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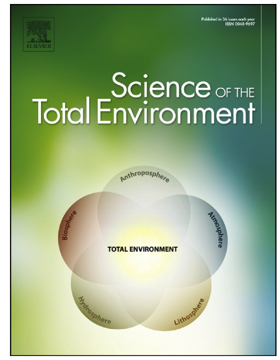

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Relevant factors in the eutrophication of the Uruguay River and the Río Negro

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Abstract

In recent decades, there has been increasing eutrophication of rivers and lagoons in Uruguay and solutions leading to water purification are being sought. The growing pollution has been attributed to nitrogen and phosphorus compounds exported from the river basins with intensification of agricultural production and the absence of tertiary treatment for urban and industrial effluents. Although nitrogen and phosphorus are relevant to eutrophication, there are also other factors that can promote eutrophication and algal blooms. This paper reports a broad analysis of water quality variables recorded over 9 years (2009-2018) at 17 sampling stations on the Uruguay River and 16 sampling stations on the Río Negro, and explores their relationship with the changes of chlorophyll a (Chl-a) concentrations using a generalized linear model and a neural network simulation (NNS). The input variables were total phosphorus; total suspended solids; electrical conductivity of water (EC_w); alkalinity; water temperature (T); water pH (pH) and sampling month. The NNS explained 79% of Chl-a variations and showed the most relevant variables to be T, EC_w, and pH. Moreover, the NNS showed that replacement of current land uses by natural prairie would not significantly reduce Chl-a concentrations. The results showed that the main factors that drive Chl-a concentrations (i.e., algae) are not directly linked to agriculture land use.

Highlights

- The algal bloom at Uruguay was promoted by the Climate Change
- Chl-a levels were increased by temperature, electrical conductivity and pH of rivers

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- Reduction in agricultural P emissions to rivers would not avoid high Chl-a levels
- The replacement of agriculture by natural prairie do not avoid the algae bloom

Keywords: neural network simulations, eutrophication, Chl-a, freshwater

1 Introduction

The contamination of freshwater bodies is one of the most important environmental impacts threatening sustainable development. This is agreed in the Millennium Development Goals (Sachs, 2012), the risk analysis of the World Economic Forum (Bakker, 2012; World Economic Forum Water, 2009), and by the International Organization for Standardization (e.g., (ISO, 2014)) through the Water-footprint Use in Life Cycle Assessment working group. All of these promote both the protection of freshwater bodies and the water quality in them, mainly against anthropic eutrophication processes.

Eutrophication is the enrichment with minerals and nutrients that increase the natural primary production (i.e., algae and macrophytes) of water bodies (lentic and lotic) (Wetzel, 2001). Therefore, concentrations of nitrogen, phosphorus and chlorophyll a (Chl-a) are monitored to assess the degree of anthropic eutrophication being promoted in water bodies (Wetzel, 2001). The eutrophication could result from point and/or diffuse pollution sources such wastewater discharges and fertilizers washed from basins, respectively. High Chl-a concentrations generally correspond to high amounts of algae in a freshwater body. Thus, it is possible to infer that increasing Chl-a concentrations are positively correlated with increasing risk of harmful cyanobacteria (Watson et al., 1997).

Since 1982, Uruguay has been reporting anthropic eutrophication, and environmental management of these impacts has focused on control of emissions of nitrogenous and phosphorus compounds (Conley et al., 2009; Wetzel, 2001). However, Wetzel (2001) has pointed out that can be other factors that promote eutrophication and thus algal blooms. Variables such as water temperature changes (Konopka and Brock, 1978; Rose and Caron, 2007; Zhao et al., 2019); loss of freshwater herbivores (Delpla et al., 2009; Yoshimura and Endoh, 2005); increasing electrical conductivity of the water (EC_w)(Casanova et al., 2009) by ions in runoff from agricultural areas (Armstead et al., 2016; Bowling, 1994; Bowling and Baker, 1996; Delpla et al., 2009; Schuytema et al., 1997); and increases in pH may all promote cyanobacteria growth (Gao et al., 2015; Zhao et al., 2019). These key influences highlight the importance of land use changes in basins. Greater soil cover can reduce soil erosion; plants protect the soil, as reflected in the (universal soil loss equation, revised universal soil less equation) USLE/RUSLE models C-factor. Better soil cover can also reduce total phosphorus export to freshwater, as identified for the Río Negro (Beretta, 2019), and the EC_w according to Carrasco-Letelier et al. (2014) and Carrasco-Letelier and Beretta-Blanco (2017).

Neural network simulation (NNS) is a data analysis tool that has recently become available for most personal computers. This methodology allows a multidimensional analysis of datasets relating diverse problems (Karul et al., 2000). NNS can identify contributing relationships with a specific variable and simulate potential scenarios (Gao et al., 2015; Huo et al., 2013). Thus, this process has been used to determine the influence of changes in several freshwater variables; a diagnostic process with less bias than when variables are defined on the basis of expert experience (Gao et al., 2015; Huo et al., 2013; Karul et al., 2000).

In the current situation, Uruguay does not have any management tool to predict the increase in Chl-a concentrations, and it was assumed that the phosphorus load is the main factor that promotes eutrophication. However, Wetzel (2001) and Allan and Castillo (2007) have pointed out that eutrophication is a multi-factor process. Therefore, to achieve sound environmental management, a tool that reduces bias and the influence of the researcher's beliefs on the diagnosis is required. In this direction, the simulation of the NNS could help both in the identification of the main variables that promote eutrophication; as in the simulation of the change in water quality due to the change in land use of the basin, if this information is used by NNS. For current freshwater problems, an NNS would offer an unbiased diagnostic tool and simulation capability to assist environmental management of the basin's land use.

If we recognize that the eutrophication process is a multidimensional event, a reductionist and unidimensional way of analysis would not identify all relevant variables linked to increasing Chl-a. Any resulting model would fail to adequately simulate the potential risk of algal blooms when key factors are modified. The hypothesis of this work is, therefore, that an NNS can identify the variables that drive increases in Chl-a concentrations, and consequently the factors that must be managed to avoid algal blooms. To explore this hypothesis, a database of freshwater variables from the Uruguay River and the Río Negro were analyzed using an NNS to identify which freshwater and land use variables are most closely linked to Chl-a changes and how the rivers would be affected if the use of the land would be restored to its natural (i.e., natural prairies).

2 Materials and Methods

2.1 Database of freshwater variables

A database of freshwater variables (Table 1) was acquired from the open database service of the National Environmental Agency (MVOTMA, 2019) for the period 2009-05-01 to 2018-11-30 for the Río Negro and for the period 2014-06-01 to 2018-11-30 for the Uruguay River. The freshwater variables included: Chl-a expressed in $\mu g\ L^{-1}$; alkalinity (ALC), expressed in $mg\ L^{-1}\ CaCO_3$; electrical conductivity of water (EC_w), expressed in $\mu S\ cm^{-1}$; total phosphorus (TP), expressed in $\mu g\ L^{-1}$; total suspended solids (TSS), expressed in $mg\ L^{-1}$; water acidity expressed in pH, and water temperature (T) expressed in degrees Celsius (^{o}C). Any measures of Chl-a higher than the 99.5% percentile were regarded as outliers and excluded. These outliers occurred at the following sampling sites: RN3 (2012-12-05), RN5 (2012-12-06 and 2012-01-19), RN6 (2012-08-15), and RN12 (2018-04-17). The average monthly radiation for each river was derived from Abal et al. (2011).

Figure 1: Uruguayan rivers analyzed in this study: Uruguay river, Río Negro and Cuareim river. The sampling points used for the database are marked (circles with centered star). The georeferecing data of each coded point were pointed out in Table 1.

Table 1: Geographic location of rivers and sampling points used in the data analyses.

River name	Sampling point	Geolocation		River name	Sampling point	Geolocation	
		Latitude	Longitude			Latitude	Longitude
Ro Cuareim	RC10	-30.694941	-56.150588	Ro Negro	RN15	-33.234717	-58.009994
Ro Cuareim	RC20	-30.503327	-56.367441	Ro Negro	RN16	-33.240824	-58.056944
Ro Cuareim	RC33	-30.40431	-56.452048	Ro Negro	RN17	-33.388324	-58.317224
Ro Cuareim	RC60	-30.27903	-57.41578	Uruguay River	RU0	-32.902139	-58.116389
Ro Cuareim	RC35	-30.395397	-56.455783	Uruguay River	RU1	-33.074944	-58.151806
Ro Cuareim	RC3C70	-30.335783	-57.046419	Uruguay River	RU2	-33.086556	-58.136611
Ro Cuareim	RC40	-30.357963	-56.547252	Uruguay River	RU3	-33.107472	-58.186444
Ro Cuareim	RC50	-30.151363	-56.784697	Uruguay River	RU4	-33.0945	-58.211889

Ro Cuareim	RCYU80	-30.347013	-57.328938	Uruguay River	RU5	-33.105167	-58.216583
Ro Negro	RN0	-31.81922	-54.459889	Uruguay River	RU6	-33.1115	-58.219361
Ro Negro	RN1	-32.109839	-54.667486	Uruguay River	RU7	-33.104111	-58.25775
Ro Negro	RN2	-32.503888	-55.505278	Uruguay River	RU8	-33.109417	-58.265111
Ro Negro	RN3	-32.621107	-55.841937	Uruguay River	RU9	-33.119361	-58.26947
Ro Negro	RN5	-32.823319	-56.419437	Uruguay River	RU10	-33.1155	-58.282139
Ro Negro	RN6	-32.835265	-56.419282	Uruguay River	RU11	-33.106111	-58.2955
Ro Negro	RN7	-32.821112	-56.5130572	Uruguay River	RU12	-33.104667	-58.301994
Ro Negro	RN9	-32.876116	-56.798615	Uruguay River	RU13	-33.118056	-58.3365
Ro Negro	RN10	-32.871883	-56.809333	Uruguay River	RU14	-33.177139	-58.359972
Ro Negro	RN11	-33.097219	-57.126662	Uruguay River	RU15	-33.165111	-58.391917
Ro Negro	RN12	-33.143322	-57.101672	Uruguay River	RU15	-33.165111	-58.391917
Ro Negro	RN13	-33.066936	-57.45417	Uruguay River	RU16	-33168	-58.358167
Ro Negro	RN14	-33.049706	-57.453616				

2.2 *Analysis of variables by linear model*

The annual trends in the water quality variables were evaluated with a generalized mixed linear model, which considered the year as a fixed effect and months and sampling sites as random effects (Eq. 1).

$$V = B \times year + month\,(S) \quad (1)$$

V, B and S correspond to any freshwater variable measured, the coefficient of annual trend analysis and the random effect nested in the sampling month, respectively.

Correlations between Chl-a level and the other freshwater variables were first determined. In addition, a boundary line was fitted for boundary points Delmotte et al. (2011); this corresponded to the maximum response of the dependent variable for each value of Chl-a and approximated a sigmoid model up to the maximal value of Chl-a and then, except for pH and T, an exponential decay pattern. Based on these boundary lines, we estimated the values of the independent variables at which one trophic state changes to another. We used the trophic categories established by the Organisation for Economic Co-operation and Development (OCDE, 1982): ultraoligotrophic state, Chl-a concentrations lower than 2.5 $\mu g\, L^{-1}$; oligotrophic state, from 2.5 to 8 $\mu g\ L^{-1}$; mesotrophic state, from 8 to 25 $\mu g\ L^{-1}$; and eutrophic state from 25 to 75 $\mu g\ L^{-1}$.

2.3 Neural network simulations

Table 2: Characteristics of the neural network that was adjusted to estimate the values of Chl-a, expressed in $\mu g\ L^{-1}$.

Input data	Transformation	Layer of hidden neurons	Response function	Output function [2]
ALC			$\frac{1}{1+2^{(-8\times10^{-6}X)}}$	$\frac{50}{10^{-(0.01Y)}}$
ECw				
TP				
pH	Normalized data			
T				
TSS				
Month	$\frac{Month\ number}{12}$			
Bias [3]				

T: water temperature (^{o}C), TSS: total solids ($mg\ L^{-1}$); ALC, alkalinity ($mg\ CaCO_3\ L^{-1}$); TP: total phosphorus ($\mu g\ L^{-1}$); EC_w, electrical conductivity of water ($\mu S\ cm^{-1}$).

(1) X represents the sum of each transformed data value multiplied by the perceptron coefficients of the neural network;

(2) Y represents the addition of each hidden layer neuron multiplied by its weight factor;

(3) bias is an input variable to the NNS that does not depend on water data (García, 2002).

Figure 2: Flux diagram of inputs, structure and output of artificial neural network.

NNS was used to identify how the different water variables linked to Chl-a concentration produce changes. The construction of NNS was made following García (2002) using Microsoft Excel® software. The NNS was set up with input of seven variables (Fig. 2, Table 2), a hidden layer of 10 neurons, and one exit neuron. First, the input variables were transformed to produce input values between 0 and 1 for each neuron, the variables ALC, EC_w, TP, pH, T and TSS were normalized, while the month variable was divided into 12. Then, each neuron of the hidden layer received as input, from each learning observation, the sum of the normalized values was multiplied by an input weight (ω) (Eq. 2). Each neuron in the hidden layer responded with a value between zero and one, given its sigmoid function, according to the value it received as input (Eq. 3). The response value of each neuron was multiplied by an input weight (Ω) to the a single exit neuron, which also used a sigmoid function, with output values from 0 to 50 (Eq. 4). The neural network was adjusted through supervised training by back-propagation looking for the smallest sum of squares error. The maximum number of neurons that did not produce overfit during learning was used, which was corroborated when estimating the testing values. The NNS was trained using values from the Río Negro and Uruguay River sampling sites (training dataset), and it was tested with Río Cuareim dataset (Table 1). The NNS simulated values of Chl-a (Chl-a $_{RN}$) were regressed against the real Chl-a values to determine whether there was a significant linear relationship and whether the regression errors had a normal distribution.

$$Input = \Sigma(Normalized\ variable\ input \times \omega_{ij}) + Bias \quad (2)$$

Where ω_{ij} is a weight of input variable i in j neurons, and be adjusted in the learning process

$$RHN_j = \frac{1}{(1+2^{-0.000008 \times intput})} \quad (3)$$

Where RHN is the response of hidden neurons j, and be between 0 and 1.

$$RN = \frac{50}{1+e^{-0.01 \times \Sigma(RHN_j \times \Omega_j)}} \quad (4)$$

Where RN is the response of exit neurons, and Ω_j is a parameter of weight of j neurons of hidden layer, and be adjusted in the learning process.

After the NNS adjustment, Chl-a $_{RN}$ values were simulated up to 2025 according to Eq. 1 for the Río Negro assuming temporal tendency of input variables using in NNS (Fig. 2). An additional simulation was carried for a land use changes that replace all agriculture with natural prairie, that would change the input values of PT and EC_w. The expected reduction of TP export from the basin to the Río Negro waters was estimated using Beretta (2019):

$$TP_{NP} = 0.834\,TP - 12.57 \quad (5)$$

where TP_{NP} is the expected TP in river waters if the basin is restored to natural prairie. Any TP_{NP} values lower than zero were recorded as zero. Similarly, EC_w changes were estimated using Eq. 6, according to Carrasco-Letelier et al. (2014) with soil loss described by Carrasco-Letelier and Beretta-Blanco (2017), assuming a C-factor of 0.02 and an annual mean rainfall of 1000 mm:

$$EC_{max} = 1,310,973.93 \times \left[\frac{rainfall(mm)}{C-factor}\right]^{-0.8025} \quad (6)$$

where EC_{max} corresponds to the highest value of EC_w ($\mu S\ cm^{-1}$) estimated for natural prairie land use.

3 Results

3.1 *Annual change analysis*

The annual values in the period 2009-2018 showed decreasing trends in pH, ALC, EC_w and TSS and an increasing trend for T in the Río Negro (Table 3). The TP and Chl-a concentrations did not show any temporal trend. In the Uruguay River, ALC, TP and T values decreased over time; pH, EC_w and TSS increased, and Chl-a did not change significantly.

Table 3: Mean monthly values, deviations, and annual changes in water quality variables from the Río Negro (May 2009 - November 2018) and the Uruguay River (June 2014 - November 2018).

	Chl-a	ALC	ECw(1)	TP	pH	TSS	T
	$\mu g\ L^{-1}$	$mg\ CaCO_3\ L^{-1}$	$\mu S\ cm^{-1}$	$\mu g\ L^{-1}$		$mg\ L^{-1}$	^{o}C
Río Negro							
Mean	2.5	39	85.7	118	7.38	122.3	20.1
Variance	5.0	19.2	34.3	114.2	0.51	55.2	5.2
Annual coefficient	0.05	-1.26	-2.73	-0.85	-0.04	-1.44	0.23
p-value	0.4212	<0.0001	<0.0001	0.1439	0.0001	0.0255	<0.0001

Degrees of freedom	251	251	251	249	251	103	251
Uruguay river							
Mean	1.9	29	66.0	99	7.31	88.6	21.2
Variance	2.0	2.7	7.4	25.5	0.2	7.5	5.2
Annual coefficient	0.02	-1.25	4.70	-9.65	0.12	3.57	-0.5
p-value	0.8073	0.0004	<0.0001	0.0024	<0.0001	0.0001	<0.0001
Degrees of freedom	124	133	251	141	140	142	120

T, water temperature; TSS, total solids; ALC, alkalinity; TP, total phosphorus; EC_w, electrical conductivity of water; ND, no data.

3.2 *Freshwater changes linked to Chl-a concentrations*

The recorded Chl-a concentrations (Fig. 3) in the studied rivers had positive, but low, correlations with: T (R^2 = 0.25; p <0.01), EC_w (R^2 = 0.14; p <0.01), pH (R^2 = 0.26; p <0.01), TSS (R^2 = 0.09; p <0.01), monthly average daily radiation (R^2 = 0.24; p <0.01), and ALC (R^2 = 0.06; p = 0.05). No correlation was found between Chl-a and TP concentrations.

Figure 3: Relationship between Chl-a concentrations and ALC (a), EC_w (b), TP (c), pH (d), TSS (e) and T(f). The solid line corresponds to the boundary of expected maximal values.

Using the Chl-a maximum values and a boundary, the relationships of this variable with the rest of studied variables were of two types. The first type exhibited a sigmoidal pattern at low variable values, with an inflection point (C_i) and a maximum value (C_{opt}). After the peak, as the studied variable increased, there was exponential decay in Chl-a concentrations. This occurred with: ALC (C_i: 27 $mg\ L^{-1}$ $CaCO_3$, C_{opt}: 49 $mg\ L^{-1}$ $CaCO_3$), EC_w (C_i: 63 $\mu S\ cm^{-1}$, C_{opt}: 120 $\mu S\ cm^{-1}$), ST (C_i: 78 $mg\ L^{-1}$; C_{opt}: 130 $mg\ L^{-1}$), and TP(C_i: 60 $\mu g\ L^{-1}$; C_{opt}: 140 $\mu g\ L^{-1}$) (Figure 3).

The second type of relationship also initially showed a sigmoidal pattern; after the inflection point (C_i) the pattern became asymptotic to the maximum value (C_{opt}). This second kind of relationship was evident in T (C_i: 18 ^{o}C) and pH (C_i: 7.0). These variables did not show exponential Chl-a decrease after a maximal value. In both rivers, month mean values of Chl-a (Table 3) showed an increasing trend related to increasing T, EC_w, and pH values (Fig. 4).

The interactions, across the sampling sites, of Chl-a with T and of ECw with pH were found to be more significant when using month means (R^2 : 0.60) than when based on individual sampling events (month) (R^2 : 0.4).

Figure 4: Mean Chl-a values for each month and year and interaction with T (^oC), EC_w ($\mu S\ cm^{-1}$), and pH for the Río Negro (triangles) and the Uruguay River (circles). Equation line is $y = 4.1\times10^{-8}x^2 - 5.3\times10^{-4}x + 2.15$; R^2 = 0.64, n = 61 (p <0.01).

The variables T and EC_w did show clear effects on maximum Chl-a concentrations: 58% of Chl-a records did not reach a mesotrophic level when EC_w was < 79 $\mu S\ cm^{-1}$ or > 141 $\mu S\ cm^{-1}$; or, in 47% of records, when T was lower than 19.1 ^oC (Table 4). No such boundaries for TSS and TP concentrations were found in the database.

Table 4: Limits of the other variables required to influence the trophic state and the observed proportion (%) of samples in each state as defined by Chl-a content (OECD, 1982).

Variable	Units	Trophic state			% of samples		
		Ultraoligo	Oligo	Meso	Ultraoligo	Oligo	Meso
T	^oC	10	13.8	19.1	1	11	35
TSS	$mg\ L^{-1}$	> 60; <365	>68; <268	>81; <173	1	3	20
pH		6.08	6.52	7.13	1	3	22
ECw	$\mu S\ cm^{-1}$	>47;<233	>61; <186	>79; <141	2	19	37
ALC	$mg\ CaCO_3\ L^{-1}$	>15.5; <89.	>21; <72.7	>28.6; <56.4	2	3	29
TP	$\mu g\ L^{-1}$	>21; <316	> 39; <244	>66; <172	4	1	17

T, water temperature; TSS, total suspended solids; ALC, alkalinity; PT, total phosphorus; EC_w, electrical conductivity of water.

The developed NNS (Fig. 4) and its adjusted coefficients (Table 3) explained 79% of the variations in Chl-a concentrations (Fig. 5), with a mean error of 0.74 $\mu g\ L^{-1}$ (p <0.01) for the Río Negro and Uruguay River and an average error of -0.68 $\mu g\ L^{-1}$ (p <0.01) for the Cuareim River. For both datasets, adjustment and validation, the relationship between observed and estimated values was 1:1 (p <0.05). The errors had acceptable values although they did not have normal adjustment distributions for the Río Negro and the Uruguay River. In validation with Cuareim River data, a normal distribution was determined using the Shapiro-Wilk test. At low values, the NNS underestimated Chl-a concentrations. The model would therefore be inappropriate for Chl-a concentrations below 5 $\mu g\ L^{-1}$; the 95th percentile of absolute errors was 4.9 $\mu g\ L^{-1}$.

Figure 5: Chl-a values estimated by NNS for the Uruguay River and the Río Negro (crosses) and the Cuareim River (squares).

Figure 6: Chl-a values from Río Negro for the period 2009-2025: recorded data (fill circles) and simulated values (fill squares) by NNS. a) means values; b) 90th percentil values.

Using the NNS to project Chl-a concentrations in the Río Negro up to December 2025 showed decreasing mean values at a rate of 0.05 $\mu g\ Chl-a\ L^{-1}$ (Fig. 6a)(p <0.001), but the 90th percentile values were unchanged (Fig. 6b). This trend reflects the interaction of Chl-a concentrations with the T, EC_w and pH variables (Fig. 4). Simulation of the effects of replacement of current land use by natural prairie in the Río Negro basin indicated that EC_w would drop below 222 $\mu S\ cm^{-1}$; however, neither the mean values of Chl-a (0.39 $\mu g\ L^{-1}$) nor the 90th percentile values would change (Fig. 7). However, if the land use would be restored to natural prairie, the 90th percentile of Chl-a values would drop from 15.73 to 15.00 $\mu g\ L^{-1}$, and the number of samples exceeding 8 $\mu g\ of\ Chl-a\ L^{-1}$, a mesotrophic state according to the OCDE (1982), would rise from 47 to 60.

Figure 7: Observed Chl-a concentrations in the Río Negro and Chl-a concentrations simulated with an adjusted neural network, assuming natural prairie land use throughout the basin.

Figure 8: Distribution of toxic units, recorded annually, for 208 imported pesticides before and after 2004, the beginning of agriculture intensification in Uruguay. For each period, previous (1999-2004) and current (2009-2018) fugacity model level 1 (Mackay, 2001) was applied to define the fraction of pesticide that could reach the water and soil (data prepared by L. Carrasco-Letelier, not published). These amounts were divided by the median lethal dose, LD_{50} (48 h), for *Daphnia magna* (pesticide properties database, University of Hertfordshire, UK) to estimate the toxic units for each mass unit of pesticide.

4 Discussion

The differences in the annual trends of freshwater variables between the Uruguay River and the Río Negro could be the result of differences in water sampling before July 2014; subsequently, a common sampling procedure (i.e., subsurface sampling) was applied to both rivers.

While the Uruguay River had lower values than the Río Negro for ALC, TSS, and EC_w, both rivers had an increasing trend in TSS and EC_w. The mean annual temperature showed a downward trend in the Uruguay River, but increased in the Río Negro. In the six warmest months (October-December and January-March) in the Uruguay River the temperature increase was $0.65\ ^{o}C\ yr^{-1}$ (p <0.001), while in the cold months, the temperature decreased at $0.58\ ^{o}C\ yr^{-1}$ (p <0.001).

The three most important variables for explaining changes in the monthly/annual means of Chl-a in both rivers were T, EC_w, and pH (Fig. 4). However, these variables did not adequately estimate the observed Chl-a values for each combination of sampling site and date. Thus, while these variables (T, EC_w, and pH) can predict the overall condition of rivers with increasing Chl-a concentrations, they can change rapidly in short periods and from one sampling station to another one. To achieve less biased forecasting of Chl-a concentrations using these variables, it may be necessary to increase the frequency and spatial density of sampling.

The increasing temperature of the river waters has been linked to increasing air temperature and/or ocean temperatures in some reports (Agency, 2016; Webb and Nobilis, 2007). The annual change in mean T in the Río Negro was approximately 10 times the 2.4 fold increase, from $0.011\,^{o}C\,yr^{-1}$ to $0.026\,^{o}C\,yr^{-1}$ for the period 1901 to 2000, reported by Webb and Nobilis (2007) or the similar values for 1901 to 2014 reported by the Agency (2016). This may be partly because of differences in measurement methods. Webb and Nobilis (2007) do not specify the water depth of their measurements, while we used surface water layer (0-5 cm from the surface) of the main flow. However, the different temporal ranges in the studies are also likely to be significant.

Konopka and Brock (1978) found that the maximum photosynthesis of algae in laboratories conditions occurs at 20-30 ^{o}C. Similarly, De León (2002) reported that cyanobacteria growth was favored by temperatures higher than 20 ^{o}C. However, the species *Microcystis aeruginosa* does not need such high temperatures for its development; because even at low temperatures the concentration of Chl-a can exceed 5 $\mu g\,L^{-1}$. Moreover, the water temperature records may not be representative of algal bloom development potential in the rivers; the shallow areas near the river banks where T could reach values higher than the mean T of the river would be more conducive to algal growth. However, the measured temperatures were sufficient for maintenance of Chl-a concentrations and presumably also the concentration of cyanobacteria. Rose and Caron (2007) concluded that in algal blooms, lower temperatures favor the growth of cyanobacteria more than that of their predators. According to these researchers, temperatures lower than 15 ^{o}C favor the growth of cyanobacteria populations, while at 20 ^{o}C the growth rate is equal to their predators growth rate. Zhao et al. (2019) reported cyanobacterial blooms in lakes and reservoirs in China occurring at temperatures of 19.5 ^{o}C to 32 ^{o}C. Moreover, Brandão et al. (2012) found that temperature could affect the presence of Daphnia. Delpla et al. (2009) similarly reported that a warmer climate promotes cyanobacteria over phytoplankton and Abal et al. (2011) observed a positive correlation between Chl-a and radiation. Although our study found a significant correlation between T and monthly radiation, the individual effect of each variable on changes in Chl-a was not clear.

The reduction in annual mean EC_w (Table 3) could be because of reduced export of cations from basin soils; EC_w levels have an inverse relationship with the USLE/RUSLE models C-factor, which reflects land use (Carrasco-Letelier et al., 2014). A high C-factor implies that the soil is less protected from rain and therefore more exposed to water erosion and ion export. Thus, recent reductions in agricultural area (DIEA (Dirección de Información y Estadística

Agropecuaria), 2018) and greater enforcement of soil conservation law (ROU, 1981, 2008) have together reduced the C-factor mean and hence reduced EC_w values and cation loss from soils (Beretta, 2019).

Casanova et al. (2009) reported a positive correlation between Chl-a and EC_w; export to water of both ions and nutrient increases EC_w while also increasing algal growth and, potentially, algal blooms. In this framework, because EC_w is linked to the ratio rainfall:C-factor (Carrasco-Letelier et al., 2014), EC_w would contribute to alga blooms when rains follow drought periods (Bowling, 1994; Bowling and Baker, 1996; Lürling et al., 2018). The soil erosion and runoff that occur during heavy rain events after a dry season increase the export of ions to freshwater (Delpla et al., 2009). The increasing EC_w can also limit the development of cyanobacterias predators. High EC_w can limit the reproduction of *Ceriodaphnia dubia* (Armstead et al., 2016) and, if EC_w is higher than 63 $\mu S\ cm^{-1}$, the growth and reproduction of *Daphnia magna*, (Schuytema et al., 1997). This EC_w level is close to that observed at the transition between the oligotrophic to mesotrophic states in our study (Fig. 3b). A second factor is the growth in use of pesticide and veterinary products (Yoshimura and Endoh, 2005) after the beginning of agriculture intensification in 2004 (Fig. 8, data prepared by Carrasco-Letelier, not published) (Céspedes-Payret et al., 2009): changes that would have increased xenobiotic export to waters and perhaps reduced the zoobenthos populations that control cyanobacteria blooms. Although in this work the availability of nitrogen (N) was not evaluated, it is feasible to assume that it contributes to the increase in EC_w and, together, to increase the Chl-a concentrations. However, this effect is unlikely to be significant because the erosion process already supplies enough phosphorus (P) (Beretta, 2019) and N. Moreover, ecosystems with low N and high P availability can be colonized by diazotrophic cyanobacteria, which themselves introduce N to the system, and the system is subsequently exploited by non-diazotrophic cyanobacteria such as *Microcystis* (Tilahun and Kifle, 2019). The sampling frequency of the database did not allow visualization of this effect.

Acidification of river water could be seen as a result of increasing atmospheric carbon dioxide (CO_2); although this effect would be insignificant given that the river CO_2 pressure is higher than the atmospheric CO_2 pressure (Wang et al., 2015). Other possible causes are the increased respiration of aquatic biota and the existence of hydroelectric dams (Wang et al., 2015). Hao et al. (2016) also observed an acidification trend in Chinas rivers attributable to increases in agricultural activity, fertilizer use, and mining. Beretta-Blanco et al. (2019) reported soil acidification between 2002 and 2014 as a result of agricultural activity; this could cause acidification of the water that reaches the channels. However, Carrasco-Letelier and Beretta (unpublished) did not observe any relationship between land use and water pH in 99 basins in Uruguay. Weiss et al. (2018) reported an increase in CO_2 in water reservoirs in Germany, to which they also attributed observed acidification. The annual magnitude of acidification observed in the Río Negro would be similar to the lowest value reported by Hao et al. (2016), who showed a decrease of approximately one unit of pH in 25 years.

The positive correlation of Chl-a with pH was also reported by De León (2002). In addition, Zhao et al. (2019) reported that the maximum risk of algal blooms is at pH values from 7.0 to 9.38. If the acidification is the product of an increase of partial pressure of CO_2 (data not available), a reduction of the *Daphnia* population, a potential predator of cyanobacteria, is also expected (Weiss et al., 2018). While the pH level can affect the development of cyanobacteria, it also changes as a consequence of them; consequently, it is possible that the relationships observed here are due to development of cyanobacteria.

No correlation was observed, in either river, between Chl-a and TP concentrations. The lack of impact of TP on Chl-a concentrations is likely to be because P levels are high most of the time. Zhao et al. (2019) wrote that the maximum risk of algal blooms is when TP is between 130 and 220 $\mu g\ L^{-1}$; a range close to the values observed in our study. Indeed, we observed that a significant limitation to the maximum concentrations of Chl-a could be expected at 220 $\mu g\ of\ TP\ L^{-1}$ in both rivers. P availability is pointed out as a limiting factor for cyanobacteria growth by various authors (Aubriot and Bonilla, 2012; Bonilla et al., 2015). However, Wan et al. (2019) concluded that *Microcystis* has the capacity to adapt to systems with low P and suggested that decreases in cyanobacterial proliferation through decreases in P are limited to diazotrophic cyanobacteria. This study found that high P concentrations could promote the development of other communities that compete with cyanobacteria; for this reason, Chl-a concentrations could decrease as TP values increase (Fig. 3). Brandão et al. (2012) observed a positive correlation between TP concentrations and the population of *Daphnia laevis*.

4.1 Estimation of Chl-a concentrations with NNS

The adjusted NNS estimated Chl-a concentrations satisfactorily and with similar results to Huo et al. (2013) and Gao et al. (2015). These authors, however, also incorporated total N and water transparency as input variables into their models. On the other hand, Gao et al. (2015) did not use total suspended solids or the effect of time. The NNS reported here is not adequate to estimate changes from ultraoligotrophic to oligotrophic conditions, given the lack of sensitivity at Chl-a concentrations lower than 5 $\mu g\ L^{-1}$. Moreover, the NNS is unable to estimate values greater than 50 $\mu g\ L^{-1}$ because this concentration was exceeded only five times from 2009 to 2018 and these were excluded as being in the 99.5th percentile. Figure 5 shows that some conditions with Chl-a concentrations near to 0 $\mu g\ L^{-1}$ were not correctly estimated. This may be because cyanobacteria populations occurred in conditions not covered by the record of water quality. Although Karul et al. (2000) reported excellent accuracy (R^2 = 0.95) of their neural network when estimating Chl-a concentration in small and homogeneous lakes, the fit of our model was better than these authors achieved for large and heterogeneous lakes (R^2 = 0.60 to 0.75).

The simulation of land use change to natural prairie in the Río Negro basin shifted the mean TP concentration to 80 $\mu g\ L^{-1}$ (Beretta, 2019): sufficient to significantly reduce Chl-a concentrations. For 95% water samples to have a mesotrophic condition, the mean concentration of TP should decrease to 17 $\mu g\ L^{-1}$ with a maximum below 23 $\mu g\ L^{-1}$. This result agrees with the current law that specifies acceptable TP values as below 25 $\mu g\ L^{-1}$ (Uruguayan Law 14,859, Decree No. 253/979). Reduction of EC_w values to a maximum of 222 $\mu S\ cm^{-1}$, would also fail to impact Chl-a concentrations. For a significant reduction in Chl-a, the EC_w should reduce by 34% (i.e., 76 $\mu S\ cm^{-1}$) or increase by 260% (i.e., 259 $\mu S\ cm^{-1}$); this would lead to 95% of samples being out of mesotrophic state. Thus, changing the entire basin land use to natural prairie would not reduce TP or EC_w to the levels required to produce a significant effect on Chl-a.

TSS is expected to reduce over the next 5 years as a consequence of the land use change and enforcement of plans and laws on the use of soils from the Uruguayan Ministry of Livestock, Agriculture and Fishery. Such environmental management would evolve towards a scenario of no increase in mean concentration of Chl-a.

As agricultural activity affects water quality, it is possible to influence the Chl-a concentrations. EC_w indicates the presence of cations and anions in solution; by decreasing export from the soil, EC_w can be reduced along with persistent Chl-a concentrations. Reports by Carrasco-Letelier et al. (2014) and Carrasco-Letelier and Beretta-Blanco (2017) suggest that decreasing the C-factor could reduce EC_w. Thus, changes in land use could help in EC_w reduction but this will not achieve the required reduction goal. A limitation of P fertilizers, however, could not contribute significantly to reduction of mean Chl-a concentrations, because the goal for freshwater concentrations is already exceeded because of P linked to natural soil erosion.

5 Conclusion

NNS was found to effectively determine the variables linked to changes in Chl-a concentrations. However, to improve the Chl-a estimation, it is necessary to increase the spatial and temporal frequency of sampling.

The average values of Chl-a in the channel waters of the Uruguay River and the Río Negro depend mainly on T, EC_w, and pH. However, when using all eight variables analyzed here, it is possible to estimate Chl-a values, with acceptable accuracy, in the range from 5 to 50 $\mu g\ L^{-1}$. Current evolution of the Río Negro suggests no increase in Chl-a extreme values (90th percentile) and the average value may decrease. By changing the current land use of the Río Negro basin towards natural prairies there would be no significant change in the average concentration of Chl-a or in extreme values.

It would also not be possible to stop the increase of Chl-a production by reduction of TP in the water, but its increase could be mitigated by decreasing the export of cations from the ground to the water courses. An increase of T, however, will continue to favor higher Chl-a concentrations and, in these conditions, agriculture would have no direct effect.

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Declaration of competing interests

X The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

~~☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:~~

CRediT author statement

Andrés Baretta-Blanco: conceptualization, Investigation, methodology, validation, formal analysis, investigation, Writing - Original Draft **Leonidas Carrasco−Letelier**: conceptualization, investigation, writing- reviewing and editing, visualization

Graphical abstract

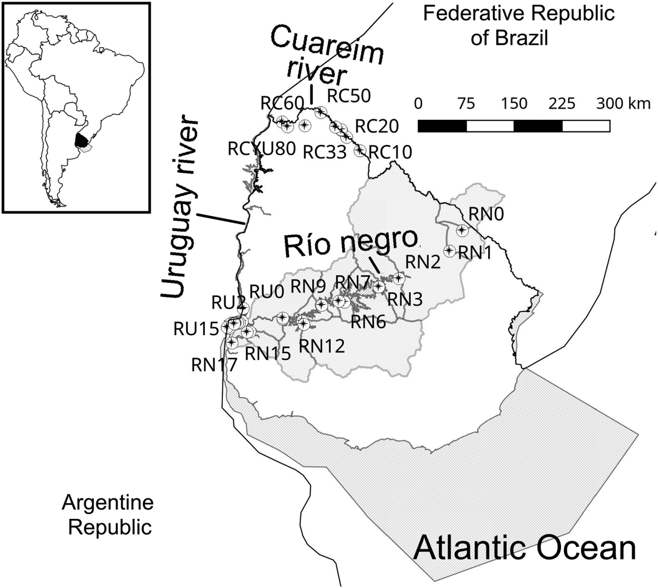
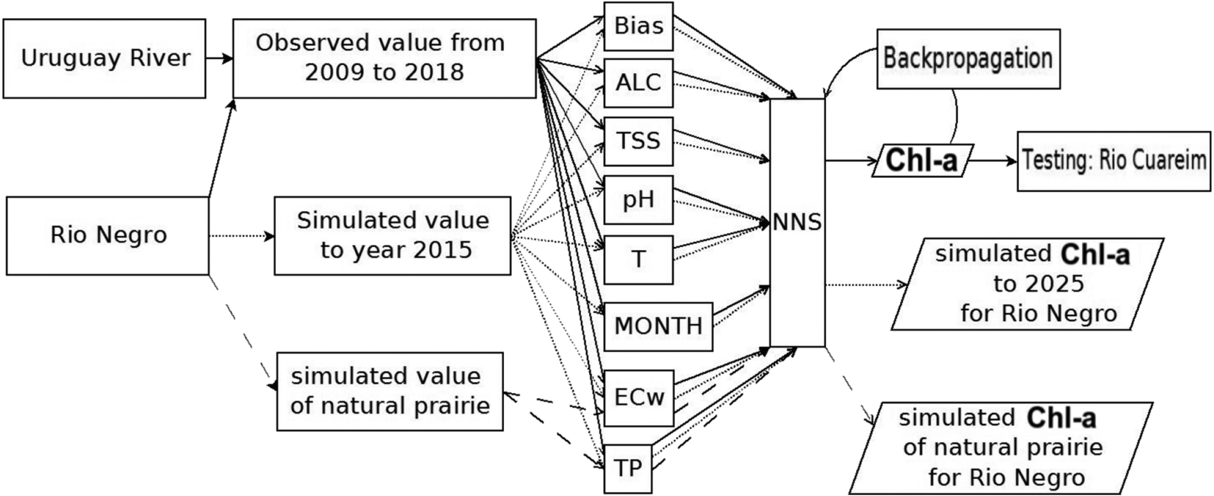

Federative Republic
of Brazil
Cuareim
river
RC60
RC50
RC20
RCYU80
RC33
RC10
0
75
150
225
300 km
Uruguay river
RN0
Río negro
RN1
RN2
RU0
RN9
RN7
RN3
RU2
RN6
RU15
RN12
RN15
RN17
Argentine
Republic
Atlantic Ocean

Figure 1



Uruguay River
Observed value from 2009 to 2018
Rio Negro
Simulated value to year 2015
simulated value of natural prairie
Bias
ALC
TSS
pH
T
MONTH
ECw
TP
NNS
Backpropagation
Chl-a
Testing: Rio Cuareim
simulated Chl-a to 2025 for Rio Negro
simulated Chl-a of natural prairie for Rio Negro

Figure 2

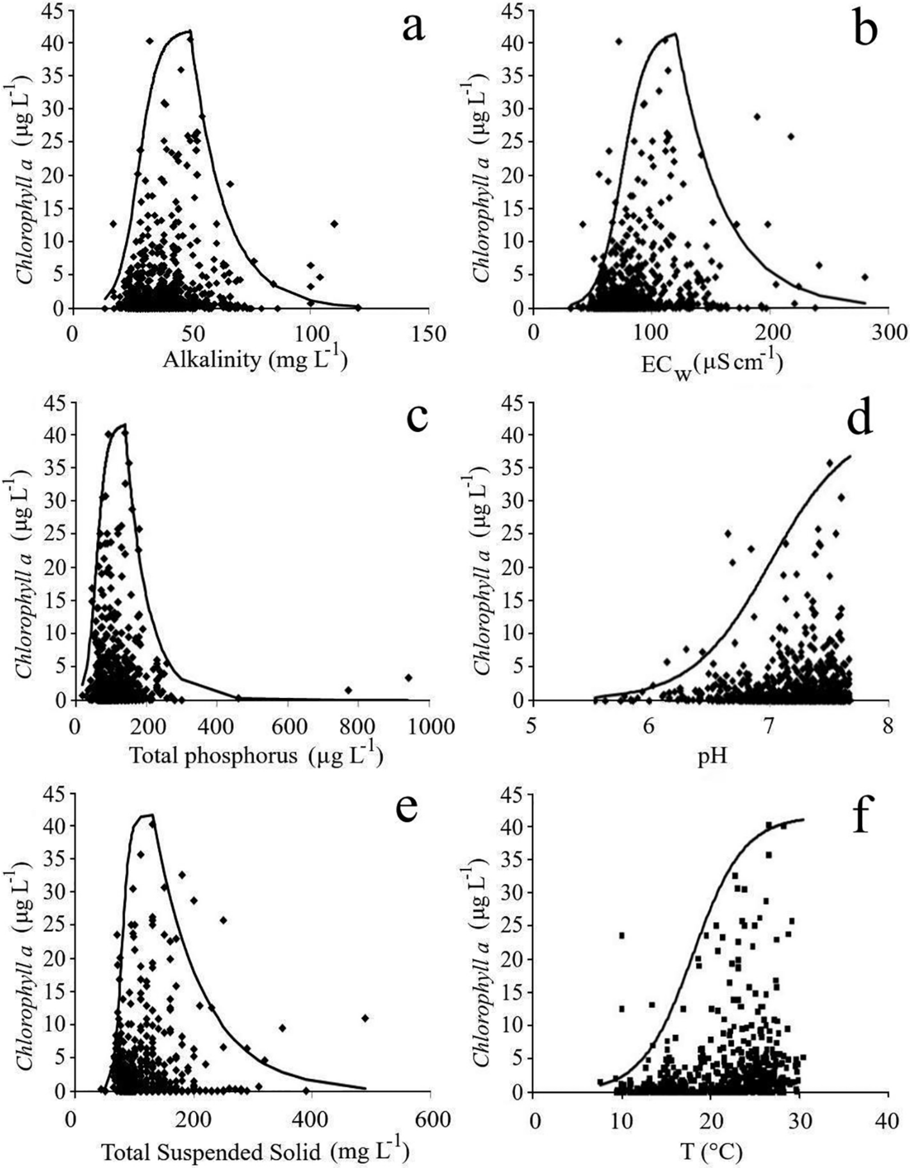

a
b
c
d
e
f
Chlorophyll a (µg L-1)
Alkalinity (mg L-1)
ECw(µS cm-1)
Total phosphorus (µg L-1)
pH
Total Suspended Solid (mg L-1)
T (°C)

Figure 3

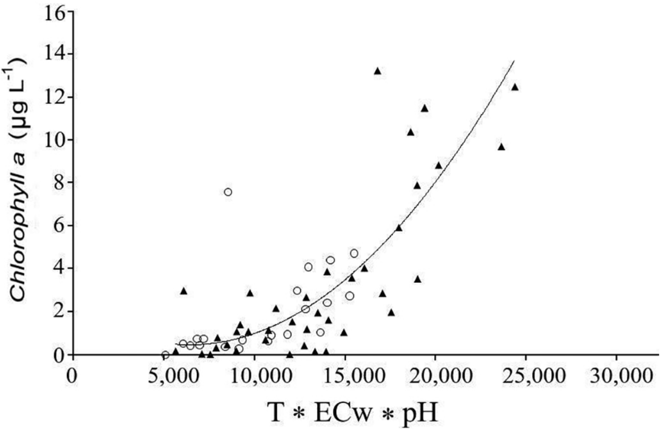
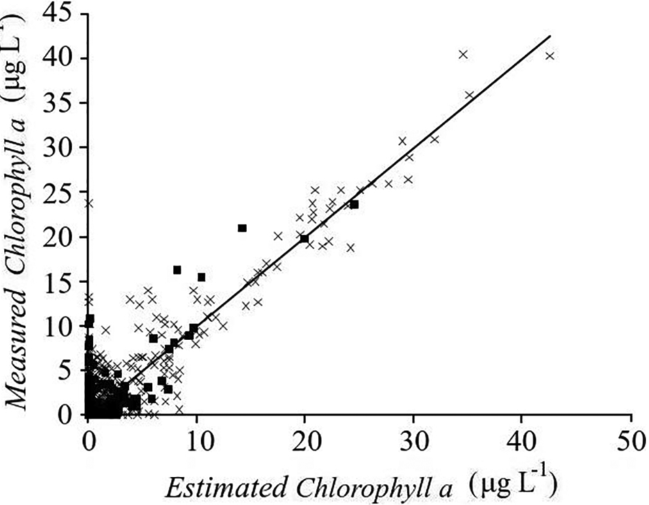

16
14
12
10
8
6
4
2
0
Chlorophyll a (μg L-1)
0
5,000
10,000
15,000
20,000
25,000
30,000
T * ECw * pH

Figure 4



45
40
35
30
25
20
15
10
5
0
0
10
20
30
40
50
Measured Chlorophyll a (μg L-1)
Estimated Chlorophyll a (μg L-1)

Figure 5

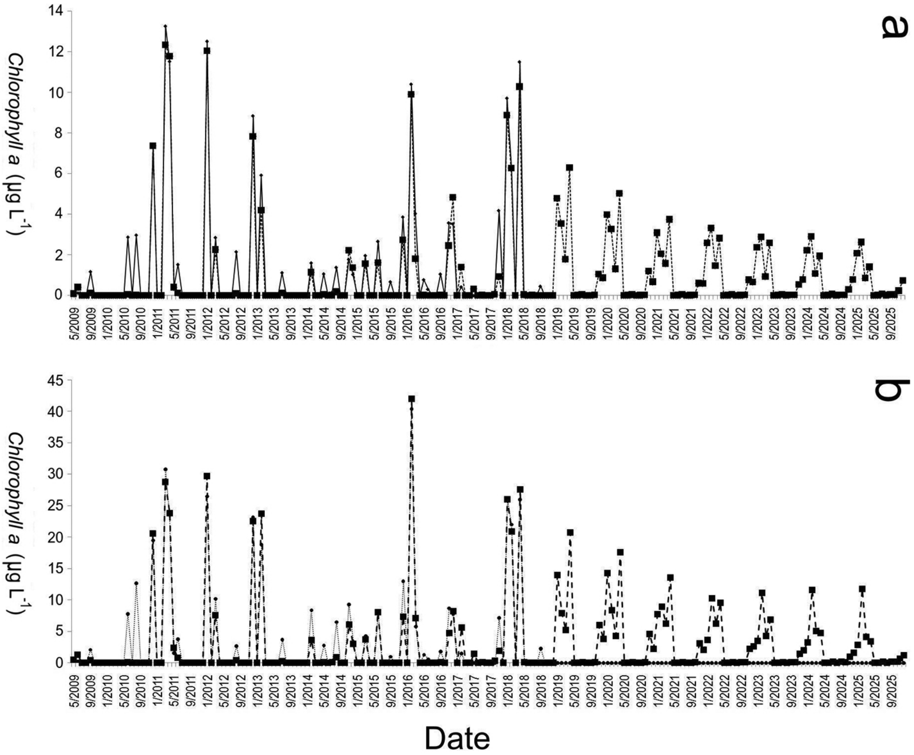
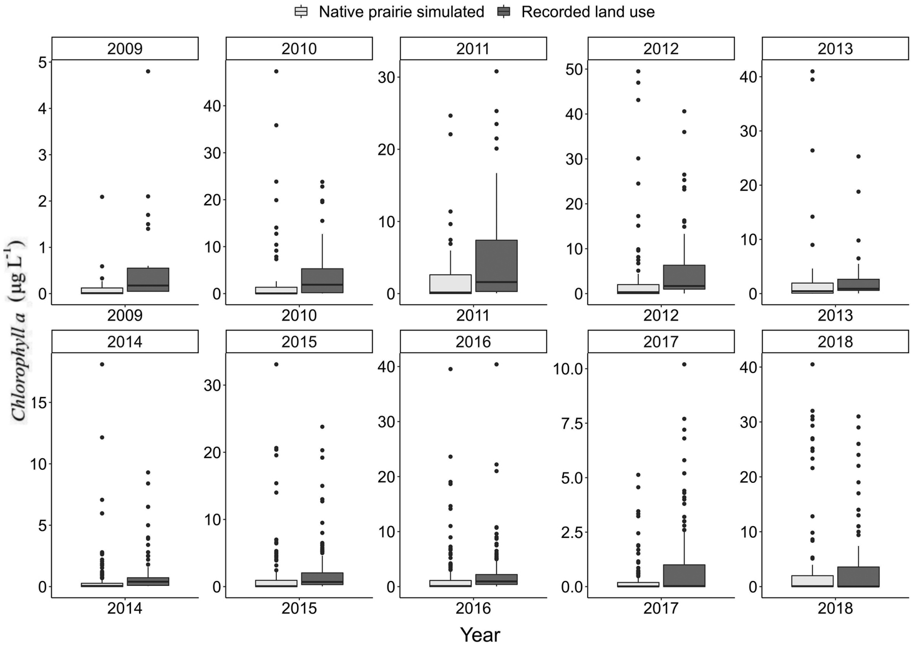


Figure 6



Native prairie simulated
Recorded land use
Chlorophyll a (μg L-1)
2009
2010
2011
2012
2013
2014
2015
2016
2017
2018
Year

Figure 7

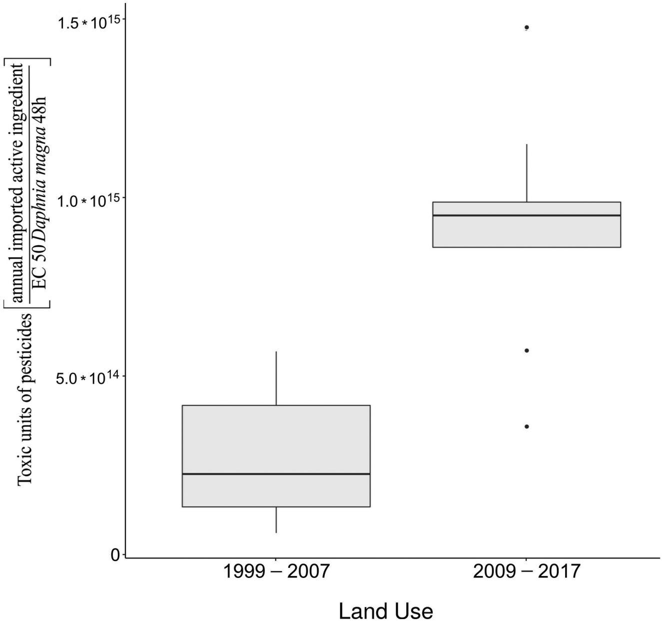

1.5 * 10^15
1.0 * 10^15
5.0 * 10^14
0
Toxic units of pesticides [annual imported active ingredient / EC 50 Daphnia magna 48h]
1999 – 2007
2009 – 2017
Land Use

Figure 8