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RESEARCH ARTICLE

Spatial distribution of pesticides, organochlorine compounds, PBDEs, and metals in surface marine sediments from Cartagena Bay, Colombia

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Abstract

Cartagena Bay is an estuarine system located in the Caribbean Sea (Colombia, South America), that receives fresh water from *Canal del Dique*, which is connected to the Magdalena River, the most important river of Colombia, with some of the most prominent Colombian cities located in its watershed, which has a high sediment yield. An analysis of persistent organic pollutants and heavy metals was carried out on marine sediments from Cartagena Bay. Cartagena Bay sediments deployed the occurrence of total levels of pesticides (thiocarbamates, bromacil, triazines, organochlorines, and organophosphorus), polybrominated diphenyl ethers (PBDEs), and polychlorinated biphenyls (PCBs), in sediments ranging from 0.83–33.67 ng/g dry-weight, 0.05–0.34 ng/g dry-weight, and 0.06–19.58 ng/g dry-weight, respectively. Their concentrations were lower than those reported in NOAA Screening Quick Reference Tables. DDTs and PCBs are banned organochlorine compounds, since, even at low levels, their presence in sediments represents a threat to aquatic organisms and, therefore, to human health through the trophic chain. Sediments showed high concentrations of strontium (50–959.6 mg/kg). All metals evaluated in the marine sediments were found in the S6 sampling point; this was near tannery and hydrocarbon industries (Pb 37.1 mg/kg, Cr 137.2 mg/kg, Cd 1.7 mg/kg, Cu 64.4 mg/kg, As 13.1 mg/kg, Sr 318.9 mg/kg); these results exceeded the accepted values of threshold effect levels (TEL) used as an indicator of their potential risk on marine life.

Keywords Pesticides · Organochlorine compounds · PCBs · PBDEs · Metals · Sediment · Pollutants · Colombia

Introduction

Cartagena Bay, located on the Caribbean coast of Colombia in South America, behaves as an estuarine system (Cogua et al. 2012). The distribution of sediments in this bay is highly influenced by *Canal del Dique* (Restrepo et al. 2013), a human-made canal connecting the bay to the Magdalena River, an important river, as it is the largest in Colombia, with a length of 1,540 km, and approximately 70% of the Colombian population (about 38 million people) is located in its watershed, which has the highest sediment yield of any other large river in South America, that is, 560 t km^{-2}. From 1984 to 2010, *Canal del Dique* has discharged approximately 52 Mt of sediments into Cartagena Bay, and 55–250 m^3 s^{-1} of freshwater (Restrepo et al. 2016). Additionally, Cartagena Bay's coastal water quality is affected by maritime transportation, as well as industrial and household waste from the coastal city of Cartagena de Indias. After 2013, the city's sewage system was directed to a drain far north of the city so as not to affect the bay (Tosic et al. 2019).

Sediments are known to become sumps for pollutants. Depending on environmental conditions, contaminants in sediments can be released into the water column and circulate in ecosystems (Tosic et al. 2019). As a result, sediment

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characterization in terms of metal and persistent organic pollutant (POP) content is used as a method to describe the environmental health status of the aquatic ecosystem. POPs such as polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and organochlorine pesticides (OCPs) have high octanol-water (K_{ow}) partition coefficients; hence, they are highly adsorbed and accumulate in sediments (Souza et al. 2018). They are harmful to the marine environment due to their detrimental effects on wildlife and humans and were added to the list of substances that should be banned or limited in the Stockholm Convention on such POPs (Commendatore et al. 2018). OCPs are also toxic, bioaccumulative in fatty tissue, become biomagnified through the food web, and are prone to long-range transport via air, water, and migratory animals (Pereira et al. 2015a). These compounds are known to cause carcinogenesis, neurotoxicity, immunotoxicity, and endocrine and reproductive disorders in living organisms (Elnar et al. 2012; Kraugerud et al. 2012). Due to their physicochemical characteristics, they are found in the environment and their destination is still of concern despite the fact that their manufacture and use have been banned in many countries (Gonzalez-Mille et al. 2013).

Other families of pesticides such as organophosphorus, triazines, thiocarbamates, and chloroacetanilides were later introduced as alternatives to OCPs because these compounds are less persistent. Nonetheless, some molecules from these new families of pesticides have also been found toxic to biota (Phyu et al. 2006; Velisek et al. 2013) and their continuous release into the environment have resulted in air, water, soil, vegetable and fruit contamination (Ferré et al. 2018; Suárez et al. 2018; Vaclavik et al. 2018).

In Colombia, during the last 30 years, pesticide registration doubled from one hundred eighty-six molecules in 1974 up to four hundred active ingredients in 2003 (Cárdenas et al. 2010), and a recent inventory of PCBs estimated that about 9.771 and 12.803 tons are still in the country (Vaca Bohórquez et al. 2014). PBDEs were used worldwide as flame retardants in everyday products such as electronic equipment, building materials, furniture, and textiles (Besis and Samara 2012). Additionally, metal pollutants are released into the environment via anthropogenic and natural sources and, contrary to most pollutants, do not undergo microbial or chemical degradation. Metals are similarly biomagnified in the food chain (Burgos-Núñez et al. 2017; Marrugo-Negrete et al. 2017), and their adsorption into sediment constitutes one of the most important processes governing their mobility and bioavailability in aquatic environments (Pinzón-Bedoya et al. 2020

Studies have reported the presence of heavy metals and persistent organic pollutants from natural, industrial sources, and accidental spills, which have found their way into ecosystems at Cartagena Bay (Aguirre-Rubí et al. 2019; Tosic et al. 2019; Jaramillo-Colorado et al. 2015). Residues of various metals have been found in the bay's surface sediments (Tosic et al. 2019; Jaramillo-Colorado et al. 2016; Alonso et al. 2000).

A multi-residue method for the analysis of semivolatile organic pollutants in marine sediments from Cartagena Bay was employed. The QUECHERS extraction technique and gas chromatography-triple quadrupole mass spectrometry (GC-MS/MS) were used for the determination of plaguicides, PCBs, and PBDEs. GC-MS/MS offers better selectivity and sensitivity than conventional quadrupole GC/MS (Payá et al. 2007; Zhang et al. 2015). Metals were analyzed by inductively coupled plasma mass spectrometry (ICP-MS), considered the best appropriate tool for determination of elements at ultratrace levels in all types of matrices (Fernandes et al. 2012).

The goals of this study were to evaluate concentrations of PCBs, PBDEs, OCPs, newer generations of pesticides, and metals from Cartagena Bay sediments, and compare the levels of these chemicals with the concentrations reported in other similar environments from other countries. This research would contribute to detect pollutant trends and improve the understanding of their sources, occurrence, risk, and destination.

Material and methods

Chemicals and materials

Analytical pesticide standards, of purity ≥ 95%, were obtained from Phenova (Golden, CO, USA) and Sigma Aldrich (St. Louis, MO, USA). Surrogate mix (2,4,5,6-tetrachloro-m-xylene and decachlorobiphenyl) was purchased from Phenova (Golden, CO, USA). Internal standards (ISTD), $^{13}C_{12}$ PCB 52 and $^{13}C_{12}$ PCB 138, were purchased from Wellington Laboratories Inc. (Ontario, Canada). PBDE standards were obtained from Accustandard (New Haven, CT, USA). The WHO-coplanar PCB mix was acquired from Cambridge Isotope Laboratories (Andover, MA). PSA (**Primary** Secondary **Amine**) **and** $\mathbf{C_{18}}$ sorbents were obtained from Agilent Technologies (Santa Clara, CA, USA). $MgSO_4$, NaCl, acetonitrile LC/MS grade, isooctane for pesticide residue analysis, and hydrogen peroxide 30% were purchased from Fisher Scientific (Pittsburg, PA, USA). Metal-grade nitric acid and standard metal mixtures (82026-108 and 82026-114 BDH Aristar® Plus) were purchased from VWR International (Radnor, PA, USA). NANOpure™ water was used in all experiments from Barnstead International (Dubuque, IA, USA).

Study area and sample collection

The Cartagena Bay has a surface area of 84 km^2, approximately, with average and maximum water depths of 16 m and 26

m, respectively (Restrepo et al. 2013; Tosic et al. 2019). Ten sampling sites along the Cartagena Bay were selected to evaluate the spatial distribution of organic and inorganic pollutants in sediments. The sampling was carried out in 2015 at ten stations, during the rainy season.

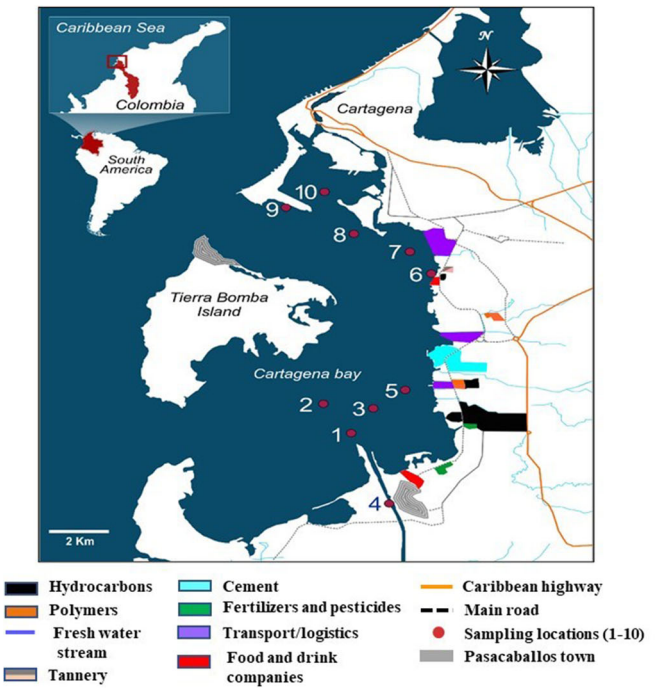
Figure 1 shows the map of the study area with sampling locations, georeference, and land use around Cartagena Bay. Surficial sediments were collected using a Van Veen-type grab sampler; three sediment sub-samples were taken to complete about 400 g of a composite sample. The water depths of the sediment samples ranged from 6 to 15 m. The samples were immediately placed in dark amber bottles, refrigerated, and transported to the Agrochemical Research Group Laboratory at the University of Cartagena. Sediments were freeze-dried, ground, homogenized, and sieved (63-μm mesh). The samples were stored at – 40 °C for transportation to the University at Buffalo and until analysis was performed.

Sample extraction for organic pollutants

The Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS^{TM}) extraction method adapted from (Payá et al. 2007) was applied by using 4 g of freeze-dried sediment, which was weighed in 50-mL centrifuge tubes, and homogenized with 10 mL water and 10 mL acetonitrile. Then, 4 g of $MgSO_4$ and 1 g of NaCl were added to promote phase separation. The mixture was agitated intensively in a vortex for 1 min and centrifuged at 3400 rpm for 8 min. An aliquot (4 mL) of the organic phase was cleaned up through dispersive solid-phase extraction (d-SPE) by adding 12.5 mg C_{18}, 25 mg of PSA, and 150 mg of $MgSO_4$ per mL extract. The mixture was shaken in a vortex for 1 min and centrifuged for 8 min at 3400 rpm. The supernatant was filtered (0.2-um PTFE), evaporated to dryness, and reconstituted with 1 mL of isooctane. An aliquot of the extract was spiked with 12.5 μL of 500 ng/mL spiking solution containing PCBs, PBDEs, and pesticides. This spiked sample was used as the single-point standard addition for quantification (Su et al. 2017).

GC/MS/MS analysis for organic pollutants

Organic compounds were analyzed using a Trace GC Ultra coupled to a TSQ Quantum XLS triple quadruple mass spectrometer (Thermo Scientific, West Palm Beach, FL) equipped with a programmable temperature vaporization injector (PTV). Separation was achieved on a DB-5HT column (30 m × 0.25 mm i.d × 0.10-μm film thickness; Agilent Technologies). The oven temperature was programmed to start at 60 °C (held for 1 min), ramped up to 160 °C at 15 °C/min (held for 2 min), then increased to 190 °C at 2.2 °C/min, ramped up to 290 °C at 50 °C/min (held for 3 min), and finally hiked up to 330 °C at 30 °C/min (held for 2 min). The carrier gas (helium, 99.99% purity) was set at 1 mL/min. Samples were injected (3 μL) using the PTV that was initially set at 89 °C and then increased at a rate of 7.5 °C /min for 0.2 min. The components were transferred to the column at a temperature of 330 °C for 1 min. A split flow of 125 mL/min and a split-less time of 1.4 min were used. The MS



Sampling locations	Georeference of sampling sites
S1	N: 10°30.926′|W: -75°.53.329′
S2	N: 10°31.992′| W: -75°.54.106′
S3	N: 10°31.836′|W: -75°. 52.688′
S4	N: 10°28.371′|W: -75°.52.220′
S5	N: 10°32.508′|W: -75°.51.775′
S6	N: 10°36.755′|W: -75°.51.044′
S7	N: 10°37.554′|W: -75°.51.658′
S8	N: 10°38.215′|W: -75°.53.246′
S9	N: 10°39.159′|W: -75°.55.196′
S10	N: 10°39.726′|W: -75°.54.094′

Fig. 1 Map of the study area, georeference of sampling locations, and land use (showing industrial influence) in the Cartagena Bay (Colombia)

ionization energy was 70 eV, the transfer line temperature was 280 °C and the ion source was 200 °C. The mass spectrometer was operated under the selected reaction monitoring mode (SRM). Table 1 summarizes MS/MS transitions, retention times, collision energies, and recoveries for the targeted compounds.

Method validation

Sensitivity and linearity

Linearity was evaluated using a seven-point matrix-matched calibration curve that proved to be linear ($r^2 \geq 0.999$) for all the studied analytes over the studied scope (1.25 to 500 ng/mL). The sensitivity of the method was evaluated in terms of method quantification limit (MQL) and method detection limit MDL values stretch from 0.07 to 4.19 ng/g for pesticides and from 0.01 to 0.05 ng/g for PCBs and PBDEs, respectively (Table 1).

Some isomers such as demeton-s-methyl and demeton-o-methyl, beta-BHC, and delta-BHC were not completely separated by the column and therefore they were quantified as one.

Accuracy and precision

Standard addition was used for the quantification of targeted compounds to account for matrix effects associated with the analysis of such analytes in sediments. Organic components were confirmed based on their retention times, the presence of singled out quantifier and qualifier ions, and their expected ratios. Retention times had to be within ± 0.1 min of the expected time of the corresponding reference standard, and qualifier-to-quantifier ion ratios of the monitored m/z had to be within ±15% for positive confirmation.

Extraction recoveries for the organic pollutants were determined at two fortification levels, 10 ng/g and 100 ng/g. The samples used for determining such enhancements were subjected to the same extraction procedure as described above. Physical-chemical parameters of sediment used for validation are shown in Table S1. More than 96% of the pesticides under study presented Recuperation values between 70% and 120%. Similarly, PCBs and PBDEs such rates ranged from 70% to 99% (Table 1).

Some isomers such as demeton-s-methyl and demeton-o-methyl, beta-BHC, and delta-BHC were not completely separated by the column and therefore they were quantified as one.

Total organic carbon and metal analysis

Total organic carbon (TOC) was determined using the modified Wakley-Black titration method described by Gaudette et al. (1974). For trace determination of metals (Pb, Cr, Cd, As, Sr, Cd), freeze-dried sediments were acid-digested (HNO_3 + H_2O_2) with a modified USEPA 3050B method (USEPA 1996), followed by metal detection using inductively coupled plasma mass spectrometry (ICP-MS). A detailed description of the metal analysis method is shown in the supplementary information.

Sample digestion for metal analysis

Freeze-dried sediment samples were digested in trace metal-grade nitric acid (Aristar Ultra) and hydrogen peroxide 30% (Fisher Scientific) following a method adapted from USEPA 3050B for 0.5 g of sample (USEPA 1996). Samples were extracted and analyzed by duplicated. Briefly, 0.5 g dry mass soil was covered with concentrated nitric acid and refluxed for 2 to 3 h in 50-mL digestion vessels, covered with reflux caps. Hydrogen peroxide was added before refluxing for an additional 1 to 3 h. Digestion was performed in a HotBlock® Pro system (Environmental Express). Samples were diluted to 50 mL with NANOpure™ water (Dubuque, IA). and filtered through 5-µm PTFE-faced polypropylene filters (Environmental Express, Charleston, SC, USA). A method blank solvent was analyzed with the samples.

Elemental metal analysis

Samples were analyzed by inductively coupled plasma mass spectrometry (ICP–MS) on a X-Series 2 instrument (SC2 DX autosampler) (Thermo Scientific). In Table S2, the operating conditions of the ICP-MS are described.

A list of the analyzed metals and the respective metal internal standard used are shown in Table S3. The isotopes used were chosen after evaluating the performance of the analysis when using the other abundant isotopes of each element. Internal standard solution of 10 ng/mL was introduced at a constant rate by the sample injection system to reduce errors due to instrument drift. Addition of 7% H_2/He gas to the collision cell was utilized in conjunction with the pole bias and hexapole bias settings to remove interfering diatomic ions.

One-point standard addition was used for accurate quantification of the target metals to minimize matrix effects. Two 3-mL aliquots were taken from each digested sample. One aliquot received 7 mL of NANOpure™ water to represent a blank sample. The other aliquot received 1 mL of 200 ng/mL standard solution mixture to create a solution with a known concentration of 20 ng/mL, then 6 mL of NANOpure™ water was added to reach a total volume of 10 mL. The *y*-intercept and slope of the line connecting the 2 points were divided to calculate the actual sample concentration in ng/mL.

Method validation

For method validation, various sediment samples were pooled and homogenized. From this pool, sediments were spiked at

Table 1 GC/MS/MS parameters of pesticides, PCBs, and PBDEs, and their method detection limits (MDL), method quantification limits (MQL) and recoveries ($n = 3$)

Compound	RT	Precursor ion (m/z)	Quantifier ion (CE, eV)	Qualifier ion (CE, eV)	Ion ratio Qual/Quant (%)	MDL (ng/g)	MQL (ng/g)	Recovery (%)	
								LS	HS
Pesticides									
Thiocarbamates									
Vernolate	7.59	161	128(5)	118(25)	14	0.15	0.49	59 ± 12	78 ± 9
Molinate	8.42	187	126(7)	98(14)	18	0.03	0.10	70 ± 12	77 ± 5
Cycloate	9.56	154	83(15)	72(15)	28	0.06	0.19	76 ± 7	81 ± 7
Uracil									
Bromacil	15.87	205	188(20)	162(10)	78	0.20	0.66	120 ± 16	117 ± 2
Triazines									
Simazine	11.23	201	172(10)	186(10)	97	1.26	4.19	93 ± 10	99 ± 11
Prometon	11.29	225	168(10)	210(10)	51	0.08	0.26	92 ± 9	100 ± 6
Atrazine	11.41	215	200(10)	173(10)	45	0.13	0.44	100 ± 6	98 ± 4
Chloroacetamides									
Alachlor	14.58	188	132(19)	160(19)	44	0.12	0.41	94 ± 7	96 ± 5
Metolachlor	16.3	238	162(14)	133(14)	12	0.08	0.25	95 ± 5	93 ± 2
Butachlor	20.94	188	132(20)	146(20)	63	0.20	0.67	89 ± 7	95 ± 2
Organophosphorous									
Dichlorvos	5.89	185	93(20)	109(20)	51	0.14	0.46	51 ± 18	70 ± 20
Mevinphos	7.52	192	127(12)	109(19)	21	0.07	0.23	92 ± 7	107 ± 15
Thionazine	9.25	143	79(17)	52(17)	58	0.09	0.31	87 ± 6	92 ± 7
Ethoprophos	9.57	200	158(8)	114(12)	36	0.04	0.14	86 ± 6	103 ± 7
Sulfotep	10.36	322	202(12)	238(12)	60	0.08	0.26	87 ± 5	96 ± 7
Phorate	10.43	260	75(8)	231(8)	45	0.05	0.16	76 ± 3	89 ± 8
Disulfoton	12.44	274	88(8)	60(17)	55	0.02	0.08	71 ± 7	82 ± 9
Diazinon	12.44	304	179(8)	162(8)	16	0.02	0.08	89 ± 4	87 ± 1
Chlorpyrifos Methyl	14.19	286	93(25)	271(25)	44	0.10	0.32	91 ± 3	81 ± 2
Methyl parathion	14.21	263	109(10)	136(20)	15	0.03	0.10	88 ± 9	97 ± 4
Fenchlorphos	14.85	285	240(25)	270 (25)	59	0.04	0.12	89 ± 5	84 ± 2
Fenthion	16.59	278	109(19)	169(19)	54	0.05	0.17	87 ± 5	96 ± 6
Chlorpyrifos	16.65	314	258(12)	286(12)	35	0.03	0.09	90 ± 5	83 ± 2
Parathion	16.69	291	109(10)	81(20)	39	0.06	0.20	90 ± 6	102 ± 6
Trichloronate	17.19	297	269(15)	223(25)	26	0.04	0.13	89 ± 5	80 ± 1
Tokuthion	21.56	309	239(15)	221(20)	37	0.02	0.07	87 ± 6	91 ± 2
Merphos oxon	22.12	258	147(8)	202(8)	33	0.06	0.20	107 ± 10	119 ± 5
Sulprofos	24.39	322	156(12)	139(12)	43	0.07	0.25	86 ± 6	96 ± 3
Famphur	24.54	218	109(17)	79(25)	25	0.08	0.28	98 ± 15	109 ± 5
Coumaphos	26.31	362	226(15)	109(15)	92	0.13	0.43	91 ± 11	109 ± 9
Chlorinated pesticides									
Alpha-BHC	10.47	219	145(14)	183(14)	72	0.06	0.21	92 ± 2	87 ± 7
Demeton S-O	10.96	170	114(7)	142(7)	26	0.16	0.54	82 ± 12	82 ± 2
Beta-delta-BHC	11.36	219	147(17)	183(17)	75	0.10	0.34	95 ± 2	101 ± 7
gamma-BHC	11.53	219	147(17)	183(17)	26	0.25	0.84	94 ± 10	93 ± 2
Heptachlor	14.26	272	237(17)	143(33)	9	0.04	0.14	86 ± 1	74 ± 3
Aldrin	15.8	263	193(25)	227(32)	9	0.07	0.23	85 ± 1	82 ± 5
Heptachlor epoxide (Isomer B)	17.94	353	263(19)	282(19)	44	0.05	0.17	88 ± 3	91 ± 5
trans-Chlordane	19.28	373	266(20)	301(20)	16	0.04	0.15	90 ± 4	89 ± 2
Endosulfan I	19.91	241	206(23)	169.5(25)	42	0.09	0.30	88 ± 3	89 ± 3

Table 1 (continued)

Compound	RT	Precursor ion (m/z)	Quantifier ion (CE, eV)	Qualifier ion (CE, eV)	Ion ratio Qual/Quant (%)	MDL (ng/g)	MQL (ng/g)	Recovery (%)	
								LS	HS
cis-Chlordane	20.16	373	266(20)	301(20)	15	0.04	0.13	90 ± 5	88 ± 3
Dieldrin	21.48	263	193(32)	227(32)	6	0.40	1.34	91 ± 1	98 ± 6
4,4′-DDE	21.9	318	246(22)	176(30)	20	0.04	0.13	94 ± 3	84 ± 1
Endrin	22.73	263	193(32)	227(32)	6	0.09	0.31	90 ± 6	99 ± 5
Endosulfan II	23.42	241	206(25)	170(25)	94	0.13	0.43	101 ± 7	102 ± 2
4,4′-DDD	23.97	235	165(23)	199(23)	18	0.03	0.09	93 ± 4	104 ± 5
Endosulfan sulfate	24.5	272	237(16)	143(32)	9	0.09	0.29	95 ± 7	97 ± 8
4,4 DDT	24.65	235	165(23)	199(23)	18	0.06	0.21	95 ± 4	101 ± 3
Endrin ketone	25.1	317	245(23)	209(23)	97	0.27	0.91	95 ± 4	93 ± 7
Methoxychlor	25.37	227	169(22)	141(22)	47	0.05	0.17	96 ± 6	97 ± 1
PBDEs									
PBDE-47	25.6	486	326 (20)	328(20)	90	0.2	0.5	80 ± 3	83 ± 7
PBDE-99	26.55	564	404(25)	406(25)	90	0.2	0.8	80 ± 10	85 ± 2
PBDE-154	27.16	484	377(40)	375(40)	90	0.4	0.13	71 ± 7	79 ± 7
PBDE-153	27.5	484	324(40)	377(40)	40	0.3	0.09	70 ± 6	77 ± 4
PBDE-183	28.84	564	457(45)	404(45)	90	0.3		82 ± 24	86 ± 5
PCBs									
PCB-81	21.46	292	220(30)	222(30)	95	0.1	0.2	99 ± 1	na
PCB-77	21.98	292	220(30)	222(30)	90	0.1	0.3	96 ± 2	na
PCB-123	23.03	326	256(25)	254(25)	60	0.1	0.2	89 ± 2	na
PCB-126	23.76	326	256(25)	254(25)	70	0.1	0.2	87 ± 2	na
PCB-118	23.81	326	256(25)	254(25)	70	0.1	0.3	91 ± 1	na
PCB-114	24.05	326	256(25)	254(25)	50	0.1	0.4	88 ± 3	na
PCB-105	24.82	326	254(25)	256(25)	60	0.1	0.4	86 ± 2	na
PCB-167	25.14	360	290(25)	288(25)	45	0.1	0.4	81 ± 2	na
PCB-156	25.41	360	290(25)	288(25)	50	0.1	0.3	82 ± 0	na
PCB-157	25.46	360	290(25)	288(25)	45	0.1	0.4	84 ± 2	na
PCB-180	25.59	396	326(25)	324(25)	95	0.1	0.2	80 ± 3	na
PCB-169	25.76	360	290(30)	288(30)	40	0.1	0.2	81 ± 2	na
PCB-170	25.84	396	326(25)	324(25)	85	0.2	0.5	76 ± 3	na
PCB-189	26.07	396	326(30)	324(30)	85	0.1	0.2	80 ± 1	na
ISTDs									
^{13}C PCB52	15.29	304	232(20)	269(20)	36	n/a	n/a	n/a	n/a
^{13}C PCB138	24.68	372	302(25)	230(40)	11	n/a	n/a	n/a	n/a

CE: Collision energy, *n/a*: not applicable, *ISTD*: internal standard, *LS*: low spiking level (10 ng/g), *HS*: high spiking level (100 ng/g)

two different levels (0.3 mg/kg and 3 mg/kg, respectively) and were digested to determine extraction recoveries of the metals (n = 3). Unspiked sediment samples were also digested and analyzed; the values from these were subtracted from the spiked samples to calculate % recoveries. The MQL and MDL were determined by pooling digested sediment and spiking them before injection at different levels. Linearity was evaluated using matrix-matched calibration over the range of 0.5 to 100 ng/mL. The MDL and MQL were defined as the minimum detectable amount of analyte with signal-to-noise (S/N) ratios of 3 and 10, respectively (Table 2). Metal extraction recovery and method performance rates are presented in Table 2. Recuperation levels overall range from 46 ± 10 % to 111 ± 7 %, while those of MDL go from 0.05 to 0.49 mg/kg.

Data processing

Spearman's correlation analysis was performed using SPSS-25 Software to examine the relationships among

Table 2 Method detection limit (MDL), method quantification limit (MQL) and recoveries for metal analysis methodology. Recovery values are reported as average ± %RSD (n = 3)

Metal	Slope	Linearity (r^2)	MDL (mg/kg)	MQL (mg/kg)	% Recovery
Pb	0.262	0.9999	0.05	0.17	111 ± 7
Cr	0.060	0.9998	0.49	1.64	73 ± 9
As	0.008	0.9999	0.17	0.56	101 ± 5
Sr	0.135	0.9997	0.35	1.15	92 ± 5
Cu	0.035	0.9999	0.45	1.52	46 ± 10
Cd	0.057	0.9999	0.05	0.15	102 ± 1

metals, TOC, and pH. To differentiate the influence caused by natural or anthropogenic sources of metals, simple and integrated indices such as contamination factor (CF), geo-accumulation index (I_{geo}) and pollution load index (PLI) were calculated according to Kalender and Çiçek Uçar (2013). The Earth's crust values were used (Lide 2008).

Principal component analysis was performed using Minitab 17.3.1 (Minitab, Inc. State College, PA). Data was pretreated using auto-scaling. A value of 0.00001 was assigned to variables exhibiting a non-detect (n.d.) to avoid loading bias. The analysis was performed using a covariance matrix to allow for full variable comparability and to account for differences in units and scales among variables. Significant principal components (PCs) were selected according to the Scree test (D'agostino and Russell 2005). Hierarchical Cluster Analysis was developed using the average linkage (between groups) method.

Results and discussion

In this study, organic pollutants were analyzed by gas chromatography-triple quadrupole mass spectrometry (GCMS/MS). With the arrival of tandem mass spectrometry detectors, sample preparation processes have been reduced and are more straightforward. Today, trends in organic pollutant residue analysis are aimed at decreasing solvent consumption, sample size, and minimum cleanup steps. One of the most used methods for the analysis of pesticide residues due to its versatility is the QuEChERS method, introduced by Annastasiades & Lehotay (Payá et al. 2007).

GC-MS/MS offers various advantages in selectivity and sensitivity at low concentrations in the most complex mixes, especially for identifying and quantifying organic contaminants in environmental samples. (Zhang et al. 2015; Fernandes et al. 2012). The utilization of tandem MS can effectively reduce co-extractive compound interference and sample matrix effects, resulting in increased signal to noise (S/N) ratio and ultimately robust limits of detection. GC-MS/MS.

Concentrations of pesticides

The concentrations of the pesticides detected in each sample are shown in Table 3. Thirty out of the forty-nine targeted pesticides were detected at least in one of the samples. Total pesticide concentrations ranged from 0.83-33.67 ng/g dry weight, with the highest levels found at the mouth of *Canal del Dique* (S1, S2, S3, and S4), and at S9. Correspondingly, these locations exhibited the highest number of pesticides detected with a significant contribution from herbicides such as atrazine, bromacil, and butachlor. Organophosphorus (OPPs) and OCPs were the main contributors to the total concentrations of pesticides detected at the remaining locations. Thiocarbamates have more affinity with water than with sediment, as indicated by their slow K_{ow} values, and were not detected in most samples, except for vernolate at S1 (28.93 ng/g) and molinate (< 0.1 ng/g) at S8 and S9.

Total OPPs concentrations ranged from 0.39 to 3.06 ng/g dw with S1, S2, and S3 showing the highest frequencies of detection for OPPs. Chlorpyrifos (0.28–1.43 ng/g) and diazinon (< 0.08–0.27 ng/g) were detected in all the samples. Chlorpyrifos exhibits a strong affinity for aquatic sediments that correlates with organic content (Etchegoyen et al. 2017; Gebremariam et al. 2012). While diazinon is a moderately mobile pesticide, its adsorption into sediments also increases with organic matter alongside organic carbon contents (Aggarwal et al. 2013), which could explain its detection in the collected sediments. These two pesticides are among the OPPs of main use in Colombia (Aguirre-Rubí et al. 2019).

The presence of chlorpyrifos at Cartagena Bay is affected by the input from *Canal del Dique* (intensive agriculture in the Magdalena River basin) and by the agrochemical industry based near the seaport (Vivas-Aguas et al. 2010). In 2011, chlorpyrifos was detected at the bay (Vivas-Aguas et al. 2014) with a toxic level at a concentration of 0.024 μg/L, higher than the reference value for acute effects on aquatic life (0.011 μg/L) (Buchman 2008). Menzies et al. (2013) found cyclodiene pesticides, including chlorpyrifos, in seawater from Colombia (Cartagena Bay = 3.7 ng/L, Rosario Island = 20.5 ng/L, Santa Martha bay = 6.6 ng/L, and Cienaga = 22.2 ng/L), Panama (Panama Canal, Gatun locks = 11.7 ng/L),

Table 3 Total concentrations (ng/g dry-weight) of organic compounds by category in the studied locations

Compound	CAS no.	Chemical formula	MW, g/mol	Sampling site									
Pesticides				S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Thiocarbamates													
Vernolate	1929-77-7	$C_{10}H_{21}NS$	203.3	28.93	nd	nd	nd	nd	nd	nd	nd	nd	nd
Molinate	2212-67-1	$C_9H_{17}NOS$	187.3	nd	nd	nd	nd	nd	nd	nd	< 0.10	< 0.10	nd
Uracil													
Bromacil	314-40-9	$C_9H_{13}BrN_2O_2$	261.1	1.44	< 0.66	4.04	0.41	0.69	nd	nd	0.71	2.38	nd
Triazines													
Atrazine	1912-24-9	$C_8H_{14}ClN_5$	215.7	1.78	2.83	3.24	2.47	nd	nd	nd	nd	nd	nd
Chloroacetamides													
Metolachlor	51218-45-2	$C_{15}H_{22}ClNO_2$	283.8	< 0.25	0.33	0.28	< 0.25	nd	< 0.25	nd	< 0.25	< 0.25	nd
Butachlor	23184-66-9	$C_{17}H_{26}ClNO_2$	311.9	0.75	2.22	3.14	1.48	nd	nd	nd	nd	nd	nd
Organophosphorous													
Dichlorvos	62-73-7	$C_4H_7Cl_2O_4P$	220.97	nd	0.68	0.64	nd	nd	nd	nd	nd	nd	nd
Mevinphos	7786-34-7	$C_7H_{13}O_6P$	224.2	< 0.23	0.53	0.29	nd	< 0.23	< 0.23	nd	nd	< 0.23	< 0.23
Thionazine	297-97-2	$C_8H_{13}N_2O_3PS$	248.2	< 0.31	0.57	nd	nd	nd	nd	nd	nd	nd	nd
Sulfotep	3689-24-5	$C_8H_{20}O_5P_{22}$	322.3	< 0.26	nd	nd	nd	nd	nd	nd	nd	nd	nd
Phorate	298-02-2	$C_7H_{17}O_2PS_3$	260.4	< 0.16	nd	nd	nd	nd	nd	nd	nd	nd	nd
Diazinon	333-41-5	$C_{12}H_{21}N_2O_3PS$	304.4	0.20	0.14	0.24	0.22	0.27	0.18	0.16	0.14	< 0.08	< 0.08
Disulfoton	298-04-4	$C_8H_{19}O_2PS_3$	274.4	< 0.08	nd	nd	nd	nd	nd	nd	nd	nd	nd
Methyl_parathion	298-00-0	$C_8H_{10}NO_5PS$	263.2	nd	0.25	0.21	nd	nd	0.22	nd	nd	nd	nd
Fenchlorphos	299-84-3	$C_8H_8Cl_3O_3PS$	321.6	0.06	nd	nd	nd	nd	nd	nd	nd	nd	nd
Famphur	52-85-7	$C_{10}H_{16}NO_5PS_2$	325.3	< 0.28	0.30	nd	nd	nd	nd	nd	nd	nd	nd
Trichloronate	327-98-0	$C_{10}H_{12}Cl_3O_2PS$	333.6	< 0.13	nd	nd	nd	nd	nd	nd	nd	nd	nd
Merphos oxon	78-48-8	$C_{12}H_{27}OPS_3$	314.5	< 0.20	nd	nd	nd	nd	nd	nd	nd	nd	nd
Bolstar (Sulprofos)	35400-43-2	$C12_2H_{19}O_2PS_3$	322.5	< 0.25	nd	nd	nd	nd	nd	nd	nd	nd	nd
Chlorpyrifos	2921-88-2	$C_9H_{11}Cl_3NO_3PS$	350.6	0.52	0.88	1.43	0.47	0.91	0.31	0.28	0.63	0.39	0.44
Coumaphos	56-72-4	$C_{14}H_{16}ClO_5PS$	362.8	< 0.43	< 0.43	0.51	< 0.43	< 0.43	nd	nd	nd	nd	nd
Chlorinated pesticides													
Heptachlor	76-44-8	$C_{10}H_5Cl_7$	373.3	< 0.14	nd	nd	nd	nd	nd	nd	nd	nd	nd
Heptachlor epoxide	1024-57-3	$C_{10}H_5Cl_7O$											
iso B			389.3	< 0.17	nd	nd	nd	nd	nd	nd	nd	nd	nd
trans-Chlordane	5103-74-2	$C_{10}H_6Cl_8$	409.8	< 0.15	< 0.15	< 0.15	< 0.15	< 0.15	< 0.15	< 0.15	< 0.15	< 0.15	< 0.15
cis-Chlordane	5103-71-9	$C_{10}H_6Cl_8$	409.8	< 0.15	< 0.15	< 0.15	nd	< 0.15	< 0.15	< 0.15	< 0.15	< 0.15	< 0.15
4,4′-DDE	72-55-9	$C_{14}H_8Cl_4$	318.0	0.26	0.43	0.51	0.39	0.55	0.68	0.28	0.39	0.32	0.84
4,4′-DDD	72-54-8	$C_{14}H_{10}Cl_4$	320.0	0.14	0.22	0.26	0.15	0.22	0.27	0.11	0.12	0.10	0.18

Table 3 (continued)

Compound	CAS no.	Chemical formula	MW, g/mol	Sampling site									
Pesticides				S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
4,4′-DDT	50-29-3	$(ClC_6H_4)_2CHCl_3$	354.5	< 0.21	< 0.21	< 0.21	0.31	< 0.21	< 0.21	< 0.21	0.22	< 0.21	< 0.21
Endosulfan_sulfate	1031-07-8	C9 H6 Cl6O4S	422.9	< 0.29	< 0.29	< 0.29	nd	nd	nd	nd	nd	nd	nd
Methoxychlor	72-43-5	$C1_6H_{15}Cl_3O_2$	345.7	< 0.17	nd	nd	nd	nd	nd	nd	nd	nd	nd
PBDEs													
PBDE-47	5436-43-1	C12 H6 Br4O	485.8	0.13	0.09	0.11	0.14	0.09	0.25	< 0.02	0.05	< MQL	0.07
PBDE-99	60348-60-9	$C1_2H_5Br_5O$	564.7	0.11	nd	< MQL	< MQL	< MQL	< MQL	nd	0.03	nd	0.08
PBDE-100	189084-64-8	$C1_2H_5Br_5O$	564.7	nd	nd	0.03	nd	nd	0.09	nd	nd	0.06	0.02
PBDE-154	207122-15-4	$C1_2H_4Br_6O$	643.6	nd	0.25	nd	nd	nd	nd	nd	nd	nd	nd
PBDE-153	68631-49-2	$C1_2H_4Br_6O$	643.6	nd	nd	< MQL	nd	nd	nd	nd	nd	nd	nd
PCBs													
PCB-77	32598-13-3	$C1_2 H_6 Cl_4$	292.0	nd	nd	nd	0.03	nd	nd	nd	nd	0.05	nd
PCB-126	57465-28-8	$C1_2 H_5 Cl_5$	326.4	nd	nd	nd	nd	0.04	0.62	0.06	0.68	0.04	3.02
PCB-114	74472-37-0	$C1_2 H_5Cl_5$	326.4	nd	nd	nd	nd	< MQL	0.26	nd	0.12	nd	0.99
PCB-105	32598-14-4	$C1_2 H_5 Cl_5$	326.4	nd	nd	nd	< MQL	< MQL	nd	nd	nd	nd	nd
PCB-167	52663-72-6	$C1_2 H_4Cl_6$	360.9	nd	< MQL	nd	< MQL	< MQL	0.18	nd	nd	0.17	0.40
PCB-156	38380-08-4	$C1_2 H_4Cl_6$	360.9	nd	nd	MQL	nd	< MQL	0.30	< MQL	0.24	nd	0.90
PCB-157	69782-90-7	$C1_2H_4Cl_6$	360.9	nd	nd	nd	nd	< MQL	0.08	nd	0.04	nd	0.16
PCB-180	35065-29-3	$C1_2H_3Cl_7$	395.3	0.05	0.08	0.06	0.03	0.33	2.08	0.29	2.46	0.14	8.95
PCB-169	32774-16-6	$C1_2H_4Cl_6$	360.9	nd	nd	nd	0.01	nd	nd	nd	nd	nd	nd
PCB-170	35065-30-6	$C1_2H_3Cl_7$	395.3	0.04	nd	nd	nd	0.17	1.15	0.20	1.46	0.10	5.01
PCB-189	39635-31-9	$C1_2H_3Cl_7$	395.3	nd	nd	nd	nd	nd	0.12	0.01	0.07	0.05	0.16
Σ Thiocarbamates				28.93	nd	nd	nd	nd	nd	nd	nd	nd	nd
Σ Uracil, triazines and chloroacetanilides				3.97	5.05	10.43	4.36	0.69	0.00	0.00	0.71	2.38	0.00
Σ Organophosphorous pesticides				0.77	3.06	2.81	0.99	1.18	0.71	0.44	0.77	0.39	0.44
Σ Chlorinated pesticides				0.40	0.94	0.77	0.54	0.77	0.95	0.39	0.73	0.42	1.02

*< LOQ values were not included, *nd*: non detected, *MW*: molecular weight (g/mol)

Costa Rica (Santa Elena = 32.2 ng/L), and Galapagos Island (Santacruz = 12.1 ng/L).

One study, on the content of chlorpyrifos in mangrove oysters from Nicaragua and Colombia, shows that chlorpyrifos was only detected in Nicaraguan oysters within the range of 5–11 ng/g dry-weight; it was not detected in oysters from Colombian localities (Aguirre-Rubí et al. 2019). Total OCP concentrations ranged from 0.39 to 1.02 ng/g in the sediments with the highest concentrations found at S2, S6, and S10. Although 13 out of the 19 OCPs targeted were detected in the samples, most of them were below the MQL. DDT-related compounds were the main OCP contributors with 4,4′-DDE (0.26–0.84 ng/g) and 4,4′-DDD (0.10–0.27 ng/g) detected in all the samples. DDT was present in all the samples but largely fell below the MQL (< 0.21–0.31 ng/g). Higher concentrations of DDE and DDD can be attributed to the degradation of DDT, which can be degraded under anaerobic and aerobic conditions to DDD and DDE, respectively (Kang et al. 2016). A DDE/DDD ratio of less than one was observed in all the sites, suggesting aerobic degradation (Table S4). The residence time of DDT can be estimated using the ratio of DDT to DDE + DDD. If DDT/(DDE + DDD) < 1, the loadings of DDT are historical, whereas a ≥ 1 ratio indicates new loadings of DDT (Kang et al. 2016). In this study, DDTs/(DDE + DDD) were in the range of 0.21–0.57, indicating that DDT residues in the bay are historical and not due to a recent introduction. Total DDT levels found in the samples were below the TEL (3.89 ng/g) for marine sediments, indicating that adverse effects to aquatic organisms are potentially rare (MacDonald et al. 1996).

The presence of pesticides in the waters, sediments, and biota of Cartagena Bay has been reported (INVEMAR 2016; Jaramillo-Colorado et al. 2015; Jaramillo et al. 2010). Previous studies have accounted for the presence of PCBs and OCPs in the Cartagena Bay water with total concentrations of 75.5 ng/L and 23.9 ng/L, respectively (Menzies et al. 2013). Residual amounts in the muscle of *M. incilis* such as β-HCH (0.00638 ng/g), γ-HCH (0.00851 ng/g), heptachlor (0.0725 ng/g), endosulfan (0.00415 ng/g), and 4,4-DDE (0.00401 ng/g), among others, were identified, indicating that the fauna of Cartagena Bay is exposed to pollutants (Jaramillo-Colorado et al. 2015).

Although OCPs have been banned in Colombia since 1993 (ICA 2004), the country still has a stock of about 160.000 kg of OCPs (García Ubaque et al. 2015), which constitute a latent risk. In Nicaragua, DDTs and their derivatives were recorded in oyster tissues in all the samples analyzed; interestingly, the highest tissue concentrations of DDT derivatives such as 4,4-DDE were recorded in Punta Lora during the rainy season (DDT = 1082) (Aguirre-Rubi, et al., 2019).

Concentrations of PBDEs and PCBs

Table 4 shows the concentrations of dioxin-like PCB congeners (77, 105, 114, 126, 156, 157, 167, 169, 170, 180, 189) and PBDE congeners (47, 99, 100, 153, 154) in the Cartagena Bay sediment from the 10 locations sampled. Total levels of PBDEs ranged from 0.02 to 0.0.40 ng/g dw. PBDE-47 and PBDE-99 were the most abundant PBDEs present in each sample, with detection frequencies of 100% and 70%, respectively. Meanwhile, in another study conducted in Colombia by Barón et al., (2013), in the Atlantic coastal area of influence of the Magdalena River, BDE-209 was detected. In the same study, marine sediments from Chile (Bio-Bio region) were analyzed. PBDEs were detected in all sediment samples from Chile at concentrations ranging from 0.03 to 2.43 ng g^{-1} dw.

BDE-47 and BDE-99 were also the most abundant PBDE congeners in settled particulates from an estuary in Argentina, but average levels of total PBDEs were 10-fold greater at 1.8 ng/g dw (Cappelletti et al. 2015). The occurrence of PBDE can occur due to the debromination of brominated congeners by biotic or photolytic pathways (La Guardia et al. 2006).

Polybrominated diphenyl ethers (PBDEs) are added to foam, textiles, plastics, television casings, computers, furniture, and carpets, all of which contain PBDEs as flame retardants and can become a source of pollution (Anim et al. 2017; Tombesi et al. 2018). Direct leaching, poor disposal of disused appliances, automotive scrap shredding, and indirect waste streams are some of the pathways of PBDE contamination in estuarine systems (Anim et al. 2017).

The total PCB concentrations in the ten sampling sites at Cartagena Bay ranged from 0.09 to 20 ng/g dw. Levels of PCBs were highest in samples 6, 8, and 10. The PCB congener with the most significant detection in the Cartagena Bay samples was PCB-180, followed by PCB-126 and PCB-170, with median levels of 1.45, 0.45, and 0.81 ng/g dw, respectively. Total levels of PCBs were far below TEL in marine (21.6 ng/g dw) and freshwater sediment (34.1 ng/g dw) in most of the samples (MacDonald et al. 1996, 2000). The concentrations of dioxin-like PCBs found in this study were similar to the sediment sample from Argentina Bay, where total concentrations reached 6.8 ng/g dry-weight (Cappelletti et al. 2015). PCBs were widely used as dielectric fluids from transformer hydraulic tools, capacitors and heat-exchange liquid, lubricants, cutting oils, surface coatings, plasticizers, carbonless copy paper, ink, waxes, dyes, and adhesives (Souza et al. 2018). PCBs reach the marine environment via dry and wet deposition, sewage sludge used as fertilizer, and leaching from landfills, river discharge, and continental runoff (Ruiz-Fernández et al. 2019).

Aguirre-Rubí et al. (2019) made a study of PCBs and PBDEs content in oyster from the Caribbean Coasts of Nicaragua and Colombia. Low concentrations of PCBs and PBDEs were found in Nicaragua. Only PCB levels were occasionally exceeded in Colombia, while PBDEs were not detected.

Table 4 Organochlorine and related compounds in sediments, water, and biota from other Colombian coastal regions and Latinomerican bays or estuaries (concentrations, ng/L)

Bay, country	∑Chlorodane-related compounds	DDT-related compounds	PCB	PBDE	References
Sediments					
Cartagena Bay, Colombia	0.30	0.57–1.33	0.06–5.07	nd–0.35	This study
Caribbean region, Colombia	na	na	na	nd–143 ng/g	Barón et al. 2013
Coastal region of Baja California, Mexico	na	na	na	0.02–5.90	Macías-Zamora et al. 2016.
Chile (Bio Bio region)	na	na	na	0.03–2.43 ng/g	Barón et al. 2013
Santos Estuary, Brazil	na	na	190.7 ng/g	na	Souza et al. 2018
Babitonga bay, Brazil	0.06–1.20	0.10–122	0.09–19.1	na	Rizzi et al. 2017
Paranagua estuary, Brazil,2018	na	nd–3.22	nd–4.78	na	Souza et al. 2018
Guaratuba bay, Brazil	na	nd–0.74	nd–562	na	
Bahía Blanca, Argentina	na	na	004–17.6	0.04–10.7	Tombesi et al. 2018.
San Blas bay, Patagonia, Argentina	na	0.07–0.65	0.02–0.88	nd–0.65	Commendatore et al. 2018
Jobos Bay, Puerto Rico,	na	na	0.42–1232	na	Alegria et al. 2016
Guaratuba bay, Brazil	nd–1.52	nd–0.49	nd–6.06	na	Combi et al. 2013
Admiralty bay King George, Antarctic	na	na	0.85–2.47	na	Montone et al. 2001
Admiralty bay King George, Antarctic	na	na	nd–2.92	na	Combi et al. 2017
Ross Island, Antarctic	na	0.19–1.15	0.32–0.83	na	Klanova et al. 2008
Sea Lots, Trinidad and Tobago	na	6.1–29	62-601	na	Mohammed et al. 2011
Crabs (*N. granulata*): San Blas bay, Patagonia, Argentina	na	0.78–85.38	nd–29.55	2.96–11.72	Commendatore et al. 2018
Olrog's gull chicks: San Blas bay, Patagonia, Argentina	na	2.8–3.0	0.7	0.8–1.3	Commendatore et al. 2018
Crassostrea rhizophorae: Caribbean coast, Nicaragua	na	134–1082	238–341	nd–325	Aguirre-Rubí et al. 2019
Crassostrea rhizophorae: Caribbean coast, Colombia	na	nd	nd–29.3	nd	Aguirre-Rubí et al. 2019
Mugil incilis: Cartagena Bay, Colombia	na	0.0040–0.0045			Jaramillo-Colorado et al. 2015
Polymesoda arctata: Caribbean coast, Nicaragua	na	4–758	nd–230	30–227	Aguirre-Rubí et al. 2019
Paralonchurus brasiliensis: Santos Bay, Brazil	na	1.01–6.27	3.32–12.61	1.07–2.97	Magalhães et al. 2017
Seawater					
Cartagena, Colombia	4.1	10	75.5	na	Menzies et al. 2013
Ustupu, San Blas Islands, Panama	6.4	3.5	5151.2	na	Menzies et al. 2013
Gatun Locks, Panama Canal	1.93	96.6	1181	na	Menzies et al. 2013
Balboa, Panama	nd	nd	18450	na	Menzies et al. 2013
Panama Canal Yacht Club	31.6	47.7	111.6	na	Menzies et al. 2013
Gamboa, Chagres River, Panama Canal	28.8	26.2	1466	na	Menzies et al. 2013
Rosario Islands, Colombia	12.1	22.2	369.4	na	Menzies et al. 2013
Santa Martha Bay, Colombia	1.9	67.9	3169.4	na	Menzies et al. 2013
Ciénaga, Colombia	nd	62	39	na	Menzies et al. 2013
Santa Elena, Costa Rica no. 2	21	nd	85.2	na	Menzies et al. 2013
Academy Bay, Santa Cruz Island, Galapagos, Ecuador	5.2	6.5	23.1	na	Menzies et al. 2013
Utila + Roatan, Bay Islands, Honduras	nd	9.6	3120.1	na	Menzies et al. 2013

nd: not detected, *na*: not applicable

Spearman's correlation analysis demonstrated significant positive correlations ($p < 0.05$) between OCPS-PBDEs ($p = 0.044$) (Table S5). Commendatore et al. (2018) reported a strong positive correlation both between total PBDEs and OCPs detected in sediment, crab, and gull samples. Their bioaccumulation was observed in marine biota, suggesting risks to upper trophic level predators (Commendatore et al. 2018).

Table 4 shows organochlorine and related compounds in sediments, water, and biota from other Colombian coastal regions, and Latinomerican bays or estuaries.

Trace metals

pH and TOC and heavy metal content of collected sediments are shown in Table 5. The pH of the samples indicates the neutral nature of the sediments, varying within a narrow range along the bay (7.2 to 8.1). Total organic content in the sediments ranged mainly from 4.18 to 8.15%, except for S6, which contained 21.64% organic carbon. These results are consistent with TOC values reported in some coastal areas around the world. However, they are above the median value (1.5%) (Seiter et al. 2004), suggesting both terrestrial and anthropogenic sources. The high sedimentation rate found in the bay is influenced by the discharge from *Canal del Dique* (Restrepo et al. 2017), which could be the primary source for organic carbon accumulation, particularly during the moderate rainy season when the samples were collected. Additionally, Cartagena Bay has mangrove ecosystems, which could provide organic-rich sediments as well (Kennedy et al. 2004).

The metal concentrations in the sampled sediments are shown in Table 6. All metals evaluated in the marine sediments were found in S6, thus exceeding the accepted values of threshold effect levels (TEL) used as indicator of their potential on marine life (Restrepo et al. 2017).

Strontium was found in all sediments from the sampling sites (32.9–959.6 mg/kg). Aghadadashi et al. (2019) report that high concentrations of Sr could be related to shell fragments, which are mostly carbonated structures. Studies show that the presence of strontium in marine sediments represents a natural geochemical footprint (Delgado et al. 2010; Sondi et al. 2017).

This trend was followed by S1 and S2. Concentrations of As, Pb, and Cr were highest in the central part of the bay (station S6), which may be associated with activities of the chemical and metallurgical industries around the Mamonal area. Besides, for Cd, the highest concentrations in the sediments were found at stations S1 and S4, near the outlet of *Canal del Dique* (2.0 and 2.4 mg/kg, respectively); Cu, Cr, As, and Sr also were found. Some of these are accumulated through the Magdalena River basin upstream of *Canal del Dique*, which indicates that Cartagena's anthropogenic activities are not the only sources of contamination at Cartagena Bay (Tosic et al. 2019). Therefore, the presence of metals in marine sediments may be due to mining and intensive agricultural activities, being the river's discharge the main input areas of pollutants to the coastal areas (Vallejo Toro et al. 2016).

When we compared our results with other studies, it can be seen the Pb, Cu, and Cr values were higher than the ones registered in other studies on the Colombian Caribbean coast (Table 6); Cd was lower than those reported by Tosic et al. (2019) and Restrepo et al. (2017), but higher than those reported by Burgos-Núñez et al. 2017, in the Cispata Bay, and Caballero-Gallardo et al. (2015) in Santa Martha Bay in Colombia. In the same Table, the results of metals in sediments from other bays of Latin America can be observed.

Physicochemical parameters in sediments are known to affect the bioavailability of metals in the environment (Benson et al. 2016). This is the degree of freedom in which

Table 5 pH, total organic carbon (TOC), and heavy metal content of collected sediments with sediment quality guidelines (SQGs) values for marine sediments. Concentrations that exceed SQGs are marked italic

Sediment location	pH	TOC[a] %	Pb (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	As (mg/kg)	Sr (mg/kg)	Cd (mg/kg)
S1	7.6	5.28 ± 3.05	19.3	*55.1*	*49.3*	*10.2*	50.0	*2.0*
S2	7.4	5.01 ± 3.21	22.9	*79.3*	*62.0*	*9.9*	128.9	*1.4*
S3	7.7	5.93 ± 3.46	19.8	43.5	*34.4*	*11.7*	63.2	*1.1*
S4	7.2	5.69 ± 3.13	21.1	*53.1*	*48.0*	*11.1*	32.9	*2.3*
S5	7.5	6.04 ± 2.78	20.4	50.4	*36.2*	*9.2*	90.4	*0.8*
S6	8.1	21.64 ± 2.06	*37.1*	*137.2*	*64.4*	*13.1*	318.9	*1.7*
S7	7.8	8.15 ± 2.23	12.1	*67.7*	*36.3*	*10.0*	282.3	0.5
S8	8	4.71 ± 4.47	7.7	22.6	*20.5*	4.1	109.4	0.2
S9	7.8	4.18 ± 2.41	8.0	38.4	*429.0*	*10.6*	278.5	0.3
S10	7.9	5.41 ± 5.56	21.1	*53.2*	*51.5*	6.5	959.6	0.7
Mean			19.0	*60.1*	*83.2*	*9.6*	231.4	*1.1*
bSQGs:								
TEL			30.2	52.3	18.7	7.2	48	0.7
PEL			112	160	108	41.6	na	4.2

na: not available, *TEL*: threshold effect level, *PEL*: probable effect level

[a] Values correspond to mean ± %RSD (n = 3, technical replicates)

[b] NOAA, 2008

Table 6 Metal concentrations in surface sediments from Cartagena Bay compared with the average metal concentration in sediments from other Colombian coastal regions and Latin American bays

Sampling	Pb	Cr	Cu	As	Sr	Cd	Ni	References
Cartagena Bay-Colombia, mg/kg	7.7–37.1	22.6–137.2	20.5–429	4.1–13.1	32.9–959.6	0.2–2.3	na	This Study
Cartagena Bay-Colombia, μg/kg	0.3–14.6	3.1–59.8	1.9–38.6	na	na	19.5–1282	10–32.7	Tosic et al. 2019
Cartagena Bay-Colombia, mg/kg	2.3–189	8.7–132.6	13.5–110	na	na	na	6.9–77.2	Restrepo et al. 2017
Cartagena Bay-Colombia, μg/L	22–96	179–360	20–30	na	na	9–14	≤ 25	INVEMAR 2016
Uraba Gulf,-Colombia, μg/g	0.17–6.9	109.6–212.4	25.08–102.9	na	na	na	28.5–72.9	Vallejo Toro et al. 2016
Cispata Bay, Cordoba province, Colombia, μg/g	0.49–1.39	na	1.63–15.36	na	na	0.009–0.14	na	Burgos-Núñez et al. 2017
Santa Martha Bay, Colombia, μg/g	5.7–12.2	30.5–141.2	3.53–29.9	2.66–11.2	216.4–464.0	0.08–0.16	7.09–46.1	Caballero-Gallardo et al. 2015
Punta Mala Bay-Panama, mg/kg	78.2	23.3	56.3	56	na	na	273	Defew et al. 2005
Morrocoy National Park-Venezuela μg/L	78.8	5.06	39.1	0.97	na	6.59	76.6	García et al. 2011
Guanabara Bay, Brazil, μg/g	14.6–107	24.6–157	na	na	na	0.47–1.80	1.1–15.9	Abreu et al. 2016
Sepetiba bay, Brazil, mg/kg	9.7–63.5	na	8.56–33.52	na	na	0.48–23.5	2.46–6.36	Rodrigues et al. 2017
Todos os Santos Bay, Brazil, mg/kg	≤ 1.76	25.4	7.75	≤ 0.05	na	na	5.09	Pereira et al. 2015b
Estero Salado-Ecuador, μg/kg	20.9–56.4	0.3–1.5	47.08–206.5	na	na	0.34–1.54	27.3–60.9	Fernandez-Cadena et al. 2014
Mar Chiquita Coastal Lagoons-Argentina, μg/L	nd–850	nd–35.2	nd–1000	na	na	nd–7.1	nd–79.84	Beltrame et al. 2009
Montevideo Bay-Uruguay, mg/kg	19.1–87.8	32.7–87.83	22.4–106.9	1.48–6.17	nd	0.19–1.11	2.65–16.7	Muniz et al. 2019
Bahia Quintero Chile, mg/kg	15–35	31–67	129–1055	9–20	388–943	na	8–21	Parra et al. 2015
Antartic Peninsule-Chile μg/g	4.9–5.8	4.2–6.5	54–82	na	na	0.56–0.69	na	Vodopivez et al. 2015
South Golf of Mexico (Yucatan), μg/g	0.1–6.8	5.4–27.9	16.3–26.4	0.5–13.1	na	na	6.7–28.7	Ruiz-Fernández et al. 2019
Golf of Mexico (Taumalipas State). mg/kg	10.7	8–63	10–25	na	222–1245	na	10–22.9	Celis-Hernandez et al. 2018
Magdalena River*, Colombia, μg/g	12.1	na	27.2	na	na	1.31	na	Tejeda-Benitez et al. 2016
Magdalena River*, Colombia, μg/g	na	15–84.7	na	2.1–9.74	19.5–75	na	na	Tejeda-Benítez et al. 2018
Magdalena River*-Dique Channel, Colombia	na	22–36.75	na	na	na	1.7–37	17.7–32.1	Espitia 2014

nd: not detected, *na*: not available

*Freshwater sediments from nonpoint source of pollution to the Cartagena Bay

an element or compound is found from a potential source to be captured by an organism (ingested or adsorbed). The accumulation of heavy metals depends on the geochemical properties of sediments and significant variations of their concentration are related to habitats. Kadhum et al. (2017) and Dehghani et al. (2018), among others, found the bioaccessibility of heavy metals influenced by pH, particle size fraction, and cation exchange capacity (CEC).

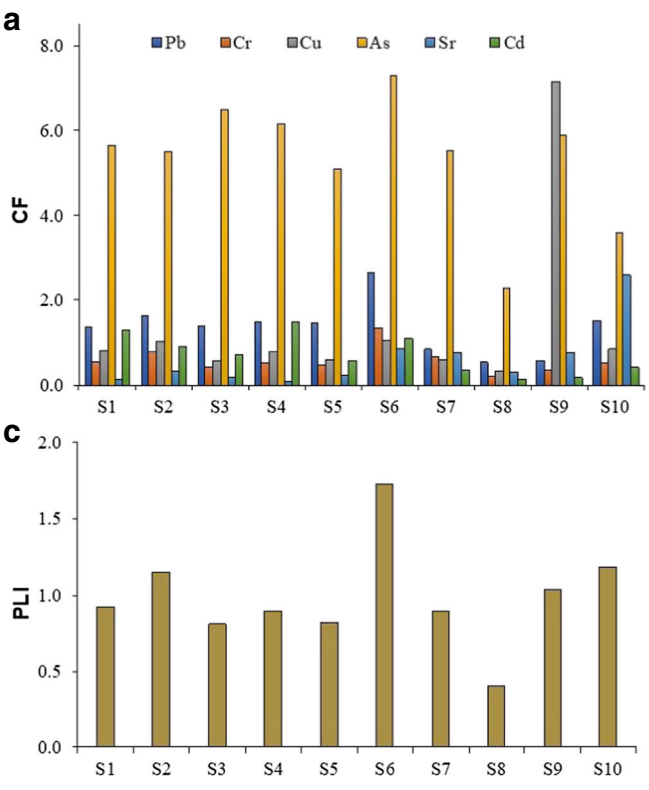
Spearman's correlation analysis demonstrated significant positive correlations ($p < 0.05$) between the metals Pb-Cr ($p = 0.026$), Pb-Cd ($p = 0.032$), TOC-Pb ($p = 0.031$), and TOC-Cr (Table S6). The results could suggest that Pb, Cr, and Cd have possible common sources and that TOC played an important role in the adsorption of Cd and Pb into the sediments collected. High organic content is related to a significant sedimentary metal affinity for humic substances, which could decrease trace metal bioavailability through complexation (Benson et al. 2016), thus explaining the positive correlation found between TOC with Cd and Pb concentrations. However, other parameters such as grain size, ligand type, presence of chelating agents, the oxidation state of mineral components, and the system's redox potential were not determined in this study, which may also influence the solubility of metals and their detected levels at the Bay (Gundersen and Steinnes 2003).

Evaluation of metal pollution in sediments and comparison to sediment quality guidelines

The results of sediment contamination indices calculated for the collected sediments and their sediment qualification description are presented in Fig. 2. The contamination factor (CF) was used to evaluate pollution by single metals in the sediments. CF values found for As indicated considerable to very high contamination (CF > 5) in eight of the ten locations. CF values for Pb and Cu indicated moderate contamination in seven and nine out of the ten sampled locations, respectively, except for Cu at location S9, where a high degree of pollution was found. This point is near beaches and neighborhoods from Cartagena city.

Contamination factors for Cr and Cd indicated moderated pollution at a few locations, while CF values for Sr indicated low contamination in nine of the ten samples. The geoaccumulation index (I_{geo}) was used to determine contamination by comparing current concentrations with pre-industrial levels. For most of the metals, all sampled locations indicated unpolluted conditions ($I_{geo} < 0$), except for As which exhibited values between 1 and 3 for nine of the locations, indicating moderate to heavy pollution in sediments.

The pollution load index (PLI) was used for assessing the integral level of metal pollution at each sampling site (Tomlinson et al. 1980). PLI values ranged from 0.5 to 2.0 in



Index description [a,b]			
CF<1	Low contamination	PLI<1	Metal pollution
1<CF<3	Moderate contamination	PLI>1	No metal pollution
3<CF<6	Considerable contamination		
CF>6	Very high contamination		
Igeo ≤ 0	Unpolluted		
0 < Igeo ≤ 1	Unpolluted to moderately polluted		
1 < Igeo ≤ 2	Moderately polluted		
2 < Igeo ≤ 3	Moderately to heavily polluted		
3 < Igeo ≤ 4	Heavily polluted		
4 < Igeo ≤ 5	Heavily to extremely polluted		
Igeo > 5	Extremely polluted		

[a](Kalender and Çiçek Uçar, 2013)
[b] (Pereira et al., 2015).

Fig. 2 Contamination factor (CF), geochemical index (I_{geo}), and pollution total index (PLI) for metals in sampled sediments and indices description of sediment quality.

the samples, with six out of the ten locations exhibiting overall metal pollution. In general, sample S6 showed the highest level of pollution for most of the tested metals and pollution indices calculated. Copper was found to be the main contributor to sediment pollution in S9. Further, Cu and As presented moderate and high degrees of pollution across the bay sediments, respectively, with an elevated anthropogenic input.

Eco-toxicological indices (SQGs) were used to assess the contamination levels of the sediments. The metal concentration values obtained were compared with the TEL and PEL of SQGs for marine sediments (Buchman 2008) (see Table 6).

In this study, most metal concentrations were within the TEL–PEL range, indicating that this can be linked to occasional adverse biological effects (Pena-Icart et al. 2017). Pb concentrations were mostly below TEL, showing that adverse effects to aquatic organisms were not expected, except at location S6 (Hubner et al. 2009). Chromium was found at concentrations above TEL at S1, S2, S4, S6, S7, S10, which is associated with occasional adverse effects. The presence of Cr at the Bay can be influenced by the tannery industry. Copper levels were found above PEL at S9 (429 mg/kg), which is associated with adverse biological effects (Pena-Icart et al. 2017).

Multivariate analysis

Principal component

The levels of POPs and metals in estuary sediments are considered a local source to the marine environment, which may affect the fish and mammals directly exposed. Therefore, there is a need to investigate contaminant relationships to identify common trends between sampling sites and potential sources of investigated compounds. Principal component analysis yielded eight significant PCs characterizing a total of 98.5% of the total variance between contaminants. The first four PCs account for approximately 80% of the total variance indicating four primary sources among the sample locations with minor contributions from other sources. Sample locations were separated organically into three groups based on sample scores from PCs 1, 2, and 4 (Fig. 3). While significant, PC3 was dominated by four of the analyzed contaminants limiting its use to visualize the reduced dataset.

Each group of related sites roughly corresponds to a different geographical area of the bay. Site S1, located at the distal end of the canal, exhibited positive loading by PC1 alone, which consists of all the analyzed pesticides except DDT, DDE, DDD, and cis-chlordane, and suggests that the contamination at S1 mainly originates from the application and runoff of pesticides upstream. Sites S2 and S3, located in the middle part of the inner bay, exhibit positive loadings in PCs 1, 2, and 4, and a negative contribution from PC3, suggesting mixed inputs from the industrial application of pesticides. PC2, which consists mainly of chloroacetanilide herbicides, Pb, Cr, As, and PBDEs, accounts for approximately 44–46%, while the remaining pesticides contribute ~ 30% to each site, and the PCBs, Cu, and Sr, pitches in with ~ 10% with all other sources making up the remainder. Sites S4, S5, and S6 demonstrated minimal contribution from the pesticides in PC1 with marked contributions from Cu, PCBs 77, 105, and 169 and DDT in PC3 (53%, 57%, and 61% for S4, S5, and S6,

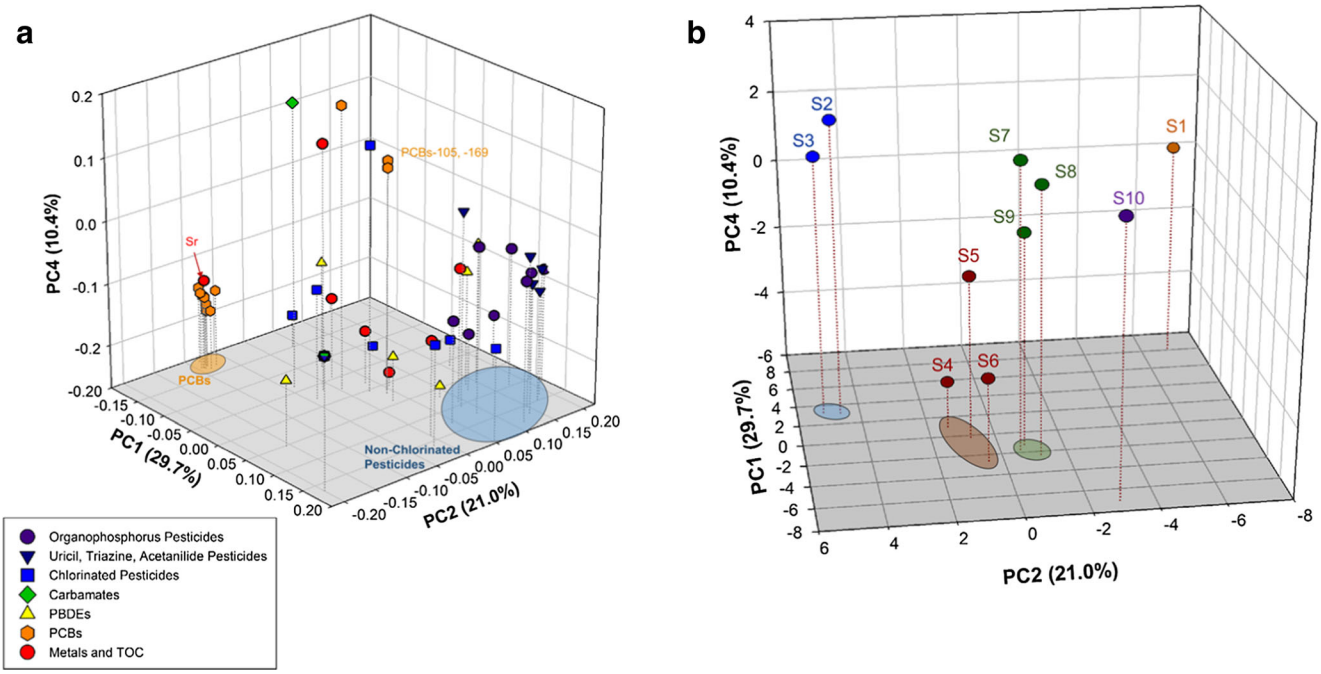


Fig. 3 **a** PCA loading plot for the contaminants detected. **b** PCA score plot for the location sites

respectively). Sites S7, S8, and S9 each exhibit positive inputs from PC3 (64–72%) and PC4 (28–36%), indicating a source contribution from the release of PCBs, Cu, Sr, and BDEs 153 and 154. Site S10 is loaded positively only with PC 4, indicating significant supplies from a single source emitting a mixture of PCBs, PBDEs, pesticides, and Cu.

Cluster analysis

In the current study, the nearest neighbor hierarchical (HCA) method was applied for the bulk sediments. The examined data matrix involves the concentrations of heavy metals and organic pollutants in the bulk sediments against the site (Marrugo-Negrete et al. 2017; Birch et al. 2001).

Cluster analysis (CA) suggests a total number of 4 groups, incorporating, from smaller to larger, group 4 (includes one site: S6) site was located in a region, which receives chromiun wastewater discharges from a tannery factory, group 2 (include one site:S10) site was in a moderate pollution region, group 3 (include three sites: S1, S2, S3, S4) were in front of *Canal del Dique* discharges (Fig. 4).

Environmental implications

Metals such as Cd, Cu, Cr, Pb, and As could become a threat to the marine ecosystem due to their persistence, inherent ecotoxicological characteristics, and tendency for biomagnification. Elevated concentrations of such elements in sediments or water are a potential threat for human health through the food chain (Pinzón-Bedoya et al. 2020; Marrugo-Negrete et al. 2017; Pereira et al. 2015b; Fernandez-Cadena et al. 2014). Colombia does not have regulations about metals in marine sediments. Nevertheless, resolution No. 122 of 2012 establishes the physicochemical, microbiological, and chemical contaminant requirements that must be met by fishery products, particularly fish, mollusks, and crustaceans for human consumption (Ministry of Health and Social Protection. 2012). Sediment quality guidelines (SQGs) are used as a screening tool to evaluate the biological significance of sediment-bound contaminants in the absence of direct biological effects data (Simpson and Batley 2016; Casado-Martínez et al. 2006,). The results obtained in this study were also compared with SQGs from other countries as can been in Table 7. This shows, for example, that Cd concentrations were greater than Spain and Hong Kong SQGs, and for Cu were higher than the USA, Australia, Canada, and Hong Kong SQGs.

As, Pb, Cd, and Hg have all been included on the top 20 list of hazardous substances by the United States Environmental Protection Agency (EPA) and the Agency for Toxic Substances and Disease Registry (ATSDR) (Kumar Rai et al. 2019). The ingestion of metals through food causes serious damage to human health, i.e., lead contamination reduces mental development and produces neurological and cardiovascular diseases (El-Kady and Abdel-Wahhab 2018). Several studies have reported that Cd, Pb, As, and Cr (VI) have carcinogenic effects and can affect the bones and nervous system, among others (Kumar Rai et al. 2019).

When comparing the concentrations of the OC pesticides obtained in this study with the different sediment quality guidelines of different countries presented in Table 7, it can be seen that at no point are the pesticide thresholds exceeded in the sediments from Cartagena Bay. OCPs, PCBs, and PBDE are ubiquitous contaminants, all of which have a high accumulation potential in marine environments, i.e., PCB concentrations in *R. mangle* tissue from Jobo Bay in Puerto Rico

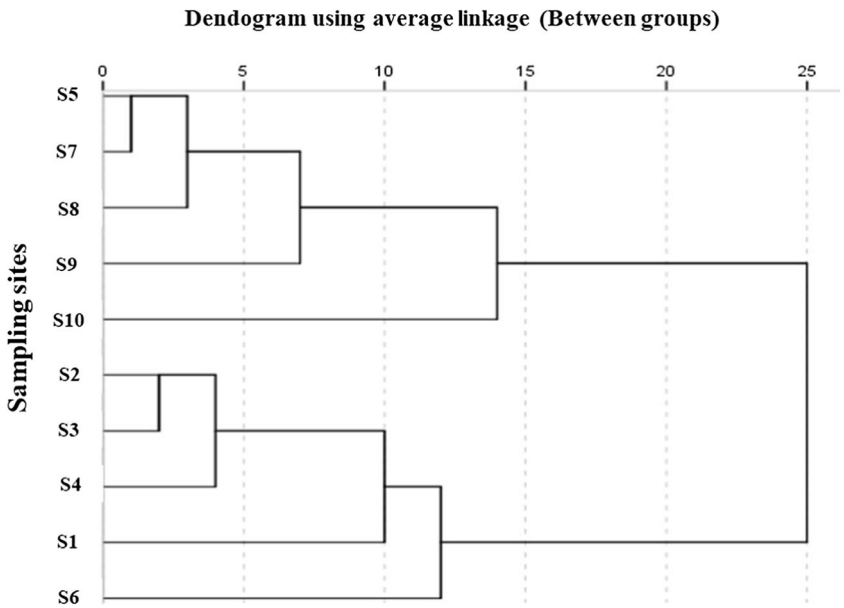


Fig. 4 Dendrogram obtained by hierarchical clustering analysis for the sampling sites on the Cartagena Bay

Table 7 Comparative table of sediment quality guidelines of different countries for marine sediments included in this study

Compound	Cartagena Bay (this study)	Spain, Riba et al. 2004		USA, Long et al. 1995, 2000		Australia-New Zealand, Simpson and Batley 2016		Canada, Canadian Council of Ministers of the Environment. 1999		Hong Kong (China), Marine Water Quality of Hong Kong 2018.		NOAA Screening Quick Reference, Buchman 2008	
		HCC	LCC	ERL	ERM	ISQG low	ISQG high	ISQG low	ISQG high	Lower chemical exceedance level (LCEL)	Upper chemical exceedance level (UCEL	TEL	PEL
Inorganic, mg/kg dry wt													
Pb	7.7–37.1	260	270	46.7	218	50	220	30.2	112	75	110	30.2	112
Cr	22.6–137.2	na	na	81	370	80	370	52.3	116	80	160	52.3	160
Cu	20.5–429	209	979	34	270	65	270	18.7	108	65	110	18.7	108
As	4.1–13.1	27.4	213	8.2	70	20	70	7.24	41.6	12	42	7.2	41.6
Cd	0.2–2.3	0.51	0.96	1.2	96	1.5	10	0.7	42	1.5	1.4	0.7	4.2
Organic, µg/kg dry wt													
-PCB	0.06–19.59	54	254	22.7	180	34	280	21.5	180	23	180	21.6	189
p,p′-DDE	0.26–0.84	na	na	2.2	27	1.4	7.0	2.07	37.4	–	–	2.1	374
Total DDT	0.21.0.31	na	na	1.58	46.1	2.0	5.0	1.19	4.77	–	–	3.89	51.7

HCC: highest concentration of a contaminant non-associated with adverse biological effects, *LCC*: lowest concentration associated with adverse biological effect, *ISQG*: the **interim** marine **sediment quality guidelines**, *TEL*: Threshold effect level, *PEL*: probable effect level

(roots, leaves, and seeds) indicate bioaccumulation in these sensitive coastal plants (Alegria et al. 2016).

Organochlorine compounds can be adsorbed in marine sediment, and bio-accumulated in fatty tissues of living organisms (Jaramillo-Colorado et al. 2015). They can produce harmful effects on aquatic organisms, such as impaired reproduction, immune suppression, and endocrine disruption and/or high occurrence of chronic lesions such as tumors in the liver and spleen (Magalhães et al. 2017; Tham et al. 2019). PCBs and PBDEs are considered potent hormonal disruptors that cause neurodevelopmental deficit, adverse reproductive effects, and possibly cancer (de Miranda et al. 2016; Taiwo 2019).

Concerning pesticides, PCBs, and PBDE, in Colombia, there is no regulation on these compounds in marine sediments, but it does exist on water and seafood. The Ministry of Health and Social Protection is the entity that ensures these regulations for fish and fishery products that are consumed in Colombia and which are intended for export, whereby the threshold is established by Colombian Resolution No 122 of 2012 (4.0 pg WHO-TEQ PCDD/F g^{-1} for PCDD/Fs and 8.0 pg WHO-TEQ g^{-1} for PCDD/Fs and dl-PCBs) (Ministry of Health and Social Protection 2012; Pemberthy et al. 2016). On the other hand, European regulation set the maximum established levels at 3.500 pg g^{-1} of dry weight WHO-TEQ PCDD/Fs and 6.500 pg g^{-1} of dry weight WHOTEQ PCDD/Fs and dl-PCBs as maximum levels for fish (shrimp) (EU 1259 2011). According to the Food and Drug Administration (FDA), the tolerance level for PCB in edible tissue of seafood is two ppm, and the action level for pesticides DDT, TDE, and DDE is five ppm (FDA 2018). In Colombia, regulations regarding the use of OCPs began in 1974, and they were completely banned in 2001 (Ministry of the Environment of Colombia 2010).

Food items must comply with the maximum residue limits of pesticides—LMR—of *Codex Alimentarius*, by resolution No. 2906 of 2007 (Ministry of Agriculture and Rural Development-Ministry of Social Protection 2007).

On the other hand, chlorpyrifos is a broad-spectrum, chlorinated, organophosphate pesticide used to control insect, tick, and mite populations. It is widely employed in Colombia in the control of insects in crops (Varela-Martíneza et al. 2019), and is being reviewed for its harmful effects (Centner 2018). This pesticide is moderately hazardous to humans (WHO 2010; Ventura et al. 2015). However, in 2014 and 2016, scientific evidence considered by the EPA showed that existing tolerances do not protect persons from dangerous levels of chlorpyrifos (EPA 2014, 2016; Centner 2018).

Our results of -PCB, p,p′-DDE, and total DDT were compared with other sediment quality guidelines from other countries (Table 7). Concentrations were below the lowest concentration associated with adverse biological effects.

Conclusions

In this study, Cartagena Bay sediments exhibited the occurrence of OCPs, PCBs, and PBDEs; their concentrations were lower than those reported in NOAA Screening Quick Reference Tables. DDTs and PCBs are banned organochlorine compounds since, even at low levels, their presence in sediments represents a hazard to aquatic organisms and subsequently to human health through the trophic chain. The prominence of dichlorodiphenyldichloroethylene (DDT) among pesticides in sediments is the result of its past use in the region and in the Magdalena River basin. Chlorpyrifos was the pesticide found in the highest level in the marine sediments from Cartagena Bay, which has not been banned yet, despite the fact that currently there are several studies on its harmfulness.

Surface sediments from Cartagena Bay have shown the presence of metals. All metals evaluated in the marine sediments were found in the S6 sampling point; this was near the tannery and hydrocarbon industries (Pb 37.1 mg/kg, Cr 137.2 mg/kg, Cd 1.7 mg/kg, Cu 64.4 mg/kg, As 13.1 mg/kg, Sr 318.9 mg/kg); these results exceeded the accepted values of threshold effect levels (TEL) used as an indicator of their potential risk on marine life which represents a potential ecotoxicological risk according to sediment quality guidelines. Metals in the bay are mainly attributed to anthropogenic activities, such as port and shipping operations, as well as the industrial sector that currently includes over seventy industries with domestic and agricultural activities on the margins of the Magdalena river that discharge into the bay. Cu and Pb are a well-known marker element of agricultural activities, mainly fertilizer application.

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Software: Edisson Duarte-Restrepo and Joshua S. Wallace

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Writing—review and editing: Edisson Duarte-Restrepo, Beatriz E. Jaramillo-Colorado

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Data availability The majority of the data generated or analyzed during this study are included in this published article (and its supplementary information files), but if some are missing, data are available from the corresponding author on reasonable request.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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Consent for publication Not applicable.

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