water MDPI

Appendix

Supplemental Methods: Methods used for watershed delineation, estimation of stream gas exchange velocity, and calculation of nutrient uptake metrics.

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Supplemental Methods

Watershed Delineation

The study watersheds were delineated based on a 30-m digital elevation model (DEM), derived from the Shuttle Radar Topography Mission (SRTM) elevation dataset, using the Hydrology Tools in the ArcMap 10.6 Spatial Analyst package. Watersheds were defined as the area upstream of the GPS location for each sampling site (i.e. the outlet or "pour point"). Landcover was determined by way of an unsupervised classification of a Landsat Thematic Mapper 8 image of the region collected on September 9, 2017. An initial classification of 25 classes was reduced to the four classes deemed pertinent to this study (intact closed canopy forest, degraded forest, cropland, and surface water). Finally, landcover statistics were extracted from the 4-class landcover map for each of the watersheds in the study.

Metabolism Modeling

Estimation of gas exchange velocity (k)

We used physically based equations to generate values of *k* which we used as priors to constrain the model-based estimation of *k*. We calculated *k* using equations derived from the Energy dissipation model and updated by Raymond et al. 2012. We compared values generated when using equations with and without stream depth, but estimates seemed overly sensitive to depth (as suggested in Raymond et al. 2012) so we used the model that had the highest explanatory power but only required only velocity and slope data. We used these calculated values (Table A3) to generate a mean and standard deviation value for *k* for each stream, which we included as a normal prior to constrain the model-generated estimates of *k* (Tables A3 & A4). In cases where we lacked data to make these estimates (e.g., stream slope), we used the grand mean and standard deviation of all streams of the same type (i.e., cropland or forest) to inform the prior.

Calculation of nutrient spiraling metrics

We calculated mass recovery as in equation 1 and based our uptake metrics off that calculation:

1) $$\boldsymbol{T_{MR} = Q \int_0^t T_c(t) dt}$$

Where T_{MR} is the tracer mass recovery (M, mg) and T_c is the time-integrated tracer concentrations of background corrected Cl or nutrient concentration (mg * L^{-1} * s), Q is discharge (L s^{-1}), and *t* is the time step. From the Cl and NO_3-N T_{MR} values, we calculated the BTC-integrated uptake length of the added nutrient (*Sw*). We calculated *Sw* by plotting the natural log of the added nutrient to Cl ratio (e.g., NO_3-N: Cl) and the BTC-integrated nutrient to Cl ratio [e.g., T_{MR} (NO_3-N): T_{MR} (Cl)] ratio against stream distance, similar to the approaches used by Covino et al. (2010) and Tank et al. (2008) The slope of the line derived from these data is the BTC-integrated longitudinal uptake rate of added nutrient (*kw*), and *Sw* is the negative inverse of *kw*. We calculated BTC-integrated nutrient areal uptake rates (*U*) and uptake velocities (*Vf*) as follows of the added nutrients (N):

2) $$\boldsymbol{U = \frac{Q * [N_{add-int}]}{S_w}}$$

3) $$\boldsymbol{Vf = \frac{U}{[N_{add-int}]}}$$

References

Covino TP, McGlynn BL, McNamara RA. Tracer Additions for Spiraling Curve Characterization (TASCC): Quantifying stream nutrient uptake kinetics from ambient to saturation. Limnol Oceanogr-METHODS. 2010 Sep;8: 484–98.

Raymond PA, Zappa CJ, Butman D, Bott TL, Potter J, Mulholland P, et al. Scaling the gas transfer velocity and hydraulic geometry in streams and small rivers: Gas transfer velocity and hydraulic geometry. Limnol Oceanogr Fluids Environ. 2012 Apr;2(1):41–53.

Tank JL, Rosi-Marshall EJ, Baker MA, Hall RO Jr. Are rivers just big streams? A pulse method to quantify nitrogen demand in a large river. Ecology. 2008 Oct;89(10):2935–45.

Table S1 – Watersheds included in the study and what was measured. LAI = leaf area index. OM = benthic organic matter.

	APP 2	APP 2a	APP M	CN	Cascavel	Nascente	APP 6	APP 3	APP 4	APP 5
	Forest	Forest	Forest	Forest	Soy	Soy	Soy	Soy-Maize	Soy-Maize	Soy-Maize
Discharge	x	x	x	x	x	x	x	x	x	x
Temp	x	x	x	x	x	x	x	x	x	x
LAI	x	x	x	x	x	x	x	x	x	x
Nutrients	x	x	x		x	x	x	x	x	x
Litter	x	x	x	x	x	x	x	x	x	x
Stream habitat	x	x	x		x	x	x			
OM	x	x	x		x	x	x			
Metabolism	x	x	x		x	x	x	x	x	

Nutrient additions	x	x	x		x	x	x		

Table S2 - Mean and variation in stream nitrate (NO_3-N) and phosphate (PO_4-P) concentrations for watersheds included in the study from 2013-2016.

Watershed	**Land Use**	**NO_3-N (mg/L)**	**PO_4-P (mg/L)**
APP2	Forest	0.042 ± 0.089	0.007 ± 0.003
APP2A	Forest	0.040 ± 0.058	0.007 ± 0.003
APPM	Forest	0.046 ± 0.065	0.006 ± 0.003
Cascavel	Soy	0.034 ± 0.147	0.005 ± 0.004
APP67	Soy	0.033 ± 0.059	0.005 ± 0.034

APP3	Soy-maize	0.022 ± 0.064	0.005 ± 0.003
APP4	Soy-maize	0.029 ± 0.057	0.006 ± 0.004
APP5	Soy-maize	0.052 ± 0.087	0.006 ± 0.004

Table S3 - Estimated gas transfer velocity standardized to 20 °C (*k20*) values from Energy Dissipation Model (EDM; Raymond et al. 2012) used as mean values of a normal prior in ecosystem metabolism model (Holtgrieve et al. 2010). nm = not measured.

Stream	**Date**	**Land Use**	**Season**	**Velocity (m/s)**	**Mean depth (m)**	**Slope (m/m)**	**EDM k20 (m/h)**
APP2	2/1/2015	Forest	Wet	0.08	0.22	0.0015	0.09
APP2	11/10/15	Forest	Dry	0.06	0.25	0.0015	0.08
APP2	1/1/2016	Forest	Wet	0.11	0.33	0.0015	0.09
APP2	10/1/16	Forest	Dry	0.08	0.27	0.0015	0.09
APP2a	11/9/2015	Forest	Dry	0.07	0.15	0.0023	0.07
APP2a	1/1/2016	Forest	Wet	0.09	0.25	0.0023	0.10

APP2a	10/1/16	Forest	Dry	0.07	0.2	0.0023	0.09
APP3	11/9/15	Crop	Dry	0.15	0.29	0.0033	0.13
APP4	2/1/2015	Crop	Wet	0.27	0.63	0.0045	0.20
APP4	11/13/15	Crop	Dry	0.29	0.52	0.0045	0.21
APP6*	1/1/2016	Crop	Wet	0.1	0.29	nm	
APP6*	10/1/16	Crop	Dry	0.04	0.25	nm	
APP67*	2/1/2015	Crop	Wet	n.d.	0.45	nm	
APPM	2/1/2015	Forest	Wet	0.15	0.25	0.0016	0.10
APPM	11/16/15	Forest	Dry	0.12	0.26	0.0016	0.09
APPM	1/1/2016	Forest	Wet	0.15	0.42	0.0016	0.10
APPM	10/1/16	Forest	Dry	0.11	0.26	0.0016	0.09
Cascavel	1/1/2016	Crop	Wet	0.11	0.39	0.0054	0.14
Cascavel	10/1/16	Crop	Dry	0.09	0.35	0.0054	0.13
Nascente	1/1/2016	Crop	Wet	0.13	0.37	0.0059	0.15
Nascente	10/1/16	Crop	Dry	0.14	0.35	0.0059	0.16

* In cases where no data were available, we used the land use mean.

Table S4. Metabolism model equations for the two-stage respiration (*R*) and photosynthesis (*P*) submodels used to estimate metabolism. *I* = irradiance data and *T* = water temperature data. K_b is the Boltzmann constant (8.62 × 10-5 J °K−1). The table shows the estimation mode for parameters.

$$P(I) = \alpha_{\mathrm{P\text{-}I}} I$$

$$R(T) = R_{ref} * e^{\frac{-Et(T - T_{ref})}{K_b T T_{ref}}}$$

Parameter	**Definition**	**Mode of estimation**	**Value**
$\alpha_{P\text{-}I}$ (mg O_2 s uE^{-1} h^{-1})	slope of photosynthesis-irradiance relationship	free parameter	
T_{Ref}(C)	Reference temperature used to standardize R_{ref}	constant	Mean stream temperature during measurement period
R_{Ref}(mg O_2 m^{-2} h^{-1})	R at a reference temperature (average stream temperature)	free parameter	
E_b (eV)	temperature sensitivity of	constant	0.65

	base respiration (Rb)		
k_{20} (m h^{-1})	gas transfer velocity standardized to 20 °C	normal prior	Mean and standard deviation based on slope and velocity (Raymond et al. 2012)
Initial O_2 concentration (mg L^{-1})		uniform prior	5 - 15
σ Initial O_2 concentration (mg L^{-1})		uniform prior	0.0001 – 1

Table S5 – Stream reach lengths used for nutrient addition experiments (in meters).

Stream	**Season**	**Nitrate**	**Phosphate**
APP2	Jan	100	100
APP2a	Jan	150	150
APPM	Jan	255	255
APP6	Jan	60	60
Cascavel	Jan	305	305
Nascente	Jan	100	100
APP2	Oct	150	150
APP2a	Oct	100	100
APPM	Oct	150	150
APP6	Oct	90	90
Cascavel	Oct	213	213
Nascente	Oct	200	200

Table S6 – Organic content (measured as ash-free dry mass (AFDM)), and the mass of carbon (C) and nitrogen (N) of litterfall components by land use and across years. P-values reflect results of two-way ANOVA testing the effects of land use and season and are indicated by bold font and *. Values given as mean ± standard error.

Annual Input	Forest		Cropland		Source of variation		
($g\ m^{-2}\ y^{-1}$)	Year 1	Year 2	Year 1	Year 2	$P_{land\ use}$	P_{year}	$P_{interaction}$
Leaf							
AFDM	489 ± 15	446 ± 19	369 ± 43	369 ± 75	0.070	0.596	0.939
C	241 ± 7	219 ± 9	180 ± 21	181 ± 37	0.069	0.599	0.939
N	5.6 ± 0.4	5.1 ± 0.5	3.3 ± 0.3	3.5 ± 0.8	**0.006***	0.627	0.943
Wood							
AFDM	25 ± 3	56 ± 24	23 ± 6	40 ± 15	0.356	0.101	0.766
C	12 ± 1	28 ± 12	11 ± 3	20 ± 715	0.357	0.101	0.766
N	0.2 ± 0.1	0.5 ± 0.2	0.2 ± 0.1	0.4 ± 0.2	0.976	0.123	0.757
Seed							
AFDM	9 ± 3	7 ± 3	48 ± 17	19 ± 12	**0.036***	0.061	0.444
C	4 ± 1	3 ± 1	24 ± 8	9 ± 6	**0.040***	0.060	0.444
N	0.1 ± 0.1	0.1 ± 0.1	0.6 ± 0.2	0.3 ± 0.1	**0.009***	0.040	0.484
Total litterfall							
AFDM	524 ± 16	509 ± 27	441 ± 53	429 ± 83	0.147	0.660	0.851
C	258 ± 8	251 ± 13	216 ± 26	211 ± 41	0.144	0.663	0.854
N	6 ± 0.3	5 ± 0.2	4 ± 0.3	4 ± 0.9	**0.022***	0.605	0.818

Table S7 – Median values of posterior metabolism estimates of for all streams across all years of the study. Gross primary production (GPP) was undetectable in several cases, which is denoted by a value of 0.1 mg m^{-2} d^{-1}. ER = ecosystem respiration, G = gas exchange, *k* = gas exchange velocity, and NEP = net ecosystem production.

Stream	Year	Land Use	Season	GPP (mg m^{-2} d^{-1})	ER (mg m^{-2} d^{-1})	G (mg m^{-2} d^{-1})	*k* (m h^{-1})	NEP (mg m^{-2} d^{-1})
APP2	2015	Forest	Dry	0.1	4,208	4,206	0.07	-4,208
APP2	2016	Forest	Dry	420	7,697	7,285	0.13	-7,277
APP2a	2015	Forest	Dry	0.1	2,223	2,217	0.02	-2,223
APP2a	2016	Forest	Dry	0.1	4,002	4,008	0.13	-4,002
APPM	2016	Forest	Dry	0.1	3,294	3,294	0.07	-3,294
			Forest - Dry	**84**	**4,285**	**4,202**	**0.08**	**-4,201**
APP2	2015	Forest	Wet	0.1	4,002	4,002	0.08	-4,002
APP2	2016	Forest	Wet	0.1	2,517	2,520	0.04	-2,517
APP2a	2016	Forest	Wet	0.1	3,408	3,406	0.04	-3,408
APPM	2016	Forest	Wet	0.1	6,141	6,127	0.11	-6,141
			Forest - Wet	**0.01**	**4,017**	**4,014**	**0.07**	**-4,017**
APP3	2015	Crop	Dry	0.1	524	523	0.04	-524
APP4	2015	Crop	Dry	1,885	2,978	1,129	0.04	-1,093
Casca-vel	2016	Crop	Dry	0.1	3,376	3,383	0.04	-3,376
Nas-cente	2016	Crop	Dry	1.0	100	99	0.15	-99
APP P	2018	Crop	Dry	1,527	11,938	10,454	0.16	-10,411
			Crop-Dry	**471**	**1,745**	**1,284**	**0**	**-1,273**

APP4	2015	Crop	Wet	1,261	3,202	1,951	0.06	-1,941
APP6	2016	Crop	Wet	0.1	6,997	6,994	0.1	-6,997
APP67	2015	Crop	Wet	0.1	1,447	1,453	0.03	-1,447
Casca-vel	2016	Crop	Wet	0.1	4,043	4,019	0.05	-4,043
Nas-cente	2016	Crop	Wet	324	8,545	8,190	0.15	-8,221
			Crop-Wet	**317**	**4,847**	**4,521**	**0.08**	**-4,530**
			Forest	**47**	**4,166**	**4,118**	**0.08**	**-4,119**
			Crop	**386**	**3,468**	**3,082**	**0.07**	**-3,082**

Table S8. AIC_c and R^2 values of models comparing the effects of land use, season and their interaction on metabolism parameters: gross primary productivity (GPP), ecosystem respiration (ER) and net ecosystem production (NEP). df = degrees of freedom, N = sample size, AIC_c = Akaike Information Criterion, ΔAIC_c = difference in AIC_c units from the best model, R^2m = marginal R-squared (fixed effects) and R^2c = conditional R^2 (full model with random effects).

	df	N	AIC_c	ΔAIC	R^2m	R^2c
GPP						
Season	5	17	258.3	0	0.01	0.87
LandUse	5	17	258.4	0.1	0.1	0.85
LandUse + Season	6	17	259.5	1.2	0.1	0.87
LandUse x Season	7	17	261.5	3.2	0.1	0.87
ER						
LandUse x Season	7	17	315.9	0	0.4	0.4
Season	5	17	317.5	1.6	0.15	0.15
LandUse + Season	6	17	319.2	3.3	0.17	0.17
LandUse	5	17	320	4.1	0.01	0.02
NEP						
LandUse x Season	6	17	314.1	0	0.42	0.42
Season	4	17	316.2	2.1	0.16	0.16
LandUse + Season	5	17	317.3	3.2	0.2	0.2

LandUse	4	17	318.4	4.3	0.04	0.04

Figure S1. Modeled photosynthetically active radiation (PAR) compared to measured PAR below the canopy in forest and cropland streams.

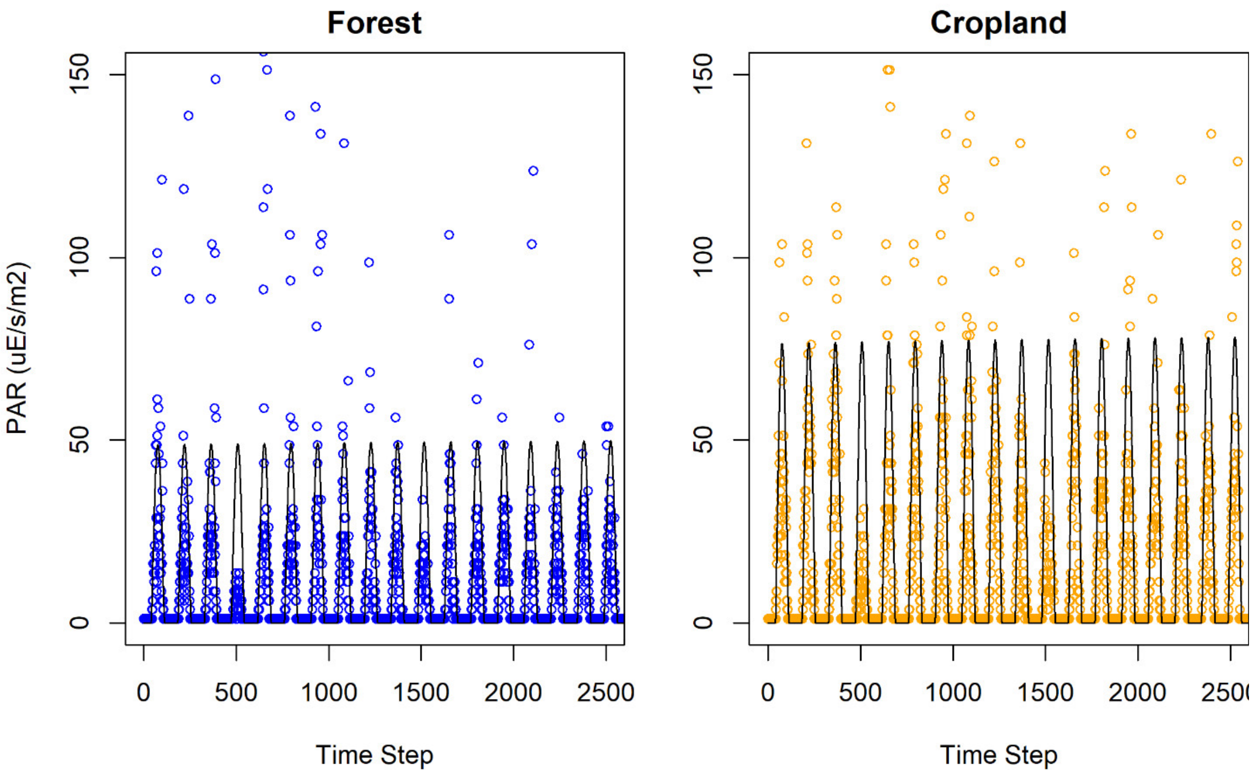


Figure S2 – % Carbon and % nitrogen of in litterfall in cropland and forest streams.

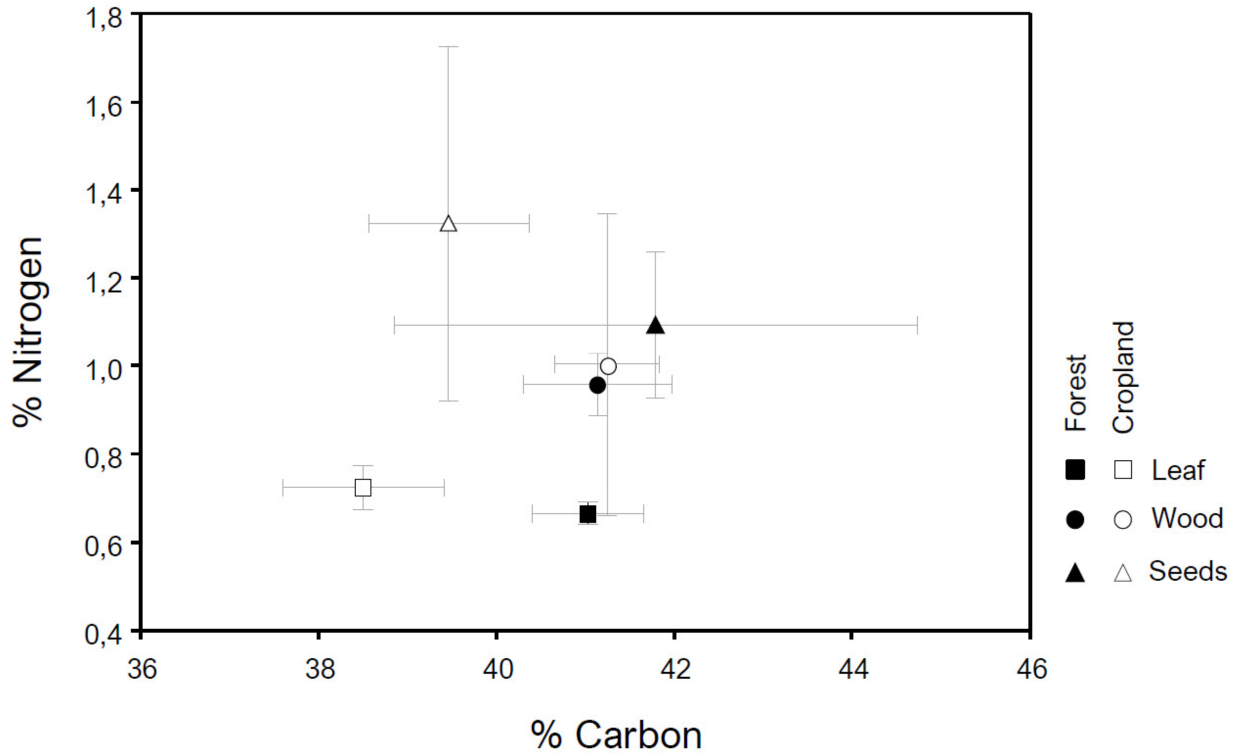


Figure S3 - % Carbon and % nitrogen of benthic organic matter in forest and cropland streams. FBOM = fine benthic organic matter.

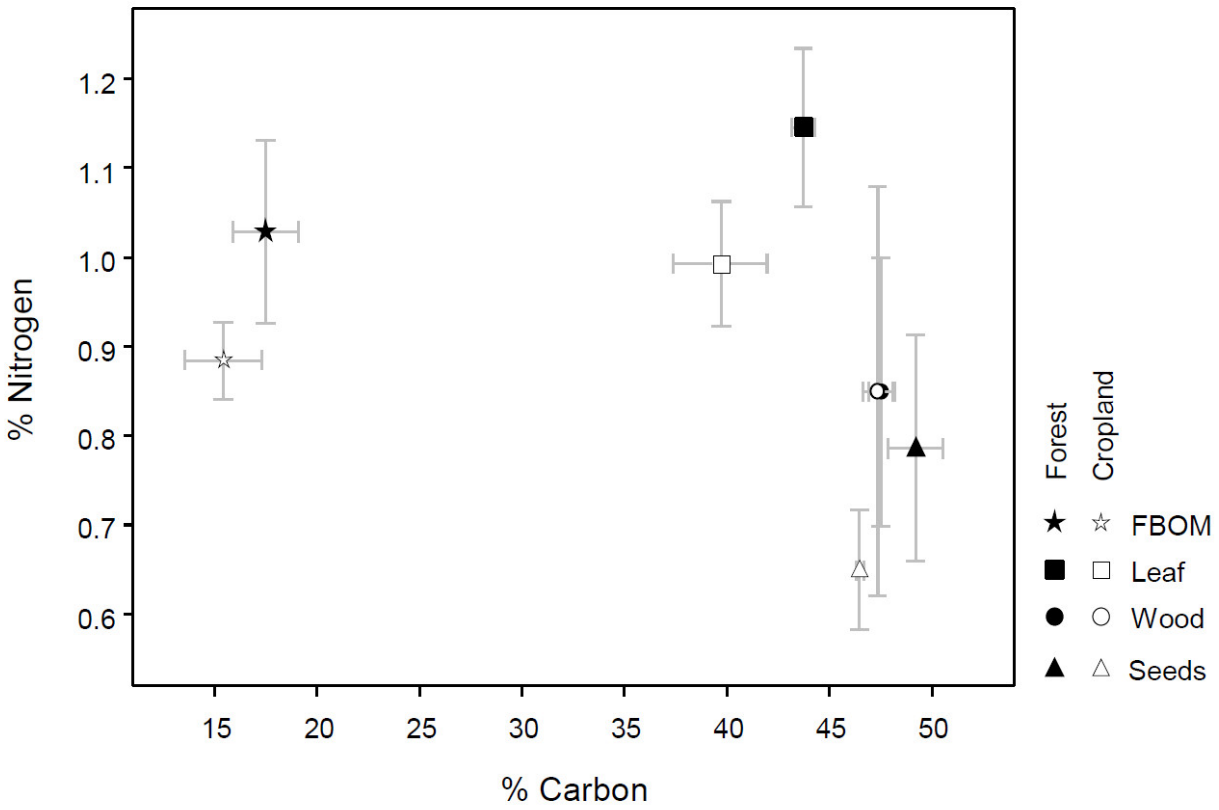
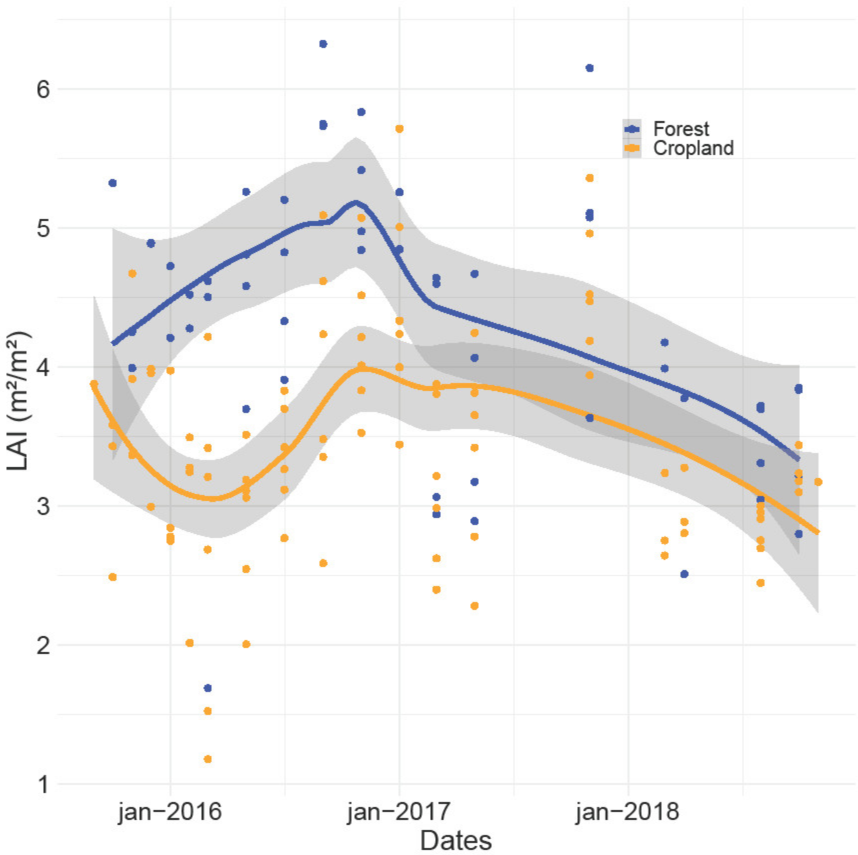


Figure S4. Leaf Area Index (LAI) measured over forest and cropland streams over two years. Points represent individual streams, bold lines indicate LOESS model fit to data for each land use and shaded regions are standard error around the model fit.


Forest
Cropland
LAI (m²/m²)
6
5
4
3
2
1
jan−2016
jan−2017
jan−2018
Dates