Supporting Information for:

Unexpected spatial stability of water chemistry in headwater stream networks

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	Couesnon	Rance
Area (km ²)	371 (4-371)	373 (7-373)
Forest (%)	6 (0-62)	7 (0-15)
Urban (%)	6 (0-9)	2.3 (0-7)
Arable land (%)	88 (37-100)	90 (81-99)
Row crops (%)	55 (24-83)	77 (57-91)
Pastureland (%)	33 (13-50)	14 (3-32)
Hedgerow density (m ha ⁻¹)	95 (87-102)	47 (32-63)
Potential wetlands* (%)	11.6 (6-23)	8.4 (6-17)
Arable land in wetlands (%)	91 (42-100)	90 (78-100)
Row crops in wetlands (%)	39 (17-73)	55 (10-92)
Pastureland in wetlands (%)	52 (15-61)	38 (0-75)
$Cows (km^{-2})^{\dagger}$	160 (45-216)	
Pigs $(km^{-2})^{\dagger}$	7 (6-335)	
Poultry $(\text{km}^{-2})^{\dagger}$	590 (27-2360)	
Nitrogen input (kg yr ⁻¹ km ⁻²) ^{\dagger}	9000 (2370-14600)	

Table S1. Mean land cover and use (range for subcatchments)

*Potential wetland area determined by topographic analysis (Medde

et al. 2014).

†Determined by field surveys in 2004 for the Couesnon. Nitrogen

input estimated by land use.

								Arable	Crops	Pasture
Couesnon	Area	Forest	Urban	Arable	Crops	Pasture	Wetlands	(wetland)	(wetland)	(wetland)
DOC		0.44	-0.41				0.48			
NO ₃ ⁻					0.52					
DIC										
PO4 ³⁻		0.65		-0.51	-0.56			-0.50	-0.45	
SUVA ₂₅₄		0.74		-0.71	-0.55			-0.68	-0.49	
NO_2^-										
SO4 ²⁻	0.53		0.53							
Cl										
F⁻					0.41					
Br										
			** 1		~	-		Arable	Crops	Pasture
Rance	Area	Forest	Urban	Arable	Crops	Pasture	Wetlands	(wetland)	(wetland)	(wetland)
DOC						-0.64			0.70	-0.79
NO ₃ ⁻		-0.45		0.58				0.43		
DIC					0.73	-0.90	0.50		0.84	-0.83
PO4 ³⁻					0.66	-0.78			0.75	-0.70
SUVA ₂₅₄						0.43	-0.57			
NO_2^-					0.68	-0.82			0.79	-0.77
SO4 ²⁻					0.62	-0.77			0.80	-0.79
Cl	0.52		0.48					-0.45		
\mathbf{F}						-0.46			0.46	-0.45
Br⁻										

Table S2. Rank correlations between land use parameters and flow-weighted mean concentrations

All reported correlation coefficients are significant at $\alpha = 0.05$ and bolded coefficients are significant at $\alpha = 0.01$.

	Overall		Q1* (<3.4)		Q2 (3.4-7.1)		Q3 (7.1-15)		Q4 (>15)	
	Couesnon	Rance	Couesnon	Rance	Couesnon	Rance	Couesnon	Rance	Couesnon	Rance
DOC	57	20	57	20	57	20	57	20	57	20
NO ₃ ⁻	57	35	68	35	57	35	57	35	57	35
DIC	216	113	216	113	216	113	216	113	216	113
PO ₄ ³⁻	22	27	22	27	22	27	22	27	22	27
SUVA ₂₅₄	68	20	68	20	68	20	68	20	68	20
NO ₂ ⁻	48	27	48	27	48	27	48	27	48	27
SO4 ²⁻	68	18	68	18	68	10	68	15	68	18
Cl	68	113	68	113	68	10	68	113	68	113
F	48	113	48	113	48	113	48	113	48	113
Br	22	72	22	8	22	12	22	23	22	35

Table S3. Spatial scales (km²) of the collapse of spatial variance as determined by change point analysis

*Hydrologic quartiles were determined from the observed range in daily discharge over the sampling period (2004-2007) and are reported in L sec⁻¹ km² based on discharge at the catchment outlets. Values that are different from the overall mean for a particular quartile are bolded.



Figure S1. Map of sampling points in the upper Couesnon and Rance catchments in northwestern France.



Figure S2. A) Flow-weighted mean values for chloride (Cl⁻), sulfate ($SO_4^{2^-}$), specific ultraviolet absorbance at 254 nm (SUVA₂₅₄), nitrite (NO_2^-), fluoride (F^-), and bromide (Br^-) from 56 subcatchments in the Couesnon and Rance catchments (Fig. S1). Error bars represent bootstrapped non-parametric 95% confidence intervals of the mean for repeat samples from each subcatchment (n=6 for the Rance, n=18 for the Couesnon). The vertical colored bands represent statistical changes in spatial variance based on change point analysis implemented for each catchment separately. Values were scaled by subtracting the mean and dividing by the standard deviation to facilitate comparison of changes in variance and evaluate convergence towards the overall mean (the 0 line). **B**)

The relationship between temporal variability (CV of repeat samplings for each subcatchment) and spatial scale for water chemistry parameters. CVs are scaled by catchment to have a SD of 1 and a mean of 0.



Figure S3. Subcatchment leverage for the Couesnon and Rance catchments. Subcatchment leverage is the percentage of outflow concentration attributable to each subcatchment, assuming conservative transport and consistent specific discharge (Equation 1). While these assumptions clearly do not hold at some spatial scales and for some parameters (e.g. PO_4^{3-} and NO_2^{-} , which show clear evidence of in-stream retention or removal downstream of the catchments with high leverage), subcatchment leverage can provide a first-order estimation of solute sources and the distributed mass balance through the stream network.



Figure S4. Concentration-discharge relationships for the 26 subcatchments of the Couesnon and the 30 subcatchments of the Rance. Note the log scale on the x-axis.



Figure S5. Concentrations of chemistry parameters through time for subcatchments in the Couesnon catchment. Units are mg L^{-1} for all parameters but SUVA₂₅₄, which is L mg C^{-1} m⁻¹. Notice the relatively high subcatchment synchrony and structure (relative rank of subcatchments) for DOC and DIC, and the low synchrony and structure for SUVA₂₅₄ and

 PO_4^{3-} . Lines between sampling dates are only shown to ease visual grouping of each subcatchment and are not meant to imply interpolation.



Figure S6. Concentrations through time for subcatchments in the Rance catchment. Units are $mg L^{-1}$ for all parameters but SUVA₂₅₄, which is L mg C⁻¹ m⁻¹. As for the Couesnon, notice the relatively high subcatchment synchrony for DOC and DIC, and the low synchrony for SUVA₂₅₄ and PO₄³⁻.



Figure S7. A and B) Spearman's rank correlations (r_s) between individual samplings and the overall flow-weighted mean for the Rance catchment. A value of 1 means that the sampling

date perfectly predicts the flow-weighted mean concentration for the whole observation period. **C**) Daily discharge of the Rance River and timing of samplings.



Figure S8. The relationship between flow-weighted mean concentration and the coefficient of variation (CV) for each subcatchment in the Couesnon and Rance catchments. Linear regression lines shown for statistically significant relationships ($\alpha = 0.05$) based on rank correlation.