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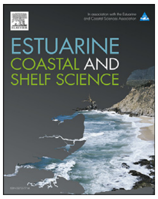

Water and sediment quality in Cartagena Bay, Colombia: Seasonal variability and potential impacts of pollution

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ABSTRACT

Cartagena Bay, one of the Caribbean's hot spots of pollution, is an estuarine system connected to the Caribbean Sea by two straits. Large freshwater discharges from the Dique Canal into the south of the bay produce estuarine conditions strongly related to the seasonal variability of runoff from the Magdalena River watershed. The bay's seasonal conditions may be characterized by three seasons: strong winds/low runoff (Jan.–April), weak winds/intermediate runoff (May–Aug.), and weak winds/high runoff (Sept.–Dec.). This coastal zone is known to be impacted by land-based sources of pollution, including continental runoff, industrial effluents and domestic wastewater. However, previous studies have not sufficiently ascertained the spatio-temporal extent of this pollution. This study addresses the following research question: What is the current extent of water and sediment pollution in Cartagena Bay and which factors control its seasonal variability? Monthly seawater samples (Sept.2014–Aug.2015) were taken from surface and bottom depths at 16 stations in and around Cartagena Bay and analyzed for physical, chemical, and biological parameters. Surface sediments were sampled from the bay's bottom every three months and analyzed for various trace metals. Seasonal variability was observed in nearly all of the water quality parameters, with higher concentrations usually coinciding with the high runoff season. Potential pollution impacts are shown by wet-season averages of total suspended solids (45.0 ± 89.5 mg/l), turbidity (26.1 ± 59.7 NTU), biological oxygen demand (1.20 ± 0.91 mg/l), chlorophyll-*a* (2.47 ± 2.17 μg/l), nitrate (171.1 ± 112.6 μg/l), phosphate (43.1 ± 63.5 μg/l), total phosphorus (85.3 ± 77.2 μg/l), phenol (2.9 ± 17.4 mg/l), faecal coliforms (798 ± 714 MPN/100 ml) and enterococci (32 ± 30 CFU/100 ml) in excess of recommended threshold values for marine conservation and recreational adequacy. The bay's hypoxic conditions are evident with low dissolved oxygen concentrations (<4 mg/l) found at bottom depths during the wet season, moderate concentrations in the windy season, and low concentrations approaching surface waters during the transitional season, showing a seasonality related to the variability of water circulation and vertical stratification. Lower chlorophyll-*a* levels found in the water column during the wet season suggest that primary productivity in this eutrophic system is not limited by nutrients, which are abundant due to land-based effluents, but rather by water transparency which is significantly reduced during the wet season due to large sediment loads discharged from the Dique Canal. Sediments from the bay's bottom were found to have concentrations of mercury, cadmium, chromium, copper and nickel in excess of the Threshold Effects Levels (TEL) used as an indicator of potential impacts on marine life.

1. Introduction

Achieving harmony between a sustainable natural environment and economical development presents a difficult challenge common to any growing human population. Anthropogenic

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development typically results in changes to the environment's water resources due to the introduction of foreign substances or excess natural substances, such as sediments and nutrients, into receiving water bodies. The capacity of a water body to assimilate these inputs is limited, which presents the risk of pollution impacts on the water resources, the aquatic ecosystem and the economies dependent on ecosystem services. This is particularly the case in the coastal zone of Cartagena, Colombia, where impacts on coastal water quality have the potential to disrupt the local economy for tourism and artisanal fisheries, and to degrade the ecosystem of the adjacent marine protected area (MPA) of the Rosario and San Bernardo Islands.

The coastal city of Cartagena, Colombia, has approximately one million inhabitants (DANE, 2016), a large number of prominent ports and shipping operations, and the country's largest coastal industrial sector that currently includes over 70 industries (Cardique & AGD, 2006). The historic city, its nearby beaches and MPA also represent Colombia's principal touristic destination while the surrounding coastal communities have traditionally depended on artisanal fisheries. The juxtaposition of these anthropogenic activities, some of which depend on ecosystem services while others degrade ecosystem function, is the essence of the conflicting use of natural resources in Cartagena Bay. Pollution issues in this bay are further compounded by runoff from the Dique Canal which drains 7% of Colombia's largest river, the Magdalena (Fig. 1; Restrepo et al., 2014), about a third of which ultimately discharges into Cartagena Bay (Restrepo et al., 2016a).

Impacts on the water and sediment quality of Cartagena Bay have been documented for decades. The local environmental authority Cardique has conducted a biannual, surface seawater quality monitoring program since the year 2000, showing high levels of coliforms, nutrients and turbidity in the canal and bay (INVEMAR, 2001–2015). Garay and Giraldo (1997), Tuchkovenko and Lonin (2003), and Cañon et al. (2007) have documented hypoxic conditions at the bottom of the bay. These studies also showed high levels of biological oxygen demand and nutrients (Cañon et al., 2007), as well as high concentrations of chlorophyll-*a* in the upper layer of the bay (Tuchkovenko and Lonin, 2003; Cañon et al., 2007).

Various metals have been found in high concentrations in the bay's surface sediments (Parra et al., 2011a). Mercury is one of the metals of most interest that has been found at high levels in the sediments (FAO & CCO, 1978; Guerrero et al., 1995; Alonso et al., 2000; Cogua et al., 2012; Parra et al., 2011a, 2011b), in marine organisms (Alonso et al., 2000; Olivero-Verbel et al., 2008; 2009; Cogua et al., 2012), as well as in coastal birds (Olivero-Verbel et al., 2013) and in human populations in the surrounding fishing communities of Caño del Oro and Bocachica (Olivero-Verbel et al., 2008). Furthermore, previous research has shown high levels of hydrocarbons in sediments and marine organisms (Garay, 1983: Parga-Lozano et al., 2002; Johnson-Restrepo et al., 2008) and the presence of pesticides in the waters, sediments, and biota of Cartagena Bay (Castro, 1997; INVEMAR, 2009; Jaramillo-Colorado et al., 2015).

These impacts on the water and sediment quality of the bay are undoubtedly related to the observed deterioration of the marine ecosystems in the bay and in the adjacent Rosario Islands. Historically, the bay's benthic ecosystem used to be composed of seagrass beds which were drastically depleted decades earlier (Díaz and Gómez, 2003; Restrepo et al., 2006). The degradation of seagrass beds, coral reefs and benthic suspension feeding invertebrates in the adjacent Rosario Islands has been shown to be related with the turbid waters coming from Cartagena Bay (Restrepo et al., 2006, 2016b). Meanwhile the hypoxic conditions found at the bottom of the bay (Garay and Giraldo, 1997; Tuchkovenko and Lonin, 2003; Cañon et al., 2007) inhibit the recovery of benthic organisms in the bay, which is likely related to drastic reductions in artisanal fisheries observed in recent decades by the communities of Ararca and Caño del Oro (personal communication with fishermen; Fig. 1).

There are not many scientific interpretations available for the effects of fluvial, industrial and domestic inputs into the Caribbean coastal systems of Colombia. To the best of our knowledge, most studies and assessments lack sufficient sampling for an integrated analysis of water quality. Even more concerning, environmental authorities do not have access to reliable data to identify sources of pollution and the spatio-temporal extents of impacts (Restrepo, 2008). Additionally, coastal ecosystem processes under the influence of fluxes from the Andean rivers of Colombia are poorly understood due to insufficient data on pre-disturbance water quality or habitat status, a lack of data from undisturbed sites and inadequacies in the measurement of water quality parameters (Restrepo et al., 2016b).

In this study, the following research question is addressed: What is the current extent of water and sediment pollution in Cartagena Bay and which factors control its seasonal variability? Results are presented of a one-year monitoring program integrating the monthly monitoring of 14 physical, chemical, and biological parameters analyzed in water samples as well as the analysis of metals in sediment samples. Previous studies have either been focused only on specific individual parameters, or have only had a limited spatial distribution of sampling stations and lower monitoring frequencies. The present study thus presents a first look at an integrated approach that covers a wide range of parameters monitored at a sufficient frequency and spatial extent to adequately reflect seasonal and spatial variability in Cartagena Bay.

2. Study area

Cartagena Bay, located on the north coast of Colombia in the Caribbean Sea, is one of the receiving estuaries of fluvial fluxes from the main Andean catchment of Colombia, the Magdalena River basin (principal panel in Fig. 1). The Magdalena River is the main contributor of fluvial fluxes to the Caribbean Sea (Restrepo and Kjerfve, 2000; Restrepo, 2008) and flows to Cartagena Bay via the Dique Canal, a 114-km-long man-made distributary channel that diverges from the Magdalena River at Calamar (lower panel in Fig. 1). The canal has been dredged since the late 1920s and because of increased sedimentation in Cartagena Bay during the 1940s, new channels were constructed from El Dique to Barbacoas Bay. Since then, the suspended sediment load has reached and impacted the coastal ecosystems of Cartagena and Barbacoas bays, as well as the coral reefs of the Rosario Islands (Mogollón, 2013; Restrepo et al., 2006) which form Colombia's major continental coral reef system and a national marine protected area.

Cartagena Bay has a surface area of approximately 84 km^2, an average depth of 16 m, a maximum depth of 32 m, a maximum meridian length of 16 km (N-S), and a latitudinal length of 9 km (E-W). The bay is connected to the Caribbean Sea by two straits, Bocachica to the south and Bocagrande to the north, and has a small internal bay, situated to the north and adjacent to the city center (Tuchkovenko and Lonin, 2003). Water exchange in the bay is governed by wind-driven circulation and tidal movement through its two seaward straits and the influent discharge of freshwater from the Dique Canal to the south (Molares and Mestres, 2012). The tides in the bay are mixed, mainly diurnal with a micro-tidal range varying between 20 and 50 cm. Freshwater discharge from the Dique Canal produces estuarine conditions in the bay characterized by a highly stratified upper water column with low salinity and high turbidity at the surface.

The Dique Canal discharges approximately 55–250 m^3/s of

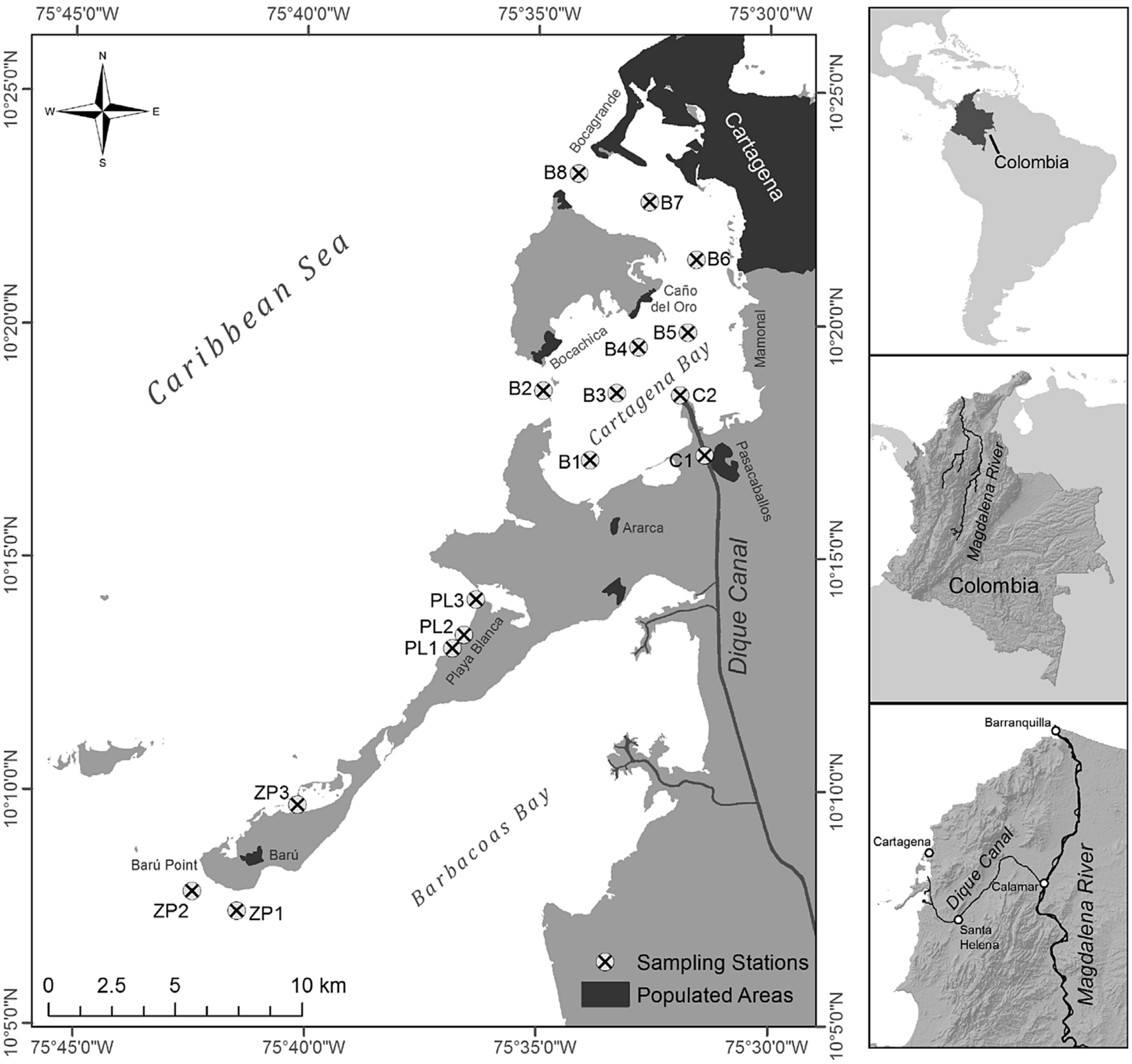

Fig. 1. Principal panel: study area showing water and sediment quality sampling stations in three zones (see section 3.1 of text for station descriptions); Cartagena Bay, "Playa Blanca" Beach, and the fishing zone of Barú Point. Secondary panels: location of Colombia (upper panel); location of the Magdalena River (middle panel); flow of the Magdalena into the Caribbean Sea and along the Dique Canal into Cartagena Bay (lower panel).

freshwater into the bay (Tuchkovenko and Lonin, 2003), the variability of which is strongly related to the seasonality of runoff from the Magdalena River watershed. The mean annual sediment load transported by the Dique Canal between 1984 and 2010 is 6.7 Mt/y, of which 1.9 Mt/y is ultimately delivered to Cartagena Bay and studies show this load is increasing (Restrepo et al., 2016a). During 26 years of monitoring, the Dique Canal has discharged approximately 177 Mt of sediment to the coast, 52 Mt of which was discharged into Cartagena Bay (Restrepo et al., 2016b).

The bay's seasonal conditions may be categorized according to the variability of winds and freshwater discharge. Fig. 2 shows multi-year average wind and discharge data from the local airport and canal gauging station, respectively. Based on daily data from 1998 to 2008, the canal gauging station at Santa Helena (approximately 35 km upstream of the bay) shows that the highest discharge levels occur from October to December and that the lowest levels occur from February to April.

Hourly METAR data from 1997 to 2015 of the Rafael Núñez International Airport (approximately 10 km north of the bay) show that from January to April the winds are strongest and predominantly northerly. This period of strong trade winds coincides with the strengthening of the southern Caribbean upwelling system which contributes to cooler water temperatures (Andrade and Barton, 2005; Rueda-Roa and Muller-Karger, 2013). From August to November, breezy conditions are observed when weaker winds come from a large range of directions, with a prominent westerly component in September and October. For the purposes of this study, months were grouped into three distinct seasons: the rainy season from Sept.–Dec., the dry/windy season from Jan.–April, and the transitional season from May–Aug.

A multitude of domestic, industrial, continental and maritime pollution sources are found in Cartagena Bay. Domestic sources of pollution include wastewater from parts of the city population not yet connected to the sewage system and about 32,500 people in the surrounding communities which discharge directly into the Dique Canal or into subterranean wells that can be susceptible to seepage or overflow during storm events. Previously, about 40% of the sewerage system (~48,000 m^3/day) was discharged directly to Cartagena Bay without treatment via an 800 m submarine outfall (UNEP, 1999; Tuchkovenko and Lonin, 2003), though since 2013 the city's sewage system has been routed to an outfall sufficiently far north of the city to not affect the bay. The city's industrial zone,

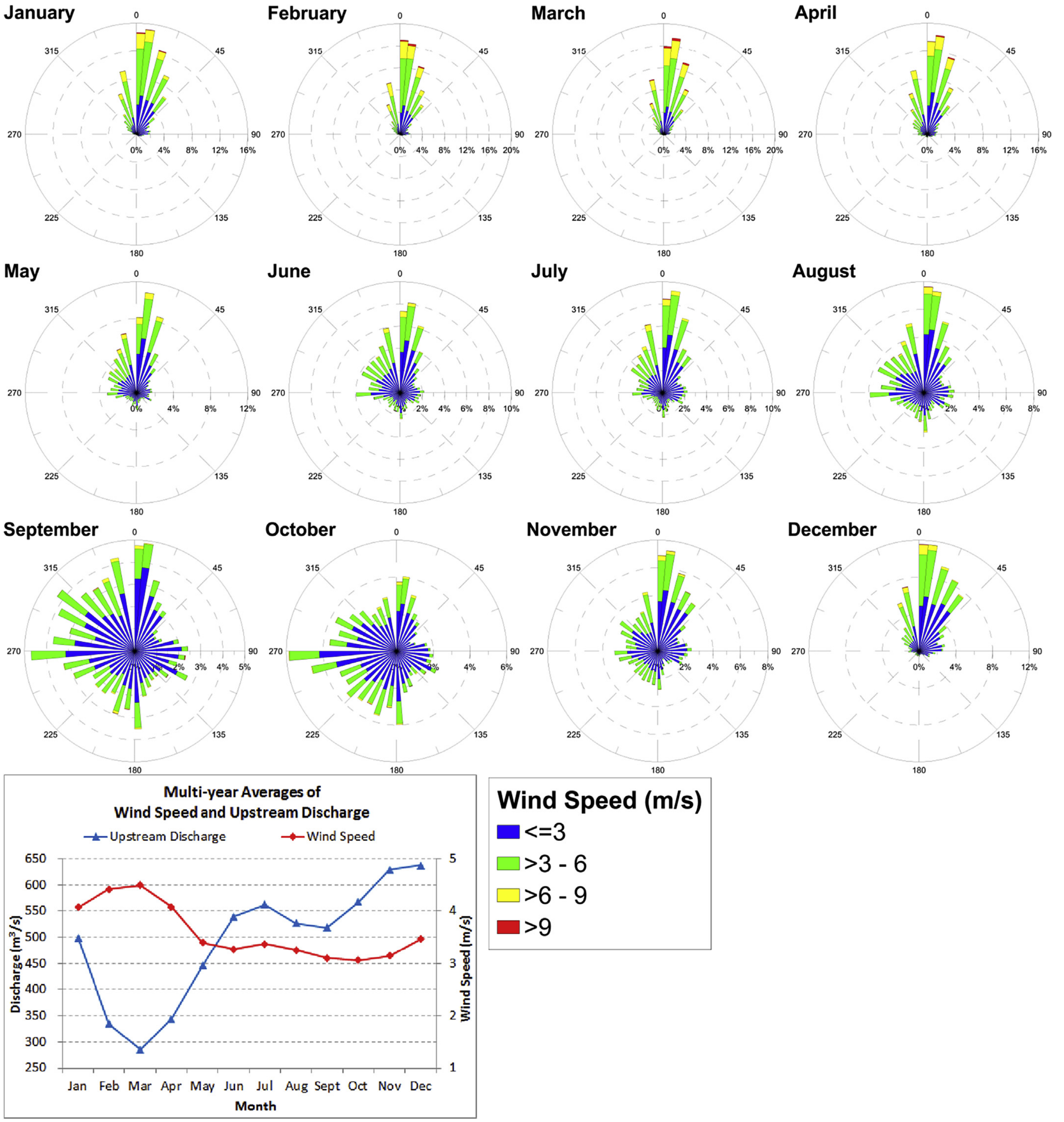

Fig. 2. Seasonality of winds and upstream discharge. Wind speed and direction data obtained from Metar station SKCG at Rafael Núñez International Airport in Cartagena for the period 1997–2015. Discharge data obtained from IDEAM gauging station at Santa Helena (see Fig. 1) approximately 35 km upstream of Cartagena Bay for the period 1998–2008.

called the “Mamonal”, extends along the east coast of the bay and includes over 70 industries which discharge directly to the bay or indirectly via small canals that ultimately discharge in the bay (UNEP, 1999). These activities include chemical plants, electric plants, petrochemical factories, a petroleum refinery, cement factories, aquaculture, pharmaceutical complexes, production of plastics and food processing industries (INVEMAR-MADS, 2011).

Runoff from the Dique Canal consists of turbid freshwater drained from the Magdalena River watershed. This watershed has an area of 260,000 km^2, covers approximately 25% of the country's land area, and includes approximately 80% of the national population along with a large number of industrial, agricultural and mining areas. Thus, the canal waters carry many potential pollutants along with a significant sediment load. Finally, marine sources of pollution are attributed to the bay's intense maritime activity. Previous reports cite more than 57 recreational and industrial docking areas and 5000 dockings per year pertaining to cargo, services, and cruise ships (Garay and Giraldo, 1997; UNEP, 1999).

3. Material and methods

3.1. Field sampling

A water quality monitoring program was undertaken in and around Cartagena Bay from Sept. 2014 to Aug. 2015. Sampling was carried out between the hours of 9:00–12:00 on a monthly basis (Karydis and Kitsiou, 2013). Samples were taken from 16 stations (principal panel, Fig. 1), including a station in the Dique Canal (C1), another at its outlet (C2), eight stations in Cartagena Bay (B1-8), three stations at the beach “Playa Blanca” (PL1-3), and three stations in the fishing areas of Barú Point (ZP1-3). Grab samples were taken from surface waters while deeper waters were sampled with a Niskin bottle. Sediment samples were obtained with a grab sampler from the same stations in March, June, Sept. and Dec. of 2015. Additional sediment samples were also taken in Nov. 2014 for mercury analysis.

In situ analyses along the water column were done with a CTD Castaway for salinity and temperature and with a YSI Pro1020 for oxygen. Water and sediment samples were delivered to three different laboratories for same-day processing. The various water and sediment quality parameters analyzed in each sample are shown in Table 1 along with the laboratories, their analytical methods and detection limits. Also, shown in Table 1 are the depths at which measurements and samples were taken along the water column. Bottom depth was defined as 22 m for all stations except B8 (5 m) and ZP1-2 (15 m), while at shallower stations (C1, C2, B2, ZP3, PL1-3) only surface water samples were taken. To optimize monitoring of the beach stations, only *in situ* parameters, turbidity, chlorophyll-*a*, and microbiological parameters were analyzed (Tosic et al., 2013).

3.2. Data analysis

Results were analyzed in comparison to two types of references values, including threshold values and background values. Threshold values consist of water and sediment quality standards defined by the Colombian legislation, international norms and scientific studies. These values indicate levels at which a parameter may pose a certain type of risk to the environment or to recreational use of the waters, and are thus used to decide whether the water or sediment presents adequate conditions for the water body's use. Background reference values consist of results found in previous studies in the area.

Statistical analyses were conducted on the water quality dataset of the bay to assess the spatio-temporal effects of the stations, seasons, and depths of samples. Only the data of three parameters displayed a normal distribution (dissolved oxygen, salinity, and temperature). A log-transformation was applied to the data of the other parameters in order to satisfy the conditions for the statistical tests. Spatio-temporal analyses of station, season and station-season interaction effects were conducted using an Analysis of Variance (ANOVA) for repeated measures in which monthly results were grouped by season: Rainy season (Sept.–Dec.), dry/windy season (Jan.–Apr.), and transitional season (May–Aug.). The effect of sampling depth was assessed using two-tailed T-tests. The results of the respective ANOVA F-tests and T-tests were compared to the 95% probability level ($p < 0.05$).

For visualization purposes, maps were created with water

Table 1

Water and sediment quality parameters measured in the coastal monitoring program, including analytical methods, detection limits and depths at which samples were taken in the water column. *S.M* indicates Standard Methods; *EPA* indicates the US Environmental Protection Agency; *EUR* indicates the European Commission.

Medium	Parameter	Code	Unit	Method	Lab Methodology	Method Reference	Detection Limit	Sample Depth
Water	Temperature	Temp	°C	CTD Castaway	In Situ	–	0.01	Multiple (every 0.3 m)
	Salinity	Sal				–	0.01	
	Dissolved Oxygen	DO	mg/l	YSI Pro 1020	In Situ	–	0.01	0.3, 3, 5, 10, 15, 22 m
	Oxygen Saturation	O_2sat	%				0.1	
	Turbidity	Tur	NTU	Lab Cardique	Turbidometry	S.M. 2130-B	0.07	0.3 m & 22 m
	Total Suspended Solids	TSS	mg/l		Filtration	S.M. 2540-D	4.21	
	Biological Oxygen Demand	BOD_5	mg/l		Membrane electrode	S.M. 5210-B, 4500-O-G	0.46	
	Nitrate-Nitrogen	NO_3-N	μg/l		Colorimetry - Cd reduction	S.M. 4500-NO3-E	10.4	
	Orthophosphates	PO_4-P	μg/l		Colorimetry - ascorbic acid	S.M. 4500-PO4	26	
	Total Phosphorus	TP	μg/l		Acid digestion, Colorimetry - ascorbic acid	S.M. 4500-P-E	32	
	Chlorophyll-*a*	Chl-a	μg/l		Spectrophotometry	S.M. 10200-H	0.25	
	Phenols	Phen	mg/l		Direct photometric method	S.M 5530 D	–	Surface
	Fecal Coliforms	FC	MPN/100 ml	Lab AcuaCar	Multiple tube fermentation	S.M. 9221-B	1.8	
	Enterococcus	ETC	CFU/100 ml		Membrane filtration	S.M. 9230-C	1	
Sediment	Cadmium	Cd	μg/kg	Lab Universidad de Cordoba	Graphite furnace atomic absorption spectrometry	EPA 3051-A - GFAAS	25	Surface Sediments
	Chromium	Cr	mg/kg		Graphite furnace atomic absorption spectrometry	EPA 3051-A - GFAAS	0.1	
	Copper	Cu	mg/kg		Flame atomic absorption spectrometry	EPA 3051-A - FLAAS	1	
	Mercury	Hg	μg/kg		Direct Mercury Analysis (DMA-80)	EPA 7473	0.1	
	Methyl Mercury	MeHg	μg/kg		Thermal decomposition, amalgamation, and atomic absorption spectrophotometry	EUR 25830 EN - 2013	2	
	Nickel	Ni	mg/kg		Flame atomic absorption spectrometry	EPA 3051-A - FLAAS	5	
	Lead	Pb	mg/kg		Graphite furnace atomic absorption spectrometry	EPA 3051-A - GFAAS	0.1	

quality results that were averaged over each season and spatially interpolated. Different interpolation methods were attempted to assess the most adequate method for each dataset. For horizontal maps, data were interpolated using the method of Inverse Distance Weighting (Xu et al., 2001) with a power of three and a search radius of three. For vertical oxygen profiles, a Kriging interpolation was applied (Buzzelli et al., 2002) based on a linear model with a slope of one.

4. Results

The monitoring program's results are summarized as annual averages in Table 2 with the results of statistical analyses presented in Table 3. Surface water salinity in the bay ranged from 9.7 to 35.8 (average: 25.0 ± 5.3) and was significantly different from bottom waters (Table 3) which ranged from 32.3 to 36.3 (average: 35.7 ± 0.6). A significant seasonal effect was found in both the bay's surface and bottom waters with lower salinity occurring in the rainy season (Fig. 3) due to the freshwater discharge from the canal (Fig. 4). Surface water salinity also showed significant spatial variability with the lowest salinity found at station B5 north of the canal. Salinity inside the bay was always lower than outside the bay at Barú Point but all stations had their highest salinity values during the dry season.

Surface water temperature was significantly different from bottom waters in the bay (Table 3) as average surface temperature was 30.0 ± 4.9 °C while average bottom temperature was 27.8 ± 0.7 °C. Seasonal variability was significant in both surface and bottom waters. Temperature was cooler at the surface and bottom of all stations during the dry/windy season (Fig. 3). Spatial variation was not observed in surface nor bottom waters.

Concentrations of total suspended solids (TSS) in the bay had a range of 6–72 mg/l with an average of 20.1 ± 12.8 mg/l. A significant difference was not detected between surface waters and bottom waters (Table 3). TSS concentrations in the canal had a range of 60–658 mg/l, an average of 242 ± 155 mg/l, and peaks during the months of October and April coinciding with the onset of periods of increased runoff (Fig. 4). Seasonal variability in the bay was significant in both surface and bottom waters with higher concentrations found during the rainy season ($p < 0.05$, Table 3). A significant spatial effect was also detected in surface waters showing higher concentrations at stations B4, B5 and B6 north of the canal's outlet which peaked at 30–72 mg/l during the rainy season (Fig. 3). Outside the bay, on average the stations at Barú Point had similar bottom water concentrations (20.9 ± 12.5 mg/l) and lower surface water concentrations (15.6 ± 8.2 mg/l) compared to the bay. In Fig. 5, spatio-temporal variability in the bay can be observed as greater TSS levels are shown to occur during the rainy season to the north of the outlet, while high levels can also be found to the west of the outlet during the dry season when strong northerly winds are prevalent.

The bay's turbidity levels showed much variability depending on season, station and depth. Surface waters were significantly different from bottom waters (Table 3) with average levels of 10.9 ± 14.4 NTU at the surface and 4.2 ± 4.4 NTU at the bottom. The canal's turbidity levels had a range of 80–450 NTU, an average of 211 ± 84 NTU, and peaks during the months of October and April coinciding with peaks of TSS and the onset of periods of increased runoff (Fig. 4). Significant seasonal variability was observed in both the bay's surface and bottom waters (Table 3). In surface waters, greater turbidity was found during the rainy season but a significant seasonal-spatial interaction effect indicates that the difference was not constant across all stations (Fig. 3), as stations west of the canal's outlet (B1-B3) were less affected by the rainy season, highlighting the northward trajectory of the canal's plume during this season (Fig. 5). In contrast, the bottom waters showed higher turbidity during the dry/windy season. Significant spatial variation was also detected in surface and bottom waters with higher surface turbidity at stations B4, B5 and B6 and higher bottom turbidity at station B5. Average turbidity outside the bay at Barú Point was similar for bottom waters (4.0 ± 3.9 NTU) and lower in surface waters (2.2 ± 2.0 NTU) compared to the bay.

Nitrate-nitrogen concentrations (NO_3-N) in the bay had a very large range of 5–389 μg/l with an average of 93 ± 88 μg/l and no significant difference between surface and bottom waters (Table 3). NO_3-N concentrations in the canal also had a large range of 114–572 μg/l and an average of 334 ± 139 μg/l (Fig. 4). A significant seasonal effect was found both in the bay's surface and bottom waters (Table 3) with higher NO_3-N during the rainy season and lower NO_3-N during the transitional season. Surface waters showed a significant spatial effect as well with greater NO_3-N found in the central part of the bay (stations B4-B6). In Fig. 5, this spatio-temporal variability in the bay's surface waters can be observed as greater NO_3-N levels can be seen to occur during the rainy season and to the north of the canal's outlet. Outside the bay at Barú Point, NO_3-N was much lower with overall average concentrations of 20 ± 18 μg/l.

Concentrations of phosphate-phosphorus (PO_4-P, also known as soluble reactive phosphorus) in the study area ranged from below detection limits (<26 μg/l) to 140 μg/l (Fig. 3). PO_4-P was highest in the canal with an average concentration of 78 ± 35 μg/l and peaks in October, May, and June, similar to TSS results. In and outside the bay, PO_4-P was significantly higher in bottom waters (average: 44 ± 19 μg/l) than in surface waters (average: 35 ± 16 μg/l; Table 3). A significant spatial effect was observed in these bottom waters with the highest concentrations found at station B7. Seasonal effects were significant both in surface and bottom waters (Table 3) with greater concentrations occurring during the transitional season.

No significant difference was found between total phosphorus (TP) concentrations in the surface and bottom waters of the bay which had an overall range of <32–140 μg/l and an average of 61 ± 32 μg/l. However, the waters off Barú Point had higher TP concentrations at bottom depths (59 ± 47 μg/l) than at the surface (39 ± 24 μg/l). TP in the canal peaked in April at 410 μg/l (Fig. 4) and TP in the bay was greatest at stations B4 and B5 north of the canal (Fig. 3). Though spatial effects were deemed insignificant ($p = 0.112$), significant seasonal effects were found both in surface and bottom waters (Table 3) with greater TP levels during the rainy season.

High concentrations of chlorophyll-*a* (Chl-*a*) were found in the surface waters of Cartagena Bay throughout the year with a range of 1.14–9.81 μg/l and an average of 3.23 ± 1.57 μg/l. While Chl-*a* concentrations in the bay's surface waters did not exhibit seasonal or station effects, they were significantly higher than the chlorophyll-*a* in the bay's bottom waters which had a range of 0.26–4.18 μg/l and an average of 0.95 ± 0.69 μg/l. These bottom waters showed significant seasonal variability (Table 3) with Chl-*a* concentrations increasing to above 1 μg/l in the dry season (Fig. 6). However, temporal variability was different at stations ZP1 and ZP2 off Barú Point where Chl-*a* at the surface and bottom depths was highest in the rainy and transition seasons (Fig. 3). Chlorophyll-*a* in the canal varied between 4.11 and 10.62 μg/l with an average of 7.39 ± 1.55 μg/l and peaks in October and April (Fig. 4).

Concentrations of biological oxygen demand (BOD) in the bay's surface and bottom waters were not significantly different and had an overall average of 1.15 ± 0.90 mg/l. Though spatial effects were not observed in the bay, both its surface and bottom waters had significant seasonal variability with greater BOD during the dry season and lower BOD in the transition season (Fig. 3; Table 3). BOD

Table 2

Summary of environmental variables measured at different depths of the water column and in surface sediments at each monitoring station. Results are presented as annual means with standard deviation in parentheses. *N* indicates number of samples collected at each station; < D.L. indicates below detection limit. Station locations are shown in Fig. 1; Parameter abbreviations are shown in Table 1.

Parameter	*N*	Station and Sample Depth (m)																								
		B1		B2	B3		B4		B5		B6		B7		B8		C1	C2	ZP1		ZP2		ZP3	PL1	PL2	PL3
		0.3	22	0.3	0.3	22	0.3	22	0.3	22	0.3	22	0.3	22	0.3	5	0.3	0.3	0.3	15	0.3	15	0.3	0.3	0.3	0.3
Water Samples																										
Temp (°C)	*12*	30.0	27.9	29.8	29.9	28.0	30.0	27.8	30.5	27.9	30.2	27.8	29.7	27.8	29.5	29.5	30.2	29.9	29.1	30.0	29.2	28.8	30.1	29.7	29.7	29.7
		(1.0)	(0.7)	(1.3)	(1.4)	(1.0)	(1.2)	(0.7)	(1.1)	(0.7)	(1.0)	(0.8)	(1.0)	(0.8)	(1.0)	(3.3)	(0.7)	(1.0)	(2.8)	(3.1)	(1.2)	(1.2)	(1.1)	(1.1)	(1.1)	(1.2)
Sal	*12*	25.3	35.2	25.6	24.6	35.1	23.9	35.3	21.0	35.9	23.7	35.9	29.1	35.8	28.5	33.3	0.1	6.6	31.4	33.9	33.6	35.4	33.6	34.5	34.5	34.6
		(5.2)	(2.3)	(5.0)	(3.9)	(2.9)	(6.1)	(2.0)	(6.0)	(0.2)	(4.0)	(0.2)	(3.7)	(0.3)	(6.3)	(3.7)	(0.1)	(6.7)	(3.4)	(2.9)	(2.1)	(0.9)	(2.1)	(1.4)	(1.4)	(1.5)
DO (mg/l)	*10*	6.4	2.7	6.7	6.9	4.5	6.8	4.6	6.6	4.3	6.7	3.8	6.4	2.9	6.6	5.6	4.8	4.8	6.1	5.6	5.9	5.7	5.8	5.8	5.9	6.0
		(1.5)	(1.1)	(1.6)	(1.9)	(1.3)	(1.7)	(1.3)	(1.6)	(1.7)	(1.2)	(1.7)	(1.3)	(1.2)	(1.5)	(1.3)	(1.0)	(1.1)	(1.7)	(1.5)	(1.4)	(1.4)	(1.2)	(1.4)	(1.4)	(1.6)
O_2sat (%)	*10*	98.0	39.4	100.6	103.9	65.0	102.4	66.4	100.1	62.4	102.7	54.8	96.3	43.8	97.7	82.43	72.7	72.3	91.3	81.0	87.4	83.9	87.4	86.8	88.2	89.2
		(13.1)	(11.0)	(10.9)	(13.9)	(10.1)	(12.1)	(10.0)	(11.6)	(20.2)	(10.8)	(19.7)	(6.6)	(18.0)	(12.7)	(8.5)	(5.9)	(9.9)	(14.3)	(6.9)	(5.6)	(5.3)	(5.1)	(9.9)	(7.2)	(10.8)
Tur (NTU)	*12*	4.8	4.2	5.0	5.7	3.5	22.6	3.0	28.9	5.5	11.4	6.7	5.4	2.6	2.8	2.5	211.2	213.7	2.8	4.1	1.3	3.8	2.4	1.7	1.9	1.3
		(1.2)	(1.8)	(1.9)	(3.6)	(1.2)	(16.8)	(0.8)	(26.0)	(4.3)	(7.1)	(9.2)	(6.0)	(1.5)	(2.2)	(1.3)	(62.2)	(105.1)	(2.9)	(3.5)	(1.0)	(4.4)	(1.5)	(1.5)	(1.2)	(0.5)
TSS (mg/l)	*12*	14.9	21.5	17.3	16.4	19.9	26.0	20.6	29.1	23.5	23.4	23.3	16.1	18.5	14.0	16.4	319.1	276.7	13.7	22.3	15.6	19.6	17.5			
		(7.9)	(18.7)	(13.9)	(7.3)	(12.8)	(15.0)	(13.5)	(16.2)	(13.8)	(18.3)	(12.8)	(7.8)	(7.1)	(7.8)	(4.9)	(406.5)	(197.3)	(8.6)	(12.3)	(8.7)	(13.1)	(7.3)			
BOD_5 (mg/l)	*12*	1.6	1.0	1.3	1.4	0.8	1.0	0.7	0.9	1.3	1.1	1.1	1.0	1.1	1.3	1.4	0.9	0.9	0.7	1.0	0.5	0.9	0.5			
		(1.4)	(0.9)	(0.8)	(1.1)	(0.6)	(0.9)	(0.6)	(0.7)	(1.0)	(0.8)	(0.8)	(0.7)	(1.0)	(0.9)	(1.1)	(0.6)	(0.8)	(0.6)	(0.9)	(0.6)	(1.0)	(0.4)			
Chl-a (μg/l)	*12*	2.7	0.8	3.0	2.7	0.9	3.1	0.8	4.2	1.1	3.8	1.2	3.2	0.9	3.3	1.6	7.5	7.2	1.9	0.8	0.9	0.8	1.0	0.6	0.6	0.6
		(1.2)	(0.3)	(1.2)	(0.9)	(0.4)	(1.1)	(0.3)	(2.1)	(0.9)	(1.9)	(1.1)	(1.3)	(0.7)	(2.2)	(1.0)	(1.3)	(1.8)	(1.9)	(0.4)	(0.7)	(0.6)	(0.4)	(0.4)	(0.4)	(0.3)
NO_3-N (μg/l)	*12*	46.2	82.1	59.2	52.6	63.9	126.4	53.0	122.4	74.9	134.6	84.2	90.8	99.3	71.4	28.1	265.9	230.6	18.9	20.5	7.5	16.4	9.8			
		(63.7)	(90.3)	(83.0)	(88.9)	(74.1)	(130.8)	(57.8)	(125.3)	(75.2)	(130.3)	(95.3)	(96.4)	(101.6)	(102.2)	(33.5)	(220.9)	(199.1)	(31.5)	(18.5)	(9.0)	(17.4)	(10.2)			
PO_4-P (μg/l)	*12*	16.6	25.0	17.4	18.3	18.5	22.8	22.8	24.1	25.9	23.6	30.0	18.8	38.4	17.4	23.9	57.5	42.5	23.6	27.8	20.5	36.7	16.6			
		(14.8)	(19.3)	(16.4)	(16.8)	(19.7)	(20.3)	(18.9)	(24.6)	(20.2)	(20.0)	(25.2)	(16.2)	(30.7)	(15.8)	(22.3)	(47.8)	(38.6)	(21.7)	(31.2)	(18.3)	(41.2)	(14.8)			
TP (μg/l)	*12*	32.2	40.0	39.7	35.7	36.4	58.4	55.0	71.7	47.5	44.2	45.0	34.2	52.5	41.3	28.7	206.8	189.2	38.8	44.7	22.8	43.5	26.2			
		(27.5)	(35.6)	(39.3)	(36.2)	(31.9)	(49.5)	(47.0)	(64.3)	(39.5)	(37.3)	(39.6)	(27.8)	(41.1)	(38.1)	(26.0)	(157.5)	(162.7)	(35.7)	(50.4)	(23.9)	(55.2)	(29.7)			
Phen (mg/l)	*12*	0.4		0.5	0.4		0.5		0.5		0.5		0.4		0.3		1.6	1.3	0.2		0.3		0.2			
		(0.4)		(0.6)	(0.3)		(0.4)		(0.8)		(0.4)		(0.4)		(0.3)		(1.9)	(1.1)	(0.1)		(0.3)		(0.4)			
FC (MPN/100ml)	*11*	43.7		126.4	193.5		191.1		573.8		419.5		229.6		236.6		1540.7	2650.6	83.2		21.5		19.6	19.5	25.6	20.6
		(68.9)		(324.3)	(379.7)		(292.5)		(869.0)		(823.0)		(456.4)		(479.9)		(1975.4)	(5167.8)	(235.6)		(39.3)		(50.1)	(25.1)	(49.0)	(49.7)
ETC (CFU/100ml)	*11*	24.2		25.6	20.1		29.0		23.5		23.0		15.5		16.3		37.0	52.5	21.6		27.5		14.5	12.9	24.7	17.8
		(29.5)		(34.3)	(27.9)		(30.2)		(23.2)		(28.2)		(20.1)		(26.5)		(41.5)	(61.9)	(21.8)		(33.3)		(13.4)	(11.5)	(31.0)	(22.9)
Sediment Samples																										
Cd (μg/kg)	*4*	191.1		43.9	331.0		400.1		540.4		272.2		149.4		21.8		1251.0	1282.6	40.0		29.3		87.4		19.5	
		(189.6)		(26.8)	(288.6)		(306.8)		(344.6)		(233.0)		(132.6)		(8.9)		(891.8)	(787.9)	(35.0)		(20.8)		(140.4)		(7.9)	
Cr (mg/kg)	*4*	44.5		5.9	42.0		50.9		54.2		59.8		52.2		17.2		38.4	42.3	33.8		24.6		8.9		3.1	
		(2.0)		(4.4)	(7.4)		(9.7)		(9.9)		(9.2)		(7.8)		(8.8)		(1.4)	(10.9)	(4.0)		(13.9)		(6.6)		(3.8)	
Cu (mg/kg)	*4*	27.4		3.1	26.0		31.0		32.5		38.6		29.4		3.4		29.9	30.3	10.3		9.2		1.9		< D.L.	
		(3.9)		(3.2)	(3.1)		(7.7)		(4.7)		(11.7)		(6.8)		(3.4)		(5.1)	(8.9)	(7.0)		(6.5)		(1.7)			
Hg (μg/kg)	*5*	117.8		24.8	136.1		116.7		351.3		141.1		164.1		20.6		97.6	83.7	52.7		41.6		32.1		5.9	
		(49.9)		(19.4)	(80.7)		(49.2)		(552.7)		(49.8)		(78.7)		(9.6)		(70.5)	(44.9)	(33.6)		(37.7)		(34.7)		(2.9)	
MeHg (μg/kg)	*4*	8.7			8.5		6.4		10.3		7.2		9.7				9.2	8.8	3.8							
		(8.9)			(9.0)		(4.6)		(9.6)		(7.3)		(6.2)				(6.9)	(8.5)	(4.2)							
Ni (mg/kg)	*4*	27.5		< D.L.	25.7		31.6		32.7		30.8		24.6		10.0		29.5	29.2	19.5		13.6		< D.L.		< D.L.	
		(4.5)			(5.4)		(7.9)		(5.6)		(5.5)		(5.1)		(3.3)		(5.7)	(6.0)	(5.6)		(7.4)					
Pb (mg/kg)	*4*	10.9		1.6	14.3		12.9		13.0		14.6		10.7		2.8		10.2	11.2	8.0		3.3		1.2		0.3	
		(7.0)		(1.2)	(2.7)		(5.2)		(5.6)		(6.5)		(6.8)		(2.6)		(6.3)	(6.6)	(4.9)		(3.7)		(0.6)		(0.2)	

Table 3
Results of the repeated measures ANOVA *F*-tests in terms of probabilities of significance for spatial (stations), seasonal (wet, dry, transition) and interaction (seasonal*spatial) effects in surface and bottom waters. Also shown are results of *T*-tests in terms of probabilities of significance for the effect of depth (surface vs bottom waters). Values in bold indicate significance ($p < 0.05$). Parameter abbreviations are shown in Table 1.

Parameter	Surface Waters			Bottom Waters			Effect of Depth (Surface vs Bottom)
	Spatial	Seasonal	Seasonal*Spatial	Spatial	Seasonal	Seasonal*Spatial	
Temp (°C)	0.2165	< **0.0001**	0.9652	0.8310	< **0.0001**	0.9543	< **0.0001**
Sal	< **0.0001**	< **0.0001**	0.7481	0.8996	**0.0004**	0.9950	< **0.0001**
DO (mg/l)	0.7576	< **0.0001**	0.9340	< **0.0001**	< **0.0001**	0.4148	< **0.0001**
Tur (NTU)	< **0.0001**	< **0.0001**	**0.0041**	**0.0011**	< **0.0001**	0.1471	< **0.0001**
TSS (mg/l)	**0.0042**	**0.0075**	0.0564	0.8455	**0.0002**	0.8567	0.1752
BOD$_5$ (mg/l)	0.6943	**0.0162**	0.3294	0.1327	< **0.0001**	0.0862	0.1805
Chl-a (µg/l)	0.2732	0.6907	0.7891	0.5969	**0.0004**	0.7234	< **0.0001**
NO$_3$-N (µg/l)	**0.0026**	< **0.0001**	0.6164	0.1232	< **0.0001**	0.5048	0.6524
PO$_4$-P (µg/l)	0.4647	< **0.0001**	0.9714	**0.0025**	**0.0019**	0.6977	**0.0037**
TP (µg/l)	0.1120	**0.0384**	0.1066	0.8333	**0.0234**	0.5699	0.6089
Phen (mg/l)	0.9912	0.1712	0.9977	–	–	–	–
FC (MPN/100 ml)	**0.0159**	< **0.0001**	0.2466	–	–	–	–
ETC (CFU/100 ml)	0.7493	**0.0476**	0.8299	–	–	–	–

concentrations in the canal had an average of 0.94 ± 0.69 mg/l (Fig. 4). Meanwhile, BOD levels were lowest in the surface waters outside the bay off Barú Point with an average of 0.55 ± 0.49 mg/l (Fig. 3).

The bay's hypoxic conditions are evident in the dissolved oxygen (DO) and O$_2$ saturation data measured along vertical profiles at each station (Fig. 7). The extent of the hypoxic conditions varied greatly by season, both in surface and bottom waters (Table 3). During the rainy season, low DO concentrations (<4 mg/l) were found at depths greater than 10–20 m, while during the transitional season such concentrations could be found below depths of 5–10 m. During the peak of the windy season (Jan.–Feb.), DO measurements were all above 4 mg/l. Similarly, adequate O$_2$ saturation values (>80%) were observed in the top 10 m of the water column during the windy season, while in other months this level of saturation was only found in the top 5 m. Bottom water DO also showed significant spatial variability (Table 3) with lower concentrations found at stations B1 and B7. Meanwhile, in November the lowest concentrations of DO were found in the bottom waters of stations B5 and B6 (Fig. 5). In contrast, outside the bay at Barú Point, DO and O$_2$ saturation values were consistently above 4 mg/l and 80%, respectively, except in the transitional season when ranges of 3.76–4.69 mg/l and 68–92% were registered.

Results of fecal coliforms in the bay varied greatly, ranging from below detection limits (<1.8 MPN/100 ml) to 2400 MPN/100 ml yielding an average value of 251.8 ± 528.4 MPN/100 ml, though a median value of just 22.5 MPN/100 ml (Fig. 3). A significant seasonal effect was observed (Table 3) with much higher concentrations found in the bay during the rainy season (median: 745.0 MPN/100 ml) than the rest of the year (median: 9.0 MPN/100 ml). While the greatest concentrations in the bay were found in the rainy season at stations B5 and B6 north of the canal, the greatest concentrations in the canal were found during the dry season (Fig. 4).

Enterococcus results in the bay had much less variability than those of fecal coliforms, with a range of <1–120 CFU/100 ml, an average of 22 ± 27 CFU/100 ml, and a median value of 14 CFU/100 ml. Enterococcus concentrations in the bay were also significantly higher during the rainy season (median: 30 CFU/100 ml) than the rest of the year (median: 7 CFU/100 ml) and peak concentrations in the canal were also found during the dry season (Fig. 4). However, contrary to fecal coliform results, enterococcus concentrations in the bay did not differ greatly from those outside the bay at "Playa Blanca" beach and Barú Point which had a range of <1–98 CFU/100 ml, an average of 20 ± 23 CFU/100 ml, and a median value of 16 CFU/100 ml.

Concentrations of phenol were found to be greatest in the canal (average: 1.4 ± 1.5 mg/l) followed by the bay (average: 0.4 ± 0.5 mg/l) and Barú Point (average: 0.2 ± 0.3 mg/l). Though spatio-temporal effects were not significant in the bay (Table 3), peak concentrations above 2 mg/l were observed during the rainy season at station B5 north of the canal (Fig. 3). Higher concentrations were found in the canal in the rainy season with a range of 1.4–6.9 mg/l (Fig. 4).

Concentrations of mercury (Hg) in the sediments at the bottom of Cartagena Bay had a range of 65–302 µg/kg and an average of 131 ± 55 µg/kg (Fig. 8). Not included in this average value is a single sample taken at station B5 in November 2014 which was analyzed in triplicate and yielded a result of 1339 ± 113 µg/kg. Mercury concentrations were lower in the Dique Canal (average: 91 ± 56 µg/kg) and much lower in the bay's straights and Barú Point (average: 29 ± 25 µg/kg). Hg levels in the bay were greatest in November 2014 and decreased with each subsequent sampling (Fig. 8). Meanwhile, methyl-mercury concentrations in the bay and the canal had a range of 1.4–24.5 µg/kg and an average of 8.6 ± 6.9 µg/kg, showing that approximately 2–20% of the total mercury detected was bio-available. Methyl-mercury in the fishing zone of Barú Point was lower with an average of 3.8 ± 4.2 µg/kg.

Concentrations of cadmium (Cd) found in the Dique Canal's sediments averaged 1267 ± 779 µg/kg. Cd levels in the bay were lower but varied greatly by season, as rainy season results had a range of 232–877 µg/kg and an average of 511 ± 208 µg/kg, while dry season results had a range of 13–244 µg/kg and an average of 60 ± 88 µg/kg (Fig. 8). Results found in the bay's straights and outside the bay at Barú Point were much lower throughout the year with an average concentration of 32 ± 21 µg/kg.

Results of chromium (Cr), copper (Cu), nickel (Ni) and lead (Pb) were highest in the central part of the bay (stations B4-6) and in the canal (Fig. 8). However, much lower concentrations were observed in the bay's straights and outside the bay. These metals did not display temporal trends, though lower concentrations were found in June 2015 for Ni and in March 2015 for Pb.

5. Discussion

5.1. Seasonal variability

The dynamics of seasonal pollution in Cartagena Bay are apparent during the rainy season when higher concentrations of fecal coliforms, enterococus, sediments and nutrients are found in the bay. This is likely related to upstream anthropogenic activities as peak concentrations in the Dique Canal are observed in October

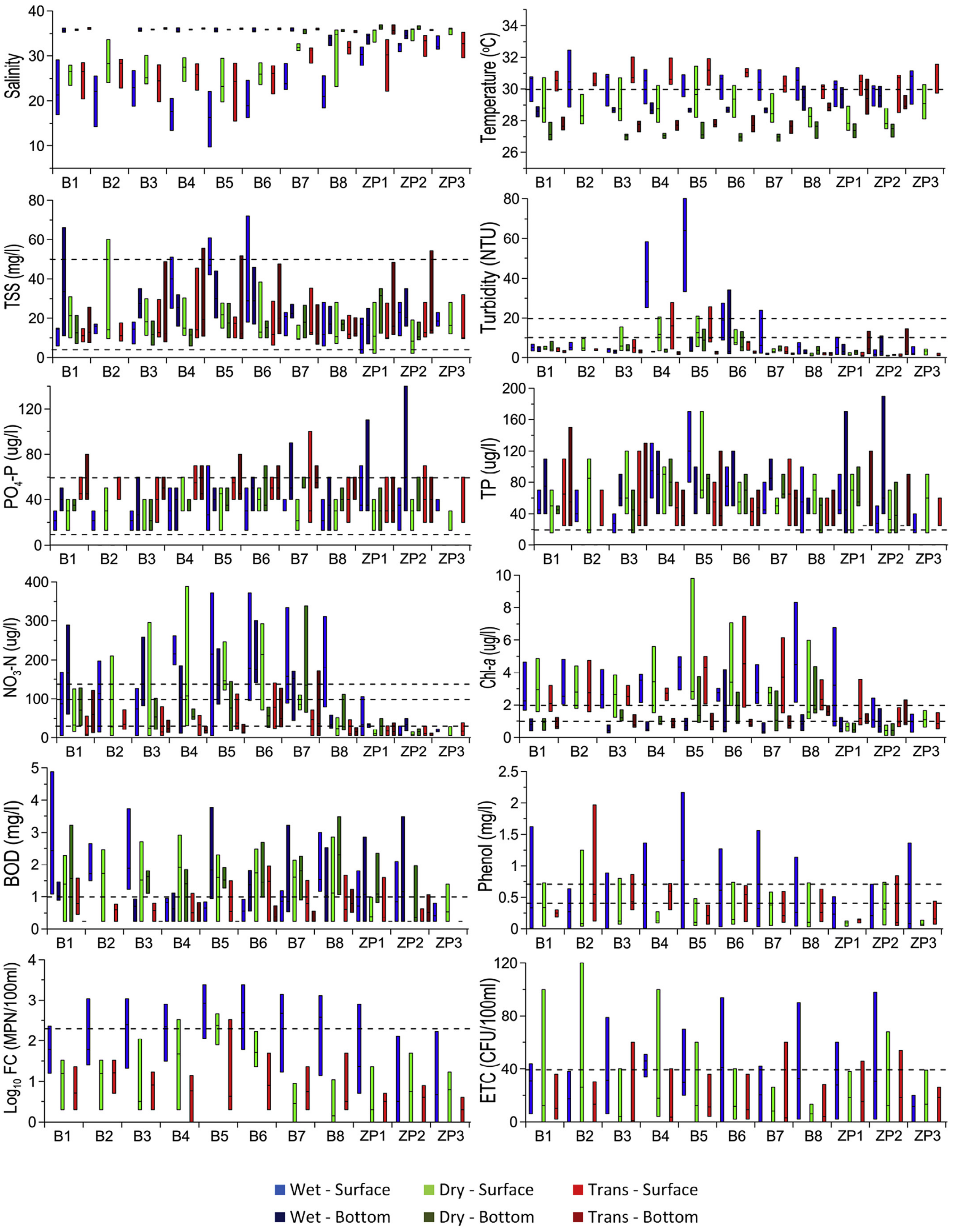

Fig. 3. Box plots of water quality parameters measured at Cartagena Bay and Barú Point. Colours differentiate the wet, dry and transitional seasons as well as surface and bottom waters (see legend). The top of each box is at the maximum value, the bottom of each box is at the minimum value, and a line is drawn across each box at the median value. Dashed lines drawn across the plots represent threshold values cited in the text. Station locations are shown in Fig. 1; Parameter abbreviations are shown in Table 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

at the onset of high discharge season, resulting in elevated concentrations in the central part of the bay where the canal's freshwater plumes tend to disperse during this season (Lonin et al., 2004). However, given that higher concentrations of NO_3-N were consistently found at station B6 (5.4 km from the canal's outlet) than at station B5 (2.5 km from the outlet), it would suggest that the waters near station B6 are also influenced by other sources of NO_3-N in addition to the canal's plume. This is likely due to domestic wastewater coming from populations along the coast, as intense rain events can result in overflow of the city's sewage system and the latrine wells used in smaller nearby communities. Nearby sources of domestic wastewater were also apparent during the dry season when the greatest concentrations of fecal coliforms and enterococus were observed in the canal. This may be a result of continuous wastewater discharges in the canal that receive less dilution in the dry season when the canal's discharge is lowest.

The influence of the windy season on the bay's water quality is evident in higher salinity values as the winds increase the seawater's vertical mixing. Temperature was cooler at the surface and bottom of all stations during this season due to increased circulation and the influence of the southern Caribbean upwelling system (Andrade and Barton, 2005; Rueda-Roa and Muller-Karger, 2013). Wind-driven circulation would also explain the seasonal improvement in oxygen levels, along with the associated lower water temperature, and may contribute to the resuspension of bottom sediments resulting in higher turbidity found in bottom waters during this period. The wind's influence on the dispersion patterns of the canal's plume is also observed as higher TSS and turbidity levels can be found to the west of the outlet during this season (Lonin et al., 2004).

The dry/windy season also resulted in increased chlorophyll-*a* concentrations in the bay's bottom waters, in agreement with previous findings of Cañon et al. (2007). This seasonal variability of Chl-*a* does not coincide with that of the nutrient concentrations (NO_3-N, PO_4-P, TP) suggesting that the bay's primary productivity is not limited by nutrients but rather by light (Tuchkovenko and Lonin, 2003). Water transparency in the bay is significantly reduced during the wet season by the canal's sediment load (Fig. 5) but once these turbid freshwater plumes decline, light penetrates deeper in the water column allowing for increased primary productivity beneath the surface. This seasonal dynamic of the bay's primary productivity may also be reflected in the higher levels of BOD and turbidity found in the bottom waters during this time.

The importance of the transitional season on coastal water quality is an aspect that has not been considered by some studies (INVEMAR, 2001–2015). Results from the transitional season in the bay showed the year's most hypoxic conditions with levels of dissolved oxygen and oxygen saturation less than 4 mg/l and 80%, respectively, reaching depths of just 5–10 m from the surface (Fig. 7). These hypoxic conditions were most prevalent at station B7 which may indicate sources of organic matter as this station is located near an old submarine outfall that discharged untreated sewage into the bay from 1960 until 2013.

Greater concentrations of PO_4-P were also found in the transitional season and in bottom waters. This may be related to lower TSS concentrations resulting in higher dissolved phosphorus concentrations due to phosphorus' high potential for sorption to sediment particles (Schlesinger, 1997). On the contrary, greater TP levels were observed during the rainy season, similar to TSS. This dynamic between TP, TSS and PO_4-P demonstrates how sediments can act as sources or sinks for phosphorus.

5.2. Threshold value comparison

Potential impacts of pollution were evident in Cartagena Bay as the majority of water and sediment quality parameters analyzed were found to exceed national and international threshold values. Occasional sanitary risks to recreational waters were found as the Colombian national water quality standard of 200 MPN/100 ml for fecal coliforms in bathing waters (MinSalud, 1984) was exceeded in the rainy season in the bay (Fig. 3). Meanwhile, the World Health Organization's guideline value of 40 CFU/100 ml for enterococus in recreational waters (WHO, 2003) was occasionally exceeded in the bay and at the beach "Playa Blanca" outside the bay.

Potential impacts to the ecosystem were evident as dissolved oxygen concentrations were often found below 4 mg/l, the minimum threshold value used for preservation of marine flora and fauna in Colombia (MinSalud, 1984), and O_2 saturation values beneath the surface were persistently less than 80%, which may be considered a minimum threshold value to maintain healthy biota (Newton and Mudge, 2005). Meanwhile, average BOD concentrations in the bay were slightly above the max threshold value of 1 mg/l for fishing resources in Cuba (NC , 1999).

Threshold values for coral health cited by Fabricius (2005) were occasionally surpassed in and outside the bay in the case of TSS (50 mg/l) and PO_4-P (62 μg/l), and often exceeded in the bay in the case of dissolved inorganic nitrogen (140 μg/l). The conservative threshold values of Barbados (1998) for coral preservation were greatly exceeded in and outside the bay in the case of TSS (5 mg/l) and turbidity (1.5 NTU). Outside the bay in the bottom waters at Barú Point, salinity never dropped below 32, a minimum threshold value for corals (Hoegh-Guldberg, 1999), although temperature exceeded 30 °C in Sept. 2014 presenting a risk of coral bleaching (Wilkinson and Souter, 2008; Vega et al., 2011).

The guideline values of Australia and New Zealand (ANZECC, 2000) for estuarine waters were frequently exceeded in and outside the bay in the case of nitrate-nitrite (NO_x-N: 30 μg/l), PO_4-P (5 μg/l) and TP 20 (μg/l), indicating ample nutrient enrichment. The bay's waters also surpassed ANZECC's threshold values for chlorophyll-*a* (2 μg/l) and turbidity (20 NTU), and were occasionally above phenol guideline values defined for species protection levels of 95% (0.40 mg/l) and 80% (0.72 mg/l).

Guideline values of the U.S. Environmental Protection Agency (U.S. EPA, 2015) for Caribbean waters would classify Cartagena Bay's waters as "poor" in the case of NO_3-N (>100 μg/l), PO_4-P (>10 μg/l) and chlorophyll-*a* (>1 μg/l), while these waters would also be classified by U.S.EPA as "poor" when compared to Gulf of Mexico waters in the case of PO_4-P (>50 μg/l).

Many of the sediment quality results were above the Threshold Effects Level (TEL) used to indicate potential risk by the U.S. National Oceanic and Atmospheric Administration (Buchman, 2008). Such was the case of concentrations of mercury (>130 μg/kg), chromium (>52.3 mg/kg), copper (>18.7 mg/kg) and nickel (>15.9 mg/kg) in the bay and canal (Fig. 8). Cadmium concentrations also exceeded the TEL value (680 μg/kg) during the rainy season, clearly showing the canal to be the source. The Probable Effects Level (PEL) for mercury (700 μg/kg) was surpassed on one occasion at station B5 in Nov. 2014, while nickel concentrations were occasionally near the PEL value of 42.8 mg/kg. Concentrations of lead (Pb) were all below the TEL value of 30.2 mg/kg.

5.3. Comparison with other studies

Nearly all of the parameters analyzed in Cartagena Bay produced data ranges similar to those of previous studies (Garay and Giraldo, 1997; Lonin and Tuchkovenko, 1998; Sierra Misco, 1999; Tuchkovenko and Lonin, 2003; Lonin et al., 2004; UniNorte and Cormagdalena, 2004; Cañon et al., 2007; Lonin, 2009; Parra et al., 2011a; Cogua et al., 2012; INVEMAR, 2001–2015; Restrepo et al., 2016b). However, there were a few exceptions such as the ranges

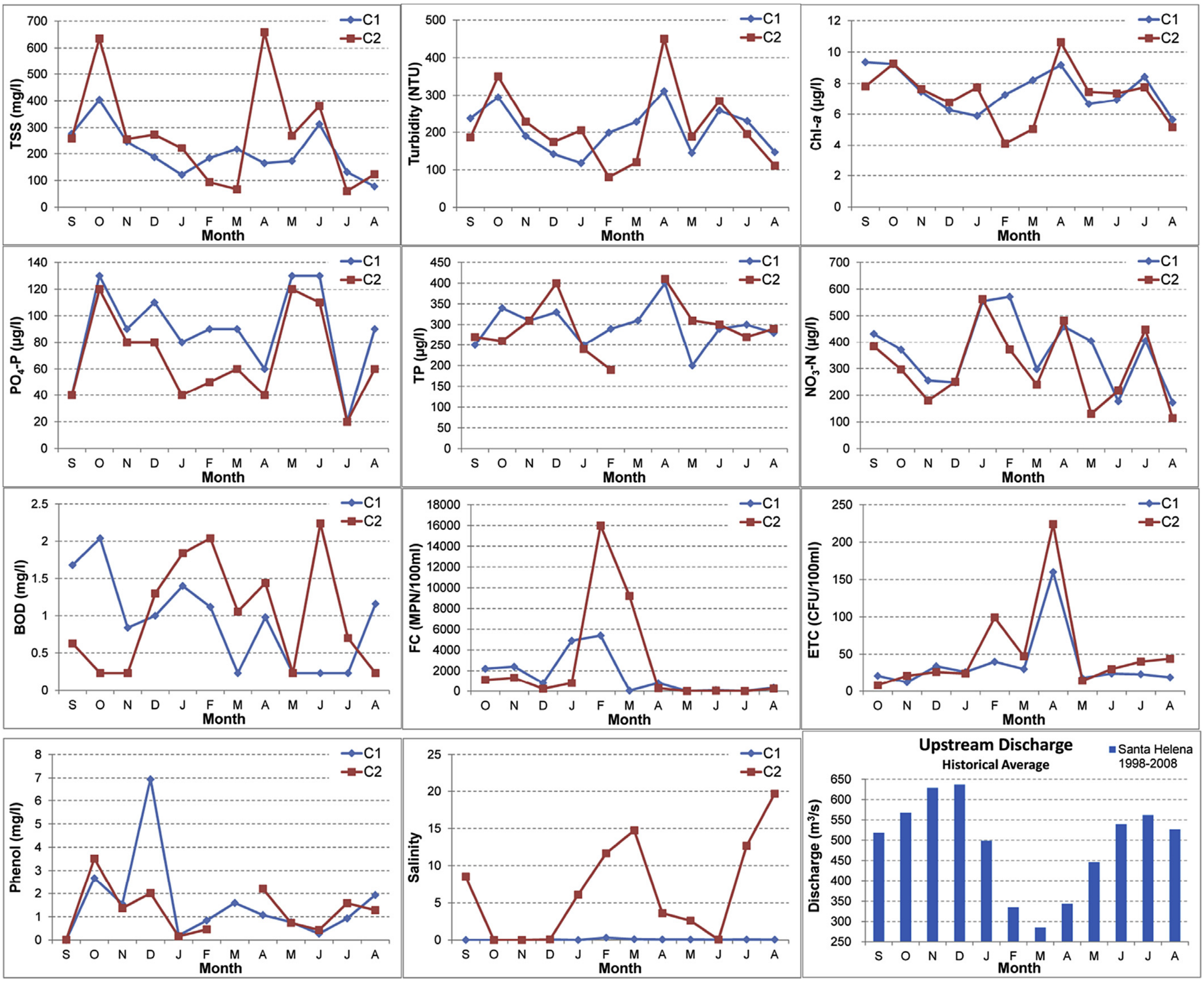

Fig. 4. Time series plots of water quality parameters measured monthly at stations C1 and C2 of the Dique Canal. Station locations are shown in Fig. 1; Parameter abbreviations are shown in Table 1. Also shown are average discharge data obtained from IDEAM gauging station at Santa Helena (see Fig. 1) approximately 35 km upstream of Cartagena Bay for the period 1998–2008.

of BOD (<0.5–4.9 mg/l), PO_4-P (<26–140 μg/l) and enterococcus (<1–120 CFU/100 ml) in the present study which were similar to those reported by Tuchkovenko and Lonin (2003), Cañon et al. (2007), and INVEMAR (2001–2015) but far below the values reported by Sierra Misco (1999) of up to 100 mg/l of BOD, 820 μg/l of PO_4-P, and 2300 CFU/100 ml of enterococcus. The maximum fecal coliform concentration found in the bay in the present study (2400 MPN/100 ml) was also much lower than previously reported maximum concentrations of 1,100,000 MPN/100 ml (Tuchkovenko & Rondón, 2002) and 240,000 MPN/100 ml (INVEMAR, 2011). These differences could be attributed to sanitary improvements in the bay such as the closure of the bay's sewage outfall in 2013. The current results of phenol concentrations up to 2 mg/l present a new maximum value reported for the bay compared to a previous maximum value of 0.6 mg/l (Sierra Misco, 1999; Lonin, 2009).

The present study's results of concentrations of Cr (31.5–57.2 mg/kg), Cu (22.1–41.2 mg/kg), and Hg (9–183 μg/kg) in the Dique Canal's sediments are higher than those previously reported by UniNorte and Cormagdalena (2004) of Cr (<1–21.3 mg/kg), Cu (2.4–26.2 mg/kg), and Hg (<4–20 μg/kg) from six sampling sessions in the canal between 1996 and 2003, though attributing this difference to long- or short-term temporal variation in the canal would be difficult. Meanwhile, Tejeda-Benitez et al. (2016) have reported similar concentrations of Cd (1.44 mg/kg), Hg (50 μg/kg) and Pb (11.3 mg/kg), along with lower concentrations of Cu (16.3 mg/kg) and Ni (12.4 mg/kg) upstream in the Magdalena River at Calamar. The present study's results in the bay were similar to previous reports of Cr (Parra et al., 2011a), Cu (Parra et al., 2011b; Restrepo et al., 2016b), Hg (Cogua et al., 2012) in Cartagena Bay. Jaramillo et al. (2016) have recently reported concentrations of Cd and Pb similar to the present study and even higher concentrations of Cr (31.2–189.2 mg/kg) and Cu (44.1–924.6 mg/kg) in the bay's sediments.

Historical levels of mercury in the bay's sediments are of particular interest due to pollution caused by a chlor-alkali plant operating from 1967 to 1978. This led to Hg concentrations between 7 mg/kg (FAO & CCO, 1978) and 33.2 mg/kg (Guerrero et al., 1995) and the plant's eventual closure in 1978. A recent study by Parra et al. (2011a, 2011b) used ^{210}Pb dating of sediment cores to reconstruct the historical levels of metals in the bay for the period

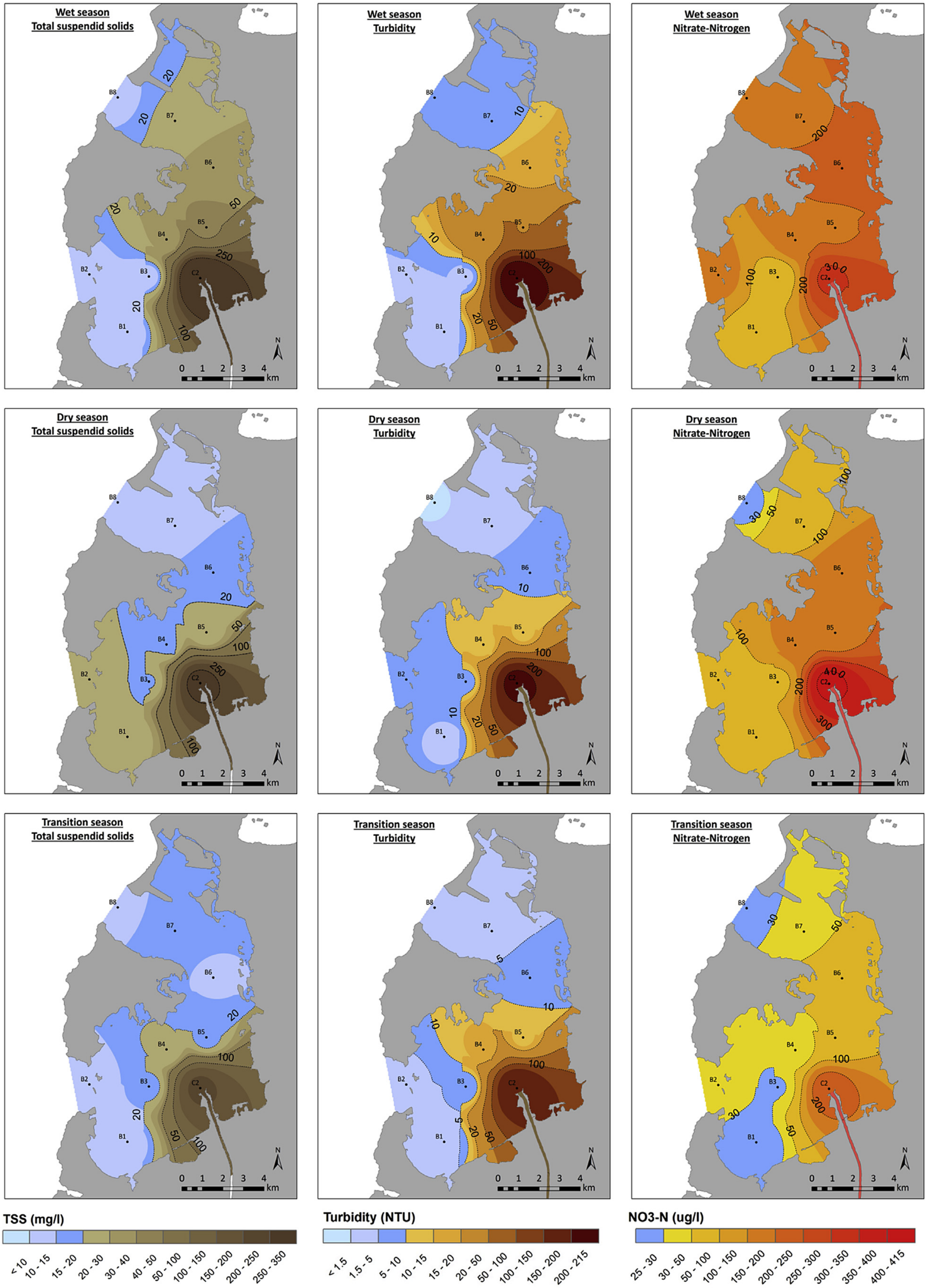

Fig. 5. Interpolated maps of total suspended solids (mg/l; left column), turbidity (NTU: center column) and nitrate-nitrogen (μg/l; right column) measured in the surface waters of Cartagena Bay and averaged over the wet (top row), dry (middle row) and transitional season (bottom row). Blue colours represent results below the threshold values cited in text. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

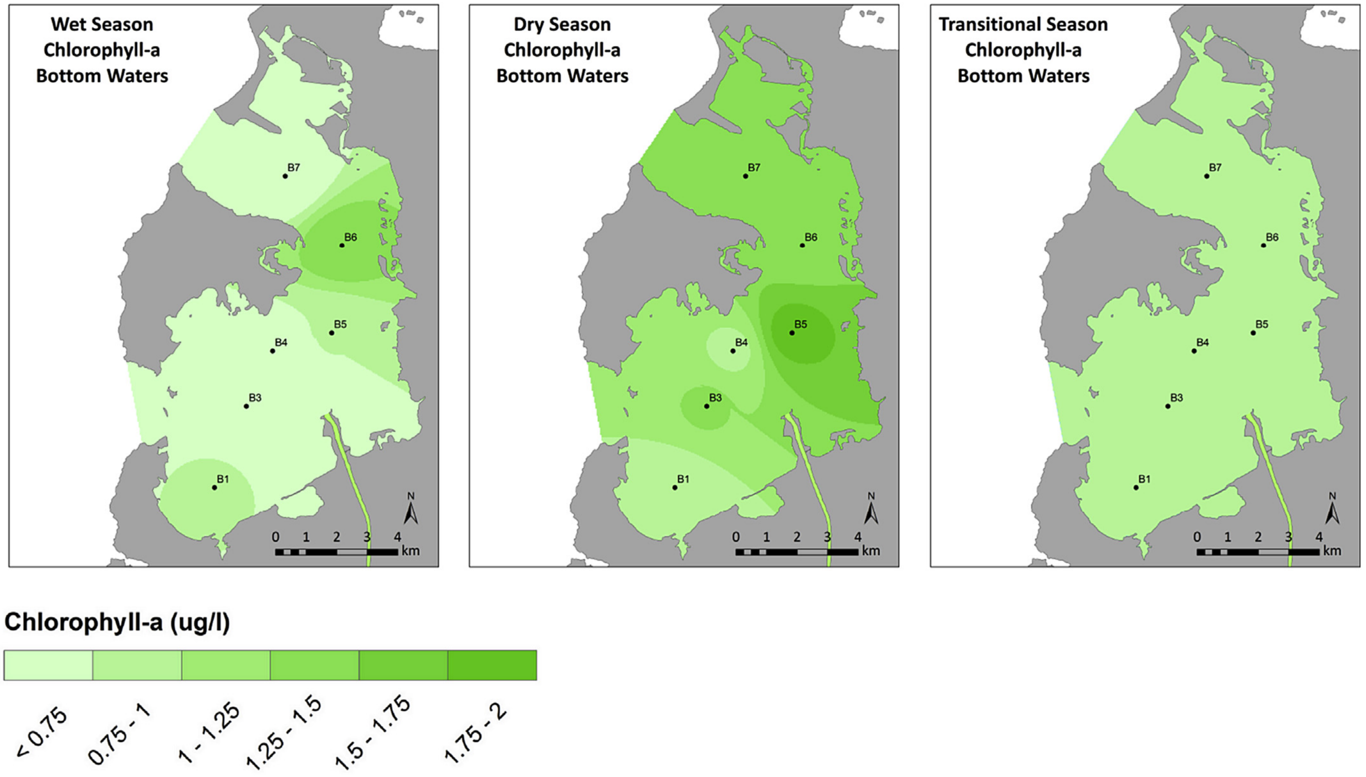

Fig. 6. Interpolated maps of chlorophyll-*a* concentration (μg/l) measured in the bottom waters of Cartagena Bay and averaged over the wet (left), dry (center) and transitional season (right).

1964–2009 and confirmed that high levels of Hg (max: 18.8 mg/kg) still exist at sediment depths of 55–65 cm, corresponding to the plant's operational period. Mercury levels have since gradually declined and recent studies have found average surface concentrations of 1.88 mg/kg (Alonso et al., 2000), 0.30 mg/kg (Parra et al., 2011a, 2011b), 0.18 mg/kg (Cogua et al., 2012) and 0.13 mg/kg (this study). Though current levels are still at the Threshold Effects Level of 0.13 mg/kg (Buchman, 2008), of more concern may be the occasional finding of Hg concentrations above the Probable Effects Level of 0.70 mg/kg (Buchman, 2008) such as the maximum value of 10.3 mg/kg found by Alonso et al. (2000) and that of the present study (1.3 mg/kg; Fig. 8). While the latter single-sample result could be considered an outlier, it is similar to the Hg concentrations found by Parra et al. (2011b) in sediments 30–40 cm beneath the surface in the same area of the bay. Consequently, this single-sample result in the present study is deemed important as it may be indicative of a pollution event, such as the resurfacing of contaminated sediments due to dredging activities that were underway in Sept. 2014, or the inflow of another land-based pollution source. Given that Hg levels in the bay decreased with each subsequent sampling following the peak value in Nov. 2014 (Fig. 8), this further supports the possibility of a pollution event prior to the start of monitoring.

This study's findings of Cr, Cu and Ni show that there are other metals of concern to the ecosystem as well. Historical data of these metals (Parra et al., 2011a) show that similar concentrations date back to the period of 1965–1975, suggesting that there are continued inputs of these metals or that such concentrations are normal in this bay. These potential risks to the ecosystem, along with that due to high Cd concentrations in the canal, are supported by previous findings of high metal concentrations accumulated in the food chain of this coastal zone, including Cd in oysters (Manjarrez et al., 2008); Cd, Pb and Hg in corals (Torres and Torres, 2004); and Hg in fish, crabs, birds and humans (Alonso et al., 2000; Olivero-Verbel et al., 2008; 2009, 2013; Cogua et al., 2012).

5.4. Recent trends of fluvial fluxes into Cartagena Bay

The downstream Magdalena and its distributary channel, the Dique Canal, show significant trends in the water discharge and sediment load records. Between 2000 and 2011, trends in fluxes were more pronounced and annual discharges increased up to 48%. For example, the Magdalena streamflow and sediment load experienced increases of 24% and 33%, respectively, with respect to the pre-2000 period. Meanwhile, fluvial fluxes from the Dique Canal were also more pronounced after 2000. A mean water discharge of 398 m^3/s before 2000 increased to about 508 m^3/s during the 2000–2010 year period, corresponding to an increase of 28%. Also, sediment load displayed an increase of 48% when comparing the mean load of 16,153 t/day during the 1984–2000 year period with the observed inter-annual mean of 23,906 t/day for the 2005–2010 year period. These results are in close agreement with the observed trends during the period between 1980 and 2010 in sediment loads of the main tributaries of the Magdalena River and also with the steep increase in deforestation during the last three decades (Restrepo et al., 2015).

The increasing behavior of sediment flux into Cartagena Bay is a major environmental concern in terms of water and sediment quality. According to a recent analysis of sedimentation and pollutant tracers (Restrepo et al., 2016b), sedimentation rates in the outlets of the Dique Canal also show major clastic fluvial sediment inputs and a remarkable transference of sediments in the inner shelf of the bays of Cartagena and Barbacoas. While the clastic sedimentation of mud in a calcareous inner shelf under natural conditions is almost undetectable, the human-induced input of muddy sediments to these bays through the Dique Canal and secondary artificial channels is high, and average sedimentation rates

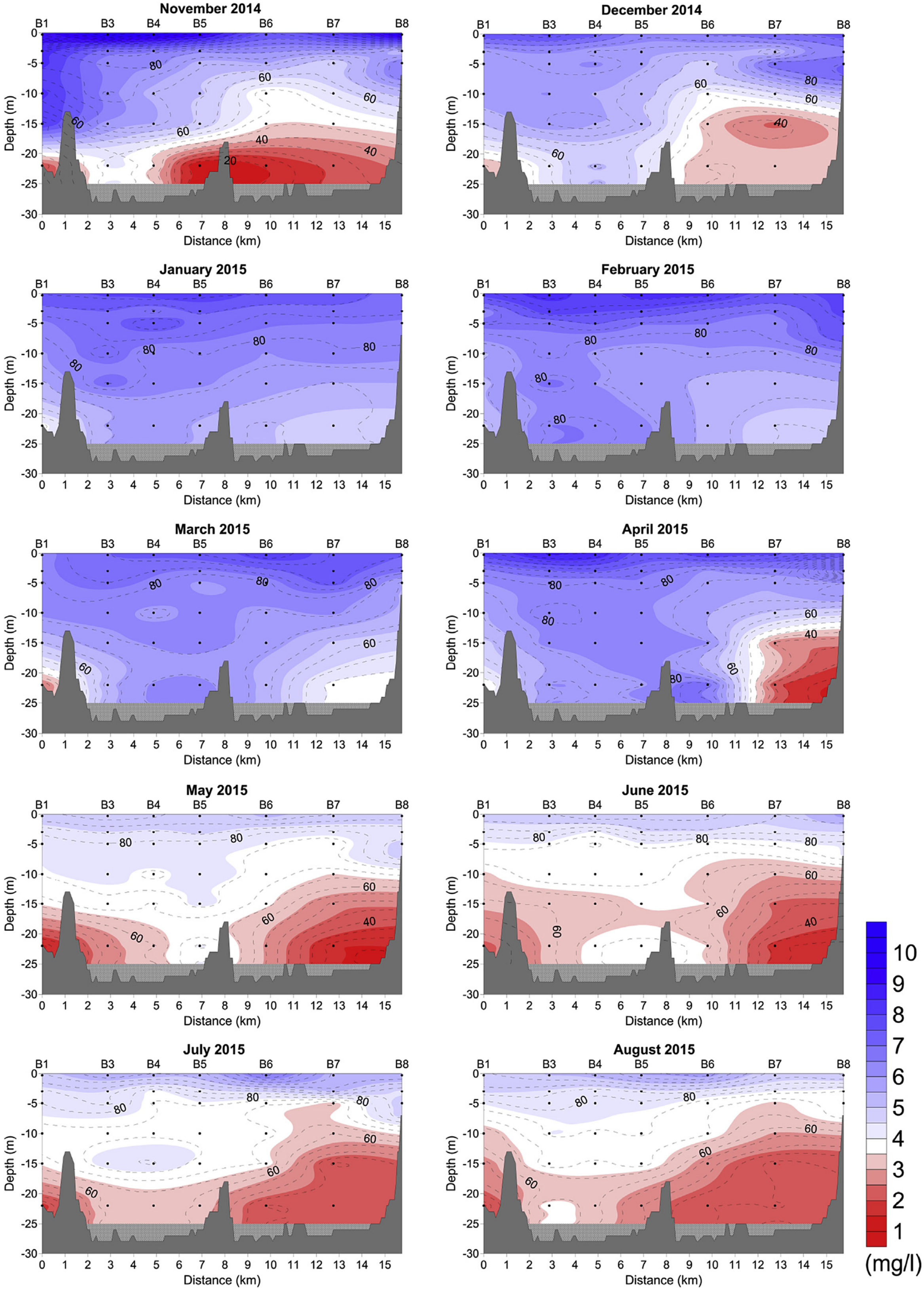

Fig. 7. Monthly measurements of oxygen profiles in Cartagena Bay. Dissolved oxygen concentration (mg/l) is shown as a colour gradient. Oxygen saturation (%) is shown as dashed contour lines. Points (●) represent measurement locations at stations (B1, B3-B8) shown in Fig. 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

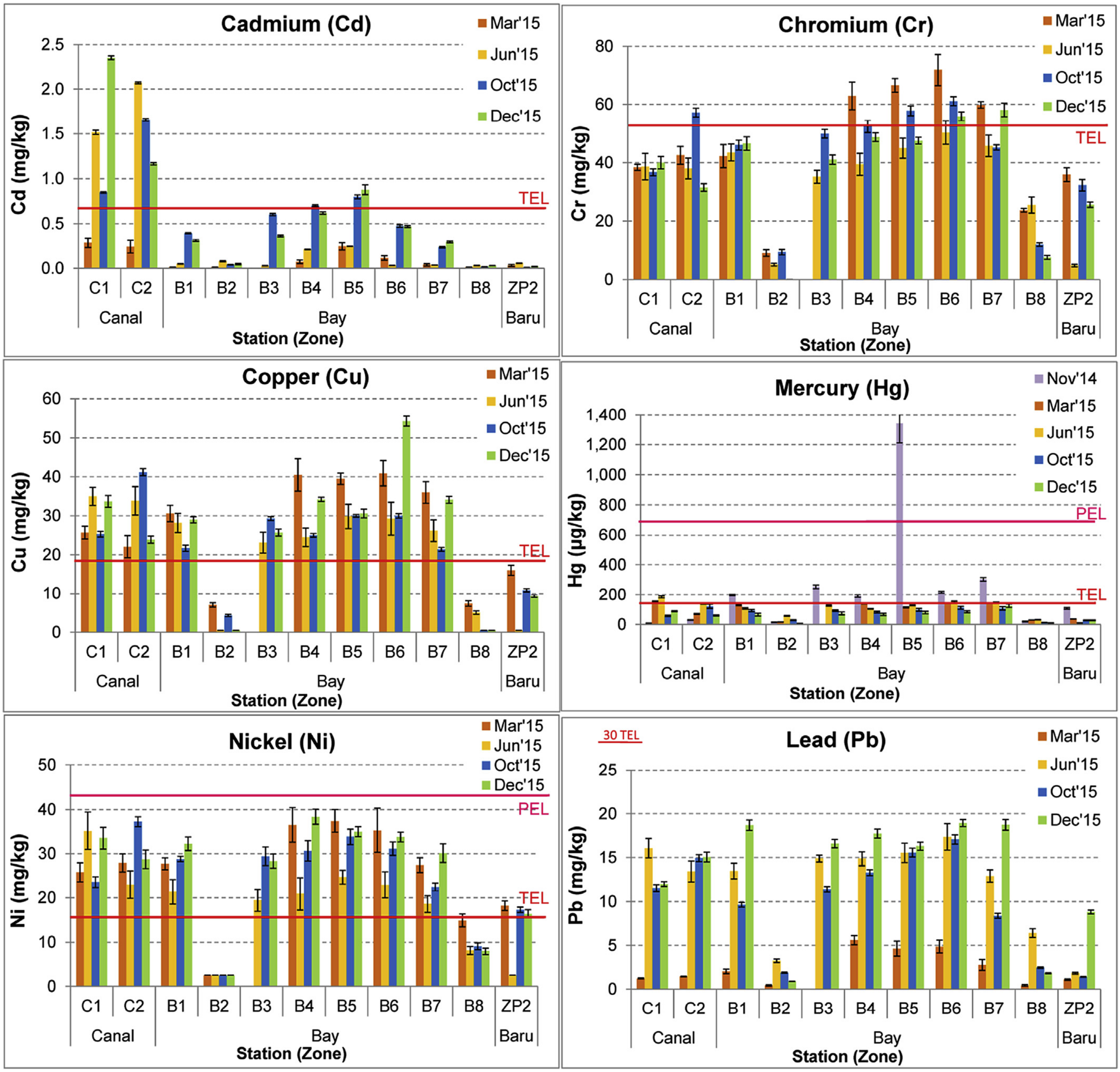

Fig. 8. Bar graphs of metal concentrations in the sediments of the Dique Canal, Cartagena Bay and Barú Point collected in March, June, October and December 2015, as well as in November 2014 for mercury. Red lines drawn across the plots show the Threshold Effects Level (TEL) and the Probable Effects Level (PEL). Station locations are shown in Fig. 1; Parameter abbreviations are shown in Table 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

are 0.7–0.8 cm/y in this coastal area. Sediment core analyses in Barbacoas Bay (Fig. 1), upstream of the city of Cartagena, also showed high levels of metals (As, Zn, Cu, Ni, Cr, Mn and Fe) that are sourced through the Magdalena Basin upstream of the Dique Canal at Calamar, showing that the anthropogenic activities around Cartagena Bay are not the only sources of coastal pollution.

6. Conclusions

This study has demonstrated various aspects of seasonal variability in the water quality of Cartagena Bay. During the rainy season (Sept.–Dec.), the bay's waters are characterized by lower salinities and greater concentrations of total suspended solids, turbidity, nitrate-nitrogen, total phosphorus, fecal coliforms and enterococcus. Increased concentrations of these parameters are particularly prevalent in the central part of the bay where freshwater plumes from the Dique Canal tend to disperse during this season. During the dry/windy season (Jan.–Apr.), lower water temperatures are found in the bay along with greater levels of biological oxygen demand and an increase in chlorophyll-*a* concentration in bottom waters. The latter result suggests that the process of primary productivity in the bay is limited by water transparency rather than nutrients which are abundant. Higher phosphate concentrations are found during the transitional season (May–Aug.), possibly due to lower concentrations of suspended solids resulting in less sorption of dissolved phosphorus. Oxygen levels were low during the rainy season, adequate during the dry/windy season, and lowest during the transitional season, evidencing the hypoxic conditions found in the bay for most of the year.

Water quality in the Dique Canal exhibited peak concentrations of total suspended solids, turbidity, chlorophyll-*a*, phosphate, total phosphorus, and phenols during the months of October and April coinciding with the onset of periods of increased runoff. On the contrary, greater concentrations of fecal coliforms and enterococcus were observed in the canal during the dry season (Jan.–Apr.) suggesting nearby sources in the canal that are otherwise diluted during high runoff conditions. Increases of cadmium concentrations both in the canal and the bay during the rainy season suggest that the canal is the principal source of cadmium to the coastal zone.

The majority of water and sediment quality parameters analyzed were found to exceed national and international threshold values. This would suggest that potential impacts of pollution to the ecosystem are likely. These water quality parameters include total suspended solids, turbidity, phosphate, total phosphorus, and chlorophyll-*a* which exceeded less-strict threshold values throughout the year and exceeded even stricter thresholds during the wet and transitional seasons. Dissolved oxygen, oxygen saturation, biological oxygen demand, and nitrate-nitrogen also exceeded threshold values during the wet and transitional seasons, demonstrating that water quality is inadequate for the ecosystem for most of the year. Increased concentrations of fecal coliforms and enterococcus during the rainy season also present a potential sanitary risk to bathers in the bay, though water quality was adequate at the beach “Playa Blanca” for the most part.

While mercury has long been studied in Cartagena, this research shows that other metals may also be of concern. Concentrations of chromium, copper, nickel, and mercury in the bay's sediments were above the Threshold Effects Level (TEL) indicating a potential risk to the ecosystem. Cadmium also exceeded the TEL during the rainy season, while nickel approached the Probable Effects Level (PEL) and lead was well-below the TEL. The finding of mercury at a concentration of nearly double the PEL in a sediment sample from November 2014 suggests a recent pollution event, such as the resurfacing of contaminated sediments due to dredging activities or the inflow of another land-based pollution source.

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