Science of the Total Environment 613–614 (2018) 866–876

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Disentangling natural and anthropogenic influences on Patagonian pond water quality

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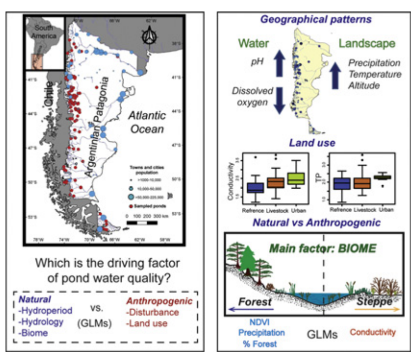
HIGHLIGHTS

- West-east variability of pond water status was mainly determined by rainfall gradient.
- Dissolved oxygen and pH showed a variation pattern from the north to the south.
- Livestock used ponds exhibited higher wet-grasses cover and total suspended solids.
- Natural variability plays a major role on Patagonian ponds ecosystems.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 June 2017
Received in revised form 13 September 2017
Accepted 14 September 2017
Available online 21 September 2017

Editor: D. Barcelo

Keywords:
Eutrophication
Land use
Land cover
Hydrology
Wetlands
Mallines

ABSTRACT

The water quality of wetlands is governed not only by natural variability in hydrology and other factors, but also by anthropogenic activities. Patagonia is a vast sparsely-populated in which ponds are a key component of rural and urban landscapes because they provide several ecosystem services such as habitat for wildlife and watering for livestock. Integrating field-based and geospatial data of 109 ponds sampled across the region, we identified spatial trends and assessed the effects of anthropogenic and natural factors in pond water quality. The studied ponds were generally shallow, well oxygenated, with maximum nutrient values reported in sites used for livestock breeding. TN:TP ratio values were lower than 14 in >90% of the ponds, indicating nitrogen limitation. Water conductivity decreased from de east to the west, meanwhile pH and dissolved oxygen varied associated with the latitude. To assess Patagonian ponds water status we recommend the measure of total suspended solids and total nitrogen in the water, and evaluate the mallín (wetland vegetation) coverage in a 100 m radius from the pond, since those features were significantly influenced by livestock land use. To evaluate the relative importance of natural variability and anthropogenic influences as driving factors of water quality we performed three generalized linear models (GLM) that encompassed the hydrology, hydroperiod and biome (to represent natural influences), and land use (to represent anthropogenic influences) as fixed effects. Our results revealed that at the Patagonian scale, ponds water quality would be strongly dependent on natural gradients. We synthetized spatial patterns of Patagonian pond water quality, and disentangled natural and anthropic factors finding that the dominant environmental influence is rainfall gradient.

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http://dx.doi.org/10.1016/j.scitotenv.2017.09.147
0048-9697/

1. Introduction

Ecosystems water quality is dependent on many factors, including land use, climate, geomorphology and soil conditions. Worldwide, the impacts of different land uses on water bodies and their relative importance compared to the effects of natural environments variability are yet to be ascertained and quantified. Landscape scale approaches are useful for exploring fundamental ecological patterns across a region and for improving our comprehension about the influence of the surrounding matrix in the ecosystems. These approaches are also useful, among others, for studying how climatic and geomorphological variation determine pond features, and for describing land use patterns to distinguish between impacted and reference areas (Céréghino et al., 2014). By studying small, isolated water bodies (ponds) it is possible to recognize the spatial variation and the main environmental controls across broad regional scales (Hefting et al., 2013).

Argentinian Patagonia is a region located at the southern end of the South American continent. This remote region shows a remarkable environmental heterogeneity, mainly determined by an exponential west-east decrease in precipitation. Thus, most of the territory is characterized by semiarid and arid conditions, supporting shrub-grass vegetation, typical of the steppe (del Valle, 1998; Paruelo et al., 1998). Patagonian wetlands, colloquially known as "*mallines*", develop in association with particular conditions of the landscape where an unusual amount of water is available (Movia et al., 1987), and are characterized by isolated small patches of hydrophytes included in a terrestrial matrix (Kandus et al., 2008). These azonal freshwater ecosystems provide the most productive soils for livestock breeding, which is the most important source of income for farmers in certain arid or heavily grazed areas (Ayesa et al., 1999).

Ecological processes in ponds play a major role in global cycles (Downing, 2010). Patagonian ponds are a key component of urban and rural landscapes because they provide several ecosystem services such as habitat for wildlife, watering for livestock, suitable environments for fish production, and recreational amenities (Jeffries et al., 2016). Patagonian ecosystems had not been grazed by domestic herbivores prior to European colonization so that the introduction of large herds of horses, cattle and sheep had a significant impact on soils, landscape processes, vegetation and fauna. It is known that decreases in vegetative cover promote the increase of evaporation rates and loss of soils by water and wind erosion (Kepner et al., 2000). These effects are inducing a desertification process, one of the main environmental problems affecting Patagonia (del Valle et al., 1998). Livestock grazing, conducted for more than a century (~130 years), has become so widespread that ungrazed areas are practically nonexistent (Golluscio et al., 1998) and most Patagonian mallines are currently threatened.

Urban development increases production of runoff, one of the largest uncontrolled sources of pollution to receiving waters (Novotny, 2003), and while discharging nutrients (such as nitrogen (N) and phosphorus (P)) accelerates the eutrophication process (Carey et al., 2013). Despite being a sparsely populated region (<3 inhabitants per km^2), the Patagonian population is concentrated in urban areas modifying the water quality of the aquatic ecosystems that surround them (e.g., Miserendino et al., 2011), and using wetland areas for disposal or treatment of domestic effluents.

Since ponds are relatively small in both size and water volume, they may be sensitive to environmental changes due to land use pressures and climate change (Declerck et al., 2006). Moreover, predictions for the Patagonia region indicate that areas suitable for mallines are likely to decrease by the middle of the century (Crego et al., 2014), accelerating the degradation processes derived from livestock overgrazing (Brinson and Malvárez, 2002). To understand the interaction between land use patterns, climate, and other changes, reliable information on land cover configurations around Patagonian ponds is needed. The effects of anthropogenic impacts are also recognized through increased transfer of nutrients from one environment to another, and alterations in the rates of transformations of nutrients within environments (Depetris et al., 2005). Previous studies, conducted at Patagonian ponds, have demonstrated that nutrient concentrations are good predictors of water quality and status conditions (Epele and Miserendino, 2015). Thus, ponds affected by urban effluents or livestock are expected to show higher levels of nutrients in the water compartment than pristine or less impacted ones.

Some recent research in Patagonian pond ecology shows greater interest in fundamental aspects of these environments and suggests some actions and conservation strategies, e.g. the fencing of some wetlands of special interest (Crego et al., 2014; Kutschker et al., 2014; Epele and Miserendino, 2016). Despite their socioeconomic value and the possible environmental vulnerability, there is a general lack of knowledge about their structure, functioning and relationships with features of the surrounding landscape (Perotti et al., 2005). Our research attempted to use a comprehensive approach to assess the effects of land use (livestock and urban) on water quality, and compare them with the effects of climatic or natural variability across the Patagonian region. Using georeferenced field data from >100 ponds sampled across the Patagonian region we: (1) identify spatial variability in Patagonian pond water quality (e.g. N-S or W-E variations); (2) determine relationships between landscape characteristics and pond water features; and (3) evaluate the relative importance of natural variability and anthropogenic influences as driving factors of water quality.

2. Material and methods

2.1. Study area

The study region, Patagonia Argentina (~800,000 km^2) is located in southern South America (Fig. 1A), extending from 36° to 55° S, ranging from the Andes Mountains on the west to the Atlantic Ocean on the east, and including five political provinces (from the north to the south: Neuquén, Río Negro, Chubut, Santa Cruz and Tierra del Fuego). The region is sparsely populated (<3 inhabitants per km^2), with 87% of the people living in cities or towns that are less populated to the south (National Government of Argentina, 2010).

The climate of Patagonia is strongly determined by the Andes Mountains, which impose a significant barrier for humid air masses coming from the Pacific Ocean. Most of the water in these maritime air masses is released on the Chilean side, and the air becomes hotter and drier through adiabatic warming as it descends on the Argentine side of the Andes (Paruelo et al., 1998). From the Andes eastward, total annual precipitation decreases exponentially, from >1000 mm to <150 mm at the eastern arid extreme. Precipitation is mainly concentrated in winter. Precipitation maximum in winter results in a strong summer deficit, excepting at the NE region. Most of the central portion of Patagonia receives <200 mm per year (Fig. 1B).

Patagonia can be defined as a temperate or cool-temperate region. A distinctive feature of the temperature pattern is the NW-SE distribution of the isotherms (Fig. 1C). Mean annual temperature ranges from 12 °C in the north-eastern part to 3 °C toward the south. The mean temperature of the coldest month (July) is >0 °C in all the extra-Andean Patagonia. However, toward the mountain parts of the southwest Patagonia, absolute minimum temperatures are lower than −20 °C (Paruelo et al., 1998). The annual range of monthly temperature is lower in Patagonia than in similar latitudes of the Northern Hemisphere.

A characteristic of the Patagonian climate is the predominance of winds from the west. In the center-west of the region, westerly winds represent between 65 and 75% of the daily observations in the year (Paruelo et al., 1998). Because of the seasonal displacement of the pressure systems, winter has a more uniform distribution of winds from the west, whereas in summer a southerly component is evident (Beltrán, 1997). Westerly winds are characterized not only by their persistence during the year but also by their intensity, with mean annual speed values that varied between 15 and 22 km h^{-1}. Low humidity content

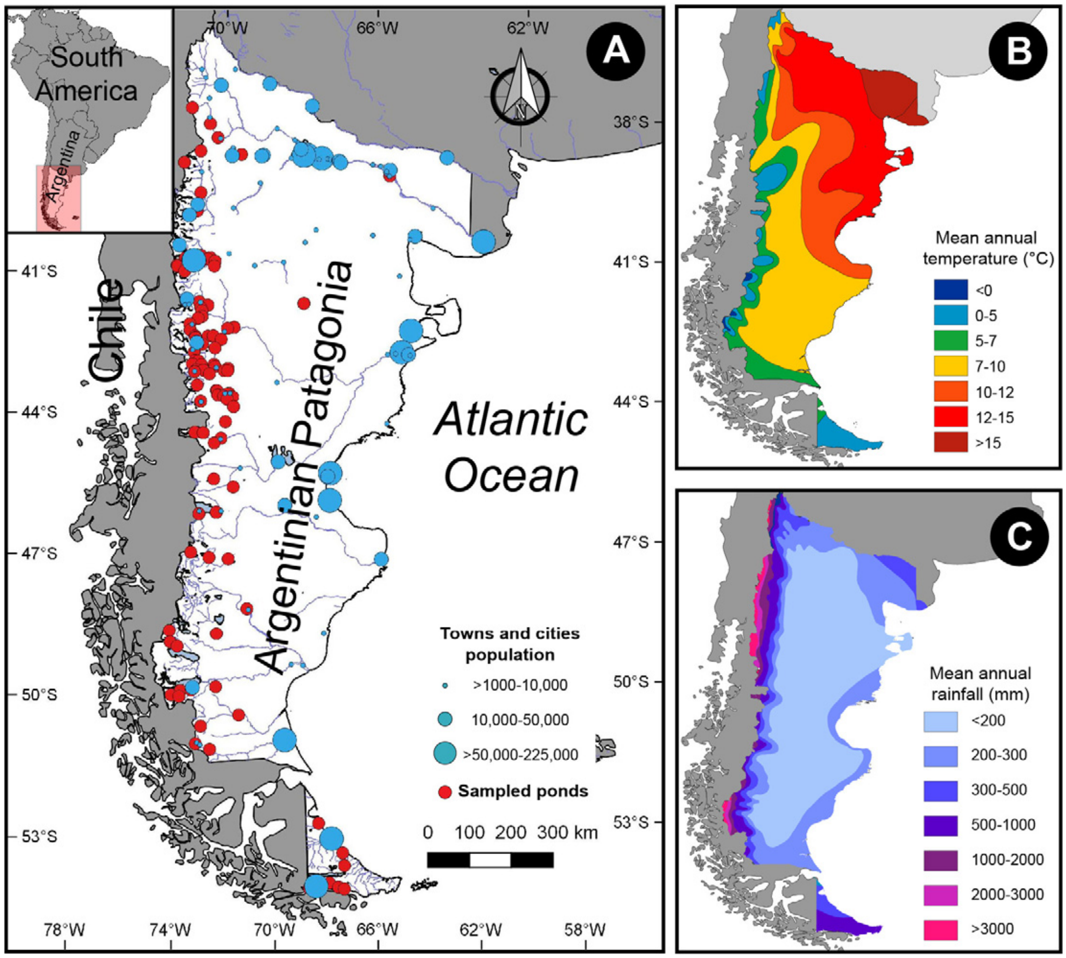

Fig. 1. (A) Map of Patagonia region, Argentina, showing the locations of the 109 ponds assessed in this study. Cities and towns with >1000 inhabitants are also represented. (B) Mean annual temperature and (C) rainfall are also represented.

characterizes both polar and westerly winds. The strong westerly winds that blow in Patagonia decrease the perception of the mean annual temperature (wind chill) by 4.2 °C over the whole region (Coronato, 1993).

The west-east rainfall gradient has shaped two main phytogeographical provinces: the Sub-Antarctic Forest (hereafter called "forest") and the Patagonian Steppe (hereafter called "steppe"). Along the gradient of decreasing precipitation, starting from the Sub-Antarctic forest border, grass steppes give way to shrub-grass steppes, and those to deserts. The forest is dominated by evergreen (*Austrocedrus chilensis*, *Nothofagus dombeyi* and *Maytenus boaria*) and deciduous trees species (*Nothofagus pumilio* and *Nothofagus antarctica*). The shrub and herbaceous strata are characterized mainly by *Chusquea culeou*, *Berberis microphylla*, *Lomatia hirsuta*, *Schinus patagonicus*, *Diostea juncea*, *Fuchsia magellanica*, *Alstroemeria aurea*, *Mutisia spinosa* and *Mutisia decurrens*. The lack of precipitation on the steppe causes vegetation coverage of xerophytic forms, dominated by an herbaceous-shrub-like steppe (*Mulimun spinosum*, *Stipa* spp., *Senecio* spp., *Colletia spinosissima*, *Adesmia* sp., *Fabiana imbricata* and *Poa* sp.) (Tell et al., 1997). Mallines in arid and semiarid areas represent 30 to 40% of the forage supply. These wetlands are dominated by a perennial C_3 tussock grass, *Festuca pallescens*, and the spaces among tussocks are dominated by exotic herbs such as *Taraxacum officinale*, native graminoids such as *Juncus balticus* and *Carex gayana*, and C_3 grasses, especially the exotic *Poa pratensis* (Boelcke, 1957). The colder areas in Patagonia have also acidic bogs, mainly dominated by *Sphagnum*. These bogs are especially widespread in the Tierra del Fuego island (Brinson and Malvárez, 2002).

Patagonia has been mainly grazed by guanacos (*Lama guanicoe*) since the end of the Pleistocene until late in the 19th century, when domestic sheep were introduced (Soriano, 1956). Grazing by domestic herbivores is the most widespread land use in the area (Gaitán et al., 2011), where ponds are very important as water sources. Vegetation degradation is the main problem for the region as a whole and salinization, soil crusting and compaction are also important problems of rangeland ecosystem degradation (del Valle et al., 1998). Anthropogenic activities also include urban run-off, oil exploration and extraction, mineral extraction, and construction operations (e.g. road building).

2.2. Study location and ponds classification

The study included 109 freshwater Patagonian ponds (study sites). To ensure that the sampled ponds were representative of Patagonian climate/geomorphological (hereafter referred to as natural) and anthropogenic pressures, site location was determined at first according to the rainfall gradient, and distributed from the north 37°50′S to the south 54°50′S of Patagonia. Study sites are principally distributed in western Argentinian Patagonia, but they cover the main rainfall gradient (Fig. 1A). We combined previous a dataset of 26 ponds (Epele and Archangelsky, 2012), with data from 83 ponds surveyed specifically for this study. Water bodies were each sampled once, between 2006 and 2014, during late spring or early summer seasons (December–January).

We classified sites in order to find possible differences in natural (hydroperiod, hydrology, biome and aridity) and anthropogenic effects (disturbance and land use) (see Appendix A in the Supporting information), adding data from the fieldtrips and the background material provided by the governmental agency Instituto Nacional de Tecnología

Agropecuaria (INTA). Thus, each site will have five possible labels (three natural classifications and two anthropogenic) (Appendix A).

2.2.1. Natural classification

We classified ponds as forest sites when they were located at the Sub-Antarctic forest and steppe when they were not. This classification is mainly an expression of the Patagonian rainfall gradient. Pond hydroperiod was assigned according to observations throughout many years, maximum depth, water supply, and data collected from interviews of landowners and environmental managers. Thus, permanent ponds are considered those that never dry completely, and temporary ponds those with a hydroperiod between 6 and 12 months. We excluded ephemeral ponds from our survey. Ponds hydrology was classified as connected or hydrologically isolated following Mitsch and Gosselink (2015). Connected ponds were those hydrologically connected with river or stream channels by surface pathways, while isolated wetlands were those located in basins with little or no outflow, no adjacent deep water systems, and an apparent lack of channels that connect them to surface water bodies or other wetlands.

2.2.2. Anthropogenic classification

Most mallines were used as pasturelands for a mix of livestock types comprised of sheep, cows, and horses; thus we classified them as livestock. We also sampled ponds used for disposal of urban effluents (diffuse, non-point source), that were classified as urban (Appendix A, "Land use"). These sites plus those used as pasture lands were classified as impacted sites ("Disturbance classification"). Reference water bodies were those not or minimally impacted by anthropogenic activities. We choose fifteen water bodies (from a total of 31 reference ponds) from protected areas (National Parks, forest biome).

2.3. Pond assessment

Each site was surveyed once at approximately the same time of day, in order to make comparisons. We performed the measurements in the inundated zone of mallines (ponds). The geographic coordinates and the altitude of each pond were measured with a handheld GPS (Garmin Etrex 10), and checked later using the elevation model of Google Earth Pro software. To evaluate the influence of natural and anthropogenic gradients on ponds conditions, we also performed morphometric and water physicochemical measurements. Morphometric descriptors were length and width, pond area (Garmin Etrex 10 or Google Earth Pro, 2015), and mean depth (calibrated stick).

In situ we measured water temperature, conductivity, total dissolved solids, salinity, pH, dissolved and percentage oxygen, with a multiparameter probe (Hach sensION156). Using field titration procedure we determined alkalinity (APHA, 1998). For planktonic chlorophyll *a* (Chl-*a*) determination, we filtered a known volume of pond water (Sartorius GF/F filter). The filters were extracted in acetone and the extracts measured with a spectrophotometer. We estimated gravimetrically, total suspended solids (TSS) in water column by filtering a known volume of water through a pre-dried and pre-weighed Sartorius GF/F, and by measuring the dry weight of the residue (after dried 24 h at 105 °C).

For all nutrient parameters, water samples were collected in the field, immediately frozen, stored in dark and analysed within 3–6 months using standard methods (APHA, 1998). We sampled water by holding the water bottle vertically 10–20 cm below the surface of the water column and sampling three different zones of each pond. Total phosphorous (TP) and total nitrogen (TN) were analysed in water samples without filtering, and soluble reactive phosphorous (SRP), nitrate + nitrite (NO_3^- plus NO_2^-) and ammonium (NH_4^+) in field-filtered water (Sartorius, cellulose acetate filter). We calculated dissolved inorganic nitrogen (DIN) as the sum of nitrate, nitrite and ammonium. We also estimated the ratio TN:TP, to check the possibility of nutrient limitations.

For each pond, we computed Carlson's (1977) and Kratzer and Brezonik (1981) trophic state index (TSI), based on three parameters TP, TN and chlorophyll *a*. According to the values reached by the TSI, four categories can be distinguished (Carlson and Simpson, 1996): oligotrophic (TSI < 30), mesotrophic (TSI 30–60), eutrophic (TSI 60–80) and hypereutrophic (TSI > 80).

We visually assessed the percentage of plant cover, including both emergent and submerged species. That percent was estimated and classified among seven categories following Daubenmire (1968) (<1%, 1–5%, 6–25%, 26–50%, 51–75%, 76–99%, and 100%).

2.4. Landscape and climatic data

We assessed land cover variables including the percentage cover of the 100 m perimeter area around each pond (López et al., 2013). The adjacent land-cover categories used here were: (1) bare soil, (2) rocks, (3) agriculture, (4) steppe grasses, (5) mallín, (6) shrubs, (7) forest, (8) water (9) urban (including roads and buildings) and (10) bog. Satellite imagery (Google Earth Pro, 2015, accessed on April 2016), was combined with ground survey information to improve the accuracy of the classification system.

Using the precipitation model developed by Gaitán et al. (2014), we obtained information of mean annual precipitation (MAP) throughout the study area (available data from 2000 to 2011). Mean annual precipitation data was estimated until the sampling date, for the ponds that were sampled before 2011.

At each pond, we estimated air temperature using the level-3 MODIS global Land Surface Temperature (LST) and Emissivity 8-day data. These data are composed from the daily 1-kilometer LST product and stored on a 1-kilometer sinusoidal grid as the average values of clear-sky LSTs during an 8-day period. MOD11A2 is composed of daytime and night-time LSTs, and provided information from January 2000 to the accessed date (April 2016). We used MOD11A2 data to obtain mean annual temperature, after adding day and night LST data. As we did with the variable precipitation we used the available data until the sampling date.

We used two MODIS vegetation indices to monitor spatial variations in vegetation among the study sites (MOD13Q1). These were the normalized difference vegetation index (NDVI) and the enhanced vegetation index (EVI), which is produced on 16-day intervals and at 250 m × 250 m pixels. We used NDVI and EVI, to perform spatial comparisons of sites regarding to vegetation canopy greenness, a composite property of leaf area, chlorophyll and canopy structure. We averaged each index (year) to obtain a mean annual value. Values were averaged from January 2000 to each sampling date.

2.5. Data analysis

We evaluated the effect of natural and anthropogenic variability on pond water and landscape characteristics. For these analyses, we focused on two types of features: (1) variables that were sampled in situ, including ponds morphometric and physicochemical features: "pond variables"; and (2) variables related with the landscape scale assessment: "landscape variables".

We obtained descriptive summary measures in order to assess the variation ranges of media values and standard errors of both, pond and landscape variables. We also performed single non-parametric correlations tests (Spearman rank) to explore the relationships among variables using *corrplot* package (Wei and Simko, 2016) in the statistical software R version 3.2.3 (R Development Core Team, 2016). A significance level of 0.05 was used for all tests. Using the nonparametric Mann-Whitney *U* Test in the statistical software R version 3.2.3 (R Development Core Team, 2016), we performed pairwise comparisons within main categories (hydroperiod, hydrology, biome, disturbance and land use).

We performed three principal component analyses (PCA) in order to reduce the pond (PCA 1), the landscape (PCA 2), and both the pond + landscape variables (PCA 3), into a small number of principal components, and to detect landscape patterns at regional scale. Prior to analysis, we $\log_{10}$ (x + 1) transformed data (except pH) to improve normality, and for the same purpose we arcsine square root transformed percentage variables. In order to avoid biased or incorrect results in the PCA, we identified and eliminated redundant (e.g. NDVI and EVI) and unimportant (e.g. percentage of bare soil and bog) variables. Also, we checked for collinearity by examining the pairwise scatter-plots comparing covariates, and the bivariate correlations among all variables (selected threshold: $r \geq 0.7$). Chl-*a*, TSS and alkalinity were discarded from these analyses, since were not measured in all sites. We carried out the analysis in the statistical software R version 3.2.3 (R Development Core Team, 2016) using ade4 package (function: dudi.pca) (Chessel et al., 2004). We performed PCA analysis on the correlation matrix (by default: center = TRUE, scale = TRUE; where center: a logical value specifying whether the variables should be shifted to be zero centered, and scale: a logical value, if TRUE, the data are scaled to unit variance before the analysis). This standardization to the same scale, avoids some variables to become dominant just because of their large measurement units (e.g. conductivity) (Chessel et al., 2004).

We analysed effects of natural and anthropogenic influences on pond water, landscape characteristics, and pond + landscape variability using generalized linear models (GLM) with a Gaussian family distribution, and identity link function between the response variable and the linear predictor (Zuur et al., 2009). We tested models that included the hydrology, hydroperiod and biome (these three variables were used to represent the natural influences), and land use (this variable was used to represent the anthropogenic influences) as fixed effects. The axis (individual scores *li*) obtained from previous PCAs (Axis 1 from: PCA 1, PCA 2 and PCA 3) were the response variables in three separate linear model analysis. Models were evaluated with a manual backward stepwise selection procedure. To supplement parameter evidence of important effects, the model parameters were bootstrapped, and confidence intervals limits (CL) of parameter estimates were calculated. In the final model, we retained explanatory variables with CL excluding zero. Interaction terms between the significant variables were added to check if they contributed to a better fit of the model. To avoid collinearity between explanatory variables, we only allowed terms with variance inflation factors ≤ 4. The standardized residuals were plotted against normal quantiles to check for normality. Also, we calculated the percentage of explained deviance by each model as a measure of the explanatory power of the model (Zuur et al., 2009). Single non-parametric correlations tests were achieved to explore the relationships between the axis, and pond and landscape variables. Also, to better visualize the relationships among variables, we made boxplots of those pond and landscape variables that were highly correlated with the axis (selected threshold: $r \geq 0.6$) and the fixed effects retained in the models. Statistical analyses were performed using R software, Version 3.2.3 (R Development Core Team, 2016), boot (Canty and Ripley, 2014), car (Fox and Weisberg, 2011) and corrplot (Wei and Simko, 2016) packages.

Pond and landscape variables that were highly correlated with the axis were tested using Receiver Operating Characteristic (ROC) curves. We used the ROC curves to find the cut-off value that separate two different levels within main categories (hydroperiod, hydrology, biome and disturbance). Thus, we also evaluate mallín land cover, TSS and TN (all used to evaluate wetland status in previous studies), to find the cut-off value of each variable, that separate reference from impacted sites. As this analysis only allow pair comparisons, we used the binary classification of reference vs. impacted (not land use). Given the ROC curve for a classifier, the area under the curve (AUC) measures its overall diagnostic performance, and was used to test the precision of the models. We also calculated sensitivity and specificity of each model. Sensitivity correspond with the true positive score, meanwhile specificity refers to 1—false positive cases (negative cases correctly classified). Thus, in the case of disturbance, sensitivity and specificity describe the ability of a pond or landscape variable to correctly diagnose impacted ponds (grazed or urban used), when perturbation is actually present and to correctly dismiss perturbation when it is truly absent (see Dos Santos et al., 2011). ROC analysis was accomplished using R version 3.2.3 (R Development Core Team, 2016) with pROC package (Robin et al., 2015).

3. Results

3.1. Ponds and landscape features

The 109 studied ponds were shallow with a mean maximum depth average of 2 m; however, 90% of the ponds were shallower than 0.85 m (Table 1). Surface area was variable, ranging from 3.1 m^2 to 7.2 ha. Most ponds were very well oxygenated, with 75% of the sites showing values between 8 and 21.5 mg L^{-1}. The set of ponds displayed a large variability for other studied variables (Table 1), and included turbid ponds (high TSS) with low aquatic plant coverage and high values of chlorophyll *a*, to well vegetated ponds with clear waters (Fig. 2).

Table 1
Summary statistics for morphometric, water and landscape variables evaluated in 109 Patagonian ponds. The number of sites (*n*) in which each variable was measured is detailed.

	n	Mean ± SE	Min	Max
Landscape variables				
Altitude (m asl)	109	708.9 ± 37	2.0	1970.0
NDVI	109	0.4 ± 0	0.1	0.7
EVI	109	0.2 ± 0	0.1	0.4
LST (°C)	109	8.2 ± 0.3	0.5	16.5
MAP (mm)	109	550 ± 42.4	98.8	2724.6
Bare soil (%)	109	5.6 ± 0.9	0	56.9
Rocks (%)	109	0.2 ± 0.1	0	7.6
Agriculture (%)	109	0.5 ± 0.4	0	37.6
Steppe (%)	109	36.5 ± 3	0	96.1
Mallín (%)	109	29.5 ± 3.1	0	99.2
Shrub (%)	109	3.1 ± 0.9	0	51.8
Forest (%)	109	9.9 ± 2.1	0	96.9
Water (%)	109	7.4 ± 1	0	57.6
Urban (%)	109	5.4 ± 0.9	0	69.5
Bog (%)	109	1.8 ± 1	0	77
Pond variables				
Morphometric variables				
Mean depth (m)	109	0.5 ± 0.03	0.07	2
Pond area (m^2)	109	4131.3 ± 1002.3	3.1	72,463
Water variables				
Temperature (°C)	109	17.8 ± 0.5	8.1	33.5
Conductivity (μS cm^{-1})	109	393.8 ± 86.9	14.8	6610
TDS (mg L^{-1})	109	207 ± 49.9	7.3	4430
Salinity (‰)	109	0.2 ± 0.1	0	4.6
pH	109	7.4 ± 0.2	3.1	11
Dissolved oxygen (mg L^{-1})	109	10.6 ± 0.3	2.2	21.5
Dissolved oxygen (%)	109	115.3 ± 3.8	22.1	232
TN (μg L^{-1})	102	599.2 ± 119.9	45	10,514
NO_2^- + NO_3^- (μg L^{-1})	108	95.6 ± 41.5	0	3331.1
NH_4^+ (μg L^{-1})	108	70.9 ± 22.3	1	2269
DIN (μg L^{-1})	108	165 ± 49.9	6.5	4008.8
TP (μg L^{-1})	102	187.4 ± 43.5	6.1	3922
SRP (μg L^{-1})	109	77.8 ± 29.7	0	3062
TN:TP	102	6.4 ± 0.7	0.2	55.5
Alkalinity (meq L^{-1})	76	2040.8 ± 240.3	4.5	8240
TSS (mg L^{-1})	74	41.3 ± 18	0	1086
Chl-*a* (mg L^{-1})	77	8.9 ± 1.9	0	89.7
Aquatic plants (%)	109	68.8 ± 2.8	5	100
Eutrophication indexes				
TSI_{TN}	63	39.8 ± 1.2	9.7	88.4
TSI_{TP}	102	69.4 ± 1.5	30.3	123.5
$TSI_{Chl\text{-}a}$	63	45 ± 1.6	17	74.4

TDS: total dissolved solids; TN: total nitrogen; DIN: dissolved inorganic nitrogen; TP: total phosphorous; SRP: soluble reactive phosphorous; TSS: total suspended solids; Chl-*a*: chlorophyll-*a*; NDVI: normalized difference vegetation index; EVI: enhanced vegetation index; LST: land surface temperature; MAP: mean annual precipitation; TSI: trophic state index.

Nutrients concentrations showed large spatial variability with the maximum values reported in sites used for livestock breeding, and showing values of total nitrogen (TN) and total phosphorous (TP) higher than 1 mg L^{-1} (Table 1). Relationships between TP and soluble reactive phosphorous (SRP) were stronger than TN–DIN, suggesting that studied ponds have a higher P availability (Fig. 3). Nevertheless, TN:TP ratio data, indicated nitrogen limitation, values were lower than 14 in >90% of the ponds. Thus, TSI based in TP was discarded, because it overestimated the trophic levels in the set of analysed ponds (94% of the ponds would be eutrophic or hypereutrophic). Results of TSI based in TN and chlorophyll *a* are detailed in Appendix B. Both indices showed consistent results, meaning that most ponds were mesotrophic (58% $TSI_{Chl\text{-}a}$; 69% TSI_{TN}), with TSI_{NT} values better distributed among the 4 trophic categories.

In general, the quantitative analysis of land cover supported the two spatial approaches used for the study design and site selection: regional scale (Google Earth Pro), and local scale (visual observations). The land cover across the areas was dominated by steppe vegetation (43 ponds), mallín (35 ponds) and forest (8 ponds) (Table 1).

3.2. Relationships among pond and landscape variables

Latitude showed negative correlations with other landscape variables (altitude, MAP and LST), and also with pH (Fig. 3). Thus, those variables tended to show lower values toward the south. NDVI showed significant positive correlations with MAP and forest coverage. This last variable was negatively related with LST and pH. On the other hand, NH_4^+ displayed positive relationships with phosphorous forms.

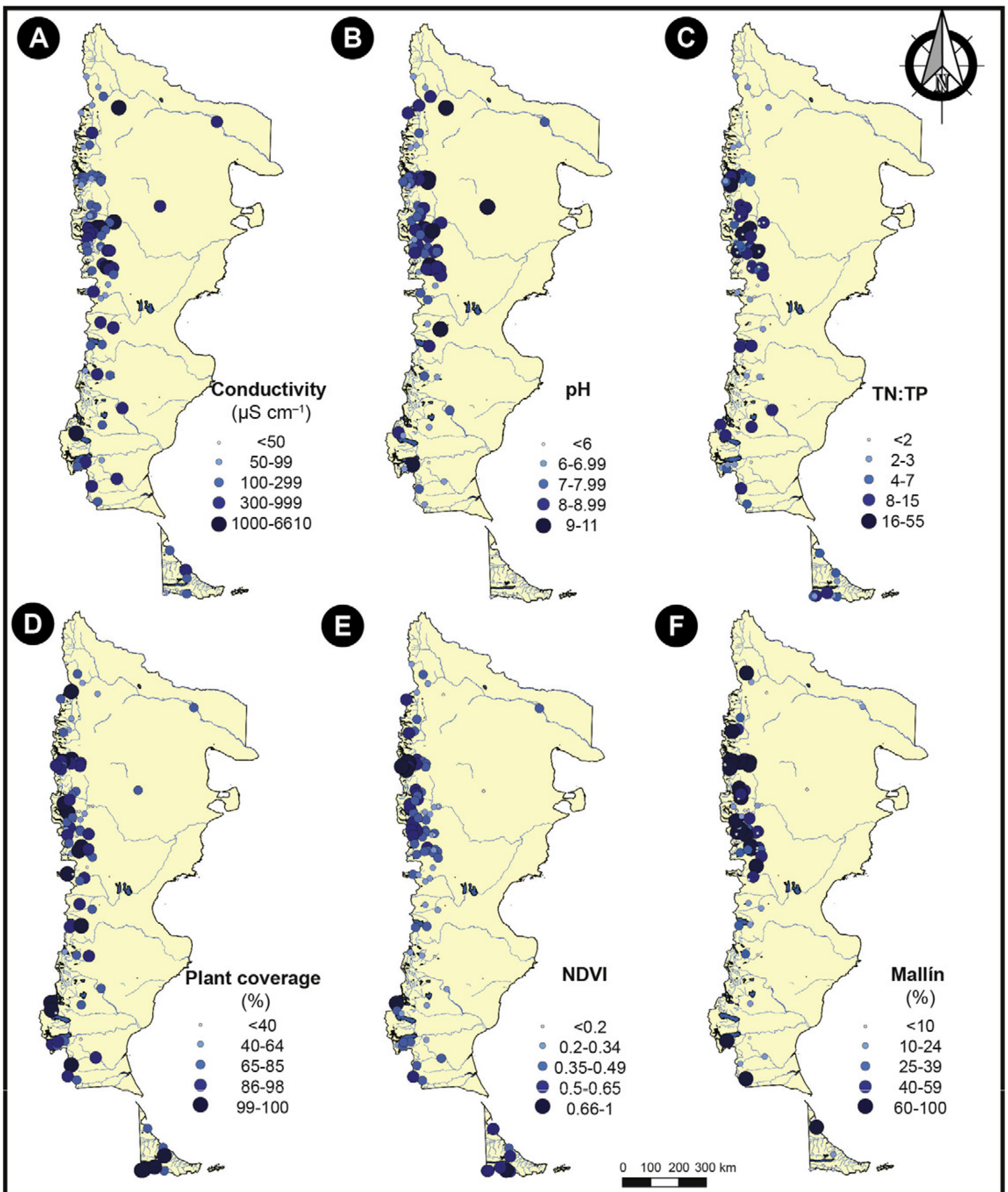

Fig. 2. Trends of water quality for (A) conductivity, (B) pH, (C) TN:TP, (D) Plant coverage, (E) NDVI (normalized difference vegetation index) and (F) mallín land cover in the Argentinian Patagonia.

Steppe cover was negatively correlated with mallín land cover and forest; showing higher land coverage in dryer and warmer sites. Moreover, Chl-*a* was strongly and positively correlated with TSS (not showed in the Fig. 3 because were recorded at 77 ponds), and was also correlated with $NO_2^- + NO_3^-$, NH_4^+ and TP. Alkalinity, was negatively correlated with NDVI.

3.3. Natural and anthropogenic patterns

A set of environmental variables were useful to distinguish among categories (Table 2). The cut off point for the most important environmental variables (estimated using the ROC curve methodology) (Table 3). Ponds showed conductivity, alkalinity and pH values significantly lower in forest and reference sites than in steppe and disturbed sites (Table 2). Landscape features were also suitable to discriminate between forest and steppe biomes. Steppe, water and bare soil land cover, and LST were higher in the steppe biome; meanwhile forest biome was characterized by greater forest (cut-off value: >2.4%) and shrubs coverage and, also higher NDVI and mean annual precipitation (MAP) (cut-off values: >0.5 and 437 mm, respectively). Moreover, aquatic plant coverage was higher at permanent, forest and reference ponds comparing with temporary, steppe and impacted (Table 2). Grazed ponds exhibited significantly higher cover of mallín and higher LST, than reference ones. Thus, sites were impacted when showed mallín land cover values higher than 11.6% (Table 3). TN and TSI_{TN} showed a decreasing trend from impacted (TN > 490 μg L^{-1}; TSI > 44.2) to reference ponds. Furthermore, this index based in TN and TP allowed to distinguish urban ponds.

3.4. Effects of natural and anthropogenic influences on pond and landscape features

The first three axes of the PCA 1 explained 61.5%, meanwhile the same axes of PCA 2 and PCA 3 explained 62.2% and 45.7% respectively (Appendix C). When considering natural and anthropogenic variables simultaneously, the landscape (model PCA 2), and pond + landscape (model PCA 3) variability was associated only with natural effects (biome, and biome and hydrology, respectively). In contrast, for pond water variability (model PCA 1), the best model included both the natural (biome and hydrology) and anthropogenic (land use) effects (Table 4). Model parameter estimates and confidence intervals indicated a negative effect of biome_steppe and land use_urban, and a positive effect of hydrology_connected and land use_reference in model PCA 1 (Table 4). For models PCA 2 and PCA 3, model parameters showed a negative effect of biome_steppe, and also a positive effect of hydrology connected (model PCA 3) (Table 4).

The relationships between the axis, and pond and landscape variables showed a negative association with conductivity, NH_4^+, TP and SRP for the model PCA 1. For model PCA 2, the response variable was negatively related with steppe, and positively with forest, MAP and NDVI, whereas the response variable from model PCA 3, showed a negative association with conductivity, TP and SRP, and a positive one with MAP and NDVI (Fig. 3). Sites located on the steppe showed greater conductivity values, and lower MAP, NDVI and forest values (Fig. 4A). According to the best-fitting models, the explanatory variable biome_steppe had a negative effect on the response variable (Table 4), and this could be translated into greater values of conductivity in these aquatic systems (for models PCA 1 and PCA 3), or sites with lower values of MAP, NDVI and forest (for models PCA 2 and PCA 3) (Fig. 3, Table 4). Connected sites had lower TP and NH_4^+ values compared with isolated ponds (Fig. 4B). The explanatory variable hydrology_connected had a positive effect on the response variable for models PCA 1 and PCA 3 (Table 4), thus lower TP and NH_4^+ values could be recorded in those ponds. The model PCA 1, was the only one that retained the explanatory variable land use. Conductivity and TP values were greater in sites subjected to urban land use compared with reference sites (Fig. 4C). Thus, the negative effect of urban land use on the response variable for model PCA 1, could be translated into ponds with greater conductivity and TP values (Fig. 3, Table 2).

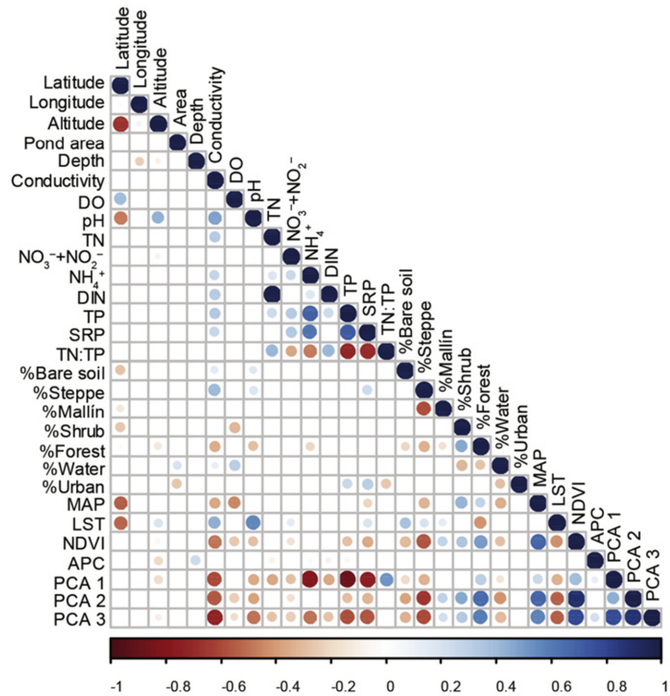

Fig. 3. Spearman rank correlation matrix for pond and landscape variables. First axis of PCA 1, PCA 2 and PCA 3 are also represented. Blue and red circles represent positive and negative relationship respectively. The size of the circles indicates the magnitude of the correlation, and when are present indicates $p < 0.05$. DO: dissolved oxygen; TN: total nitrogen; TP: total phosphorous; SRP: soluble reactive phosphorous; MAP: mean annual precipitation; LST: land surface temperature; NDVI: normalized difference vegetation index; APC: aquatic plant coverage.

4. Discussion

4.1. Pond water features landscape characteristics

Wetlands provide many important functions and ecosystem services in the landscape, but anthropogenic impacts have led to considerable changes in chemical cycling in many of them (Mitsch and Gosselink, 2015). There are a number of key drivers influencing water quality such as climatic conditions, geological weathering, hydrologic and geomorphic processes, physical, chemical and biological processes, and anthropogenic land use (Carr and Nearly, 2008). The combination and interaction of these processes produces dynamic systems that vary spatially within landscapes, and require careful use to ensure ecosystem functions. Our study presents the evaluation and interpretation of a broad scale dataset, about the water quality of freshwater ponds of Argentinian Patagonia, in a complex scenario of climatic and anthropogenic variability.

In our study, water conductivity decreased from de east to the west, meanwhile pH and dissolved oxygen (DO) varied associated with the latitude. Previous studies in Patagonia have demonstrated a positive relationship of groundwater conductivity, pH and cation concentrations, as the precipitation decreased (Chimner et al., 2011), pattern also exposed for other temperate regions (Stewart and Kantrud, 1971). Our study revealed a negative relationship between conductivity and mean annual precipitation. Since it would be naturally influenced (e.g., aridity of the ponds surrounded area) and at the same time positively affected by anthropogenic activities (mainly livestock breeding) (Schmutzer et al., 2008), it should be cautiously used to asses ponds water quality. On the other hand, pH tended to decrease to the south, associated to the presence of acidic bogs in the Tierra del Fuego Island (located at the southern extreme of South America). The DO is commonly used to evaluate freshwater quality (Sánchez et al., 2007), however Patagonian ponds where well oxygenated, even when the sites were disturbed. This pattern was found in previous Patagonian studies (Kutschker et al., 2014), and could be explained for the fact that most of our sampled ponds were shallow, thus affected by the constant and strong winds, and also due to the daytime release of oxygen by aquatic plants and algae. This feature augmented to the south, probably associated with lower mean annual temperatures.

Another important factor influencing Patagonian ponds ecology is nutrients. Nutrient inputs to ecosystems have increased over the past century in many parts of the world. The resulting nutrient enrichment often has significant effects, including increased productivity, higher rates of nutrient leaching and shifts in the dominance, and composition, of species (Vaithiyanathan and Richardson, 1999). As was predicted by Abell et al. (2012) for the Patagonian latitudes, the absolute amount of nutrients was relatively low. Nevertheless, the TN:TP ratio was unexpectedly low (lower than 15 at 93% of the sites), suggesting N limitation. Naturally nutrient-poor (i.e. oligotrophic) systems react more drastically than do naturally eutrophic systems (Verhoeven et al., 2006). Thus, our results suggest that special attention should be dedicated to potential sources of N contamination (at least twelve ponds would be eutrophic or hypereutrophic; $TSI_{TN} > 50$), since could be the limiting nutrient, systems might be less resilient to a larger change in N.

4.2. Measures to determine a reference pond

Given the myriad of available water pond and landscape measures, ecologists face the important task of identifying a subset of statistically independent metrics that allow quantification of the anthropogenic impacts (Foley et al., 2005). All ecological studies conducted in Patagonia were performed after the introduction of exotic species, both terrestrial (e.g., livestock) and aquatic (e.g., trout), and this problem confounds separation of natural from anthropogenic effects. The task is not trivial, and there might not be easy to determine a pool of variables that can capture the effects of urban and livestock impacts on Patagonian wetlands. Consequently, from the total of 15 pond and 19 landscape features assessed, only total suspended solids (TSS) could appropriately and significantly separated between reference and impacted ponds. Many natural factors (e.g., shallowness, wind exposure, frequent mixing, bioturbation) and anthropogenic (e.g. livestock trampling) can affect water turbidity (Fairchild et al., 2005). Nevertheless, since TSS increases were not associated with hydrology, hydroperiod and biome classifications, we consider that turbidity mostly augmented by the stocking trampling in ponds shorelines and urban land use.

We also propose TN (including TSI_{TN}) and mallín land coverage as reliable variables to assess ponds health, since both are features easy to determine, significantly separate reference and impacted ponds, but are not strongly affected by natural variability. Thus, to assess Patagonian water status we recommend the measure of TSS (values $< 8.05\ mg\ L^{-1}$ in reference ponds) and TN (values $< 490\ \mu g\ L^{-1}$ in reference ponds) in the water, and evaluate the mallín coverage in a 100 m radius from the pond (values < 11.6% in reference ponds). Golluscio et al. (1998) recognized that Patagonian mallines are such an important

Table 2
Statistical comparisons between 109 Patagonian ponds natural and anthropogenic categories.

	Natural			Anthropogenic	
	Hydroperiod	Hydrology	Biome	Disturbance	Land use
Landscape variables					
Altitude					
NDVI	$P > T^{*}$		$F > S^{***}$		
LST			$S > F^{***}$	$Im > R^{***}$	$L > R^{***}$
MAP			$F > S^{***}$		
Steppe			$S > F^{***}$		
Mallín		$C > I^{**}$		$Im > R^{**}$	$L > R^{***}$
Shrub			$F > S^{***}$		
Forest			$F > S^{***}$	$R > Im^{*}$	$R > L^{*}$
Water			$S > F^{*}$		
Pond variables					
Mean depth	$P > T^{***}$			$R > Im^{*}$	$R > L^{*}$
Pond area		$I > C^{***}$			
Temperature		$I > C^{***}$			
Conductivity			$S > F^{***}$	$Im > R^{***}$	$U,L > R^{**}$
pH			$S > F^{***}$	$Im > R^{***}$	$U,L > R^{**}$
Dissolved oxygen			$S > F^{*}$		
TN	$T > P^{*}$			$Im > R^{**}$	$U > L > R^{*}$
$NO_2^- + NO_3^-$		$I > C^{**}$			$U > L^{*}$
NH_4^+	$T > P^{*}$	$I > C^{**}$			
DIN		$I > C^{***}$			
TP		$I > C^{**}$			$U > L,R^{*}$
SRP			$S > F^{*}$		
TN:TP		$C > I^{**}$			
Alkalinity	$T > P^{*}$		$S > F^{***}$	$Im > R^{***}$	$L > R^{***}$
TSS				$Im > R^{***}$	$U > R^{*}$
Chl-*a*					
Aquatic plants	$P > T^{**}$		$F > S^{**}$	$R > Im^{*}$	$R > L^{*}$
TSI_{TN}	$T > P^{*}$			$Im > R^{**}$	$U > L,R^{*}$
TSI_{TP}		$I > C^{**}$			$U > L,R^{*}$
$TSI_{Chl\text{-}a}$	$T > P^{*}$				

Statistically significant differences Mann-Whitney U test ($^{*}\ p < 0.05$; $^{**}\ p < 0.01$; $^{***}\ p < 0.001$). P: permanent; T: temporary; C: connected; I: isolated; F: forest; S: steppe; R: reference; Im: impacted; L: livestock; U: urban.

Table 3
Summary statistics for the cut-off (ROC curve) analysis, based on 109 Patagonian ponds variables. Biome, hydrology, and disturbance are the natural and anthropogenic ponds classifiers. The significance (area under the curve (AUC)), sensitivity and specificity of each analysis are included. Scenarios with AUC < 0.5 show "ns" (non-significant).

Classification	Variable	Pond labels	Cut-off value	AUC	Specificity	Sensitivity
Biome	NDVI	F > S	0.51	0.86	0.69	0.92
	MAP	F > S	437	0.84	0.82	0.70
	Forest	F > S	2.4	0.79	0.67	0.87
	Conductivity	S > F	98.7	0.8	0.67	0.83
Hydrology	NH_4^+	I > C	14.9	0.61	0.62	0.65
	TP	I > C	161.1	0.63	0.82	0.4
Disturbance	Mallín	Im > R	11.6	0.68	0.66	0.71
	Conductivity	Im > R	93	0.77	0.80	0.65
	TN	Im > R	490	0.66	0.38	0.96
	TP			ns		
	TSS	Im > R	8.05	0.66	0.42	0.89
	TSI_{TN}	Im > R	44.2	0.66	0.38	0.96

Variable abbreviations: NDVI: normalized difference vegetation index; MAP: mean annual precipitation (mm); TN: total nitrogen ($\mu g\ L^{-1}$); TSS: total suspended solids ($mg\ L^{-1}$); TSI: trophic state index. Pond label abbreviations: P: permanent; T: temporary; C: connected; I: isolated; F: forest; S: steppe; R: reference; Im: impacted.

Table 4
Generalized linear models results for the effect of natural and anthropogenic influences on pond (Model PCA 1), landscape (Model PCA 2), and pond + landscape (Model PCA 3) variability. Explanatory variables, parameter estimates (β) (±Standard Error), and confidence intervals (CL) are shown.

Model	Explanatory variables	β ± SE	t value	*p*-Value	CL: lower	CL: upper
PCA 1	Intercept	0.2 ± 0.3	0.7	0.5	−0.4	0.8
	Biome_Steppe	−1 ± 0.3	−3	0.004	−1.6	−0.4
	Hydrology_Connected	1.3 ± 0.4	3.2	0.002	0.5	2.1
	Land use_Reference	0.8 ± 0.4	2.2	0.03	0.09	1.4
	Land use_Urban	−1 ± 0.6	−1.6	0.1	−1.7	−0.3
PCA 2	Intercept	1.7 ± 0.2	8.6	$8.4e^{-14}$	1.3	2.1
	Biome_Steppe	−2.6 ± 0.2	−10.7	$2e^{-16}$	−3.1	−2.1
PCA 3	Intercept	1.7 ± 0.3	6.4	$4.7e^{-9}$	0.9	2.4
	Hydrology_Connected	0.9 ± 0.4	2.3	0.03	0.1	1.6
	Biome_Steppe	−2.9 ± 0.3	−8.8	$3e^{-14}$	−3.5	−2.2

Explanatory variables with CL including zero were excluded from the final model. Percentage of explained deviance by each model: 22% (PCA 1), 52% (PCA 2), and 42% (PCA 3).

forage resource that livestock density is positively correlated with their proportion in the landscape. Such management might be unsustainable over time, even more if predictions of precipitations decreases are fulfilled (Crego et al., 2014). Hence, in the landscape matrix it would be desirable that ponds having greater adjacent cover of mallín be specially considered in conservation policies and actions.

In Patagonia, the population is mainly concentrated in cities and towns, causing numerous impacts to the adjacent aquatic environments (Miserendino et al., 2011). Urban development results in the increased production of runoff, consequently increasing discharges of nutrients (Wang et al., 2014). In urban land used ponds, we detected higher concentrations of TP (PCA 1 model), even higher than livestock used ones. The TP of the ponds seems to be naturally in excess, but urban land use in Patagonia increased it deteriorating water quality.

4.3. Rainfall gradient, a strong predictor of environmental variability

Our findings pointed the importance of the forest and steppe biomes (or Andes Mountains-steppe) as the main drivers of the Patagonian ponds status (retained in all in GLM models). These biomes are primarily determined by the west-east rainfall gradient, affecting not only landscape features (e.g. MAP and NDVI), but also some water ponds attributes (e.g., conductivity). Various studies have conducted intensive investigations of relationships between land uses and water quality, with most reporting strong ties between them (e.g., Tong and Chen, 2002). Nevertheless, we must consider distinct regional or local characteristics of Patagonia human aspects (e.g., farming patterns, crop types, and irrigation and drainage systems) and environmental conditions (e.g., precipitation) that might influence these relationships.

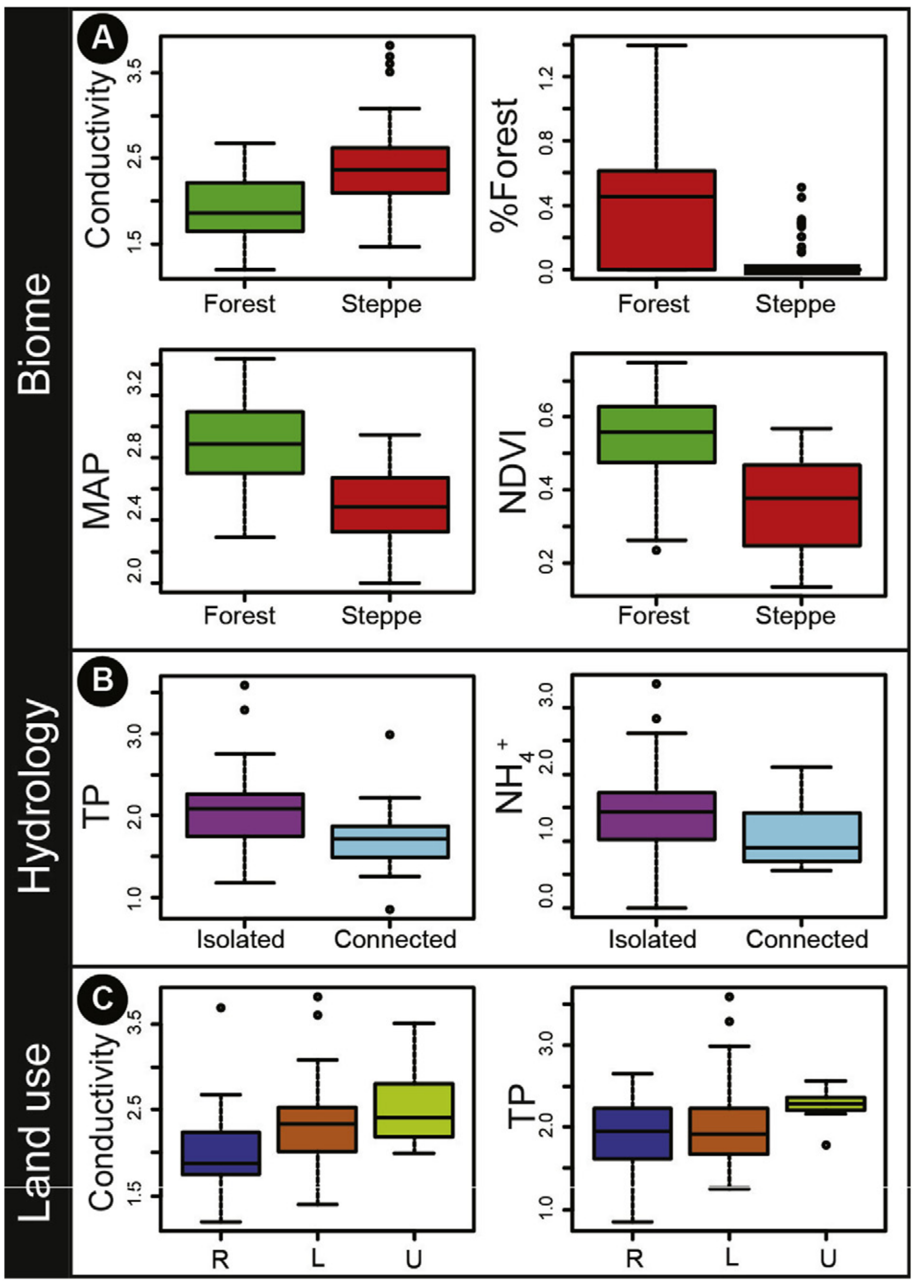

Fig. 4. Pond and landscape variables highly correlated with the PCA axis (selected threshold: r ≥ 0.6) and the fixed effects retained in the three models, based in 109 Patagonian ponds data. (A) Ponds located at forest or steppe (Biome); (B) Isolated and connected ponds (Hydrology); (C) Reference (R), livestock grazed (L) and urban (U) ponds (Land use). TP: total phosphorous; MAP: mean annual precipitation; NDVI: normalized difference vegetation index.

Livestock grazing in Patagonia is driving a vegetation homogenization that could have profound impacts on the desertification process (Paruelo et al., 2004). Kutschker et al. (2014) and Epele and Miserendino (2015), studied 30 mallines of the NW Chubut Province (a Patagonian Province). Those mallines were used as pasture lands for livestock, and some were highly impacted, showing high nutrient values. Despite nutrients are good predictors of anthropogenic disturbance (Trebitz et al., 2007), and in our study we demonstrated that were useful to segregate between reference and impaired sites, nutrient effects were subordinate to natural variability (measured as: biome and hydrology of ponds) at a higher Patagonian scale. This region is a particular scenario, with characteristics that distinguish it from other regions of the world. Is sparsely populated and mainly impacted by livestock breeding, an activity that affected the ecosystem quality, but for sure is less intense than for example, the agriculture land use (Gleason et al., 2008) and drainage of the Prairie Potholes wetlands (National Wetlands Working Group, 1988), or urban land use in other temperate regions such as the UK (Gledhill et al., 2008). Even at those heavily impacted regions, natural variability (e.g. precipitation and temperature) plays a major role in water quality wetlands (Dahl, 2014), outweighing influences of anthropogenic land use practices (Tangen et al., 2003). Thus, at Patagonian scale, ponds water quality would be strongly dependent of patterns that hydrology and principally rainfall gradient attributes impose on them.

5. Conclusions

South America has a long way to go in order to preserve ponds integrity and it is clear that at present, there are not strong actions to protect them in Patagonian region, and this is particularly marked at the arid zone (steppe). Moreover, in a climate change scenario, predictions for southern South America indicate a decrease in the surface area of wetlands (Crego et al., 2014) and this is due, in part, to the unsustainable management of natural resources (Newbold et al., 2015). Our results intended to highlight the importance of Patagonian ponds, within a complex mixture of anthropogenic and natural landscapes. For further studies would be desirable to improve the understanding of how natural and anthropogenic factors constrain pond water conditions at different temporal scales (e.g., seasonal or inter annual). However, we consider that this study, performed at regional scale level, synthetized spatial patterns of Patagonian pond water quality, and disentangled natural and anthropic factors finding that the main one would be rainfall gradient. Water resource managers may target landscape and pond factors for the improvement of water quality management efforts, including adequate livestock (e.g., controlled grazing in the surrounding catchment areas) and practices to manage urban effluent.

Acknowledgments

We thank INTA personnel for access and field assistance to some of the study sites, particularly V. Nakamatsu, G. Ciari and W. Opazo. We also thank C. Brand, C.Y. Di Prinzio, M. Archangelsky, Y. Assef, M. Grech, R. Suarez, A.M. Kutschker and N. Nakamura for the assistance in the field and lab work. We thank the private landowners who gave us gate and road access. J.J. Gaitán and M. Schiaffini, helped with the estimation and interpretation of the precipitation models. D.A. Dos Santos helped with the models selection. We thank Dr. Alistair Blachford for English language revision and helpful comments. This work was partially supported by the project R/8, No. 108/2013 UNPSJB. L.B.E, L.M.M., M.G.G., L.L. and M.L.M. were funded by CONICET. We thank the National Parks and Provinces administrations for sampling permits. The MOD13Q1 and MOD11A2 were courtesy of the NASA EOSDIS Land Processes Distributed Active Archive Center (LP DAAC), USGS/Earth Resources Observation and Science (EROS) Center, Sioux Falls, South Dakota. We would also like to thank reviewers of this paper for their helpful suggestions and comments. This is Scientific Contribution no. 134 from LIESA.

Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.scitotenv.2017.09.147. These data include Google map of the most important areas described in this article.

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