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## ***Interactive comment on* “Phosphorus sorption and buffering mechanisms in suspended sediments from the Yangtze Estuary and Hangzhou Bay, China” by M. Li et al.**

**M. Li et al.**

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Response to comments (BG-2012-504): Anonymous Referee 2 Received and published: 2 January 2013 General comments: The manuscript focuses on sorption of phosphorus to suspended sediments in the Yangtze estuary in China, where the impact of sewage outfalls is large. Sorption experiments were performed and isotherms were fitted using known equations (Langmuir, Freundlich, Temkin) or an exponential expression. The authors show differences in the sorption behavior of the different sediments related to grain size and suggest the occurrence of precipitation of  $\text{CaHPO}_4$ . Incubations were also performed at lower phosphorus concentrations and different temper-

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atures to understand the buffer capacity of the sediments. The zero equilibrium concentration and the linear adsorption coefficient increased with temperature suggesting a higher buffering capacity at higher temperatures. The experimental design seems adequate and provides interesting information concerning phosphorus sorption to suspended sediments in the Yangtze estuary. I suggest some improvements in the figures and tables and a few questions about the text should be addressed. I recommend this manuscript for publication after minor revisions. Specific comments: Abstract. I find the first sentence confusing. What/Which are the mechanisms of the buffering effect? And the adsorption isotherms are not controls on the phosphorus behavior (but they are indeed useful to estimate phosphate concentrations in aquatic environments). I suggest a rephrasing of this sentence.

We apologize for the confusing description. We have changed it to “The buffering effect of phosphorus (P) by sediments is one of the most important controls on soluble P concentration in estuaries, while the adsorption isotherms are often used to estimate P concentration in aquatic environments”.

Section 2.1 Sampling. The title refers to suspended sediments but in the experiments bottom sediments were used. Some explanation on the assumptions made and on the extrapolation of the results from bottom sediments to suspended sediments would be helpful. Information on the natural suspended sediment concentrations typical for this area and how that relates to the particle concentrations used in the experiments would be helpful.

Thank you for your advices. (1) In this area, the bottom sediments exchanged with suspended sediments frequently and their particle size distributions were similar to those of suspended sediments. Another reason that we used the bottom sediments in our experiments was because the bottom sediments were easy to be collected. During experiments, conical flasks containing sediments and artificial sea water were shaken continuously to ensure all particles were suspended, so we used suspended sediments in our manuscript. (2) The particle concentrations in the bottom of this estuary are

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between 0.3g/L and 27g/L, so we chose 5g/L in our experiments, which is a common particle concentration in this area. Hope we have made the referee's concerns clear and we accordingly have modified the manuscript.

Table 1. I believe the DIP concentrations refer to the water column and not porewater. That could be stated more clearly. Information on the porewater phosphate concentrations would be helpful since that's the concentration at which the sediments were equilibrated after deposition.

Thank you very much for your suggestions. The DIP concentrations in Table 1 are indeed about the water column samples. We have modified the footnote under Table 1. We will consider the porewater phosphate concentrations in our subsequent study.

Section 2.2 Isothermal adsorption isotherms. Why were the sediments ground? I see no advantage in that and it will potentially bias the results by increasing the surface area available for sorption. 24h of incubation might be a short period to achieve equilibrium based on previous literature (van Raaphorst and Kloosterhuis 1994, Leote et al. 2012). Was this checked?

The sediments were ground after transported to laboratory for a better storage. Since we could not conduct all the experiments immediately, it would be better to store the ground sediments for subsequent experiments. Previous studies used the same approach as far as we know. 24h of incubation was based on our previous experiments and we had cited the reference in the revised manuscript. Actually, as the referee mentioned that 24h might not be enough for a real equilibrium, but it could reach 95-98

Section 3.1 Adsorption isotherm models. Lines 5, 7, 10, 21 and 24. The use of P adsorption density is more adequate than P adsorption capacity. Line 18-Ion product calculation. I have the impression that the concentration given (12 mg l<sup>-1</sup>) refers to phosphate concentration. However, it is divided by the molecular weight of phosphorus. Shouldn't the molecular weight of HPO<sub>4</sub> (96 g mol<sup>-1</sup>) be used instead?

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Thank you for your suggestions. We have checked some literatures about adsorption and found that “adsorption capacity” was used more frequently than “adsorption density”, so we didn’t change it. We used the phosphorus concentration not the phosphate concentration in our experiments regardless of the existing form of phosphate, so 12 mg l<sup>-1</sup> represented the phosphorus concentration, that’s why we used 31 as the molecular weight. Hope this can clarify the referee’s question.

Section 3.2 Buffering effects. Line 22-The nomenclature for the equilibrium phosphate, PS-EPC0, induces in error because it seems to be PS minus EPC0. This becomes particularly confusing in the equation (line 25). I suggest replacing it by NAP (native adsorbed phosphorus) or another equivalent expression. It would be interesting to have some information about the sediment porewater concentrations of phosphorus, since the adsorbed fraction was lastly equilibrated in the bottom and not in suspension and at a different particle concentration.

Thank you for your advices. We have changed “PS-EPC0” to “PS<sub>EPC0</sub>” in the revised manuscript. *Hope this would be clearer. We will also consider the sediment porewater concentration so*

Section 3.3 Influence of temperature on sediment buffer capacity to phosphorus. Line 11- “The rate of both adsorption and desorption will increase with temperature.” This statement cannot be inferred by the increasing K with increasing temperature and no kinetic data is provided. Therefore, references should be provided.

Thanks. We have added and cited some references in the revised manuscript.

Technical corrections:

Page 17521 – Line 9. Maintains instead of maintain.

Thanks. We have modified it.

Page 17522 – Line 14. I suggest replacing three sediments by sediment triplicates or three sediment samples.

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Thank you for your advice. We have replaced “three sediments” by “three sediment samples”.

Page 17523 – Line 5. Was instead of were

Thanks. We have changed it.

Page 17523 – Line 21. “: : : except using very low initial P concentrations: : :” sounds odd. I suggest using something like: ‘with the difference that very low P concentrations were used’

Thank you very much. We have revised the original sentence to “with the difference that very low initial P concentrations of 0, 0.04, 0.08, 0.12, 0.2, 0.3, 0.4 and 0.5 mg P/L were used.”

Page 17527 – Line 11. Adsorb instead of absorb

Done.

Table 2. For clarity, I suggest moving the columns of r and S from the Temkin equation to the right so that they are in line with the ones obtained for the other equations. A description of what n and K from the Freundlich equation, and R, T, beta, Q0 and C0 from the Temkin equation, are should be provided in the end of the table, similarly to the parameters from the Langmuir equation.

Thank you very much for your advice. We have moved that two columns to the right part of Table 2 and added a description of the parameters in isotherm equations at the footnote of Table 2.

Figure 1. Changjiang estuary in the map should be replaced by Yangtze estuary since this might be confusing for many readers.

Thanks. We have replaced it by “Yangtze Estuary”.

Figure 2. The indication of plots a and b should be in capital letters to make it more

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clear. The data points in plot B should follow the same symbols as in plot A, i.e. triangles and circles for samples B and F, instead of squares and triangles. In the legend adsorption capacity should be replaced by adsorption density.

Thanks. We have modified all the referee's concerns.

Figure 3. What do the lines represent in the plot? Which equations were used for the fit?

The lines in Figure 3 represent the trend of the data for samples A, B, F and Z4, which fitted the logarithmic equations.

Figure 4. The indication of plots a, b and c should be in capital letters for higher clarity.

Thanks. We have modified it.

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/9/C8717/2013/bgd-9-C8717-2013-supplement.pdf>

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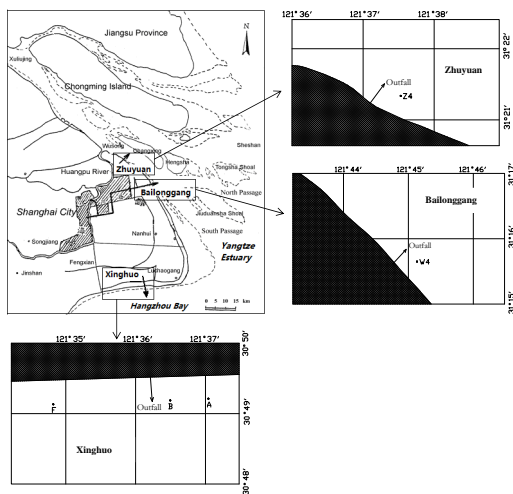
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**Figure 1** Sketch map of sediment sampling site locations for the Zhuyuan, Bailonggang and Xinghuo outfalls.

**Fig. 1.**

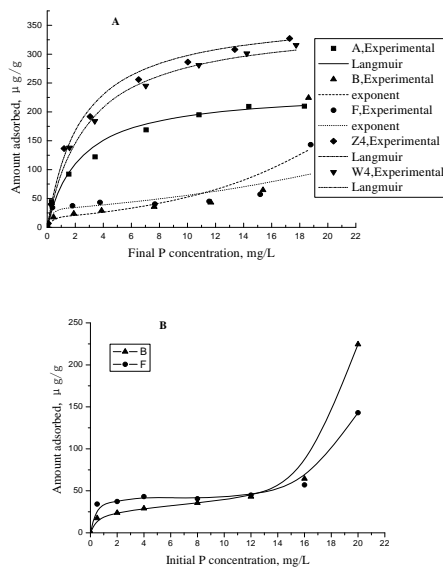
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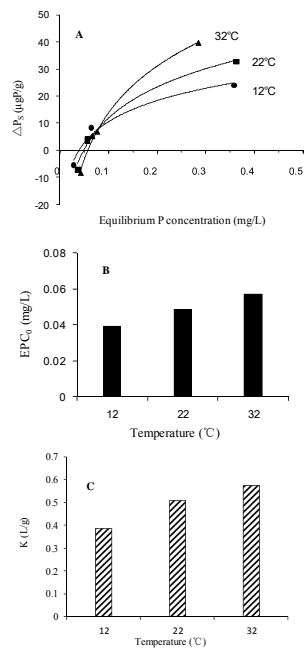




**Figure 2** (A) Adsorption isotherms of different sediments; (B) Adsorption capacity versus initial liquid-phase phosphate concentrations of samples B and F.

**Fig. 2.**





**Figure 4** Relationship between equilibrium solution P concentration (mg/L) and the amounts of adsorbed or desorbed P ( $\mu\text{g P/g}$ ) under different temperatures for sediment sample Z4 (A). Changes of  $\text{EPC}_0$  (B) and  $K$  (C) with temperatures for sediment sample Z4.

**Table 2** Langmuir, Freundlich, Temkin isotherm equations and constants for adsorption of phosphate by different sediments.

Sample	Langmuir equation				
	$\frac{c}{F} = \frac{c}{F_{\infty}} + \frac{1}{F_{\infty}b}$	$F_{\infty}$ ( $\mu\text{gP/g}$ )	$b$ (L/mg)	$r$	$S$
A	$\frac{c}{F} = 0.0042c + 0.0098$	238.09	0.428	0.996	12.632
B	$\frac{c}{F} = 0.0062c + 0.0969$	161.29	0.064	0.463	63.425
F	$\frac{c}{F} = 0.0101c + 0.0557$	99.01	0.181	0.711	35.791
Z4	$\frac{c}{F} = 0.0027c + 0.0066$	370.37	0.409	0.992	12.885
W4	$\frac{c}{F} = 0.0028c + 0.0081$	357.14	0.346	0.997	13.461
Sample	Freundlich equation				
	$\lg F = \frac{1}{n} \lg c + \lg k$	$K$	$n$	$r$	$S$
A	$\lg F = 0.3899 \lg c + 1.8721$	74.49	2.567	0.995	11.075
B	$\lg F = 0.5067 \lg c + 1.2752$	18.845	1.974	0.801	64.842
F	$\lg F = 0.2282 \lg c + 1.5456$	35.124	4.382	0.655	35.171
Z4	$\lg F = 0.7297 \lg c + 1.78$	60.286	1.37	0.968	71.921
W4	$\lg F = 0.4974 \lg c + 1.9392$	86.936	2.01	0.974	30.954
Sample	Temkin equation				$S$
	$F = \frac{RT}{bQ_{\infty}} \ln(C_{\infty}c)$			$r$	
A	$F = 43.38 \ln c + 84.588$			0.987	11.433
B	$F = 32.103 \ln c + 10.449$			0.585	64.829
F	$F = 15.316 \ln c + 33.008$			0.556	35.094
Z4	$F = 56.739 \ln c + 147.12$			0.988	22.037
W4	$F = 68.553 \ln c + 113.41$			0.994	11.648

$F$ : equilibrium P adsorption amount;  $c$ : equilibrium P concentration in liquid phase;  $F_{\infty}$ : maximum adsorption amount;  $b$ : adsorption equilibrium constant;  $r$ : correlation coefficient;  $S$ : standard deviation;  $K$ : empirical constant;  $n$ : empirical constant;  $R$ : universal gas constant;  $T$ : temperature;

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