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Supplement of

How do inorganic nitrogen processing pathways change quantitatively at daily, seasonal, and multiannual scales in a large agricultural stream?

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Supplement

Supplementary Information includes SI Text for estimation of discharges from the tributaries, calculation of NO_3^- and NH_4^+ uptake rates, and comparison of N uptake results among different studies, SI Figures S1-S8, and SI Tables S1-S3.

SI Text

1. Estimation of discharges from the tributaries and water balance

The discharges of 8 tributaries within the study reach were only measured bi-monthly, which would bring large uncertainties in boundary conditions by interpolating such coarse resolution datasets with highly temporal heterogeneous characteristics. However, a tributary Geesgraben, about 500 m upstream of HAD, has a gauge station, which provides daily discharge. Since the geology, soil structure, elevation, and precipitation pattern are homogeneous in the study area, we assume that the area specific discharges of the tributaries in the study reach are similar to that of Geesgraben. Based on the assumption, the daily discharge ($m^3\ s^{-1}$) of each tributary ($Q_{Trib,i}$) was calculated by the area specific method (eq. S1)

$$Q_{Trib,i} = \frac{Q_{Gees}}{A_{Gees}} \times A_{Trib,i} \qquad \text{(eq. S1)}$$

where Q_{Gees} donates the daily natural discharge of Geesgraben ($m^3\ s^{-1}$); A_{Gees} and $A_{Trib,i}$ represent catchment areas (km^2) of Geesgraben and i^{th} tributary, representatively. The catchment areas are provided in Table S1. What needs to be mentioned is that sewage from a large sugar refinery continuously discharged into Geesgraben. For an accurate area specific discharge calculation, Q_{Gees} was obtained by subtracting the sewage flow from the measured daily flow of Geesgraben.

We also considered the situations that the small tributaries can dry out in the summer months. The tributaries with the catchment size below 30 km^2, namely Roethe, Suelzgraben, Hecklinger Hauptgraben, and Boernecker Graben, were assumed to dry out when the discharge of the Geesgraben fell beneath its base flow value of 0.05 $m^3\ s^{-1}$. Finally, to test the reliability of the calculated values, a hydrological budget with a percentage error of discharge ($Error$, in %) was derived as

$$Error = \left(Q_{Up} + \sum_{i}^{8} Q_{Trib,i} - Q_{Down} \right) \Big/ Q_{Down} \times 100\% \qquad \text{(eq. S2)}$$

where $\sum_i^8 Q_{Trib,i}$ is the sum of the 8 tributary discharges; Q_{UP} and Q_{DOWN} represent the mean daily discharge at the upstream and downstream stations.

The discharge at the upstream and downstream stations show very close values (Figure S1). This demonstrates the limited contribution fraction of the lateral inputs in the study reach. There are two potential N diffuse sources, namely tributaries and direct groundwater inputs. In the study, we considered the lateral input from the tributaries. According to our water balance calculation results over the five years, we found that the mean percentage balance error for 5 years was +0.97%[1]. Targeting on the low flow period, we calculated the water balance for the extreme summer low flow period in 2018 and got the result of animbalance percentage of +0.59%. These small percentage values both on a multi-annual basis and for an extreme summer low flow period suggest the direct evidence that groundwater-surface water exchange does not play a significant role for the water balance in our study reach. In fact, the 8 small tributaries

[1] The positive value means that discharge at the outlet was lower than the input.

are used as drainage of the corresponding sub-catchments. The flow and N concentration at the outlet of the tributaries are the results of hydrological cycle including the groundwater exchanges in the sub-catchments. The direct exchange with groundwater of the main stem of the study reach in the Lower Bode is therefore very limited.

The uncertainty of uptake calculation in the Lower Bode caused by the estimation of the lateral boundary conditions are small because of three reasons. First, most inflow and loading come from the upstream boundary (Figure S1), which is well constrained by the high-frequency discharge and nitrate measurements. Second, the water imbalance is very small (0.59% in summer 2018), see also Figure S1. During the extreme low flow conditions in 2018 the tributaries were all dry as documented by personal visual inspections and the state water authority monitoring, which means errors of calculating these discharge inputs can be neglected. If we further assume that at extreme low flows lateral inflows should be highest our well-balanced discharge during this extreme discharge conditions suggest that there are no significant inflows not only during this low flow conditions but also during higher flow stages. Third, the net uptake percentage of the total input loadings is high during the summer low flow periods (nearly 30% in summer 2018). During winter high flow periods, the loading contribution percentage of the tributaries to the Lower Bode was higher than that of low flow conditions. However, in this season nitrogen processing in the study reach was mainly controlled by hydrological processes and nitrate was simply transferred downstream with no noticeable net uptake.

2. Calculation of NO_3^- and NH_4^+ uptake rates

Because many studies measured uptake rates for specific N form (i.e., NO_3^- and NH_4^+) separately or only, in order to better compare the uptake rate results of this study with others, we also calculated the nitrate gross uptake rate ($U_{GROSS,NO3}$), nitrate net uptake rate ($U_{NET,NO3}$), ammonia gross uptake rate ($U_{GROSS,NH4}$), and ammonia net uptake rate ($U_{NET,NH4}$) separately. All process rates have the same unit of mg N m^{-2} d^{-1}.

$$U_{GROSS,NO3} = U_D + U_{A,P,NO3} + U_{A,B,NO3} \quad \text{(eq. S3)}$$

$$U_{NET,NO3} = U_D + U_{A,P,NO3} + U_{A,B.NO3} - U_{NIT} \quad \text{(eq. S4)}$$

$$U_{GROSS,NH4} = U_{A,P,NH4} + U_{A,B.NH4} + U_{NIT} \quad \text{(eq. S5)}$$

$$U_{NET,NH4} = U_D + U_{A,P} + U_{A,B} - R_P - R_B + U_{NIT} - U_{MIN} \quad \text{(eq. S6)}$$

where $U_{A,P,NO3}$ and $U_{A,B,NO3}$ represent the assimilatory NO_3^- uptake rate by phytoplankton and benthic algae, respectively; $U_{A,P,NH4}$ and $U_{A,B,NH4}$ represent the assimilatory NH_4^+ uptake rate by phytoplankton and benthic algae, respectively; U_{NIT} is the nitrification rate. NH_4^+ is a preferred DIN form for algae due to the lower energy required to assimilate into biomass. The preference percentage for ammonia uptake of total DIN uptake by phytoplankton (P_{NH3}) and benthic algae (P_{NH4b}) are calculated as:

$$P_{NH3} = \frac{C_{NH4}\, C_{NO3}}{(K_{mN} + C_{NH4})(K_{mN} + C_{NO3})} + \frac{C_{NH4}\, K_{mN}}{(C_{NH4} + C_{NO3})(K_{mN} + C_{NO3})} \quad \text{(eq. S7)}$$

$$P_{NH4b} = \frac{C_{NH4}\, C_{NO3}}{(K_{hnxb} + C_{NH4})(K_{hnxb} + C_{NO3})} + \frac{C_{NH4}\, K_{hnxb}}{(C_{NH4} + C_{NO3})(K_{hnxb} + C_{NO3})} \quad \text{(eq. S8)}$$

where K_{mN} is the half-saturation constant for N uptake for phytoplankton and K_{hnxb} is the ammonia preference factor for benthic algae showed in Table S3.

3. Comparison of N uptake results among different studies

We compared our instream DIN uptake rates with the results of other studies. Our results of $U_{NET,NO3}$ in the growing season (i.e., spring and summer) are comparable to those measured in 4-5th order streams (9.1-376.7 mg N m^{-2} d^{-1}) with nutrient addition methods summarized by Ensign and Doyle (2006). Exceptions that exceeded this range were for a few days at the spring phytoplankton peaks. Our results are also comparable with the measured $U_{NET,NO3}$ in rivers of similar size by longitudinal profiling method (Hensley et al., 2014; Kunz et al., 2017). Ensign and Doyle (2006) reported $U_{NET,NH4}$ of 3.6-228.5 mg N m^{-2} d^{-1} for 4-5th order streams, which is comparable to the rates estimated for the Lower Bode in the growing seasons (Table 4).

SI Figure

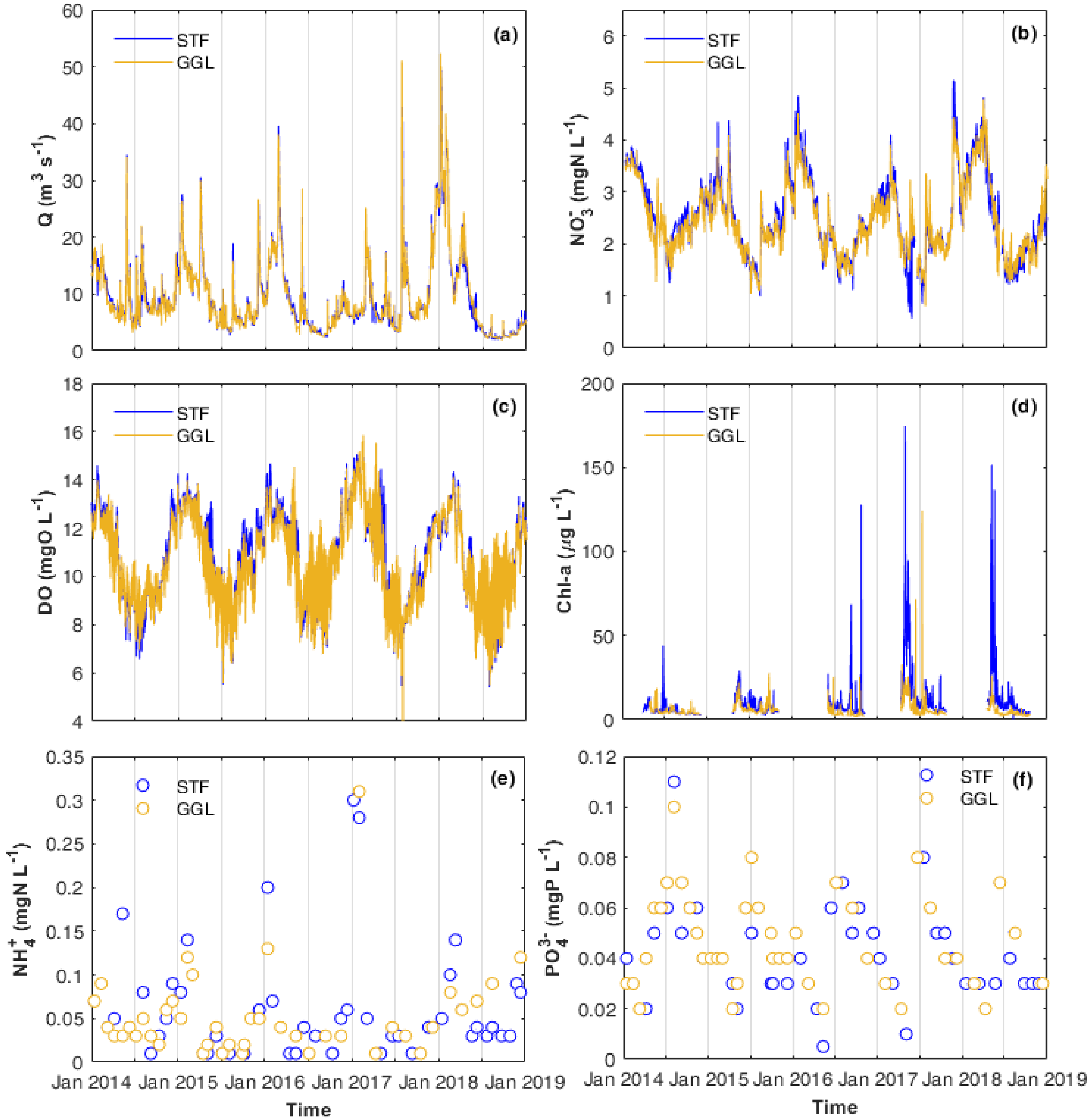

Figure S1. Comparison of discharge & water quality variables measured at GGL and STF stations

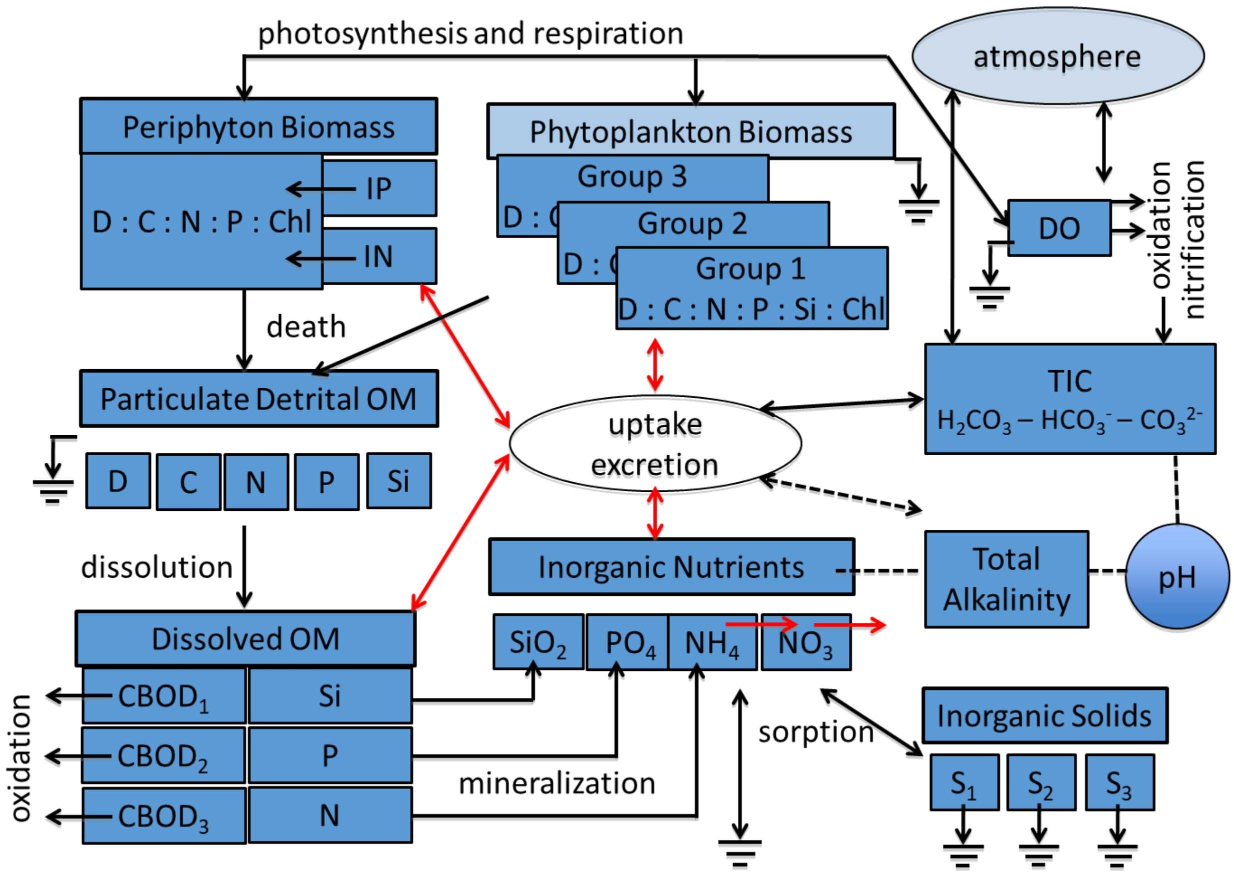

Figure S2. Schematic description of the kinetic model for WASP Advanced EUTRO Module. The red lines represent the N cycling processes we focused on in this study. The schematic chart was adopted from Wool et al. (2020).

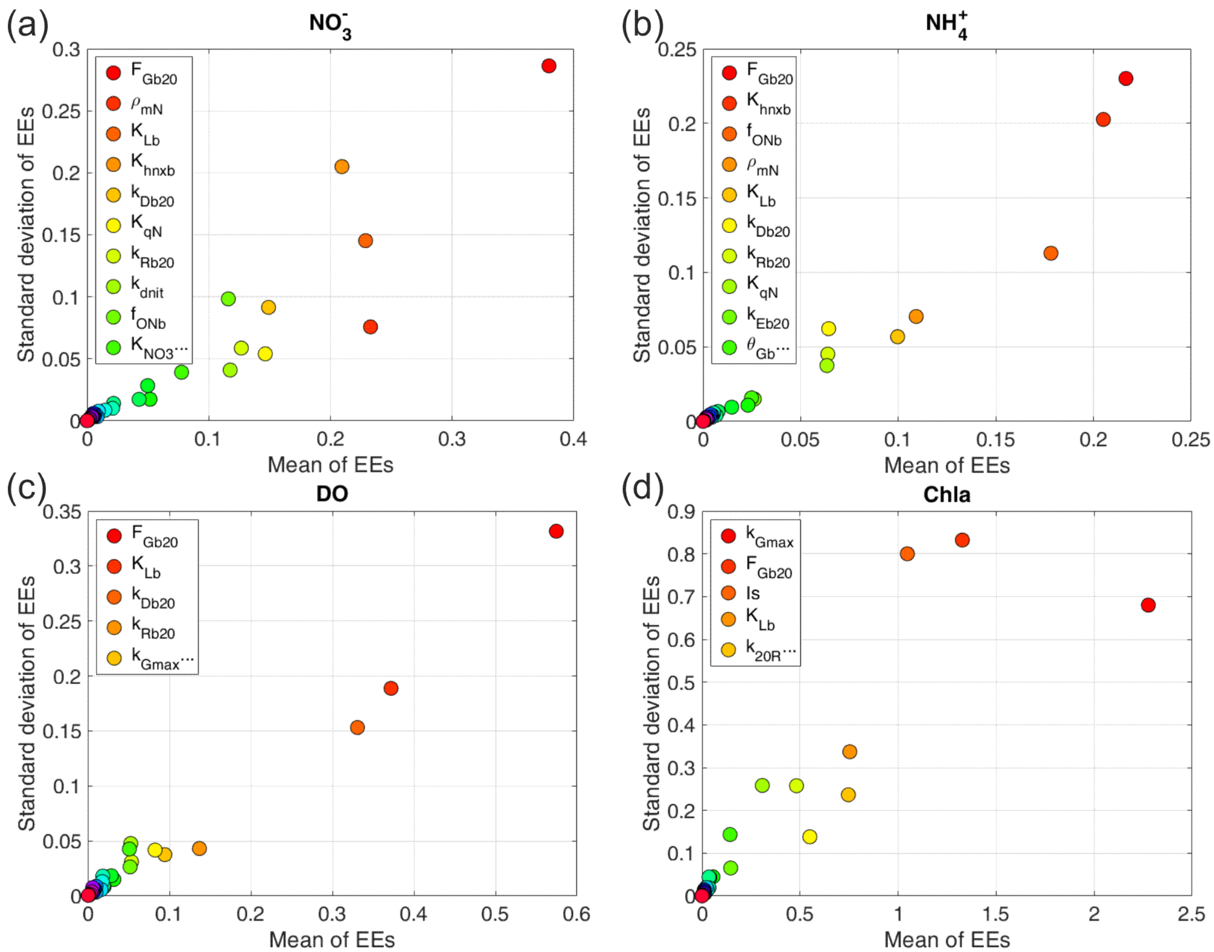

Figure S3. Parameter sensitivity ranking by Elementary Effects (EE) method with different objective functions defined respectively by the RMSE of (a) NO_3^-, (b) NH_4^+, (c) DO, and (d) Chl-a. The more to the right a point along the horizontal axis, the more influential the parameters. The higher up a point along the vertical axis, the larger its degree of interactions with other parameters. The most sensitive parameters for each objective function are shown in the legends.

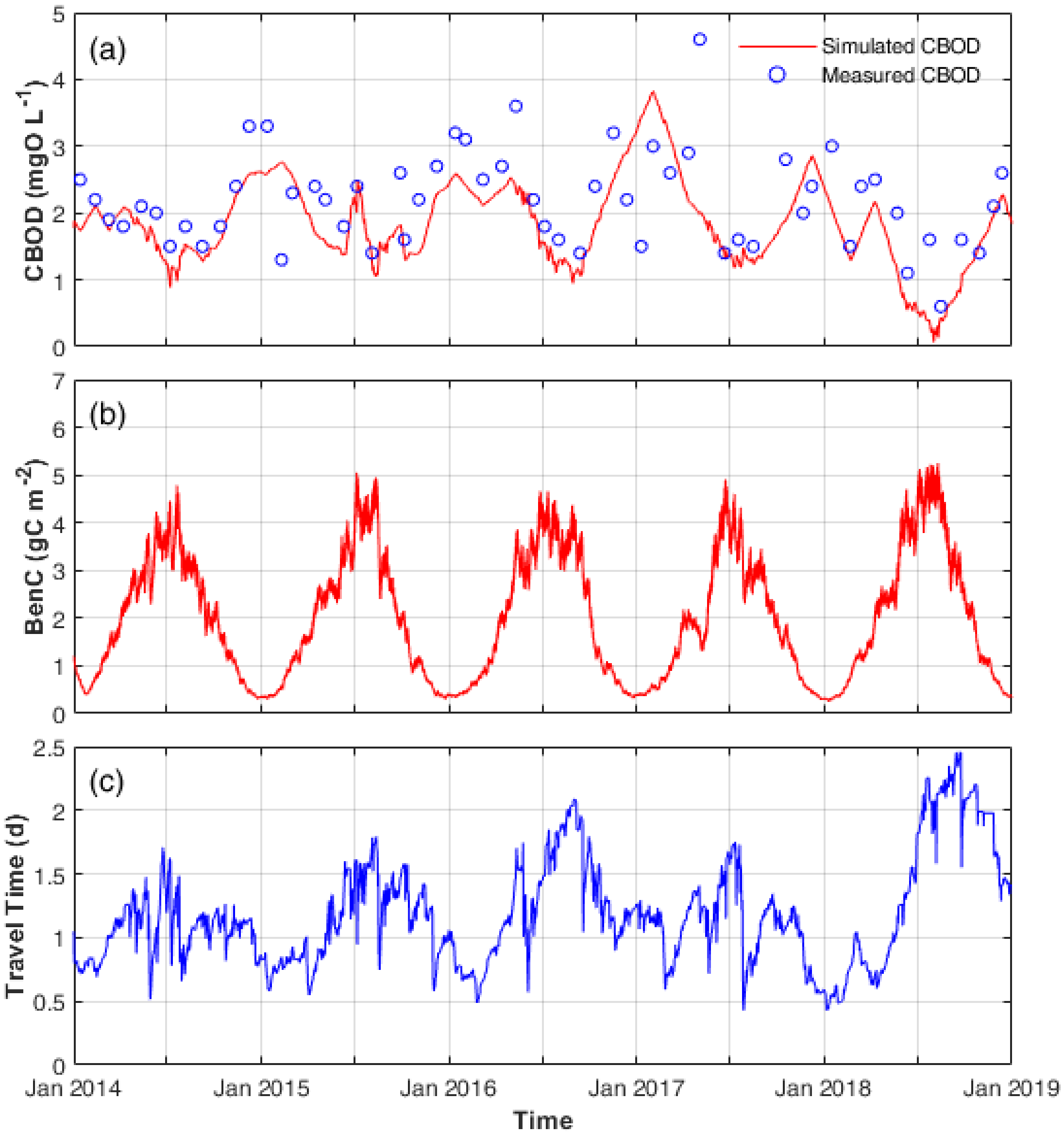

Figure S4. Measured and simulated (a) CBOD, (b) simulated benthic algae biomass carbon concentrations and (c) travel time in calibration and validation periods at the STF station.

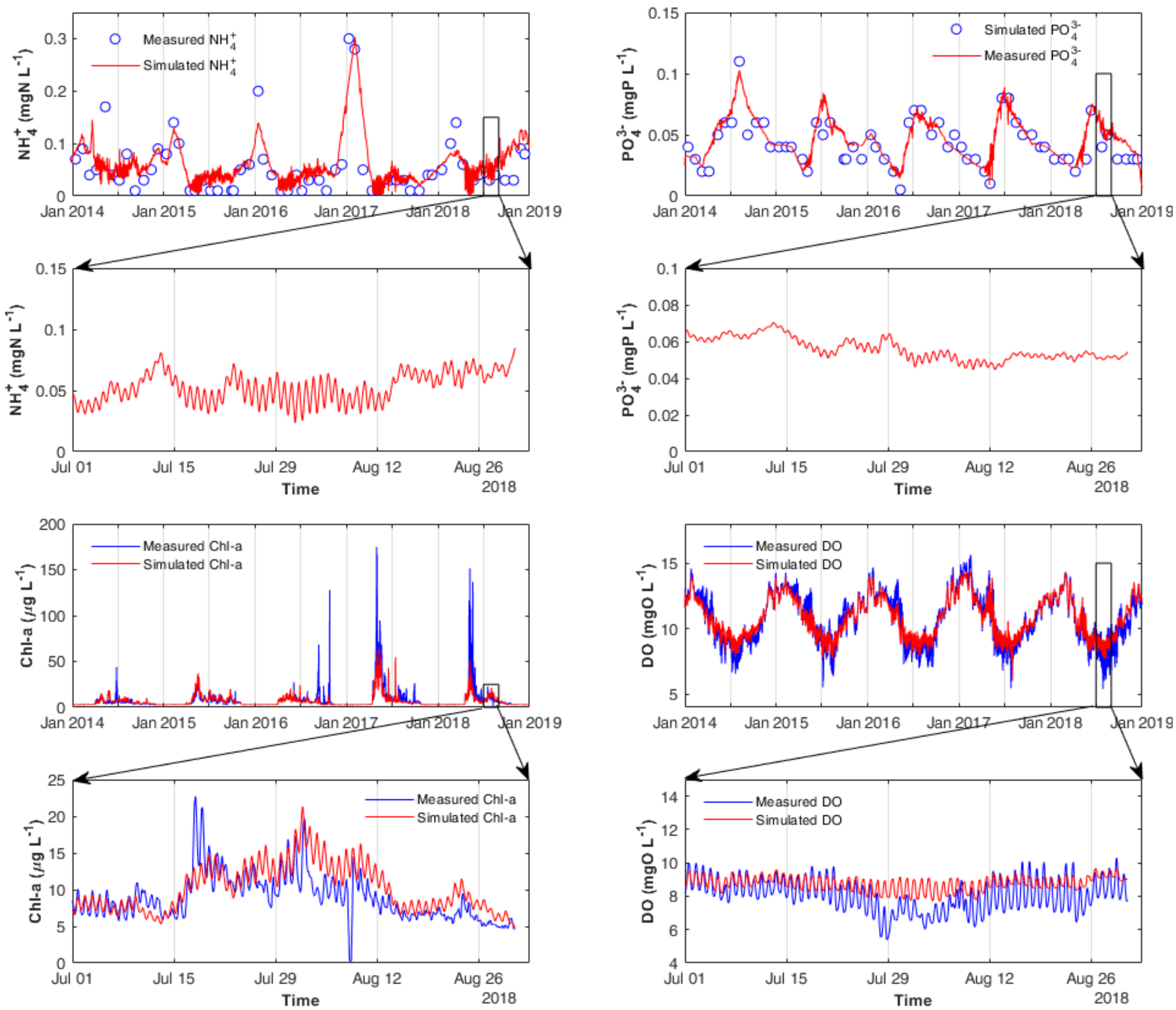

Figure S5. PO_4^{3-}, NH_4^+,Chl-a & DO concentrations from 2014 to 2018 and zoom-in views during the extreme summer low flow in July and August 2018.

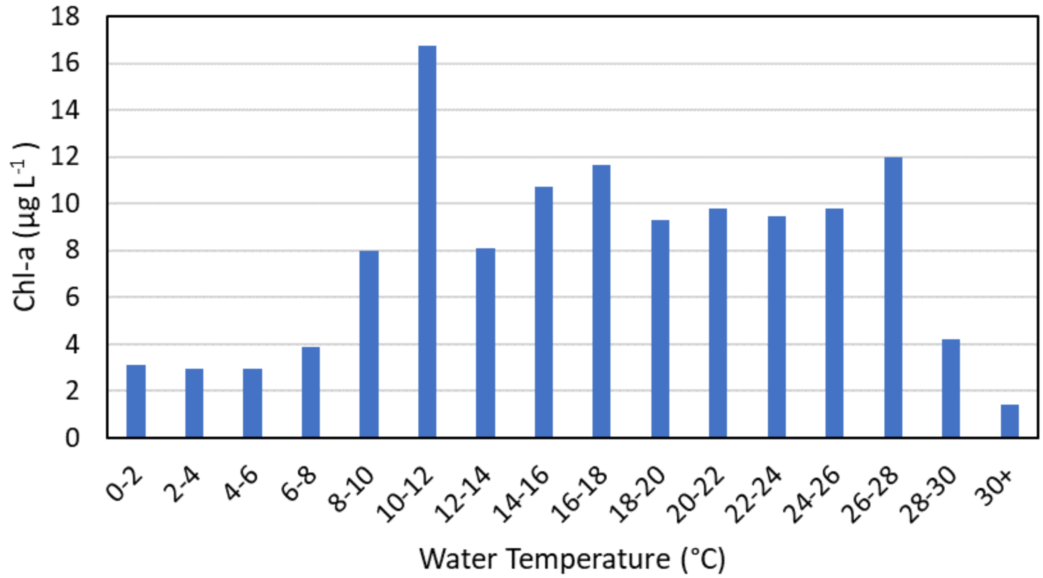

Figure S6. Measured average Chl-a concentration at different water temperatures at STF.

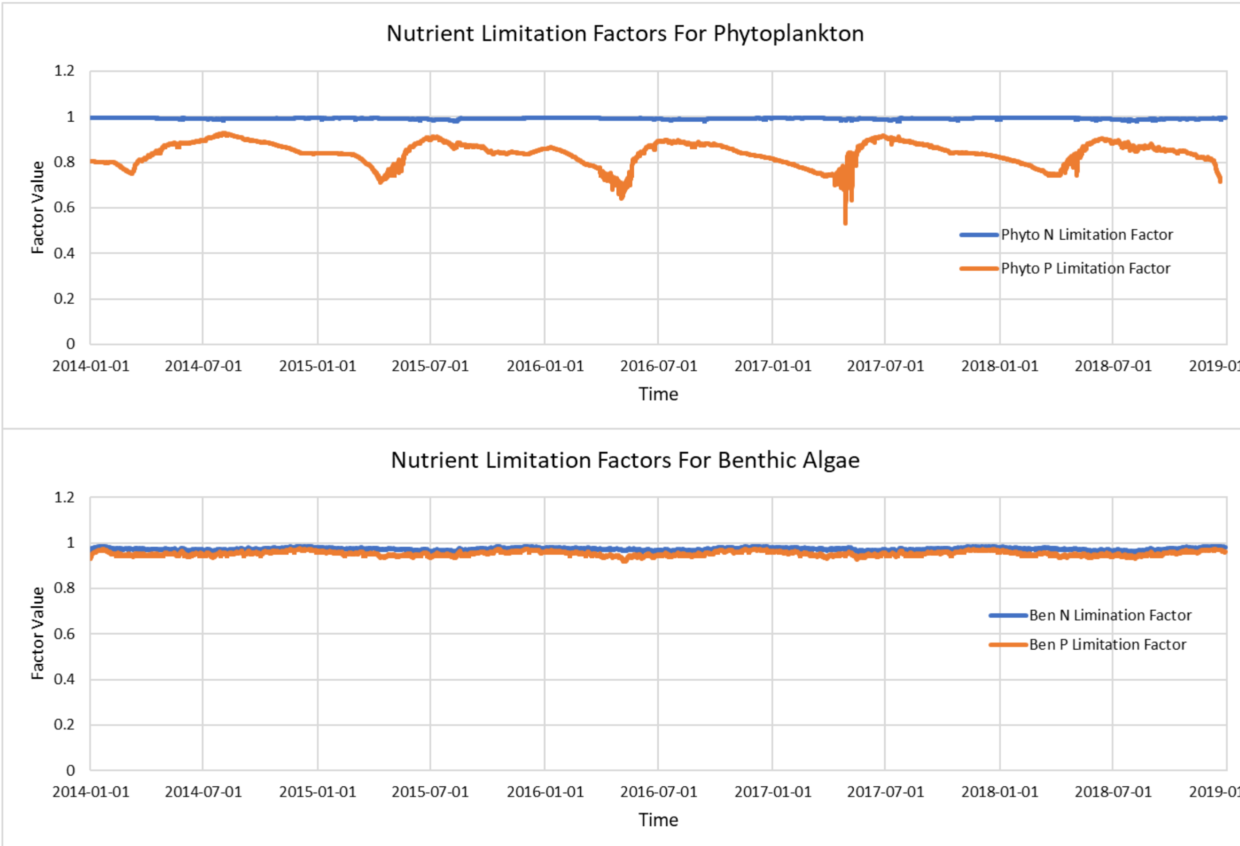

Figure S7. Nutrient limation factors calculated in the WASP model for phytoplankton and benthic algae. In our model, the nutrient limitation factor is calculated as the minimum value of the N and P limitation factors. As shown in the figure, the P-limitation factor values are below N-limitation factor values in the whole simulation period.

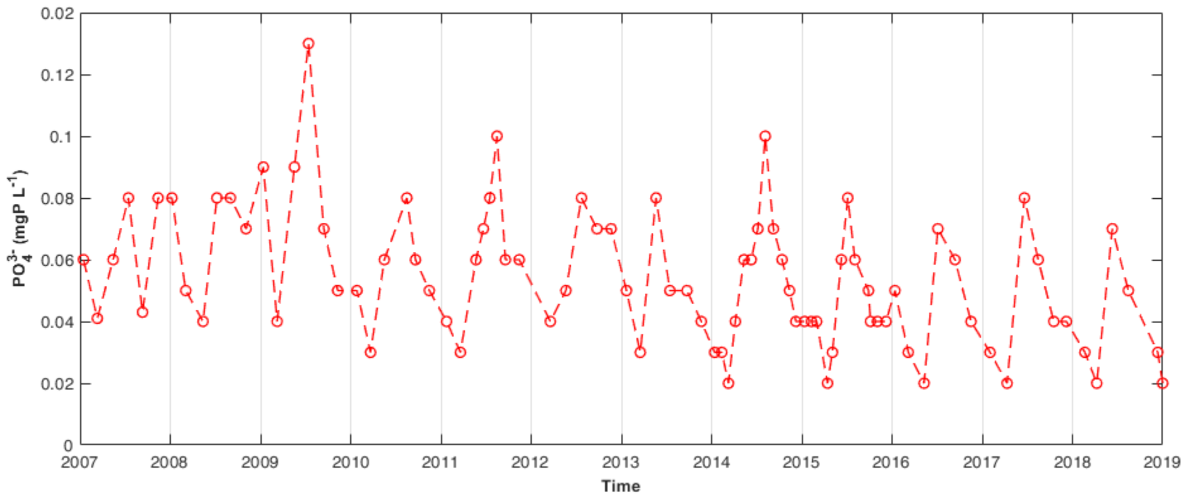

Figure S8. Monthly PO_4^{3-} concentration at GGL from 2007 to 2018

SI Table

Table S1. Summary of C-Q analysis for the tributaries of Lower Bode.

	Watershed area (km^2)	**Slope for C-Q linear regression**[#]	**Offset for C-Q linear regression**	**R^2 for correlation of Q and NO_3^-**
Sarre	70.89	13.31	3.48	0.51
Sülzgraben	23.43	75.93	6.17	0.14
Röthe[1]*	22.01	-	-	-
Ehle	118.74	3.33	1.25	0.44
Marbegraben	77.98	7.95	-0.07	0.18
Börnecker Graben[2$]	27.24	-	-	-
Hecklinger Hauptgraben	10.81	22.66	0.42	0.26
Beek	51.95	2.38	8.28	0.005

[*,$] No water quality data are available for Röthe and Börnecker Graben. For these two streams for which no regression could be made, their equations were adopted by those of the most similar streams in catchment size or NO_3^- concentration, i.e., Röthe by Sülzgraben and Börnecker Graben by Hecklinger Hauptgraben.

[#] Positive slopes indicate enrichment, and negative slopes indicate dilution.

Table S2. Stoichiometry and kinetic parameters related to N processes in the WASP model.

Symbol	Kinetic Constant	Units	Value	Range[$]
k_{nitr}	Nitrification rate constant at 20 °C	d^{-1}	0.4	0-0.4
θ_{nitr}	Nitrification temperature coefficient	--	1.07	1.04-1.1
K_{nit}	Half saturation constant for nitrification oxygen limit	mg O L^{-1}	2	0-5
k_{dnit}*	Denitrification rate constant at 20 °C	d^{-1}	0.15	0-0.4
θ_{dnit}	Denitrification temperature coefficient	--	1.1	1.04-1.1
K_{NO3}	Half saturation constant for denitrification oxygen limit	mg O L^{-1}	1	0-5
F_{Gb20}*	Benthic algae maximum growth rate	gD m-2 d^{-1}	6.5	5 – 100
θ_{Gb}	Temp coefficient for benthic algal growth	--	1.08	1.05 - 1.1
k_{Rb20}*	Benthic algae respiration rate constant	d^{-1}	0.2	0.05 – 0.2
θ_{Rb}	Temperature coefficient for benthic algal respiration	--	1.05	1.05 – 1.08
k_{Eb20}*	Internal nutrient excretion rate constant for benthic algae	d^{-1}	0.1	0.02 – 0.1
θ_{Eb20}*	Temperature coefficient for benthic algal nutrient excretion	--	1.05	1.05 – 1.08
k_{Db20}*	Benthic algae death rate constant	d^{-1}	0.02	0.001-0.2
θ_{Db20}	Temperature coefficient for benthic algal death	--	1.05	1.05 – 1.08
K_{sNb}	Half saturation uptake constant for extracellular N for benthic algae	mg N L^{-1}	0.2	0.05-0.8
K_{Lb}*	Light constant for benthic algal growth	Ly d^{-1}	130	50-300
K_{hnxb}*	Ammonia preference for benthic algae	mg N L^{-1}	0.025	0.01 – 0.5
q_{0N}	Minimum cell quota of internal N for benthic algal growth	mgN/gD	7	4-20
ρ_{mN}*	Maximum N uptake rate for benthic algae	mgN/gD-d	720	200 – 2000
K_{qN}*	Half saturation uptake constant for intracellular N for benthic algae	mgN/gD	9	5 – 20
f_{ONb}*	Fraction of benthic algae recycled to organic N	--	0.21	0 – 0.5
NCRB	Phytoplankton N to carbon ratio	gN/gC	0.25	0.15-0.25
CChla	Phytoplankton carbon to chlorophyll ratio	gC/gChl	50	25-125
k_{Gmax}*	Phytoplankton maximum growth rate constant at 20 °C	d^{-1}	2.5	0.5 – 4.0
θ_G	Phytoplankton growth temperature coefficient	--	1.07	1.05-1.1
k_{20R}	Phytoplankton respiration rate constant at 20 °C	d^{-1}	0.1	0.05 – 0.25
θ_R	Phytoplankton respiration temperature coefficient	--	1.05	1.05 – 1.08
k_D	Phytoplankton death rate constant (non-zoo predation)	d^{-1}	0.02	0.003 – 0.1
K_{mN}	Phytoplankton half-saturation constant for N uptake	mg N L^{-1}	0.02	0.005-0.4
Is	Phytoplankton optimal light saturation	Ly d^{-1}	250	100 – 500
f_{ON}	Fraction of phytoplankton death recycled to organic N	--	0.2	0.05 – 0.5
k_{min}	Mineralization rate constant for organic N	d^{-1}	0.1	0.01 – 0.2
θ_{min}	Temperature coefficient for mineralization	--	1.07	1.04 – 1.1
K_{mpc}	Algal half-saturation constant for mineralization	mg C L^{-1}	0.025	0.01 – 0.5
a_{NC}	Benthic algae N to carbon ratio	gN/gC	0.18	0.06 – 0.3

ROC	Oxygen to carbon ratio	gO2/gC	2.67	--
ADC	Detritus to carbon ratio	gD/gC	2.5	2 – 5
G_p	Phytoplankton growth rate	d^{-1}	$k_{Gmax} X_{RT} X_{RI} X_{RN}$ [#]	
D_p	Phytoplankton death rate	d^{-1}	$k_{20R} \theta_R^{T-20} + k_D$	
F_{Gb}	Benthic algal zero-order growth rate	d^{-1}	$F_{Gb20} \varphi_{Tb} \varphi_{Lb} \varphi_{Nb}$ [%]	

* The most identifiable parameters used for auto-calibration.

[$] Sources of literature values: Wool et al. (2002) and Martin et al. (2017).

[#] X_{RT}, X_{RI} and X_{RN} refer to dimensionless temperature adjustment factor, light, and nutrient limitation factor for phytoplankton, respectively.

[%] φ_{RT}, φ_{RI} and φ_{RN} refer to dimensionless temperature adjustment factor, light, and nutrient limitation factor for benthic algae, respectively. T represents water temperature. More details on the calculation of G_p, D_p and F_{Gb} are provided in the WASP manual.

Table S3. Statistics calculated on uptake rates and efficiency: minimum (Min), median, mean, and maximum (Max) values.

Variable	Unit	Min	Median	Mean	Max
U_{GROSS}	mg N m^{-2} d^{-1}	7.9	74.0	124.1	707.9
U_{NET}	mg N m^{-2} d^{-1}	-17.4	19.9	56.8	553.9
E_{GROSS}	%	0.03	2.7	6.0	43.3
E_{NET}	%	-1.3	0.7	2.7	29.1
U_{D}	mg N m^{-2} d^{-1}	0.2	4.3	14.1	117.1
$U_{NET,A,P}$	mg N m^{-2} d^{-1}	-4.7	6.7	28.4	536.9
$U_{NET,A,B}$	mg N m^{-2} d^{-1}	-21.6	11.5	14.3	77.9
$U_{GROSS,NO3}$	mg N m^{-2} d^{-1}	1.3	35.7	60.5	485.2
$U_{NET,NO3}$	mg N m^{-2} d^{-1}	-49.7	23.6	49.2	481.4
$U_{GROSS,NH4}$	mg N m^{-2} d^{-1}	5.7	45.6	63.6	257.1
$U_{NET,NH4}$	mg N m^{-2} d^{-1}	-42.0	4.0	7.6	161.3

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