Biogeosciences Discuss., 6, S126–S135, 2009
www.biogeosciences-discuss.net/6/S126/2009/

Biogeosciences
Discussions

Interactive comment on "Nutrient budgets for large Chinese estuaries and embayment" *by* S. M. Liu et al.

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Received and published: 20 February 2009

General comments

This paper reports potentially valuable data of nutrient elements in 18 rivers emptying into the Chinese marginal seas; it also reports nutrient data in coastal embayment and adjacent marginal seas. Based on these data sets, calculations of nutrient budgets are made with the LOICZ-type steady-state box models constrained by salinity balance. It is evident that the authors spent much effort to compile the large dataset and even more effort to make box-model calculations for each of the 7 estuarine and 8 embayment systems receiving discharges from these Chinese and Korean rivers. However, the authors did little more than listing the data as they are without interpreting the meaning of the rich data; they also present the model output without justifying the fluxes they derive from box models. The conclusions reached by the authors are either well known facts or assertions unsubstantiated by the evidence they present. In fact, some of the model results are puzzling and probably erroneous. The authors appear to have missed the problems standing out of the results and do not provide any argument to explain anomalous findings. Some of the problematic results apparently stem from the data themselves, casting serious doubt over the data quality. Some of the findings indicate that the simple steady state approach is not applicable in many cases.

To raise this contribution above the level of a data report, the authors are encouraged to limit the scope of their study to the interpretation of their most important data set, namely, nutrient concentrations in river discharges. They may adopt some of the approaches recently employed by several groups in analyzing nutrient data from numerous river systems. They need to demonstrate similarities and differences between their systems and other systems. If there is consistency between this dataset and others or the differences can be reasonably well explained, the authors may start to work on the models to explore implications of their dataset on the coastal ecosystem. In the process, I believe new findings and better understanding of the nutrient dynamics in the studied watersheds will emerge. Otherwise, the authors would fail to do justice to the potentially valuable dataset they possess.

Specific comments

1. Introduction:

The authors rightfully note that the delivery of river borne nutrients has been strongly modified by changes in land use and by anthropogenic emissions. They continue to stress the wide latitudinal coverage of the study area and diverse climate conditions, which make their study area ideal in delineating how natural conditions may affect the nutrient loads in rivers. Unfortunately they scarcely discuss how these natural and human factors may have influenced the nutrient data presented in the manuscript. If they practice what they preach, their contribution will be very valuable. Several recent synthesis papers (e.g., Smith et al., 2003; Seitzinger et al. 2005), which seem to have been missed by the authors, serve as good examples for the authors to follow.

In my opinion, the box model calculation should be presented in a separate paper, leaving this paper to deal with only the river loads of nutrients, which deserve a paper dedicated to the rich meanings buried in their data. For the box model paper, it is strongly recommended to include figures illustrating each of the estuarine or embayment systems. The water turnover in the coastal water bodies is critically dependent on their geometric features, such as the channel width or constrictions. The figures would provide the much needed background information to readers outside the circle familiar with the Chinese and Korean coastal environments.

2. Materials and methods: Since most of the data seem to have been taken from other published papers, the brief sketch of the sampling and analytical methods is acceptable. However, the single most important fact that must be clearly stated is the accuracy or, at least, the precision of the reported data. It is simply unacceptable to merely state, [All the nutrient data were measured by spectrophotometric method with precision $<$3%.] (p. 395 Line 18) Accuracy of the data is critical, when some derived quantities are concerned. For instance, the authors repeatedly stress the very high N/P ratio up to 2800. I could not find the data that may substantiate this high value. The closest I can get is the Daguhe data that the total dissolved inorganic nitrogen concentration is 160.05 uM and the phosphate concentration is 0.08 uM. There is no way that the precision of the phosphate value can be better than +/-3%, which corresponds to absolute values as low as +/-0.0024 uM. For example, in the Strickland and Parsons classical manual, they report the precision of phosphate analysis to be +/-0.03 uM for phosphate concentration at 3 uM and +/-0.02 uM for 0.3 uM. If the phosphate concentration of the Daguhe has a precision of +/-0.02 uM, then the uncertainty of the N/P ratio is as large as +/-500.

Moreover, the box model calculation is constrained mainly by the salt balance, which is critically dependent on the accuracy of the salinity data of the coastal system and the adjacent open sea. Therefore, description of the salinity determination method (CTD

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measurements or salinometer determination) and the accuracy of the measurements should be provided.

3. Biogeochemical modeling approach: The formulation of the box model is inaccurate and confusing in several aspects. The problems indicate that the authors are probably sloppy about their modeling exercise or, worse, misunderstand the model.

3.1. Exchange flow (Vx): The original formulation of Gordon et al. (1996) is as follows:

Vx = [V1dS1/dt + Vr*Sr]/(S1-S2), (1)

where V1 is the volume of the system, which is assumed constant, S1 and S2 are the salinity of the system and the adjacent open sea, VR is the residual flow and SR is the salinity of the residual flow. For the steady state condition, the differential term is zero. The resultant equation becomes the following.

Vr*Sr = Vx (S1-S2), (2)

or

Vr*Sr = Vs (Ssys-Soce), (3)

The right hand term has the opposite sign of that in Eq. (2) of the manuscript. This difference could be due to differences in definition. In the original definition of Gordon et al. (1996) as shown in Eq. (3), Vr and Vx usually have opposite signs because SR is always positive while (Ssys-Soce) is usually negative. If the authors definition is the opposite of Gordon et al., then Vr and Vx should be mostly of the same sign. Oddly, the listing of Vr and Vx in Tables 5a and 5b show them mostly in opposite signs.

3.2. Non-conservative flux: The non-conservative flux, such as DeltaDIP, in the paper is defined in the opposite sign of the original definition (Gordon et al., 1996). This is OK as long as the authors stick to their definition. If so, they should note the difference so that the readers will not get confused. However, there are signs to be discussed later that the authors are confused themselves about the signs.

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3.3. Steady state: The authors skip the original mass balance equations, such as Eq. 1 listed above. Consequently, they fail to qualify the conditions that may allow simplification of the time-dependent model to the steady-state case. The time-dependent term, V1dS1/dt, may be ignored, if the following is true.

V1 |dS1/dt| $<<$ |Vr*Sr|, (4)

The time-dependent term may be assessed through the following approximation:

|dS1/dt| = (|S1(t2)- S1(t1)|) /(t2-t1), (5)

where (t2-t1) represent the time span of the period examined by the model. In this study, the winter or summer conditions are examined. Then the time span is 6 months. Thus Eq. 5 may be expressed as the following:

(t2-t1)(V1/(|S1(t2)- S1(t1)|) $<<$ |Vr*Sr|, (6)

This condition may be examined with the data presented by the authors. If the condition does not hold, then the steady state approximation cannot be applied.

4. Results and discussion

4.1. Nutrients in rivers:

4.1.1 The authors repeatedly stress two facts, high N/P ratio in Chinese rivers and weathering controlled silicate concentrations, which are all well known. They also repeat 3 times in the paper that the N/P ratio could be as high as 2800, but the data listed in Table 2a give the maximum N/P ratio of 2000 instead of 2800. Aside from the unsubstantiated claim, they never once mention the very large range of the N/P ratio, from 23 (for Huaihe) to 2000 (for Daguhe) nor do they provide any explanation of the very large range. The authors suggest that the high N/P ratio is attributed to the high N/P ratio in fertilizers used in China (p. 398 Line 20) and the stronger tendency of nitrogen leaching (p. 398 Line 21). Then, why is it the case the large North American and European rivers with strong agricultural input show considerably higher N/P ratios and DIP concentrations? In other words, the Chinese rivers appear to be depleted in phosphate. This may contribute to the very high N/P ratio in addition to nitrogen enrichment. It is also puzzling why some of the rivers have drastically different N/P ratio in different seasons. For example, Daguhe has N/P ratio of 2000 in March but less than 300 in August, while Daliaohe is the other way around, 188 in May and 64 in August. What kind of nutrient dynamics could have caused such contrasting behavior. The wild fluctuations of the properties make readers wonder how reliable or representative the data are.

4.1.2. As for the increasing silicate concentration in the southern rivers due to warmer climate, the authors do not give any explanation why the silicate concentrations of Huanghe are almost the same as those of Zhujiang, the southernmost river (Table 2a). The authors also claim that warmer and wetter climate favor faster silicate weathering. Then it is perplexing why the silicate yields of the Changjiang and Zhujiang watersheds are at the same level as the Yalujiang watershed.

4.1.3. Another interesting feature barely mentioned by the authors is the contribution of ammonium to the nitrogen load. Some of the rivers have very high ammonium contributions. Two of the Korean rivers, Han and Jun, have ammonia concentrations accounting for more than half of the DIN loads. Jiulongjiang also has quite high ammonium contribution. This is rarely seen in North American or European rivers and deserves attention.

4.1.4. It is useful to calculate the nutrient yields of different watersheds, but the meaning of seasonal values is not clear to me. Production of nutrients in watersheds is usually a slow process. Even fertilizers have a retention time in farm lands longer than just one season. Although the calculation is straightforward mathematically, what the authors try to illustrate is not stated in the manuscript. It is most baffling that the silicate yields change so much seasonally in the two southernmost watersheds, Jiulongjiang and Zhujiang (Table 2c). It is inconceivable that silicate weathering which usually undergoes in the subterranean environment should change so much from summer to

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winter.

4.2. Nutrients in coastal waters:

4.2.1. Tables 3 and 4 list nutrient concentrations in coastal embayment and shelf waters. It is uncertain what the data represent because no background information about the data can be found. Are they average values of the whole water body or just the surface water? For the adjacent shelves, some of which are huge, what is the meaning of averaging over the entire shelf? For this study, only the shelf water close to the river mouth should be of concern because of its potential interaction with the estuarine processes. In other words, only the river plume is of significance to the nutrient budget of the estuarine system.

Since the authors intend to assess the impact of river carried nutrients on coastal ecosystem, it is worthy to discuss the elemental ratios of nutrient loads in coastal waters. However, judgment simply based on N/P ratio of dissolved inorganic species may end in unsound conclusions. Dissolved phosphate may be released from particulate species discharged from rivers. It has been shown that DIP availability may increase by as much as five times, once particulate phosphorus enters saline environment (Froelich 1988). Some fractions of dissolve organic phosphorus can also be utilized by algae readily (Cotner and Wetzel, 1992). The meaning of Fig. 2 is obscure to me. Why should an exponential relationship exist between N/P and P/Si? Or is it rather a simple inverse relationship because of P in the inverse position of the mathematical expressions? If it does not lend any support to the argument, it should be deleted.

4.2.2. The scope of the manuscript is further stretched to include nutrient exchange with the open ocean off the shelf edge. Inevitably the presentation is superficial and filled with random and trivial statements. Some of them are false. An example (p. 403, Lines 8-14) is given below.

[In the Bohai, horizontal movement of water and spatial variations tend to determine the

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distribution of chemical parameters. While vertical structure of nutrients is concerned, the South China Sea shows the typical open-ocean nutrient profiles with vertical distribution stable and unchanged,...]

Is it not generally true to all shelf waters that distribution of chemical parameters is determined by horizontal movement of water? On the other hand, it is false to say that nutrient profiles remain unchanged in the South China Sea.

It is best to limit the scope of this manuscript to river discharged nutrients and the coastal water adjacent to the river mouth. The cursory discussion on nutrients in the marginal seas is irrelevant and should be eliminated.

4.3. Nutrient transports to open seas:

4.3.1. The arguments here depend on the model output, which is not critically examined by the authors but taken as truth. First of all, the applicability of steady state approach need be examined. An easy criterion derived from Eq. 6 is as follows.

(t2-t1)(V1/(|S1(t2)- S1(t1)|)/|Vr*Sr| $<<$ 1, (7)

where t1 and t2 stand for summer and winter, respectively. For Table 5b, I found the index expressed as the left hand side of Eq. 7 ranging between 0.001 to 0.58. If taking 0.1 as the cut-off point, five cases out of the 16 in Table 5b do not qualify for steady state approach.

The calculated residence time provides another way to look at the issue. In five cases, the residence time is longer than six months, which is the maximum separate between the two seasons treated as two individual cases. If the water residence time is longer than the time separation, it means more than 37% of water from one season will remain until the next season. This is a clear contradiction to the steady state assumption, which presumes the salt and nutrient budgets are balanced within the season, when the data were taken. The erroneous approach is illustrated by the example of Jiaozhou Bay, for which the estimate is almost 3 years long for the winter case.

Although Jiaozhou Bay has a constricted entrance, it is inconceivable that it takes 3 years for its water to exchange with the open shelf. The estimate for the summer case, 13 days, is more reasonable.

On the other hand, some of the estimated values of residence time are very long for both winter and summer cases. For example, the estimates are about 3 and 10 months, respectively, for the summer and winter cases of Hangzhou Bay. It is hard to imagine that Hangzhou Bay with its very open bay mouth needs 3-10 months to turn its water over. The implausible estimates put the applicability of the model in doubt. Because the model is too simple to include tidal effects, the usefulness of model estimates is sometimes questionable. Some discussion may be in the paper by Asselin and Spaulding (1993).

4.3.2. The authors calculate the nutrient transport to the open sea by the following expression:

Fmodel = Cr*Vr + Cx*Vx,

where CX = Csys - Coce (p. 397 Line 14), which should be positive in most, if not all cases. It is puzzling that most entries of Cx*Vx in Tables 6a and 6b are negative, while both factors in the expression are positive.

There are cases that the calculated seaward transports of nutrients appear unaccountable. An example is the summer case for the Yalujiang. Its transport of nitrate to the shelf is shown to be -39.6 megamole per day (Table 7a). The river load, Cq*Vq, is 29.2 megamole per day (Table 6a). All other terms are negligible except the non-conservative flux, which is shown to be 10.4 megamole per day. As stated by the authors (p. 397 Line 14-16), a positive value of the non-conservative flux represents a sink that means removal of the nutrient. If that much of nitrate is removed in the estuary, how could it be possible to export more nitrate from the estuary than the river load? The modeling part of the paper is very confusing. The authors must think out thoroughly before they present the model results.

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Interactive comment on Biogeosciences Discuss., 6, 391, 2009.

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