Response to Referees

Authors are grateful for comments and suggestions from the two referees. All raised issues were listed below and carefully answered.

We had to run several other simulations to address some comments (especially the first comment from Referee 1). This did not affected results in the manuscript. Only descriptions and interpretations were modified.

Referees' comments are shown in blue. Authors' responses are in red.

Response to referee 1

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 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).

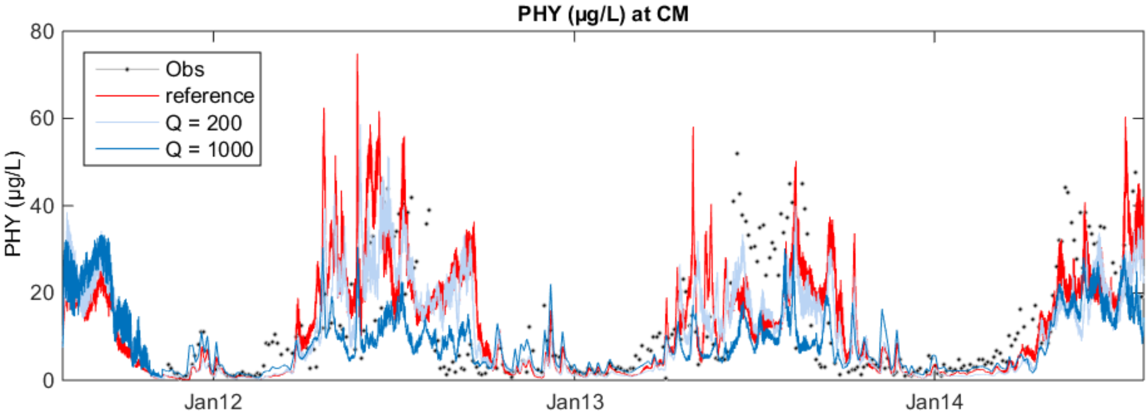


Figure A1. Phytoplankton concentration at S2 observed and estimated by QUALNET for three different simulations: the reference simulation used in the paper, a constant flow run with Q = 200 m3s-1 in the Loire River, and a constant flow run with Q = 1000 m3s-1 in the Loire River.

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°C (i.e. the median water temperature simulated in the Loire River by T-NET module).

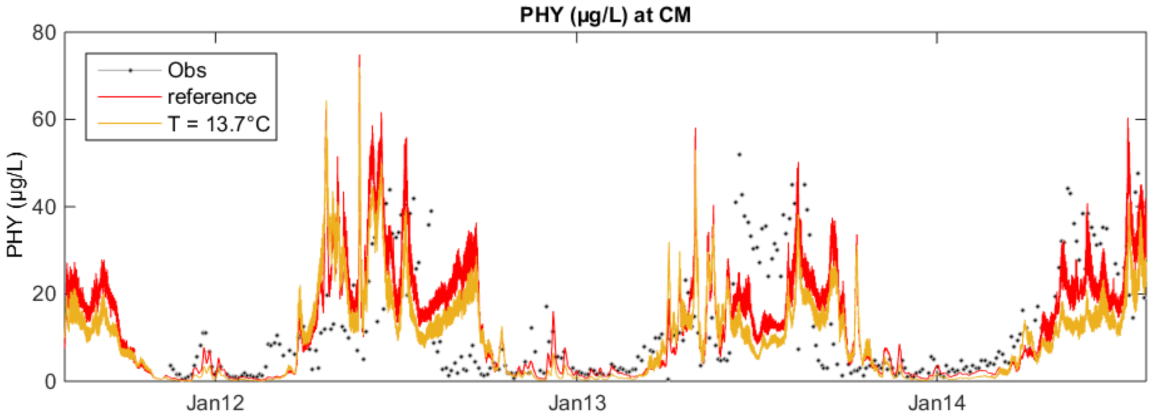


Figure A2. Phytoplankton concentration at S2 observed and estimated by QUALNET for three different simulations: the reference simulation used in the paper, and a constant temperature run with T = 13.7°C everywhere in the Loire River

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.

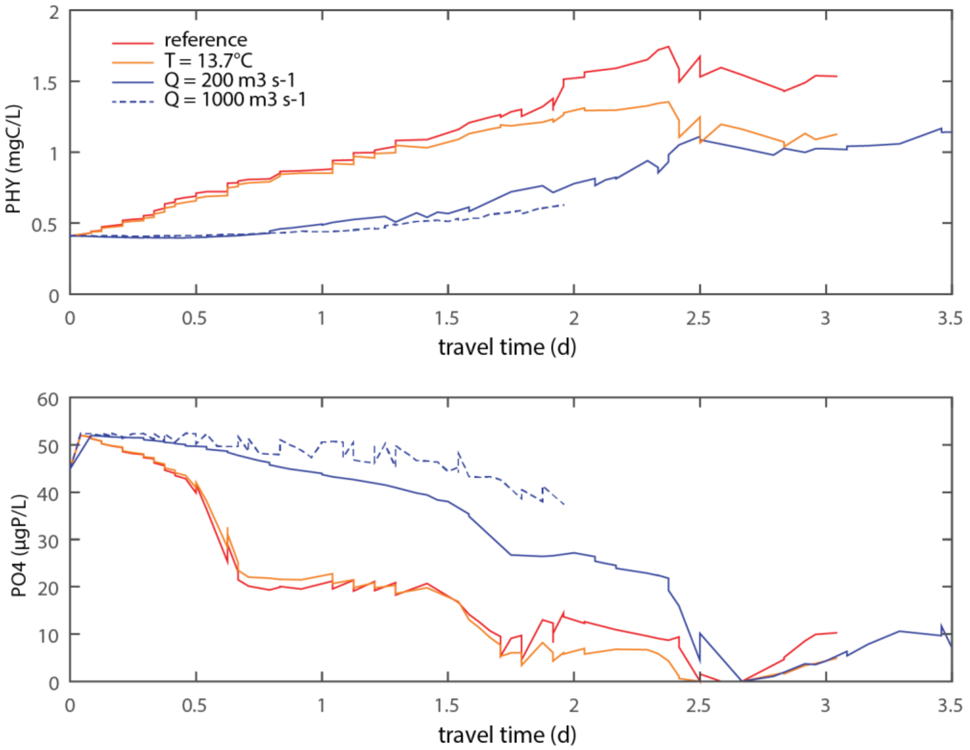


Figure A3. Lagrangian view from S1 to S2 of phytoplankton and PO4 concentrations for 4 different scenarios: the reference simulation, a constant T°C simulation where T = 13.7°C in the Loire River, and two constant flow simulations where Q = 200 or 1000 m3 s-1

It was decided to add Figure A3 as a Supplement file S1.

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.

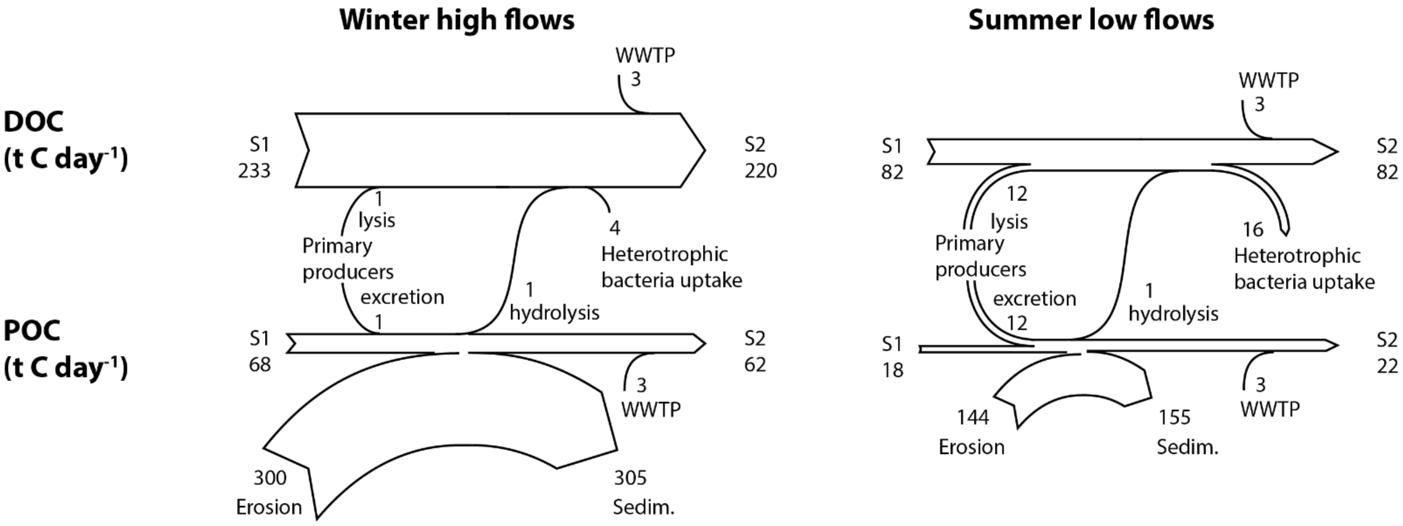


Figure A4. DOC and POC budgets assessed with QUAL-NET between S1 and S2

Figure A4 was added to Figure 7.

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.

This was modified in the manuscript, refer to page 7 lines 5-11 of the marked-up manuscript.

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.

This was modified in the manuscript, refer to page 7 lines 14-16 of the the marked-up manuscript.

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.
This was modified in the manuscript, refer to page 11 lines 1-2 of the marked-up manuscript.

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.
This was highlighted in the manuscript, refer to page 12 line 3 of the marked-up manuscript.

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:

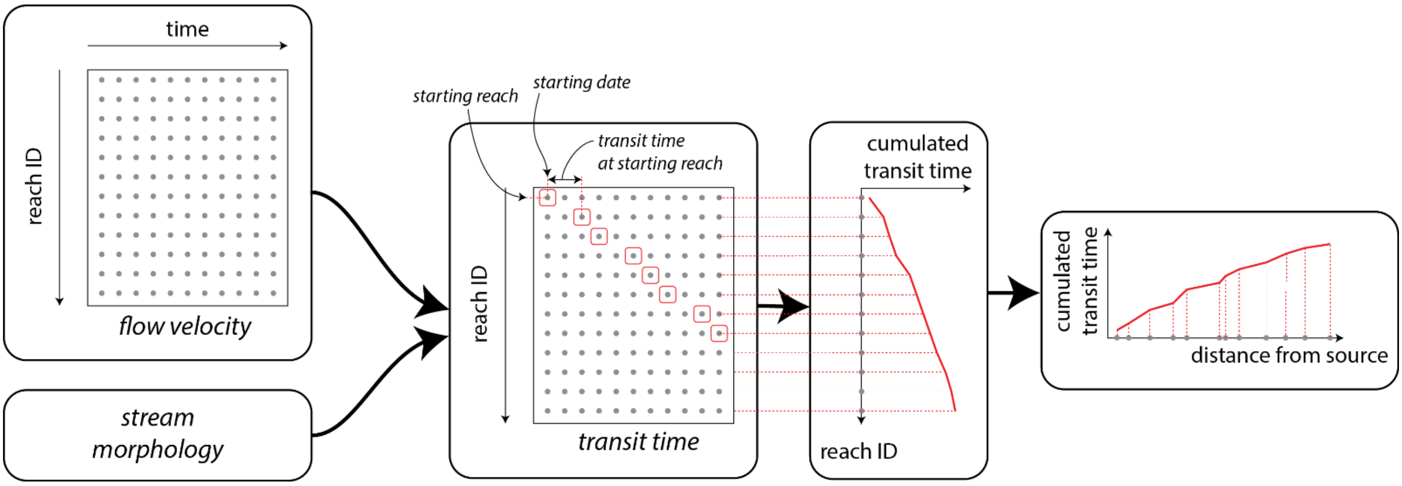


Figure A5. Successive steps to produce Lagrangian longitudinal profiles

This was added to the manuscript, refer to page 13 lines 16-17 of the marked-up manuscript.

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.

$$Err_{std} = std(observation - model)$$

$$Err_{bias} = \sum_{i=1}^{n} \frac{observation(i) - model(i)}{n}$$

This was added to the manuscript, refer to page 13 lines 6-7 of the marked-up manuscript.

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.

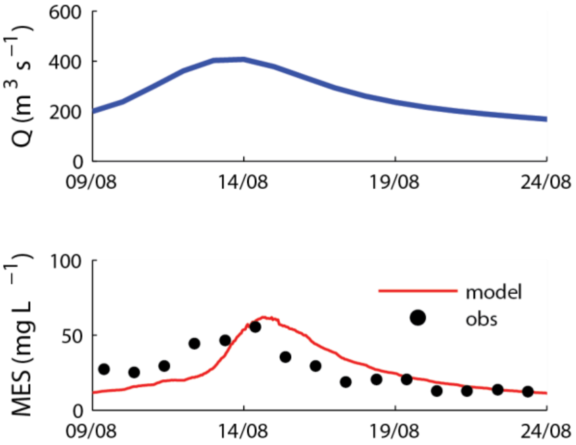


Figure A6. Discharge and observed and modeled TSS concentration during the selected storm event.

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 O_2 (e.g. SRP concentration fluctuated between 0 and 15 µg 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)."

This was added to the manuscript, refer to page 15 lines 15-28 of the marked-up manuscript.

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.

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.

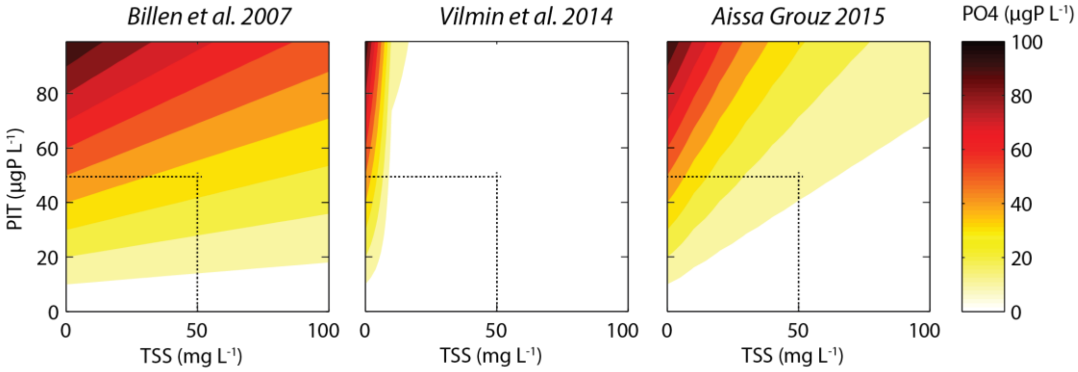
This was modified in the manuscript, refer to the legend of Figure 5.

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 = 0.18 µmolP/mgMES
Kpads = 22 µmol/L

Pac = 0.41 µmolP/mgMES
Kpads = 0.32 µmol/L

Pac = 0.10 µmolP/mgMES
Kpads = 1.3 µmol/L

$PO4_{PIT = 50, MES = 50} = 36$ µgP/L $PO4_{PIT = 50, MES = 50} = 0{,}8$ µgP/L $PO4_{PIT = 50, MES = 50} = 13$ µgP/L

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

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.

Response to referee 2

R2C1: The hypothesis and purpose of the study is somehow unclear. I do not really understand what the objective of this paper. Does the paper focus on the new modeling approach or the eutrophication in the modelling study?
A: The main objective was to assess the hydrological versus biological control of water quality in a eutrophic system. We proposed an original model to determine the controlling factors based on high temporal frequency. Thus, presenting the new model approach had to be a second objective in this paper.

R2C2: I found the manuscript written with unclear messages. The manuscript seems were written without final editing. I think it needs a language editing. Also, please avoid repetition of adverb such as "yet" and "additionally" in the text.
A: A native speaker went carefully through the manuscript to clarify as much as possible our messages.

R2C3: The manuscript states that most of biogeochemical processes are water temperature dependent, however, I found that it does not provide modeling result on temperature variable. How does the daily temperature look like? During the travel time from S1 to S2, does it highly fluctuated? During summer, does the temperature at S2 close to the temperature value at S1?
A: That is correct. We agree that presenting results of water temperature estimations is necessary.

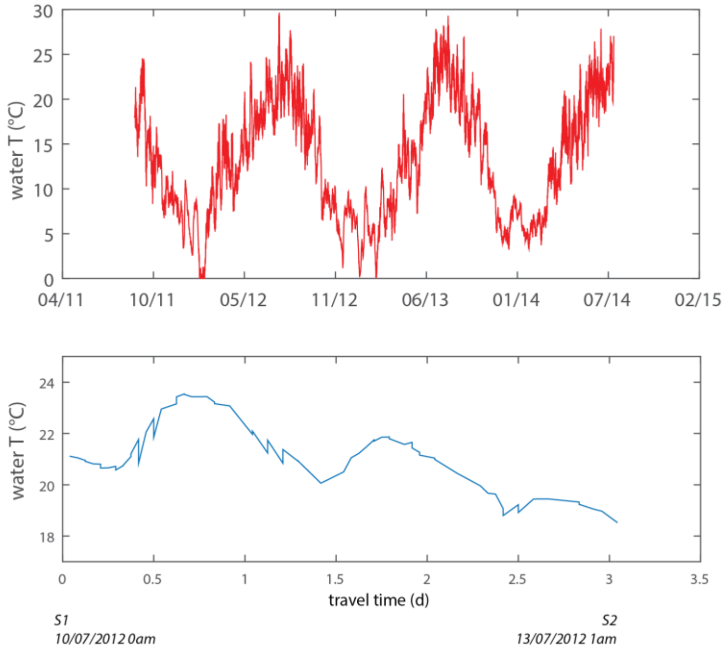


Figure A8. Water temperature estimated with T-NET module: top panel presents hourly variations at station S2 over the period considered. Bottom panel plots the evolution of water temperature when the water moves downstream from S1 to S2 during summer

Water temperature was highly seasonal and fluctuates between 0 and 30°C (Figure A8). In summer in the Loire River, amplitude of diel cycles ranged between 0.2 and 1.5°C.

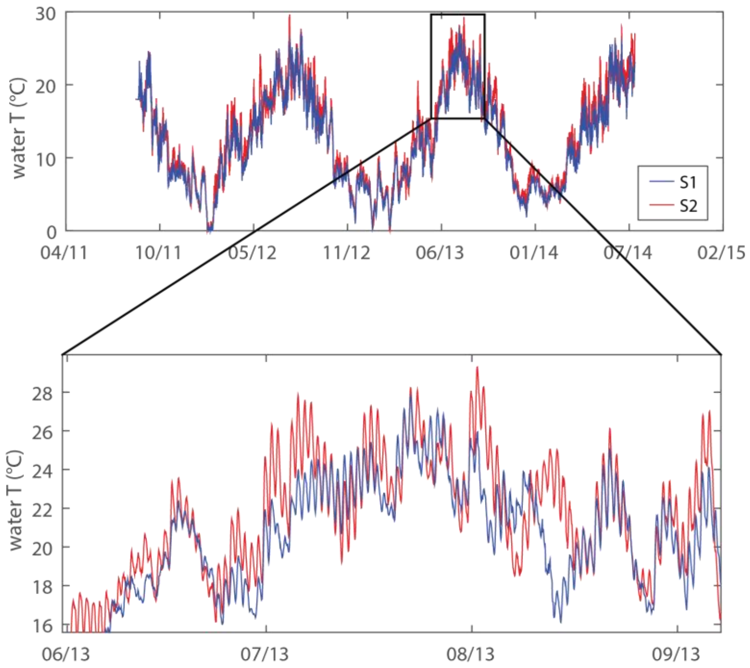


Figure A9. Water temperature estimated by T-NET module at S1 and S2

Seasonal variations between S1 and S2 were very close (Figure A9). Temperature variations at the daily scale were highly contrasted at the two stations, highlighting meteorological and hydrological controls on water temperature.

This was added to the manuscript, refer to Figure 5 in the marked-up manuscript.

R2C4: The fluxes and concentration of point sources were considered constant over the time in the model. Further explanation on how much and how fluxes and concentration were estimated is needed.

A: The regional Water Agency ("Agence de l'Eau Loire Bretagne") publishes N-P-C and total effluent fluxes exiting WWTP for all domestic and industrial effluents.

It was estimated in 2010 that point sources represent in the Middle Loire sub-catchment (our study) 322 kgP day-1 and 1.9 tN day-1. Model QUAL-NET uses directly this data.

We would add this information to the manuscript.

This was added to the manuscript, refer to page 9 lines 12-13 of the marked-up manuscript.

R2C5: The manuscript does not discuss how the model treats the nutrient source coming from re-suspended sediment and nutrient fluxes between water and sediment interface. I think a paragraph discussing this would be helpful for the reader.

A: This might have been unclear in our manuscript.

The model estimates for each river reach and at each time-step quantities of suspended particles eroded or that settled on the river bed (based on sedimentation velocities). Particles are both inorganic and organic with three levels of lability. Re-suspension might fuel the water column with soluble reactive phosphorus via desorption processes from suspended matter.

Diffusion processes for nutrients between the two layers are also considered. The benthic compartment can be either a source or a sink of nutrients, depending on redox conditions. All these processes are 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 was considered compact and not erodible, the other one could potentially be re-suspended. Nutrient fluxes between these two sediment layers were also considered in our model.

This was added to the manuscript, refer to page 7 lines 5-11 of the marked-up manuscript.

R2C6: (Page 1: Line 19) Change "or" to "end"

A: there was no "or" page 1 line 19

R2C7: (2:15-30) "Yet" and "additionally" adverbs were used extensively.

A: We carefully read the manuscript and tried to avoid these adverbs.

R2C8: (2:31) Instead of “context”, perhaps use “study”?
A: We really meant “context”, but this was modified in the manuscript to:

“The objectives of our study were twofold: firstly, develop a model able to simulate hydrological and biogeochemical processes in drainage networks at the regional scale (over 104 km^2), with hourly resolution and water temperature explicitly determined to allow potential climate change impact assessment; secondly, disentangle the different processes involved in eutrophication in a large river and identify their main drivers. To achieve this, the model QUALity-NETwork (QUAL-NET) was developed based on the integration of a biogeochemical model, RIVE (Garnier et al., 2002), in a thermal model, T-NET (Beaufort et al., 2016). This new model was tested on a selected portion of the Loire River basin, the Middle Loire River Corridor, draining 43x103 km^2, where the river main stem (270 km long) is prone to eutrophication in summer (Descy et al., 2011; Lair and Reyes-Marchant, 1997; Minaudo, 2015; Minaudo et al., 2015).”

Refer to page 4 lines 18-25 of the marked-up manuscript.

R2C9: (3:3, 7, 26) Missing multiply mark “x”. Also, in the figure 1.
A: OK, this was modified.

R2C10: (3: 18-20) Please reorganize these unclear sentences.
A: OK
“Chlorophyll-a concentration was often over 250 µg L-1 in the 1980s, and many efforts were conducted since 1990 to limit phosphorus point and non-point sources and counteract eutrophication: since 1990, phosphorus concentrations were divided 2.5-fold and phytoplankton blooms declined 3-fold (Floury et al., 2012; Minaudo et al., 2015; Oudin et al., 2009). Even if phytoplankton in the Loire system is now clearly P-limited, algal blooms still occur (Abonyi et al., 2012), questioning the source of phosphorus and suggesting potential recycling processes.”
This was modified, refer to page 6 lines 10-15 of the marked-up manuscript.

R2C11: (3: 22) Change “the fusion” to “a couple”
A: We changed it to:
“It is the coupling between a thermal model T-NET (Beaufort et al., 2016), and a biogeochemical model, RIVE (Garnier et al., 2002).”
This was modified, refer to page 6 lines 17-18 of the marked-up manuscript.

R2C12: (4: 16) In Figure 2, switch delta x with delta t.
A: OK

R2C13: (7: 19) In Figure 3, change the color lines and add a list of abbreviations to improve the figure clarity.
A: We don’t think this is needed: variable names already have abbreviations and are organized. Our objective with this figure really was to show the complexity of our model and the fact that variables are highly inter-dependent.

R2C14: (7: 31) What and how many variables were calibrated?
A: Two variables were calibrated: TSS and Total Inorganic P concentrations. To achieve this, 5 coefficients in total were manually calibrated (see Table 1 in the manuscript).
This was added to the manuscript, refer to page 12 lines 4-5 of the marked-up manuscript.

R2C15: (page 11, 12, and 13) I do not think lower roman numbering is necessary in the text.
A: OK
This was modified.

R2C16: (13, 21) Consider improving “At finer resolution” words in the conclusion. What resolution? Time or space? Finer from what?
A: You are right, we meant “higher temporal resolution”
This was modified, refer to page 18 lines 21-22 of the marked-up manuscript.

QUAL-NET, a high temporal resolution eutrophication model ~~in~~for large hydrographic networks

Camille Minaudo[1,2], Florence Curie[1], Yann Jullian[3], Nathalie Gassama[1], Florentina Moatar[1]

[1]E.A. 6293 GeHCO, François Rabelais de Tours University, Tours, 37000, France
[2]OSUR-CNRS, Rennes 1 University, Rennes, 35000, France
[3]CaSciModOT, UFR Sciences et Techniques, François Rabelais de Tours University, Tours, 37000, France

Correspondence to: Camille Minaudo (camille.minaudo@univ-tours.fr)

Abstract. To allow climate change impact assessment ~~on river system~~of water quality in river systems, the scientific community lacks efficient deterministic models able to simulate hydrological and biogeochemical processes in drainage networks at the regional scale, with ~~a fine~~high temporal resolution and~~ with~~ water temperature explicitly determined. The model QUALity-NETwork (QUAL-NET) was developed and tested on the Middle Loire River Corridor, a sub-catchment of the Loire River ~~(~~in France~~)~~, prone to eutrophication. Hourly variations computed efficiently by the model helped disentangle the complex interactions existing between hydrological and biological processes across different timescales. ~~Phytoplankton variations~~Phosphorus (P) availability was the most constraining factor for phytoplankton development in the Loire River~~ were governed by phosphorus availability and transit time. Model ~~, but simulating bacterial dynamics in QUAL-NET ~~showed that a~~surprisingly evidenced large ~~amount~~amounts of ~~phytoplankton cells growing in the upper part of the studied corridor was~~ organic matter recycled within the water column through the microbial loop, which delivered significant fluxes of available P and enhanced phytoplankton growth~~, explaining~~. This explained why severe blooms still occur in the Loire River despite large P input reductions since 1990. QUAL-NET could be used to study past evolutions or predict future trajectories under climate change and land use scenarios.

~~1 Introduction~~

~~River eutrophication has become a rising problem over the past decades, especially in India, Asia or South America, constituting a major risk for ecosystems and human health (e.g. Braga et al., 2000; Dixit et al., 2017; Némery and Garnier, 2016; Yin et al., 2016). Significant efforts to reduce non-point and point sources of nitrogen (N) and phosphorus (P) were done in Europe and North America, leading to eutrophication decline in several large rivers (Friedrich and Pohlmann, 2009; Hardenbicker et al., 2014; Hartmann et al., 2007; Howden et al., 2010; Minaudo et al., 2015, 2016). Yet, eutrophication crises are still occurring in many freshwater areas.~~

~~Previous studies often tried to assess which controlling factor of eutrophication prevails over the others, and often opposed nutrients availability to supposedly favorable physical conditions. Conflicting results shown in the literature did not help solve this issue. Indeed, in some rivers chlorophyll-*a* concentration could directly be assessed confidently from P concentration (e.g. Basu and Pick, 1996; Dodds, 2006), whereas river flow conditions in other systems clearly constrained and determined the algal biomass (Biggs and Smith, 2002; Istvánovics et al., 2009). A few studies identified a combination of variables co-controlling phytoplankton blooms like the association of river flow conditions, water temperature and sunshine duration over the preceding days (Bowes et al., 2016), flow and light intensity (Hardenbicker et al., 2014), and flow, temperature and nutrients availability (Van Vliet and Zwolsman, 2008). If reducing P inputs has proved to be efficient to limit phytoplankton blooms in rivers, many recent studies show that both N and P availability must be considered as key elements to determine trophic state in streams and rivers (Dodds and Smith, 2016; Paerl et al., 2016). Apart from nutrients availability, numerous other factors control phytoplankton composition and abundance in rivers, such as water residence time (directly linked to the river morphology, with potential presence of flow velocity dead-zones), penetration of solar radiation into the water column (depth and turbidity), water temperature variations (hydrological and climate forcing), invertebrate grazing from endemic and invasive species and self-shading effects by the phytoplankton colony itself (Reynolds, 2006; Reynolds and Descy, 1996).~~

~~Disentangling the relative influence of so many chemical, biological and physical factors on the river biogeochemistry can hardly be captured confidently through a simple water quality monitoring and often requires the help of numerical modelling. Many deterministic water quality models at the catchment scale were developed and used initially to estimate nutrient source inputs into receiving waterbodies, and support watershed stakeholders and decision-makers to tackle eutrophication issues (Wellen et al., 2015). Yet, a limited number of models propose a mechanistic module simulating phytoplankton community dynamics and its impact on eutrophication. One can cite RIVERSTRAHLER (Billen et al., 1994; Garnier et al., 2002), ProSe (Even, 1995; Even et al., 1998; Flipo et al., 2004; Vilmin et al., 2015), PEGASE (Deliège et al., 2009), QSIM (Kirchesch and Schöl, 1999; Schöl et al., 1999), WaterRAT (McIntyre and Wheater, 2004), QUAL2KW (Pelletier et al., 2006), WASP7 (Ambrose and Wool, 2009), QUASAR (Whitehead et al., 1997) or RWQM1 (Reichert et al., 2001). However, many of these models are only able to simulate river stretches, and not the entire river network. The main reason is that very few models work at the catchment scale with a subdaily timestep (Wellen et al., 2015), mostly because program developers have to face long calculation time, and usually make a compromise between large spatial scale and high temporal and/or spatial resolution. Yet, the use of a fine temporal resolution is required to account for hydrological and biogeochemical processes occurring over short periods of time (e.g. storm events, or subdaily phytoplankton growth variations). Additionally, water temperature is a key factor for phytoplankton abundance and assemblage (Reynolds, 2006) which needs to be simulated at high temporal frequency to assess the impact of potentially drier streams and warmer summers under climate change (Quiel et al., 2010). Developing methods appropriate to the regional scale is also required to account for instream processes in large rivers which control N, P and carbon (C) variations, and constrain water quality in estuarine and coastal zones. Additionally, models' scales also have to match with the scale of actions undertaken by water body stakeholders and catchment managers.~~

~~In this context, the model QUALity-NETwork (QUAL-NET) was developed to simulate hydrological and biogeochemical processes in drainage networks at the regional scale (over 10^4 km²), with a sub-daily temporal resolution and water temperature explicitly determined to allow potential climate change impact assessment. QUAL-NET was based on the integration of a biogeochemical model, RIVE (Garnier et al., 2002) in a thermal model, T-NET (Beaufort et al., 2016). This approach was tested on a selected portion of the Loire River basin, the Middle Loire River Corridor, draining 43 10^3 km², where the river main stem (270 km long) is prone to eutrophication in summer (Lair and Reyes-Marchant, 1997; Minaudo, 2015; Minaudo et al., 2015).~~

1 Introduction

River eutrophication has become a rising problem over the past decades, especially in India, Asia or South America, constituting a major risk for ecosystems and human health (e.g. Braga et al., 2000; Dixit et al., 2017; Némery and Garnier, 2016; Yin et al., 2016). Significant efforts to reduce non-point and point sources of nitrogen (N) and phosphorus (P) were done in Europe and North America, leading to eutrophication decline in several large rivers (Friedrich and Pohlmann, 2009; Hardenbicker et al., 2014; Hartmann et al., 2007; Howden et al., 2010; Minaudo et al., 2015, 2016; Poisvert et al., 2017; Powers et al., 2016). However, eutrophication crises are still occurring in many freshwater areas.

Previous studies often tried to assess which controlling factor of eutrophication prevails over the others, and often opposed nutrients availability to supposedly favorable physical conditions. Conflicting results in the literature did not solve this issue. In some rivers chlorophyll-*a* concentration could directly be assessed confidently from P concentration (e.g. Basu and Pick, 1996; Dodds, 2006), whereas river flow conditions in other systems clearly constrained and determined the algal biomass (Biggs and Smith, 2002; Istvánovics et al., 2009). A few studies identified a combination of variables co-controlling phytoplankton blooms like the association of river flow conditions, water temperature and sunshine duration over the preceding days (Bowes et al., 2016), flow and light intensity (Hardenbicker et al., 2014), and flow, temperature and nutrients availability (Van Vliet and Zwolsman, 2008). If reducing P inputs has proved to be efficient to limit phytoplankton blooms in rivers, many recent studies show that both N and P availability must be considered as key elements to determine trophic state in streams and rivers (Dodds and Smith, 2016; Paerl et al., 2016). Apart from nutrients availability, numerous other factors control phytoplankton composition and abundance in rivers, such as water residence time (directly linked to the river morphology, with potential presence of flow velocity dead-zones), penetration of solar radiation into the water column (depth and turbidity), water temperature variations (hydrological and climate forcing), invertebrate grazing from endemic and invasive species, and self-shading effects by the phytoplankton colony itself (Abonyi et al., 2018; Reynolds, 2006; Reynolds and Descy, 1996).

Disentangling the relative influence of so many chemical, biological and physical factors on the river biogeochemistry can hardly be captured confidently through a simple water quality monitoring and often requires the help of numerical modelling.

Many deterministic water quality models at the catchment scale were developed and used initially to estimate nutrient source inputs into receiving waterbodies, and support watershed stakeholders and decision-makers to tackle eutrophication issues (Wellen et al., 2015). Only a limited number of models propose a mechanistic module simulating phytoplankton community dynamics and its impact on eutrophication. One can cite RIVERSTRAHLER (Billen et al., 1994; Garnier et al., 2002), ProSe (Even, 1995; Even et al., 1998; Flipo et al., 2004; Vilmin et al., 2015), PEGASE (Deliège et al., 2009), QSIM (Kirchesch and Schöl, 1999; Schöl et al., 1999), WaterRAT (McIntyre and Wheater, 2004), QUAL2KW (Pelletier et al., 2006), WASP7 (Ambrose and Wool, 2009), QUASAR (Whitehead et al., 1997) or RWQM1 (Reichert et al., 2001). However, many of these models are only able to simulate river stretches, and not the entire river network. The main reason is that very few models work at the catchment scale with subdaily timesteps (Wellen et al., 2015), mostly because program developers have to face long calculation times, and usually compromise between large spatial scale and high temporal and/or spatial resolution. The use of high temporal resolution is however required to account for hydrological and biogeochemical processes occurring over short periods of time (e.g. storm events, or subdaily phytoplankton growth variations). Water temperature is also a key factor for phytoplankton abundance and assemblage (Reynolds, 2006) which needs to be simulated at high temporal frequency to assess the impact of potentially drier streams and warmer summers under climate change (Quiel et al., 2010). Developing methods appropriate to the regional scale is also required to account for instream processes in large rivers that control N, P and carbon (C) variations, and constrain water quality in estuarine and coastal zones. Finally, models need to be appropriate for regional studies, i.e. the scale at which actions are undertaken by water body stakeholders and catchment managers.

The objectives of our study were twofold: firstly, develop a model able to simulate hydrological and biogeochemical processes in drainage networks at the regional scale (over 10^4 km²), with hourly resolution and water temperature explicitly determined to allow potential climate change impact assessment; secondly, disentangle the different processes involved in eutrophication in a large river and identify their main drivers. To achieve this, the model QUALity-NETwork (QUAL-NET) was developed based on the integration of a biogeochemical model, RIVE (Garnier et al., 2002), in a thermal model, T-NET (Beaufort et al., 2016). This new model was tested on a selected portion of the Loire River basin, the Middle Loire River Corridor, draining 43x10^3 km², where the river main stem (270 km long) is prone to eutrophication in summer (Descy et al., 2011; Lair and Reyes-Marchant, 1997; Minaudo, 2015; Minaudo et al., 2015).

2 Study site

~~The Loire River (110 10^3 km²) is the largest river flowing in France. The selected Middle Loire Corridor is a subcatchment located in the lowland section of the river main stem (Figure 1). It separates the Upper Loire (a mountainous area where anthropogenic pressures are highly impacting the river water quality but where eutrophication is only visible in lakes and reservoirs), from the Lower Loire River where the river main stem meets its major tributaries (Cher, Indre, Vienne, Maine). The Middle Loire River Corridor (MLRC) starts 450 km from the source of the River and runs over 300 km, increasing in~~

~~length by 50% while meeting only minor tributaries. From the beginning of the MLRC to its outlet, i.e. stations S1 to S2 respectively on Figure 1, the cumulated catchment area increases by only 26%. The MLRC has a high eutrophication potential, combining most of the conditions favoring phytoplankton growth: low water level in summer (≈1m) and a river morphology with multiple channels and numerous islands slowing down flow velocity which increases the water travel time (Latapie et al., 2014). Many efforts have been conducted since 1990 to limit phosphorus point and non-point sources and counteract eutrophication which was reaching some extreme levels (chlorophyll-*a* concentration often over 250 µg L^{-1} in the 1980s). Phosphorus concentrations were since divided 2.5-fold and phytoplankton blooms declined 3-fold (Floury et al., 2012; Minaudo et al., 2015; Oudin et al., 2009). Yet, algal blooms are still occurring from time to time, questioning the source of phosphorus.~~

~~3 Methods~~

~~The model QUALity NETwork (QUAL-NET) was developed based on a deterministic approach. It is the fusion between a thermal model T-NET (Beaufort et al., 2016), and a biogeochemical model, RIVE (Garnier et al., 2002).~~

~~Model T-NET is a physically based model able to estimate the water temperature in each reach of a large hydrographical network (10^5 km²) with an hourly resolution (Beaufort, 2015; Beaufort et al., 2016). It has previously been developed specifically for the Loire River Basin (110 10^3 km² and over 50 10^3 river reaches from headwaters to the estuary). The temperature in the river network is computed as follows: i) resolution of the heat budget in a given reach and estimation of the equilibrium temperature; ii) longitudinal propagation downstream of the thermal signal according to the estimated water velocity throughout the river reach; iii) discharge-weighted mix of the thermal signal when two or more streams meet in one node.~~

~~Model RIVE is a mechanistic model describing many of the biogeochemical interactions occurring in the river between the water column, and the benthos. It simulates the dynamic of dissolved and particulate organic matter, nutrients (N, P, Si), dissolved oxygen, the phytoplankton biomass (three algae groups: green algae, diatoms, and cyanobacteria), zooplankton and bacteria. RIVE is the core of RIVERSTRAHLER (Billen et al., 1994) and ProSe (Even et al., 1998) models. RIVERSTRAHLER was largely used in past studies to simulate with a 10-day time step the biogeochemical functioning of large lowland eutrophic rivers under varying climate conditions, e.g. the Seine basin, the Danube River, the Red River in Vietnam, and over large periods of time (Billen et al., 2001; Billen and Garnier, 2000; Garnier et al., 1995, 2002, 2005; Quynh et al., 2010). The numerous variables included in the model and equations are extensively described in Billen et al. (1994) and Garnier et al. (2002). Both the water and the benthic components are considered, including chemical and physical exchanges in-between these two components, according to Billen et al. (2014) formulation.~~

The Loire River ($110 x 10^3$ km²) is the largest river flowing in France. The selected Middle Loire River Corridor (MLRC) is an intermediate subcatchment located in the lowland section of the river main stem (Figure 1). It separates the Upper Loire (a mountainous area where anthropogenic pressures are highly impacting the river water quality but where eutrophication is only visible in lakes and reservoirs (Jugnia et al., 2004)), from the Lower Loire River where the river main stem meets its major tributaries (Cher, Indre, Vienne and Maine Rivers). The MLRC starts 450 km from the headwaters and runs over 270 km, increasing in length by 50% while meeting only minor tributaries: from its entrance to its outlet (stations S1 to S2 on Figure 1), the cumulated catchment area in the MLRC increases by only 26%. This section of the river has a high eutrophication potential, combining most of the conditions favoring phytoplankton growth: high N and P concentrations (Minaudo et al., 2015), low water level in summer (≈1m) and a morphology with multiple channels and numerous islands slowing down flow velocity which increases the water travel time (Latapie et al., 2014). Chlorophyll-*a* concentration was often over 250 µg L^{-1} in the 1980s, and many efforts were conducted since 1990 to limit phosphorus point and non-point sources and counteract eutrophication: since 1990, phosphorus concentrations were divided 2.5-fold and phytoplankton blooms declined 3-fold (Floury et al., 2012; Minaudo et al., 2015; Oudin et al., 2009). Even if phytoplankton in the Loire system is now clearly P-limited, algal blooms still occur (Abonyi et al., 2012), questioning the source of phosphorus and suggesting potential recycling processes.

3 Methods

The model QUALity NETwork (QUAL-NET) was developed based on a deterministic approach. It is the coupling between a thermal model, T-NET (Beaufort et al., 2016), and a biogeochemical model, RIVE (Garnier et al., 2002).

Model T-NET is a physically based model able to estimate the water temperature in each reach of a large hydrographical network (10^5 km²) with an hourly resolution and low errors, especially in the lowland area (Beaufort et al., 2015, 2016; Loicq et al., 2018). It has previously been developed specifically for the Loire River Basin ($110 x 10^3$ km² and over $50 x 10^3$ river reaches from headwaters to the estuary). The temperature in the river network is computed as follows: i) resolution of the heat budget in a given reach and estimation of the equilibrium temperature (Bustillo et al., 2014); ii) longitudinal propagation downstream of the thermal signal according to the estimated water velocity throughout the river reach; iii) discharge-weighted mix of the thermal signal when two or more streams meet in one node.

Model RIVE is a mechanistic model describing many of the biogeochemical interactions that occur in the river between the water column, and the benthos. It simulates the dynamic of dissolved and particulate organic matter, nutrients (N, P, Si), dissolved oxygen, the phytoplankton biomass (three algae groups: green algae, diatoms, and cyanobacteria), zooplankton and bacteria. Equations from model AQUAPHY (Lancelot et al., 1991) were used to describe primary producers variations. Model RIVE is the biogeochemical module of RIVERSTRAHLER (Billen et al., 1994) and ProSe (Even et al., 1998) models. RIVERSTRAHLER was largely used in past studies to simulate with a 10-day time step biogeochemical variations in large lowland eutrophic rivers under varying climate conditions, e.g. the Seine basin, the Danube River, the Red River in Vietnam, and over large periods of time (Billen et al., 2001; Billen and Garnier, 2000; Garnier et al., 1995, 2002, 2005; Quynh et al., 2010). Equations and variables included in the model are extensively described in Billen et al. (1994) and Garnier et al. (2002). Both the water and the benthic components were considered, including chemical and physical exchanges in-between these two components, according to Billen et al. (2014) formulation. Equations in this formulation provided estimates of nitrogen, phosphorus, silica and dissolved oxygen fluxes across the water – sediment interface. The sediment layer was split into two sub-layers. The one at the bottom was considered compact and not erodible, the other one could potentially be re-suspended. Nutrient fluxes between these two sediment layers were also considered in our model. The model estimated for each river reach and at each time-step quantities of eroded particles or that settled on the river bed. Particles were considered as both inorganic and organic with three levels of lability. Re-suspension could potentially fuel the water column with soluble reactive phosphorus via desorption processes from suspended matter.

Temporal resolution of QUAL-NET ~~is hourly even if biogeochemical variations were computed every 15 minutes to avoid potential numerical drifts~~was hourly. QUAL-NET was coded in C++ language and allowed parallel computing, i.e. the simultaneous use of several processors in order to reduce as much as possible computation time. Simulating hourly biogeochemical evolutions of 3361 stream segments over a 3 year period took nearly 4 hours on a 2 processors platform (Intel(R) Xeon(R) CPU E5-2670 0 @ 2.60GHz) with 16 cores (64 Go, DDR3 = 1600 MHz).

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3.1 Data inputs and main spatialization choices

Hydrological, geomorphological and meteorological forcing variables were determined and used on the basis of T-NET model implementation on the Loire Basin (Figure 2). Thus, a more detailed description is available in ~~Beaufort et al. (2016)~~Beaufort et al. (2016), except for nutrient sources forcing variables.

3.1.1 Meteorological variables

Hourly meteorological variables were taken from SAFRAN atmospheric reanalysis ~~(Quintana-Segui et al., 2008), produced by the French Meteorological Services (Meteo-France). Spatial resolution was 8x8 km^2. Meteorological variables were used to compute the hydrological model (see below) for both thermal and biogeochemical modules: air temperature, specific humidity, wind velocity and atmospheric radiation were used to compute water temperature; most~~(Quintana-Segui et al., 2008), produced by the French Meteorological Services (Meteo-France). Spatial resolution was 8x8 km^2. Meteorological variables were used to compute the hydrological model (see below) for both thermal and biogeochemical modules. Air temperature, specific humidity, wind velocity and atmospheric radiation were used to compute water temperature. Most biogeochemical variables were water-temperature dependent, and phytoplankton photosynthesis processes were directly linked to atmospheric radiation variations.

3.1.2 Hydrology

Daily mean discharge and groundwater flows were simulated by the semi-distributed hydrological model EROS ~~(Thiéry and Moutzopoulos, 1995)~~(Thiéry and Moutzopoulos, 1995) at the outlet of 17 ~~subwatersheds.~~sub-watersheds. Within each of these ~~subwatersheds~~sub-watersheds, flows were redistributed into the hydrographic network according to the corresponding drainage area of each river reach. This approach proved its efficiency and reliability at the regional scale in the Loire Basin ~~(Beaufort et al., 2016)~~(Beaufort et al., 2016). Discharge and groundwater flows were considered constant over 24 h even if the water quality model output was hourly.

3.1.3 Geomorphology

The hydrographical network was determined from the Carthage® database (French Ministry of Environment and regional water agencies cartography, ~~Carthage, 2012), after transforming multiple channels into single channels. In the MLRC, we counted 3361 reaches, every one of them being defined as the river section between two confluences. Slopes for each reach were assessed based on a 25 m resolution digital terrain model (BD ALTI®, 2012). Streams transversal morphology were assumed to be rectangular, while depth and width were assessed on a daily time step but differently for the Loire River main stem and other streams: i) depth in the Loire River main stem reaches was assessed based on field measurements conducted during both low and high flow periods (Latapie, 2011; Latapie et al., 2014) and considering Manning-Strickler formulation with a Strickler coefficient to be calibrated numerically; ii) in all other rivers and streams, where no field measurements were done, depth and width were assessed daily based on the ESTIMKART application (Lamouroux et al., 2010) which uses reach~~Carthage, 2012), after transforming multiple channels into single channels. In the MLRC, we counted 3361 reaches, every one of them being defined as the river section between two confluences. Slopes for each reach were assessed based on a 25 m resolution digital terrain model (BD ALTI®, 2012). Transversal morphology in streams were assumed to be rectangular, while depth and width were assessed on a daily time step but differently for the Loire River main stem and other streams: i) depths in the Loire River main stem reaches were assessed based on field measurements conducted during both low and high flow periods (Latapie, 2011; Latapie et al., 2014) combined with Manning-Strickler formulation (Strickler coefficient was calibrated numerically); ii) in all other rivers and streams, where no field measurements were available, depth and width were assessed daily based on the ESTIMKART application (Lamouroux et al., 2010) which uses stream slope, watershed area, daily and inter-annual discharge to estimate streams morphology.

3.1.4 Non-point sources

Non-point sources of nutrients and exports of TSS were defined based on land use (European Corine Land Cover dataset, ~~2006)~~2006), climate characteristics, lithology ~~(LITHO®, 2008)~~(LITHO®, 2008) and previous observations conducted in 108 streams located in the Loire headwaters, upstream any potential point sources ~~(Blanchard, 2007).~~(Blanchard, 2007). Overall, land use categories were grouped into seven large categories (urban, arable land, cultivated land, prairie, forest, wetland, other types), and associated with a corresponding non-point source concentration for the following variables: nitrate, ammonium, total inorganic phosphorus, biogenic silica, dissolved and particulate organic carbon for three different biodegradability classes, total suspended solids, and fecal matter. The MLRC basin was divided into 479 small sub-catchments (the average was 27 km²), and diffuse sources concentrations were applied homogenously for all streams located in a given sub-catchment as a combination of concentrations originating from all the different land use types. Land use was considered constant over time, leading to constant nutrient concentrations for non-point sources. Thus, it was hypothesized that the hydrological variability alone could be responsible for ~~seasonal and event-based~~temporal variations of non-point nutrient fluxes.

3.1.5 Point sources

Industrial and domestic point sources of nutrients and TSS fluxes originated from Loire Basin water authorities (AELB) surveys conducted in 2010. In the MLRC basin, 641 waste water treatment plant (WWTP) were recorded. Datasets provided total organic carbon, total nitrogen and total phosphorus fluxes~~ for all of them. Fluxes~~. It was estimated in 2010 that point sources represented in the Middle Loire sub-catchment (our study) 322 kgP day^{-1} and 1.9 tN day^{-1}. These fluxes were divided into the different chemical forms for C, N and P, according to ~~Servais and Billen (2007) depending on the type of point sources and the characteristics of the waste water treatment. Fluxes and concentration of point sources were considered constant over time.~~Servais and Billen (2007), depending on the type of point sources and the characteristics of WWTP. Fluxes of point sources were considered constant over time.

3.1.6 Upstream boundary in the Loire River and validation dataset at catchment outlet

A daily survey was conducted at S1 (Saint-Satur-sur-Loire) and S2 (Cinq-Mars-la-Pile) in the Loire River during the period August 2011-July 2014~~(Minaudo, 2015).~~ (Minaudo, 2015). Data collected at S1 was used as data input for the model, and data at S2 was used for both calibration and model performances assessment. Samples were collected every day from a bridge using the same procedure at each station~~.~~. Total suspended solid concentrations (TSS) were measured every day. The following parameters were ~~analysed~~analyzed on a 3-day frequency basis: dissolved and particulate organic carbon (DOC and POC), total and dissolved inorganic phosphorus (TP and SRP), nitrate (NO_3^-), dissolved silica (Si) and chlorophyll-*a* concentrations. Filtrations were immediately made on-site using a 0.45 µm cellulose acetate membrane filters for chemical parameters and 0.70 µm glass filter (Whatman GFF) previously burned at 500°C during 6 hours for chlorophyll-*a* and POC analysis. Total suspended solids concentrations where determined by filtration of a precise volume of each water sample through pre-weighed filters and by drying them at 105°C. After filtration, water samples and filters were stored at -80°C in polypropylene tubes after acidification of aliquots for NO_3^-, SRP and DOC analysis. Tubes and filters were unfrozen on the day of the analysis. DOC concentrations were measured with a carbon ~~and ~~analyzer (Shimadzu TOC-V CSH/CSN). The NO_3^- concentration was determined by ionic chromatography. Phosphorus was measured by colorimetry after solid digestion in the case of TP analysis (potassium-persulfate digestion~~) in the case of TP analysis.~~). Dissolved silica (Si) was measured by colorimetry. For POC analyses,~~ the~~ filters were first treated with HCl 2N to remove carbonates, dried at 60°C for 24 hours and then measured with a C/S analyzer (LECO C-S 200). Chlorophyll-*a* was measured by fluorimetry at a wavelength > 665 nm after an excitation step between 340 and 550 nm. Chlorophyll-*a* concentrations were expressed in mg C L^{-1} considering C:Chl-a ratio ~~equals~~of 31, according to ~~Minaudo et al. (2016)~~Minaudo et al. (2016), and constituted the variable hereafter named 'PHY'.

3.2 Computation steps in the model~~ based on a network topology~~

Computation in the model was based on a network topology: each reach in the hydrographic network corresponded to the stream segment between two confluences. Each reach ~~was constituted by~~had an upstream (or upper) and a downstream (or lower) node (Figure 1). ~~Then, except~~Except for first Strahler order streams in the headwaters, upper nodes were always connected to two ~~downstream~~lower nodes.

3.2.1 Initialization at upper node and boundary conditions

All variables were initialized at the upper node of first Strahler order streams. Water component variables were initialized according to non-point sources estimated for hillslope catchments located upstream the upper nodes. ~~Sediment~~Variables in the sediment component~~ variables~~ were initialized homogeneously everywhere in the stream network, ~~based on the hypothesis~~assuming that the model should quickly ~~modify values in the sediment component, depending~~reach its equilibrium based on the interactions with variables from the water component. The upstream boundary in the Loire River (S1) was determined based on the daily survey conducted at S1 (see ~~above~~ section 3.1.6).

3.2.2 Propagation downstream

All variables computed at one reach in the water component were transferred downstream according to travel time estimated from discharge and stream morphology. Variables from the benthic component interacted with the water component but were not transferred downstream. For a given time step, a given reach was discretized depending on the estimated travel time. If travel time ~~was less~~shorter than 1 hour, the reach was not segmented: thermal and biogeochemical equations were solved at the downstream node~~ considering all forcing variables as constant because their resolution was at best hourly.~~. If travel time exceeded ~~one~~1 hour, the reach was segmented into as many sub-segments as needed to get ~~one~~1 hour travel time sub-segments. ~~This allowed calculation with a hourly resolution, and in the latter case, thermal and biogeochemical equations were solved downstream each sub-segment considering varying forcing variables with time.~~ Within one hour time step, all biogeochemical equations were solved with a 15 minutes sub-time step~~, all other variables being considered constant~~ to avoid potential numerical resolution drifts. When two streams met, ~~the thermal and~~ biogeochemical signals were mixed with respect to ~~their~~streams discharge~~ and this~~. This determined ~~all~~ the~~ variables~~ values for the next downstream upper node. Because the exact location of ~~the~~potential WWTP input within a segment was ~~unknown,~~not always known, it was assumed that location of point sources ~~fluxes were considered to happen~~occurred at the downstream node~~ only~~.

~~3.3 Calibration step~~

~~The thermal model was fully deterministic and no calibration step was needed. Despite the fact that RIVE was built as a universal representation of the mechanisms occurring in rivers, some processes were based on empirical relationships. Nearly 150 coefficients were counted overall (Fig. 3), the majority of them were used to describe bacteria and phytoplankton dynamics depending on light intensity, water temperature, and nutrient availability. Most coefficients are currently accepted as universal constants, but several studies pointed out that hydro-sedimentary and P sorption/desorption processes needed experimental or numerical calibration (Vilmin et al., 2015), especially because the processes involved highly impacted performances on phytoplankton and water quality predictions (Aissa-Grouz, 2015). Phosphorus dynamic in the water compartment was based on the Langmuir equilibrium concept (Limousin et al., 2007), a description largely found in the literature for water quality models (e.g. Chao et al., 2010; Rossi et al., 2012; Vilmin et al., 2015). Very different values for P sorption/desorption coefficients according to Langmuir equilibrium equations were found experimentally or numerically in the literature, with up to 5 orders of magnitude differences from one study to another (Vilmin et al., 2015). No specific laboratory experiments were conducted in the Loire River, leading us to deploy numerical optimization methods to calibrate TSS and SRP dynamics. Because SRP computation relies on TSS dynamic, the first variable to be calibrated was TSS. Calibration was conducted by changing the values of the different coefficients to be calibrated over a range of values found in the literature. The best set of coefficients was selected when results minimized root mean square errors (RMSE) of the calibrated variable. Among the period of records (August 1st 2011 to July 31st 2014), the period selected for calibration was the first year, i.e. August 1st 2011 to July 31st, 2012, and the remaining time series served as validation.~~

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The thermal model was fully deterministic and no calibration step was needed. Even if RIVE was built as a universal representation of the mechanisms occurring in rivers, some processes were based on empirical relationships. Nearly 150 coefficients were counted overall (Figure 3), the majority of them were used to describe bacteria and phytoplankton dynamics depending on light intensity, water temperature, and nutrient availability. Most coefficients are currently accepted as universal constants, but several studies pointed out that hydro-sedimentary and P sorption/desorption processes needed experimental or numerical calibration (Vilmin et al., 2015), especially because processes involved highly impacted performances on phytoplankton and water quality predictions (Aissa-Grouz, 2015). Phosphorus dynamic in the water compartment was based on the Langmuir equilibrium concept (Limousin et al., 2007), a description largely found in the literature for water quality models (e.g. Chao et al., 2010; Rossi et al., 2012; Vilmin et al., 2015). Very different values for P sorption/desorption coefficients were found experimentally or numerically in the literature, with up to 5 orders of magnitude differences from one study to another (Vilmin et al., 2015). No specific laboratory experiments were conducted in the Loire River, leading us to deploy numerical calibration methods to calibrate TSS and SRP dynamics. Because SRP computation relies on TSS dynamic, the first variable calibrated was TSS. Calibration was conducted manually by changing the values of the different coefficients to be calibrated over a range of values found in the literature. In total, five coefficients were calibrated. The best set of coefficients was selected when results minimized root mean square errors (RMSE) of the calibrated variable. Among the recorded time series (August 1st 2011 to July 31st 2014), the period selected for calibration was the first year, i.e. August 1st 2011 to July 31st, 2012, and the remaining data served for validation.

3.3.1 Calibration of TSS dynamic

Total suspended solids concentration increments ($dTSS$) were computed based on a simple difference between eroded matter from the river bed ($eros_{TSS}$) and ~~sedimentated~~settled particles ($sedim_{TSS}$), as described in Equ. ~~(1-4~~(1-4). Erosion was defined as a power law function of flow velocity (Equ. 2 and 3).

$$dTSS(t) = eros_{TSS}(t) - sedim_{TSS}(t) \tag{1}$$

$$eros_{TSS}(t) = \frac{Vs_{TSS}}{depth(t)}\left(Cap_{TSS}(t) - TSS(t-1)\right)^{\frac{SED(t-1)-SED_0}{SED_0}} \tag{2}$$

$$Cap_{TSS}(t) = Veli_0 + Veli_1 \cdot V(t)^3 \tag{3}$$

$$sedim_{TSS}(t) = \frac{Vs_{TSS}}{depth(t)} TSS(t-1) \tag{4}$$

where Vs_{TSS} was the sedimentation velocity; $depth(t)$ was the water depth at time t; Cap_{TSS} was the erosion capacity depending on coefficients $Veli_0$, $Veli_1$, and flow velocity $V(t)$; SED was the height of the layer of sediments potentially erodible, SED_0 was the layer of sediments set during initialization step.

Thus, TSS concentration depended on coefficients $Veli_0$, $Veli_1$ and Vs_{TSS}~~, and were chosen as variables for TSS dynamic calibration~~. These three coefficients were calibrated.

3.3.2 Calibration of P dynamic

~~The~~ SRP concentration was estimated based on sorption/desorption equations originating from Langmuir equilibrium displayed by Equ. (5) and (6). This formulation requires the maximal sorption capacity of P onto suspended solids (Pac, in mg P g^{-1}) and a half-saturation constant ($Kpads$, in mg P L^{-1}) that needed to be defined.

$$dSRP(t) = \frac{1}{2}\left[\left[A(t)^2 + 4 \cdot TIP(t) \cdot Kpads\right]^{\frac{1}{2}} - A(t)\right] \tag{5}$$

$$A(t) = Kpads - TIP(t) + TSS(t) \cdot Pac \tag{6}$$

~~Where~~where TIP corresponded to total inorganic phosphorus concentration at time step t, $Kpads$ and Pac were the two parameters needing to be calibrated.

3.4 Model performance criteria for validation

~~Bias~~To estimate model performances and define criteria for model validation, bias and standard deviation errors ~~for~~ were used, following Equ. 7 and 8:

$$Err_{std} = std(observation - model) \qquad (7)$$

$$Err_{bias} = \sum_{i=1}^{n} \frac{observation(i) - model(i)}{n} \qquad (8)$$

where std was the standard deviation, and n the total number of observations. These metrics were calculated for each variable observed at S2 over the entire period of validation (August 1st 2012 to July 31st 2014~~) were calculated for each variable observed at S2. They~~), and were also computed seasonally~~ over the period~~: “summer” corresponded to the bloom season~~,~~ from April to October; “winter” corresponded to the remaining part of the year.

3.5 Lagrangian ~~point of view~~representation and fluxes budgets

In addition to more common ~~way~~ways of presenting results longitudinally~~ along the main river main stem~~, we proposed two other graphical representations of transfers and biogeochemical transformations from S1 to S2~~.~~ along the Loire River. One representation consisted in following the same water body transferred from S1 to S2, ~~as~~i.e. a Lagrangian ~~point~~representation. Lagrangian profiles were estimated from the matrix of ~~view.~~travel time computed for each reach and at each time-step from measured discharge and river morphology estimates (see section 3.1.3). This representation was both spatial and temporal since it displayed longitudinal variations according to travel time going downstream. It was used for two typical situations~~,~~: one in winter (starting on February 9th 2013 during a high-flow period), and another one during a phytoplankton bloom (starting on July 10th 2012).

Additionally, average seasonal ~~average~~ fluxes budgets of all the main processes ~~and potential~~ (inputs ~~occurring~~and outputs) simulated between S1 and S2 over “winter” or “summer” periods were computed for a selection of variables (TSS, NO_3^-, total inorganic P, Si, PHY, DOC, POC and O_2). In those graphs, arrow widths were proportional to the corresponding calculated flux, allowing ~~to compare~~the comparison between the two different seasons.

3.6 Constant flow and constant water temperature simulations

It was tested to assess the sensitivity of phytoplankton variations to constant flow conditions in the Loire River for both low-flow and high flow conditions (200 and 1000 m^{3}s^{-1}, respectively). A similar approach was tested with constant water temperature (13.7°C, i.e. the average temperature). Lagrangian profiles during a phytoplankton bloom (starting on July 10th 2012) of these simulations can be found as a Supplement file (Figure S1).

4 Results

4.1 Calibration step

The best set of coefficients that minimized errors over the period are displayed in Table 1. RMSE on calibrated variables were 15 mg L^{-1} for TSS and 14 µgP L^{-1} for SRP. The selected values for TSS coefficients largely differed from other values found in the literature, justifying the need for this calibration step. Compared to the Seine River, it appeared necessary to increase the erosion capacity ($Veli_1$) but also to reduce considerably suspended solids sedimentation rates (Vs_{TSS}), which resulted on an increased sediment reactivity ~~in~~within the Loire system. Values calibrated for P sorption processes were close to the values found experimentally in the neighboring Seine basin ~~(Aissa-Grouz, 2015)~~(Aissa-Grouz, 2015).

4.2 Model performances at station S2

Over the study period, discharge variations at S2 presented highly seasonal variations (~~Fig.~~Figure 4): Q ranged between 60 and 150 m^3 s^{-1} in summer low flows, and peaked over 1200 m^3 s^{-1} in winter high flows. ~~Observed TSS concentrations co-variated with discharge, and ranged between nearly 0 in summer to 150 mg L^{-1} during high flows. The model predicted well TSS dynamic and errors bias ± standard deviation over the entire study period (August 2011 to July 2014) were 8 ± 13 mg L^{-1}. A few storm events that were observed with the daily survey were however not represented by the model, especially for several storm events that occurred during low flow periods.~~

Water temperature simulated by T-NET was highly seasonal and fluctuated between 0 and 30°C. In summer, amplitude of water temperature diel cycles ranged between 0.2 and 1.5°C. Phytoplankton concentrations presented three clearly delimited bloom events~~,~~ between March and September~~ of each hydrological year surveyed.~~. The maximum ~~concentrations recorded were between~~observed each year was 60 to 70 µg chl-*a* L^{-1} corresponding to 1.6 and 1.9 mgC L^{-1}. ~~Phytoplankton variations simulated by the model succeeded at representing seasonal variations. Errors over the entire period were 0 ± 0.4 mg C L^{-1}. One event at the end of summer 2012 was simulated but this did not correspond to the observations.~~

Observed TSS concentrations was correlated with discharge, and ranged between nearly 0 in summer to 150 mg L^{-1} during high flows. Nitrate concentrations presented a clear seasonal signal, fluctuating between ≈ 1.5 mgN L^{-1} in summer to ≈ 3.5 mgN L^{-1} in winter. ~~The model successfully reproduced these seasonal variations, and errors were 0.1 ± 0.4 mg N L^{-1}.~~

~~Recorded dissolved~~Dissolved silica concentrations ranged between nearly 0 and 8 mg Si L^{-1}. Concentrations always peaked in winter during high flows, and dropped in spring, concomitantly with the start of phytoplankton activity. ~~Errors from model were large for this element (0.2 ± 1.7 mg N L^{-1}), especially for winter periods.~~

Soluble reactive P concentrations presented a clear seasonal cycle, with very low concentrations reached during summer (< 10 µg P L^{-1}) and relatively high concentrations in winter (≈ 60 µg P L^{-1}). ~~The model represented successfully these seasonal variations; results were subject to -2 ± 14 µg P L^{-1}. Diel fluctuations in summer estimated with model QUAL-NET fluctuated between 0 and 15 µg P L^{-1}.~~

~~Recorded particulate~~Particulate organic carbon concentrations ranged between 0.4 to 5 mg C L^{-1}, with ~~a~~ strong ~~correlation on the one hand~~correlations between POC and TSS in winter, and ~~on the other hand~~ between POC and phytoplankton biomass during algae blooms ~~(Minaudo et al., 2016). Errors from the model were 0.3 ± 1 mg C L^{-1}, especially due to POC overestimation in May 2012.~~

~~Recorded dissolved~~(Minaudo et al., 2016). Dissolved organic carbon concentrations ranged between 4 and 10 mg C L^{-1}. The highest concentrations were observed during high flow periods, but no clear seasonal variations could be deciphered. ~~Model QUAL-NET provided results within the measured range of values, but errors over the entire period were 0.4 ± 1.5 mg C L^{-1}.~~

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 storm events that occurred under low flow conditions. A phytoplankton bloom event at the end of summer 2012 was simulated but did not correspond to our observations. Dissolved oxygen was not measured, but ~~concentration~~ concentrations simulated by QUAL-NET presented a clear seasonal cycle, with ~~high values (≈~~≈ 12 mg O_2 L^{-1}~~) reached during~~ estimated in winter, and ~~low values (~~6 to 9 mg O_2 L^{-1}~~) found~~ in summer. During phytoplankton blooms, ~~simulated O_2 concentrations were subject to large~~the model provided interesting diel fluctuations~~, with~~ for PHY, SRP and O_2 concentrations. For instance, SRP concentration fluctuated between 0 and 15 µg P L^{-1} and O_2 concentrations presented a minimum ~~occurring around~~at midnight, and a maximum ~~reached by~~at noon.

~~Model performances~~Unfortunately, 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 ~~much~~ lower absolute errors in winter ~~but this corresponded to~~(a period with very low PHY concentrations~~.~~).

4.3 Lagrangian views of winter versus summer dynamics

The Lagrangian views of the evolution of the different biogeochemical species highlighted different hydro-biogeochemical functioning depending on the season, (Figure 5).

~~i)~~ The selected winter event corresponded to a high-flow period: Q at S1 was 940 m^3 s^{-1} and increased to 1110 m^3 s^{-1} by the time the water arrived at S2. It took almost 2 days for the water to travel between S1 and S2 (≈ 250 km). Most elements were simply transferred downstream, with no significant transformation or alteration between S1 and S2. Concentration of TSS presented a decreasing evolution from 33 mg L^{-1} at S1 to 25 mg L^{-1} at S2. Nitrate concentration slightly increased from 2.8 to 3.1 mg N L^{-1} (+11%), and so did SRP (+40%). Dissolved silica concentration decreased (-12%). Phytoplankton activity remained very low and declined steadily (5 to 2 µg chl. *a* L^{-1}). Dissolved oxygen slightly increased (+8%).

~~ii)~~ During the selected summer event, discharge was much lower: Q was 330 m^3 s^{-1} when the water left S1 on July 10th, 2012, and increased to 340 m^3 s^{-1} when the water reached S2. The model estimated that it took nearly 3 days for the water to cover the distance ~~between~~ from S1 to S2, and ~~the~~all biogeochemical variables were largely modified ~~while travelling~~when the water moved downstream. Two steps were identified~~.~~:

- The first 2.5 days, total phytoplankton concentration increased from 0.5 to 1.7 mg C L^{-1}. Simultaneously, SRP was dramatically depleted from 50 to nearly 0 µg P L^{-1}. Nitrate, silica and oxygen concentrations slightly decreased (≈ -10%). The amount of P released from organic matter mineralization remained limited but reached a first peak concomitantly with a large P uptake from the phytoplankton colony. Phytoplankton mortality rates kept increasing ~~while going downstream~~, and peaked when growth rate reached its maximum (0.15 mgC L^{-1} h^{-1}~~)~~), i.e. when travel time from S1 was 2.3 days.
- Then, during the next 24 hours~~, i.e.~~ (the time needed for the water to reach S2~~,~~), phytoplankton concentration started to decrease (-15%), SRP remained very low under 5 µg P L^{-1} and presented a diurnal fluctuation with a minimum reached during the afternoon, and rising concentrations when ~~arriving~~the water arrived at S2 by night. During this phase, organic matter mineralization as a source of inorganic P increased substantially from 2 to 13 µg P L^{-1} h^{-1} and, phytoplankton growth rates first dropped from 0.15 to near 0 mgC L^{-1} h^{-1} and then rose again to 0.1 mgC L^{-1} h^{-1} when SRP input from mineralization counteracted phytoplankton uptake.

4.4 Storm event disturbance during a phytoplankton bloom

A storm event occurred in August 2013, during a phytoplankton bloom. Over five days (August 9th to 14th), discharge at S2 increased from 200 to 406 m^3 s^{-1} and then declined to reach 230 m^3 s^{-1} on August 19th. This largely disturbed TSS, SRP and PHY dynamics (~~Fig.~~Figure 6).

Mis en forme : Normal, Sans numérotation ni puces

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Mis en forme : Espace Avant : 0 pt, Après : 0 pt, Ne pas ajouter d'espace entre les paragraphes du même style, Avec puces + Niveau : 1 + Alignement : 0,63 cm + Retrait : 1,27 cm

This storm event ~~entailed~~caused a suspended solids peak which propagated over the entire ~~studied~~ river stretch. TSS concentration peak amplitude decreased from 120 to 50 mg L^{-1} ~~while flowing~~when the water moved downstream from S1 to S2, and the peak width widened. At the beginning of the event, SRP concentration profile was showing a complete P depletion starting approximately 80 km downstream S1. This P limitation threshold progressively moved further downstream when the storm event hit. SRP slightly increased at S2, but concentrations remained very low. When the discharge peak hit S2 (August 14th), SRP concentrations presented a steady longitudinal decline from 50 µg P L^{-1} down to nearly 0. Before the storm event, phytoplankton concentrations ~~were showing~~showed a limited longitudinal increase, from 0.5 to 1.2 mg C L^{-1}~~. When~~, but when the discharge peak event ~~hit~~occurred, PHY concentrations decreased in the upper part of the ~~Middle Loire River Corridor~~MLRC, but clearly increased in the lower part~~. Phytoplankton~~ suggesting that phytoplankton was flushed away by the storm event~~, and~~. PHY concentrations during discharge recession ~~were showing~~presented an increasing longitudinal profile from 0.1 to 1.1 mg C L^{-1}~~. PHY concentrations~~ and began to increase again everywhere along S1 to S2 when hydrological conditions stabilized.

4.5 Fluxes, transfers and transformations in the Middle Loire River Corridor

~~Results were similar to the Lagrangian analysis, i.e. proportions~~Proportions of the different contributions or biogeochemical transformations ~~were~~ largely ~~depending~~depended on the season (~~Figure~~Figures 7~~).~~

and 8). In winter, most of the biogeochemical species entering the MLRC at S1 were transferred downstream, with non-significant interactions with the biological component. Suspended solids and particulate P showed an almost balanced budget between erosion and sedimentation processes. Lateral contribution between S1 and S2 remained small compared to the upstream flux at S1, except for nitrate because tributaries and lateral non-point sources inputs contributed to 25% of the total NO_3^- flux at S2. Reaeration of the water body represented a significant portion of dissolved oxygen budget at S2 (14 %).

In summer low flows, the biological component largely modified the river biogeochemistry in the studied sector.

~~i)~~ Nitrate fluxes were 15% higher at S2 (38 t N day^{-1}) than at S1 (28 t N day^{-1}) despite N uptake by phytoplankton (3.2 t N day^{-1} ≈ 11% S1 flux) and a moderate contribution from the lateral streams (12 t N day^{-1}). Diffuse sources in the tributaries ~~corresponded~~contributed to 94% of total lateral inputs.

~~ii)~~ Inorganic phosphorus loads were divided 3-fold between S1 and S2 (from 1 t P day^{-1} to 0.3 t P day^{-1}) due to phytoplankton and bacteria uptakes (respectively 2.6 and 0.4 t P day^{-1}). ~~Interestingly,~~ P recycling from organic matter mineralization (phytoplankton dead cells) supplied 1.3 t P day^{-1}, i.e. more available phosphorus than both upstream and lateral P inputs. Inorganic P inputs from WWTPs within the MLRC ~~subbasin~~sub-basin represented less than a third of P load in the Loire at S1 (0.3t P day^{-1} compared to 1 t P day^{-1}~~) despite the presence of 2 10^6 inhabitants equivalent within the sub-catchment.~~). Particulate inorganic P ~~represented~~constituted a very small amount of total inorganic P,~~ and~~ most of it was balanced between erosion and sedimentation processes. The river bed acted like a source of inorganic P (299 kg P day^{-1}).

~~iii)~~ Dissolved silica fluxes were slightly affected by phytoplankton activity: 20% of the flux at S1 was assimilated by diatoms. Lateral streams contribution represented 13% of the flux quantified at S2. Phytoplankton increased 4-fold between S1 and S2 during summer blooms~~,~~, (Figure 8), from 4.3 to 17.1 kg C day^{-1}~~. However~~ but this calculation took only~~ took~~ into account the surviving cells when the water body reached S2. A larger proportion of phytoplankton actually grew but part of it decayed and was eventually recycled: the model estimated that 50% of green algae and 25% of diatoms that grew between S1 and S2 decayed. Additionally, approximately 25% diatoms ~~were deposited on the river bed. Since the lateral contributions by the Loire river tributaries were not significant (only 0.1 kg C day^{-1}), we can estimate that phytoplankton only grew within the MLRC.~~

~~iv)~~ deposited on the river bed. The lateral contributions by the Loire river tributaries were not significant (only 0.1 kg C day^{-1}), indicating that phytoplankton grew only within the river main stem. Approximately 100 t of organic C enter the system at S1 every day under low flow periods (see also Minaudo et al., 2016). Approximately 80% of it was dissolved, the rest was particulate. It was estimated that 16 t C day^{-1} in summer of DOC was bioavailable and consumed by heterotrophic bacteria. Part of this organic matter was eventually mineralized, depending on oxygen content. Dissolved oxygen budget was balanced between S1 and S2 (respectively 192 and 208 t O_2 day^{-1}), with oxygen inputs from primary producers (phytoplankton, 136 t O_2 day^{-1}) similar to oxygen depletion by bacteria and zooplankton respiration processes (137 t O_2 day^{-1}).

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5 Discussion

Inter-annual, annual and seasonal variations of the main water quality variables simulated by QUAL-NET corresponded to the observations, proving the efficiency of the model at both transferring the different biogeochemical species and also modelling the main ~~biogeochemical~~ processes instream~~ when they start to control the river biogeochemical variations. At finer~~. High temporal resolutions~~, QUAL-NET~~ provided reasonable daily variations and ~~was able to~~made possible estimate biogeochemical variations during short-term ~~and~~(but highly impacting) events such as storm ~~events occurring in summer~~ during a phytoplankton bloom. These performances were considered good enough to allow us investigate confidently the different processes ~~occurring in the river and discuss the controlling variables of eutrophication in the Loire River.~~and their drivers. This is highlighted in paragraphs 5.1 and 5.2. Additionally, QUAL-NET was subject to several weaknesses, and potential improvements ~~could~~shall be brought; this is detailed in sections 5.3 and 5.4.

5.1 Drivers of eutrophication in the Middle Loire River Corridor

5.1.1 Biological versus hydrological control of the river biogeochemistry

The model showed that the Loire River biogeochemistry ~~is~~was the result of complex interactions between nutrients availability and hydrological variations. In winter, the MLRC was mainly controlled by hydrological processes, and nutrients were simply transferred downstream, with no noticeable control ~~of~~by biological processes. ~~During lower~~Under low flow ~~period~~conditions and warmer water temperature~~ increased~~, C, N, P and oxygen dynamics were dominated by biological processes. ~~The stream~~Stream algae were clearly P-limited and never reached N or Si limitations, supporting previous studies ~~(Descy et al., 2011; Minaudo et al., 2015).~~(Descy et al., 2011; Minaudo et al., 2015). In the MLRC, lateral inputs during summer were not significant compared to the magnitude of fluxes within the Loire River main stem~~ and the intensity of the processes that occurred.~~. The highest phytoplankton concentration was not necessarily observed at the ~~Corridor~~catchment outlet: during ~~a~~ phytoplankton ~~bloom~~blooms, P was often depleted before the water could reach S2, and when this occurred, lower phytoplankton growth and higher mortality rates started to cause a decline of phytoplankton concentration. ~~This maintained low SRP concentrations downstream the point where~~As soon as phytoplankton started to be P-limited, and bacterial activity caused the decrease of oxygen concentration ~~(Li et al., 2014).~~(Li et al., 2014). When a storm event entered the Middle Loire system, the phytoplankton colony ~~developed in the lower part of the Corridor ~~was flushed downstream, and, as long as physical conditions for phytoplankton growth remained degraded (shorter transit time, increased turbidity), available P was not totally assimilated~~ by ~~. Thus, SRP concentrations increase in the lower section during such event was rather the consequence of lower phytoplankton~~, and the river discharged higher SRP concentration downstream S2 in addition to a peak of suspended solids, a vector for particulate P that might be partly ~~ activity than increased inputs. Storm events in summer simply move the available ~~for the biomass ~~P-exhaustion point further downstream~~ due to desorption processes. ~~.

5.1.2 P recycling within the ~~Middle Loire River Corridor~~MLRC

~~Most inorganic P entering the MLRC was assimilated by phytoplankton and bacteria biomasses. However, mineralization of organic matter in summer constituted a significant source of inorganic P. The model suggested that P originating from mineralization represented a P share equivalent to all fluxes entering the MLRC (point and non-point sources) (≈ 1.3 tP day^{-1}). Additionally, 40% of the phytoplankton that grew between S1 and S2 was lost due to P-limitation. It suggested that a large portion of inorganic P recycled within the water during the transfer through the MLRC (from S1 to S2). In summer, SRP was most of the time completely assimilated by phytoplankton, but the phytoplankton subjected to mortality could eventually be partially recycled and constitute a new source of available P. Re-mineralization of autochthonous labile organic particulate P, known as part of the 'microbial loop', is described in the literature of phytoplankton ecology (Li et al., 2014; Reynolds, 2006) and mostly identified in lakes, reservoirs or estuarine systems (James and Larson, 2008; Jossette et al., 1999; Song and Burgin, 2017) but also in rivers (Withers and Jarvie, 2008). On the one hand bacteria compete with phytoplankton for SRP availability,~~

~~and on the other hand, bacterial mineralization recycles P and supports phytoplankton growth. These observations, sparsely documented in rivers, comfort the necessity of considering bacterial activity as a major driver of carbon cycling in large eutrophic rivers.~~

~~5.2 High temporal resolution is needed in water quality models~~

~~Model QUAL-NET identified several key processes occurring over a fine temporal scale such as diel fluctuations of SRP (daily variations oscillated between 0 and 15 µgP L-1 during phytoplankton blooms) and of dissolved oxygen. Diel fluctuations of~~ ~~O_2~~ ~~were often observed and described in previous studies, directly linked to primary producers' activity (Moatar et al., 2001; Rode et al., 2016; Wade et al., 2012). Sub-daily fluctuations of inorganic phosphorus are sparsely observed, but this is due to limited measurements of high-frequency variations of P concentration. Similar diel fluctuations were found in some other lowland eutrophic rivers; but these cycles were mostly explained as a balance between P contributions from direct sources and non-point sources (Wade et al., 2012).~~

~~In the case of the Loire River, model QUAL-NET simulates these diel fluctuations due to a complex interaction between biological uptake and P inputs from instream mineralization, lateral and point-sources inputs or diffusion from the benthos: phytoplankton growth rates during the night is nil, while lateral contributions (both point and non-point sources) still occur, and P keeps being diffused from the benthic compartment, resulting in an increased SRP concentration in the water column. After sunrise, as soon as the biological compartment starts to assimilate more P than the amount of P originating from the different P sources, SRP concentration starts to decrease again. These subtle variations, revealed by the model, could not be seen based on the daily-scale survey and need to be confirmed with higher-frequency sampling measurements.~~

~~High-frequency measurements were also needed to validate the complex interactions between hydrological variations and P-availability simulated by the model when a storm event occurs during a period of phytoplankton bloom.~~

In summer, most of the inorganic P entering the MLRC was assimilated by phytoplankton and bacteria biomasses. However, mineralization of organic matter constituted a significant source of bioavailable P. The model estimated that P releases from mineralization was equivalent to all fluxes entering the MLRC (point and non-point sources) i.e. ≈ 1.3 t P day^{-1}. Besides, the phytoplankton concentration peak in-between S1 and S2 corresponded to inorganic P exhaustion. This caused a 15% decrease of PHY concentration when the water moved further downstream. Thus, SRP was most of the time fully assimilated by phytoplankton in summer, but phytoplankton was also subject to mortality and could partly be recycled to eventually constitute an autochthonous source of available P. Re-mineralization of autochthonous labile organic particulate P, known as part of the 'microbial loop', is described in the literature of phytoplankton ecology (Li et al., 2014; Reynolds, 2006) and mostly identified in lakes, reservoirs or estuarine systems (James and Larson, 2008; Jossette et al., 1999; Song and Burgin, 2017), and sparsely in rivers (Descy et al., 2002; Withers and Jarvie, 2008). On the one hand bacteria compete with phytoplankton for SRP availability, and on the other hand, bacterial mineralization recycles P and supports phytoplankton growth. These observations, comfort the necessity of considering bacterial activity as a major driver of carbon cycling in large eutrophic rivers.

5.2 High temporal resolution is needed in water quality models

The high temporal resolution in QUAL-NET enabled to disentangle the interactions between hydrological and biogeochemical processes when a storm event occurred in summer low flow. Besides, the model identified diel fluctuations of O_2 or SRP (daily variations oscillated between 0 and 15 µg P L-1 during phytoplankton blooms). Diel fluctuations of O_2 were often observed and described in previous studies, directly linked to primary producers' activity (Moatar et al., 2001; Rode et al., 2016; Wade et al., 2012). Sub-daily fluctuations of inorganic phosphorus are sparsely observed, but this is due to limited measurements of high-frequency variations of P concentration. Similar diel fluctuations were found in some other lowland eutrophic rivers; but these cycles were mostly explained as a balance between P contributions from direct sources and non-point sources (Wade et al., 2012). In the case of the Loire River, QUAL-NET simulates these diel fluctuations are likely to be the result of complex interplay between biological uptake, P mineralization instream, lateral inputs and diffusion from the benthos. During the night, phytoplankton growth was nil, while lateral contributions from point and non-point sources still occurred. Additionally, P kept being diffused from the benthic compartment, resulting in an increased SRP concentration in the water column. After sunrise, as soon as the biological compartment started to assimilate more P than the amount of P originating from the different P sources, SRP concentration decreased again. These subtle variations, revealed by the model, could not be seen based on the daily-scale survey and need to be confirmed with higher-frequency sampling measurements.

5.3 Sensitivity to phosphorus sorption/desorption representation

During the calibration step, QUAL-NET showed a high sensitivity to the formulation of phosphorus sorption/desorption processes. Compared to other studies using the same formulation, the optimized values found manually for our study appeared relatively close to ~~the values~~those determined experimentally in the Seine River (Table 1). However, the large variability in the results when one of these two coefficients was modified ~~questioned~~challenged the use of the model~~ with the current values~~: if modifications are conducted on the model (in terms of data inputs and/or processes), these coefficients ~~must~~should be re-calibrated. This appears ~~to be~~as an important weakness in the model until an experimental survey is deployed to assess ~~the~~ spatial and temporal ~~variations in the Loire River~~heterogeneities of P sorption-desorption characteristics ~~according to Langmuir equilibrium concept~~in the Loire River.

5.4 Issues and potential improvements for model QUAL-NET

~~Results showed that the deterministic approach provided many useful insights to understand the biogeochemical functioning of the river and the interaction between hydrological and biological factors that control the river biogeochemistry. Some~~

~~improvements could be made on the model, and the following paragraph lists what appeared to us as the most important changes that could be made.~~

5.4.1 Conflicting time steps between forcing variables and output resolution

The use of high temporal resolution in QUAL-NET proved its usefulness to model processes that occur ~~on a fine~~over short temporal ~~scale~~scales. However, the only forcing variables with such a fine resolution were the meteorological variables, allowing to compute hourly water temperature and light availability in the water column.

Flows, and therefore water depth and velocity, were daily based, and spatial discretization for discharge was based on catchments that were on average 27 km². Flows within each of these 17 catchments were redistributed into the hydrographic network according to the corresponding drainage area of each river reach. If this method ~~might provide~~provided reasonable values of average flow in each stream of the ~~river~~ network, it ~~considers the~~ assumed simultaneous temporal dynamic ~~to be simultaneous~~ within each of the 17 catchments. This~~, misses a certain spatial heterogeneity in terms of flow contribution and sources, and also might~~ could provoke conflicting signal propagation ~~of the signal from headwaters to downstream~~through the hydro-system during storm events~~ and high-flow periods~~. A semi-distributed hydrological model could address some potential propagation issues during storm events, even if the output frequency remains daily because of the lack of ~~observations~~discharge estimation on a sub-daily basis.

Nutrients fluxes discharged from point sources were considered constant through time. Waste water treatment plants efficiency in treating sewage can be seasonal (biological processes, variation of population in touristy areas…) and sometimes highly impacted by storm events. Therefore, we urge local and national water basins authorities to provide at least monthly concentrations and fluxes for the different waste water treatment plants, especially for plants treating sewage from the biggest cities.

Non-point sources concentrations were constant through time. ~~Therefore, it was hypothesized that only hydrological variability drove its input. This representation proved its reliability with a 10-days time step (Garnier et al., 2002), but misses many processes occurring at least at the seasonal scale, such as for instance nutrient retention by the riparian vegetation during spring and summer (Peterjohn and Correll, 1984; Pinay et al., 1993), denitrification increased during warmer conditions, peaks of nutrient concentrations during soil-rewetting events and when groundwater connects with streams (Dupas et al., 2015a, 2015b). QUAL-NET proved to be efficient to model in-stream processes and would certainly benefit if coupled with land-use models that predict more reliably nutrient non-point inputs such as SWAT (Douglas-Mankin et al., 2010), or HSPF (Fonseca et al., 2014). This would allow to model the biogeochemical variations for the whole drainage system, not forcing the system with daily-scale measurements at S1, but instead, modelling water quality in the entire basin at S2. To upscale the model to the entire Loire Basin, the influence of lakes and reservoirs have to be considered since they largely modify the transfer of nutrients~~

~~downstream.~~Therefore, it was assumed that only hydrological variability could modify non-point fluxes. This representation proved its reliability with a 10-days time step (Garnier et al., 2002), but misses many processes occurring at least at the seasonal scale, such as ~~for instance~~ nutrient retention by the riparian vegetation during spring and summer (Peterjohn and Correll, 1984; Pinay et al., 1993), denitrification increase~~d~~ during warmer conditions, peaks of nutrient concentrations during soil-rewetting events and when groundwater connects with streams (Dupas et al., 2015a, 2015b). QUAL-NET proved to be efficient to model in-stream processes and would certainly benefit if coupled with land-use models that predict more reliably nutrient non-point inputs such as SWAT (Douglas-Mankin et al., 2010), or HSPF (Fonseca et al., 2014). This would allow to model the biogeochemical variations for the whole drainage system, instead of forcing the system with daily-scale measurements at S1. To upscale the model to the entire Loire Basin, the influence of lakes and reservoirs have to be considered since they largely modify nutrients transfers downstream. This raises another issue, because the connection between streams/rivers with lakes/reservoirs is hardly considered in water quality models at the catchment scale.

5.4.1 New eco-hydrological issues~~ that should be considered~~

~~In eutrophic rivers, several recent studies clearly showed the increasing concern on the Asian *Corbicula* clams *spp.* that invaded the river networks in South and North America and later in Europe over the past decades (Cataldo and Boltovskoy, 1998; Cohen et al., 1984; Phelps, 1994; Pigneur et al., 2014). This clam plays a significant role in the dynamic of phytoplankton (and thus, on nutrients) for several rivers in Europe, and for instance seems to be responsible for 70% decrease in the phytoplankton biomass of the Meuse River (Pigneur et al., 2014). The main issue to take into account this grazer is the lack of dataset, both spatially and temporally. In the Loire River, Descy et al. (2011) determined that a *Corbicula* population density of 2.5 to 10 g C m^{-2} was needed to explain the phytoplankton variations, but clams density was then uniformly distributed depending on the river reach due to lack of data. This was not tested in QUAL-NET yet, since very few surveys have been conducted, and spatial distributions of *Corbicula* spp. population are still unknown.~~

~~In addition, aquatic fixed vegetation are able to extract nutrients from the sediment and might keep growing even if the phytoplankton has reached its phosphorus limitation in the water column (Carignan and Kalff, 1980; Hood, 2012). Thus, despite low P availability, macrophytes might keep growing, especially when there is a high P legacy in the river bed sediments. We lack data about macrophytes in the Loire River, but a few unpublished observations in the MLRC presented very significant densities of *Ranunculus fluitans*, *Myriophyllum spicatum* and *Elodea nuttallii* (Michel Chantereau, personal comm.). Their impact on the Loire River biogeochemistry could be significant, and further developments in the model QUAL-NET should be able to model this biological compartment. However, a reliable monitoring has to be set up, at least in the MLRC.~~

In eutrophic rivers, several recent studies clearly showed the increasing concern with Asian *Corbicula* clams *spp.* that invaded river networks in South and North America and later in Europe over the past decades (Cataldo and Boltovskoy, 1998; Cohen et al., 1984; Phelps, 1994; Pigneur et al., 2014). This clam plays a significant role in the dynamic of phytoplankton for several rivers in Europe. Pigneur et al. (2014) estimated for instance that *Corbicula* was responsible for 70% decrease in the phytoplankton biomass of the Meuse River. The main challenge with *Corbicula* is the lack of dataset, both spatially and temporally. In the Loire River, Descy et al. (2011) determined that a population density of 2.5 to 10 g C m^{-2} was needed to explain the phytoplankton variations, but clams density was then uniformly distributed depending on the river. This was not tested in QUAL-NET yet, since very few surveys have been conducted, and spatial distributions of *Corbicula* spp. population remain unknown. In addition, aquatic fixed vegetation are able to extract nutrients from the sediment and might keep growing even if phytoplankton has reached its phosphorus limitation in the water column (Carignan and Kalff, 1980; Hood, 2012). Despite low P availability, macrophytes might keep growing, especially under high P legacy in the river bed sediments. We lack data about macrophytes in the Loire River, but few unpublished observations in the MLRC presented very significant densities of *Ranunculus fluitans*, *Myriophyllum spicatum* and *Elodea nuttallii* (Michel Chantereau, personal comm.). Their impact on the Loire River biogeochemistry is likely significant, and further developments in the model QUAL-NET should consider this biological compartment and macrophyte biomass within the MLRC need to be surveyed properly.

6 Conclusions

The deterministic modelling approach we developed ~~allowed to~~helped disentangle the interactions ~~existing~~ between hydrological ~~processes~~ and biological ~~activity~~processes in the Loire River. Results from ~~model~~ QUAL-NET fitted the available daily observations, and the main driving processes could be identified. The Middle Loire River Corridor functions as a biogeochemical reactor in summer during low water period. The system clearly reaches a P-limitation, and our model indicate that internal loadings of P due to bacterial mineralization ~~enhance~~enhances phytoplankton blooms. The use of high temporal resolution ~~allowed~~enabled to study the impact of a storm event during a phytoplankton bloom, and identified large diel fluctuations for C, P and O_2, but these variations still need to be confronted to high-frequency *in situ* measurements. QUAL-NET simulated realistic sub-daily variations from low-frequency forcing variables, and could be applied at a larger scale (e.g. the entire Loire Basin, ~~110 10^3~~110x10^3 km²). It could be used to study past evolutions using low frequency dataset as data input, or predict future evolutions under climate change and land use scenarios.

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Author contribution

C. Minaudo and F. Curie designed the model structure. C. Minaudo and Y. Jullian developed the model code. F. Moatar and N. Gassama and C. Minaudo designed and conducted the daily sampling and the chemical analysis. C. Minaudo prepared the manuscript with contributions from all co-authors.

Acknowledgements

This work started within the “Eutrophisation-Trends” project (funds from “Agence de l’Eau Loire Bretagne, “Plan Loire Grandeur Nature” and FEDER European funds) and continued within the project “Risque Eutrophisation Plans d’Eau” funded by “l’Office Nationale des Eaux et Milieux Aquatiques”. Authors are very thankful to Gilles Billen (Paris Sorbonne-UPMC Univ.) for sharing with us the code of model RIVE and for his careful read of our manuscript. Comments and suggestions from Gilles Pinay (Rennes 1 Univ.) also contributed to improve the manuscript.

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Table 1. Values optimized for TSS and Langmuir coefficients during the calibration step, and compared to other values found in ~~other studies~~literature

	RMSE	Coefficient name	Unit	Optimized value for this study	~~Values found in other~~Other studies for rivers or streams
TSS	15 mg L^{-1}	$Veli_0$	mg TSS L^{-1}	20	20^1
		$Veli_1$	mg TSS L^{-1}	500	50^1
		Vs_{TSS}	m h^{-1}	0.1	0.5^1
SRP	14 µg L^{-1}	*Kpads*	mg P L^{-1}	0.15	0.68^1 0.04^2 0.01^3 1.89 to 200^4
		Pac	mg P (g $TSS)^{-1}$	5.5	5.6^1 3.1^2 12.8^3 0.3 to 3.0^4

1. Billen et al., (1994), Seine River, France
~~2. Aissa-Grouz, (2015), Seine River, France~~
~~3. Vilmin et al., (2015), Seine River, France~~
~~4. Jalali and Peikam, (2013), Abshineh River, Iran~~
2. Aissa-Grouz, (2015), Seine River, France
3. Vilmin et al., (2015), Seine River, France
4. Jalali and Peikam, (2013), Abshineh River, Iran

Code de champ modifié

Mis en forme : Français (France)

Table 2. Model performances (bias ± s.d. errors) for different time scales: over the entire period of validation (August 1st 2012 to July 31st 2014), in "summer" (April to October) and "winter" (November to March).

~~element~~parameter	unit	entire period	"summer"	"winter"
TSS	mg L^{-1}	7.6 ± 13	5.4 ± 11	10.3 ± 14.8
NO_3^-	mg N L^{-1}	0.1 ± 0.4	0.1 ± 0.4	0.1 ± 0.5
SRP	µg P L^{-1}	-2 ± 14	-2.2 ± 15	-1.9 ± 13
Si	mg Si L^{-1}	0.2 ± 1.7	0.4 ± 1.3	-0.1 ± 2.1
PHY	mg C L^{-1}	0.0 ± 0.4	-0.1 ± 0.5	0.1 ± 0.1
POC	mg C L^{-1}	0.3 ± 1.0	0.0 ± 1.1	0.6 ± 0.7
DOC	mg C L^{-1}	0.4 ± 1.5	0.2 ± 1.3	0.7 ± 1.8

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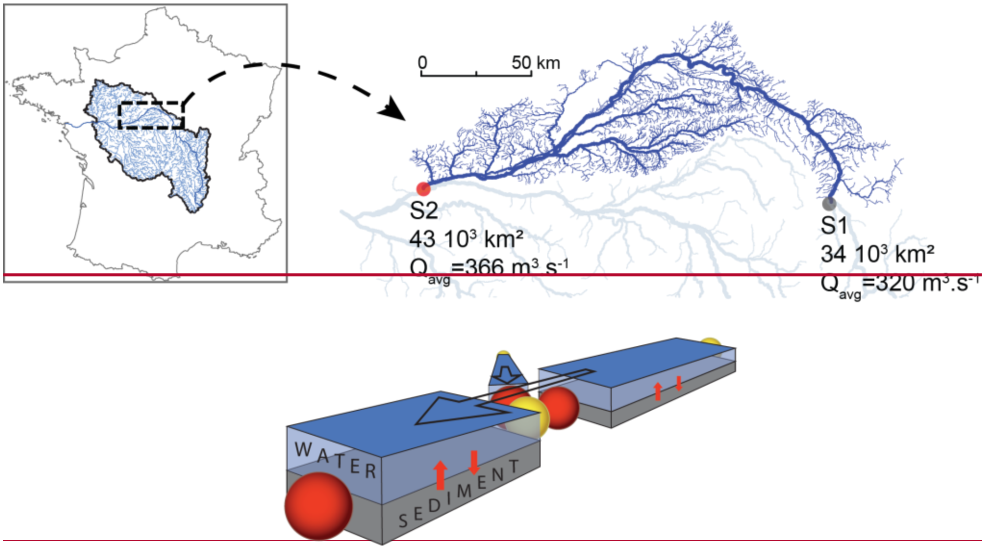

0
50 km
S2
43 10³ km²
Q avg =366 m³.s-1
S1
34 10³ km²
Q avg =320 m³.s-1
WATER
SEDIMENT

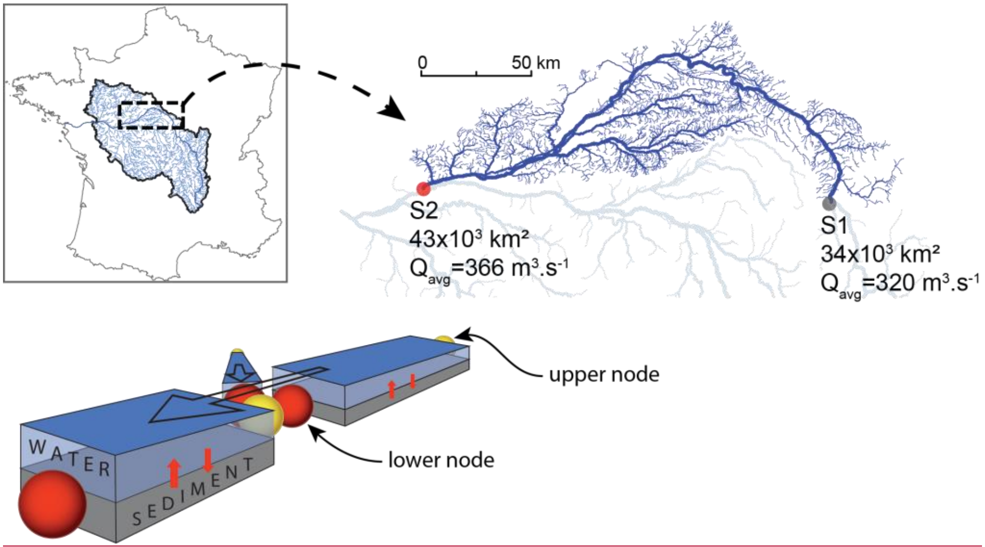
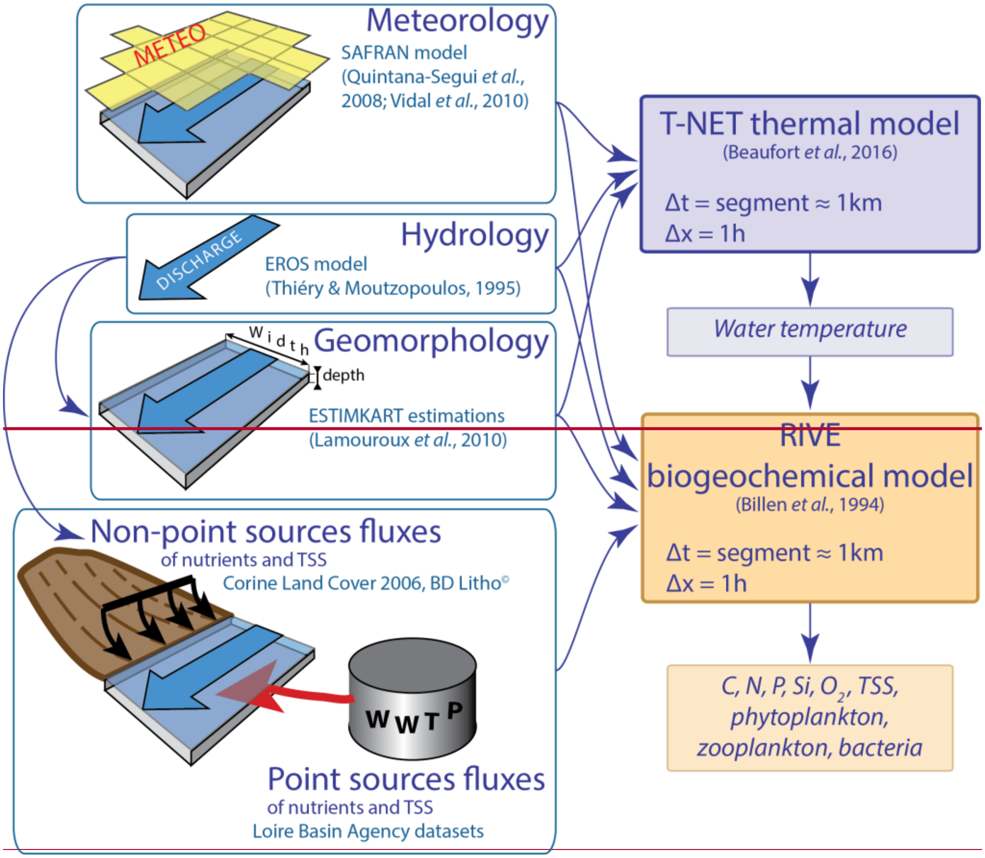

0
50 km
S2
43x10³ km²
Q avg =366 m³.s-1
S1
34x10³ km²
Q avg =320 m³.s-1
upper node
lower node
WATER
SEDIMENT

Figure 1. Study area,~~ i.e.~~ the Middle Loire Corridor sub-catchment defined between stations S1 and S2, and network topology concept used in the model.


Meteorology
METEO
SAFRAN model
(Quintana-Segui et al., 2008; Vidal et al., 2010)
Hydrology
DISCHARGE
EROS model
(Thiéry & Moutzopoulos, 1995)
Geomorphology
Width
depth
ESTIMKART estimations
(Lamouroux et al., 2010)
Non-point sources fluxes
of nutrients and TSS
Corine Land Cover 2006, BD Litho©
WWTP
Point sources fluxes
of nutrients and TSS
Loire Basin Agency datasets
T-NET thermal model
(Beaufort et al., 2016)
Δt = segment ≈ 1km
Δx = 1h
Water temperature
RIVE
biogeochemical model
(Billen et al., 1994)
Δt = segment ≈ 1km
Δx = 1h
C, N, P, Si, O2, TSS,
phytoplankton,
zooplankton, bacteria

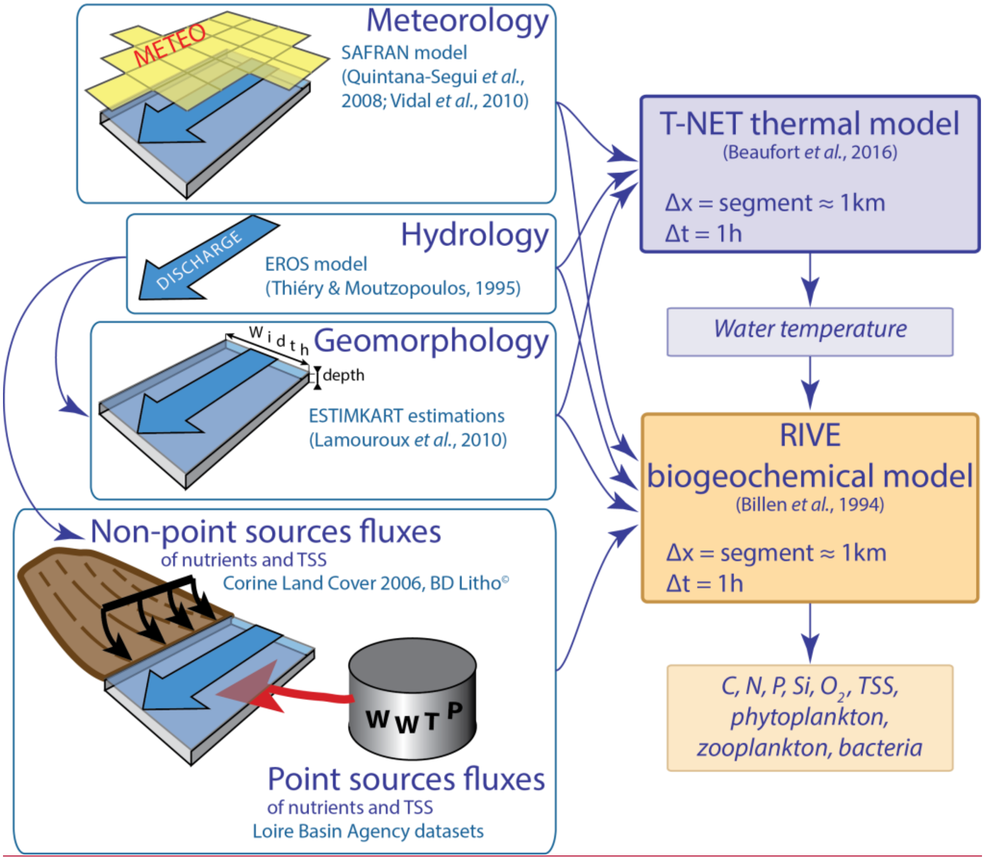


Figure 2. Architecture of QUAL-NET and data sources~~for the different types of forcing variables~~.

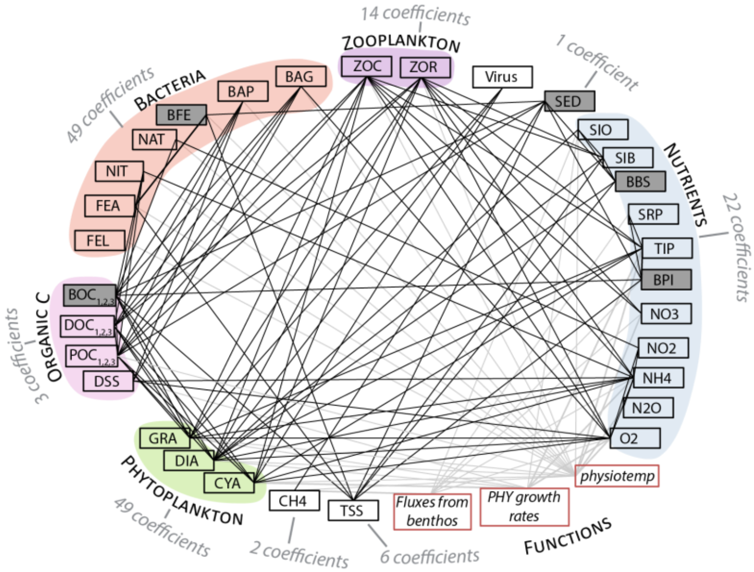
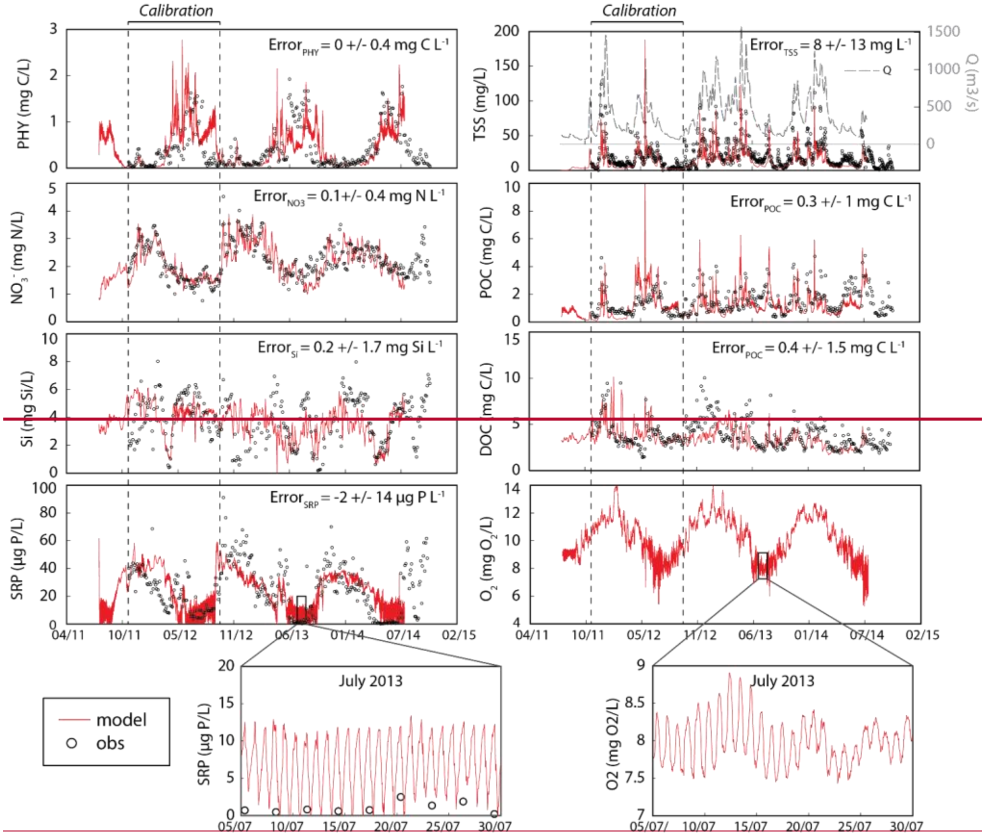


Figure 3. Main variables interdependency in the biogeochemical model RIVE and associated ~~counted~~ coefficients. Grey plain rectangles identify variables ~~in~~describing the benthos component, red rectangles are generic functions often called within the code.


Calibration
Calibration
PHY (mg C/L)
Error_PHY = 0 +/- 0.4 mg C L-1
NO3- (mg N/L)
Error_NO3 = 0.1+/- 0.4 mg N L-1
Si (mg Si/L)
Error_Si = 0.2 +/- 1.7 mg Si L-1
SRP (µg P/L)
Error_SRP = -2 +/- 14 µg P L-1
TSS (mg/L)
Error_TSS = 8 +/- 13 mg L-1
Q
Q (m3/s)
1500
1000
500
POC (mg C/L)
Error_POC = 0.3 +/- 1 mg C L-1
DOC (mg C/L)
Error_POC = 0.4 +/- 1.5 mg C L-1
O2 (mg O2/L)
04/11
10/11
05/12
11/12
06/13
01/14
07/14
02/15
July 2013
SRP (µg P/L)
05/07
10/07
15/07
20/07
25/07
30/07
July 2013
O2 (mg O2/L)
model
obs

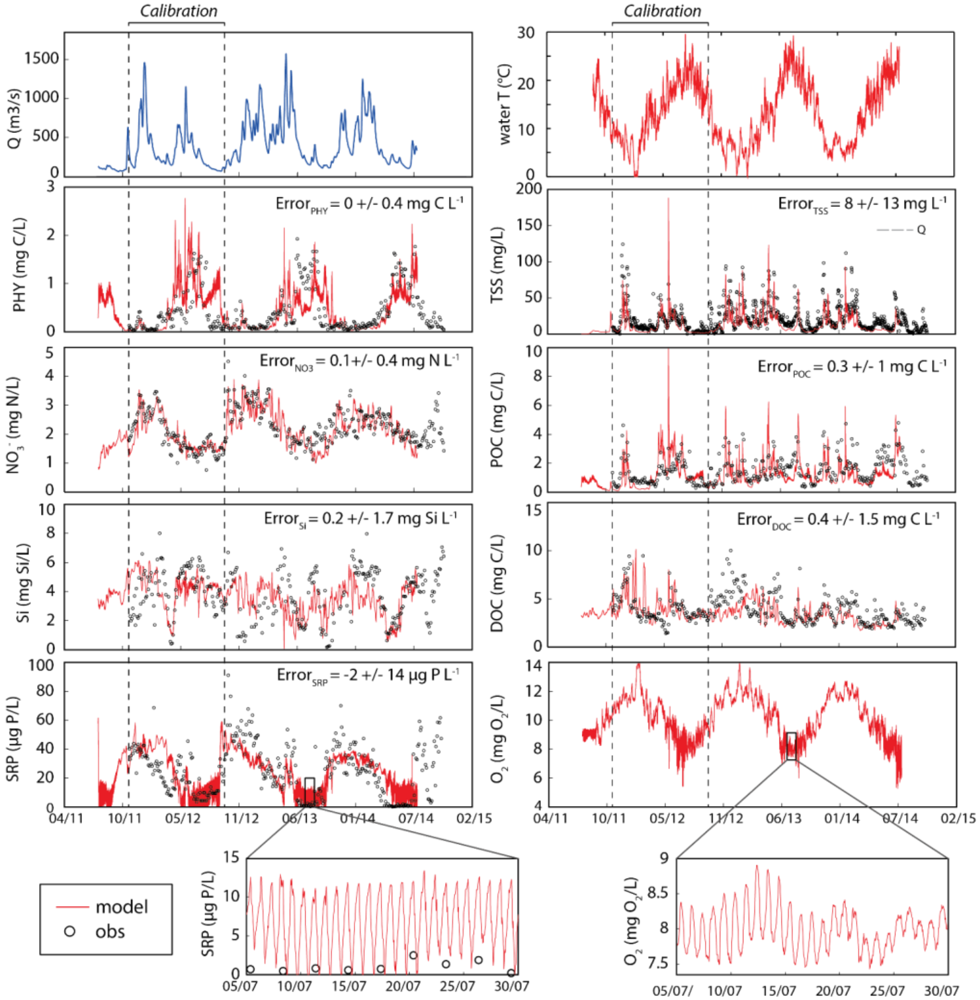


Figure 4. Results at station S2 after calibration for the main variables in the model: discharge (Q), phytoplankton (PHY), nitrate (NO_3^-), dissolved silica (Si), soluble reactive phosphorus (SRP), water temperature, total suspended solids (TSS~~) and discharge (Q~~), particulate organic carbon (POC), dissolved organic carbon (DOC), dissolved oxygen (O_2). Last row zooms in on ~~July 2013 for~~ SRP and O_2 concentrations in July 2013 to show simulated diel fluctuations.

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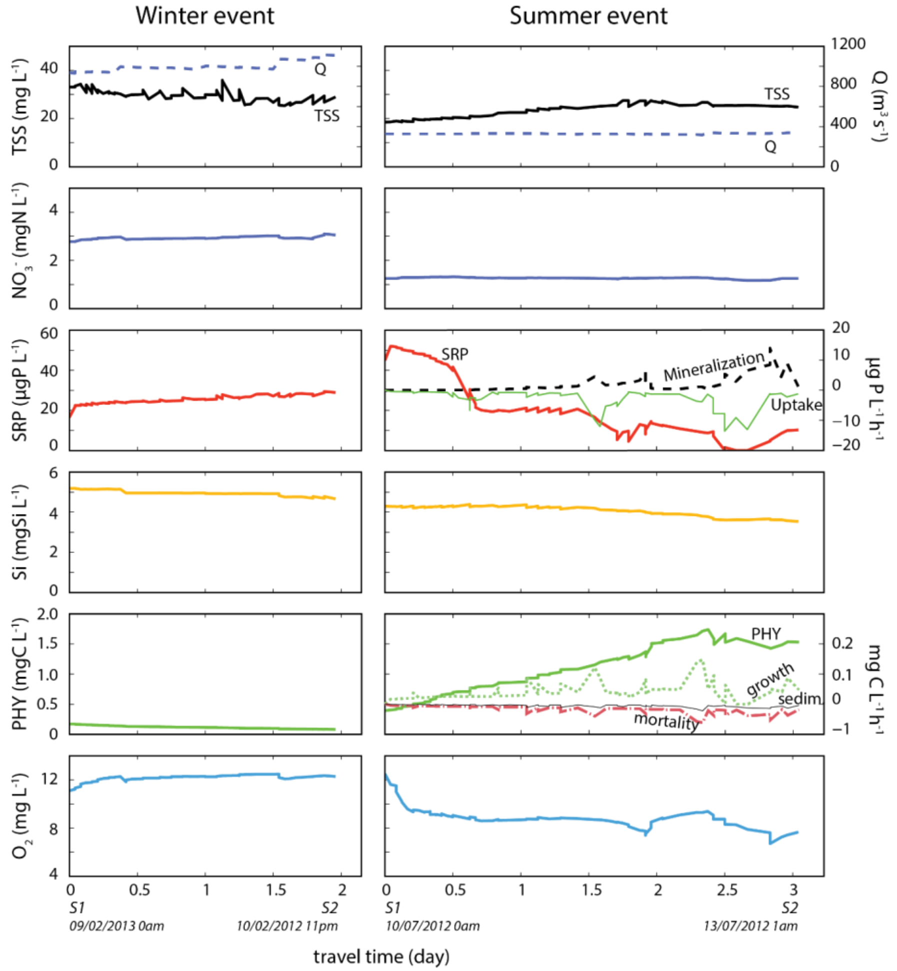
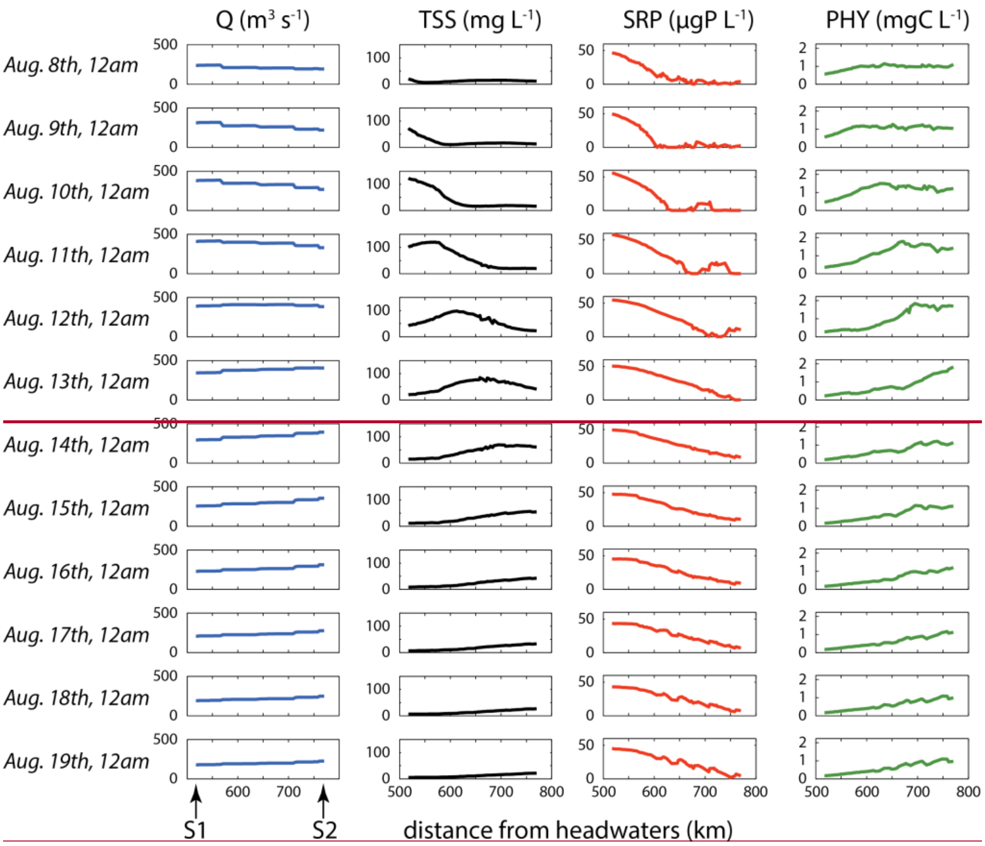


Figure 5. Lagrangian ~~view~~profiles from S1 to S2 of TSS, NO_3^-, SRP, Si, PHY and O_2 during two selected events. For the summer event, are also displayed on the right axis P input from mineralization processes, P uptake from phytoplankton, phytoplankton growth~~, sedimentation and mortality. For the winter event, the model estimated that water left S1 on February 9th 2013 at midnight and reached S2 on February 10th at 1pm. For the summer event, water left S1 on July 10th 2012 at midnight and reached S2 on July 13th at 1am~~ rate (availability of intracellular carbon and nutrients), sedimentation and mortality rates.


Q (m³ s⁻¹)
TSS (mg L⁻¹)
SRP (µgP L⁻¹)
PHY (mgC L⁻¹)
Aug. 8th, 12am
Aug. 9th, 12am
Aug. 10th, 12am
Aug. 11th, 12am
Aug. 12th, 12am
Aug. 13th, 12am
Aug. 14th, 12am
Aug. 15th, 12am
Aug. 16th, 12am
Aug. 17th, 12am
Aug. 18th, 12am
Aug. 19th, 12am
500
0
100
50
2
1
600
700
800
S1
S2
distance from headwaters (km)

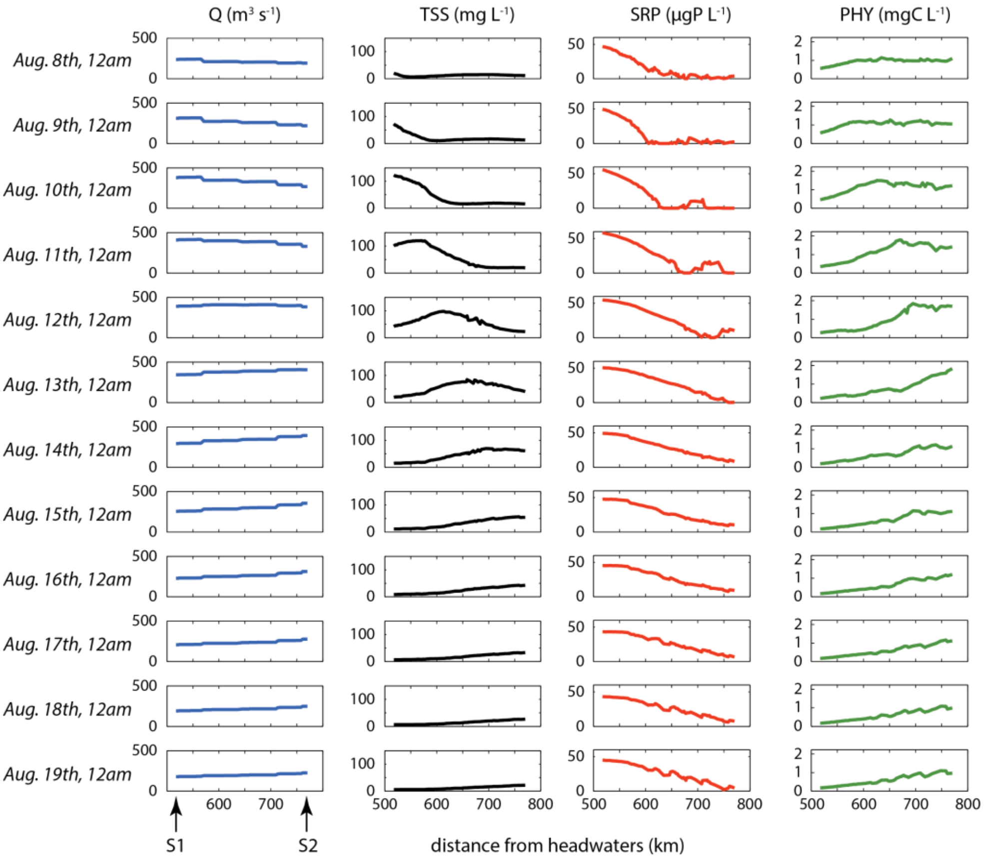
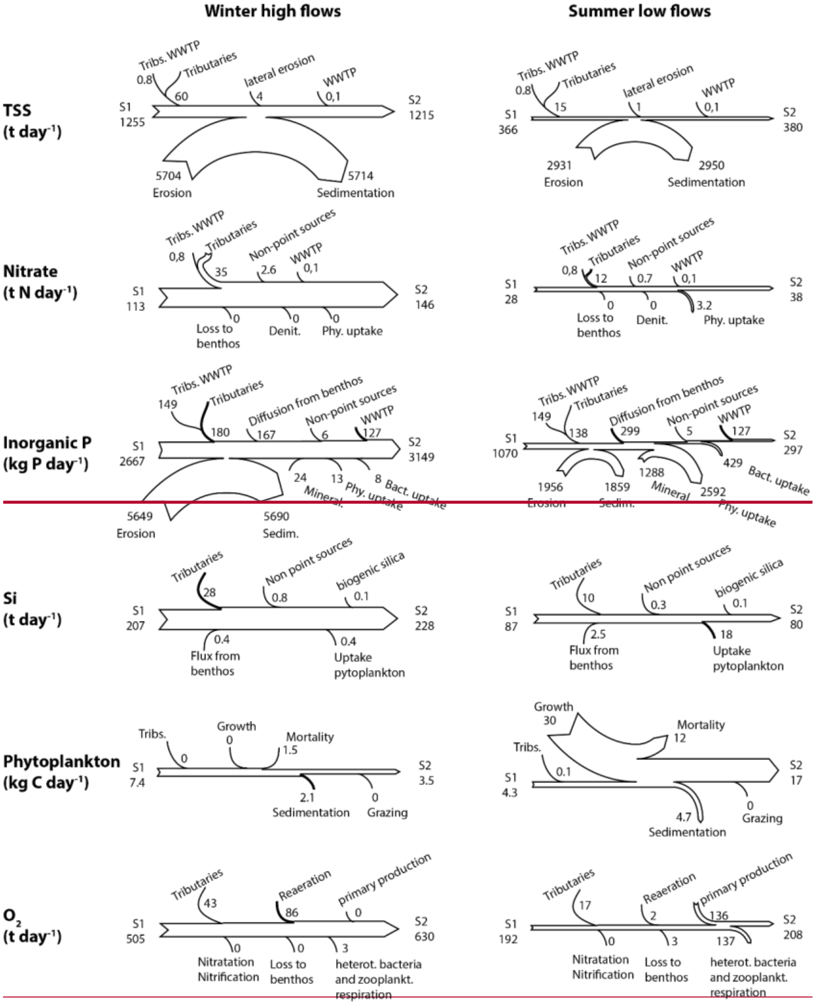


Figure 6. Longitudinal evolution of discharge Q, TSS, SRP and PHY concentrations when a storm event occurred between August 8th and August 19th 2013.


Winter high flows
Summer low flows
TSS (t day⁻¹)
Tribs. WWTP 0.8
Tributaries 60
lateral erosion 4
WWTP 0,1
S1 1255
S2 1215
5704 Erosion
5714 Sedimentation
Tribs. WWTP 0.8
Tributaries 15
lateral erosion 1
WWTP 0,1
S1 366
S2 380
2931 Erosion
2950 Sedimentation
Nitrate (t N day⁻¹)
Tribs. WWTP 0,8
Tributaries 35
Non-point sources 2.6
WWTP 0,1
S1 113
S2 146
0 Loss to benthos
0 Denit.
0 Phy. uptake
Tribs. WWTP 0,8
Tributaries 12
Non-point sources 0.7
WWTP 0,1
S1 28
S2 38
0 Loss to benthos
0 Denit.
3.2 Phy. uptake
Inorganic P (kg P day⁻¹)
Tribs. WWTP 149
Tributaries 180
Diffusion from benthos 167
Non-point sources 6
WWTP 127
S1 2667
S2 3149
24 Mineral.
13 Phy. uptake
8 Bact. uptake
5649 Erosion
5690 Sedim.
Tribs. WWTP 149
Tributaries 138
Diffusion from benthos 299
Non-point sources 5
WWTP 127
S1 1070
S2 297
1956 Erosion
1859 Sedim.
1288 Mineral
2592 Phy. uptake
429 Bact. uptake
Si (t day⁻¹)
Tributaries 28
Non point sources 0.8
biogenic silica 0.1
S1 207
S2 228
0.4 Flux from benthos
0.4 Uptake pytoplankton
Tributaries 10
Non point sources 0.3
biogenic silica 0.1
S1 87
S2 80
2.5 Flux from benthos
18 Uptake pytoplankton
Phytoplankton (kg C day⁻¹)
Tribs. 0
Growth 0
Mortality 1.5
S1 7.4
S2 3.5
2.1 Sedimentation
0 Grazing
Growth 30
Mortality 12
Tribs. 0.1
S1 4.3
S2 17
4.7 Sedimentation
0 Grazing
O2 (t day⁻¹)
Tributaries 43
Reaeration 86
primary production 0
S1 505
S2 630
0 Nitratation Nitrification
0 Loss to benthos
3 heterot. bacteria and zooplankt. respiration
Tributaries 17
Reaeration 2
primary production 136
S1 192
S2 208
0 Nitratation Nitrification
3 Loss to benthos
137 heterot. bacteria and zooplankt. respiration

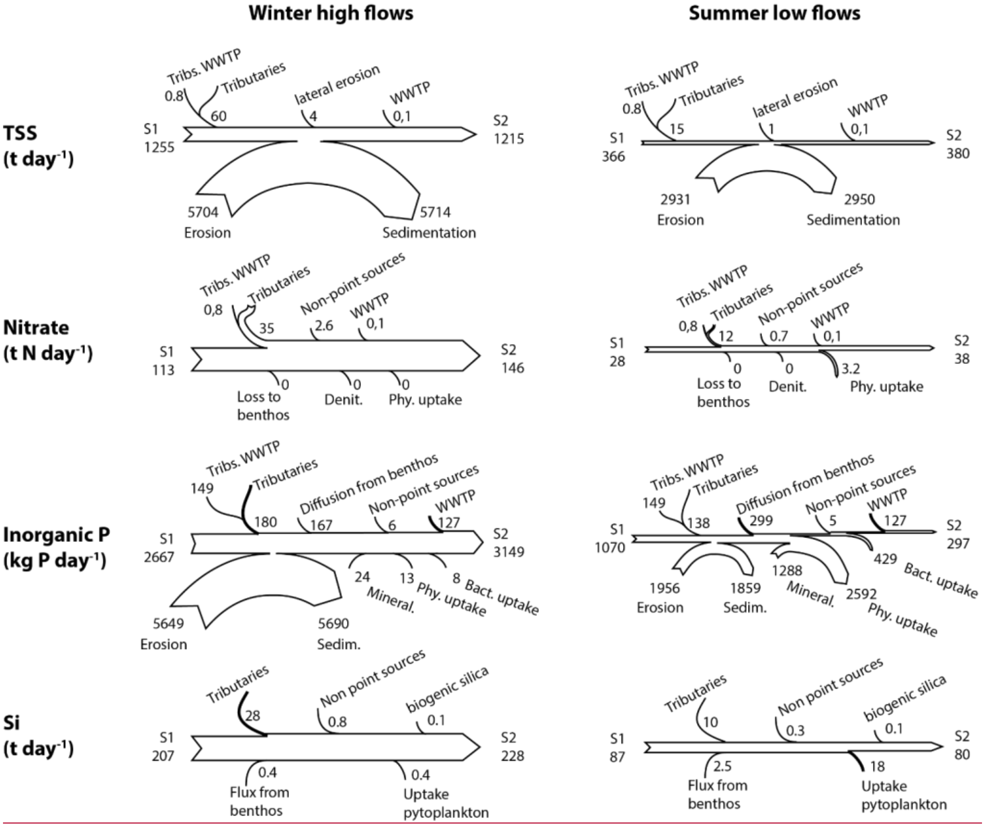


Figure 7. Average “winter” and “summer” budgets between S1 and S2 for TSS, nitrate, inorganic P, dissolved silica~~, phytoplankton biomass and dissolved oxygen. Arrow~~. All arrow widths are~~ all~~ proportional to calculated fluxes, allowing the visual comparison between “winter” and “summer” periods.

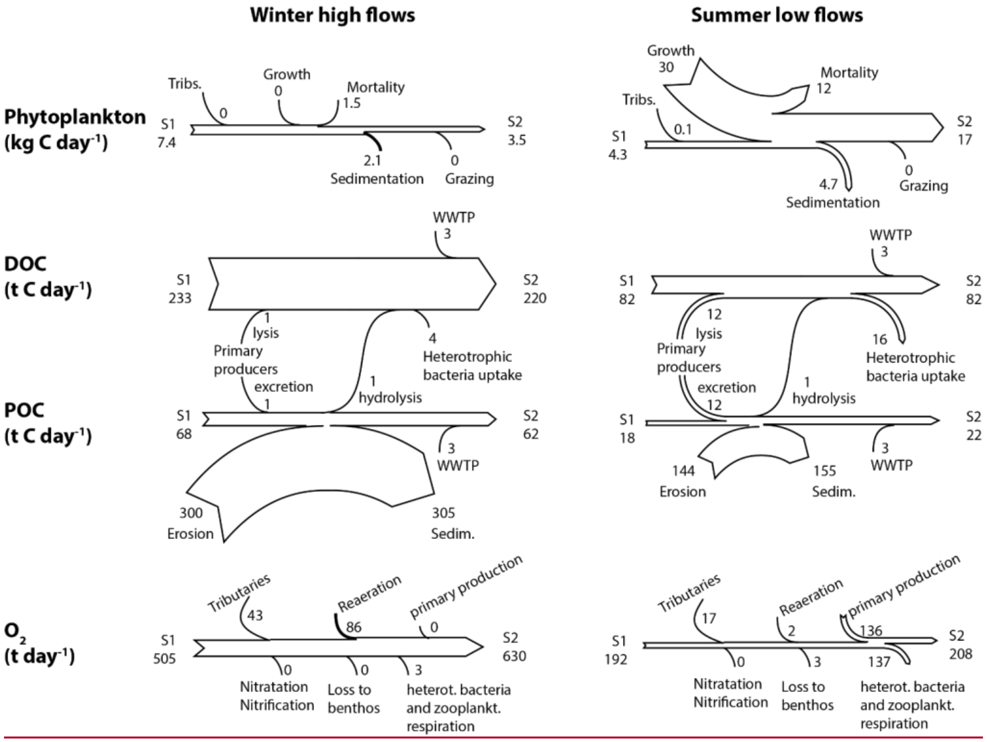


Figure 8. Average "winter" and "summer" budgets between S1 and S2 for phytoplankton biomass, dissolved and particulate organic carbon, and dissolved oxygen. All arrows widths are proportional to calculated fluxes, allowing the visual comparison between "winter" and "summer" periods.

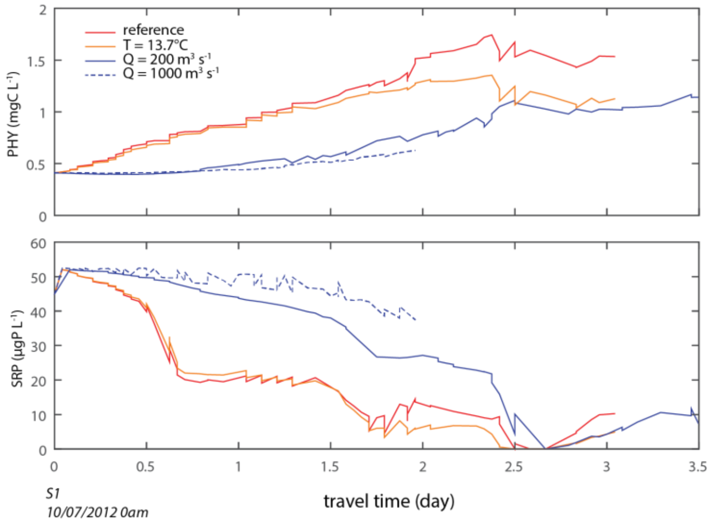


Figure S1. Lagrangian profiles from S1 to S2 of phytoplankton and SRP concentrations for four contrasted simulations to show phytoplankton and phosphorus sensitivity to flow and water temperature conditions: i) reference simulation used throughout the manuscript; ii) constant low-flow in the Loire at S1 forced at 200 m^3 s^{-1} and forced at 0.1 m^3 s^{-1} in all other streams; iii) constant high-flow in the Loire at S1 forced at 1000 m^3 s^{-1} and forced at 0.1 m^3 s^{-1} in all other streams; iv) constant water temperature simulation, T = 13.7°C in all streams at all time. Phytoplankton development was much more affected by shorter travel times than by colder water temperature. P availability played a major role, and SRP exhaustion was reached 2.5 days after the starting date from S1 for all simulations except for the high-flow simulation where no P limitation was simulated because travel time from S1 to S2 was not long enough.