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Interactive comment on "Interactions of local climatic, biotic and hydrogeochemical processes facilitate phosphorus dynamics along an Everglades forest-marsh gradient" *by* T. G. Troxler et al.

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Author Final Response to Referee #1 (C3246)

We thank the referee very much for the very constructive comments to improve the manuscript. In response to the two issues raised in the General comments regarding (1) redox potentials and (2) P limitation of the oligotrophic marshes. With regard to redox potential, we are very grateful to the referee for raising this critical point and will clarify that, given the evidence that some proportion of the TP is Fe-bound, there is a

possibility that redox state contributes to P dissolution related to the reductive dissolution of Fe(III)-oxides. We will further clarify that while redox can have a significant effect on P availability, the difference in mineral content (and Ca-P) is greater in magnitude than the difference in hydrology between the two sites. Similarly, while DO only differs at 0.5-0.6m depth between high head and wet head soils, TDP and SRP at this depth are similar. We will also add references to bring forth that generally, in an unimpacted state, the influence of limestone bedrock governs P dynamics in the Everglades. With regard to P limitation in adjacent, oligotrophic marshes, we will provide text and references (i.e. Noe et al, 2001; McCormick et al. 2009) to bring forth studies that test for the oligotrophic status of freshwater marsh in the region where the study was conducted.

In response to specific comments, we address them point-by-point in the following section.

p.10292/l.20-p.10293/l.4: No information of replicate measurements is given for the various parameters analyzed.

To insert in line 21 numbers of replicates for each of the communities and reference to Supplementary material, Table 3 where this information is cited.

p.10292/l.20: The core locations are not described despite the opportunity to include these in Figure 1. Core distributions among communities are listed only in Table 3 of the supplementary material. Yet, the text does not refer to this table. Core numbers per community given in the supplement do not fit to the piezometer and well distributions (Figure 1). Thus, core locations obviously do not match given piezometer and well locations and are therefore apparently not described.

As referred to in response above, the number of cores per community is now provided, and reference made to Table 3 of the Supplementary material. It was not clear whether the cores collected were representative of the communities characterized by the piezometers/wells. Since the tree island communities are described on the Figure

1, and piezometer/well locations provided, with cores now similarly described, we've provided clarification that relates the core samples with the piezometer/well locations.

p.10292/l.28: For this study, the fractionation method by Hieltjes and Lijklema has been modified (KCl instead of NH4Cl). However, the rationale for this modification is not explained. Further, a brief description of the extraction conditions would be advisable for each pool despite citation of the corresponding articles.

The rationale for KCl and the extraction concentrations will be revised as such in methods section to address the referees notable concern: "Soil fractionation followed an inorganic P fractionation scheme using a modified Hieltjes and Lijklema (1980) method as described in Reddy et al. (1998). Briefly, instead of 1M NH4Cl, 1M KCl was used and the 0.1 M NaOH extract was analyzed for TP, with the difference between TP and Pi assumed to be organic P associated with humic and fulvic acids (Reddy et al., 1998). Like NH4Cl, KCl is a neutral salt and commonly used to measure exchangeable NH4-N. As a result, some researchers have replaced NH4Cl with KCl in this extraction scheme, thus allowing measurement of exchangeable N and P simultaneously, though only P used here. Soil P was fractionated into five compounds: labile P (KCl-Pi), Fe/Al-boundP (NaOH-Pi), organic P (NaOH-Po = NaOH-TP−NaOH-Pi), Ca/Mg bound P (HCl-Pi, 0.5 M HCl), and calculated residual P. The TP concentration in the NaOH extract solutions was assessed via standard Pi methods following acid digestion.

p.10293/l.1: The NaOH extract was analyzed for "moderately resistant organic P forms". A reference is missing, which verified the quantification of moderately resistant organic P by NaOH-Po. Although total organic P was not determined in this study, an estimate for the approximate content of NaOH-Po relative to total organic P would be useful (i.e. Is NaOH-Po generally a main fraction of total organic P or just a marginal part?). However, the main issue in that context is the apparently missing description of the method used for conversion of Po into Pi in order to determine NaOH-TP. For the determination of the overall TP content of the soil (given in Fig. 2A), acid-digested samples were used. Whether this method was also used for NaOH-TP is not described.

The reviewer raises an interesting point regarding the use of the term "moderately resistant organic P forms". While this is used throughout the literature it is more accurate to state that we assume the difference between NaOH TP and NaOH Pi is organic P and we will rewrite the text accordingly, along with the citation it came from. We also added that NaOH extracts were digested with acid prior to analysis for Pi.

p.10293/l.4: For low residual P contents, suggestions for potential P forms of the residual pool are less important. However, residual P was by far the predominant P fraction at all investigated communities (Fig. 2A), and the entire text does not respond to this issue. As extraction conditions are not sufficiently described within the Methods section (e.g. concentrations of extractants), it is not instantly clear whether HCl-Pi and NaOH-Pi comprise most of the inorganic P pool and, consequently, whether residual P contains primarily organic or inorganic P.

As the reviewer notes, what is left in the residual pool is a function of the extraction scheme used. The addition of the concentrations that will be provided in the revised text of the different extractions allows the potential for extraction of different P groups clearer.

p.10294/l.21-23: Which equipment/methods were used to determine these values (e.g. which electrodes)?

The instrument and probes used for these water quality parameters were provided.

For the district sampling we have been using (our preferred sonde) the Hach Quanta with: pH probe-part # B6pH DO/cond probe-part #004484 Circulator-part # 004508 Reference probe (no part # found)

p.10295/l.5-8: As two different computer programs were used to determine saturation indices the rationale for selecting these programs should be explained. Further, it is necessary to document, which compounds were used to chemically define the system (e.g. for ion-pairing; probably some of the parameters given in Table 2). Moreover, selected apparent solubility products (with corresponding references) for each mineral and information about the calculation of activity coefficients (ionic strength correction) maybe required for traceability of those computer-based calculations.

To address the first point, we will add a line to articulate that two equivalent modelling programs were used to cross-check results and calculate an additional saturation index that was hydroxyapatite.

To address the second point, we will add text in line 8, of p. 10295 that defines the chemical parameters used for calculating the indices of mineral saturation and in table 2 for clarity.

p.10299/l.2-5: As redox potential has generally considerable influence on P compositions (see e.g. Hutchison and Hesterberg, 2004; Mortimer, 1971), the large water level differences between High Head and Wet Head may have caused some of the observed geochemical differences (e.g. the low TP level at the Wet Head as compared to the High Head). Although redox potentials were not measured, it may be reasonable to discuss whether the redox state may have contributed to the differences between High Head and Wet Head or not.

We will add text to discuss the potential impact of redox state on differences in TP between High Head and Wet Head, starting line 9, p. 10305. As the referee notes, given the important effect of redox state on P availability, this is a very important clarification to provide. Given the evidence that some proportion of the TP is Fe-bound, there is a possibility that redox state contributes to P dissolution related to the reductive dissolution of Fe(III)-oxides, citing the references kindly provided. We will further clarify that while redox can have a significant effect on P availability, the difference in mineral content (and Ca-P) is greater in magnitude than the difference in hydrology between the two sites. It will be noted also, that despite the variation in DO between high head and wet head at the same depth (0.5 – 0.6m), TDP and SRP are similar. Finally, we will also add references to bring forth that generally, in an unimpacted state, the influence

of limestone bedrock governs P dynamics in the Everglades.

Figure 6: What is meant by "no evidence of mineral exchange" or "minerals are absent from the shallow soils" (P-minerals or "non-carbonate minerals")?

It will be clarified that what is meant is non-carbonate minerals.

p.10303/l.8-10: This implies that the "non-carbonate component" of the soils is just composed of Ca-bound P. However, other P pools maybe also part of the noncarbonated component. Likewise, the non-carbonate mineral content may comprise various other minerals (see Ross and Sah, 2011). It is described that "Ca bound phosphate comprised approximately 50% of the soil by mass". This percentage seems to be extremely high. It is necessary to document the corresponding calculation.

We will revise the text of these lines to clarify nearly 50 % of the non-carbonate component of the total soil phosphorus is Ca-P. A reference to Figure 2B will also be provided. As the referee notes, the text as presenting is not clearly worded to articulate this.

p.10303/l.12: Bioapatite is structurally similar and frequently termed as HAP but shows also considerable chemical and structural differences (see Wopenka and Pasteris, 2005). When referring to a specific formula, probable substitutions and their potential effects for saturation indices should be mentioned (e.g. indicating saturation indices for other apatites). However, it is still advisable to use hydroxylapatite as a reference compound.

As the referee correctly notes, the chemical formula for hydroxylapatite is a general formula and similarly can to apatites in general. The potential for alternative substitutions, i.e. Cl, F, will be presented in the text as possible and additional justification for using hydroxlyapatite as a reference compound will be provided.

p.10305/l.26-27: The statement "strong potential for hydroxyapatite dissolution but potential for mineral precipitation" should be rephrased. Hydroxylapatite is also a mineral.

To clarify, we will substitute “calcite” with “mineral”.

Table 2: Two columns of Table 2a are unnecessarily repeated in the supplementary material (Table 2a; some values differ slightly for some reason). Instead of repeating measured values, it would be useful to present raw data for all four seasons at least for key parameters such as TDP, SRP, pH, Ca and Cl. One of the main goals of this study is to validate that a temporal trigger (precipitation) explains fluxes of a limiting nutrient. Thus, it would be worthwhile to present temporal phosphorus distribution changes (as raw data in the supplementary material) despite presented flux calculations (Table 3).

We are grateful to the referee for this important observation and will provide the temporal variation in the key parameters listed as suggested in a supplementary table.

Figure 6: To me, the explanation of this figure in the text is not sufficient (p.10302/l.24-26).

We will supplement the discussion of the figure, cross-referencing the specific elements described in each note of figure 6, and elaborate discussion text on those notes.

Entire MS: The usage of the same abbreviation for two different parameters is disadvantageous (P: Precipitation, e.g. Fig. 5; P: Phosphorus), especially when these parameters are correlated.

We will correct figure 5 and tables, text to change precipitation to the alternative abbreviation “Pre”

Technical corrections: p.10297/l.5: "P" is missing after "labile". p.10300/l.14: I guess TDP is meant here instead of TP because TP is quite low at the Wet Head (See Table 3).

We will implement these technical corrections.

Interactive comment on Biogeosciences Discuss., 10, 10287, 2013.