

## Hydrochemistry and carbonate sediment characterisation of Bacalar Lagoon, Mexican Caribbean

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**Abstract.** The aim of the study is to determine the distribution of trace and major elements in the water and in the sediments of the south part of the Bacalar Lagoon and to identify the sources of the trace elements and their changes over time. The western part of the lagoon water column is characterised by high concentrations of  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$  and  $\text{Sr}^{2+}$ , derived from groundwater input. In contrast, the eastern part of the lagoon is characterised by high concentrations of  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{Cl}^-$ . The lagoon is not affected by present-day seawater intrusion. Water column and sediment geochemical analyses performed in Bacalar Lagoon show clear spatial distribution of different parameters. The saturation index of the water column indicates three main groups: (1) a zone oversaturated with regard to aragonite, calcite and dolomite; (2) an undersaturated area where all three minerals are dissolving; and (3) an area with calcite equilibrium and undersaturation with regard to the other minerals. Herein we present the first measurements of trace element ( $\text{Ba}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ) concentrations in carbonates obtained from sediments in Bacalar Lagoon. In order to evaluate whether the trace elements are derived from natural or anthropogenic sources, four pollution indices were calculated. The results confirmed that Bacalar Lagoon sediments are not contaminated with  $\text{Ni}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mn}^{2+}$  and  $\text{Ba}^{2+}$ , and that the  $\text{Zn}^{2+}$  seems to have a predominantly anthropogenic origin.

**Additional keywords:** carbonate mineral solubility, groundwater, sediment geochemistry.

Received 15 February 2018, accepted 31 July 2018, published online 23 October 2018

### Introduction

Surface and groundwater systems in the Mexican Caribbean are being affected by contaminants, particularly heavy metals, due to poor or a lack of proper waste water treatment and an increase in activities related to growth in population, tourism, agriculture and livestock (Díaz 2005; Medina *et al.* 2014; Ochoa *et al.* 2016). The economy of Quintana Roo is based on tourism, and its population has increased 17-fold over the past 40 years (Dixon *et al.* 2001; Bauer-Gottwein *et al.* 2011; Instituto Nacional de Estadística y Geografía 2016). This represents substantial infrastructure needed for clean water supply and waste water treatment, and improperly functioning or non-existent infrastructure results in the discharge of waste water into surface waterbodies, such as the coastal ocean and lagoons (Hernández-Terrones *et al.* 2011). Moreover, the karst nature of the area promotes waste water infiltration and mixing with groundwater (Beddows 2002).

Bacalar Lagoon (south Quintana Roo) is a very popular place for tourism. Bacalar Lagoon is unique in the region due to the presence of carbonate structures called stromatolites. The lagoon's stromatolites are one of the largest freshwater microbialite occurrences in the world (10 km; Gischler *et al.* 2008; Centeno *et al.* 2012) and preserve past information about climatic and microbial life conditions and processes at the time of sedimentation, so it is important to ensure that these formations are not affected by water pollution. The growth of stromatolites depends on the physicochemical conditions of the water; they are sensitive to changes in the environment, and any change in water quality could affect their development (Dupraz *et al.* 2011). The main activities around the lagoon are tourism, agriculture (sugarcane, pineapple, rice and maize), livestock (cattle, swine, sheep) and aquaculture (Instituto Nacional de Estadística y Geografía 2002; Díaz 2005). Bacalar town became a municipality in 2014 and is planning regulation to

ensure tourism activities will not stress the lagoon's ecosystem; however, the lagoon has not been declared a protected area. The current lack of regulation for infrastructure and tourism may result in degradation of the water quality of the lagoon, ecosystem structure and possibly the integrity of stromatolites (Díaz 2005). Previous studies in Bacalar Lagoon provided physical information about the lagoon, but none focused on water quality and sources of pollution (Díaz 2005; Gischler *et al.* 2008, 2011; Pérez *et al.* 2011; Siqueiros-Beltrones *et al.* 2013; Castro-Contreras *et al.* 2014; González *et al.* 2014; Sánchez *et al.* 2015; Oliva *et al.* 2016).

Pollution from trace elements may be of particular concern. Trace metals can occur as dissolved or colloidal phases, or they may be present in association with suspended particles in the water column and within sedimentary phases (Katip *et al.* 2011). Many trace metals are present at higher concentrations in sedimentary phases than in the water column (Nriagu and Pacyna 1988; Pradit *et al.* 2010). Trace metal concentrations in the water are controlled by inputs from land through weathering processes, groundwater discharge and atmospheric deposition (Salomons and Förstner 1980), as well as from anthropogenic activities, and each input can change over time. Therefore, sediments (including stromatolite beds) can serve as archives of environmental changes through time, and changes in the chemical composition of the sediments may be informative of changes in natural and anthropogenic sources and fluxes of trace metals (Boyle 2001). The chemical composition of sediments and water can also be used to identify the rock–water interaction and mineralogical composition of aquifer rocks (Elango and Kannan 2007).

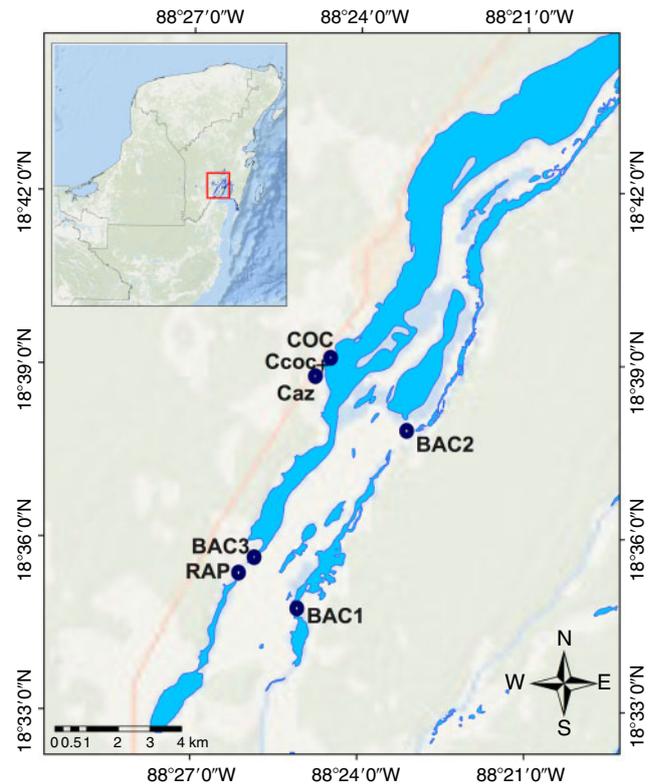
Herein we report, for the first time, the distribution of trace and major elements in the water column (along with hydrography) and in the sediments of the south part of the lagoon (near the location of the stromatolites). Through these analyses we identify the sources of the trace elements and their changes over time in Bacalar Lagoon.

## Materials and methods

### Study area

Bacalar Lagoon is located in the south-eastern part of Quintana Roo, Mexico (from 18°56'26.5"N, 88°9'28.6"W to 18°32'38.6"N, 88°27'48.6"W); 1.5 m above sea level; Fig. 1). This area is characterised by a humid tropical climate with a mean annual air temperature of 26.0°C. Three meteorological seasons dominate the region: (1) the 'nortes' season between October and April, characterised by cold fronts; (2) the dry season between April and May; and (3) the wet season from June to October, when tropical storms and hurricanes result in high rainfall. The average annual rainfall in the region ranges between 100 and 1500 mm year<sup>-1</sup>, with mean temperatures during winter and summer being ~28.0 and ~29.0°C respectively (Comisión Nacional del Agua 2015).

The lagoon has a surface area of 42.0 km<sup>2</sup> (length 40.0 km, width ~1.0–2.0 km; Comisión Nacional del Agua 2002; Castro-Contreras *et al.* 2014). It is an oligotrophic freshwater system (electrical conductivity (EC) <2.3 mS cm<sup>-1</sup>) and has a pH between 7.6 and 8.3 (Beltrán 2010). The maximum water depth of the lagoon is 15 m, but the water level of the lagoon can increase by up to ~30.0 cm during the wet season (June–October; Gischler *et al.* 2011).



**Fig. 1.** Location of Bacalar Lagoon, showing sampling sites. Site details are given in Table 1. BAC1, Bacalar 1; BAC2, Bacalar 2; BAC3, Bacalar 3; Caz, cenote Azul; Ccoc, cenote Cocalitos; COC, Cocalitos; RAP, Los Rápidos.

Bacalar Lagoon is situated in Hydrological Region number 33 (RH33; Comisión Nacional del Agua 2012). Five sinkholes (locally called *cenotes*) are located inside and near the lagoon (Gischler *et al.* 2008). The *cenotes* Cocalitos, Esmeralda and Negro are located inside the lagoon, whereas *cenote* Azul (with a maximum water depth of 90.0 m) is located outside the lagoon but has an underground connection to the lagoon. *Cenote* Xul-Ha is connected to the lagoon through a surface channel in the south-west area (Perry *et al.* 2009; Beltrán 2010; Gischler *et al.* 2011; Pérez *et al.* 2011).

The lagoon is located along the Bacalar fault system, and surrounding rocks are mostly from the Bacalar Formation that have been assigned a Neogene age. To the north, the outcrops are of marine Pliocene to Holocene age, whereas Miocene age rocks are observed to the south. Upper Cretaceous outcrops have also been identified, particularly along the west side of the lagoon (Kenkmann and Schönian 2006). Based on Sr isotopes, Perry *et al.* (2009) suggest that in this region the slow-moving groundwater derives its ion chemistry from relatively soluble aquifer rocks including gypsum, calcite, dolomite and accessory minerals such as celestite (SrSO<sub>4</sub>). Perry *et al.* (2009) also observed that water Sr isotope analyses of Bacalar Lagoon and *cenote* Azul suggest that these waterbodies derive their Sr from dissolution of minerals of Cretaceous–Eocene age.

### Field sampling

Seven sampling sites were selected along the southernmost 10.0 km of Bacalar Lagoon, with five sites located on the

western side of the lagoon and two located on the eastern side (Fig. 1). Two sampling campaigns were performed. The locations of the sites were determined using a global positioning system (GPS; (NOMAD; Trimble, Sunnyvale, CA, USA), with the World Geodetic System (WGS) 84 datum. Temperature, pH, depth, total dissolved solids (TDS), EC and dissolved oxygen (DO) were measured in the field (during both sampling campaigns) using a multiparameter sonde (Model 6600; YSI, Control Técnico y Representaciones, México City, México). Temperature profile data were collected using a CastAway-CTD (SonTek Xylem, San Diego, CA, USA). The field parameters were measured as close to sediment core and water sample collection points as possible.

The first sampling campaign was conducted in November 2016. Five sediment cores of variable length (between 11 and 41 cm) were collected using a steel push core with 5.0-cm diameter plastic liners. Three sediment cores were taken at the western side of the lagoon (COC, RAP and BAC3), and two cores were taken at the eastern side (BAC1 and BAC2; Fig. 1). The samples were kept at 4.0°C. The sediment cores were sectioned into 4.0-cm intervals for a total of 27 samples. Samples were dried at 50°C in an oven and powdered using an agate mortar and pestle. In addition, surface water samples were collected at each of the seven study sites (Fig. 1). All water samples were collected in acid-washed polyethylene bottles (Nalgene, Sigma-Aldrich México, Toluca, México) rinsed with sample at the time of collection. Samples were filtered using 0.45- $\mu\text{m}$  syringe filters and analysed for alkalinity, nutrients, cations and anions.

The second sampling campaign was conducted in June 2017. During this campaign, water samples were taken from sites at *cenote* Azul (Caz) and *cenote* Cocalitos (Ccoc; Fig. 1). At each site, two water samples (surface and at a depth of 15.0 m) were collected by divers. All samples collected during both campaigns were kept at 4.0°C and transported to the Hydrogeochemistry and Water Quality Laboratory of the Water Sciences Unit, Centro de Investigación Científica de Yucatán.

#### Laboratory analysis

Alkalinity was measured by the titration method using 0.2 N sulfuric acid ( $\text{H}_2\text{SO}_4$ ). Nutrients ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{PO}_4^{3-}$ ), cations ( $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Sr}^{2+}$ ) and anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ) were determined using ion chromatography with an 882 Compact Plus IC Metrohm (Metrohm México, México City, México) and certified standards (TraceCERT, Sigma-Aldrich México) for calibration. For determination of  $\text{NH}_4^+$ , a spectrophotometer (LaMotte, Análisis y Soluciones Ambientales, México City, México) was used. Water analyses were performed at the Hydrogeochemistry and Water Quality Laboratory of the Water Sciences Unit, Centro de Investigación Científica de Yucatán A.C. The concentrations of major elements (Al, Fe, Ca, Mg, Ti, Sr and K) and trace elements (Mn, Ba, Ni, Zn, and U) in sediment samples were determined after sample dissolution using inductively coupled plasma-mass spectrometry (ICP-MS; XR Thermo Scientific, San Diego, CA, USA) at the Institute of Marine Sciences at the University of California – Santa Cruz (UCSC). Prior to these analyses, 100 mg of homogenised sediment was dispersed in 1.5 mL of MilliQ water and digested using 15.5 N nitric acid ( $\text{HNO}_3^-$ ). A 100- $\mu\text{L}$  subsample was diluted 200-fold using 1%  $\text{HNO}_3^-$  for analysis. Instrumental drift was corrected with Sc

and Rh standards; Rh was used as the internal standard correction for Sr, Ba and U, whereas Sc was used as the internal standard correction for all other elements. Counts per second values were converted to concentrations using a standard curve prepared from a homemade rendition of the NIST1D (National Institute of Standards and Technology, NIST) standard reference material (argillaceous limestone). An average of three procedural blanks was subtracted from final concentration values.

To determine the sediment mineralogy, sediment samples (2.0 g) were analysed using a Panalytical X'Pert Pro X-Ray Diffraction (XRD) Spectrometer (Royston, UK) with a 1-h rotating platter in the Marine Sciences Laboratory, UCSC. Sample 2-theta peaks were identified using the Panalytical Spectrometer mineral spectrum database as a reference. The most prominent peaks for all samples occurred near 29.5° with a pair of peaks near 46 and 47°.

## Results and discussion

### Physicochemical parameters

The main physicochemical features of shallow water in Bacalar Lagoon are presented in Table 1. The low EC values (2.65–3.19  $\text{mS cm}^{-1}$ ) indicate a freshwater system, with pH ranging from 6.6 to 7.3 at the sampling sites (mean pH = 7.05). Water temperature was relatively stable in the study area during our sampling campaigns (27.5–29.7°C). The EC, temperature and pH ranges measured in this study are consistent with measurements made by Gischler *et al.* (2008), Beltrán (2010), Pérez *et al.* (2011), Castro-Contreras *et al.* (2014) and Sánchez *et al.* (2015) in this system.

Fig. 2 shows the temperature profiles along the southern side of Bacalar Lagoon. The relatively small temperature variability among lagoon sites (28.5–28.8°C) suggests a near-homogeneous temperature with depth for both seasons (Fig. 2b). This indicates a well-mixed water column consistent with the shallow depth of the lagoon where the samples were collected.

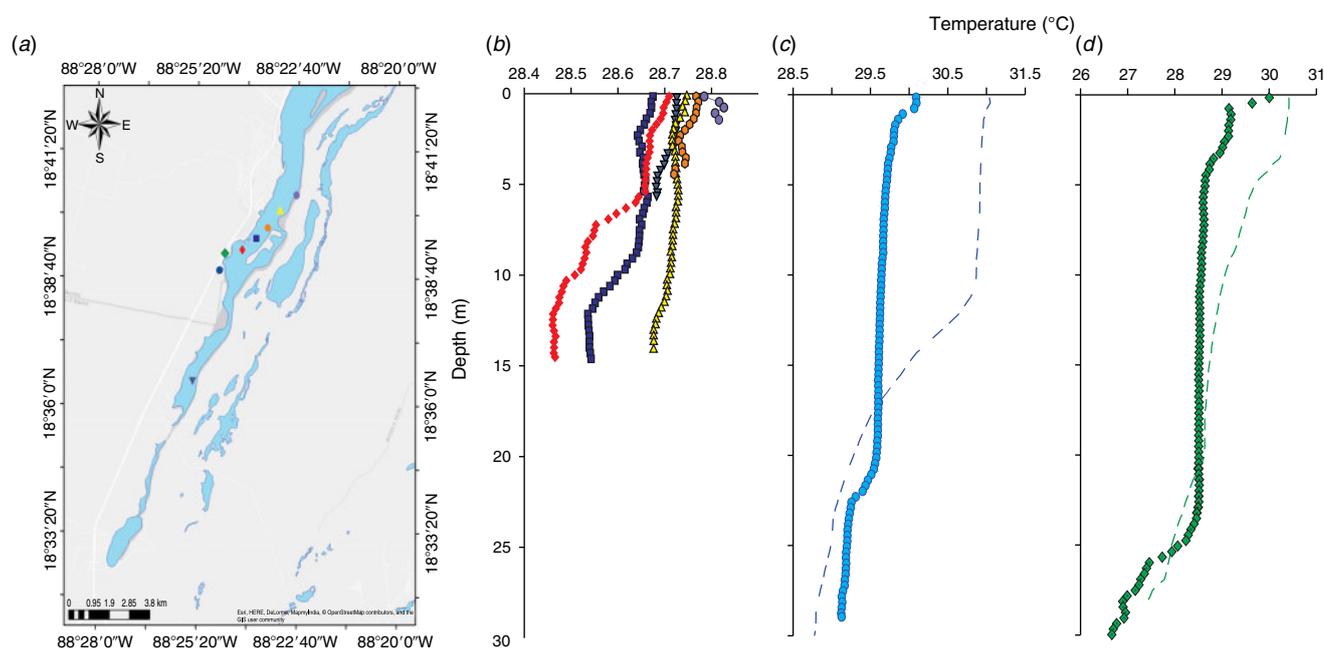
In contrast, the water column profiles of the *cenotes* show slight variability between sampling campaigns; in June the temperature of *cenotes* Azul and Cocalitos was higher (31.0 and 30.4°C respectively) compared with November temperatures (30.0°C). During both sampling campaigns, the *cenotes* clearly show stratification with two thermoclines. During June, the *cenote* Azul thermoclines are at depths of 0.5 and 12.0 m, whereas in November they are at 2.3 and 29.0 m (Fig. 2c). At *cenote* Cocalitos, the June thermoclines are at 3.8 and 29.0 m, whereas in November they are at 2.0 and 24.0 m (Fig. 2d). For both *cenotes*, the first thermocline is related to diurnal changes in solar radiation (heating of surface waters), whereas the second is derived from distinct mixing that varies seasonally and between years. During winter (November), water column mixing extends deeper due to wind action, whereas during summer (June) the changes in thermocline depth are due to an increase in temperature over the warm months, allowing for water column stratification and shallowing of the thermocline.

$\text{NO}_3^-$  concentrations ranged from 0.1 to 2.7  $\text{mg L}^{-1}$ , whereas  $\text{NO}_2^-$  and  $\text{PO}_4^{3-}$  concentrations were below the limits of detection of the method used in the present study (0.01 and 0.1  $\text{mg L}^{-1}$  respectively). These results are consistent with the oligotrophic designation of Bacalar Lagoon. It has been

**Table 1. Main physical and chemical parameters of water samples in Bacalar Lagoon**

Standard deviation for the elements is as follows:  $\text{Na}^+$  0.97%,  $\text{K}^+$  0.13%,  $\text{Mg}^{2+}$  2.98%,  $\text{Ca}^{2+}$  14.29%,  $\text{Sr}^{2+}$  0.34%,  $\text{Cl}^-$  2.11%,  $\text{SO}_4^{2-}$  9.0%,  $\text{SiO}_2^-$  2.6%,  $\text{NO}_3^-$  0.19%, and  $\text{NH}_4^+$  0.04%. BLD, below the limit of detection; NA, data not available. Ionic balance <10%. The locations of each of the sample sites are shown in Fig. 1

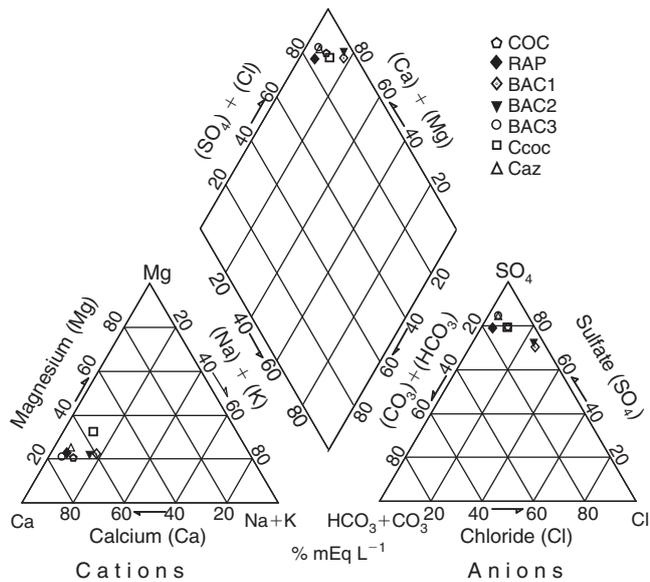
	COC	RAP	BAC1	BAC2	BAC3	Ccoc	Caz		
Site	Cocalitos	Los Rápidos	Bacalar 1	Bacalar 2	Bacalar 3	Cenote Cocalitos	Cenote Azul		
Depth (m)	0.5	0.5	0.5	0.5	0.5	0.5	15.0	0.5	15.0
pH	6.58	6.97	7.31	7.34	NA	6.54	NA	6.85	NA
Temperature (°C)	29.26	28.91	27.47	29.67	29.20	29.3	28.50	30.84	29.60
EC ( $\text{mS cm}^{-1}$ )	2.93	2.65	3.15	3.19	2.50	2.68	NA	2.67	NA
TDS ( $\text{mg L}^{-1}$ )	1.76	1.60	1.95	1.90	NA	1.57	NA	1.56	NA
Chemical composition ( $\text{mg L}^{-1}$ )									
$\text{Na}^+$	63.0	32.47	133.57	108.11	32.73	47.40	34.10	31.30	33.60
$\text{K}^+$	0.75	0.41	1.80	1.74	0.25	3.58	2.97	2.82	3.05
$\text{Mg}^{2+}$	71.20	73.20	89.0	83.65	75.60	73.40	77.50	76.80	78.10
$\text{Ca}^{2+}$	393.0	376.0	386.0	386.0	422.0	208.0	354.0	342.0	365.0
$\text{Sr}^{2+}$	5.46	6.31	7.15	4.39	2.70	4.76	5.92	5.45	5.52
$\text{Cl}^-$	100.74	41.66	283.17	226.40	41.65	91.0	47.0	41.0	42.0
$\text{SO}_4^{2-}$	962.0	1015.0	1091.0	962.0	1174.0	913.0	1237.0	1107.0	1284.0
$\text{SiO}_2^-$	16.25	22.0	22.25	23.50	15.75	32.0	30.0	36.0	31.0
$\text{HCO}_3^-$	156.70	270.90	86.50	61.90	225.30	155.0	244.0	214.0	241.0
$\text{NO}_3^-$	1.40	1.74	2.68	0.10	2.67	2.0	1.28	2.55	2.83
$\text{NO}_2^-$	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD
$\text{NH}_4^+$	0.18	0.13	0.28	0.19	0.14	0.20	0.26	0.21	0.23
$\text{PO}_4^{3-}$	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD



**Fig. 2.** Temperature profiles in the lagoon and cenotes. (a) Sampling locations. Each symbol corresponds to the traces shown in the graphs on the right. (b) Temperature profiles at the different study sites in Bacalar Lagoon. (c, d) Temperature profiles of cenote Azul (c) and cenote Cocalitos (d). Grey (dots and diamonds) correspond to the November 2016 sampling campaign; dashed lines correspond to the June 2017 sampling campaign.

suggested (Beltrán 2010) that the low concentrations of bioavailable nitrogen ( $\text{NH}_4^+$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$ ) promote  $\text{N}_2$  fixation in the lagoon. The lower nutrient concentrations also favour the growth of stromatolites (Beltrán 2010).

Cation abundance in Bacalar Lagoon water follows the order  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{Sr}^{2+} > \text{K}^+$ ; anion abundance is in the order  $\text{SO}_4^{2-} \gg \text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^-$  (see Table 1). In order to determine the main hydrochemical features of the lagoon, a



**Fig. 3.** Piper diagram and groundwater composition. Each symbol correspond to lagoon sites, white square and white triangle points correspond to *cenotes* samples, which represent the groundwater in the region. BAC1, Bacalar 1; BAC2, Bacalar 2; BAC3, Bacalar 3; Caz, *cenote* Azul; Ccoc, *cenote* Cocalitos; COC, Cocalitos; RAP, Los Rápidos.

Piper diagram was made in Aquachem (ver. 3.7, Waterloo Hydrogeologic, Kitchener, ON, Canada) using the proportions of major cations and anions (Fig. 3). All samples cluster together in a group corresponding to a sulfate–calcium (Ca–SO<sub>4</sub>) water type. Studies performed by Sánchez *et al.* (2015) reported a Ca–HCO<sub>3</sub> water type in the northern part of the lagoon, and Oliva *et al.* (2016) showed that the north side of Bacalar Lagoon is characterised by muddy sediments with murky water all year long. In contrast, the south of the lagoon is associated with sandy sediments and high water transparency. We attribute the observed differences in water chemistry in the lagoon to the effects of sulfate-rich groundwater inputs in the south compared with the north, where lower groundwater input and sulfate concentrations were measured by Sánchez *et al.* (2015). The water chemistry in the south can have a direct effect on the formation of stromatolites, which are more abundant in the southern part of the Bacalar Lagoon. Pacton *et al.* (2015) showed that stromatolites appear to prefer fresh water rather than turbid and brackish lake waters, and turbidity is one of the most important factors restraining stromatolite development.

According to the Piper diagram (Fig. 3), the water type of Bacalar Lagoon is dominated by sulfates (962.0–1174.0 mg L<sup>-1</sup>). The SO<sub>4</sub>:Cl ratio may be indicative of water origin, and the ratio at the western side ranged between 6.96 and 20.55, higher than at the eastern side (2.81–3.10). All the SO<sub>4</sub>:Cl ratios in Bacalar Lagoon are between 27- and 197-fold greater than those of seawater (0.103; Perry *et al.* 2002), indicating that the sulfate source in the lagoon is not seawater intrusion. Therefore, we interpret the findings to indicate high sulfate originating from dissolution of evaporites.

Although all the lagoon water samples cluster into one group, spatial differences are present within the lagoon and may

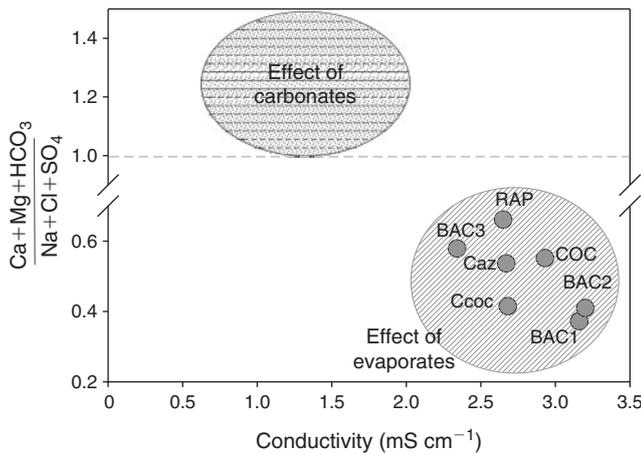
suggest differences in input sources or fluxes, as well as in processes affecting solute concentrations within the lagoon. The western side of the lagoon is characterised by higher alkalinity and calcium concentrations (157.0–270.0 mg CaCO<sub>3</sub> L<sup>-1</sup> and 376.0–422.0 mg L<sup>-1</sup> respectively) compared with the eastern side (62.0–86.0 mg CaCO<sub>3</sub> L<sup>-1</sup> and 86.0 mg L<sup>-1</sup> respectively). The alkalinity of the western side is similar to the alkalinity measured at Caz and Ccoc (244.0 and 241.0 mg CaCO<sub>3</sub> L<sup>-1</sup> respectively at a depth of 15.0 m). A gradient of increasing alkalinity is seen from north to south. Because high alkalinity is associated with groundwater input and the waters are undersaturated with regard to carbonate minerals, this alkalinity gradient indicates a diminishing effect of groundwater towards the north of the lagoon. Schmitter-Soto *et al.* (2002) reported other factors that can affect alkalinity in the Yucatan Peninsula, including the contribution of meteoric water (rich in carbonate and bicarbonate) and precipitation, which promotes the dissolution of carbonates and therefore affects alkalinity.

The concentrations of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> are lower on the eastern than western side of the lagoon, potentially explaining the formation of stromatolites in the western part of the lagoon, where external sources of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> are present. To reach the saturation necessary for precipitation of microbialites, Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> are needed, which has been reported in other systems (Chagas *et al.* 2016). The EC (3.15–3.19 mS cm<sup>-1</sup>) and Na<sup>+</sup> (4.7–5.8 mg L<sup>-1</sup>) and Cl<sup>-</sup> (41.0–283.0 mg L<sup>-1</sup>) concentrations on the eastern side of the lagoon are higher than on the western side (2.65–2.93 mS cm<sup>-1</sup>). These differences most likely occur because the eastern part of Bacalar Lagoon is shallower (0.4–0.6 m) than the western part (1.0–2.2 m), promoting higher evaporation on the eastern side. Marfia *et al.* (2004) identified high-calcium, high-sulfate water in the south-eastern area of Quintana Roo, including north-eastern Belize, likely from gypsum dissolution; when the groundwater is mixed with seawater, the mixture forms a caliche barrier, preventing seawater intrusion characteristic of the north-east coast.

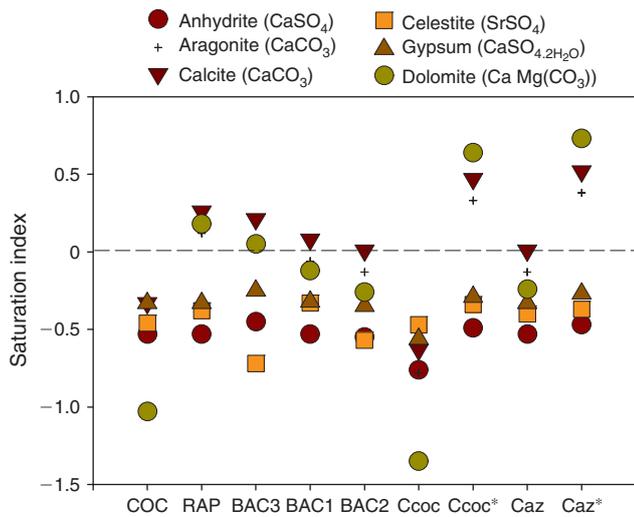
The (Ca<sup>2+</sup> + Mg<sup>2+</sup> + HCO<sub>3</sub><sup>-</sup>) to (Na<sup>+</sup> + Cl<sup>-</sup> + SO<sub>4</sub><sup>2-</sup>) ratio has been used to determine the effect of carbonate and evaporite solute sources in groundwater and surface waters (Appelo and Postma 2005; Khedidja and Boudoukha 2016). When plotting this ratio against EC (Fig. 4), it is clear that dissolution of evaporitic substratum is the dominant source of cations in this system. The lower EC (fresh water) and a carbonate to sulfate ion ratio <1.0 also indicate that evaporite dissolution and not seawater intrusion controls ion composition in Bacalar Lagoon.

The saturation indices (SI) for the different mineral species considered in our system (calcite, dolomite, aragonite, gypsum and celestite) were calculated based on field pH and temperature measurements using PHREEQC (ver. 3.7, US Geological Survey, Denver, CO, USA) (Fig. 5). Our calculations allowed us to determine the SI of Bacalar Lagoon water (note, SI = 0 signifies equilibrium; SI > 0 signifies oversaturation and thus mineral precipitation; and SI < 0 signifies undersaturation and thus mineral dissolution (Appelo and Postma 2005).

According to the SI calculations, three trends were identified (Fig. 5). The first corresponds to four sites (RAP, BAC3, Caz and Ccoc; 15 m deep) and shows oversaturated conditions with regard to aragonite, calcite and dolomite. In the second group (Coc and Ccoc; surface sample), all the minerals are

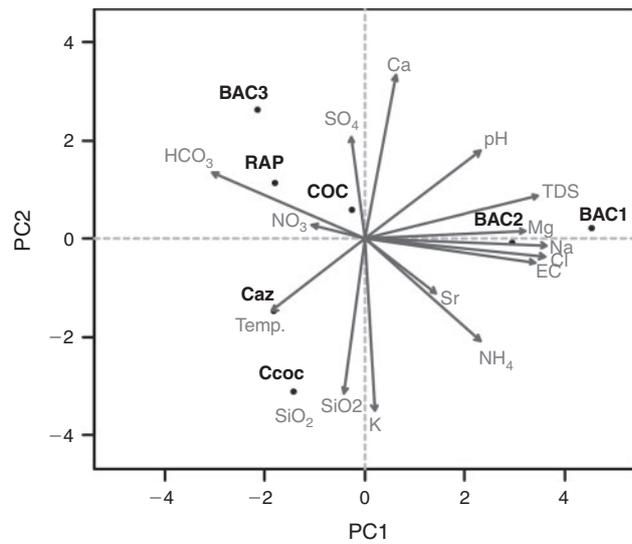


**Fig. 4.** Mineralisation effect on water chemistry. Dark grey points represent the sampling sites; dashed circular areas indicate the range in which the electrical conductivity and major element ratios are interpreted as resulting from mineralisation of evaporites or carbonates according to [Khedidja and Boudoukha \(2016\)](#). BAC1, Bacalar 1; BAC2, Bacalar 2; BAC3, Bacalar 3; Caz, *cenote* Azul; Ccoc, *cenote* Cocalitos; COC, Cocalitos; RAP, Los Rápidos.



**Fig. 5.** Saturation index (SI) calculated for each sample site for all relevant minerals. Note, SI = 0 indicates the mineral equilibrium (grey line), SI > 0 indicates oversaturation and SI < 0 indicates undersaturation. Asterisks indicate *cenote* water samples at a depth of 15 m. BAC1, Bacalar 1; BAC2, Bacalar 2; BAC3, Bacalar 3; Caz, *cenote* Azul; Ccoc, *cenote* Cocalitos; COC, Cocalitos; RAP, Los Rápidos.

experiencing dissolution (undersaturation). Finally, the third group (BAC1 and BAC2) is associated with calcite equilibrium and undersaturation of the other minerals. Bacalar Lagoon is located in a region where Miocene rocks containing gypsum and anhydrite are common and water–rock interaction results in the dissolution of evaporites ([Perry \*et al.\* 2002; 2009](#)). The high concentrations of  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$  and  $\text{Sr}^{2+}$  could be derived from the dissolution of these minerals. The water samples in Bacalar



**Fig. 6.** Principal component analysis based on 15 chemical variables (grey arrows) at different sampling sites (lagoon and *cenotes*). PC1, principal component 1; PC2, principal component 2; EC, electrical conductivity; TDS, total dissolved solids; Temp., temperature; BAC1, Bacalar 1; BAC2, Bacalar 2; BAC3, Bacalar 3; Caz, *cenote* Azul; Ccoc, *cenote* Cocalitos; COC, Cocalitos; RAP, Los Rápidos.

**Table 2.** Eigenvalues of principal component analysis components and variance explained

Principal component	Eigenvalue	Variance explained (%)
1	7.06	47.12
2	3.38	22.58
3	2.10	14.02
4	1.27	8.51

Lagoon are all undersaturated with regard to gypsum and anhydrite, indicating that these minerals would not precipitate within the lagoon. [Ceballos Martínez \(2002\)](#) indicated that gypsum and limestone in the Bacalar formation tend to be concentrated in the surface due to weathering, forming lamellar caliche.

The  $\text{Sr}^{2+}$  concentrations in samples from the western side are quite similar to concentrations measured at the *cenotes*, indicating an input of this element from groundwater. The same was suggested by [Perry \*et al.\* \(2002, 2009\)](#) when they compared concentrations of  $\text{Sr}^{2+}$  and  $\text{SO}_4^{2-}$  and Sr isotopes in the lagoon to those of *cenote* Azul.

Standardised principal component analysis (PCA) was performed using R (ver. 3.4.0, R Foundation for Statistical Computing, Vienna, Austria) to identify the dominant limnological gradients in the dataset. [Fig. 6](#) shows the results of a PCA applied to the 15 hydrochemical variables measured here (water temperature, pH, EC, TDS,  $\text{SiO}_2^-$ ,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{Sr}^{2+}$ ). We present only the first two components (PC1 and PC2) because these explained 47 and 22% of the total variance respectively ([Table 2](#)). PCA represents standard deviations, and when the distance among

samples is greater than 2 units, this indicates that the physicochemical conditions are distinct (Massaferro *et al.* 2018); hence, variations could be interpreted as significant differences between sites.

Samples along PCA Axis 1 show two distinctive patterns within the lagoon, which are separated by pH, EC, TDS, Na<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> distribution. The spread of samples within PC1 is relatively large, suggesting significant differences among sites. This spread reflects the distinct distributions of physicochemical features at the different sides of the lagoon: the western side (Axis 1; from -4 to 0 units) is characterised by a high HCO<sub>3</sub><sup>-</sup> content (COC, RAP, BAC3, Ccoc and Caz), whereas the eastern side (Axis 1; from 0 to 4 units) is characterised by high EC, Na<sup>+</sup>, pH and TDS and corresponds to the BAC1 and BAC2 sites.

PC2 is associated with SiO<sub>2</sub><sup>-</sup> and K<sup>+</sup> concentrations. PC2 shows two groups, with the first group corresponding to samples with low SiO<sub>2</sub><sup>-</sup> and K<sup>+</sup> concentrations (COC, RAP, BAC1, BAC2 and BAC3) and positive values of Axis 2 (from 4 to 0). The second group is characterised by high SiO<sub>2</sub><sup>-</sup> and K<sup>+</sup> concentrations (Ccoc and Caz samples) and corresponds to negative axis values (from 0 to -4). PC2 is associated with silica content due to higher silica concentrations in the *cenotes* compared with the rest of the lagoon samples. This can be explained by more rapid Si uptake in the sun-lit lagoon where diatoms are abundant.

Changes in pH and transparency by sediment disturbance can have an effect on stromatolites. Sulfate-reducing bacteria participate in the formation of stromatolites and appear to always be associated with Mg calcite and low-salinity and low-turbidity waters. Although stromatolites were not analysed in the present study, we recommend that a water monitoring program be established to survey nutrients and measure other variables, such as transparency, tourist and boat activity weathering, disturbance of sediments, and trace elements at least twice a year to ensure that the stromatolites are not negatively affected.

### Sediment characterisation

#### X-Ray diffraction

The results from the XRD analyses indicate that the main mineralogical composition for all sediment samples was calcite (CaCO<sub>3</sub>), dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>) and SiO<sub>2</sub> (quartz and possibly minor amounts of coesite). In general, calcite was in highest abundance in all cores. Dolomite was present in all samples at lower proportions.

These results are in accordance with the SI, where calcite is oversaturated in the western part of the lagoon and Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> concentrations are elevated throughout the lagoon. Coesite forms under conditions of high pressure (3–10 GPa; Hemley *et al.* 1994), and the presence of this mineral could be related to the impact of the Chicxulub meteorite (Lounejeva *et al.* 2002). Fouke *et al.* (2002), with an estimated diameter of its effect ~360 km. The presence of coesite in Bacalar Lagoon could be associated with this event. Fouke *et al.* (2002) and Kenkmann and Schönian (2006) reported Chicxulub ejecta deposited in Belize and in some regions of the Rio Hondo (near Bacalar Lagoon). However, identifying the origin of this mineral in Bacalar Lagoon requires additional detailed studies with longer scan times to confirm the presence of coesite. Other minerals that we found in lower proportions are barite (BaSO<sub>4</sub>)

and a few samples with sphalerite (ZnS), with higher proportions of barite in the western than eastern side of the lagoon.

### Geochemistry

Elemental concentrations in the sediment samples are shown in Fig. 7. All sediment cores had high concentrations of Ca<sup>2+</sup>, Mg<sup>2+</sup> and Sr<sup>2+</sup>, which were one to three orders of magnitude higher than concentrations for the rest of the elements, consistent with carbonate minerals (calcite) dominating the sediment.

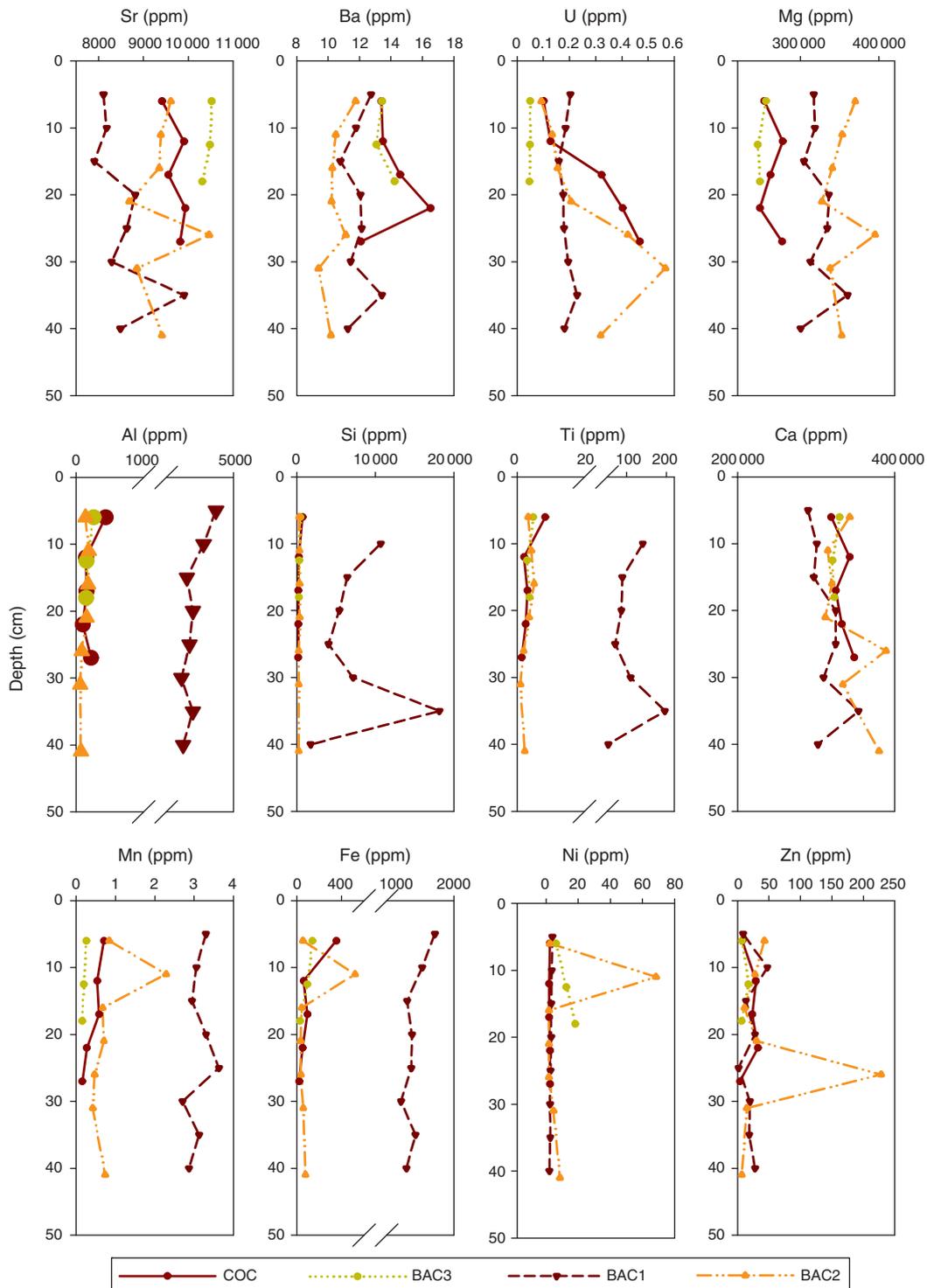
Element abundance was similar in cores of sites located in the western part of the lagoon (COC, RAP and BAC3), in the order Ca<sup>2+</sup> > Mg<sup>2+</sup> >> Sr<sup>2+</sup> > Si<sup>4+</sup> > Al<sup>3+</sup> > Fe<sup>3+</sup> > Zn<sup>2+</sup> > K<sup>+</sup> > Ba<sup>2+</sup> > Ti<sup>4+</sup> > Ni<sup>2+</sup> > Mn<sup>2+</sup> > U<sup>6+</sup>. The order of element abundance for the eastern cores (BAC1 and BAC2) was similar, except that Mg was more abundant than Ca (Mg<sup>2+</sup> > Ca<sup>2+</sup> >> Sr<sup>2+</sup> > Si<sup>4+</sup> > Al<sup>3+</sup> > Fe<sup>3+</sup> > Zn<sup>2+</sup> > K<sup>+</sup> > Ni<sup>2+</sup> > Ba<sup>2+</sup> > Ti<sup>4+</sup> > Mn<sup>2+</sup> > U<sup>6+</sup>). These relative abundances suggest that cores from the western side are dominated by Ca<sup>2+</sup> carbonate minerals (likely calcite), whereas those from the east side contain more dolomite. The BAC1 core had the highest concentrations of Al<sup>3+</sup>, Si<sup>4+</sup>, K<sup>+</sup>, Ti<sup>4+</sup>, Mn<sup>2+</sup> and Fe<sup>3+</sup>, likely representing some silicates and iron–manganese oxides from terrigenous sources. The highest Ni<sup>2+</sup> and Zn<sup>2+</sup> concentrations were measured in the core from BAC2 and may represent anthropogenic pollutant inputs. The other elements analysed had similar distributions in all cores.

In general, concentrations of Ba<sup>2+</sup>, U<sup>6+</sup> and Zn<sup>2+</sup> were higher in deeper sections of the cores, and this may suggest temporal changes in the input of these elements. The rest of the elements (Ca<sup>2+</sup> and Mg<sup>2+</sup>) did not show variations with depth down the core ( $r^2 < 0.5$ ).

The concentrations of elements span orders of magnitude, therefore the data do not satisfy the assumption of normality. A Spearman correlation was performed using STATISTICA (ver. 13.3, Palo Alto, CA, USA) to test the relationship between the trace elements in each core with significance level at  $P < 0.05$ .

Except for BAC3, the most significant correlation was for Al–(Fe–Ti) ( $r^2 > 0.90$ ). In the BAC2 core, significant correlations were found for Sr–Mg, Al–Ti, K–Ni and Si–Ti ( $r^2 = 0.90, 0.90, -0.88$  and  $0.86$  respectively). For BAC1, the highest correlations were found for Sr–Ca, Al–(Fe, Ni), K–(Fe, Ni) and Ba–Mg ( $r^2 = 0.95, 0.98, 0.98$  and  $0.81$  respectively). Negative correlations were found at the COC site ( $r^2 = -0.90$ ) for Al–(Zn, Sr), Fe–(Ca, U), Mn–(U, Ca), U–Si and Ba–Zn, but a positive correlation was found for Ti–(Mn, Fe), with  $r^2 = 0.90$ . In the BAC3 core, relationships were found for only four elements: U–Sr and Ca–Mg ( $r^2 = 0.99$ ).

The relationship for Al–(Ti, Fe) in almost all cores is derived from the fact that these elements represent silicates and other refractory minerals, and hence aeolian or fluvial input of particulate matter from land (Drever 2005). The correlation for Ca–(Sr–Mg) in most cores is consistent with the main carbonate mineralogy of these sediments. Other correlations are not universal and, in general, no pattern in spatial distribution was found in the correlation between elements among all cores, suggesting that these elements are not controlled by the same parameters at each site.



**Fig. 7.** Concentrations of trace and major elements in sediment cores. BAC1, Bacalar 1; BAC2, Bacalar 2; BAC3, Bacalar 3; COC, Cocalitos.

*Sediment pollution*

Some trace elements in Bacalar Lagoon sediments may reflect anthropogenic pollution. Here we used four indices

following [Manoj and Padhy \(2014; see Table 3\)](#). We normalised concentrations to Al because it is a conservative lithogenic element and is resistant to chemical weathering; hence, it does

**Table 3. Indices as indicators of sediment quality based on Manoj and Padhy (2014) and Javan *et al.* (2015)** $M_s$ , sample element concentration;  $M_b$ , background concentration of the element

Index	Equation	Sediment quality
Index of geoaccumulation	$I_{geo} = \ln(M_s/1.5 \times M_b)$	<0 = unpolluted 0–1 = unpolluted to moderately polluted 1–2 = moderately polluted 2–3 = moderately polluted to highly polluted 3–4 = highly polluted 4–5 = highly polluted to very highly polluted >5 = very highly polluted
Contamination factor	$CF = M_s/M_b$	<1 = low CF 1 ≤ CF <3 = moderate CF 3 ≤ CF <6 = considerable CF
Contamination degree	$CD = \sum_{i=1}^n CF$	≥6 = very high CF <6 = low CD 6 ≤ CD <12 = moderate CD 12 ≤ CD <24 = considerable CD ≥24 = high CD (anthropogenic contamination)
Pollution load index	$PLI = (CF_1 \times CF_s \times \dots \times CF_n)^{1/n}$	0 = unpolluted 1 = baseline levels of pollutants present >1 = progressive deterioration of site

not actively participate in the dominant geochemical cycles and does not have a significant anthropogenic source (Boës *et al.* 2011; Dautović *et al.* 2014).

For normalisation to Al, values for the Earth's crust were taken from Turekian and Wedepohl (1961), in which the values are mean concentrations in carbonates rocks of the upper crust: K = 2700.0 ppm; Mn = 1100.0 ppm; Ni = 20.0 ppm; Zn = 20.0 ppm; and Ba = 10.0 ppm.

To determine whether the elements are from lithological or anthropogenic sources, the trace element concentrations were compared with the crustal composition (Hernandez *et al.* 2003):

$$[M]_{lithogenic} = [Al]_s \times ([M]/[Al]_c) \quad (1)$$

$$[M]_{anthropogenic} = [M]_T - [M]_{lithogenic} \quad (2)$$

where the lithogenic input ( $[M]_{lithogenic}$ ) is estimated through the concentration of Al in the sample ( $[Al]_s$ ) and the ratio of the average of the Earth's crust ( $[M]/[Al]_c$ ). The anthropogenic input ( $[M]_{anthropogenic}$ ) was calculated based on the total concentration ( $[M]_T$ ) and the lithogenic input.

The results of these calculations are summarised in Table 4. For all cores,  $U^{6+}$ ,  $Mn^{2+}$  and  $K^+$  show negative values for the index of geoaccumulation ( $I_{geo}$ ), whereas the values of CF (contamination factor) and CD (contamination degree) are lower than 2.0. All factors indicate that the sediment is not polluted with these elements, which are likely of lithogenic origin. For  $Ni^{2+}$ , the  $I_{geo}$  (<0), CF (<1) and CD (<6) indices also indicate low pollution, except for the upper samples (depths of 0–6 and 6–11 cm) of the BAC2 core, where the CF is >3.0 and  $I_{geo}$  is >1.0, suggesting unpolluted to moderately polluted conditions. In contrast, the values of these indices for  $Zn^{2+}$  and  $Ba^{2+}$  show some spatial variability.

The CD of  $Zn^{2+}$  at all sites is >1.5. The eastern samples (BAC1 and BAC2) show higher CD values (8.22 and 18.05

respectively), suggesting moderate to considerable contamination of the sediment. The  $Ba^{2+}$  concentration exhibits a spatial distribution; the western sites (COC, RAP and BAC3) have higher  $Ba^{2+}$  concentrations compared than the eastern sites, and the calculated indices were correspondingly higher for the western side of the lagoon. However, overall, the indices indicated that the sediments on both sides of the lagoon are unpolluted with regard to Ba and the differences are likely due to higher barite content on the western side. Based on these indices, no influence of human activities was detected in eastern core samples (BAC1 and BAC2).

The higher  $Zn^{2+}$  and  $Ba^{2+}$  concentrations may be due to a higher input of these elements into the area close to these sites. However, water column distributions have to be assessed to confirm this.  $Zn^{2+}$  and  $Ba^{2+}$  in Bacalar Lagoon sediments could be derived from two sources: (1) authigenic minerals found in the sediment, which, on the western side, contain barite ( $BaSO_4$ ) and some sphalerite ( $ZnS$ ); and (2) anthropogenic sources, such as agricultural fertiliser or cattle feed. Commercial fertilisers contain micronutrients, such as  $Zn^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{3+}$ ,  $Cu^{2+}$ ,  $Mo^{6+}$  and  $Ba^{2+}$  in concentrations ranging from trace to several ppm, which could infiltrate and cause pollution in the soil and groundwater (Adriano 1986). Baize (1997) indicated that Zn is found in animal feed used for pigs that are raised domestically and commercially in the region. The waste water generated by this industry has been poorly handled, resulting in adverse effects on the environment (Drucker *et al.* 2003). Near the town of Bacalar, fertilisers and agrochemicals are used regularly (Álvarez-Legorreta 2009). The agriculture practices in the municipality include maize, sugarcane and pepper, and more than 40 products are spread annually on these crops (fertilisers, herbicides and pesticides; Euán-Ávila *et al.* 2002). García-Ríos and Gold-Bouchot (2002) identified Fe, V, Ni, Pb, Zn, Cu and Cd in sediments of nearby Chetumal Bay. Indeed, Bacalar and Othón P. Blanco municipalities have the highest fertilised area

**Table 4. Index of geoaccumulation ( $I_{geo}$ ), anthropogenic (A.) input, contamination factor (CF) and contamination degree (CD) for Ba, U, K, Mn, Ni and Zn in the sedimentary record of the Bacalar Lagoon**

NA, data no available; PLI, pollution load index; BAC1, Bacalar 1; BAC2, Bacalar 2; BAC3, Bacalar 3; COC, Cocalitos; RAP, Los Rápidos

Site	Depth (cm)	Ba		U		K		Mn		Ni		Zn		PLI									
		$I_{geo}$	A. input																				
COC	0-6	-0.16	12.36	1.34	7.01	0.65	-6.88	-246.29	0.01	0.03	-11.19	-113.61	0.001	0.002	-3.71	0.21	0.11	0.53	-2.03	5.29	0.37	4.79	0.05
	6-12	-0.15	13.14	1.35		0.06	-6.75	-55.69	0.01		-11.60	-37.53	0.000		-4.09	1.07	0.09		-0.04	28.46	1.46		0.06
	12-17	-0.04	14.21	1.46		0.15	NA	-100.01	0.00		-11.47	-40.16	0.001		-4.05	1.07	0.09		-0.37	22.54	1.16		0.00
	17-22	0.14	16.27	1.65		0.18	-11.58	-62.88	0.00		-12.57	-25.88	0.000		-3.62	1.96	0.12		0.10	31.74	1.61		0.04
	22-27	-0.31	11.56	1.21		0.21	NA	-141.25	0.00		-13.38	-57.39	0.000		-3.67	1.32	0.12		-3.01	2.67	0.19		0.00
RAP	0-6	-0.39	10.74	1.15	2.64	0.09	-8.89	-188.18	0.00	0.02	-10.67	-79.12	0.001	0.001	-5.08	-0.57	0.04	0.14	-1.56	8.70	0.51	2.84	0.04
	6-11	-0.01	13.60	1.49		0.06	-6.51	-317.21	0.02		-11.89	-146.91	0.000		-3.91	-0.69	0.10		0.63	43.90	2.33		0.07
BAC1	0-5	-0.24	2.67	1.27	9.56	0.69	-2.30	-1893.64	0.31	1.61	-8.96	-1103.98	0.003	0.023	-3.00	-16.39	0.19	1.15	-1.74	-11.18	0.45	8.22	0.14
	5-10	-0.35	3.02	1.18		0.08	-2.76	-1766.36	0.22		-9.07	-960.21	0.003		-3.11	-14.04	0.17		0.66	29.82	2.37		0.17
	10-15	-0.48	3.82	1.08		0.07	-3.07	-1398.30	0.18		-9.13	-763.41	0.003		-3.27	-10.83	0.16		-1.19	-0.74	0.66		0.13
	15-20	-0.31	4.44	1.21		0.08	-2.95	-1531.79	0.19		-8.96	-834.86	0.003		-3.30	-12.20	0.15		-0.13	12.25	1.37		0.15
	20-25	-0.31	4.88	1.21		0.08	-3.01	-1457.41	0.19		-8.83	-794.49	0.003		-3.51	-11.89	0.13		-4.24	-12.93	0.08		0.09
BAC2	25-30	-0.39	5.04	1.14		0.09	-3.20	-1289.17	0.16		-9.25	-701.52	0.002		-3.63	-10.37	0.12		-0.61	6.89	0.98		0.13
	30-35	-0.16	5.81	1.34		0.10	-2.99	-1546.25	0.19		-9.04	-834.54	0.003		-3.53	-12.64	0.13		-0.69	3.37	0.93		0.14
	35-40	-0.41	4.67	1.13		0.08	-3.13	-1317.72	0.17		-9.17	-721.83	0.003		-3.92	-11.20	0.10		-0.12	14.46	1.38		0.13
BAC3	0-6	-0.35	11.41	1.17	7.34	0.86	-7.43	-66.89	0.01	0.06	-10.94	-35.96	0.001	0.006	-3.74	1.57	0.11	4.44	0.51	42.03	2.14	18.05	0.07
	6-11	-0.52	10.05	1.05		0.06	-8.34	-106.94	0.00		-9.49	-46.38	0.002		1.19	67.64	3.43		-0.12	26.66	1.38		0.12
	11-16	-0.55	9.84	1.03		0.07	-7.50	-92.68	0.01		-11.26	-46.17	0.001		-4.20	0.78	0.08		-1.44	10.18	0.55		0.05
	16-21	-0.55	9.85	1.02		0.09	-5.97	-34.26	0.02		-11.19	-39.62	0.001		-4.21	0.89	0.08		0.01	29.53	1.51		0.08
	21-26	-0.43	10.93	1.11		0.19	-8.28	-38.39	0.00		-11.78	-20.46	0.000		-4.12	1.35	0.09		2.93	227.85	11.41		0.09
BAC3	26-31	-0.68	9.25	0.94		0.26	-8.32	-25.78	0.00		-11.94	-15.24	0.000		-2.73	4.24	0.23		-1.04	14.34	0.73		0.06
	36-41	-0.56	10.01	1.02		0.14	-8.75	-35.56	0.00		-11.13	-17.59	0.001		-1.82	8.19	0.43		-2.19	6.26	0.33		0.06
	0-6	-0.16	12.83	1.34	4.07	0.07	-6.82	-129.43	0.01	0.02	-12.66	-67.06	0.000	0.001	-5.53	-0.57	0.03	0.08	-2.11	5.72	0.35	1.52	0.03
	6-12	-0.20	12.70	1.31		0.02	-9.89	-95.45	0.00		-13.08	-40.43	0.000		-5.80	-0.20	0.03		-0.81	16.39	0.86		0.02
	12-18	-0.08	13.89	1.42		0.02	-8.91	-86.95	0.00		-13.41	-38.72	0.000		-5.93	-0.21	0.02		-2.23	5.67	0.32		0.02

in Quintana Roo state (Instituto Nacional de Estadística y Geografía 2016). Owing to the karstic nature of the area, these products can immediately infiltrate the aquifer and therefore could be affecting the lagoon. Because the concentration of ZnS minerals was low in the cores, it is suggested that the source of  $Zn^{2+}$  could be derived from human activities. Although the results from the pollution load index (PLI) ( $<1$ ) for all samples indicate that the sites are not highly polluted, the excess  $Zn^{2+}$  in the sediment suggests some local pollution with regard to this element. Conversely, the concentrations of  $Ba^{2+}$  can be explained by the variable occurrence of barite in the cores.

Minimal trace metal pollution is consistent with previous metal work in the lagoon. Castro-Contreras *et al.* (2014) reported heavy metal concentrations in Bacalar Lagoon water below the maximum limits of the Mexican legislation (NOM-127-SSA1-1994) and ecological water quality criteria (CE-CCA-001/89) that establish the limits of heavy metals for drinking water, irrigation and recreational activities.

Nevertheless, organochloride compounds (pesticides and polychlorinated biphenyls) and hydrocarbons in sediments have been identified by Noreña-Barroso *et al.* (1998) in the Chetumal Bay area, near Bacalar Lagoon. Organochlorine pesticides (OCPs) are used in agriculture in the region (Álvarez-Legorreta 2009). Furthermore, heavy metals and OCPs have been detected in crocodilian eggs near Chichorro Atoll (Charruau *et al.* 2013; Buenfil-Rojas *et al.* 2015).

## Conclusions

Bacalar Lagoon is a shallow and oligotrophic system (low-nutrient waters), with a mineralogical composition dominated by calcite, dolomite and evaporites dissolution. Water geochemical analyses show a clear spatial distribution of different parameters. The western part of the study area is characterised by high alkalinity and calcium and sulfate concentrations; the ratios of these constituents indicate groundwater sources and no seawater intrusion. The decreases in these parameters towards the north indicate a gradient in groundwater influence throughout the lagoon. The eastern part of the study area is characterised by a shallower water column resulting in high evaporation and high electrical conductivity compared with the western side.

We present the first measurements of trace elements in carbonate sediments in Bacalar Lagoon. The sediment exhibits only moderate contamination with  $Zn^{2+}$  on the western side of the lagoon. The high Ba concentration in the sediment corresponds to barite, but further work is necessary to identify the source of  $Ba^{2+}$  and  $Zn^{2+}$ . This study can be useful for Bacalar municipality to make decisions and define actions regarding the management and development of Bacalar Lagoon.

## Conflicts of interest

The authors declare that they have no conflicts of interest.

## Declaration of funding

This investigation was financed by the ‘Water Security Project in the South-east Mexico in the face of two climate change scenarios’ project (CONACYT 247565) and ‘Project networks CONACYT’ (282240). The authors acknowledge a grant from CONACYT

towards a Masters of Water Sciences degree (awarded to Nidia Tobón Velázquez).

## Acknowledgements

The authors thank technical staff Daniela Ortega (Water Sciences Unit, Centro de Investigación Científica de Yucatán) and Kimberly Bitterwolf (University of California—Santa Cruz).

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Handling Editor: Russell Frew