Authors' responses to reviewers' comments (bg-2016-42)

Biogeosciences Manuscript #: bg-2016-42

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Title: The silica-carbon biogeochemical cycle in the Bohai Sea and its responses to the changing terrestrial nutrient loading

Dear Reviewer,

Thank you very much for your attention and the useful comments and suggestions for improvement on our paper BG-2016-42. Based on the comments, we have made extensive modifications (point by point) of the original manuscript. We attach the revised manuscript with changes marked as PDF, as well as the document with our responses to your comments.

Kind regards,

Jun Liu, Lex Bouwman, Jiaye Zang, Chenying Zhao, Xiaochen Liu, Zhigang Yu, Ran Xiangbin

General comments:

The manuscript describes the results from two campaigns in the Bohai Sea, China and computes Si and C budgets for the coastal system. There were many measurements made, but also data from the literature was necessary to compute budgets. The methods section is not clear, so it is difficult to partly understand how the measurements were made and how many samples were collected. Although large spatial gradients were observed in water column Si and C concentrations, a 1D box model integrated over the coastal bay was used to calculate the budgets. The primary production of the system was then related to the water, sediment and nutrient inputs from riverine inputs. I am not confident in the adequacy of the measurements or the budget produced. Details regarding the results and calculations in the manuscript are not well described. The manuscript requires extensive revisions. However, once revised it will not make a significant contribution to the biogeosciences.

Response: Thanks for the reviewer's constructive and insightful suggestions, which make a significant improvement on the manuscript. We have made extensive modification according to the comments. We focused more on the details of methods and discussing the Si-C budget, and impact processes in the revised manuscript. The method was reorganized, and the sample number and data from this study and references were added in the Method and Table 1, 2 and 3. For the budget, the exchanges between the Bohai and Yellow seas were recalculated using our data (spring and fall) and other available data from latest published works to make the budget robust. In addition, a new section "*4.4 The uncertainty of budget*" was added to evaluate the accuracy of our budget. Additional, some original data were attached in "*SUPPLEMENTARY INFORMATION*".

Though the connection between the changes in nutrient loading and ecosystem variation in coastal areas has been widely studied (Humborg et al., 1997; Bernard et al., 2011), but unfortunately the study in Bohai Sea did not cover riverine Si input to coastal marine ecosystems and consequences for the C cycle. In addition, the water and sediment regulation of the Yellow River since 2002 has greatly changed the nutrient input to the Bohai Sea in the time scale, resulting in a large proportion of total annual silicate (30-60%), DOC (36%) and POC (86%) input to the Bohai Sea during the water-sediment regulation event (Wang et al., 2012; Gong et al., 2015; Liu et al., 2015), and also enhances the annual Si and C fluxes in comparison with that in the period 1990-2001, when zero flow was frequently observed in the Yellow River. Thus, the magnitude of nutrient input under a dam-orientated artificial regulation within a short period would bring significant influence on the ecosystem, which is the dominant difference to the other marine systems affected by rivers in the world. Therefore, our work quantifying the influence of changing terrestrial loadings on the Si and C cycles and primary production in the Bohai Sea would provide a new insight on the land-sea interaction. So, we believe the revised manuscript can make a significant contribution to the Biogeosciences.

Specific comments:

(1) How many water samples were taken in Bohai Bay and where were they located?

Response: There were no samples in the Bohai Bay of the two campaigns in 2012. The diffusive fluxes in the Bohai bay were referred from Liu et al. (2011), and exchanges between the Bohai and Yellow Seas were calculated based on the Si-C concentrations from southern Bohai Sea and northern Yellow Sea.

In the revised manuscript, the numbers of samples were added in the Method and Tables.

(2) Lines 66-76: This paragraph is difficult to understand. Both changes in the river and in the Sea are mixed together. They present the idea that river regulation of the Yellow River has changed, but do not mention what changes were made.

Response: This suggestion was followed. We stated the changes were produced by the regulation of the Yellow River, and have corrected and reorganized this paragraph and the following two paragraphs in the revised manuscript. The new text is as follows:

The Bohai Sea is a semi-enclosed, shallow shelf water body of the northwestern Pacific Ocean, with a surface area of 77,300 km^2 and an average depth of 18 m. A large number of rivers drain into the Bohai Sea, typically with densely populated and industrialized coastal areas. The Yellow River is the largest river draining into the Bohai Sea. Human activities (dam construction, agriculture and industry) have induced important changes in the river discharge, sediment load and nutrient concentrations in the past decades (Gong et al., 2015; Liu, 2015). A substantial decrease of Si/N ratio in the Bohai Sea is attributed to the reduction of the Yellow river discharge (Ning et al., 2010) and dam construction (Liu, 2015; Ran et al., 2015).

The water residence time in the Bohai Sea is about 3 years (Liu et al., 2012). Changes of nutrient inputs from rivers in the semi-enclosed Bohai Sea therefore have a larger and more prolonged influence on the ecosystem than in open seas. The phytoplankton abundance in the Bohai Sea had decreased in the period of 1959–1999 (Tang et al., 2003) and a shift from a system dominated by diatoms to one dominated by non-diatoms has been observed in the 1980s and 1990s (Lin et al., 2005). However, the primary production has been increasing (Tan et al., 2011) since the regulation of water and sediment in the Yellow River started in 2002.

There may be a close connection between the changes in nutrient loading and primary production in coastal marine ecosystems (Bernard et al., 2011). The C cycle in shelf seas is sensitive to changing riverine loading due to anthropogenic perturbations (Li et al., 2014; Woodland et al., 2015), but unfortunately the effect of changing riverine Si export on the C cycle was not studied. The most important change was a result of the dam-based water and sediment regulation of the Yellow River since 2002; this regulation caused a large proportion of total annual DSi (30-60%), DOC (36%) and POC (86%) input to the Bohai Sea to be concentrated in the months of June and July with a slight increase of the annual fluxes (Wang et al., 2012; Gong et al., 2015; Liu et al., 2015) and with important impacts of the Bohai Sea ecosystem.

(3) Line 93: Two campaigns for water column measurements are inadequate to produce meaningful mass balances.

Response: Thanks for the reminding. Few campaigns for water column measurements may be inadequate to Si and C budgets in the Bohai Sea, which is more significant to the exchanges between the Bohai and Yellow Seas (F_E) and diffusive fluxes (F_B). We therefore added some available data from other seasons to make sure our budget robust. The main revision is as follows:

The RSi and OC fluxes through the Bohai Strait were calculated using the water flux together with the measured RSi and OC concentration data from the Southern Bohai Sea and the Northern Yellow Sea (Table 1). DSi are collected from this study (May and November 2012) and Yang et al. (2014) (June and July 2013); BSi are collected from this study (May and November 2012); DOC are collected from this study (May and November 2012) and Zhao et al. (2015) (September 2010); and POC are collected from this study (May and November 2012) and Shang et al. (2011) (September 2010). Diffusive fluxes of DSi were from Liu et al. (2011) and this study. In addition, the sample number and data from this study and references were added in the Method and Table 1.

(4) Lines 103-105: Were the filters cleaned using this method or were the samples processed using this method?

Response: Filters were cleaned using this method. It has been rewritten as follows:

Water samples were filtered with 200 μm Nylon sieves to remove zooplankton, subsequently filtered with 0.45 μm polyethersulfone filters Filters were pretreated according to the following four steps: cleaned with 1:1000 HCl for 24 h; rinsed with Milli-Q water to achieve a neutral pH; oven-dried at 45°C for 72h; weighed after cooling in a dryer with desiccant. Then filters with particulate matter were stored at -20°C for determination of suspended particulate matter (SPM) and BSi, and filtrates were stored at 4°C after adding drops of chloroform for determination of DSi.

(5) Line 225: Was atmospheric deposition from a model or from measurements?

Response: Atmospheric deposition was from measurements referred to Zhang et al. (2004) and Xu et al. (2016).

(6) Lines 277-284 Using satellite remote sensing to calculate primary productivity in a coastal area with sediment inputs is difficult. Further, extrapolation of uptake rates from standard nutrient ratios is not sufficient.

Response: Primary production was estimated from the average primary production in the euphotic layer, obtained by satellite remote sensing technology calibrated against measured productivity (Tan et al., 2011), in which the chlorophyll-a concentrations are very close to the data from Fu et al. (2016) using the same method.

The rates of DSi uptake by phytoplankton and BSi regeneration rate were calculated using the Redfield ratio (C: Si=106: 15, atom basis, Brzezinski, 1985), which is also close to the molar ratio of BSi: POC (0.12) in the suspended particulate matters in the Bohai Sea from our measured results. Thus using the standard nutrient ratio to calculate uptake rates is reasonable in this study. And the method using Si: C in the suspended particulate matters to evaluate DSi uptake rates and BSi production rates has been applied in the Jiaozhou Bay (Liu et al., 2008) and East China Sea (Liu et al., 2005).

(7) Lines 368-369: If there was a large spring diatom bloom, couldn't the high bottom water column concentrations be due to settling?

Response: This suggestion is followed. We added the relative text in the revised manuscript. The new text is as follows:

The main reason why BSi in the bottom water exceeds that in the surface water in parts of the Bohai Sea is largely due to sediment resuspension (Liu et al., 2005) and diatom deposition (Wei et al., 2008).

(8) Lines 480-482: The dissolved silica concentrations show not evidence for Si limitation of DIATOMS. However, even if the Bay becomes dissolved silica limited there are other algae that do not require Si, so I do not understand how the system is not limited by N and/or P.

Response: Thanks for the reminding. As the referee said, the DSi concentrations show not evidence for Si limitation of diatoms in the Bohai Sea, currently. Meanwhile, there is almost no evidence of P limitation on the basis of P concentrations (>0.1 μmol L^{-1}). But a substantial decrease of Si/N ratio and Si concentration in the Bohai Sea is attributed to the reduction of the Yellow river discharge from 1960 to 1996 (Ning et al., 2010), which may bring negative consequence in the study area.

Since 2002, the Yellow Rive has been witnessed 14 times water and sediment regulation, which has greatly changed the nutrient input to the Bohai Sea in the time scale, resulting in a large proportion of total annual DSi (30-60%), DOC (36%) and POC (86%) input to the Bohai Sea (Wang et al., 2012; Gong et al., 2015; Liu et al., 2015) during the water-sediment regulation event (generally in June and July). Thus, the magnitude of nutrient input under a dam-orientated artificial regulation within a short period would bring significant influence on the ecosystem, which is the dominant difference to the other marine systems affected by rivers.

Therefore, anthropogenic perturbations on the silicon cycling and their influence on phytoplankton and primary production in the Bohai Sea needs to further study, and this is an important work for us in the future.

(9) There are an excessive number of references.

Response: This suggestion is followed. We removed some irrespective or old references in the revised manuscript.

(10) The BSi data in Table 3 has extremely low numbers in the sediments and surprisingly low standard deviations, especially when you compare it to the data in Figure 4 that has large spatial variations in BSi. In addition, sediment BSi concentrations then to be relatively invariant with time, but there are large differences spatially in BSi concentrations between the spring and fall samplings. I find it difficult to believe these numbers.

Response: We have carefully checked the data, and there is no mistake in Table 3.

Actually, Sediment BSi concentrations in surface sediments of the same stations between seasons have no significant difference at the 95% confidence level. Maybe the scale of legend brings a confusing signal in Figure 4 (Figure S3 in the revised manuscript), which enhances gain to show the variation among different stations. The original data of sedimentary BSi and TOC were provided below in order to solve these problems (Table R1 for response only).

Additional, the measurements for DSi, BSi and POC were calibrated with different methods; we have addressed this point in No. 10 response for the first referee.

Table R1. Biogenic silica (%) and total organic carbon contents (%) of the surface sediment in the Bohai Sea.

Spring			Fall		
Station	BSi	TOC	Station	BSi	TOC
B36	0.31	0.20	B39	0.20	0.10
B45	0.51	0.37	B41	0.42	0.60
B49	0.41	0.10	B42	0.40	0.27
B50	0.61	0.48	B43	0.51	0.45
B61	0.41	0.66	B45	0.54	0.53
B65	0.31	0.26	B47	0.51	0.37
B71	0.29	0.19	B49	0.29	0.20
			B50	0.60	0.67
			B53	0.42	0.50
			B54	0.27	0.19
			B63	0.69	0.60
			B64	0.33	0.55
			B65	0.41	0.44
			B66	0.21	0.21
			B68	0.21	0.10
			B69	0.41	0.44
			B70	0.21	0.17
			YD01	0.21	0.24

References:

Bernard, C. Y., Laruelle, G. G., Slomp, C. P., and Heinze, C.: Impact of changes in river fluxes of silica on the global marine silicon cycle: a model comparison, Biogeosciences, 7, 441-453, doi:10.5194/bg-7-441-2010, 2010.

Brzezinski, M. A.: The Si: C: N ratio of marine diatoms: interspecific variability and the effect of some environmental variables, J. Phycol., 21, 347-357, doi:10.1111/j.0022-3646.1985.00347.x, 1985.

Fu, Y. Z., Xu, S. G., and Liu, J. W.: Temporal-spatial variations and developing trends of Chlorophyll-a in the Bohai Sea, China, Estuar. Coast. Shelf S., 173, 49-56, doi:10.1016/j.ecss.2016.02.016, 2016.

Gong, Y., Yu, Z. G., Yao, Q. Z., Chen, H. T., Mi, T. Z., and Tan, J. Q.: Seasonal Variation and Sources of Dissolved Nutrients in the Yellow River, China, Inter. J. Env. Res. Pub. Heal., 12, 9603-9622, doi:10.3390/ijerph120809603, 2015.

Humborg, C., Conley, D. J., Rahm, L., Wulff, F., Cociasu, A., and Ittekkot, V.: Silicon retention in river basins: far-reaching effects on biogeochemistry and aquatic food webs in coastal marine environments, AMBIO, 29:45–50, doi:abs/10.1579/0044-7447-29.1.45, 2000.

Humborg, C., Ittekkot, V., Cociasu, A., and Bodungen, B. V.: Effect of Danube River dam on Black Sea biogeochemistry and ecosystem structure, Nature, 386, 385-388, 1997.

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

Li, Z. Y., Bai, J, Shi, J. H., and Gao, H. W.: Distributions of inorganic nutrients in the bohai sea of china, J. Ocean

Univ. China, 2, 112-116, doi:10.1007/s11802-003-0038-8, 2003.
Lin, C. L., Ning, X. R., Su, J. L., Lin, Y., and Xu, B.: Environmental changes and the responses of the ecosystems of the Yellow Sea during 1976–2000, J. Marine Syst., 55(3), 223-234, doi:10.1016/j.jmarsys.2004.08.001, 2005.
Liu, D., Pan, D. L., Bai, Y., He, X. Q., Wang, D., F. and Zhang, L.: Variation of dissolved organic carbon transported by two Chinese rivers: The Changjiang River and Yellow River, Marine Pollution Bulletin, 100(1), 60-69, doi:10.1016/j.marpolbul.2015.09.029, 2015.
Liu, S. M., Li, L. W., and Zhang, Z.: Inventory of nutrients in the Bohai, Cont. Shelf Res., 31, 1790-1797, doi:10.1016/j.csr.2011.08.004, 2011.
Liu, S. M., Ye, X. W., Zhang, J., Zhang, G. S., and Wu, Y.: The silicon balance in Jiaozhou Bay, North China, J. Marine Syst., 74, 639-648, doi:10.1016/j.jmarsys.2008.06.001, 2008.
Liu, S. M., Zhang, J., and Li, R. X.: Ecological significance of biogenic silica in the East China Sea, Mar. Eco-Prog. Ser., 290, 15-26, 2005.
Liu, S. M.: Response of nutrient transports to water–sediment regulation events in the Huanghe basin and its impact on the biogeochemistry of the Bohai, J. Marine Syst., 141, 59-70, doi:10.1016/j.jmarsys.2014.08.008, 2015.
Liu, Z., Wang, H. Y., Guo, X. Y., Wang, Q., and Gao, H. W.: The age of Yellow River water in the Bohai Sea, J. Geophys. Res., 117, C11006, doi:10.1029/2012JC008263, 2012.
Nelson, D. M., Tréguer, P., Brzezinski, M. A., Leynaert, A., and Quéguiner, B.: Production and dissolution of biogenic silica in the ocean: revised global estimates, comparison with regional data and relationship to biogenic sedimentation, Global Biogeochem. Cy., 9, 359-372, doi: 10.1029/95GB01070, 1995.
Ning, X., Lin, C., Su, J., Liu, C., Hao, Q., Le, F., and Tang, Q.: Long-term environmental changes and the responses of the ecosystems in the Bohai Sea during 1960–1996, Deep-Sea Res. Pt. II, 57, 1079-1091, doi:10.1016/j.dsr2.2010.02.010, 2010.
Ran, X. B., Che, H., Zang, J. Y., Yu, Y. G., Liu, S., and Zheng, L. L.: Variability in the composition and export of silica in the Huanghe River Basin, Sci. China: Earth Sci., 58: 2078-2089, 10.1007/s11430-015-5064-z, 2015.
Rodellas, V., Garcia-Orellana, J., Masqué, P., Feldman, M., and Weinstein, Y.: Submarine groundwater discharge as a major source of nutrients to the Mediterranean Sea, P. Natl. Acad. Sci., 112, 3926-3930, 2015.
Shang, R. L.: The distribution and influence factors of Organic Carbon in the Bohai Sea and Yellow Sea of 2010, Master's thesis, China: Ocean university of China, 2011. (in Chinese)
Tan, S. C., Shi, G. Y., Shi, J. H., Gao, H. W., and Yao, X.: Correlation of Asian dust with chlorophyll and primary productivity in the coastal seas of China during the period from 1998 to 2008, J. Geophys. Res.: Biogeosciences, 116, G02029, doi:10.1029/2010JG001456, 2011.
Tang, Q., Jin, X., Wang, J., Zhuang, Z., Cui, Y., and Meng, T.: Decadal-scale variations of ecosystem productivity and control mechanisms in the Bohai Sea, Fish. Oceanogr., 12, 223-233, DOI: 10.1046/j.1365-2419.2003.00251.x, 2003.
Wei, G.. F., Tang, D. L., Wang, S. F.: Distribution of chlorophyll and harmful algal blooms (HABs): A review on space based studies in the coastal environments of Chinese marginal seas, Adv. Space Res., 41(1), 12-19, doi:10.1183/09031936.97.10071530, 2008.
Willey, J. D., Kieber, R. J., Eyman, M. S., and Avery, G. B.: Rainwater dissolved organic carbon: concentrations and global flux, Global Biogeochem. Cy., 14, 139-148, doi:10.1029/1999GB900036, 2000.
Xu, C. L., Lou, C. L., Xue, Y. J., Ge, T. T., and Wang, X. C.: Concentration and source assessment of dissolved organic and inorganic carbon and dissolved nitrogen in snow and rainfalls in Shandong Province, Acta Sci. Circum., 36(2), 658-666. doi:10.13671/j.hjkxxb.2015.0540, 2016.

Yang, G. P., Song, Y. Z., Zhang, H. H., Li, C. X., and Wu, G. W.: Seasonal variation and biogeochemical cycling of dimethylsulfide (DMS) and dimethylsulfoniopropionate (DMSP) in the Yellow Sea and Bohai Sea, J. Geophys. Res.: Oceans, 119(12), 8897-8915, doi:10.1002/2014JC010373, 2014.

Zhang, J., Yu, Z. G., Raabe, T., Liu, S. M., Starke, A., Zou, L., Gao, H. W., and Brockmann, U.: Dynamics of inorganic nutrient species in the Bohai seawaters, J. Marine Syst., 44, 189-212, doi:10.1016/j.jmarsys.2003.09.010, 2004.

Zhang, X. L., Wu Z. M., Li, J., G. Y., Zhang, Z. N., and Gao, S. H.: Modeling study of seasonal variation of the pelagic-benthic ecosystem characteristics of the Bohai Sea, J. Ocean Univ. China, 5, 21-28, 2006.

Zhao, B. Z., Yang, G. P., Xie, H., Lu, X. L., and Yang, J.: Distribution, flux and photoproduction of carbon monoxide in the Bohai and Yellow Seas, Mar. Chem., 168, 104-113, doi:10.1016/j.marchem.2014.11.006, 2015.