

Biogeosciences Discuss., author comment AC1
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Reply on RC1

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-AC1>, 2021

RC1: 'Comment on bg-2021-100', Anonymous Referee #1, 11 Jun 2021 reply

The manuscript titled "Identification of the natural background of phosphorus in the Scheldt river using tidal marsh sediment cores" by Lauryssen et al., is a good piece of work to justify the possible sedimentary records of dissolved phosphate-P in river water in the past. Authors have analysed two types (old and young) of sediment cores from the river flood-land to establish the fact that bottom sediment retains the signature of phosphate concentration in overlying water without much alteration over the period of time. And based on those sedimentary records authors have tried to predict the "natural background" value of phosphate-P prevailed during the age of pre-industrialisation and/or any major human intervention. For this objective, one should be very careful about the possible artifacts in prediction of such background value; because that may cause unexpected errors.

The authors would like to thank reviewer 1 for his/her kind comments and feedback and the time and energy spent reviewing the manuscript. The careful consideration will benefit the quality of this article. We appreciate the recommendations and understand the care needed in predicting a background value.

No doubt it is an innovative attempt; but the present manuscript has some shortfalls and queries. The text language is fine but some longer statements can be avoided.

With this reply, we solved the shortfalls and answered the questions addressed. In addition, the text was adjusted to improve flow, and clarify long statements.

In present study it was assumed that the immobile nature of P helps in retaining water column signature in sediment. From this basic idea it is expected that the past time-zones which correspond the phosphate peaks in water should precisely match with the peaks of P_{ox} or DPS found in core sediment. In Figure 2, the maximum dissolved phosphate peak appears immediately after 1980s but the most of the DPS profiles (except Young-1) in Figure 3 have peaks before 1980 (between 1920-70). In this regards some suitable explanations have to be included in the discussion section.

We thank the reviewer for noticing the importance the identification of P preservation.

Section 3.3 describes the sediment core selection and represents the considerations for

selecting the representative cores. Further in the manuscript, section 3.5 describes the model selection regarding the different cores to fit the model.

The fitting of the sorption model excluded Old2 and Young2. The DPS peaks of both cores did not correspond with what was observed in the surface water. This was indicating P migration, as was addressed in section 3.3, line 275-285.

The time series of Old1 displayed a DPS peak around 1960, indicating a shift of only 20 years (Figure 2). Thus the shift of Old1 is smaller than the maximal shift up to 1920 Reviewer 1 noticed. However, the core Old1 was included in the model fitting. That core is essential to predict the background because the core dates back to 1800 at the deepest levels. Furthermore, the DPS concentrations stabilised before 1920, indicating that P has not migrated to these depths, making it suitable for background prediction.

Furthermore, the sorption model used to predict the surface water concentrations using observations from both cores Old1 and Young1 (model 3b, Table 2) performed better at predicting recent surface water concentrations, at relatively low concentrations. If the observations from Old1 are removed from the dataset, the background would be slightly lower with $51 \mu\text{g PO}_4\text{-P L}^{-1}$ [49; 54]. However, that model only including the observations from Young1 that underestimated recent PO_4 (2007-2019) values by 28%, while the model 3b had only 15% underestimation.

Section 3.3 was supplemented in the manuscript with part of the discussion above:

“The time series of Old1 displayed a DPS peak around 1960, indicating a shift of 20 years (Figure 2). However, the core Old1 was taken up for the prediction of the model fitting. That core is essential to predict the background because the core dates back to 1800 at the deepest levels. Furthermore, the DPS concentrations stabilised before 1920, indicating that P has not migrated to these depths, making it suitable for background prediction.”

Authors have estimated the level of P-saturation in sediment samples following a relation (as mentioned in the Equation 1); actually verified for the porewater-soil system of typical agricultural fields. This similar relation could be applicable to the estuarine sediment also?? Specially, I have doubt about the factor of 0.5 in this Equation 1. It may differ for sediments in aquatic environments; characterised with different geochemical settings as compared to those from agricultural lands.

The DPS was verified for porewater-soil systems and was developed by (van der Zee et al., 1990). The 0.5 is an empirical value based on pore water measurements of non-calcareous sandy soils and is considered the sorption capacity of the soil. Lexmond et al., (1982) illustrated that the maximal sorbed P was about half the pool available after a long-term precipitation experiment. So they concluded the α was set at (0.5 ± 0.1) . However, even among terrestrial soils this parameter varied between 0.3 and 0.6.

Because the dataset in this study had a lot of noise and a limited number of observations, we decided only to fit the parameter K, i.e. one and not two adjustable parameters. Furthermore, the two parameters α and K are correlated by fitting, if α is reduced, then K must be increased to fit the same data. The parameter α primarily affects the maximum sorption capacity, while the parameter K determines the slope between zero and the maximal capacity. The maximum is only reached at high PO_4 (not relevant) concentrations. We focussed on background concentrations where K is most important.

We can speculate that the solution-particulate P relationships are different between soils and surface water for various reasons (e.g. soil-leachates have PO_4 concentrations but P has equilibrated longer than in water), however we do not want to elaborate too much to keep focus on the identification on the background, all we wanted to identify is a

translator between sediments and water, the validity of the "soil" model is simply the statistical validity of the predictions. In this study we chose to use the 0.5 value, but that further research is needed to assess the exact value for tidal marsh sediments.

Ln 79-80: "In lowland rivers with tidal influence, also called estuaries such as the Scheldt estuary in Flanders, tidal marshes....." The statement is not clear; use simpler sentences.

We used shorter sentences to clarify the statement.

"In Lowland rivers with tidal influence, tidal marshes develop along the river banks. tidal flooding accumulates sediment on these marshes. The process is similar to the development of river floodplains but at a much faster sedimentation rate (i.e. mm to cm per year)."

Ln 106-07: Author has mentioned that they restrict their observation within the freshwater areas of the Scheldt estuary. Is there any specific reason for selection of only freshwater segments of that estuary?? -Here they should cite those actual reasons for such site selection in context to the aims of the present study.

Thanks for pointing us the importance of mentioning to clarify why we restricted our research to freshwater systems.

The following reasons was cited in the text:

"The brackish portion of the estuary experiences mixing of freshwater from upland sources and seawater, making it difficult to distinguish between the anthropogenic sources of PO_4 from seawater influence. Furthermore, brackish and saltwaters in the North Sea have PO_4 concentrations about a factor 10 lower compared to freshwater (Burson et al., 2016). Too low concentrations could lead to an undetectable signal in the sediment. Our research was focussed on freshwater and lowland river systems, and the human influence on the PO_4 concentrations. "

Ln 120-121: Authors should mention about the site specific sedimentation rates (as obtained from radiometric dates) at four sampling locations. As the sediment accretion rates in this estuarine system are quite variable (e.g. 0.3-3.2 cm/yr); this information would provide better perception regarding the 'young' and 'old' settings.

We agree with reviewer 1 that comparing specific sedimentation rates associated with young and old marshes gives a better perception of the setting. These data were collected from literature and will be added to the text:

"For example, between 1931 and 1951 young marshes accumulated at rates of 1.58 to 3.22 $cm\ yr^{-1}$, during the subsequent period 1955-2002 they accumulated at lower rates of 0.4-1.84 $cm\ yr^{-1}$. In contrast to the young marshes, the elevation of old marshes is at any time very close to MHWL of 0.32 to 0.58 $cm\ yr^{-1}$ in the Western Scheldt (Temmerman et al., 2003)."

Ln 150-155: This section of sediment analyses needs more details. It has ".....solid-liquid ratio of 1 g in 50 ml....". What is that solid-liquid ?? Here, it looks solid-liquid refers sediment-oxalate solution. Provide the details about the liquid and its purity, concentration etc used for this leaching experiment.

We understand reviewer 1, and therefore will clarify the purity of the liquids and concentrations used for the oxalate extraction.

"The extractant was made with Milli-Q® grade water and all glassware used was acid

washed prior to remove all P. That acid oxalate extractant, a mixture of ammonium oxalate and oxalic acid at pH = 3, targets poorly crystalline oxyhydroxides of Fe, Al and Mn and the associated P.

...

The preparation of extraction solution and dilutions were made with ultrapure water; all glassware used was acid-soaked overnight in a 1% HCl acid bath. The extraction solution is composed of a mixture of 0.2 M ammonium oxalate and 0.2 M Oxalic acid at pH 3, as described by Schwerzman (1964). The extraction was done with 1 g of dry sediment in 50 ml of extraction solution."

Ln 250: In the Table 1, authors should provide the estimated Fe_{ox} and Al_{ox} values for each samples. This would help reader to verify the DPS values presented in the table.

The addition of Fe_{ox} and Al_{ox} concentrations to table 1 allows the reader to calculate and verify the DPS values presented in the text. We agree with the reviewer that this will benefit the interpretation of the value. The concentrations will be added to the final table.

Ln 295: In Table 2, there are two background values (for 1800 and 1930) have been presented. Its bit confusing; which one represents the natural background value. Is 1930s value is really essential??

We thank reviewer for pointing out that confusion, we kept 1800 defined as pre-industrial background but did not use any longer the term background for the 1930 estimate, we merely defined it as the concentrations around 1930. The concentrations near 1930 is used because it refers to a time before the widespread application of mineral fertilisers, industrialisation and sewage connection. Therefore PO_4 concentrations were considered to be lower than today. However, the authors were surprised that the values presented in 1930 were already at levels similar to today.

Secondly, in the Table 2 caption, it has mentioned that the profiles of only one site (Old-1) has used for prediction of background phosphate concentration. However, in same table, the model 3b is based on Young-1 and Old-1 data set). This is also confusing.

We thank reviewer 1 for mentioning another confusing statement in table 2. The only core dating back to pre-industrial times (1800) was Old1, with a DPS of 20% at the bottom of the core. However, model 3b converted DPS to surface water PO_4 was fitted on both Old1 and young1 core data. The data of core Young1 is valuable for fitting the model but does not go back in time long enough as it was formed after 1945. So, the model fitted on both cores (Old1 + Young1) was applied to the deeper layers of the Old1 core, to predict the background.

Caption change

"Table 2: The predicted concentrations of phosphate (PO_4 -P μgL^{-1}) in the Scheldt river based on the Degree of Phosphate Saturation (DPS) in the sediment layers of marsh Old1, dating back to 1800 (pre-industrial), where DPS values stabilised with depth at 20% , and the predicted concentration dated to 1930 where DPS stabilised at 36%. The Pbias measures the average tendency of the simulated data to be larger or smaller than their observed counterparts, expressed as a percentage (Moriassi et al., 1983). Conversion of DPS to river phosphate concentration based on the association of DPS with PO_4 -P calibrated to data 1967-2016, thereby using different calibration for sediment-water models; the details of models are in Table S2. Model 3b (in bold), is proposed as the most accurate one (see text).

Ln 309-310: The models using mean DPS and individual PO₄ are considered more useful for evaluating the factor "K". Here authors should mention the proper reasons for this choice.

We use DPS (in X-axis) to predict solution P (Y-axis). Both X and Y are prone to sampling error, hence we are investigating allometric relationships. Allometry is not commonly used and certainly not in non-linear allometric relationships. Hence, we reduced it to regression and try to limit error in the X-axis, the assumed independent variable. To limit that variation, we averaged data. A sediment analysis gives an average DPS signal over a deposition period. However, due to variation in the marsh surface, the age-depth relation can vary slightly. By taking an average DPS concentration, we compensate for this natural variation. The mean DPS over different replicate cores, therefore, corresponded to each surface PO₄ measurement. Moreover, as we had described from line 311, single DPS value requires the need to duplicate/ triplicate solution P data (e.g. three DPS values for one year of water P data), which incorrectly increases the number of observations in the dataset.

Part of this reasoning was already described in lines 311-313 of the reviewed manuscript.

The following statement will be added to the text:

"A single sediment sample analysis gives an average P signal over a deposition period. However, due to variation in the marsh surface, the age-depth relation can vary slightly. By taking an average DPS from replicate cores, we reduced the the variation in the independent variable with which the dependent variable (PO₄ in water) is predicted. Furthermore, in most models, the prediction error increased by relating individual rather than mean DPS values with individual PO₄ measurements."

Ln 356-357: The summer anoxia induced oxide dissolution has projected for excess P loads in river water and thus explained for higher projected background value of 62 microgm/l. Summer anoxia is generally short-term seasonal process and therefore is it really could be effective to maintain higher background over the long run?? Or, it is some other processes responsible for such projected higher values in river water relative pristine lakes. Similar effects of seasonal anoxia are not evident in those lake waters??

We thank the reviewer for questioning the effect of summer anoxia on the background concentrations. Hereby we clarify the importance of this process in lowland rivers.

The summer peak of PO₄ is present for five months of the year in Flanders, thereby significantly influencing the mean P concentrations in the rivers (Smolders et al., 2017). Therefore, we expect the summer anoxia to be the main driver behind the elevated P concentrations.

Also, lowland rivers in Flanders are primarily groundwater-fed; on average, 73% of streamflow can be attributed to base flow. Natural groundwaters in Belgium have a median P concentration between 150 - 320 µg P L⁻¹. Groundwater feeding river waters will increase P levels. Conversely, primarily rain-fed lakes will have lower P concentrations, ranging between 1.5 and 120 µg L⁻¹.

Summer anoxia also occurs in eutrophic lakes, or sometimes oligotrophic brown water lakes (Nürnberg, 1995). For 75 in the US lakes anoxia occurred between zero and 83 days a year, less than the five months or 150 days in Flemish rivers (Nürnberg, 1995; Smolders et al., 2017).

The reasoning presented above will be added to the manuscript.

Ln 400: "Our data estimated that the pre-industrial background concentration is about half of the....." In this conclusionary statement, mention the actual predicted background value i.e., 62microgm PO₄-P/l along with confi. Intervals.

Reviewer 1 brought up a good point to add the numerical value and confidence limits to the conclusion statement; we agree that it is crucial to mention there.

The sentence at line 400 will be changed to: "Our data estimated that the pre-industrial background concentration is 62 µg PO₄-P [95% CI (57; 66)] which is about half of the environmental limits set for surface waters in Flanders and neighbouring countries. "

The plots of Figure S9 are easy to visualise as compared to those in Figure S7 and S8. Therefore, S7 and S8 can be presented in similar format of S9. Furthermore, in these depth profiles, the extremes (Highs and lows) should be marked with corresponding ages. In my opinion instead of supplementary documents, these depth profiles would be good to present as the part of the main text.

We thank reviewer 1 for proposing a more convenient way to visualise figures S7 and S8. The orientation of S7 and S8 has changed accordingly.

However, we decided not to add the figure to the main text as it contains very similar information as Figure 3, presenting the DPS timeline calculated based on the depth profiles from Figure S7. The peaks and corresponding dates are presented in Figure 3.

Please also note the supplement to this comment:

<https://bg.copernicus.org/preprints/bg-2021-100/bg-2021-100-AC1-supplement.pdf>