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Baseline

Evaluation of water quality and heavy metal concentrations in the RAMSAR Wetland El Yali (Central Chile, 33°45′S)



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ABSTRACT

The EYNR is the most important wetland in central Chile because it is protected as a RAMSAR site. It includes coastal lagoons, estuaries and saltmarshes, sustaining an important biodiversity. The chemical complexity was described using water and soil samples, which are characterized by high levels of alkalinity and soil cations. In addition, high concentrations of Cu $(0.01-0.080\,\mathrm{mg\,L^{-1}})$ and Pb $(0.120-0.566\,\mathrm{mg\,L^{-1}})$ in water were measured. Using a simplified index of water quality for oxygen demand, the ecological status of the wetland was classified as bad quality due to the existing use of land. Multivariable analyses and heavy metal index classified this wetland as having low to intermediate deterioration due to the combination of heavy metals. If this trend is allowed to continue unabated, the food web complexes in this wetland are likely to be at the highest risk of induced heavy metal contamination.

Wetlands are among the most productive and vulnerable ecosystems in the world, sustaining an important biodiversity of flora and fauna, including rare and threatened species (Mitsch and Gosselink, 2000; Van den Broeck et al., 2015; Wu et al., 2018). Additionally, wetlands perform many important ecosystem services, including water storage, mitigating floods and storms, controlling erosion and playing an important role in carbon sequestration by preventing long-term build-up of organic carbon (i.e. blue carbon ecosystem) (Tockner and Stanford, 2002; Junk et al., 2006; Silva et al., 2007; Daniels and Cumming, 2008; Kaur et al., 2014; Bassi et al., 2014; Fu et al., 2015; Mojica et al., 2018; Román et al., 2018). Wetlands also are extremely sensitive environments with regard to climate change due to the impacts of sea level rise (Gilman et al., 2008; Erwin, 2009; Mojica et al., 2018) or tsunami inundation (Morton et al., 2011). However, wetlands are negatively influenced by different types of environmental alterations, which may include the continuing encroachment of urban development on wet heaths and seasonal wetlands and wetland-associated habitats or land reclamations, causing changes in the hydrological regimes, eutrophication, nutrient enrichment, salinization, and pollution with organic compounds, pesticides and heavy metals (e.g. Davis and Froend, 1999; Lee et al., 2006; Li et al., 2015; Tian et al., 2016; Wu et al., 2018).

Among the short-term anthropogenic impacts on coastal wetlands, heavy metal pollution is one the most important due to potential biomagnification in food webs. Heavy metals such as copper (Cu), lead (Pb) and cadmium (Cd) are persistent and potentially toxic in aquatic ecosystems, and most heavy metals are bioaccumulated in aquatic food webs (Peters et al., 2013; Tang et al., 2014; Singh et al., 2017). Heavy metals may enter aquatic ecosystems in different ways, including industrial or domestic sewage, storm runoff, leaching from landfills, shipping and harbor activities and atmospheric deposits, thereby affecting water quality and the trophic structure and functions of pelagic and benthic communities (Nair et al., 2006; Peters et al., 2013; Tang et al., 2014).

El Yali National Reserve (EYNR) is a wetland complex and one the most important freshwater ecosystems in the semiarid region of Central Chile, which includes coastal lagoons, estuaries, streams and saltmarshes (Figueroa et al., 2009; Vidal-Abarca et al., 2011; Fariña et al., 2012; Flores-Toro and Contreras-López, 2015). The EYNR is a euryhaline ecosystem with eutrophic or hypertrophic status due to high levels of nitrogen and organic phosphorus input from eucalyptus forests, livestock farms and wastewater inputs (Vidal-Abarca et al., 2011). The EYNR is a RAMSAR site of international significance (Möder et al., 2002; Flores-Toro and Contreras-López, 2015). In fact, the EYNR is protected by Chilean law as a national reserve and, since 1996, as a RAMSAR site (RAMSAR, 2004). However, the main regulation for water quality is related to physical, chemical and bacteriological properties

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for drinking water (NCh409/2005 norm) or for irrigation water quality (NCh1333 norm), and there are not secondary environmental quality standards, generating important problems in the water quality regulation framework in the country (Valdés-Pineda et al., 2014). More than 110 migratory species have been recorded in this wetland, which is also one of the most relevant sites for both Nearctic and Neotropical shorebirds, but vulnerable to hydrological change (Vilina and Lopez-Calleja, 1992; Vilina and López-Calleja, 1996; Dussaillant et al., 2009; Fariña et al., 2012). The EYNR is also highly influenced by the hydrological regimen, whose precipitation trends show high interannual variations due to the periodic occurrence of the El Niño Southern Oscillation (ENSO) cycle, increasing rainfall and therefore affecting coastal habitat irrigation (Fariña et al., 2009). Despite being an ecosystem of great cultural and ecological significance, important weaknesses can be identified in its conservation status (Flores-Toro and Contreras-López, 2015). Henceforth, the purpose of this study was to evaluate water quality and heavy metal concentrations using multivariable analyses to provide an insight into the current pollution status, which may help to monitor the patterns of bioaccumulation and biomagnification of heavy metals in this ecosystem.

Soil and water sampling were carried out at twelve stations covering four water bodies in the EYNR wetland complex (Fig. 1; Table 1). Water

samples were collected at Albufera Lagoon (W1 and W2), Yali River (W3), Colejuda Lagoon (W4) and Matanzas Lagoon (W5, W6 and W7), and soil samples were collected at five stations: Albufera Lagoon (S1), Colejuda Lagoon (S2) and Matanzas Lagoon (S3, S4 and S5).

In this study, water samples (5 L) were collected just below the surface water in the wetland using acid-cleaned polyethylene bottles in summer (January 2013) and winter (August 2013), and they were preserved at 4 °C before analysis. At all sampling stations, surface water temperature, depth, pH, alkalinity, conductivity, salinity and water hardness were measured (Table 2). For water quality, total suspended solids (TSS), dissolved oxygen (DO), biochemical oxygen demand (BOD₅), nitrate (NO₃⁻), nitrite (NO₂⁻), ammonium (NH₄⁺), phosphate (PO₄⁻³), nitrate/phosphate ratio (NO₃⁻/PO₄⁻³), total organic phosphorus (TOP), oil-fats, sodium (Na), potassium (K), F-ratio (Na/K), copper (Cu) and lead (Pb) were measured. In addition, pH, salinity, electrical conductivity, temperature and DO were measured in situ. All water analyses described above were conducted according to Standard Methods (APHA, 1985). DO was measured using in situ electrodes (JENWAY Model 9070), which were calibrated with the Winkler method (Williams and Jenkinson, 1982). To classify the water quality of different water bodies in the study area, a simplified index of water quality (IWQ) was used (Queralt, 1982). The IWQ was calculated using

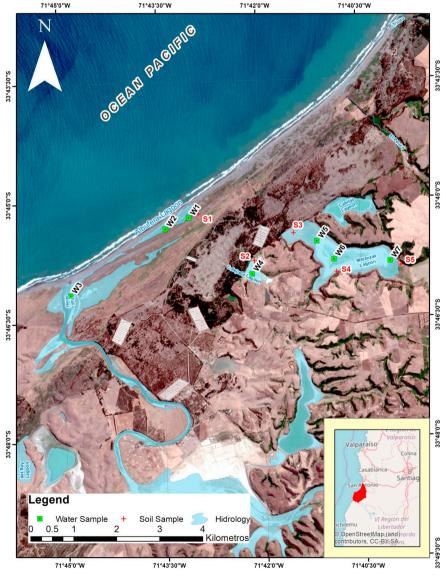


Fig. 1. Locations of the sampling sites in the wetland complex of El Yali (Central Chile). Water samples (W) and soil samples (S).

 Table 1

 Water sampling sites and hydrological and chemical parameters measured in the study area.

Location Station Latitude ("S) Longitude ("W) Date Depth	10 10 10 10		SWT AT Cla (°C) (°C) (°C) 22.2 0.0 39. 25.0 0.0 39. 21.3 0.0 22. 28.1 -0.1 20.	ΔΤ* Clarity (°C) (cm) 0.0 39.0 0.0 22.0 0.0 22.0	Hd lity pH 8.5 8.5 8.9 8.9	Alkalinity Hardness (mg L ⁻¹) (mg L ⁻¹) 160 8500 460 7500 420 8250 200 13,000		Salinity (mg L ⁻¹) 37,000 37,000 43,000	COD (mgL ⁻¹) (22.4 (20.8 ((mgL ⁻¹) (0.22 5 0.24 6 0.34 4	DO CO (mgL ⁻¹) (6.5 6 6 6.5 6 6.5 6 6.1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	Conductivity (µS/cm) (65,800 56,500 183,000	Classification IWQ (salinity) Mesohaline 52.9 Mesohaline 48.9 Mesohaline 48.9		Ecological status Bad quality Bad quality Unacceptable Unacceptable
ry 16, ry 16,	1	148 2	22.8 – 5	-5.5 35.0 -6.2 33.0	9.5	550	2400 5	5000	17.6 (0.01 6	6.7 8	8740	Mesohaline Hipohaline	54.6	Bad quality Bad quality
January 16, 2013	115	. 4		~									Hipohaline	54.8	Bad quality
71'43'04.30" August 28, 89 2013 71'43'25.08" August 28, 68			15.9 13.1 16.1 12.9	.1 18.5 .9 38.0	8.5	300	5600 3	33,200	33.6	1.15 8	8.0 2 9.7 2	28,300	Hipohaline Hipohaline	54.1	Bad quality Bad quality
t 28, 24		5	19.6 8.0	24.0	8.8	250	0009	37,200	46.4	1.18 2	21.5	44,400	Mesohaline	54.6	Bad quality
71°42′08.20″ August 28, 22 23 2013		83	23.3 4.7	22.0	8.3	300	4100 4	47,300	43.2	1.56 8	9.6	67,800	Mesohaline	50.0	Bad quality
71°41′09.00" August 22, 110 1 2013			15.2 4.2	18.0	8.9	200	1600 4	4200	169.6	0.05	15.4	1800	Subhaline	55.3	Bad quality
71°40′53.09″ August 22, 128 1! 2013		=:	15.7 –(-0.5 17.0	8.7	550	1540 4	4300	147.2 (0.10	16.6 1	1300	Freshwater	52.0	Bad quality
71°40′30.20″ August 22, 85 15 2013		u.,	15.4 –2	-2.1 15.0	8.8	525	2400 4	4400	140.8 (0.07	8.7	1300	Freshwater	74.0	Utilizable

SWT: surface water temperature, $\Delta \Gamma^*$: difference between air temperature and sea water temperature, Alk: alkalinity, COD: chemical oxygen demand, Cond: conductivity, IWQ: index water quality. TSS: total suspended solids, DO: dissolved oxygen.

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Organic and inorganic parameters measured in the water in the str

Organic and morg	same parar	organic and morganic parameters incasared in the water in the study area.	IIC water III	ure study a	.ca.											
Location	Station	Date	Nitrate	Nitrite	Ammonium	Phosphate	N/P	TOP	Oil-fats	BOD_5	Sodium	Potassium	F-Ratio	Cu	Pb	HEI
			$(mg L^{-1})$	$(mg L^{-1})$ $(mg L^{-1})$ $(mg L^{-1})$	(mgL^{-1})	$(mg L^{-1})$	(NO^{3-}/PO_4^{-3}) $(mg L^{-1})$	(mgL^{-1})	(mgL^{-1})	(mgL^{-1})	$(mg L^{-1})$	$({\rm mgL^{-1}})$	(Na/K)	$({\rm mg}{\rm L}^{-1})$	$(mg L^{-1})$	
Summer																
Albufera Lagoon	W1	January 15, 2013	12.8	0.05	25.4	29.0	0.05	0.04	4.3		11,596.0	512.0	22.6	0.062	0.566	14.4
Albufera Lagoon	W2	January 15, 2013	13.1	0.05	19.5	4.37	0.33	0.05	1.8		19,366.0	1800.0	10.8	0.043	0.443	11.0
Yali River	W3	January 15, 2013	3.8	0.08	20.2	4.34	1.14	90.0	1		9107.0	713.0	12.8	0.020	0.250	0.9
Colejuda Lagoon	W4	January 15, 2013	50.0	0.03	75.5	0.18	0.01	0.04	6.1		3130.0	0.299	4.7	0.020	0.420	9.4
Matanzas Lagoon	W5	January 16, 2013	14.4	90.0	1.8	756	52.50	0.24	6.7	11	1373.0	246.0	5.6	0.010	0.120	2.9
Matanzas Lagoon	M6	January 16, 2013	15.8	90.0	2.4	724	45.82	0.31	6.7		1186.0	270.0	4.4	0.020	0.120	3.4
Matanzas Lagoon	W7	January 16, 2013	16.4	0.10	2.1	721	43.96	0.29	4	10	1203.0	312.0	3.9	0.080	0.240	8.8
Winter																
Albufera Lagoon	W1	August 28, 2013	2.0	0.01	12.0	0.34	0.17	3.20	3.2	21	9557.0	342.4	27.9	n.d.	0.005	0.1
Albufera Lagoon	W2	August 28, 2013	1.6	0.01	14.1	0.33	0.21	0.50	19.7	31	8817.5	319.2	27.6	n.d.	0.005	0.1
Yali River	W3	August 28, 2013	2.1	0.00	12.1	0.03	0.01	2.20	9.3	29	11,994.5	385.8	31.1	n.d.	0.005	0.1
Colejuda Lagoon	W4	August 28, 2013	7.0	0.00	37.5	0.04	0.01	0.50	8.9	27	16,889.2	267.0	63.3	n.d.	0.020	0.4
Matanzas Lagoon	W5	August 22, 2013	6.7	0.01	2.5	320	32.99	0.08	13.4	106	1613.0	49.9	32.3	n.d.	0.050	1.0
Matanzas Lagoon	M6	August 22, 2013	6.6	0.01	3.0	570	57.58	80.0	5.9	92	1497.2	54.9	27.3	n.d.	0.050	1.0
Matanzas Lagoon	W7	August 22, 2013	13.0	0.01	3.3	310	23.85	80.0	14	88	1515.8	57.7	26.3	n.d.	0.050	1.0
																ĺ

TOP: total organic phosphorous, freshwater cations ratio (K/Na), BOD₅: biochemical oxygen demand, HEI: heavy metal index (H_{mac} Cu = 0.02 and Pb = 0.05).

five environmental variables: water temperature, TSS, conductivity, DO, and chemical oxygen demand (COD), which was estimated from BOD_5 . For completely contaminated water, this index is close to 0, while for excellent water quality the index is 100.

For the measurement of heavy metals such as cadmium (Cd), lead (Pb), and copper (Cu) in the soil, nitric acid digestion with perchloric acid and spectrophotometry by direct aspiration was used. Note that for arsenic (As), nitric acid digestion with perchloric acid was used and determined with a hydride generator, in accordance with the procedures recommended. All chemical analyses of water and soil were conducted in the Chemistry Faculty of the Universidad de Playa Ancha (Chile). Additionally, we used a heavy metal index (HEI) in order to estimate the overall quality of the water with respect to heavy metals (Edet and Offiong, 2002). The HEI was computed as: HEI = $\Sigma_{n=1}^{i}$ Hc/Hmac, where Hc is the monitored value of the i_{th} parameter and Hmac the maximum admissible concentration of the i_{th} parameter (Cu = 0.02 mg L⁻¹; Pb = 0.05 mg L⁻¹; WHO standards).

Univariate and multivariate statistical methods were used to analyze data gathered. For univariate tests, normality was determined with the Shapiro-Wilk test to determine parametric and non-parametric treatments, with significance levels set at 5%; significant differences between the sampling sites for water and soil variables were determined with analysis of variance (ANOVA); the Kruskal-Wallis test with a post-hoc Dunn's test (Zar, 1999) was used for nonparametric information processing. For multivariate analyses, Principal Component Analysis (PCA) was used to search for associations between the sampling stations and geochemical variables and heavy metal concentrations (Jongman et al., 1987). We also correlated water quality variables (i.e. temperature, alkalinity, conductivity, salinity, TSS and hardness) with variables related to the organic matter content (nitrate, nitrite, ammonium, phosphate, TOP and oil-fats), cations (sodium and potassium), and heavy metals (Pb) using Spearman correlation analysis after $\log_{10}(x + 1)$ transforming environmental variables. The multivariable analyses were carried out using the statistical package Past 3.22 (Hammer et al., 2001).

The physical and chemical characteristics of the water bodies of the EYNR are shown in Tables 1 and 2. The results showed that the water bodies are shallow, ranging between 20 and 172 cm, the shallowest being Colejuda Lagoon (W4). No significant differences in depth between summer and winter were observed (Kruskal-Wallis test; p > 0.05). The ΔT° exhibited a maximum in winter at Albufera Lagoon $(13.0 \pm 0.1 \,^{\circ}\text{C})$ and a minimum at Colejuda Lagoon $(4.7 \pm 0.1 \,^{\circ}\text{C})$. In contrast, the Matanzas Lagoon showed higher differences during summer (-6.3 ± 0.07 °C). pH, alkalinity, conductivity, salinity and total hardness in the water column did not show significant differences between summer and winter (Kruskall-Wallis test; p > 0.05). pH varied between 8.3 and 9.5, with alkalinity values ranging between 160 and 610 mg L⁻¹ (Table 2). It is important to note that total hardness varied between 1540 and $13,000 \, \text{mg} \, \text{L}^{-1}$, exceeding 5.8 times the normal concentrations for Chilean environmental regulations $(266-569\,\mathrm{mg\,L}^{-1})$. Albufera Lagoon (W1 and W2) exhibited higher levels of salinity and conductivity in summer (from 37,000 mg L⁻¹ to 67,800 µS cm⁻¹) than in winter, varying from a mesohaline to a hyposaline system (Table 2). Yali River showed less variability in its $(43,000-37,200 \text{ mg L}^{-1})$ and conductivity $(44,400-56,500 \,\mu\text{S cm}^{-1})$, classifying it as a mesohaline system. In terms of salinity and conductivity, for Colejuda Lagoon (W4) concentrations of $47,300-151,000 \,\mathrm{mg} \,\mathrm{L}^{-1}$ and $44,400-183,000 \,\mu\mathrm{S} \,\mathrm{cm}^{-1}$, respectively were measured, and the lagoon exhibited significant seasonal changes of these parameters, but was classified as a mesohaline system (Table 2). In contrast, at Matanzas Lagoon (W5, W6 and W7), salinity varied from 4200 to 5000 mg L^{-1} and conductivity varied from 1300 and $8990\,\mu S\,cm^{-1},$ resulting in a wide range of variability of salinity and classifying the lagoon as mesohaline to freshwater. Clarity is related to the level of turbidity and chlorophyll concentration. Significant seasonal differences in clarity levels were measured (KruskalWallis test; p < 0.05), particularly in Matanzas lagoon, where clarity decreased to approximately 84.3% \pm 2.52% (Table 2).

The ecological status of the all water bodies was classified as bad quality (IWQ: 50.0–54.8) and unacceptable (IWQ: 48.3–48.9), with exception of the Matanzas Lagoon (W7) in winter (IWQ: 74.0), which was classified as utilizable (Table 2). It is important to note that conductivities were similar to those reported by Vidal-Abarca et al. (2011), although Albufera Lagoon (W5, W6 and W7) showed a less saline condition (subhaline and mesohaline), probably related to increasing levels of river discharges and rainfall in the Maipo river basin, characterized by maximum values in August of $75.6\,\mathrm{m}^3\,\mathrm{s}^{-1}$ ($\pm\,13.8\,\mathrm{m}^3\,\mathrm{s}^{-1}$) and $13.3\,\mathrm{mm}$ ($\pm\,6.7\,\mathrm{mm}$), respectively. In contrast, minimum values of river discharges and precipitation have been recorded in January with mean values of $52.4\,\mathrm{m}^3\,\mathrm{s}^{-1}$ ($\pm\,15.2\,\mathrm{m}^3\,\mathrm{s}^{-1}$) and $0.76\,\mathrm{mm}$ ($\pm\,0.06\,\mathrm{mm}$; Dirección de General de Aguas, Ministerio de Obras Públicas de Chile; http://www.dga.cl).

Furthermore, nitrogenous (NO₃⁻ and NH₄⁺) and phosphorous compounds (phosphate and total organic phosphorus) in the study area exhibited marked significant spatial differences, with higher concentrations in the Matanzas lagoon (PO_4^{-3} : 310–756 mg L⁻¹; NO_3^{-1} : $1.6-12.8 \,\mathrm{mg} \,\mathrm{L}^{-1}$; $\mathrm{NO_3}^{-}/\mathrm{PO_4}^{-3} > 32.99$) and lower concentrations in Albufera Lagoon and Yali River $(0.03-4.37 \text{ mg L}^{-1}; \text{NO}_3^{-})$ PO_4^{-3} < 1.14). Colejuda Lagoon registered higher concentrations of nitrate and ammonium in January (NO₃⁻: 7-50 mg L⁻¹; NH₄⁺: $37.5-75.5 \text{ mg L}^{-1}$; Table 2). TOP varied between 0.04 mg L^{-1} (January) and 3.20 mg L⁻¹ (August) in Albufera Lagoon. Albufera Lagoon, Colejuda Lagoon and Yali River showed higher levels of ammonium, ranging from 12.0 to $37.5 \,\mathrm{mg}\,\mathrm{L}^{-1}$, and lower $\mathrm{NO_3}^-/\mathrm{PO_4}^{-3}$ ratios (Table 2). It is important to mention that nitrogen compounds and phosphate concentrations exceeded 151 times the concentrations measured previously at other sites in the EYNR (Vidal-Abarca et al., 2011), which coincide with higher biochemical oxygen demand measurements (BOD₅ > 21 mg L^{-1}), particularly in August (Table 2). These concentrations of nitrogenous compounds (NO₃⁻ and NH₄⁺), phosphate and total organic phosphorous are associated with livestock farms, eucalyptus forest and migratory birds, whose wastewater and feces may affect negatively the water quality, contributing to the eutrophication of this ecosystem (Khadse et al., 2008; Noorhosseini et al.,

In soil, electrical conductivity (EC) ranged from 3.1 to 112 dS m⁻¹ in Albufera Lagoon and Colejuda Lagoon, respectively (Table 3). Nitrate varied between 7.8 mg Kg⁻¹ (Matanzas Lagoon) and 85.1 mg Kg⁻¹

(Albufera Lagoon), and phosphate varied between $12.2\,\mathrm{mg\,Kg}^{-1}$ (Colejuda Lagoon) and $38.1\,\mathrm{mg\,Kg}^{-1}$ (Colejuda Lagoon). High concentrations of iron (2.6 to $4.5\,\mathrm{mg\,Kg}^{-1}$) were measured, reaching > 90 mg Kg $^{-1}$ in the Matanzas Lagoon (Table 3), coinciding with concentrations reported by Vergara (2014), which were associated with the presence of magnetite (Fe $_3$ O $_4$) deposits. In addition, higher concentrations of different cations and heavy metals were associated with the loss of soil structure and desiccation, which may affect the ability of soil of maintain cations. EC also affects the nutritive characteristics of soil and, in turn, is associated with salinity. In the study area, the concentrations of Ca (3.6–22.6 cmol + Kg $^{-1}$), Mg (5.3–11 cmol + Kg $^{-1}$) and K (76.3–1210 mg Kg $^{-1}$) were slightly higher than mean values reported and related to higher level of EC (Allaire et al., 2012; Cortés-D et al., 2013).

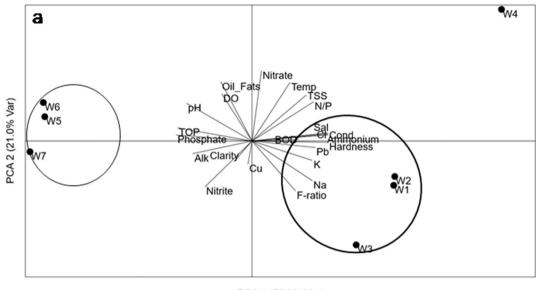
In general, Cu and Pb concentrations ranged from 0.01 to 0.080 mg L^{-1} and from 0.120 to 0.566 mg L^{-1} , respectively (Table 2). However, maximum mean concentrations of Cu (0.037 mg $L^{-1} \pm 0.026$ mg L^{-1}) and Pb (0.308 mg $L^{-1} \pm 0.171$ mg L^{-1}) in January were observed. These concentrations are considered above the permissible limit according to Chilean (CONAMA, 2005). It is important to note that higher concentrations of heavy metals were registered in January, probably associated with the desiccation of the lagoons in summer. Wetlands are sensitive to freshwater input associated with the hydrologic water cycle (Gambrel, 1994). In addition, the EYNR is heavily influenced by lithology, urbanization, and local agriculture activity, modifying the use of land (Soto et al., 2011; 2009; Meza et al., 2015). In soil, higher concentrations of heavy metals were measured for Colejuda Lagoon (Cu: 32.2 mg Kg $^{-1}$; Pb: 34.8 mg Kg $^{-1}$; Cd: 2.4 mg Kg $^{-1}$; As: 11.2 mg Kg $^{-1}$) and Matanzas Lagoon (Cu: 17.9; Pb: 18.8 mg Kg $^{-1}$; Cd: 1.1 mg Kg $^{-1}$; As: 5.4 mg Kg $^{-1}$; Table 3).

PCA ordination and Spearman correlation analyses were performed based on twenty-three environmental variables (pH, alkalinity, conductivity, water hardness, TSS, OD, BOD $_5$, nitrate, nitrite, ammonium, phosphate, TOP, oil-fats, Na, K, Cu, Pb) for January and August (Fig. 2). The first two PCA axes accounted for 77.3% and 80.8% of the total variance in January (Fig. 2a) and August (Fig. 2b), respectively. In general, the environmental variables such as water ammonium, BOD $_5$ conductivity, hardness and K were associated with Albufera Lagoon (W1 and W2), whereas pH, phosphate, alkalinity and TOP exhibited a stronger association with Matanzas Lagoon (W5, W6 and W7). However, Cu and Pb showed seasonal variations with high concentrations of Pb in Matanzas Lagoon and Colejuda Lagoon in January, and high concentrations of Cu for Albufera lagoon and Matanzas Lagoon in

Table 3
Soil sample sites and chemical and heavy metal concentrations measured in the study area.

Location	Albufera Lagoon	Colejuda Lagoon	Matanzas Lagoon	Matanzas Lagoon	Matanzas Lagoon
Station	S1	S2	S3	S4	S5
Date	March 23, 2013	January 17, 2015	November 21, 2014	January 17, 2015	March 23, 2013
pH	7.37	7.7	7.9	7.6	8.1
Electrical conductivity (dS/m)	3.1	112.0	8.1	23.0	5.5
Organic matter (%)	3.9	4.2	1.0	0.5	4.0
N (mg/Kg)	85.1	11.5	7.8	9.5	20.0
P (mg/Kg)	17.4	38.1	12.3	27.9	27.1
K _{Exchangeabled} (mg/Kg)	190.0	1210.0	249.0	262.0	76.3
Ca _{Exchangeabled} (cmol + /Kg)	3.6	22.6	17.0	20.1	15.4
Mg _{Exchangeabled} (cmol + /Kg)	5.3	11.0	8.0	7.5	8.3
Zn _{Availability} (mg/Kg)	n.d.	1.6	0.4	0.5	1.5
Mn _{Availability} (mg/Kg)	n.d.	8.5	12.4	8.7	27.7
Fe _{Availability} (mg/Kg)	n.d.	44.3	93.4	56.0	65.1
B _{Availability} (mg/Kg)	n.d.	7.6	0.8	0.7	0.5
Cu _{Availability} (mg/Kg)	n.d.	4.7	2.1	2.5	2.0
Cd _{Total} (mg/Kg)	n.d.	2.4	n.d.	1.1	n.d.
Pb _{Total} (mg/Kg)	n.d.	34.8	n.d.	18.8	n.d.
Cu _{Total} (mg/Kg)	n.d.	32.2	n.d.	17.9	n.d.
As _{Total} (mg(Kg)	n.d.	11.2	n.d.	5.4	n.d.

n.d.: no data.



PCA 1 (56.3% Var)

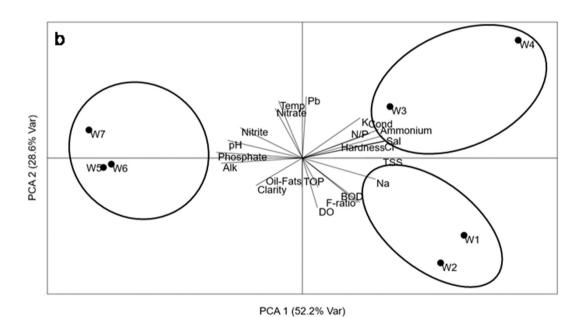


Fig. 2. Principal component analysis of hydrological and chemical parameters in the water during January (a) and August (b).

August (Fig. 2a, b). This situation can be associated with the higher freshwater input from rainfall and freshwater from tributaries, although changes in salinity, biological processes and other physical phenomena affect the cycling, mobility and fate of trace metals (Morabito et al., 2017). The Spearman correlation analyses exhibited a positive correlation between the alkalinity and phosphate levels, as well as between water hardness and Cl⁻ and K. Nitrogenous compounds such as nitrate and ammonium appeared to be positively correlated with K/Na ratio and conductivity (Table 4). There are many chemical processes that directly or indirectly involve organic matter and heavy metal concentrations in the water, including both dissolved and colloidal forms (Morabito et al., 2017). According to PCA analyses, higher concentrations of Pb were associated with low concentrations of TOP and TSS, suggesting that organic matter concentrations are not influencing the heavy metal concentrations measured in the study area (Fig. 2a).

In general, heavy metals have been reported to be well concentrated in the water column in wetlands (Everall et al., 1989; Brraich and Jangu, 2015). These metals in trace amount may play important roles in the biochemical life processes of aquatic organisms (Libes, 2009). However, at high concentrations they become lethal to fish and other aquatic organisms when the duration of exposure is prolonged. It is well known that copper has a high bioaccumulation factor in water (ASTDR, 1990). In our study area, we used a heavy metal evaluation index (HEI) for a better understanding of pollution. The mean value of HEI was 8.0 (ranging from 2.9 to 14.4) in January. The proposed HEI criteria for the samples are as follows: low (HEI < 10), intermediate (HEI = 10-20) and high (HEI > 20). Thus, the HEI shows that the water quality falls within low and intermediate of heavy metal pollution. Heavy metals may be transferred from the abiotic environment to living organisms, accumulated in biota at different trophic levels (i.e. bioaccumulation), and thus contaminate the food webs (i.e. biomagnification; Hazrat and Khan, 2018). In the study area, heavy metal concentrations in organisms were not measured. Further research in this area is badly needed. However, higher heavy metal concentrations in plant and soil samples

organic matter and heavy metal variables in the study area.
 Table 4

 Spearman correlation analysis between

	the properties of the properti			1															Ì
STW pH Alk	Alk		Cond	Sal	Hard	CI	Clarity	TSS	OD	DBO_5	NO ³⁻	NO^{2-}	$\mathrm{NH^{4}}^{+}$	PO_4^{-3}	TOP	Oil-fat	Na	K	K/Na
0.07																			
0.53																			
-0.47		-0.74																	
-0.49		-0.70	0.95																
-0.45		-0.80	0.87	0.85															
-0.58		-0.71	0.94	0.93	0.83														
	_	-0.11	0.43	0.33	0.41	0.30													
	_	-0.68	0.73	0.79	09.0	0.79	-0.03												
	,_	-0.03	-0.20	-0.16	-0.37	-0.06	-0.12	0.23											
	~	-0.02	-0.39	-0.33	-0.34	-0.19	-0.62	60.0	0.56										
		0.42	-0.03	-0.11	-0.11	-0.16	0.12	-0.36	-0.47	-0.54									
		0.47	-0.09	-0.13	-0.01	-0.17	0.33	-0.55	-0.66	-0.73	0.65								
		-0.81	98.0	0.84	0.81	0.88	0.10	0.75	-0.16	0.00	-0.24	-0.31							
		0.88	-0.70	-0.75	-0.65	-0.70	0.02	-0.85	-0.21	-0.23	0.53	0.69	-0.82						
		0.27	-0.28	-0.19	-0.50	-0.31	-0.26	90.0	0.42	0.10	-0.24	-0.31	-0.45	0.04					
		0.03	-0.28	-0.26	-0.29	-0.25	-0.19	0.00	0.40	0.55	-0.19	-0.54	-0.16	-0.14	0.10				
		-0.76	0.70	99.0	0.65	0.71	0.23	0.58	0.11	0.15	-0.51	-0.50	92.0	-0.78	-0.10	-0.17			
		-0.57	0.77	0.77	0.88	0.71	0.51	0.51	-0.35	-0.48	-0.02	0.18	0.63	-0.48	-0.36	-0.58	0.57		
		0.41	0.01	-0.01	0.09	-0.11	0.36	-0.31	-0.60	-0.75	0.81	0.85	-0.25	0.55	-0.29	-0.43	-0.53	0.30	
		0.04	0.32	0.20	0.36	0.24	0.39	-0.26	-0.68	-0.65	69.0	0.79	0.19	0.32	-0.64	-0.58	-0.06	0.45	0.71

STW: surface water temperature, Alk: alkalinity, Cond: conductivity, Sal: salinity, hard: hardness, TSS: total suspended solid, OD: oxygen dissolved, BOD₅: biochemical oxygen demand. TOP: total organic phosphorous.

Bold numbers indicate significant levels (p < 0.05).

were detected in our study area (Meza et al., 2018). The biological component in the EYNR is composed of commonly marine species, which indicates a close relationship between the marine environment and the wetland. The benthic communities are dominated by gastropods (Lymnaeidae and Physidae), followed by Ostracoda, Trichoptera and larvae of Chironomidae (Rudolf, 2004). In addition, Diptera (Orthorrapha and Ephidridae), Plecoptera and Coleoptera (Insecta), Copepoda, Cladocera and Amphipoda (Crustacea) and Physidae (Mollusca) are present but in lower abundances (Rudolf, 2004). High concentrations of heavy metals in the surrounding environment can also result in reduce relative abundance and diversity of organisms by affecting the balance of the food web, resulting in a considerable potential risk to the wetland ecosystem.

In summary, water and soil samples in the study area showed different levels of heavy metal concentrations, which varied from low to intermediate heavy metal pollution, in comparison with other wetlands in Chile (CONAMA, 2005; Meza et al., 2018). If this trend is allowed to continue unabated, the food web complexes in this wetland are likely to be at the highest risk of induced heavy metal contamination. In fact, high levels of Cu and Pb in sediments (Cu: $11-48 \mu g g^{-1}$; Pb: $0.08-20 \,\mu g \, g^{-1}$) and in the nereidid polychaete *Perinereis gualpensis* (Cu: $13.6-112.4 \,\mu g \, g^{-1}$; Pb: $0.3-2.2 \,\mu g \, g^{-1}$) have been reported from several estuaries in central Chile; these heavy metals provoke oxidative stress in the organisms and potentially constitute a risk for the aquatic organisms inhabiting coastal estuarine ecosystems (Chandía and Salamanca, 2012; Gaete et al., 2017). In addition, approximately 56 locations of wastewater discharges, including point and non-point, have been reported in the study area, mainly associated with livestock farms and occasional agriculture farms, which are producing important environmental changes in the water reserves, affecting their water quality (Castro and Aliaga, 2010; Meza, 2010; Meza et al., 2015). Hence, strict management actions should be taken into consideration in order to protect the ecological sustainability of this RAMSAR site.

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References

- Allaire, S.E., Lange, S.F., Lafond, J.A., Pelletier, B., Cambouris, A.N., Dutilleul, P., 2012. Multiscale spatial variability of CO2 emissions and correlations with physico-chemical soil properties. Geoderma 170, 251–260.
- APHA, 1985. Standard Methods for the Examination of Wastewater and Water, 19th edition. American Public Health Association, Washington DC.
- Bassi, N., Kumar, M.D., Sharma, A., Pardha-Saradhi, P., 2014. Status of wetlands in India: a review of extent, ecosystem benefits, threats and management strategies. J. Hydrol. Reg. Stud. 2, 1–19.
- Brraich, O.S., Jangu, S., 2015. Evaluation of water quality pollution indices for heavy metal contamination monitoring in the water of Harike Wetland (Ramsar site). India. Internat. J. Sci. Res. Publ. 5 (2), 1–6.
- Castro, C.P., Aliaga, C., 2010. Evaluación de la pérdida de suelo, asociada al proceso de expansión urbana y reconversión productiva. Caso: comunas de Los Andes, Quillota y Concón, valle del Aconcagua. Rev. Geograf. Norte Grande. (45), 41–49.
- Chandía, C., Salamanca, M., 2012. Long-term monitoring of heavy metals in Chilean coastal sediments in the eastern South Pacific Ocean. Mar. Poll. Bull. 64, 2254–2260. https://doi.org/10.1016/j.marpolbul.2012.06.030.
- CONAMA, 2005. Estrategia y Plan de Acción Para la Conservación de la Diversidad Biológica. Ministerio del Medio Ambiente de Chile, Región de Valparaíso, pp. 160.

- Cortés-D, D.L., Pérez-B, J.H., Camacho-Tamayo, J.H., 2013. Relación espacial entre la conductividad eléctrica y algunas propiedades químicas del suelo. U.D.C.A Act. Divul. Cient. 16 (2), 401–408.
- Daniels, A.E., Cumming, G.S., 2008. Conversion or conservation? Understanding wetland change in northwest Costa Rica. Ecol. Appl. 18 (1), 49–63.
- Davis, J.A., Froend, R., 1999. Loss and degradation of wetlands in southwestern Australia: underlying causes, consequences and solutions. Wetlands Ecol. Manag. 7, 13–23.
- Dussaillant, A., Galdames, P., Sun, C.-L., 2009. Water level fluctuations in a coastal lagoon: El Yali Ramsar wetland, Chile. Desalination 246, 202–214.
- Edet, A.E., Offiong, O.E., 2002. Evaluation of water quality pollution indices for heavy metal contamination monitoring. A study case from Akpabuyo-Odukpani area, Lower Cross River Basin (Southeastern Nigeria). GeoJournal. 57, 295–304.
- Erwin, K.L., 2009. Wetlands and global climate change: the role of wetland restoration in a changing world. Wetl. Ecol. Manag. 17 (1), 71–84. https://doi.org/10.1007/s11273-008-9119-1.
- Everall, N.C., MacFarlane, N.A., Sedgwick, R.W., 1989. The interactions of water hardness and pH with acute toxicity of zinc to brown trout, S. trutta L. J. Fish Biol. 35, 27–36.
- Fariña, J.M., Silliman, B.R., Bertness, M.D., 2009. Can conservation biologists rely on established community structure rules to manage novel systems?. Not in salt marshes. Ecol. Appl. 19 (2), 413–422.
- Fariña, J., Bertness, M., Silliman, B., Aragoneses, N., Gayo, E., 2012. Historia natural y patrones ecológicos del humedal costero El Yali, Chile Central. In: Fariña, J.M., Camaño, A. (Eds.), Humedales costeros de Chile. Ediciones UC, Santiago de Chile, pp. 215–250.
- Figueroa, R., Suarez, M.L., Andreu, A., Ruiz, V.H., Vidal-Abarca, M.R., 2009. Caracterización ecológica de humedales de la zona semiárida en Chile Central. Gayana 73 (1), 76–94.
- Flores-Toro, L., Contreras-López, M., 2015. Suaeda foliosa Moq. (Caryophyllales: Amaranthaceae) first record of the genus and species for Valparaíso Region, Chile. Rev. Chil. Hist. Nat. 88 (2), 1–4.
- Fu, B., Pollino, C.A., Cuddy, S.M., Andrews, F., 2015. Assessing climate change impacts on wetlands in a flow regulated catchment: a case study in the Macquarie Marshes, Australia. J. Environ. Manag. 157, 127–138.
- Gaete, H., Álvarez, M., Lobos, G., Soto, E., Jara-Gutiérrez, C., 2017. Assessment of oxidative stress and bioaccumulation of the metals Cu, Fe, Zn, Pb, Cd in the polychaete *Perinereis gualpensis* from estuaries of central Chile. Ecotox. Environ Safety 145, 653–658.
- Gambrel, R.P., 1994. Trace and toxic metals in wetlands a review. J. Environ. Qual. 23, 883–891.
- Gilman, E.L., Ellison, J., Duke, N.C., Field, C., 2008. Threats to mangroves from climate change and adaptation options: a review. Aquat. Bot. 89, 237–250. https://doi.org/ 10.1016/j.aquabot.2007.12.009.
- Hammer, O., Harper, D.A.T., Ryan, P.D., 2001. PAST: paleontological statistic software package for education and data analysis. Paleontol. Elect. 4 (1), 1–9.
- Hazrat, A., Khan, E., 2018. Trophic transfer, bioaccumulation, and biomagnification of non-essential hazardous heavy metals and metalloids in food chains/webs—concepts and implications for wildlife and human health. Human and Ecological Risk Assessment: An International Journal. https://doi.org/10.1080/10807039.2018. 1469398.
- Jongman, R., Ter Braak, C., van Tongeren, O., 1987. Data Analysis in Community and Landscape Ecology. PUDOC. Wageningen.
- Junk, W.J., Brown, M., Campbell, I.C., Finlayson, M., Glopal, B., Ramberg, K., Warner, B.G., 2006. The comparative biodiversity of seven globally important wetlands: a synthesis. Aquat. Sci. 68, 400–414.
- Kaur, J., Chaudhary, A., Kaur, R., 2014. Assessment of mutagenic, genotoxic, and cytotoxic potential of water samples of Harike wetland: a Ramsar site in India using different ex vivo biological system. Ecotoxicology 23, 967–977.
- Khadse, G.K., Patni, P.M., Kelkar, P.S., Devotta, S., 2008. Qualitative evaluation of Kanhan river and its tributaries flowing over central Indian plateau. Environ. Monit. Assess. 147, 83–92.
- Lee, S.Y., Dunn, R.J.K., Young, R.A., Connolly, R.M., Dale, P.E.R., Dehayr, R., Lemckert, C.J., Mckinnon, S., Powell, B., Teasdale, P.R., Welsh, D.T., 2006. Impact of urbanization on coastal wetland structure and function. Austral Ecol. 31, 149–163.
- Li, D., Sharp, J.O., Drewes, J.E., 2015. Influence of wastewater discharge on the metabolic potential of the microbial community in river sediments. Micro. Ecol. 71, 78.
- Libes, S., 2009. Introduction to Marine Biogeochemistry. Second Edition. Academic Press. Meza, M., 2010. Evaluación del recurso suelo como indicador de degradación ambiental por uso y manejo en el contexto de la reconversión productiva, cuenca de Quillota, curso medio del río Aconcagua. Tesis para optar al grado de Magíster en Geografía. Universidad de Chile, Chile.
- Meza, V., Bustillos, G., Contreras-López, M., 2015. Análisis fertilidad de suelos en la reserva El Yali, Santo Domingo, Chile Central (33°45′S). Rev. Geog. Valp. 51, 25–34 (In Spanish).
- Meza, V., Lillo, C., Rivera, D., Soto, E., Figueroa, R., 2018. Sarco cornianeei as an indicator of environmental pollution: a comparative study in coastal wetlands of Central Chile. Plants 7, 66–74. https://doi.org/10.3390/plants7030066.
- Mitsch, W.J., Gosselink, J.G., 2000. The value of wetlands: landscapes and institutional perspectives. Ecol. Econ. 35, 25–33.
- Möder, L., Gallardo, H., Vilina, Y., 2002. Ficha informativa de los humedales Ramsar. (Humedal El Yali).
- Mojica, J.M., García, S.R., Tenorio, A.E., 2018. Policies in coastal wetlands: key challenges. Environ. Sci. Pol. 88, 72–82.
- Morabito, E., Radaelli, M., Corami, F., Turetta, C., Toscano, T., Capodaglio, G., 2017.
 Temporal evolution of cadmium, copper and lead concentration in the Venice Lagoon water in relation with the speciation and dissolved/particulate partition. Mar. Poll. Bull. 129 (2), 884–892. https://doi.org/10.1016/j.marpolbul.2017.10.043.

- Morton, R.A., Gelfenbaum, G., Buckley, M.L., Richmond, B.R., 2011. Geological effects and implications of the 2010 tsunami along the central coast of Chile. Sediment. Geol. 242, 34–51.
- Nair, M., Jayalakshmy, K.V., Balachandran, K.K., Joseph, T., 2006. Bioaccumulation of toxic metals by fish in a semi-enclosed tropical ecosystem. Environ. For. 7, 197–206.
- Noorhosseini, S.A., Allahyari, M.S., Damalas, C.A., Moghaddam, S.S., 2017. Public environmental awareness of water pollution from urban growth: the case of Zarjub and Goharrud rivers in Rasht. Iran. Sci. Total Environ. 599–600.
- Peters, K., Bundschuh, M., Schäfer, R.B., 2013. Review on the effects of toxicants on freshwater ecosystem functions. Environ. Poll. 180, 324–329.
- Queralt, R., 1982. La calidad de las aguas de los ríos. Tecnología del agua. 4, 49–57. RAMSAR (Ed.), 2004. The Ramsar Convention Manual: A Guide to the Convention on Wetlands (Ramsar, Iran, 1971), 3rd ed. Gland, Switzerland, Ramsar Convention Secretariat
- Román, M., Rendal, S., Fernández, E., Méndez, G., 2018. Seasonal variability of the carbon and nitrogen isotopic signature in a Zosteranoltei meadow at the NW Iberian Peninsula. Wetlands 38, 739–753. https://doi.org/10.1007/s13157-018-1019-4.
- Rudolf, J.P., 2004. Análisis del estado de conservación de los cuerpos mayors del humeda El Yali y criterios para su sustentabilidad. Trabajo de tesis para optar al título professional de biólogo marino. Chile, Universidad de Valparaíso (88 pp).
- Silva, J.P., Phillips, L., Jones, W., Eldridge, J., O'Hara, E., 2007. Life and Europe's wetlands, restore a vital ecosystem. European Commission Environment Directorategeneral 68.
- Singh, N., Kaur, M., Katnoria, J.K., 2017. Spatial and temporal heavy metal distribution and surface water characterization of Kanjli Wetland (a Ramsar site), India using different indices. Bull. Environ. Contam. Toxicol. 99, 735–742. https://doi.org/10. 1007/s00128-017-2194-3.
- Soto B., Victoria M., González A., Correa JC, Paz C., Michael M., & G. 2011. Relación entre el cambio de uso del suelo en la cuenca del Aconcagua y su litoral arenoso correlativo: Chile central. Rev. Geog. Norte Grande, (50), 187–202.

- Tang, W., Shan, B., Zhang, W., Zhang, H., Wang, L., Ding, Y., 2014. Heavy metal pollution characteristics of surface sediments in different aquatic ecosystems in Eastern China: a comprehensive understanding. PLoS One 9 (9), e108996.
- Tian, B., Wu, W., Yang, Z., Zhou, Y., 2016. Drivers, trends, and potential impacts of long-term coastal reclamation in China from 1985 to 2010. Estuar. Coast. Shelf Sci. 170, 83–90.
- Tockner, K., Stanford, J.A., 2002. Riverine flood plains: present state and future trends. Environ. Conser. 29 (3), 308–330.
- Valdés-Pineda, R., Pizarro, R., García-Chevesich, P., Valdés, J.B., Olivares, C., Vera, M., Balocchi, F., Pérez, F., Vallejos, C., Fuentes, R., Abarza, A., Helwig, B., 2014. Water governance in Chile: availability, management and climate change. J. Hydrol. 519, 2538–2567. https://doi.org/10.1016/j.jhydrol.2014.04.016.
- Van den Broeck, M., Waterkeyn, A., Rhazi, L., Grillas, P., Brendonck, L., 2015. Assessing the ecological integrity of endorheic wetlands, with focus on Mediterranean temporary ponds. Ecol. Indic. 54, 1–11. https://doi.org/10.1016/j.ecolind.2015.02.016.
- Vergara, H., 2014. Características sedimentológicas y mineralógicas de playa El Yali. Región de Valparaíso. Anal. Museo Hist. Nat. Valparaíso. Vol. 27, 68–78.
- Vidal-Abarca, M.R., Suárez, M.L., Figueroa, R., Enríquez, M., García, V., Domínguez, C., Arce, M.I., 2011. Caracterización hidroquímica del complejo de humedales El Yali. Chile Central. Limnetica 30 (1), 43–58.
- Vilina, Y.A., López-Calleja, M.V., 1996. The Neotropical plovers of Estero El Yali in central Chile. International Wader Studies 8, 85–92.
- Williams, P.J.leB., Jenkinson, N.W., 1982. A transportable microprocessor controlled precise Winkler titration suitable for field station and shipboard use. Limn. Oceanogr. 27 (3), 576–584.
- Wu, W., Yang, Z., Tian, B., Huang, Y., Zhoua, Y., Zhan, T., 2018. Impacts of coastal reclamation on wetlands: loss, resilience, and sustainable management. Estuar. Coast. Shelf Sci. 210, 153–161.
- Zar, J.H., 1999. Biostatistical Analysis, 4th edn. Prentice-Hall, Upper Saddle River, NJ.