Spatial and temporal variation in the water quality of an urban drainage system in Ciudad del Carmen, México

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Abstract

Anthropogenic activities generate pollutants that are often discharged, untreated, into bodies of water. The drainage system, known as the Caleta in Ciudad del Carmen, Mexico, is surrounded by an urban area and receives immense amounts of industrial and sewage discharge. Physicochemical analyses were conducted for the water and sediment samples taken along this drainage system to understand its hydrological dynamic and pollutant load. The drainage channel communicates with Terminos Lagoon, a Natural Protected Area, and the Gulf of Mexico. Water and sediment samples were taken at fifteen stations along the drainage channel during the three local seasons: northwinds (January); dry (May); and rainy (October). Physicochemical parameters (pH, temperature, salinity, dissolved oxygen, and total dissolved solids), as well as biological oxygen demand (BOD_5), chemical oxygen demand (COD) and total suspended solids (TSS) were measured in the water samples. Heavy metals concentrations (Fe, Cr, Cu, Zn, Cd and Pb) were quantified in the sediment samples. No differences were observed in the physicochemical parameters between sample stations, although differences ($P < 0.05$) were observed between seasons. Dissolved oxygen levels at all stations and in all seasons were near or below hypoxia levels (< 2.0 mg/l). Biological oxygen demand and COD were highest during the rainy season, particularly near industrial effluent discharges. Heavy metals concentrations varied spatially, with higher levels nearest the drainage outlet and lower levels further inland. Lead and iron levels were extremely high, and all heavy metals concentrations far exceeded legal limits. The Caleta is clearly heavily impacted by discharge from the surrounding urban area containing pollutants generated by anthropogenic

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activities. Any possible recovery of this drainage ecosystem will be contingent on treating and controlling any discharges into it.
Keywords: Terminos Lagoon, water quality, heavy metals, drainage, Ciudad del Carmen.

1 Introduction

Hydrology within Terminos Lagoon, Mexico, is influenced by the interaction between marine water entering from the Gulf of Mexico through inlets and freshwater influx from the Grijalva and Usumacinta river systems. Water circulation in the lagoon is most strongly affected by the east to west winds prevailing in the region (Graham *et al*. [1]). Ciudad del Carmen, Campeche, is located at the western tip of an island forming a barrier between the Gulf of Mexico and the lagoon. The city is a logistics center for petroleum extraction activities on offshore oil platforms in the southern Gulf. A drainage known as the Caleta runs east to west through the city, connecting to the lagoon at the west end. It is an ecologically important drainage, particularly because it interacts with the waters of the lagoon, which is classified as a natural protected area (NPA). Over time, pollution in the drainage has increased in response to anthropogenic activities. The primary pollutant sources are petroleum industry activities, which generate heavy metals and hydrocarbons, and agriculture, which contributes chemical run-off from fertilizers and pesticides. Residues from commercial and fishing activities also wash into the drainage. After years of rapid population growth in Ciudad del Carmen, it is now completely surrounded by urban area, and receives largely untreated sewage from the city's sewage system. Flora and fauna in the Caleta ecosystem have suffered extremely negative impacts from this pollution, and are considered pollutant bioindicators because they concentrate persistent, bioaccumulative toxic substances (Instituto Sindical de Trabajo, Ambiente y Salud [2]).

Its environmental matrix strongly influences the Caleta's hydrology. This determines material import and export rates within the system, and controls internal processes such as nutrient assimilation, organic matter storage, benthonic regeneration and nutrient release. Geological, physical, chemical, climatic and biological factors add their effects to anthropogenic activities, determining how the Caleta, and the greater Terminos Lagoon, functions.

The present study objective was to use water and sediment physicochemical parameters to characterize the Caleta drainage's hydrology and pollutant load during the three regional seasons.

2 Methods

2.1 Study area

The Caleta in Ciudad del Carmen is a surface drainage that connects to Terminos Lagoon at its western outlet (Figure 1). Located at the southern extreme of the Gulf of Mexico, in southeast Mexico (91°15′, 92°00′W; 18°25′ and 19°00′N), the Terminos Lagoon measures approximately 70 km long and 28 km wide (2500 km^2). This coastal lagoon system contains approximately fourteen minor coastal lagoons, and is encompassed by the “Gulf coastal plain” and “Yucatan Peninsula” physiographic provinces (Gutiérrez-Estrada and Castro del Río [3]). It is separated from the Gulf by Carmen Island (approx. 37.5 x 3 km), a barrier island (Tamayo [4]).

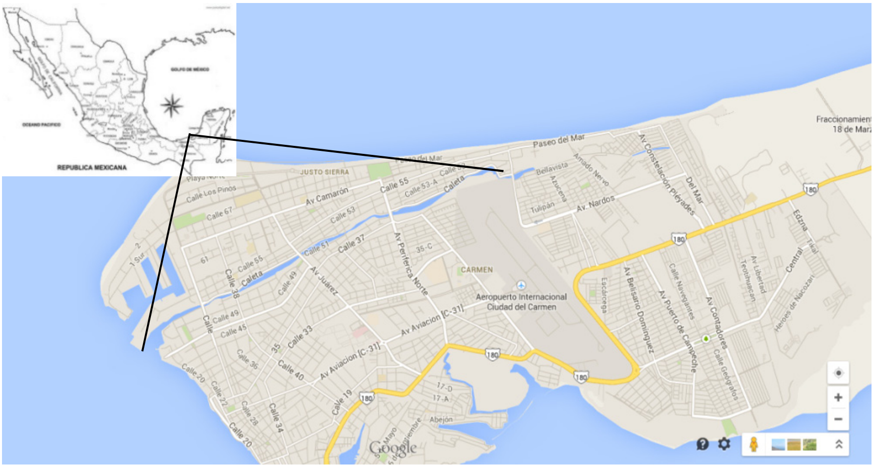

Figure 1: Study area: western end of Carmen Island, showing Ciudad del Carmen and the Caleta.

2.2 Sample station locations

Fifteen sample sites were placed along the 7.5 km length of the drainage.

Table 1: Sampling station locations.

Stations	Positions	
	Latitude	Longitude
1	(18°39’45.4”)	(91°48’13.7”)
2	(18°39’47.8”)	(91°48’23.5”)
3	(18°39’41.8”)	(91°48’35.4”)
4	(18°39’34.5”)	(91°48’50.5”)
5	(18°39’30.6”)	(91°49’05.5”)
6	(18°39’24.1”)	(91°49’21.3”)
7	(18°39’18.9”)	(91°49’35.7”)
8	(18°39’10.3”)	(91°49’48.0”)
9	(18°39’07.4”)	(91°49’57.4”)
10	(18°39’01.2”)	(91°50’07.7”)
11	(18°38’56.4”)	(91°50’20.4”)
12	(18°38’50.1”)	(91°50’35.9”)
13	(18°38’49.3”)	(91°50’45.3”)
14	(18°38’43.2”)	(91°50’37.6”)
15	(18°38’38.1”)	(91°50’42.3”)

2.3 Sample analysis

Soil and water samples were collected during each of the three regional seasons: northwinds (January 2014); dry (May 2014); and rainy (October 2014). A multiparameter probe (Hanna HI 9828 PH/ORP/EC/DO) was used to run triplicate, in situ analyses of pH, temperature (°C), salinity ($^0/_{00}$), dissolved oxygen (O_2) and total dissolved solids (TDS). Water samples were returned to the laboratory to calculate biological oxygen demand (BOD_5) using an electrometric test (NMX-AA-028-SCFI-2001), chemical oxygen demand (COD) with the closed flow test (NMX-AA-034-SCFI-2001) and total suspended solids (TSS) with the gravimetric test (NMX-AA-034-SCFI-2001).

Surface sediment samples were taken at each station using a 6 x 6 x 6" Ekman dredge. Presence of six heavy metals (Fe, Cu, Mn, Zn, Cd, and Pb) was determined following EPA method 3050-B (US EPA [5], for acid digestion of sediments, muds and soils. Final metals concentrations were quantified using a double beam atomic absorption device (GBC-Avanta 3000, Flama) with an air-acetylene flame and deuterium background corrector. A calibration curve was prepared for each metal using recognized standard, analytical quality patterns within the analytical range (Table 2).

Table 2: Wavelength and application intervals.

Element		Wavelength (nm)	Working range μgL^{-1}	Detection limit
Iron	(Fe)	248.3	2.0-145	0.1
Chrome	(Cr)	357.9	0.1-50	0.02
Zinc	(Zn)	213.9	0.1-10	0.2
Cadmium	(Cd)	228.8	0.1-20	0.02
Lead	(Pb)	283.3	5.0-200	0.1
Copper	(Cu)	324.8	0.1-180	0.07

2.4 Statistical analyses

Data were interpreted using the Past ver. 3.5 statistical package. A completely random analysis of variance (ANOVA) was run to identify significant differences between sampling stations. Unequal variances were analyzed with the Kruskall-Wallis (KW) non-parametric method in which the dependent variable was season and the significance level was $P \leq 0.05$. Differences between the means were identified with a Duncan multiple range test (Duncan [6]), and standard error (SE) calculated by mean squared error.

3 Results and discussion

Average physicochemical variable data for the three seasons showed no differences in pH between stations (KW = 21.17), with values ranging from 7.1 to 8.7 (Table 3). However, differences (KW = 442.06, $p \leq 0.05$) were observed in pH between seasons. Values were highest during the rainy season, particularly in stations nearer the drainage mouth.

Table 3: Physicochemical parameters recorded by station.

Station	Season	pH		T (°C)		Sal ($^0/_{00}$)		O_2 (mg/l)		TDS (mg/l)	
		Avg	SE	Avg	SE	Avg	SE	Avg	SE	Avg	SE
SS 1	Northwind	7.9	0.05	23.94	1.25	3.63	0.94	1.50	0.01	1743	83.29
	Dry	7.2	0.04	31.50	1.00	4.12	0.75	1.80	0.01	1985	66.63
	Rainy	8.3	0.11	30.29	2.75	3.05	2.06	2.35	0.02	2245	183.23
SS 2	Northwind	7.4	0.03	23.65	0.75	5.32	0.56	1.93	0.01	1789	49.97
	Dry	7.6	0.05	31.55	1.25	6.18	0.94	2.10	0.01	1973	83.29
	Rainy	8.5	0.05	30.12	1.25	4.56	0.94	2.45	0.01	2376	83.29
SS 3	Northwind	7.1	0.12	23.69	3.00	5.45	2.25	1.98	0.02	1675	199.89
	Dry	7.6	0.11	31.54	2.75	6.21	2.06	2.15	0.02	1950	183.23
	Rainy	8.7	0.14	30.15	3.50	5.12	2.63	2.98	0.03	2419	233.20
SS 4	Northwind	7.9	0.13	23.78	3.25	6.74	2.44	2.17	0.02	1872	216.54
	Dry	7.2	0.07	31.55	1.75	6.99	1.31	1.95	0.01	1975	116.60
	Rainy	8.4	0.09	29.99	2.25	5.36	1.69	3.12	0.02	2489	149.91
SS 5	Northwind	7.3	0.06	23.30	1.50	5.95	1.13	2.41	0.01	1213	99.94
	Dry	7.6	0.05	31.58	1.25	6.82	0.94	2.52	0.01	1325	83.29
	Rainy	8.1	0.07	29.95	1.75	5.49	1.31	2.98	0.01	1828	116.60
SS 6	Northwind	7.2	0.08	23.55	2.00	5.99	1.50	1.98	0.01	2190	133.26
	Dry	7.7	0.09	31.60	2.25	6.37	1.69	1.25	0.02	2135	149.91
	Rainy	8.5	0.07	30.12	1.75	5.79	1.31	2.27	0.01	2318	116.60
SS 7	Northwind	7.9	0.08	23.78	2.00	6.78	1.50	2.13	0.01	2145	133.26
	Dry	7.4	0.09	31.62	2.25	7.18	1.69	2.56	0.02	1958	149.91
	Rainy	8.3	0.12	29.89	3.00	6.15	2.25	3.56	0.02	2456	199.89
SS 8	Northwind	7.1	0.08	23.65	2.00	9.85	1.50	2.19	0.01	1987	133.26
	Dry	7.5	0.09	31.59	2.25	10.20	1.69	2.35	0.02	1875	149.91
	Rainy	8.2	0.11	29.95	2.75	9.35	2.06	2.18	0.02	2531	183.23
SS 9	Northwind	7.6	0.05	23.69	1.25	11.95	0.94	2.99	0.01	1983	83.29
	Dry	7.8	0.04	31.55	1.00	12.45	0.75	3.38	0.01	1770	66.63
	Rainy	8.7	0.10	29.91	2.50	10.29	1.88	3.95	0.02	2431	166.57

Table 3: Continued.

Station	Season	pH		T (°C)		Sal ($^0/_{00}$)		O_2 (mg/l)		TDS (mg/l)	
		Avg	SE	Avg	SE	Avg	SE	Avg	SE	Avg	SE
SS 10	Northwind	7.3	0.09	23.85	2.25	12.95	1.69	3.10	0.02	1863	149.91
	Dry	7.8	0.08	31.68	2.00	13.83	1.50	3.45	0.01	1662	133.26
	Rainy	8.5	0.13	29.87	3.25	12.56	2.44	4.10	0.02	2387	216.54
SS 11	Northwind	7.9	0.05	23.79	1.25	15.12	0.94	3.99	0.01	1982	83.29
	Dry	7.7	0.06	31.65	1.50	16.54	1.13	4.20	0.01	1532	99.94
	Rainy	8.1	0.09	29.75	2.25	14.90	1.69	4.87	0.02	2764	149.91
SS 12	Northwind	7.4	0.09	23.81	2.25	17.35	1.69	4.10	0.02	2239	149.91
	Dry	7.6	0.07	31.56	1.75	17.98	1.31	4.85	0.01	1459	116.60
	Rainy	8.7	0.10	29.90	2.50	16.98	1.88	4.91	0.02	2691	166.57
SS 13	Northwind	7.9	0.08	23.80	2.00	24.10	1.50	4.95	0.01	1243	133.26
	Dry	7.8	0.05	31.59	1.25	24.56	0.94	5.10	0.01	991	83.29
	Rainy	8.7	0.09	29.92	2.25	23.45	1.69	5.15	0.02	1963	149.91
SS 14	Northwind	7.2	0.08	23.79	2.00	26.75	1.50	4.87	0.01	982	133.26
	Dry	7.5	0.06	31.61	1.50	27.48	1.13	5.15	0.01	1012	99.94
	Rainy	8.2	0.13	29.95	3.25	25.56	2.44	5.23	0.02	1873	216.54
SS 15	Northwind	8.1	0.07	23.80	1.75	29.56	1.31	4.99	0.01	1002	116.60
	Dry	7.9	0.05	31.60	1.25	31.25	0.94	5.31	0.01	995	83.29
	Rainy	8.3	0.12	29.99	3.00	27.89	2.25	5.59	0.02	1110	199.89

Dissolved oxygen (O_2) exhibited no differences between stations, although all O_2 values were near or below concentrations constituting hypoxia (2.0 mg/l). Levels were notably lower at stations near urban wastewater discharges. For instance, station 6 had the lowest overall value (1.25 mg/l), one clearly favored by the nearby discharge and decomposition of large quantities of organic matter.

Temperature varied according to season. It was lowest (23°C) at almost all stations during the northwinds season, which is to be expected since cold north winds during this season lower air and water temperature. Temperatures were highest (31.68°C) during the rainy and dry seasons in response to increased solar radiation.

As expected, salinity varied between stations (KW = 51.26 $p \leq 0.05$). Those nearest the drainage mouth, and therefore to the marine influence of the Gulf, had the highest values (23.45–31.25$^0/_{00}$). Between seasons, salinity levels at all stations were higher during the dry season due to a greater marine water influx (particularly at stations 10 to 15) in response to less freshwater outflow, higher solar radiation levels and consequent evaporation of the water column (Yañez-Arancibia and Day [7].

Total dissolved solids levels were highest during the rainy season due to wastewater discharge into the drainage (particularly at station 6).

The parameters BOD_5 (mg/l), TSS (mg/l), and COD (mg/l) are required by law NOM-001-SEMARNAT-1996 [8] in Mexico to establish permissible pollutant levels in wastewater discharge into type A bodies of water, specifically artificial reservoirs and natural lakes. These three variables are used to represent wastewater conditions because conventional treatments can mitigate them and/or fix them at established levels. Regulations in Mexico include levels determined by the National Water Commission (Comision Nacional de Agua – CNA) that must be met by the party responsible for the discharge, or for a specific receiving body of water (e.g. the Caleta), to comply with the National Water Law. Legal maximum concentrations are 150 mg/l BOD_5, 125 mg/l SST, and 320 mg/l COD. Concentrations recorded for these three variables along the Caleta drainage significantly exceeded these legal maximum levels (Table 4). Clearly, this drainage receives immense amounts of polluting discharge from the surrounding urban area, as well as from the many companies in Ciudad del Carmen with permits allowing them to discharge wastewater into the Caleta.

Table 4: Physicochemical parameters (NOM-001-SEMARNAT-1996).

Station	Season	TSS mg/l		BOD_5 mg/l		COD mg/l	
		Avg	SE	Avg	SE	Avg	SE
SS 1	Northwind	159	1.23	270	80	810	63.3
	Dry	185	0.99	315	64	945	50.7
	Rainy	256	2.71	435	176	1305	139.3
SS 2	Northwind	142	0.74	242	48	726	38.0
	Dry	174	1.23	295	80	885	63.3
	Rainy	230	1.23	391	80	1173	63.3
SS 3	Northwind	184	2.96	312	192	936	152.0
	Dry	175	2.71	298	176	894	139.3
	Rainy	235	3.45	399	224	1197	177.3
SS 4	Northwind	175	3.21	297	208	891	164.6
	Dry	188	1.73	319	112	957	88.6
	Rainy	306	2.22	521	144	1563	114.0
SS 5	Northwind	182	1.48	310	96	930	76.0
	Dry	229	1.23	390	80	1170	63.3
	Rainy	288	1.73	489	112	1467	88.6

Table 4: Continued.

Station	Season	SST mg/l		BOD_5 mg/l		COD mg/l	
		Ave	E.E	Ave	E.E	Ave	E.E
SS 6	Northwind	234	1.97	398	128	1194	101.3
	Dry	257	2.22	437	144	1311	114.0
	Rainy	361	1.73	614	112	1842	88.6
SS 7	Northwind	160	1.97	272	128	816	101.3
	Dry	174	2.22	295	144	885	114.0
	Rainy	217	2.96	369	192	1107	152.0
SS 8	Northwind	95	1.97	162	24	486	18.7
	Dry	111	2.22	189	27	567	21.0
	Rainy	154	2.71	261	33	783	25.7
SS 9	Northwind	85	1.23	145	15	436	11.7
	Dry	104	0.99	177	12	531	9.4
	Rainy	138	2.47	235	30	704	23.4
SS 10	Northwind	110	2.22	187	26.63	243	21.04
	Dry	105	1.97	179	23.67	232	18.70
	Rainy	141	3.21	239	38.47	311	30.39
SS 11	Northwind	105	1.23	178	14.80	232	11.69
	Dry	113	1.48	191	17.76	249	14.03
	Rainy	184	2.22	313	26.63	406	21.04
SS 12	Northwind	109	2.22	186	26.63	242	21.04
	Dry	138	1.73	234	20.71	304	16.36
	Rainy	173	2.47	293	29.59	381	23.38
SS 13	Northwind	140	1.97	239	23.67	310	18.70
	Dry	154	1.23	262	14.80	341	11.69
	Rainy	217	2.22	368	26.63	479	21.04
SS 14	Northwind	96	1.97	163	23.67	212	18.70
	Dry	104	1.48	177	17.76	230	14.03
	Rainy	130	3.21	221	38.47	288	30.39
SS 15	Northwind	195	1.73	332	20.71	431	16.36
	Dry	214	1.23	364	14.80	473	11.69
	Rainy	298	2.96	369	35.51	480	28.05

Heavy metals concentrations exhibited a value gradient with the highest values nearest the drainage outlet (Table 5). This suggests that these metals most probably originate in discharge from areas surrounding the drainage, direct influents into it, and rainfall wash from the urban area. Lead and iron had significantly high levels. The former is an indicator of anthropogenic activity and the latter is a mobile element. Both can form precipitates with other heavy metals and are indicative of

Table 5: Heavy metal values in sediments, Caleta drainage, Ciudad del Carmen, Campeche.

Station	Season	Heavy metals (µg/g)					
		Fe	Cr	Cu	Zn	Cd	Pb
SS 1	Northwind	66.5	21.45	1.38	0.32	1.76	95.00
	Dry	50.25	16.21	1.24	0.25	1.59	71.79
	Rainy	71.4	23.03	2.00	1.78	2.57	91.54
SS 2	Northwind	73.15	23.60	1.51	0.35	1.94	104.50
	Dry	55.28	17.83	1.36	0.27	1.75	78.96
	Rainy	78.54	25.34	2.20	1.96	2.82	100.69
SS 3	Northwind	79.80	25.74	1.65	0.38	2.12	114.00
	Dry	60.30	19.45	1.48	0.30	1.90	86.14
	Rainy	85.68	27.64	2.40	2.14	3.08	109.85
SS 4	Northwind	83.13	26.81	1.72	0.40	2.20	118.75
	Dry	62.81	20.26	1.55	0.31	1.98	89.73
	Rainy	89.25	28.79	2.50	2.23	3.21	114.42
SS 5	Northwind	86.45	27.89	1.79	0.41	2.29	123.50
	Dry	65.33	21.07	1.61	0.32	2.06	93.32
	Rainy	92.82	29.94	2.60	2.31	3.34	119.00
SS 6	Northwind	89.78	28.96	1.86	0.43	2.38	128.25
	Dry	67.84	21.88	1.67	0.33	2.14	96.91
	Rainy	96.39	31.09	2.70	2.40	3.47	123.58
SS 7	Northwind	99.75	32.18	2.06	0.48	2.64	142.50
	Dry	75.38	24.31	1.86	0.37	2.38	107.68
	Rainy	107.10	34.55	3.00	2.67	3.85	137.31
SS 8	Northwind	103.08	33.25	2.13	0.49	2.73	147.25
	Dry	77.89	25.13	1.92	0.38	2.46	111.27
	Rainy	110.67	35.70	3.10	2.76	3.98	141.88
SS 9	Northwind	106.40	34.32	2.20	0.51	2.82	152.00
	Dry	80.40	25.94	1.98	0.40	2.54	114.86
	Rainy	114.24	36.85	3.20	2.85	4.11	146.46

Table 5: Continued.

Station	Season	Heavy metals (µg/g)					
		Fe	Cr	Cu	Zn	Cd	Pb
SS 10	Northwind	109.73	35.40	2.27	0.53	2.91	156.75
	Dry	82.91	26.75	2.04	0.41	2.62	118.45
	Rainy	117.81	38.00	3.30	2.94	4.24	151.04
SS 11	Northwind	113.05	36.47	2.34	0.54	3.00	161.50
	Dry	85.43	27.56	2.10	0.42	2.70	122.04
	Rainy	121.38	39.15	3.40	3.03	4.37	155.62
SS 12	Northwind	116.38	37.54	2.41	0.56	3.09	166.25
	Dry	87.94	28.37	2.17	0.43	2.78	125.63
	Rainy	124.95	40.31	3.50	3.12	4.49	160.19
SS 13	Northwind	119.70	38.61	2.48	0.57	3.17	171.00
	Dry	90.45	29.18	2.23	0.45	2.86	129.21
	Rainy	128.52	41.46	3.61	3.20	4.62	164.77
SS 14	Northwind	123.03	39.69	2.54	0.59	3.26	175.75
	Dry	92.96	29.99	2.29	0.46	2.93	132.80
	Rainy	132.09	42.61	3.71	3.29	4.75	169.35
SS 15	Northwind	126.35	40.76	2.61	0.60	3.35	180.50
	Dry	95.48	30.80	2.35	0.47	3.01	136.39
	Rainy	135.66	43.76	3.81	3.38	4.88	173.92
Mean	Northwind	99.75	32.18	2.06	0.48	2.64	142.50
	Dry	75.38	24.31	1.86	2.34	2.38	107.68
	Rainy	107.10	34.55	3.00	4.56	3.85	137.31
Std. Dev.	Northwind	5.87	1.89	0.12	0.03	0.16	8.38
	Dry	4.43	1.43	0.11	0.14	0.14	6.33
	Rainy	6.30	2.03	0.18	0.27	0.23	8.08

general eutrophication processes (Aulio [9]). These metals are widely used by a number of companies in the city and its environs providing services to the state petroleum company, Petróleos Mexicanos (Pemex). Bioavailable metals such as zinc and cadmium exhibited higher concentrations near the drainage outlet during the rainy season than previously reported levels (Aguilar-Ucán *et al.* [10]). Heavy metal concentrations were also higher during the northwind season than during the dry season, mainly because high winds lead to sediment suspension which makes metals available for biota and allows them to circulate throughout the drainage. As mentioned, overall heavy metals concentrations and bioavailable metals concentrations far exceeded legal limits; concentrations this high are probably due largely to anthropogenic sources within Ciudad del Carmen.

4 Conclusions

The present results clearly indicate that the Caleta drainage in Ciudad del Carmen, Mexico, receives an immense pollutant load from the surrounding urban area. Pollutant accumulation was highest in sediments, which could have detrimental long-term effects. When combined with environmental and seasonal conditions in the area, these pollutants have created extremely unfavorable conditions for the area's biota. Spatial and temporal variation within the Caleta drainage were determined by mixing processes caused by a number of factors: marine water from the Gulf; freshwater influx from rivers; pollutant discharges from industry and irregular human settlements; and internal circulation patterns caused by seasonal weather, particularly northwinds. Understanding how these factors interact is vital to quantifying the impacts suffered by this drainage. Influence from Terminos Lagoon and the Gulf of Mexico slightly mitigate the impact of anthropogenic pollution in the Caleta, but only control and treatment of sewage and industrial discharge will stop further deterioration of this ecosystem.

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