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Interactive comment on "Tidal variability of nutrients in a coastal coral reef system influenced by groundwater" *by* Guizhi Wang et al.

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

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: Data from groundwater close to the time-series station and the estuary for nutrients and Ra isotopes are available to confirm the submarine groundwater input. These data are going to be presented in a manuscript under preparation focused on submarine groundwater discharge (SGD) traced by Ra, and can be shown in this manuscript to confirm SGD input. It is true that desorption of radium isotopes occurs at mid-salinities. In the case of Sanya Bay the salinity in the bay is over 33, so desorption is negligible. Desorption is usually significant in estuaries, such as the Sanya River estuary where mid-salinity occurs. Diffusion from sediments is one source of radium, but it is much smaller for 228Ra than submarine groundwater discharge based on our calculation, which will be shown in our SGD manuscript. This manuscript is a sister paper of that published in Environmental Science &Technology (Wang et al., 2014, ES&T, p. 13069-13075). 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 some 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 3.4. The rationale is that the 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. As summarized on Line 23, "the biological influence seems to be less as inferred from the less significant correlations during the spring tide." As stated on Page 6 Line 3, " Greater groundwater discharge appeared during the ebb flow in the spring tide than in the neap tide as indicated by the higher activity of 228Ra, bringing more groundwater into the reef system." On Page 8 Line 8, "the groundwater discharge was characterized by higher nitrate and phosphate and lower nitrite than the offshore water. The daily maximum concentration of NOx, 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 3.3 & 3.4, 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 water 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 water. Therefore, the mixing of tidally-driven groundwater with lower nitrite and offshore water with higher nitrite results in the positive correlation of nitrite with water depth.

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 R2 of >=0.9. Nitrite is positively correlated with salinity, while nitrate and phosphate are negatively correlated with salinity. This will be explained briefly here and elaborated in the discussion in the revision 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 the 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 precipitation at the reef station, which will be further clarified in the revision. 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 will be clarified in the revision.

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

Response: the suggestion will be taken.

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: all of the information suggested will be provided in the revision.

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

Response: the suggestion will be taken.

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 will be presented in the revision. 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 will be clarified in the revision.

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

Response: the suggestion will be taken.

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 will be provided in the revision.

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: the suggestions will be taken in the revision.

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 suggestion will be taken in the revision.

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 will be provided.

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 suggestions will be taken.

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 the software SigmaPlot. Reference will be provided.

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 re-suspension of sediments, without biological observations. This sort of information will be provided with references to support our discussion.

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: references will be provided.

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 will be made. Good catch.

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 will be combined into one figure.

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 R2 just implies that the correlation is not as good as that with a greater R2. The value of R2 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 will be taken.

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 will be taken.

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

Response: the suggestion will be taken.

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 R2 just implies that the correlation is not as good as that with a greater R2. The value of R2 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 will be taken.

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 dis-

charge 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 calciïňĄcation/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 inïňĆuenced 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 ïňĆow 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 already presented in the ES&T paper were 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 at least one week before our sampling. So the only possible source of fresh water at this station is groundwater. This is confirmed by the significant negative correlation between 228Ra and salinity as presented in Fig. (5b). Water exchange with the adjacent ocean water was already considered in the manuscript. In the revision horizontal distributions will be plotted to cover the time-series station. At Station CT, because it is so close to the coast, the groundwater discharge from the seabed is that from the coast. Although nutrients peaks appeared around the highest 228Ra activity (the greatest groundwater discharge), the correlation between nutrients and 228Ra is not significant.

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 ïňĆow and ïňĆood tide of the spring tide, the difference between nitrite and nitrate (or phosphate) during the ïňĆood 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 of the spring tide on Feb. 7, when the full moon occurred, were selected as shown in Fig. 8 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 water would be most obvious from data on this day. These are the reasons why only data on this day were selected. There are 5 data points for the ebb flow of the spring tide on Feb. 7, 2012. As Fig. 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 Fig. 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. The logic is clear here. From the water depth vs. date plot (Fig. 3), the tidal speed can be estimated from the difference in water depth divided by the difference in date (i.e., deltah/deltat), the slope of the curve. This will be added in the revision when mentioning faster or slow speed of the tide for clarity.

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 ïňĄltering, storage, and measurement processes.

Response: the blanks were directly set up as the baselines during the measurement process and subtracted. This will be added here in the revision. 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 mmol kg-1 for nitrate, 0.0-0.6 mmol kg-1 for nitrite, 0.0-3.0 mmol kg-1 for phosphate, 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 our measurements are reliable.

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: We do have tidal level data. But it is kind of subjective to separate the spring tide period from the neap tide period for these continuous days. For a full-moon day and a quarter-moon day it is easy to tell them apart. 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 m2 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 period of the full-moon day (Feb. 7, 2012) to the quarter-moon day (Feb. 14, 2012). That is how we cut the line between Feb. 9 and Feb. 10, 2012. In the revision the formula of variance will be provided for clarity.

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

Response: Silicate was accidently cut in Fig. 4. Thanks for catching this. It will be added back. That silicate was not significantly correlated with NOx during the spring tide, while was significantly correlated with NOx during the neap tide was 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 biological processes were predominant in regulating the composition of nutrients. This is consistent with our conclusions.

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

clear enough.

Response: Significant digits will be checked and corrected. Fig. 1b will be plotted with higher resolution.

Interactive comment on Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-156, 2017.

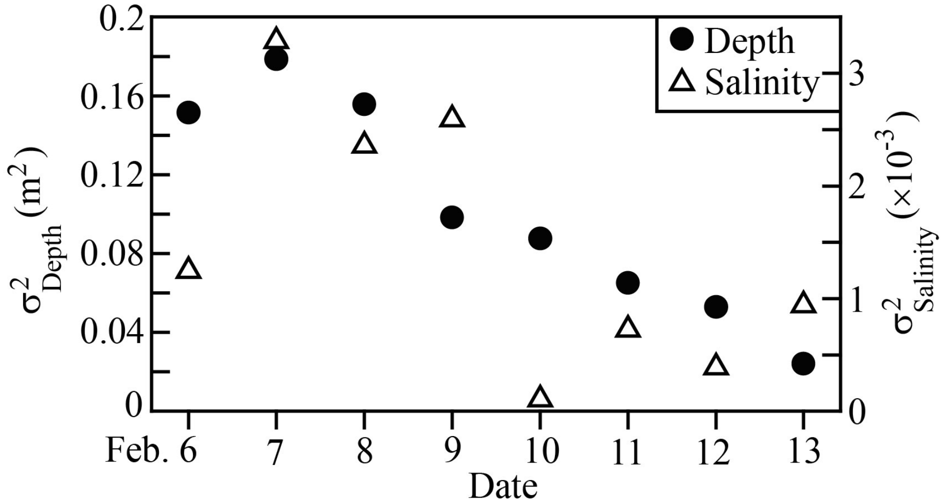

Fig. 1. Figure 2: Daily variance of water depth (ïĄş2Depth) and salinity (ïĄş2Salinity) at the coastal reef station CT during February 6-13, 2012.

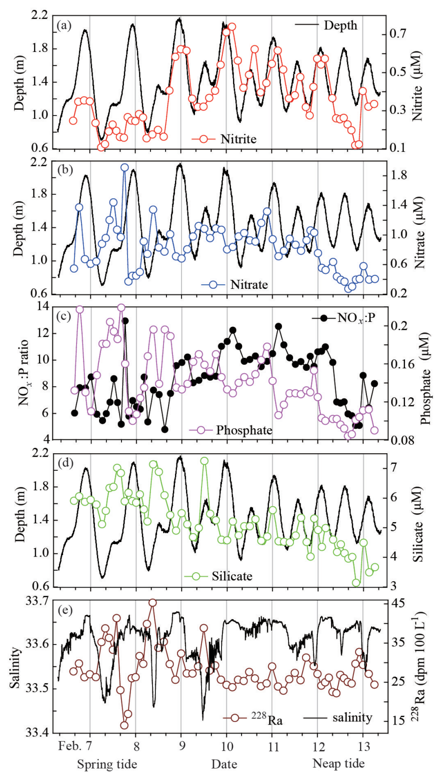

Fig. 2. Figure 3: Time-series observations of nutrients and 228Ra at Station CT in the Luhuitou reef of Sanya Bay, China during February 6-13, 2012.

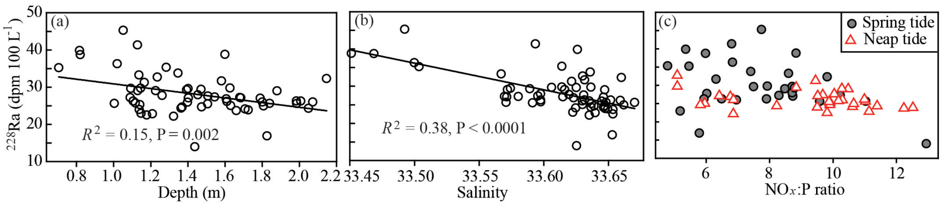

Fig. 3. igure 5: The activity of 228Ra against water depth, salinity and the NOx:P ratio in the water column at Station CT during February 6-13, 2012.

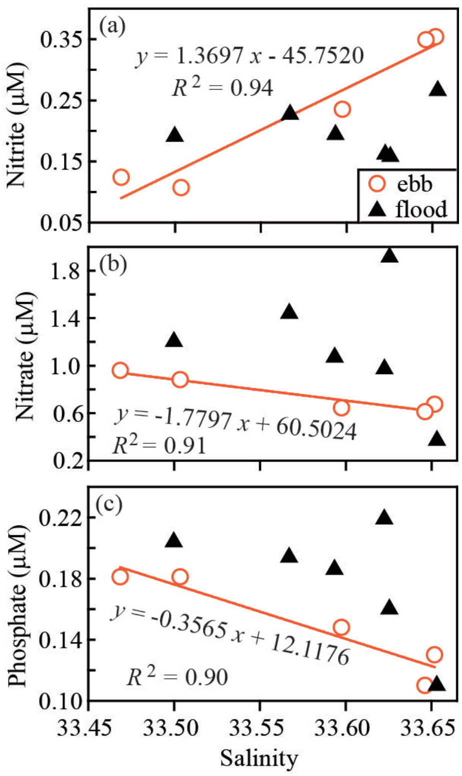

Fig. 4. Figure 8: Behaviours of nutrients with salinity during the ebb flow and flood tide of the spring tide at Station CT.

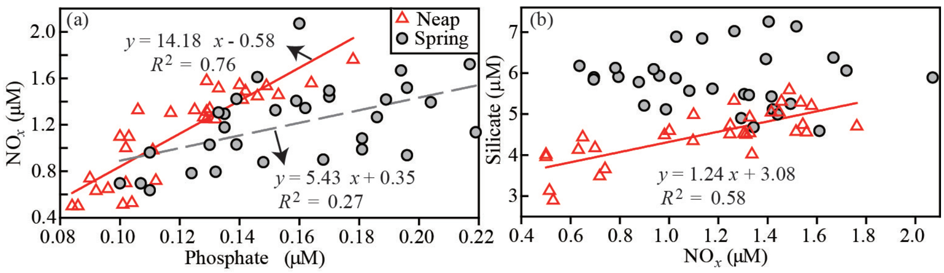

Fig. 5. Figure 7: Concentrations of nutrients in the water column against each other during the spring tide and neap tide at Station CT during February 6-13, 2012.

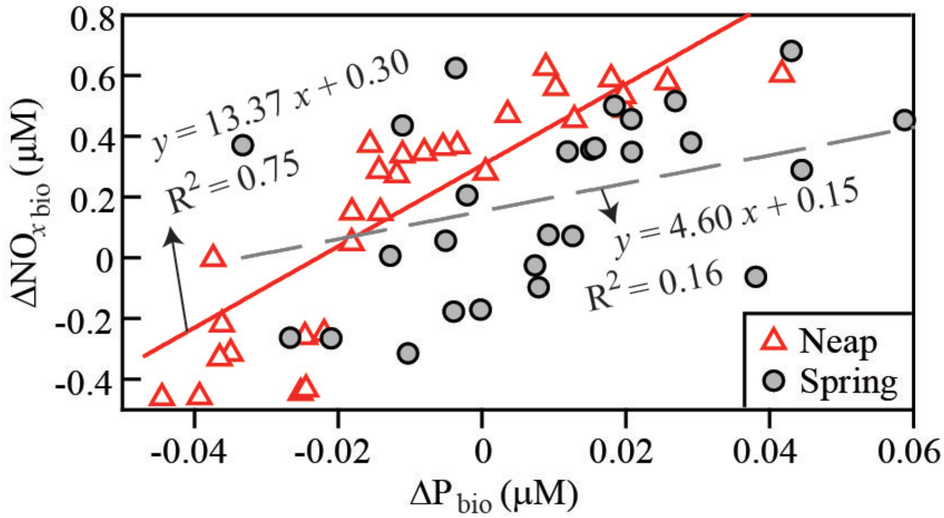

Fig. 6. Figure 10: Relationship between biologically contributed NOx and phosphate during the spring tide and neap tide at Station CT in the Luhuitou fringing reef in February 6-13, 2012.