Biogeosciences Discuss.,
https://doi.org/10.5194/bg-2017-229-AC1, 2018


Biogeosciences Discussions
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# *Interactive comment on* "QUAL-NET, a high temporal resolution eutrophication model in large hydrographic networks" *by* Camille Minaudo et al.

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Received and published: 25 January 2018

Authors are grateful for comments and suggestions from Referee 1. All raised issues were listed below and carefully answered. We had to run several other simulations to address some comments (especially the first comment). This did not affect results in the manuscript. Only descriptions and interpretations were modified.

//——Referee 1 Comment 1: In my opinion the difference in time is very small in relation to the time it takes for biological reactions to occur such as organic matter remineralization. Without the authors presenting any reaction rates, especially for P remineralization and uptake, it is hard to judge whether the author's physics vs biology explanation is supported. In addition, the authors neglect to discuss temperature



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variation in the two seasons and the impact it would have on the reaction rates and phytoplankton growth. I would argue that low temperature and thus reactivity of constituents in the winter months can largely determine the distribution in the reach of the river. A thorough explanation of reaction rates and there relation to transport rates would help address these issues. In addition, the authors could do a model run with constant flow and see if the same patterns emerge. If they do, then their conclusion would be supported.

//——A: We thank Referee 1 for this thoughtful comment. We agree that the difference between travel times in winter compared to summer is too small to fully explain seasonal variations observed at the downstream station S2. We also know that changes in reactivity rates are triggered by warmer water temperature, and this must play a role. Almost every single variable in the model is temperature dependent. Phytoplankton dynamic also depend on light availability (conditioned indirectly by suspended sediment concentrations, governed by hydrological variations) and, of course, nutrients availability. As suggested by Referee 1, we ran a constant flow simulation with Q in the Loire itself = 200 m3 s-1, and Q = 0.1 m3 s-1 everywhere else. We compared this run with another simulation where Q in the Loire River was 1000 m3 s-1 (Figure A1).

Results showed for all simulations strong seasonal variations with phytoplankton blooms in summer and very low phytoplankton concentration in winter. Phytoplankton development was similar between the reference simulation and the constant low-flow simulation. However, results with a constant high-flow presented much lower PHY concentrations. This proved how much travel time impacts phytoplankton blooms occurrences. However, the fact that phytoplankton concentration remained low during winter with constant low-flow conditions proves that Q can't be the only key driver, especially because nutrient concentrations are highest in winter.

We also ran a simulation with normal flow variations but constant water temperature throughout the entire period with T = 13.7$^{\circ}$C (i.e. the median water temperature simulated in the Loire River by T-NET module). Results showed (Figure A2) that the intensity of PHY (peaks values) was sensitive to water temperature: we observed lower PHY concentrations in the constant T°C run. However, the dynamic of PHY remained very close to the reference simulation, proving that water temperature, just like travel time, can't be qualified as the main driver of PHY variations. Phytoplankton variations in the Loire River are co-controlled by Q, T°C, nutrients and light availabilities, and all these variables interact with each other. Viewed in a Lagrangian way during a summer event (starting date at Q1 = 17th July, 2012same date as in the paper on Figure 5), we observed that phytoplankton development was much more affected by shorter travel times (run with Q = 1000 m3 s-1) than with colder water temperature (see Figure A3 below). P availability played a major role, and P exhaustion was reached 2.5 days after the starting date from S1 for all simulations except with the high-flow simulation where no P limitation was simulated, because travel time from S1 to S2 was too short.

//——R1C2: What is the source of the organic matter that is fueling the enhanced release of phosphorus? Is it autochthonous to this river reach, from sediments, from the watershed? More detail on the source of the P needs to be added, because if the reach of the river was in a steady state during summer i.e. recycling from algae, there wouldn't necessarily be algae blooms; the population would be constant in time.

//——A: Large amounts of organic matter enter the Middle Loire at its upper limit S1: it is estimated with our daily measurements that approximately 80t of organic C enter the system at S1 every day under low flow periods (see also Minaudo et al. 2016 in Environmental Monitoring Assessment). Approximately 80% of it is dissolved organic carbon, the rest is particulate. Model QUAL-NET tells us that a significant proportion of DOC is bioavailable and consumed by heterotrophic bacteria (16 tC day-1 in summer, see Figure A4). Part of this organic matter is eventually mineralized, depending on oxygen conditions. This constitutes another pathway for P, and, combined with P recycling processes from dead algae, it explains that blooms may still occur despite P limited conditions. These processes are explicitly represented in the model, and can be seen in the C budget, as depicted in the figure below. This also highlights how important it is to explicitly represent bacteria in our water quality models. We would add this analysis to our manuscript.

//——R1C3: How the sediment and water column interact biologically and chemically needs to be further explained. What is the sediment model and how is it coupled with the water column? What happens to porewater in the stream sediment when it is resuspended during erosion?

//——A: the following interactions between the sediment layer and the water column are considered: Sedimentation/erosion processes of particles depending on flow energy. Particles are both inorganic and organic with three levels of lability. Diffusion processes for nutrients between the two layers. The benthic compartment can be either a source or a sink of nutrients, depending on redox conditions. All these processes were modeled using Billen et al. 2014 (Ann. Limnol). Equations in this formulation provided estimates of $NH_4$, $NO_3$, $PO_4$, $SiO_2$ and $O_2$ fluxes across the water – sediment interface. The sediment layer was split into two sub-layers. The one at the bottom is considered compact and not erodible, the other one might potentially be re-suspended. Nutrient fluxes between these two sediment layers were also considered in our model.

The sediment model is a simple power law model based on the flow velocity. Equations are already explained in section 3.3.1, thus we did not believe it had to be clarified. Although fluxes from and to the benthic compartment were considered (see above), pore-water was not explicitly considered as an object in our model. Only the physical dynamic of sediment particles was considered.

//——R1C4: How long does a model simulation take and on what platform? More information could be helpful to the reader to see if this is a tool they might want to use in the future

//——A: It takes approximately 4 hours to simulate hourly biogeochemical evolutions of 3361 stream segments over a 3 year period on a 2 processors platform (Intel(R) Xeon(R) CPU E5-2670 0 @ 2.60GHz) with 16 cores (64 Go, DDR3 = 1600 MHz).

Computing time could be reduced on a more efficient platform.

//——R1C5: Why were the WWTP locations not known? Surely the coordinates exist? //——A: Coordinates of WWTP buildings are well known, but not the exact location of WWTP discharge points for all plants in the studied zone. That is why we had to make assumptions.

//——R1C6: Page 7 lines 27-30: Was this optimized numerically or by hand (manually)? //——A: All calibration steps were conducted manually based on sensitivity analysis.

//——R1C7: how was the Lagrangian view captured, specifically? How was the water mass tracked? //——A: Lagrangian views were produced based on travel time estimated for each reach and at each time-step. The matrix of travel time was estimated based on known discharge and river morphology (estimated for most reaches, except for the Loire River itself were we used measured values from previous studies). The following figure A5 explains the successive steps we considered to compute Lagrangian profiles:

//——R1C7: Page 9 lines 27: First mention of statistics, how do you calculated bias and error?

//——A: Bias and std errors are mentioned in section 3.4 but equations were not shown. Err_std=std(observation-model) Err_bias=$\sum\_(i = 1ton)(observation(i) - model(i))/n$

//——R1C8: Does the lack of the ability for the model to capture storms complicate the interpretation of the storm flow results in section 4.4?

//——A: We chose to describe the results of a storm event that was satisfactorily predicted on a sediment dynamic point of view (see Figure A6 below). We do not think that because the model underestimates sediment variations for several storms impacted our interpretations in section 4.4.

//——R1C9: Page 10: This entire section reiterates information in Table 2, it can probably be summarized in a sentence or two.

//——A: OK. We still think it is necessary to describe temporal variations over the studied period, but we decided to extract key messages from Table 2 as follows: "QUAL-NET provided reasonable estimations for the main variables (report to Table 2 for bias and standard deviation errors). Seasonal variations were correctly simulated for all variables. At the scale of the storm event, a few events were observed with the daily survey but were not represented by the model, especially for several events that occurred under low flow conditions. A phytoplankton bloom event at the end of summer 2012 was simulated but this did not correspond to our observations. The model provided interesting diel fluctuations in summer for PHY, SRP and O2 (e.g. SRP concentration fluctuated between 0 and 15 $\mu$g P L-1), but the reliability of these variations could not be verified with our measurements. Performances appeared similar between seasons (Table 2) with approximately the same range of errors in winter or summer, except for dissolved silica whose simulated concentrations in winter were subject to higher imprecisions (2.1 against 1.3 mgSi L-1 in summer) and for PHY with lower absolute errors in winter (a period with very low PHY concentrations)."

//——R1C10: page 10, line 21: It is interested that DOC varied with flow, and flow is seasonal, but the DOC concentration wasn't seasonal. Maybe expand on this a little bit more...

//——A: As it is shown in the DOC budget assessed during high flow and low flow periods (see above response to comment R1C2), DOC is only slightly transformed by biogeochemical processes within the Middle Loire River Corridor. Unlike POC, DOC variations at S2 are very close to variations at S1. QUAL-NET cannot fully explain why DOC isn't seasonal at the entrance of the Middle Loire River Corridor. However, we can hypothesize based on QUAL-NET results that DOC variations are largely driven by upstream soil leaching, and metabolic activities within the water column play only a minor role.





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//——R1C11: page 11, line 6: In figure 5, it is curious to me that the phytoplankton are growing at night. Shouldn't primary production go to 0, or is this a different measure of growth?

//——A: "phytoplankton growth" in Figure 5 represents phytoplankton growth controlled by the availability of intracellular carbon and nutrients, and not photosynthesis activity which, we agree, goes to zero at night. Phytoplankton growth is mostly driven by water temperature and nutrients availability. We would add this explanation in the manuscript, along with the reference of the model AQUAPHY (Lancelot et al. 1991) which serves as a basis in QUALNET biogeochemical module to describe primary producers dynamic. This formulation is also used in models RIVERSTRHALER or ProSe.

//——R1C12: page 14, line 18: "lost due to P-limitation" what do the authors mean by lost? Clarify

//——A: "lost" was not the right term. We meant that "PHY concentration declined by 40% due to P-limitation".

//——R1C13: page 15, lines 15-21: Can the authors quantify how sensitive the model was to these parameters? Can the authors speculate how useful this parameterization would be? Similar river systems, similar environments or would the model always have to be recalibrated?

//——A: During the calibration step, we observed that the sensitivity to phosphorus sorption/desorption coefficients was large. A previous study (in Camille Minaudo's PhD thesis) describes this sensitivity. In the model, PO4 is determined based on Langmuir equilibrium concept which uses TSS and Total Inorganic P concentrations and two coefficients Kpads and Pac that needs to be either calibrated or measured experimentally. Very different values were found in the literature for these coefficients, and largely impacts the estimation of PO4: Figure A7 shows differences in PO4 estimations for three different sets of values for Kpads and Pac extracted from 3 different studies on the Seine River.

Pac and Kapds values have never been assessed experimentally in the Loire River sediment. Our manual calibration found values very close to what AIssa Grouz (2015) has found experimentally in the neighboring Seine basin, showing that our parametrization could be used on other systems. However, if no specific measurements were conducted on the river sediment, we highly recommend to calibrate these coefficients within reasonable ranges.

//———————————— Figures Captions————————————————————-//

Figure A1. Phytoplankton concentration at S2 observed and estimated by QUALNET for three different simulations: the reference simulation used in the paper, a constant flow run with Q = 200 m3s-1 in the Loire River, and a constant flow run with Q = 1000 m3s-1 in the Loire River.

Figure A2. Phytoplankton concentration at S2 observed and estimated by QUALNET for three different simulations: the reference simulation used in the paper, and a constant temperature run with T = 13.7°C everywhere in the Loire River

Figure A3. Lagrangian view from S1 to S2 of phytoplankton and PO4 concentrations for 4 different scenarios: the reference simulation, a constant T°C simulation where T = 13.7°C in the Loire River, and two constant flow simulations where Q = 200 or 1000 m3 s-1

Figure A4. DOC and POC budgets assessed with QUAL-NET between S1 and S2 (would be included in Figure 7)

Figure A5. Successive steps to produce Lagrangian longitudinal profiles

Figure A6. Discharge and observed and modeled TSS concentration during the selected storm event.

Figure A7. Sensitivity of PO4 estimations from total inorganic P (PIT) and suspended solids concentrations (MES) based on the Langmuir equilibrium concept

Interactive comment on Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-229, 2017.

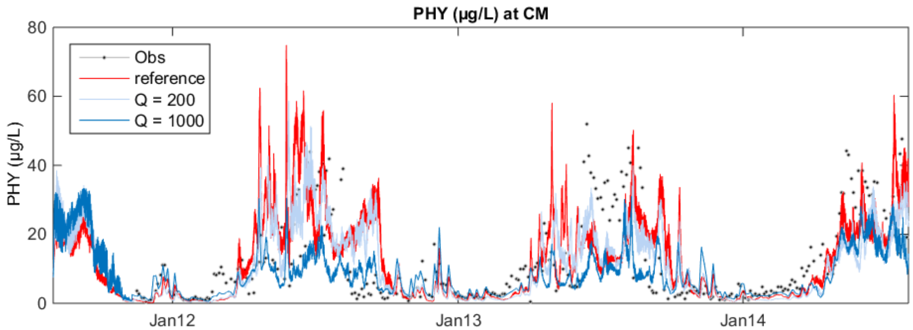


**Fig. 1.** Figure A1. Phytoplankton simulation sensitivity to hydrological conditions



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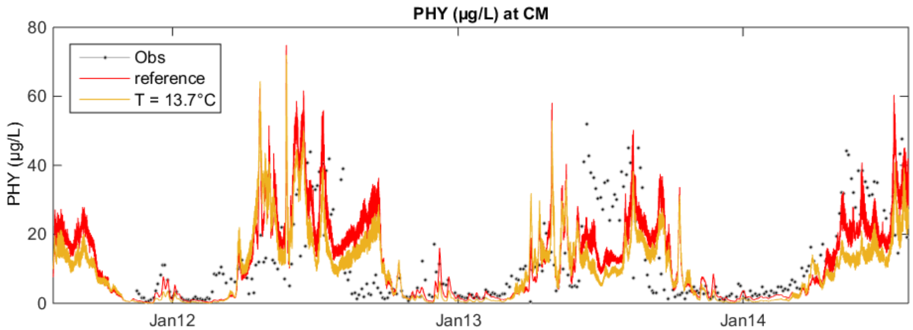


**Fig. 2.** Figure A2. Phytoplankton simulation sensitivity to water temperature conditions



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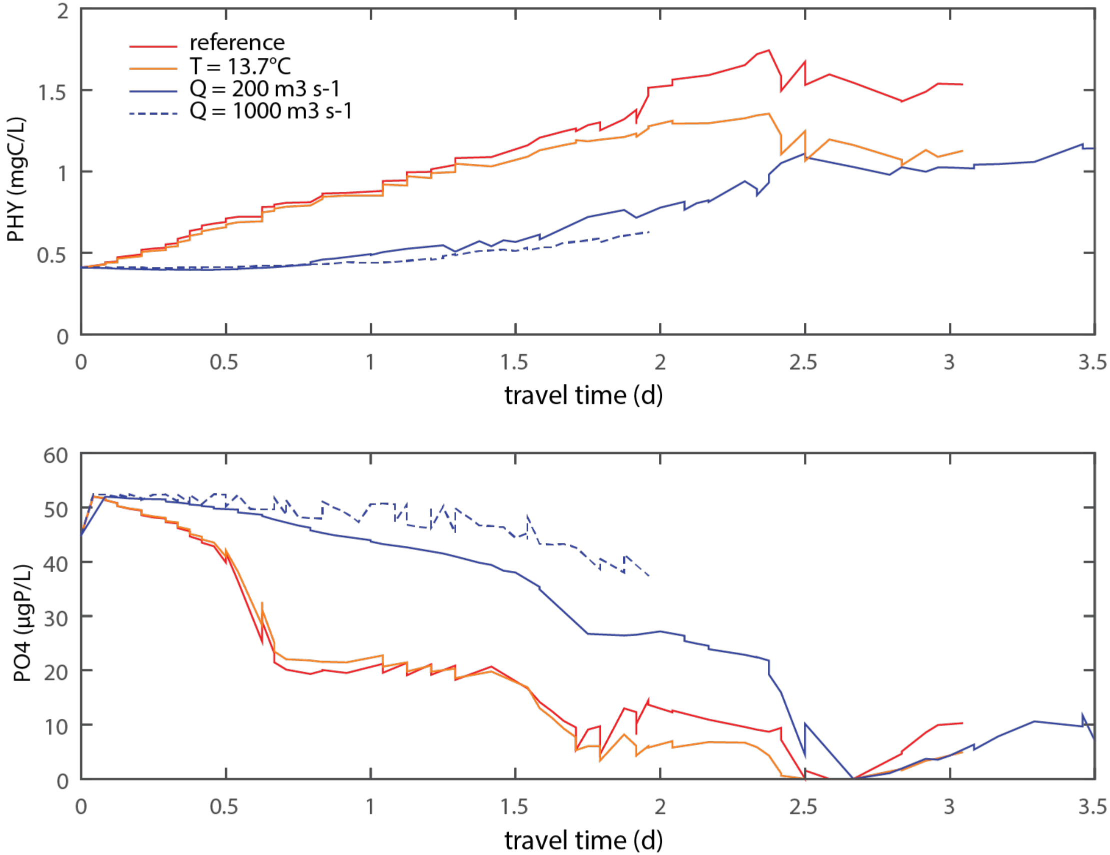


**Fig. 3.** Figure A3. Lagrangian view from S1 to S2 of phytoplankton and PO4 concentrations for 4 different scenarios





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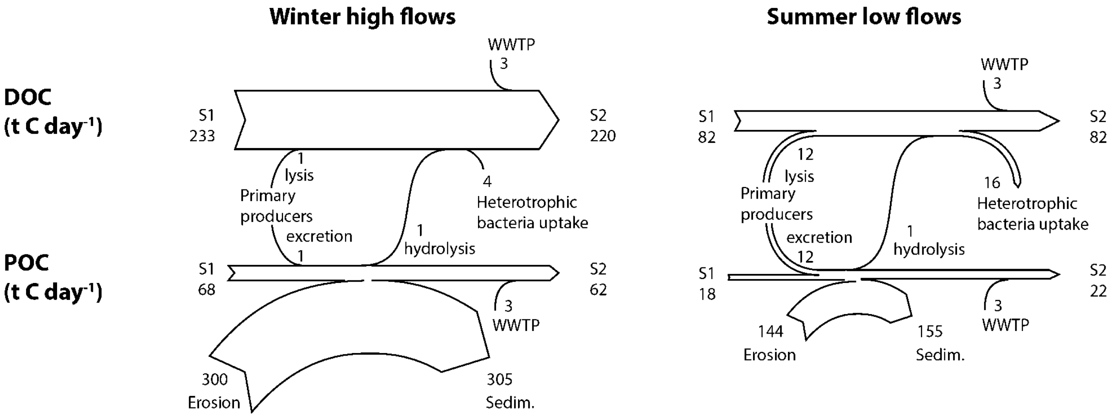


**Fig. 4.** Figure A4. DOC and POC budgets assessed with QUAL-NET between S1 and S2 (would be included in Figure 7)

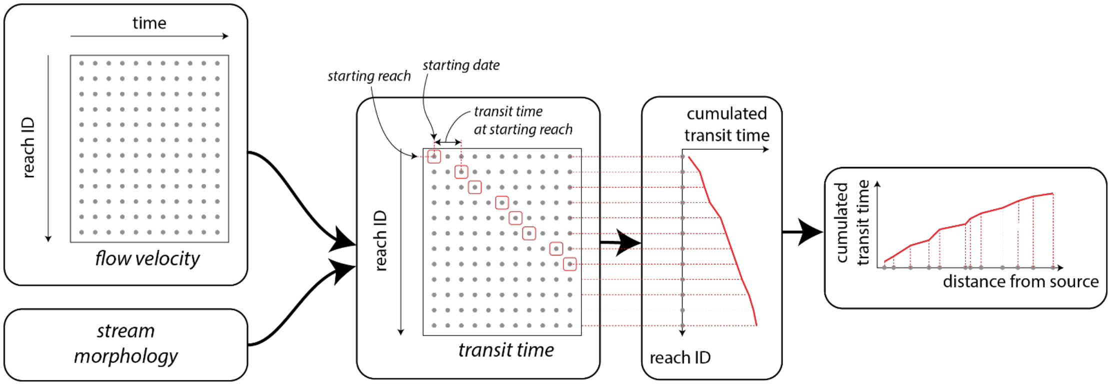


**Fig. 5.** Figure A5. Successive steps to produce Lagrangian longitudinal profiles

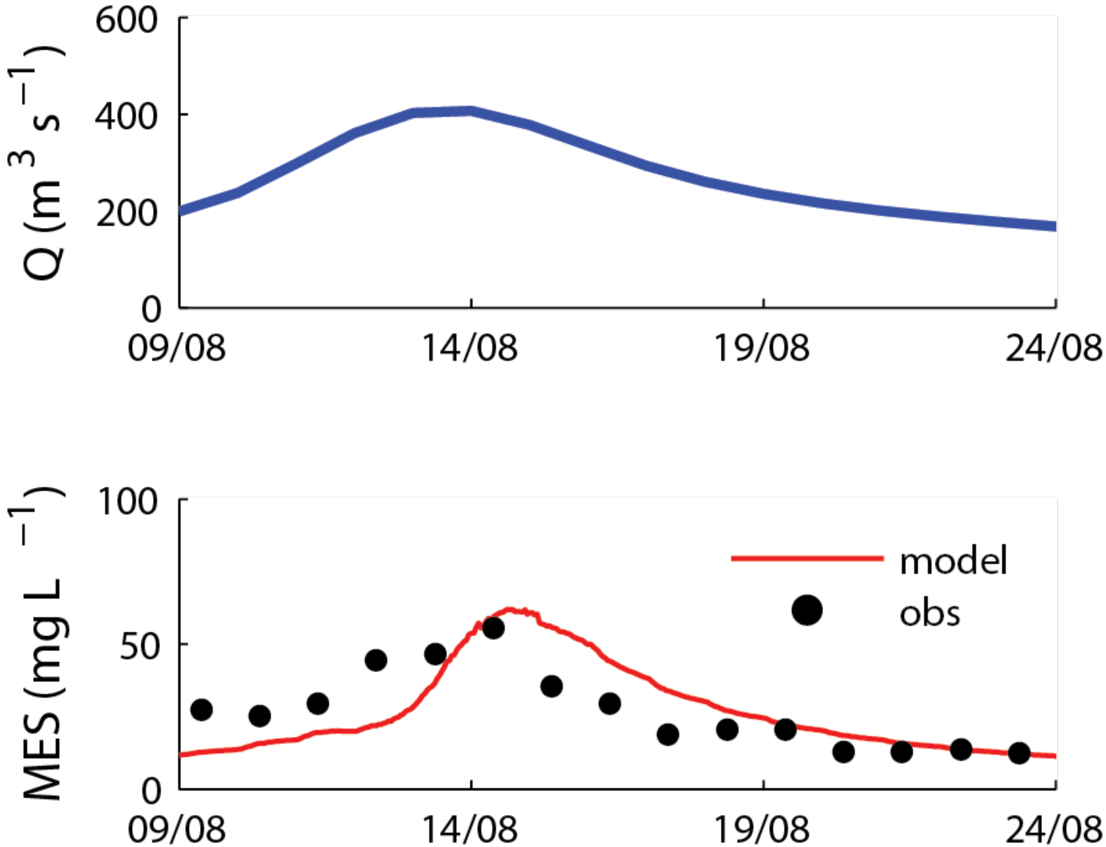


**Fig. 6.** Figure A6. Discharge and observed and modeled TSS concentration during the selected storm event

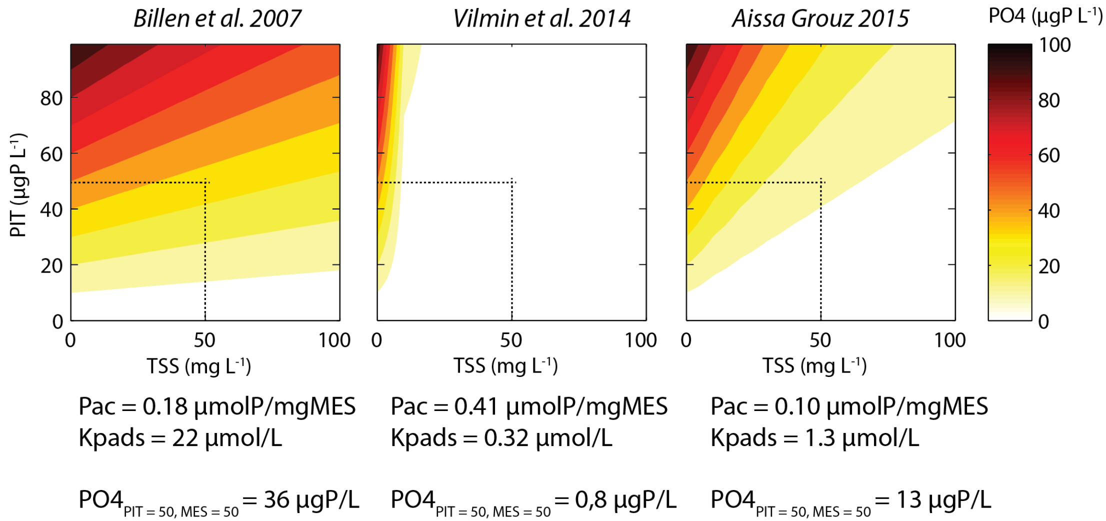


**Fig. 7.** Figure A7. Sensitivity of PO4 estimations from total inorganic P (PIT) and suspended solids concentrations (MES) based on the Langmuir equilibrium concept



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