

Biogeosciences Discuss., author comment AC2
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Reply on RC2

Florian Lauryssen et al.

Author comment on "Estimation of the natural background of phosphate in a lowland river using tidal marsh sediment cores" by Florian Lauryssen et al., Biogeosciences Discuss., <https://doi.org/10.5194/bg-2021-100-AC2>, 2021

RC2: 'Comment on bg-2021-100', Anonymous Referee #2, 30 Aug 2021 reply

The paper does address relevant and appropriate scientific questions which are very important to environmental P cycling and the journal. The authors propose to use sediment cores as a chemical archive to estimate historical surface concentrations of orthophosphate (orthoP) using a Langmuir-type sorption model in order to test statements regarding orthoP pre-industrial levels in freshwater rivers.

We thank reviewer 2 for noticing the value and importance of our work. Furthermore, we highly appreciate the effort put into the review and formulation of constructive comments.

The manuscript is relevant and valuable work, but the manuscript as submitted needs significant work with regard to the Introduction and language throughout. There are many areas where the language struggles and the meaning of the sentence is lost. I would recommend authors seek editing advice for English language, as many of the difficulties maybe due to language barriers.

The manuscript was revised on language, and complex sentences were adjusted to clarify their meaning.

Because the paper uses a model to predict pre-industrial orthoP concentrations the authors should be careful to use language to that effect throughout the document. Language such as estimates, predictions, suggestions rather than words like identification (title). The name of the model should be mentioned in the abstract - after reading the abstract I had no idea a model was being used as the main methodology.

We thank reviewer 2 for pointing out the importance of the language used to describe background predictions. We understand the importance of language in this context.

Therefore we adjusted the title to: "Phosphorus natural background estimation in the Scheldt river using tidal marsh sediment cores."

The specific model used in the manuscript was not described in the abstract.

Therefore the following sentence was added at line 21:

“By combining the sediment-P and water-PO₄ data, the sorption characteristics of the sediment could be described using a Langmuir-type sorption model.”

The Introduction needs to be rewritten with current literature on global P problems in the world's waterways and why estuaries/lowland rivers need to be studied to determine P capacity and/or leakage. I would recommend that the Introduction be rewritten to include some of the literature referenced in the methods section. I had a much better idea about what the authors were investigating after reading the methods section – and that should be reflected in the Introduction. For example, the Introduction should introduce why P is a problem globally, and why estuaries/lowland rivers are particularly a problem for both P storage and leakage – although not enough is known about either problem in these areas. There also needs to be a thorough discussion of why P in sediments would reflect overlying orthoP concentrations – leading the reader as to why you chose to use the methods described. And finally, a thorough discussion of the specific P problems related to this area of Belgium. After reading the Abstract and Introduction compared to the Methods section I had very different ideas about what was going to be discussed in the paper.

We thank reviewer 2 for the valuable suggestion to improve the Introduction. The idea about the investigation was clarified, and the Abstract – Introduction and methods were aligned.

The Introduction was rewritten according to the suggestions discussed, the latest literature was consulted.

The following structure was followed:

- The global P problem, importance to limit P concentrations
- EU Water framework directive, maximum P concentrations are defined.
- Importance of lowland regions, P holding capacity and leakage?
 - Excessive P levels are especially a problem in lowland rivers as they exceed However, the natural background for P in rivers is largely unknown. These background values are important to develop nutrient limits.
- Correlation P sorption & Pore water concentrations (including Literature from Methods section)
 - The relation between soil characteristics and pore water PO₄ concentrations have been described by several authors in the Belgium and the Netherlands. However the relation between sediments and surface waters has not yet been investigated.
- Why is P in sediment reflecting overlying ortho P concentrations (DPS relation)
- Importance of Sediment analysis for Long term reconstruction of P loading
- Measuring P using new method (tidal marsh sediment cores)
 - Specifically Tidal marshes along the Scheldt have been investigated regarding tidal marsh growth and carbon sequestration, however P storage analysis are lacking.
 - Therefore we will analyse the P accumulation in tidal marsh sediment cores to combine knowledge from both soil sorption models and tidal marsh elevation models. The goal is then to estimate the pre-industrial background to serve as method to develop regionally specific nutrient limits for lowland rivers.

I will try and identify specific examples regarding my overall comments above as well as highlight the great parts of the manuscript.

We appreciate the addressing the specific examples regarding language statements and the general appreciation of the manuscript.

Recommend defining P forms early in the manuscript (Introduction) and sticking to that nomenclature throughout the document. For example, orthophosphate for dissolved P or

reactive P (Line 38), Total P as organic, and inorganic – all forms of P. I would also recommend using the nomenclature L^{-1} rather than /L (Line 41) - unless that is mandated by the journal.

The author agrees that one nomenclature should be used consistently throughout the document, we chose for ortho phosphate (PO_4).

The nomenclature L^{-1} was changed throughout the document (Corrected)

The sentence on line 38 will be replaced by:

“As different P forms occur in surface waters, we focussed on ortho-phosphate (PO_4), which is almost identical to the reactive P determined by a colour reaction. Other P forms present in surface water include organic P fractions and P sorbed to mineral colloids. Total P refers to all P forms together. ”

The use of historical orthoP data from collections using DPS sediment data from adjacent marshes is a novel concept of how to predict pre-industrial level orthoP concentrations – and will help with predictions on P loading for the future in these types of environments.

We thank the author for addressing the relevance of our research.

Recommend a sentence in the abstract from Discussion 4.2 Limitations of the model such as careful consideration for P-migrations, checks or correlations on DPS and orthoP peaks when recreating orthoP levels or history in areas prone to excess orthoP or eutrophication.

The following sentence was added to the abstract:

“The model requires a careful consideration of vertical P migration and correlates sediment DPS and water PO_4 to reconstruct historical concentrations”

Specific examples of rough or misguided or language barriers includes Line 181, Line 215, Line 324-325, Line 357.

Line 181: “Therefore, we rescaled the modelled marsh surface elevation by fitting it through the observed depth-age points from the GPS measured marsh surface elevation in 2016 and previously published radiometric and paleoenvironmental dating (Temmerman et al. 2003; 2004).”

The statement was reformulated in the final manuscript:

Because this study focussed on the time of sediment deposition, the original age-depth relation calculated by MARSED was recalibrated by using the observed age-depth point. The observed age-depth points originate from GPS measured marsh elevation in 2016 (Van de Broek, unpublished data) and previously published radiometric and paleoenvironmental dating and act as ground truth (Temmerman et al. 2003; 2004).

Line 215: We did not use the existing sorption models for soils directly, and instead, the parameter K, in Eq. (2), was calibrated to the most recent Scheldt water data. So that, the K-value adapted to the geochemistry of the tidal marsh sediments.

The statement was reformulated in the final manuscript

As the parameters ($K - L \text{ kg}^{-1}$) of existing soil models had been calibrated for soil - pore water concentrations, the sediment-water relation is unlikely equal. Therefore, the model

was calibrated by fitting parameter K on sediment DPS measurements and recent Scheldt water PO₄ measurements. As a result, the fitted parameter K is adapted to the local chemistry of tidal marsh sediments and of the surface water.

Line 324-325: In contrast, half of the observations were underestimated by at least 25% for model 2b and by 11% for model 3b (Table 2). The actual by predicted plots illustrate the same (Fig. S10). Based on these observations, model 3b was considered as the best model, although the residual standard error (RSE) was lower for model 2b (Table S2). Model 3b predicted recent PO₄-concentrations best, with median underestimation of only 11% (Table 2). The selected model 3b succeeds to reconstruct the rise and fall in surface water PO₄-concentrations based on the sediment characteristic DPS (Fig. 4).

We thank the reviewer for pointing out that the paragraph about the model performance was hard to read. Therefore, we rewrote the passage and included the Pbias as a model evaluation.

Section Evaluation Model Performance:

"Additionally, the Percent bias (Pbias) was calculated for data points between 2007 and 2016. The Pbias measures the average tendency of the simulated data to be larger or smaller than their observed counterparts, expressed as a percentage (Moriasi et al., 1983; Eq. 3)."

Line 324-325 will be replaced by the following paragraph:

"Model 3b was considered the most suitable for predicting background concentrations. The Pbias was the lowest for recent observations of model 3b, as simulated data was underestimating the observations by -14.9 %, which is within the acceptable range of $\pm 25\%$ (Moriasi et al., 1983). However, model 2b had an average underestimation of more than 28% and model 1b overestimated recent observations by more than 60%, which is unwanted for calculating the background, and therefore both model fits were considered unsuitable (Table 2). The actual by predicted plots illustrate the same (Fig. S10). Based on these observations, model 3b was considered as the best model, although the residual standard error (RSE) was lower for model 2b (Table S2). The selected model 3b successfully reconstructed the rise and fall in surface water PO₄-concentrations based on the sediment characteristic DPS (Fig. 4)."

The methods section is well written. The language in the methods with regard to calculations of P-saturation and P sorption capacity is great – it would be great to see some of this language put into the Introduction as to why measuring P this way is important in gauging effects of long-term P loading – correlations between P sorption and pore water concentrations. The authors also used a published Langmuir-type sorption model to predict orthoP concentrations that had been used before for sediments and water in this area – which makes it very relevant in this study.

The authors appreciate the positive comments on the methods section. The literature on P saturation was partly taken up in the Introduction to bring a complete story.

Two topics will be discussed in the Introduction as well, as was mentioned in the fourth comment of reviewer 2.

- Correlation P sorption & Pore water concentrations (Literature Methods)
- Why is P in sediment reflecting overlying ortho P concentrations (DPS relation)

Expected a discussion of why previously reported/estimated values for background orthoP

in this lowland river is larger than estimates for background P in other lakes/streams (15-35 $\mu\text{g P/L}$) what might be causing excess surface orthoP concentrations in these lowland areas pre-industrial era.

The comment was already addressed in the reply to the comment of reviewer 1 about Ln 356-357

- The specific conditions in lowland rivers – slow flow, summer anoxia in small rivers is present for 5 months a year
- Rivers are largely fed by baseflow (75%) bringing in a significant source of P. The average groundwater P concentrations are 145-325 $\mu\text{g/L}$
- Lakes fed by rainwater will have lower P concentrations at rainwater P varies between (5 and 120 $\mu\text{g L}^{-1}$)

The results from sediment core selection – the discussion on P-migration for the two samples (Old2 and Young2) and why they should be eliminated from the analysis of DPS and PO₄ relationship is appropriate, understandable, and very relevant.

The elimination of two cores showing issues with P preservations are indeed important for the results. Thanks for pointing this out. We also mentioned the importance of core selection in the abstract.

Please also note the supplement to this comment:

<https://bg.copernicus.org/preprints/bg-2021-100/bg-2021-100-AC2-supplement.pdf>