

Supplementary Information

Long-Term Variation of Hydrochemical Parameters in a Medium-Sized Tropical River: Effects of a Severe Drought

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Table S1. Mann-Whitney test (W) results for the variables analyzed in the period before (2009-2013) and after (2014-2019) the drought

Variable	W	<i>p</i> -Value
Discharge	14616	< 0.001
pH	7834	0.661
EC	4212	< 0.001
DO	12056	< 0.001
TA	14607	< 0.001
SPM	13524	< 0.001
Chl-a	4372	< 0.01
DOC	49901	< 0.001
NO ₂ ⁻	5648	< 0.01
NO ₃ ⁻	5586	< 0.001
NH ₄ ⁺	11157	< 0.001
PO ₄ ³⁻	5619	< 0.01
Cl ⁻	707	< 0.001
Na ⁺	3928	< 0.001
Ca ²⁺	2127	< 0.001
K ⁺	2375	< 0.001
Mg ²⁺	3570	< 0.001

EC: electrical conductivity; DO: dissolved oxygen; TA: total alkalinity; SPM: suspended particulate matter; Chl-a: chlorophyll-a; DOC: dissolved organic carbon; NO₂⁻: nitrite; NO₃⁻: nitrate; NH₄⁺: ammonium; PO₄³⁻: phosphate; Cl⁻: chloride; Na⁺: sodium; Ca²⁺: calcium; K⁺: potassium; Mg²⁺: magnesium.

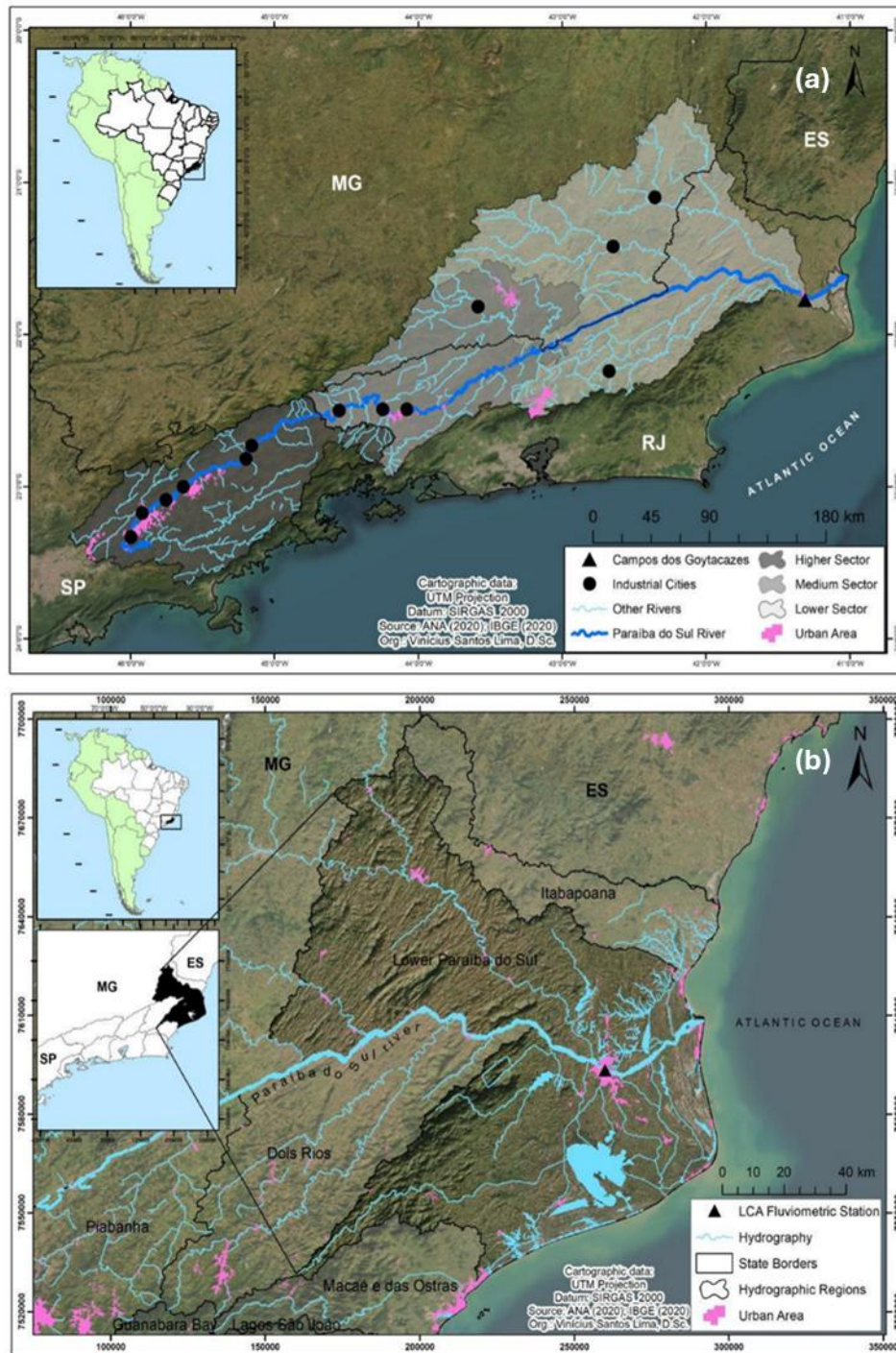


Figure S1. (a) Map of the Paraíba do Sul River basin highlighting mesoregions (Upper, Middle, and Lower) and industrial cities; (b) map of the Lower Paraíba, located in the Lower Paraíba sector, highlighting the sampling site ($21^{\circ}45'06.9''\text{S}$ $41^{\circ}19'33.0''\text{W}$) and urban areas in pink.

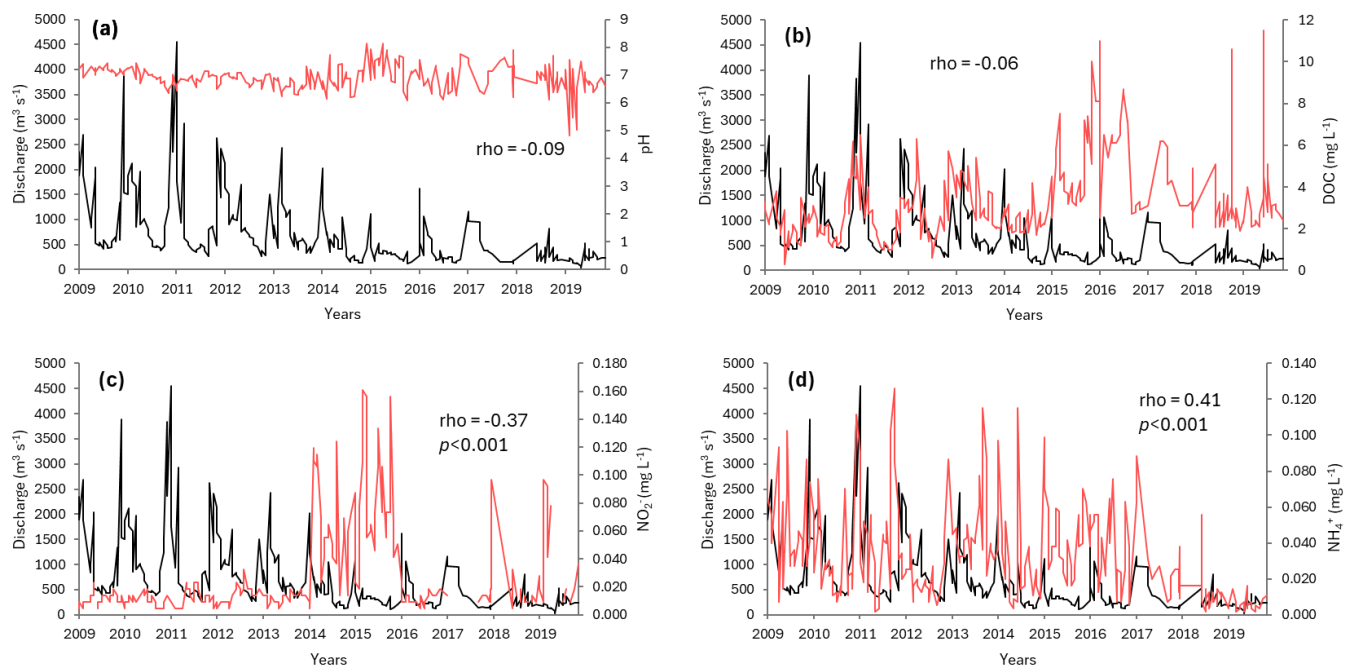


Figure S2. Annual variation in flow (black) and variables of interest (red). Correlation between: (a) flow and pH; (b) flow and dissolved organic carbon (DOC); (c) flow and nitrite (NO_2^-); (d) flow and ammonium (NH_4^+).

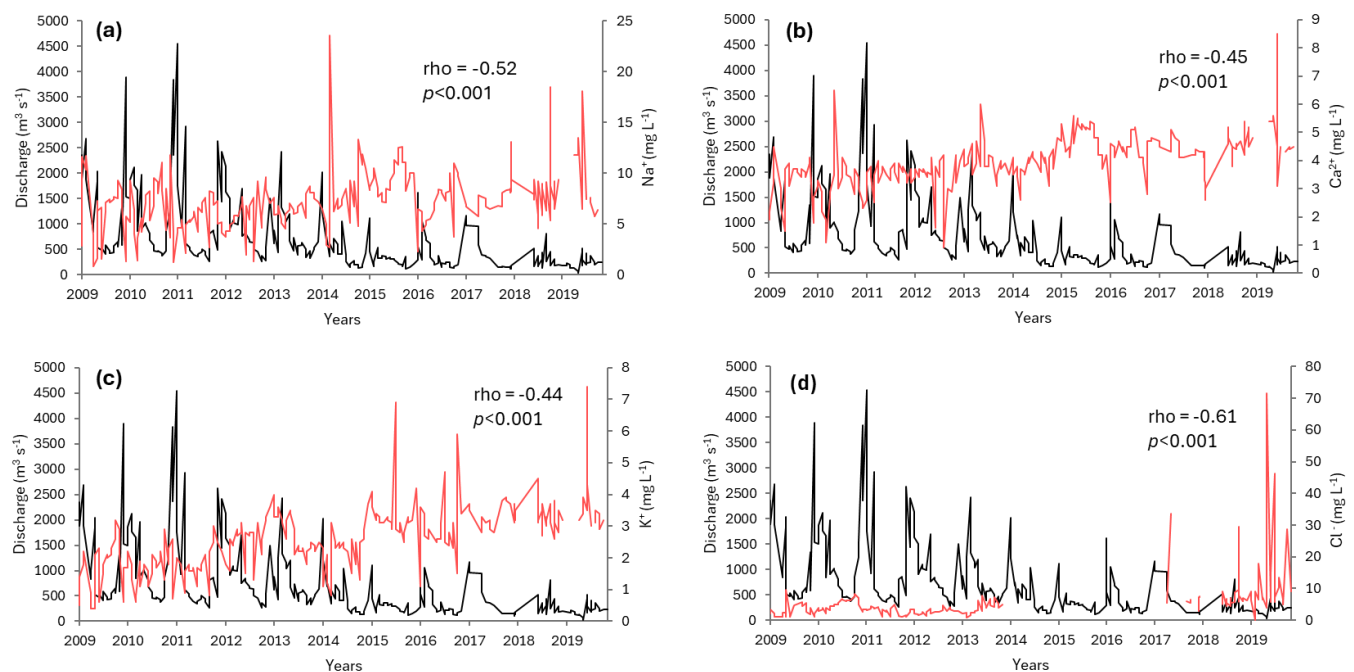


Figure S3. Annual variation in flow (black) and variables of interest (red). Correlation between: (a) flow and sodium (Na^+); (b) flow and calcium (Ca^{2+}); (c) flow and potassium (K^+); (d) flow and chloride (Cl^-).

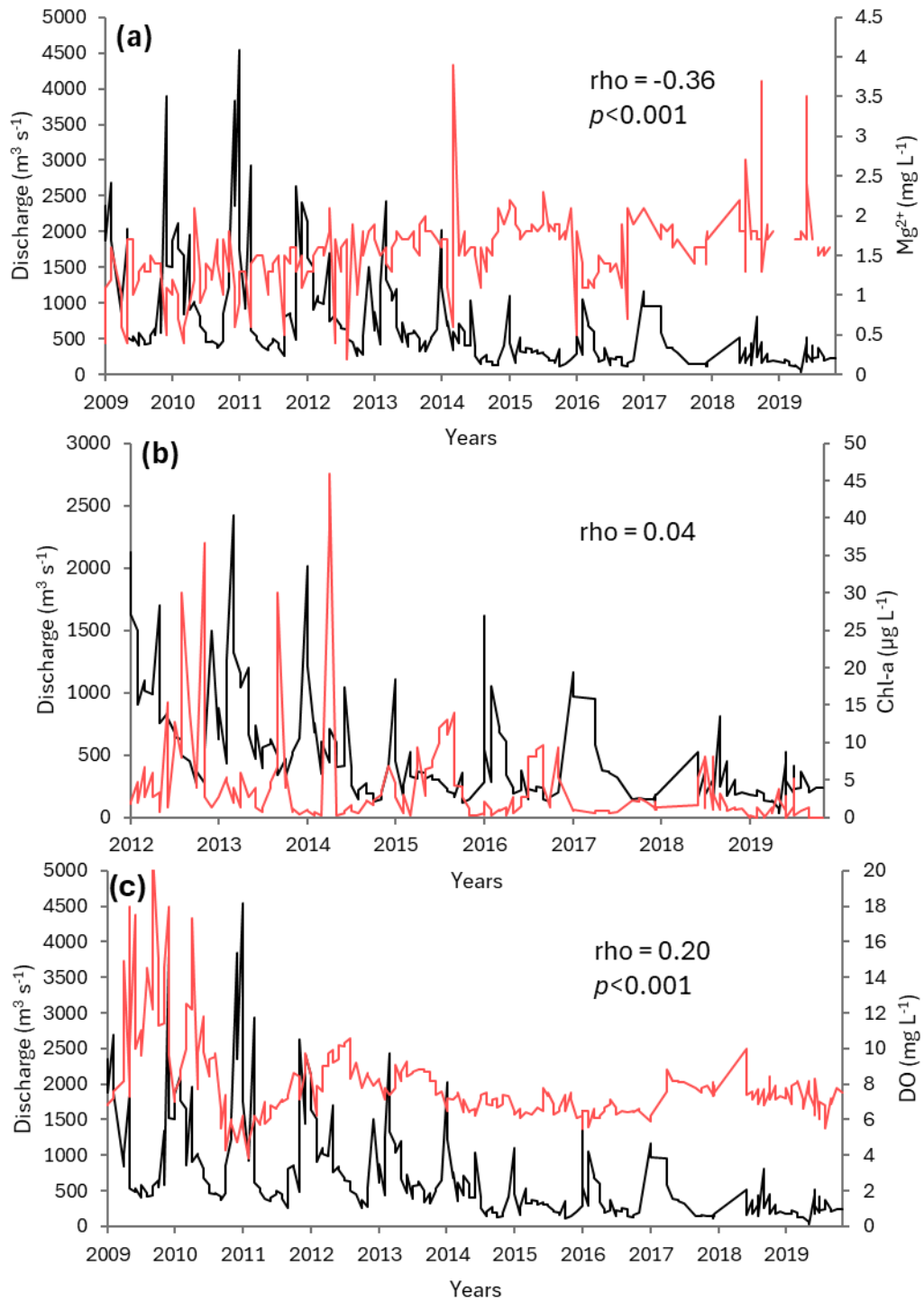


Figure S4. Annual variation in flow (black) and variables of interest (red). Correlation between: (a) flow and magnesium (Mg^{2+}); (b) flow and chlorophyll-a (Chl-a); (c) flow and dissolved oxygen (DO).

Table S2. Instrumental conditions used in atomic emission spectrometry with inductively coupled plasma (ICP OES; Varian 720 ES)

Instrument parameter	ICP OES
RF power / kW	1.0
Plasma flow / (L min ⁻¹)	15.0
Nebulizer pressure / kPa	200
Auxiliary flow / (L min ⁻¹)	1.50
Replicate read time / s	1.0

RF: radiofrequency power.

Table S3. Analytical wavelength of determined elements

Element	Analytical wavelength / nm
Na ⁺	589.592
Ca ²⁺	317.933
K ⁺	769.897
Mg ²⁺	279.553

Na⁺: sodium; Ca²⁺: calcium; K⁺: potassium; Mg²⁺: magnesium.

Table S4. Correlation matrix of the variables analyzed with signs for significant correlations ($p < 0.05$)

	Discharge	pH	EC	DO	TA	SPM	Chl-a	DOC	NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	PO ₄ ³⁻	Cl ⁻	Na ⁺	Ca ²⁺	K ⁺	Mg ²⁺
Discharge	–																
pH	–0.096	–															
EC	–0.586***	0.128*	–														
DO	0.205***	0.139*	–0.122	–													
TA	0.416***	0.001	–0.152*	0.385***	–												
SPM	0.726***	0.009	–0.489***	0.129*	0.329***	–											
Chl-a	0.041	0.119	0.056	0.106	0.387***	–0.104	–										
DOC	–0.060	–0.195**	0.055	–0.327***	–0.261***	–0.087	–0.066	–									
NO ₂ ⁻	–0.375***	0.103	0.351***	–0.083	–0.263***	–0.434***	0.036	–0.071	–								
NO ₃ ⁻	–0.426***	–0.1	0.419***	–0.215***	–0.053	–0.468***	0.306***	–0.012	0.330***	–							
NH ₄ ⁺	0.419***	–0.016	–0.171**	–0.027	0.224***	0.221***	0.045	0.174**	–0.162*	–0.186**	–						
PO ₄ ³⁻	–0.203**	–0.158*	0.067	0.166*	–0.189**	–0.097	–0.183*	0.11	–0.179**	0.031	–0.367***	–					
Cl ⁻	–0.612***	–0.061	0.455***	–0.180*	–0.333***	–0.504***	–0.434***	0.088	0.164*	0.390***	–0.508***	0.568***	–				
Na ⁺	–0.524***	0.192**	0.525***	–0.083	–0.203**	–0.447***	0.162*	0.051	0.325***	0.364***	–0.125	0.101	0.462***	–			
Ca ²⁺	–0.452***	–0.002	0.297***	–0.222***	–0.369***	–0.376***	0.092	0.315***	0.198**	0.335***	–0.171**	0.247***	0.425***	0.497***	–		
K ⁺	–0.440***	0.025	0.307***	–0.121	–0.436***	–0.309***	–0.002	0.426***	0.192**	0.193**	–0.170**	0.400***	0.368***	0.546***	0.680***	–	
Mg ²⁺	–0.366***	0.094	0.402***	–0.076	–0.306***	–0.345***	0.106	0.218***	0.332***	0.240***	–0.124	0.256***	0.426***	0.662***	0.654***	0.698***	–

EC: electrical conductivity; DO: dissolved oxygen; TA: total alkalinity; SPM: suspended particulate matter; Chl-a: chlorophyll-a; DOC: dissolved organic carbon; NO₂⁻: nitrite; NO₃⁻: nitrate; NH₄⁺: ammonium; PO₄³⁻: phosphate; Cl⁻: chloride; Na⁺: sodium; Ca²⁺: calcium; K⁺: potassium; Mg²⁺: magnesium; * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$.

