Fig. 9c). The greatest diel variation during the spring tide in ΔP_{bio} appeared on February 7, 2012 when ΔP_{bio} varied from -0.027 to 0.088 μM, while during the neap tide the greatest variation occurred on February 10, 2012 when ΔP_{bio} ranged from 0.009 to 0.056~~-~~ μM. Net phosphate consumption occurred throughout the period of February 12-13, 2012.

The relationship between $\Delta NO_{x\mathrm{bio}}$ and ΔP_{bio} during the spring tide differed from that during the neap tide. During the spring tide there was significant correlation between ΔN_{bio} and ΔP_{bio}, with a regression slope of 4.60 and R^2 of 0.16 (Fig. 10). During the neap tide, however, the correlation was much more significant with a regression slope of 13.37 and R^2 of 0.75. The regression slope of the regression between biologically contributed $NO_{x\mathrm{bio}}$ ~~-~~and phosphate was similar to that of the significant regression between $NO_{x\mathrm{bio}}$ and phosphate in the water column, which was 5.43 ~~-~~during the spring tide and 14.18 during the neap tide. This similarity indicates that the composition of nutrients in the water column was closely related with biological processes during both tidal periods, but the biological effect appeared to be less during the spring tide as inferred from the less significant correlations. The net release of nutrients during the neap tide with a very Redfield-like ratio suggests that the net nutrient fluxes in this system were likely to be dominated by the uptake and remineralization of plankton/oceanic organic particles by benthic filter feeders as observed in other reefs (e.g., Ayukai, 1995; Ribes et al., 2005; Southwell et al., 2008; Genin et al., 2009; Monismith et al., 2010). The net uptake of nitrate and phosphate was mainly made by reef primary producers. Thus, the composition of nutrients in the water column seemed to be directly related with biological contributions from the spring to neap tide. The biological influence was less during the spring tide most~~ly~~ likely due to groundwater discharge. This confirms our proposal that biological processes predominantly controlled the composition of nutrients in the reef system, but the impact was less due to groundwater discharge.

Successive uptake rates of NO_x were approximated by the depth-integration of the biologically contributed NO_x divided by the sampling time interval from the spring to neap tide. The uptake rate ranged from -9.04 to 19.07 mmol m^{-2} d^{-1}, which compares well with the sum of nitrate and nitrite fluxes over Ningaloo Reef, a fringing reef in Australia, -24 to 15 mmol m^{-2} d^{-1} (Wyatt et al., 2012). It is significantly correlated with the concentration of NO_x in the water column (Fig. 11), with a slope of 14.47 and R^2 of 0.94 (P<0.0001), indicating the mass-transfer limitation of NO_x uptake. The slope (in m d^{-1}) falls in the range of the typical uptake rate coefficient for dissolved inorganic nitrogen reported in Falter et al. (2004).

4.3~~3.5~~ Seasonal and regional extrapolations~~ and expectations~~

This study was carried out in winter. Seasonal variations are present in the river discharge as inferred from precipitation (Wang et al., 2005) and there might be increase in the groundwater discharge and associated nutrient fluxes in summer as in other coastal systems (e.g., Lewis, 1987; Costa et al., 2006; Kelly and Moran, 200~~1~~2; Wang et al., 2015). However, the relative changes in the groundwater discharge and associated nutrient fluxes would be much smaller than those of the river. The tidally-driven feature of the groundwater discharge in this reef system might make our conclusions applicable to other seasons. But it is likely that what we observed in a dry season might be different from what would happen in a wet season due to the involvement of other forces, e.g., upwelling in summer (Wu et al., 2012a; Wang et al., 2016), which merits further studies.

In relatively oligotrophic coastal systems with coral reefs, such groundwater-associated nutrient fluxes may sustain the reef community production (Cuet et al., 2011), result in increases in diversity and occurrence of algae and sponge where relatively low salinity is present (Houk and Starmer, 2010), or induce the proliferation of diatom and cyanobacteria (Blanco et al., 2011). In addition, tidally-driven groundwater into nearshore ecosystems was found to be negatively correlated with seagrass habitat condition (Houk et al., 2013). Nutrients loads via groundwater discharge may affect the community structure to move towards macroalgal blooms via bottom-up control (Lapointe, 1997) and likely play a role in the displacement of slow-growing benthic flora with fast-growing species observed in Sanya Bay in the last two decades (Titlyanov et al., 2015). Future changes in these fluxes, likely caused by climate change and human activities, might make the situation worse and need to be monitored in reef protection programs and be considered in assessing the environmental health of coral reef systems, especially in regions with expected higher inputs of anthropogenic nutrients into the groundwater.

4 Conclusions

The variability of nutrients in a spring-neap tidal cycle in a coral reef system in winter was revealed for the first time under the synergistic control of tidally-driven groundwater discharge and biological processes. The activity of ^{228}Ra was significantly correlated with water depth and salinity, indicating tidally-driven groundwater discharge at this site. Nitrate and phosphate were negatively correlated with salinity at the ebb flow of the spring tide, indicating that groundwater discharge was enriched in nitrate and phosphate. Nitrate, phosphate and silicate in the water column showed greater diurnal variations during the spring tide than during the neap tide, while the diel change in the concentration of nitrite demonstrated no consistent pattern. The nutrient composition in the water column seemed to differ between the spring tide and neap tide, but was similar to their biological uptake/release in either tidal period for oxidized nitrogen (NO_x) and phosphate. This similarity indicates that variations in nutrients in the water column in the reef system were mainly regulated by biological processes. However, correlations between NO_x and phosphate in the water column and between biologically contributed NO_x and phosphate were less significant during the spring tide when groundwater discharge was more prominent. The concentration of silicate in the water column was significantly correlated with that of NO_x during the neap tide, but they were not significantly correlated during the spring tide. This indicates that the composition of nutrients in the water column was also affected by tidally-driven groundwater discharge, especially during the spring tide. Therefore, biological processes predominantly controlled the composition of nutrients in the reef system, but the impact was less due to groundwater discharge.

The stoichiometric relationship of NO_x and phosphate from the spring to neap tide in this reef system is important in understanding how biologically processes predominantly affected these nutrients variations under the influence of tidally-driven groundwater discharge. The composition of silicate and NO_x during the neap tide when groundwater discharge was less was comparable to the elemental ratio of diatoms. The release/consumption ratio of NO_x:P by biological processes followed a Redfield-like ratio during the neap tide, but about one third as much during the spring tide. Whether this change in the biological release/uptake ratio of NO_x:P is associated with a change in the community structure needs further study.

Supplement Time-series data are provided in Table S1.

Author contribution Guizhi Wang and Minhan Dai wrote the main text of the manuscript. Guizhi Wang, Shuling Wang, Zhangyong Wang, Wenping Jing, Yi Xu, and Zhouling Wang collected samples in the field and measured the parameters. Guizhi Wang analyzed the data and did the calculations. Ehui Tan drew some of the figures.

Competing interests The authors declare that they have no conflict of interest.

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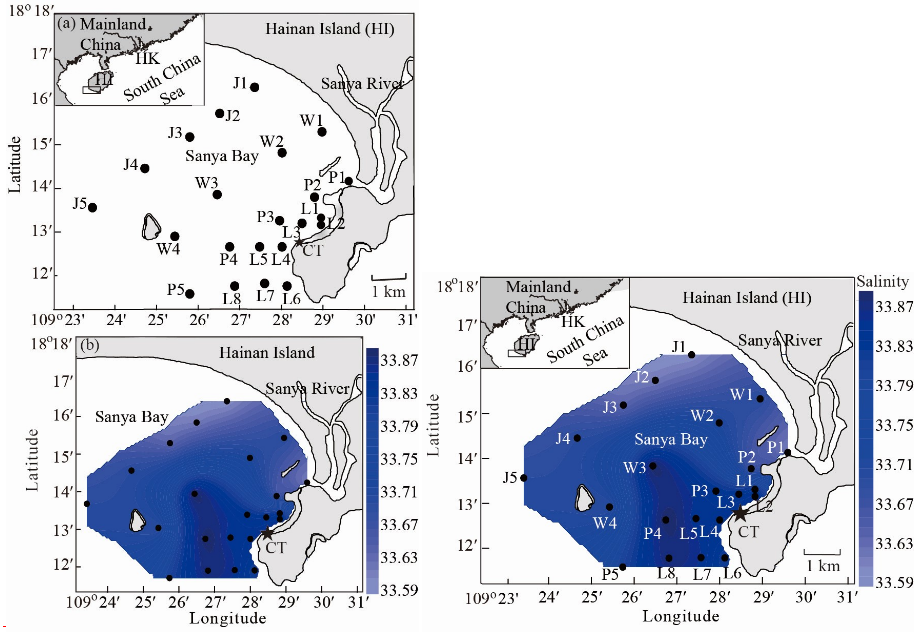


Figure 1: Study area, sampling stations and salinity distribution in February 2012 in Sanya Bay, Hainan Island (HI) in the South China Sea. ~~(a) study area and sampling stations; and (b) salinity distribution.~~ HK represents Hong Kong. CT is the coastal reef time-series station.

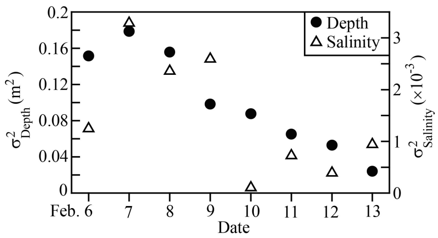


Figure 2: Daily variance of water depth (σ^2_{Depth}) and salinity ($\sigma^2_{Salinity}$) at the coastal reef station CT during February 6-13, 2012.

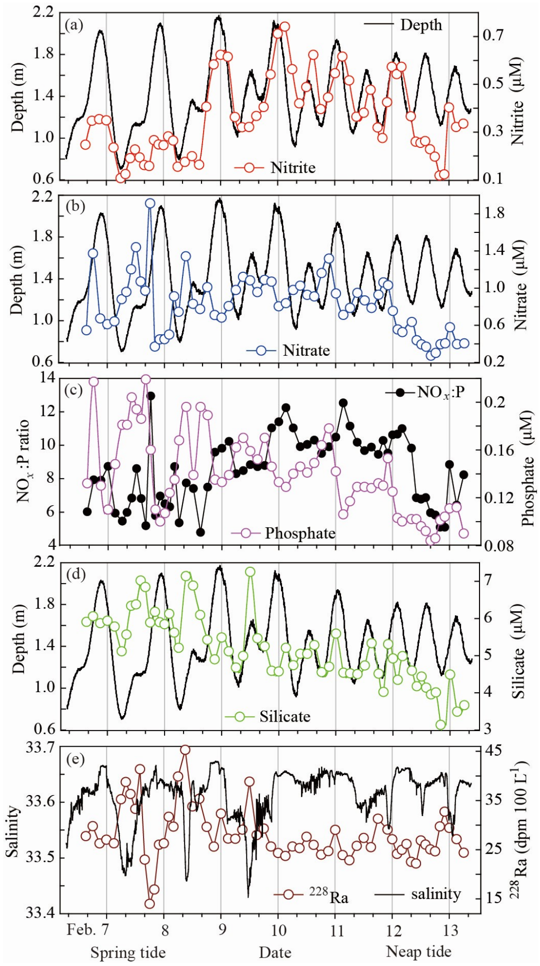
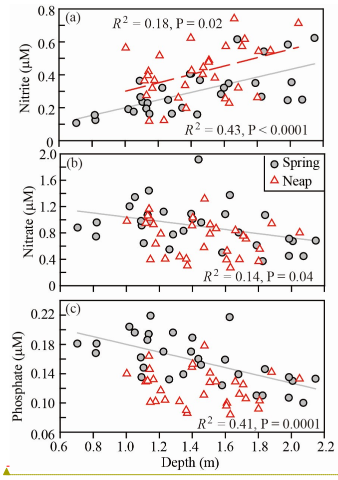


Figure 3: Time-series observations of nutrients and ^{228}Ra at Station CT in the Luhuitou reef of Sanya Bay, China during February 6-13, 2012. (a) Nitrite; (b) nitrate; (c) phosphate and NO_x:P ratio; (d) silicate; and (e) ^{228}Ra. Lines connecting the symbols are to show trends. Water depth and salinity were reported in Wang et al. (2014).



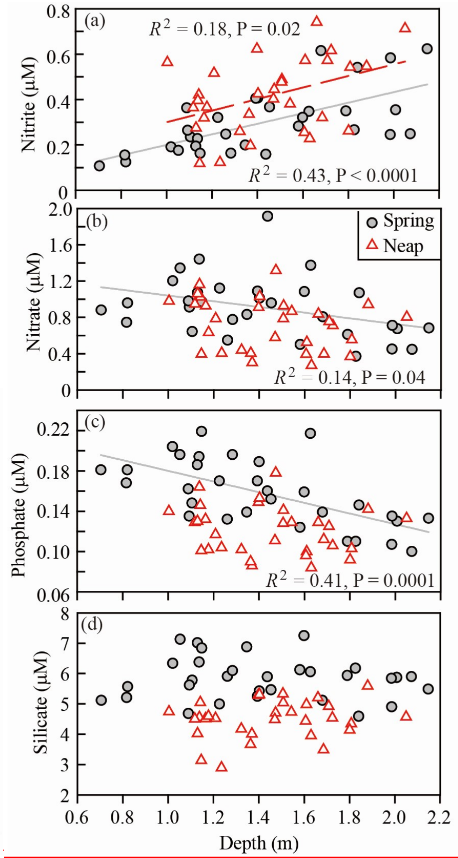


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Figure 4: Concentrations of nutrients in the water column against water depth during the spring tide and neap tide at Station CT in the Luhuitou reef during February 6-13, 2012. (a) nitrite; (b) nitrate; ~~and~~ (c) phosphate; and (d) silicate.

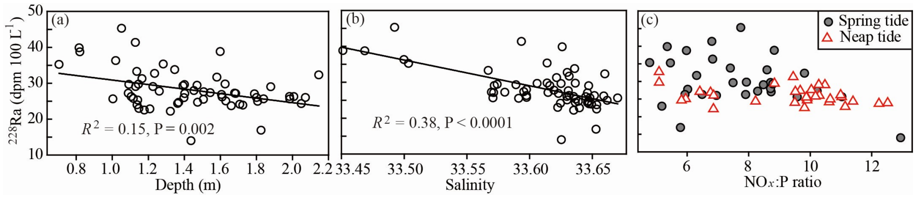
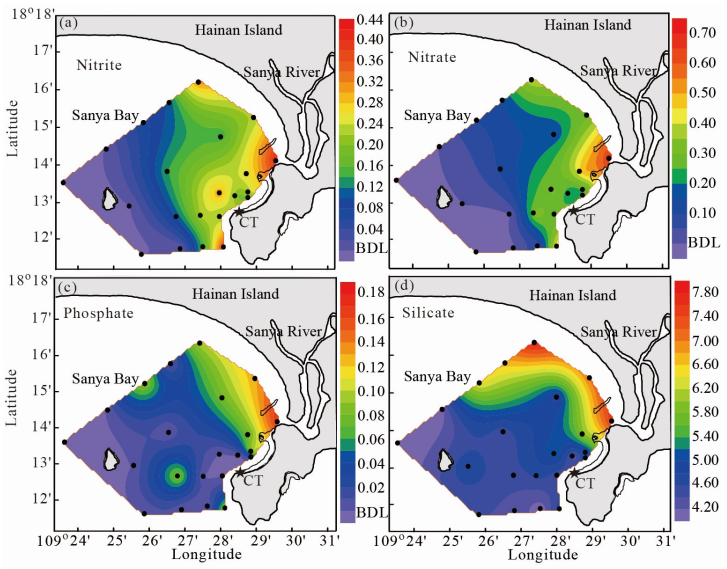


Figure 5: The activity of ^{228}Ra against (a) water depth, (b) salinity, and (c) the NO_x:P ratio in the water column at Station CT during February 6-13, 2012. ~~(a) ^{228}Ra vs. water depth; (b) ^{228}Ra vs. salinity; and (b) ^{228}Ra vs. the NO_x:P ratio.~~



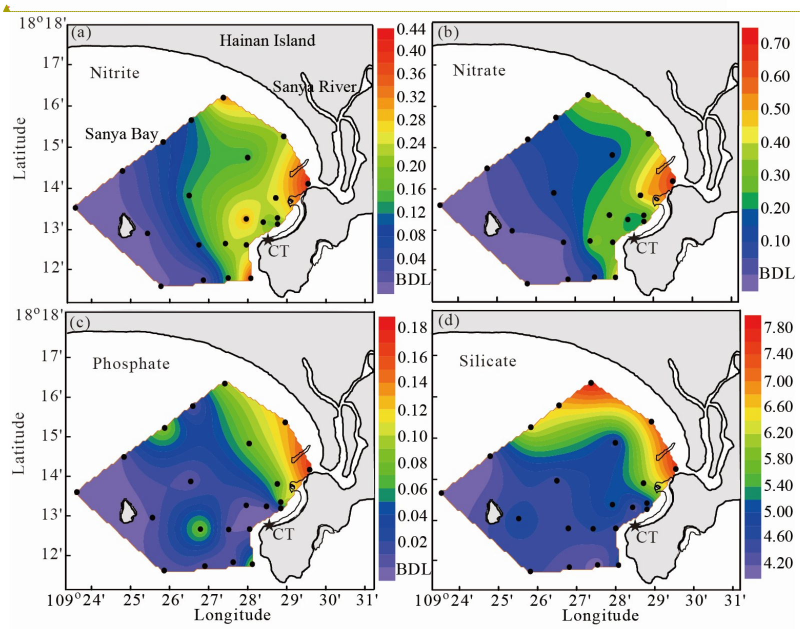


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Figure 6: Surface distributions of nutrients in Sanya Bay in February 2012. (a) Nitrite; (b) nitrate; (c) phosphate; and (d) silicate. The units are in µM. BDL is below the detection limit, which is 0.04 µM for nitrate and nitrite and 0.08 µM for phosphate.

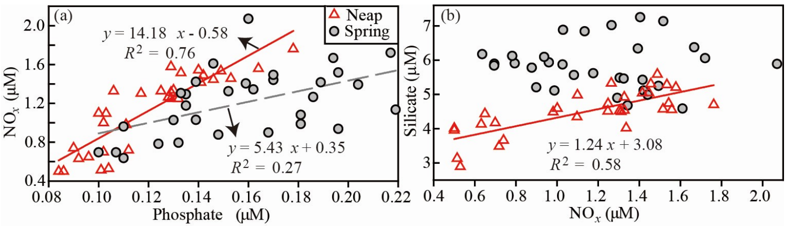

Figure 7: Concentrations of (a) NO_x against phosphate and (b) silicate against NO_x ~~nutrients~~ in the water column ~~against each other~~ during the spring tide and neap tide at Station CT during February 6-13, 2012. ~~(a) NO_x against phosphate; and (b) silicate against NO_x~~.

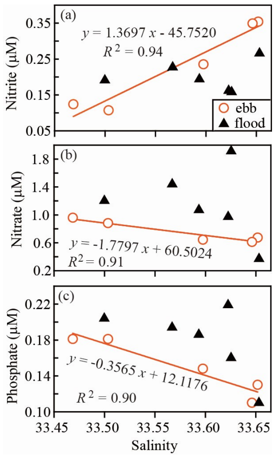

Figure 8: Behaviours of nutrients with salinity during the ebb flow and flood tide of the spring tide at Station CT. (a) nitrite; (b) nitrate; and (c) phosphate.

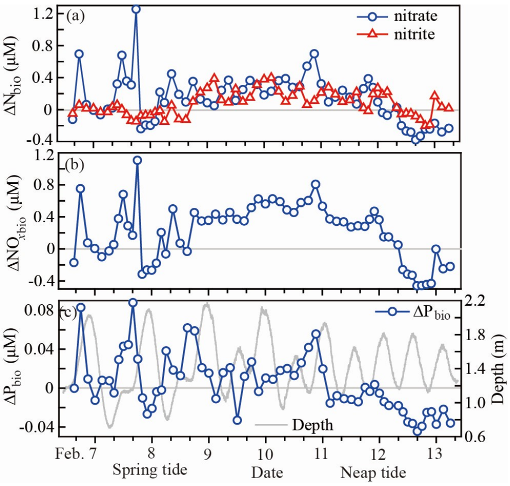

Figure 9: Variations of nutrients contributed by biological processes in a spring-neap tide during February 6-13, 2012 at the coastal reef station CT. (a) nitrite and nitrate; (b) NO_x; and (c) phosphate (P). Water depth was reported in Wang et al. (2014).

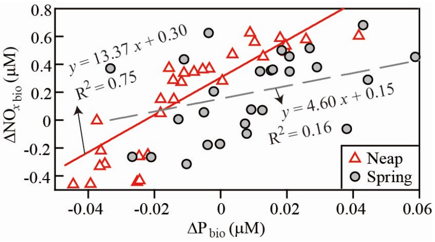

Figure 10: Relationship between biologically contributed NO_x and phosphate during the spring tide and neap tide at Station CT in the Luhuitou fringing reef in February 6-13, 2012.

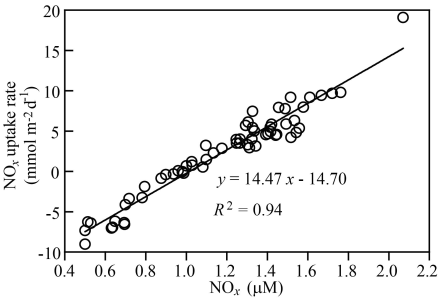

Figure 11: Uptake rate of NO_x against the concentration of NO_x in the water column at reef Station CT in a spring-neap tide during February 6-13, 2012.

Table 1. Sampling stations and data collected in Sanya Bay in February 2012.

Station	Latitude (°N)	Longitude (°E)	Bottom Depth (m)	Sample Depth (m)	Temperature (°C)	Salinity	NO_2^- (μM)	NO_3^- (μM)	PO_4^{3-} (μM)	SiO_3^{2-} (μM)
J1	18.2718	109.4565	8	0.5	22.80	33.60	0.328	0.410	0.104	7.916
				6.5	22.74	33.60	0.298	0.343	0.098	7.485
J2	18.2623	109.4423	9	0.5	22.66	33.62	0.103	0.149	BDL	6.708
				8.0	22.64	33.63	0.124	0.162	BDL	6.531
J3	18.2531	109.4298	12	0.5	22.70	33.64	0.073	0.104	0.090	6.472
				11.0	22.69	33.65	0.104	0.067	0.108	6.318
J4	18.2409	109.4118	11	0.5	22.81	33.70	BDL	BDL	BDL	4.069
				12.4	22.81	33.70	BDL	BDL	BDL	4.095
J5	18.2261	109.3909	15	0.5	22.90	33.70	BDL	BDL	BDL	4.058
				14.0	22.88	33.74	BDL	BDL	BDL	4.126
W4	18.2154	109.4244	17	0.5	22.90	33.70	BDL	BDL	BDL	4.768
				17.5	22.73	33.75	BDL	BDL	BDL	4.760
W3	18.2306	109.4413	16	0.5	22.97	33.89	0.136	0.112	BDL	4.476
				16.0	23.40	33.60	0.063	0.098	BDL	5.188
W2	18.2466	109.4672	12	0.5	22.93	33.72	0.147	0.158	0.081	4.724
				9.5	22.76	33.73	0.075	0.127	BDL	5.179
W1	18.2555	109.4832	5	0.5	23.12	33.70	0.228	0.299	0.131	7.136
				3.0	22.92	33.73	0.228	0.234	0.102	6.317
P3	18.2213	109.4660	16	0.5	22.75	33.84	0.300	0.309	BDL	5.172
				16.0	22.87	33.76	0.132	0.144	BDL	4.655
P2	18.2296	109.4797	11	0.5	23.01	33.67	0.262	0.496	0.082	6.035
				11.0	22.90	33.77	0.206	0.204	BDL	4.569
P1	18.2355	109.4940	5	0.5	22.98	33.62	0.426	0.699	0.178	7.726
				2.8	22.97	33.64	0.350	0.525	0.157	7.671
P4	18.2105	109.4464	12	0.5	22.71	33.89	0.108	0.002	0.081	4.519
				19.0	22.67	33.89	0.200	0.013	0.130	4.935
P5	18.1931	109.4296	26	0.5	22.69	33.81	BDL	BDL	BDL	4.428
				26.0	22.74	33.87	0.054	0.076	BDL	4.522
L8	18.1964	109.4476	25	0.5	22.78	33.88	BDL	BDL	BDL	4.282
				25.5	22.75	33.88	0.191	0.005	0.082	4.528
L7	18.1966	109.4601	32	0.5	22.83	33.86	0.171	0.092	BDL	4.093
				30.7	22.78	33.87	0.077	0.081	BDL	4.400
L6	18.1965	109.4694	23	0.5	22.79	33.82	0.420	0.516	0.097	4.859
				27.0	22.77	33.87	0.405	0.431	0.112	4.839
L5	18.2111	109.4582	21	0.5	22.74	33.85	0.231	0.326	BDL	4.643
				18.0	22.79	33.86	0.355	0.392	0.097	4.480
L4	18.2105	109.4674	20	0.5	22.76	33.85	0.219	0.248	BDL	4.484
				21.0	22.77	33.87	0.285	0.309	BDL	4.645
L3	18.2201	109.4749	12	0.5	22.79	33.84	0.194	0.193	BDL	4.315
				12.8	22.79	33.86	0.202	0.183	BDL	4.444
L2	18.2193	109.4812	11	0.5	22.81	33.85	0.192	0.309	BDL	5.006
				11.0	22.80	33.86	0.195	0.218	BDL	4.639
L1	18.2219	109.4812	11	0.5	22.76	33.84	0.244	0.253	0.101	4.887
				11.0	22.81	33.87	0.353	0.235	0.107	5.252

Note: BDL is below the detection limit.

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Manuscript Details

Manuscript number	MARSYS_2017_259
Title	Significance of submarine groundwater discharge in nutrients budget in tropical Sanya Bay, China
Article type	Research Paper

Abstract

To quantify the contribution of submarine groundwater discharge (SGD) to the nutrients budget in tropical embayments, naturally occurring radium isotopes (223Ra, 224Ra, 226Ra, and 228Ra) were investigated as SGD tracers in Sanya Bay, China in the northern South China Sea. Higher activities of radium were present along the north coast and near the Sanya River estuary. Using the activity ratio of 224Ra/228Ra, the apparent water age in Sanya Bay was estimated to be 0-13.2 days, with an average of 7.2±3.2 days. Based on the mass balance of 226Ra and 228Ra, SGD was calculated to be 2.76-5.03×106 m3 d-1 (or 4.3-7.7 cm d-1), which accounted for more than half of the respective radium source flux into Sanya Bay. SGD associated dissolved inorganic nutrient fluxes into Sanya Bay were estimated to be 3.91-7.11×105 mol NOx d-1, 5.03-9.15×105 mol P d-1, and 6.55-11.9×105 mol Si d-1. The estuarine nutrients flux from the Sanya River was equivalent to the phosphate flux via SGD, but a few times smaller the nitrogen and silicate fluxes carried by SGD. SGD was also more important than atmospheric deposition and nitrogen fixation in the nutrients budget. Our results demonstrate that SGD contributed at least 38% phosphate, 90% nitrogen, and 83% silicate in Sanya Bay. SGD could thus supply almost all nitrogen and silicate required by phytoplankton growth in the bay.

Keywords	submarine groundwater discharge; radium isotopes; residence time; nutrients; China, Hainan Island, Sanya Bay

Corresponding Author	Guizhi Wang
Corresponding Author's Institution	Xiamen University
Order of Authors	Guizhi Wang, Shuling Wang, Zhangyong Wang
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Research Data Related to this Submission

There are no linked research data sets for this submission. The following reason is given:
Data will be made available on request

Dear Editor,

My co-authors and I would like to submit the manuscript entitled "Significance of submarine groundwater discharge in nutrients budget in tropical Sanya Bay, China " for consideration as a research article in *Journal of Marine Systems*.

This study revealed the significance of submarine groundwater discharge (SGD) in the nutrients budget in Sanya Bay, China in the dry season using radium isotopes as SGD tracers. From our results SGD contributes at least 90% nitrogen, 83% silicate, and 38% phosphate in Sanya Bay. SGD is more important than the estuarine export from the Sanya River, the atmospheric deposition and nitrogen fixation. SGD would satisfy almost all requirements of nitrogen and silicate by phytoplankton growth in the bay. We believe that our study would be of interest to broad readers of *JMS*.

The manuscript has not been previously published, in whole or in part, and it is not under consideration by any other journal. All authors have seen the manuscript and approved the submission to your journal.

For contributions of authors: Guizhi Wang wrote the main text of the manuscript. Guizhi Wang, Shuling Wang, and Zhangyong Wang collected samples in the field and measured the parameters. Guizhi Wang analyzed the data and did the calculations.

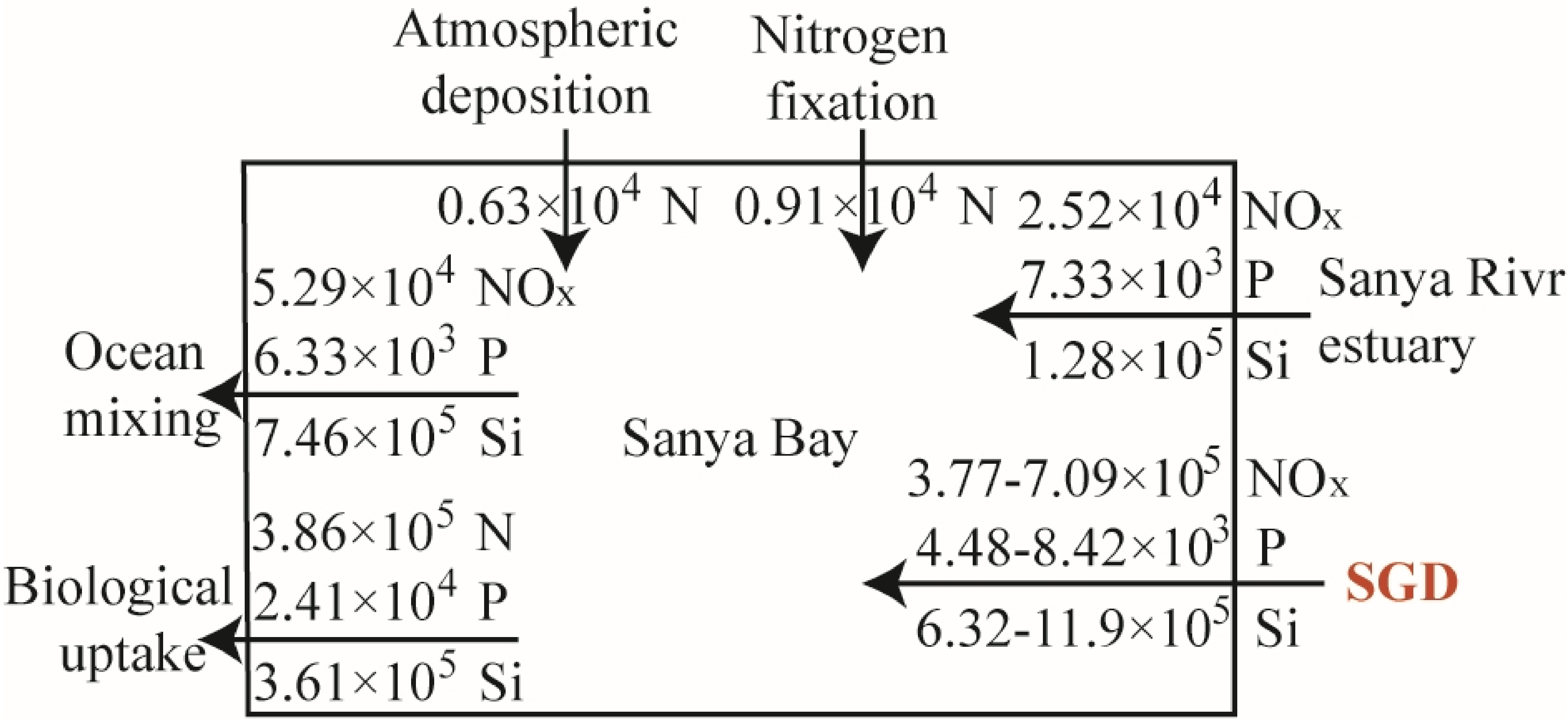
Thank you very much in advance for considering our manuscript for potential publication at *JMS*.

Sincerely yours,

Guizhi Wang
Corresponding Author

Highlights

- Radium isotopes were used to trace SGD in Sanya Bay, China
- Nutrients flux via SGD was equivalent to or more than the estuarine export flux
- SGD is a major source of N and Si and contributes at least 38% P in Sanya Bay
- SGD could satisfy almost all requirements of N and Si by phytoplankton growth



Nutrients budget in Sanya Bay (Unit: mol d^{-1})

Significance of submarine groundwater discharge in nutrients budget in tropical Sanya Bay, China

Guizhi Wang[1,2]*, Shuling Wang[1], Zhangyong Wang[1]

[1]State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen, 361102, China

[2]College of Ocean and Earth Sciences, Xiamen University, Xiamen, 361102, China

*Corresponding author: Guizhi Wang, email: gzhwang@xmu.edu.cn

Abstract

To quantify the contribution of submarine groundwater discharge (SGD) to the nutrients budget in tropical embayments, naturally occurring radium isotopes (^{223}Ra, ^{224}Ra, ^{226}Ra, and ^{228}Ra) were investigated as SGD tracers in Sanya Bay, China in the northern South China Sea. Higher activities of radium were present along the north coast and near the Sanya River estuary. Using the activity ratio of $^{224}Ra/^{228}Ra$, the apparent water age in Sanya Bay was estimated to be 0-13.2 days, with an average of 7.2±3.2 days. Based on the mass balance of ^{226}Ra and ^{228}Ra, SGD was calculated to be 2.76-5.03×10^6 m^3 d^{-1} (or 4.3-7.7 cm d^{-1}), which accounted for more than half of the respective radium source flux into Sanya Bay. SGD associated dissolved inorganic nutrient fluxes into Sanya Bay were estimated to be 3.91-7.11×10^5 mol NO_x d^{-1}, 5.03-9.15×10^5 mol P d^{-1}, and 6.55-11.9×10^5 mol Si d^{-1}. The estuarine nutrients flux from the Sanya River was equivalent to the phosphate flux via SGD, but a few times smaller the nitrogen and silicate fluxes carried by SGD. SGD was also more important than atmospheric deposition and nitrogen fixation in the nutrients budget. Our results demonstrate that SGD contributed at least 38% phosphate, 90% nitrogen, and 83% silicate in Sanya Bay. SGD could thus supply almost all nitrogen and silicate required by phytoplankton growth in the bay.

Key words: submarine groundwater discharge; radium isotopes; residence time; nutrients; China, Hainan Island, Sanya Bay

1. Introduction

Coastal waters are prone to deterioration under a global context of climate change and changes in ocean and land-source forces, such as acidification and hypoxia induced by upwelling [*Booth et al.*, 2012; *Feely et al.*, 2008; *Glenn et al.*, 2004; *Grantham et al.*, 2004; *Peterson et al.*, 2013] and eutrophication and hypoxia caused by increasing terrestrial nutrient loadings from catchment areas [*Zhang et al.*, 2010]. Among these interacting forces submarine groundwater discharge (SGD) has been recognized as an important carrier of water often featured with high concentrations of nutrients, dissolved inorganic and organic carbon, and metals [*Cai et al.*, 2003; *Charette et al.*, 2001; *Liu at al.*, 2012; *Moore*, 2010; *Moosdorf et al.*, 2015; *Porubsky et al.*, 2014]. Thus, SGD is a key factor to quantify in evaluating material budgets of any coastal system.

Naturally occurring radioactive radium isotopes (^{223}Ra, ^{224}Ra, ^{226}Ra, and ^{228}Ra) have been widely used to trace SGD because they are not chemically active in coastal waters and their activities in SGD are at least an order of magnitude greater than in the receiving coastal waters [*Burnett and Dulaiova*, 2003; *Dulaiova et al.*, 2008; *Liu et al.*, 2012; *Moore*, 2010; *Schwartz*, 2003]. Radium is regenerated from decay of particle-reactive thorium isotopes and released from particles when encountering brackish or saline waters. The short-lived radium isotopes, ^{223}Ra (half-life =11.4 days) and ^{224}Ra (half-life =3.66 days), also work well in estimating apparent water ages on the shelf on time scales of a few to tens of days [*Gu et al.*, 2012; *Moore*, 2000; *Moore and Krest*, 2004].

Sanya Bay is a tropical bay located at the southern tip of Hainan Island, China in the northern South China Sea under the influence of the Southeast Asian monsoon (Fig. 1). Coral reefs account for 30% of its coastline [*Huang et al*., 2003]. The Sanya River flows into the bay in the northeast. Seasonal investigations in the bay demonstrate that the inner bay is influenced by the discharge of the Sanya River with relatively high nutrient levels, and the central and outer bay is dominated by oceanic forces from the South China Sea [*Wu et al.*, 2012a]. Our time-series studies demonstrate that tidally-driven SGD occurred at the Luhuitou fringing reef in the bay in a dry season, which caused coastal acidification and affected nutrient dynamics of the reef system [*Wang et al*., 2014; 2017]. The flux of SGD into Sanya Bay based on mapping data, however, has never been reported.

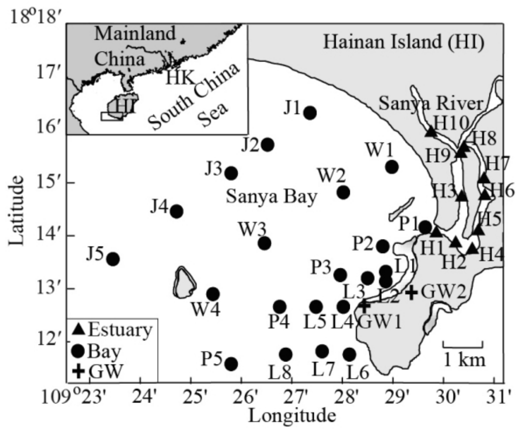


Figure 1. Study area and sampling stations in Sanya Bay and the Sanya River estuary. HK represents Hong Kong.

To quantify SGD and evaluate its geochemical impacts on Sanya Bay, a study was designed and implemented in Feb. 2012, using radium isotopes as SGD tracers. This study includes time-series observations at the Luhuitou fringing coral reef and a mapping investigation in the bay. The time-series observations were reported in *Wang et al*. [2014; 2017]. The present work is focused on interpretations of the mapping data. Briefly, the residence time and the flux of SGD in Sanya Bay were estimated based on distributions of radium isotopes in the bay. Nutrients fluxes into the bay via SGD were subsequently quantified and compared with other sources and sinks.

2. Materials and Methods

2.1. Study area

Sanya Bay has an average water depth of 16 m [*Huang et al.*, 2003] and irregular diurnal tides with a mean tidal range of 0.9 m [*Zhang*, 2001]. The annual mean surface water temperature is 26.8°C and the annual precipitation is around 1600-1800 mm [*Zhang*, 2001]. The Sanya River discharges into Sanya Bay in the northeast with an annual average discharge of 5.86 m^3 s^{-1} [*Wang et al.*, 2005]. 95% of the rainfall occurs in May to October [*Li et al.*, 2013], so that the river discharge in the dry months is even lower than the annual average. Fringing reefs develop along the east coast and around the islands in the bay. Sanya Bay is oligotrophic under the influence of the northern South China Sea [*Wu et al.*, 2012b]. Multiple habitats, coral reefs, mangroves, mudflats, and rocky and sandy beaches, are present in the bay [*Huang et al.*, 2003]. Holocene deposits of coral debris, sand, and silt surround the coast [*Zhao et al.*, 1979]. The sediments in the bay are mostly sands (>60%) [*Che et al.*, 2010], composing a highly permeable surface quifer.

2.2. Sampling and measurements

Surface water samples were collected for radium using a plastic barrel in Sanya

Bay during Feb. 2-3, 2012 and at the lower Sanya River estuary station H1 on Feb. 4, 2012 (Fig. 1). Samples for nutrients were collected using a 5 L Niskin bottle at the same time in the Sanya River estuary in order to evaluate the estuarine export nutrients fluxes. Temperature and salinity were measured using a multiparameter sonde YSI 6600. The salinity was measured using the Practical Salinity Scale.

Groundwater samples were taken at domestic wells using a submersible pump. Groundwater Station GW1 is about 50 m away from the coast. Details of GW1 are provided in *Wang et al* [2014] and samples were taken at this station every 2 hours from the morning of Feb. 7 to the morning of Feb. 8, 2012 for 24 hours to catch the diurnal variation of the groundwater. Station GW2 is about 100 m away from the coast and was sampled on Feb. 9, 2012. At this station the well was about 40 cm in diameter and 2.33 m deep and the water was 0.83 m deep. Samples for dissolved nitrate and nitrite, phosphate, silicate, and radium isotopes were taken at both groundwater stations.

Radium samples were passed through a 1 μm cartridge filter followed by a MnO_2-impregnated acrylic fiber (Mn-fiber) column to extract the dissolved radium [*Rama and Moore*, 1996]. The Mn-fiber was measured for ^{223}Ra and ^{224}Ra with a radium delayed coincidence counter [*Moore and Arnold*, 1996] with an error less than 13%. After the measurements were finished in two months, the Mn-fibers were leached for ^{226}Ra and ^{228}Ra, which were then co-precipitated with $BaSO_4$ and measured in a germanium gamma detector (GCW4022, Canberra)[*Moore*, 1984] with an error less than 7%. To estimate radium desorbed from particles of the estuary water, total suspended matter (TSM) was collected at Station P1 on pre-weighed and pre-combusted 47-mm-diameter GF/F filters (pore size of 0.7 μm) and measured by weighing after drying.

Nutrient samples were filtered through 0.45 μm cellulose acetate membranes and preserved with 1-2‰ chloroform. One filtrate was stored at 4°C before measurement for silicate, and one was kept at -20°C for nitrate, nitrite, and phosphate measurements. In the laboratory, nitrate, nitrite, silicate and phosphate were measured with a Technicon AA3 Auto-Analyzer (Bran-Luebbe, GmbH) following the same methods in *Han et al.* [2012]. The analytical precision was better than 1% for nitrate and nitrite, 2% for phosphate, and 2.8% for silicate.

2.3. Radium mass-balance model and residence time estimation

The decay of the long-lived radium isotopes, ^{226}Ra (half-life = 1600 yrs) and ^{228}Ra (half-life = 5.75 yrs), can be ignored in studying coastal and estuarine processes [*Moore et al.*, 2006]. Under the assumption of steady state of the system investigated, long-lived radium loss via mixing was equal to gains from river, SGD, and sediment diffusion, i.e.,

$$F_R \cdot {}^iRa_R + {}^iF_{sed} \cdot A_B + F_R \cdot f_d \cdot {}^iRa_p \cdot C_{TSM} + F_{SGD} \cdot {}^iRa_{GW} = V_B \cdot ({}^iRa_B - {}^iRa_O) \cdot \frac{1}{\tau} \qquad (1)$$

where on the left-hand side are the source terms: the first term represents the dissolved radium flux from the river, where F_R is the river water discharge, ${}^iRa_R$ is the activity of dissolved ${}^iRa$ of the estuary water, i=226 and 228; the second term represents the sediment diffusion flux of radium, where ${}^iF_{sed}$ is the areal diffusive flux of ${}^iRa$ from the sediments, and A_B is the sediment surface area of the bay investigated;

the third term represents the desorbed radium flux from the river, where f_d is the fraction of radium exchangeable from particles, $^{i}Ra_p$ is the activity of ^{i}Ra on particles, and C_{TSM} is the concentration of TSM of the estuary water; and the fourth term represents the radium flux via SGD, where F_{SGD} is the SGD flux, and $^{i}Ra_{GW}$ is the average activity of dissolved ^{i}Ra of the groundwater; on the right-hand side are the sink terms: where V_B is the volume of the bay under investigation, $^{i}Ra_B$ is the average activity of dissolved ^{i}Ra in the bay, $^{i}Ra_O$ is the activity of dissolved ^{i}Ra of the ocean water, and τ is the residence time in the bay.

The residence time in the bay can be estimated by the activity ratio of ^{224}Ra and ^{228}Ra under the assumption of steady state as derived by *Moore et al.* [2006]:

$$\tau = \frac{F\left(\frac{^{224}Ra}{^{228}Ra}\right) - I\left(\frac{^{224}Ra}{^{228}Ra}\right)}{I\left(\frac{^{224}Ra}{^{228}Ra}\right)\cdot \lambda_{224}} \qquad (2)$$

where $F\left(\frac{^{224}Ra}{^{228}Ra}\right)$ is the ratio of the flux of ^{224}Ra over that of ^{228}Ra into the system, equivalent to the activity ratio of ^{224}Ra to ^{228}Ra of the flux into the system, and $I\left(\frac{^{224}Ra}{^{228}Ra}\right)$ is the ratio of the inventory of ^{224}Ra over that of ^{228}Ra in the system, which is equal to the activity ratio of ^{224}Ra to ^{228}Ra in the system.

3. Results

3.1. Radium isotopes in Sanya Bay

Activities of ^{223}Ra ranged 0.4-1.8 dpm 100 L^{-1} (i.e., 0.07-0.3 Bq m^{-3}), decreasing offshore and southward with the maximum in the north of the bay (Fig. 2a). The activity of ^{228}Ra showed a similar pattern, varying in the range 23.1-38.0 dpm 100 L^{-1}

(Fig. 2d). ^{224}Ra and ^{226}Ra demonstrated the highest activities in the northeast bay off the Sanya River estuary. The range of activity was 11.9-42.6 dpm 100 L^{-1} for ^{224}Ra and 9.6-11.9 dpm 100 L^{-1} for ^{226}Ra (Figs. 2b,c). In general, activities of radium isotopes were higher in the northern Sanya Bay and outside the Sanya River estuary, coincident with lower salinities of 33.60-33.62 at these stations (Table 1). These higher radium signals were reflective of the Sanya River plume and other land sources.

Station	Latitude	Longitude	Water Depth (m)	Temp (°C)	Salinity	^{223}Ra	σ	^{224}Ra	σ	^{226}Ra	σ	^{228}Ra	σ
						dpm 100 L^{-1}							
J1	18.2718	109.4565	8	22.80	33.60	1.79	0.20	33.86	0.36	10.81	0.45	33.73	1.30
J2	18.2623	109.4423	9	22.66	33.62	0.80	0.13	21.52	0.68	10.50	0.39	31.74	1.09
J3	18.2531	109.4298	12	22.70	33.64	1.56	0.16	30.04	0.38	10.91	0.50	37.95	1.44
J4	18.2409	109.4118	11	22.81	33.70	0.60	0.14	11.92	0.40	10.78	0.39	28.24	1.02
J5	18.2261	109.3909	15	22.90	33.70	0.52	0.15	17.61	0.89	10.19	0.41	28.02	1.10
W1	18.2555	109.4832	5	23.12	33.70	1.36	0.23	26.66	0.39	12.04	0.49	30.35	1.23
W2	18.2466	109.4672	12	22.93	33.72	0.83	0.13	12.88	0.32	10.92	0.41	26.22	1.02
W3	18.2306	109.4413	16	22.97	33.89	0.59	0.13	11.93	0.53	10.63	0.43	23.11	1.06
W4	18.2154	109.4244	5	23.12	33.70	0.52	0.11	12.82	0.30	10.73	0.39	24.03	0.98
P1	18.2355	109.4940	5	22.98	33.62	1.22	0.19	42.60	0.85	11.93	0.54	28.87	1.34
P2	18.2296	109.4797	11	23.01	33.67	0.97	0.17	23.57	0.34	10.56	0.49	31.94	1.27
P3	18.2213	109.4660	16	22.75	33.84	0.54	0.13	15.49	0.59	10.99	0.41	24.26	1.08
P4	18.2105	109.4464	12	22.71	33.89	0.77	0.11	15.32	0.36	10.83	0.32	28.14	0.85
P5	18.1931	109.4296	26	22.69	33.81	1.38	0.11	18.51	0.65	10.95	0.33	28.90	0.89
L1	18.2219	109.4812	7	22.76	33.84	0.65	0.10	13.65	0.40	9.71	0.42	26.42	1.15
L2	18.2193	109.4812	11	22.81	33.85	0.74	0.11	22.99	0.67	11.98	0.44	26.33	1.16
L3	18.2201	109.4749	12	22.79	33.84	0.78	0.11	14.49	0.28	9.77	0.41	25.24	1.06
L4	18.2105	109.4674	20	22.76	33.85	0.70	0.11	13.82	0.42	10.59	0.42	25.53	1.13
L5	18.2111	109.4582	21	22.74	33.85	1.17	0.13	17.63	0.33	11.27	0.38	25.90	0.96
L6	18.1965	109.4694	23	22.79	33.82	0.84	0.12	16.34	0.38	10.21	0.43	23.77	0.95
L7	18.1966	109.4601	32	22.83	33.86	0.84	0.18	14.26	0.76	10.53	0.41	26.03	1.08
L8	18.1964	109.4476	25	22.78	33.88	0.43	0.15	12.18	0.40	9.58	0.43	27.01	1.20
H1	18.2348	109.4977	nd*	22.88	31.70	1.69	0.50	64.75	0.74	15.45	0.70	43.75	1.85

*nd– not determined

Table 1. Sampling stations and data for surface water in Sanya Bay and the lower Sanya River estuary in Feb. 2012.

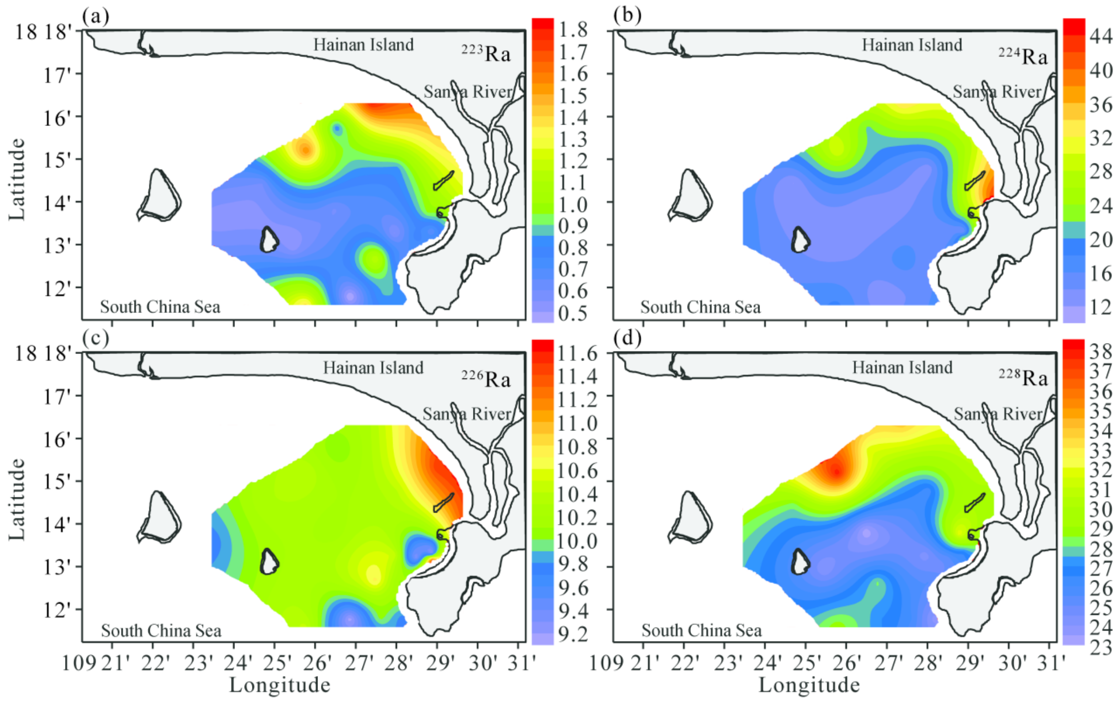


Figure 2. Surface distributions of radium isotopes (in dpm 100 L^{-1}) in Sanya Bay, (a) ^{223}Ra, (b) ^{224}Ra, (c) ^{226}Ra, and (d) ^{228}Ra.

3.2. Parameters of the estuary water and of the groundwater

The salinity in the investigated Sanya River estuary increased from 6.06 downstream to 31.70 at the estuary outlet. Temperature ranged from 23.12-24.00. Nutrients decreased consistently with salinity for oxidized inorganic nitrogen (NO_x) and silicate, from 36.6 to 6.72 μM for NO_x with nitrite accounting for one third of NO_x and from 271 to 30.1 μM for silicate (Fig. 3a). For phosphate a general decreasing trend was present (Fig. 3b), however, the peak concentration, 11.0 μM, appeared at the mid-salinity station H8, where the salinity was 15.60, and the minimum concentration, 1.45 μM, showed at Station H3, where the salinity was 28.91. The deviation from conservative mixing of phosphate in the mid-salinity in estuaries has been proposed to be due to particle sorption/desorption [*Froelich et al.*, 1982; *van der Zee et al.*, 2007]. The estuarine station H1 had a salinity of 31.70 and relatively high activities of radium isotopes (in dpm 100 L^{-1}) compared with the bay water, 1.7 for ^{223}Ra, 64.8 for ^{224}Ra, 15.5 for ^{226}Ra, and 43.8 for ^{228}Ra. TSM of the estuary water was 25.3 mg L^{-1}.

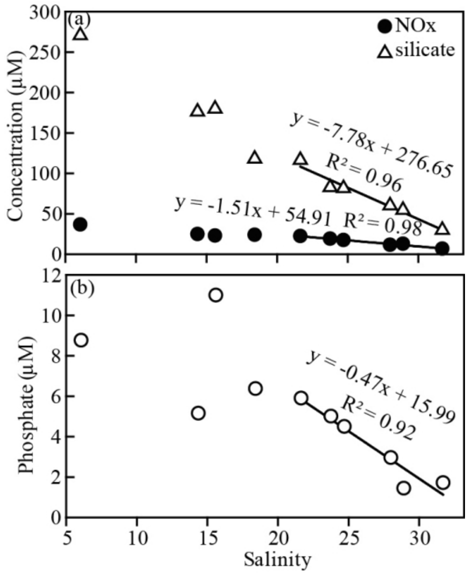


Figure 3. Concentrations of nutrients against salinity in the Sanya River estuary, (a) oxidized inorganic nitrogen (NO$_x$) and silicate (b) phosphate.

A weekly observation of temperature and salinity at groundwater Station GW1 indicated that groundwater properties were relatively constant with time, without apparent tidal resonances and the salinity varied in the range of 20.06-20.49 [*Wang et al.*, 2014]. NO$_x$ was mostly nitrate with nitrite less than 0.1% (i.e., <0.1 μM). The average concentrations of NO$_x$, phosphate, and silicate (in μM) were 141.5±14.2, 1.68±0.53, and 237.2±2.2, with n=13, respectively. The average activities of radium isotopes (in dpm 100 L^{-1}) were 30.6±7.2 for ^{223}Ra, 624.2±25.8 for ^{224}Ra, 245.9±25.9 for ^{226}Ra, and 434.9±17.3 for ^{228}Ra. At Station GW2 the salinity was 0.20. The activities of radium isotopes (in dpm 100 L^{-1}) were much lower than at Station GW1, 1.96 for ^{223}Ra, 62.4 for ^{224}Ra, 17.7 for ^{226}Ra, and 42.9 for ^{228}Ra; while concentrations of nutrients were about twice higher for NO_x than at Station GW1, twice as high for silicate, but half as much for phosphate.

4. Discussion

4.1. Residence time in Sanya Bay

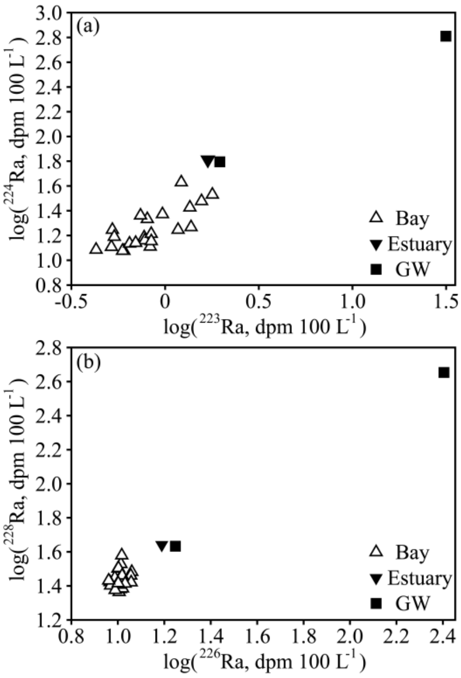


Figure 4. Activities of ^{224}Ra vs. ^{223}Ra (a) and ^{228}Ra vs. ^{226}Ra (b) of Sanya Bay water, the lower Sanya River estuary water, and nearby groundwater in Feb. 2012.

Dissolved radium in Sanya Bay appeared to have the same source as that of the estuary water and of the groundwater with ^{224}Ra vs. ^{223}Ra and ^{228}Ra vs. ^{226}Ra falling not far from a linear line (Fig. 4). The activity ratio of ^{224}Ra/^{228}Ra ranged 0.42-1.48 in Sanya Bay with the maximum occurring at Station P1 outside the Sanya River estuary, with higher values in the north and northeast of the bay (Fig. 5a), indicating sources of radium from the coastline. The intrusion of the northern South China Sea water into the bay caused the lower activity ratio of $^{224}Ra/^{228}Ra$ in the south of the bay. In terms of the sources of radium into Sanya Bay, the activity ratio of $^{224}Ra/^{228}Ra$ was almost the same for the Sanya River plume and SGD, 1.48 for Sanya River estuary water and 1.44±0.07 for the groundwater. Considering that the radium flux from sediment diffusion is usually less than SGD [*Liu et al.*, 2012; *Moore et al.*, 2006], the residence time in the bay was estimated using Eq. (2), taking 1.48 to represent the activity ratio of radium input fluxes from the river plume and SGD. The residence time ranged 0-13.2 days in Sanya Bay with an average of 7.2±3.4 days, relatively short near the north and northeast coast of the bay and increasing offshore (Fig. 5b).

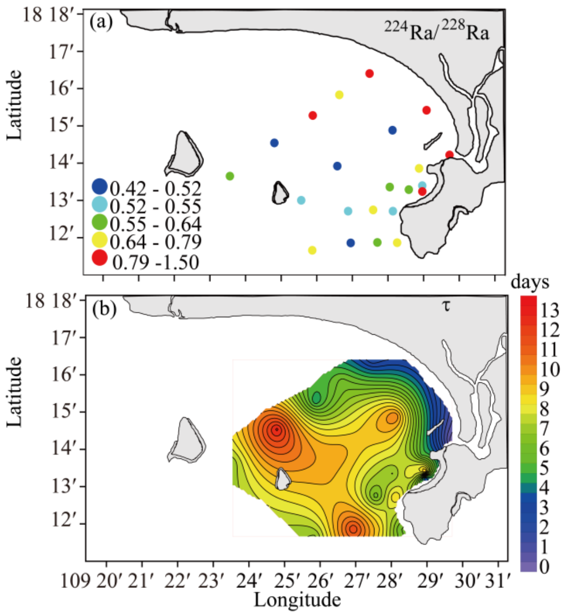


Figure 5. Activity ratio of $^{224}Ra/^{228}Ra$ (a) and residence time (τ) (b) in Sanya Bay in Feb. 2012.

4.2. SGD estimation using radium isotopes

To estimate SGD into Sanya Bay, the mass balance of ^{226}Ra and ^{228}Ra was set up as illustrated in Eq. (1). The average salinity of the bay water was 33.77±0.10. Thus, groundwater Station GW1, a well much closer to the coast, where the average salinity was 20.22, was more representative of SGD water directly interacting with the bay water. Therefore, data from Station GW1 were taken as the SGD end-member. The annual Sanya River discharge was taken into Eq. (1) for a minimum SGD estimate. The parameters at the lower estuarine station H1 were taken to calculate the river/estuarine contribution of radium to the bay. Diffusive fluxes of radium were taken from the literature. Radium data at an offshore station (110 ºE, 18 ºN) were taken to represent the ocean water radium. All the parameters used in Eq. (1) to estimate SGD are listed in Table 2 and sources and sinks of radium in the bay were quantified and are listed in Table 3. The SGD flux was estimated to be 2.67×10^6 m^3 d^{-1} (or 4.1 cm d^{-1}) based on ^{226}Ra and 5.01×10^6 m^3 d^{-1} (or 7.7 cm d^{-1}) based on ^{228}Ra, which accounted for 98% of the respective radium source flux into Sanya Bay. This was comparable to the SGD rate along the eastern coast of Hainan Island and in other embayments (Table 4). The rate estimated using mapping data of long-lived radium isotopes in the bay fell in the range of seepage rates derived from time-series observations of ^{226}Ra in a coastal station in Sanya Bay, 0-44 cm d^{-1} [*Wang et al.*, 2014].

	Parameter		Value	Unit	Reference
Estuary	F_R	River discharge	5.86	m^3 s^{-1}	*Wang et al.*, 2005
	$^{226}Ra_R$	Estuary water ^{226}Ra	15.45	dpm 100 L^{-1}	This study
	$^{228}Ra_R$	Estuary water ^{228}Ra	43.75		
	C_{TSM}	Concentration of total	25.33	mg l^{-1}	

		suspended matter			
	f_d	Fraction of desorbed radium from particles	0.43	-----	*Wang et al.*, 2015
	$^{226}Ra_p$	^{226}Ra on particles	2.5	dpm g^{-1}	*Krest and Moore*, 1999
	$^{228}Ra_p$	^{228}Ra on particles	2.09		
Sediment	$^{228}F_{sed}$	^{228}Ra diffusive flux	2.1	dpm m^{-2} d^{-1}	
	$^{226}F_{sed}$	^{226}Ra diffusive flux	0.27		*Charette et al.*, 2001
Groundwater	$^{226}Ra_{GW}$	Groundwater ^{226}Ra	255.8	dpm 100 L^{-1}	This study
	$^{228}Ra_{GW}$	Groundwater ^{228}Ra	454.0		
Sanya Bay	$^{226}Ra_B$	Bay water ^{226}Ra	10.75		
	$^{228}Ra_B$	Bay water ^{228}Ra	27.81		
	V_B	Volume of the bay investigated	1.04×10^9	m^3	
	A_B	Surface area of the bay investigated	6.49×10^7	m^2	
	τ	Residence time	7.24	day	
Ocean	$^{226}Ra_O$	Ocean water ^{226}Ra	5.92	dpm 100 L^{-1}	
	$^{228}Ra_O$	Ocean water ^{228}Ra	11.70		

Table 2. Parameters used in the mass balance Eq. (1) of ^{226}Ra and ^{228}Ra.

Radium			Formula in Eq.(1)	Value	Unit
^{226}Ra	Sources	Sanya River	$F_R \cdot {}^{226}Ra_R$	7.82×10^7	dpm d^{-1}
			$F_R \cdot f_d \cdot {}^{226}Ra_p \cdot C_{TSM}$	1.31×10^7	
		Sediment diffusion	$A_B \cdot {}^{226}F_{sed}$	1.75×10^7	
		Groundwater	$F_{SGD} \cdot {}^{226}Ra_{GW}$	6.82×10^9	
	Sink	Mixing	$V_B \cdot ({}^{226}Ra_B - {}^{226}Ra_O)/\tau$	6.93×10^9	
^{228}Ra	Sources	Sanya River	$F_R \cdot {}^{228}Ra_R$	2.22×10^8	
			$F_R \cdot f_d \cdot {}^{228}Ra_p \cdot C_{TSM}$	1.10×10^7	
		Sediment diffusion	$A_B \cdot {}^{228}F_{sed}$	1.36×10^8	
		Groundwater	$F_{SGD} \cdot {}^{228}Ra_{GW}$	2.27×10^{10}	
	Sink	Mixing	$V_B \cdot ({}^{228}Ra_B - {}^{228}Ra_O)/\tau$	2.31×10^{10}	

Table 3. Sources and sinks of long-lived radium (^{226}Ra and ^{228}Ra) in Sanya Bay.

Region	SGD rate (cm d^{-1})	References
Manila Bay, Philippines	0-26	*Taniguchi et al.*, 2008
Jamaica Bay, USA	1.5-17	*Beck et al.*, 2007

Masan Bay, Korea	6.1-7.1	*Lee et al.*, 2009
Yeogil Bay, Korea	20	*Kim et al.*, 2007
Eastern coast of Hainan Island, China	10-29	*Ji et al.*, 2013
Sanya Bay, China	4.1-7.7	This study

Table 4. The SGD flux in Sanya Bay compared with SGD rates in other embayments and along the eastern Hainan Island.

4.3. Nutrients fluxes via SGD into Sanya Bay and their contributions to the nutrients budgets

Nutrients fluxes via SGD into Sanya Bay were calculated using the flux of SGD estimated from surface distributions of long-lived radium in the bay multiplied by nutrients concentrations at the groundwater Station GW1. Thus, nutrients fluxes via SGD were 4.48-8.42×10^3 mol d^{-1} for phosphate, 3.77-7.09×10^5 mol d^{-1} for NO_x, and 6.32-11.9×10^5 mol d^{-1} for silicate. Sanya Bay is relatively oligotrophic with concentrations of nutrients in the range of below the detection limit (BDL) to 0.17 μM for phosphate, BDL to 1.13 μM for NO_x, and 4.06-7.92 μM for silicate [*Wang et al.*, 2017]. The inventory of nutrients in Sanya Bay was estimated, taking the average concentration of nutrients in the bay and multiplied by the water volume under investigation, to be 4.58×10^4 mol P, 3.83×10^5 mol NO_x, and 5.40×10^6 mol Si. The inventory was then divided by the residence time in the bay, 7.24 d, and a removal rate of nutrients by mixing was estimated to be 6.33×10^3 mol P d^{-1}, 5.29×10^4 mol NO_x d^{-1}, and 7.46×10^5 mol Si d^{-1}. Comparisons with SGD-associated nutrients fluxes indicated that SGD could supply all NO_x and almost all phosphate and silicate removed by mixing in Sanya Bay. The average planktonic primary production in

Sanya Bay in winter is 39.36 mmol C m^{-2} d^{-1} [*Dong et al.*, 2008]. Assuming an uptake ratio of C:N:P:Si of 106:16:1:15 [*Brzezinski*, 1985; *Redfield*, 1960], the corresponding nutrient uptake rates would be 2.41×10^4 mol d^{-1} for P, 3.86×10^5 mol d^{-1} for N, and 3.61×10^5 mol d^{-1} for Si. SGD seemed to provide more than enough N and Si and at least 19% of the P necessary to support this planktonic primary production. In addition, nitrite, nitrate, and phosphate at offshore stations were below detection limits [*Wang et al.*, 2017], indicating that the ocean provided negligible, if any, nutrients to Sanya Bay. The average nitrogen fixation rate in the bay is 0.14 mmol m^{-2} d^{-1} in winter [*Dong et al.*, 2008], at most 2% equivalent to that contributed by SGD. The estuarine export nutrients fluxes from the Sanya River estuary were estimated, using an effective concentration multiplied by the annually-average river discharge, to be 7.33×10^3 mol d^{-1} for phosphate, 2.52×10^4 mol d^{-1} for NO_x, and 1.28×10^5 mol d^{-1} for silicate. The effective concentration was the *y* intercept of a linear regression of the concentration in the estuary against salinity at mid to high salinity [*Officer*, 1979]. As shown in Fig. 3, the linear regressions were significant for these nutrients with $R^2>0.9$ and the effective concentration was 16.0 μM for phosphate, 54.9 μM for NO_x, and 277 μM for silicate. The estuarine export phosphate flux was comparable to the SGD-associated flux, while the fluxes of NO_x and phosphate from the Sanya River estuary were less than that contributed by SGD. Another source of nutrients is atmospheric deposition. Since there was no rain during the two weeks before our sampling, a higher dry deposition rate of nitrogen for the south China from the literature, 9.72×10^{-5} mol N m^{-2} d^{-1} [*Wai et al.*, 2010], was considered, which gave a deposition flux of 6.31×10^3 mol N d^{-1}. The deposition flux is about two orders of magnitude smaller than SGD-contributed nitrogen. Thus, SGD is a main nutrient contributor to Sanya Bay at least as important as the Sanya River.

In the nutrients budgets of Sanya Bay (Fig. 6), the source terms include the Sanya River estuarine export, SGD, atmospheric deposition, and nitrogen fixation. The sink terms are ocean mixing and biological uptake. The total sink is 4.39×10^5 mol N d^{-1}, 2.78×10^4 mol P d^{-1}, and 1.11×10^6 mol Si d^{-1}, while the total source is $4.18\text{-}7.50\times10^5$ mol N d^{-1}, $1.18\text{-}1.58\times10^4$ mol P d^{-1}, and $0.76\text{-}1.32\times10^6$ mol Si d^{-1}. Apparently, the source and sink terms of nitrogen and silicate can be balanced in Sanya Bay. A deficit in phosphate is present. At least 1.20×10^4 mol P d^{-1} is required to fill the gap. We propose two reasons for this deficit: a) benthic flora of about 150 species were found in Sanya Bay [*Titlyanov et al.*, 2015] and macroalgae usually demonstrate an N:P ratio of about 30 in their tissues [*Atkinson and Smith*, 1983]; if this ratio were considered in estimating the biological uptake rate of phosphate based on the nitrogen uptake rate, a much lower biological uptake rate of phosphate would have been obtained; and b) benthic release of phosphorus due to remineralization or grazing of organic matter may be a phosphate source.

Nutrients carried by SGD contributed 90-95% nitrogen, 38-53% phosphate, and 83-90% silicate to the nutrients source of Sanya Bay. Our results substantiate the regulation of SGD on nutrient composition in a coral reef system of Sanya Bay found in our time-series studies [*Wang et al.*, 2017]. Nutrient enrichments have caused worldwide coastal environmental issues of eutrophication and hypoxia [*Chislock and*

Doster, 2013; *Howarth et al.*, 2011]. As a major nutrient source, with frequencies and areas of eutrophication and associated hypoxia increasing around the world coast [*Diaz and Rosenberg*, 2008], SGD and its associated material fluxes need to be monitored in the long term in environmental protection programs of any coastal ecosystems.

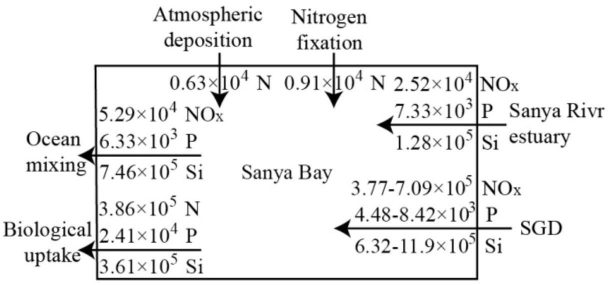


Figure 6. Nutrients budgets in Sanya Bay. Unit is in mol d^{-1}.

5. Conclusions

Contribution of SGD-associated nutrients to the nutrients budget in Sanya Bay in the dry season was investigated for the first time using naturally occurring radium isotopes as SGD tracers. The following was concluded from this study:

a) In Sanya Bay, radium isotopes (^{223}Ra, ^{224}Ra, ^{226}Ra, and ^{228}Ra) had higher activities along the north coast and in the northeast near the Sanya River estuary, indicating sources of radium from the coast and the river.

b) The residence time in Sanya Bay ranged 0-13.2 days, with an average of 7.2±3.4 days, relatively short near the north and northeast coast of the bay and increasing offshore.

c) SGD associated dissolved inorganic nutrient fluxes into Sanya Bay were estimated to be 3.91-7.11×10^5 mol NO_x d^{-1}, 5.03-9.15×10^5 mol P d^{-1}, and

6.55-11.9×10^5 mol Si d^{-1}. SGD could satisfy all nitrogen and silicate requirements and 20% of phosphate requirement by phytoplankton growth in Sanya Bay. The nutrients fluxes via SGD are at least comparable to the estuarine export fluxes from the Sanya River.

d) SGD is a major source of nitrogen and silicate and contributes at least 38% phosphate in Sanya Bay.

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