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Metals in *Thaisella chocolata* from the Callao Bay, Perú

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Abstract

The concentration of Al, As, Ba, B, Cd, Ca, Co, Cr, Cu, Sr, P, Fe, Li, Mg, Mn, Hg, Ni, Ag, Pb, K, Se, Na, Ti, V and Zn in water, sediment and Thaisella chocolata muscle in three sampling zones during the four seasons of the year (autumn, winter, spring, and summer) in the Bahía del Callao, Perú. The concentration of heavy metals in T. chocolata by sampling area was compared with environmental standards, and the bioconcentration factor for each element was determined. A correlation matrix was made for the concentrations of metals analyzed and the physicochemical parameters of the water. The average concentrations of As, Cd, Cu, Cr, Hg, Pb, and Se in all zones and stations exceeded the minimum limit concentration among the regulations consulted, except for Cu in P1. Likewise, the FBCwater and FBCsediment of As and Cd were among the highest values. It was found that Cu in T. chocolata was positively correlated with Sb, As, Co, Cu, Mg, Ag, and V in sediment; on the other hand, the Hg in T. chocolata was negatively correlated with the Ca, Sr, Li, Mg, Mo, K and Na of the surface water. The results indicate that the consumption of T. chocolata from the bay of Callao would be a severe problem for people's health.

Keywords: *bioconcentration, Potentially toxic elements, quality standard, Thaisella chocolate*

1. Introduction

The Bay of Callao in Perú presents a tremendous industrial, tourist, and recreational importance; However, it also has problems of contamination by potentially toxic elements in its coastal waters, mainly from domestic, industrial, and agricultural collectors, mineral sediments resulting from the loading and unloading of mineral concentrates and from discharges by the Chillón and Rímac rivers [1]. In addition, the presence of heavy metals has been recorded in continental and marine water, sediments, and soil in the Callao region [2-4].

Heavy metals represent a significant problem due to their abundance, persistence, and environmental toxicity [5 - 9]. In likewise, metal contamination of aquatic ecosystems is increasing due to urbanization and industrialization [10 - 14]. The increase in contamination by heavy metals generates a significant adverse effect on the health of aquatic invertebrates [14] and, being located at the top of the food chain in marine ecosystems, molluscs considerable amounts of heavy metals can accumulate in soft tissues and shells through oral intake, and through the skin through water and food [15, 16].

Molluscs are frequently used as biomonitors of contamination by heavy metals in fresh and marine water [15,17]. In particular, members of the Muricidae family are bioindicators of contamination by toxic chemicals in coastal areas [18]. *Thaisella chocolata* is a gastropod of the Muricidae family for local consumption and export distributed from Paita in Perú to the Valparaiso Region in Chile, with Callao being among the four main landing ports for this hydrobiological resource [19].

In addition, *T. chocolata* helps monitor heavy metals and other marine organic pollutants [18,20-24]. Various metal studies have been carried out in Chile and Perú, including the muscle in *T. chocolata* [20-23, 25]. The objective of this study was to evaluate the concentration of heavy metals in the power of *T. chocolata* from the bay of Callao, Perú.

2. Material and methods

2.1. Sample extraction

Samples of *T. chocolata*, water, and sediment were extracted from three zones (P1, P2, and P3) during four seasons of the year (autumn, winter, spring, and summer) between the years 2015-2016, in the area between 12 2'34.10 "S - 12 ° 5'16.57" S and 77 ° 9'15.40 "W - 77 ° 11'52.03" W of Callao Bay. The P1 zone was located between the San Lorenzo Islands and the Frontón (12 ° 5'16.57 "S; 77 ° 11'52.03" W), the P2 zone in front of IMARPE (Instituto del Mar del Perú) (12 ° 3'56.20 "S; 77 ° 9'30.70" W) and zone P3 in the area of influence of the Callao Pier (12 ° 2'34.10 "S; 77 ° 9'15.40 "O) (Figure 1).

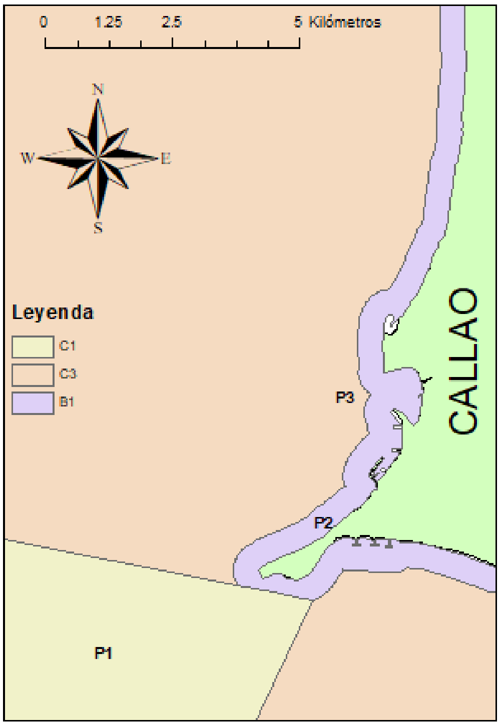

Figure 1. Distribution of the sampling and classification areas of the marine-coastal water bodies of the Bahía del Callao, Perú. P1 = between the San Lorenzo Islands and the Frontón (12 ° 5'16.57 "S; 77 ° 11'52.03" W) and it was located in C1, space destined to the extraction and cultivation of molluscs , P2 = in front of IMARPE (Instituto del Mar del Perú) (12 ° 3'56.20 "S; 77 ° 9'30.70" W) and it was located in B1 space destined to the recreation of primary contact, P3 = area of influence of the Callao Wharf (12 ° 2'34.10 "S; 77 ° 9'15.40" W), and it was located in C3, space destined to marine port, industrial or sanitation activities.

According to the classification of coastal-marine water bodies in Perú, P1 was located in C1, a space for the extraction and cultivation of molluscs; P2 was located in B1, a space intended for primary contact recreation and P3 was located in C3, a space intended for marine port, industrial or sanitation activities [25,26].

2.2. Water

The extraction of the water samples was carried out under the standards established by the National Protocol for the Monitoring of the Quality of Surface Water Resources [25,26]. 500 mL of water were extracted in polyethylene containers, washed and treated with nitric acid until reaching pH 2.0, and kept at 4°C until the determination of heavy metal concentrations.

2.3. Sediment

500 g of surface sediment were extracted using the 0.04 m^2 Van Veen dredge and stored in polyethylene bags at 4°C until the determination of heavy metal concentrations.

2.4. Thaisella chocolata

Thirty specimens of *T. chocolata* were captured by diving with a compressor in each season of the year and sampling area. The muscles of these snails were placed in polyethylene bags and stored at -4°C until their transfer to the laboratory where they were kept at -20°C until the determination of heavy metal concentrations.

2.5. Physico-chemical characteristics of water

The values of sea surface temperature (SST) (°C), pH, electrical conductivity ($mS.cm^{-2}$), salinity ($g.L^{-1}$), total dissolved solids (STD) were obtained in each sampling area. ($mg.L^{-1}$), dissolved oxygen (DO) ($mg.L^{-1}$), transparency (m), turbidity (FTU), oxide reduction potential (mRV), ammonia ($mg.L^{-1}$), ammonia ($mg.L^{-1}$) and nitrates ($mg.L^{-1}$) using the EXO 2 multiparameter probe (YSI brand, United States). Chlorophyll ($ug.L^{-1}$) and phycocyanin ($ug.L^{-1}$) were determined by the AlgaeTorch Fluorometer (brand EIJKELKAMP, The Netherlands).

2.6 Potentially toxic elements

The concentrations of 24 metals in surface water such as Al (Aluminum), As (Arsenic), Ba (Barium), B (Boron), Cd (Cadmium), Ca (Calcium), Co (Cobalt), Cu (Copper), Cr (Chromium), Sr (Strontium), P (Phosphorus), Fe (Iron), Li (Lithium), Mg (Magnesium), Mn (Manganese), Ni (Nickel), Ag (Silver), Pb (Lead), K (Potassium), Se (Selenium), Na (Sodium), Ti (Titanium), V (Vanadium) and Zn (Zinc) were determined by inductively coupled plasma mass spectrometry (ICP-MS, NexION 2000B, PerkinElmer, USA). For the water samples, the EPA method 200.7 [26] was used. An aliquot was digested with nitric acid and hydrochloric acid; then, the chelation-extraction technique is used with APDC (pyrridolin ammonium dithiocarbamate) and MIBK (methyl isobutyl ketone) [27]. For the determination of Hg (mercury) in surface water, the EPA 245.1 procedure [28] was carried out.

To obtain 24 metals in sediments, a sample of one g in dry weight was taken, and 10 mL of a mixture of nitric acid and hydrochloric acid in a ratio of 6: 2 was added during two h of exposure or until complete digestion [29]. Hg was digested by adding a mixture of acids: sulfuric acid (H_2SO_4), nitric acid (HNO_3), and potassium permanganate ($KMnO_4$), and its analysis was performed by inductively coupled plasma mass spectrometry (ICP-MS, NexION 2000B, PerkinElmer, USA) [30].

To determine 24 metals in *T. chocolata* tissues, they were dried in an oven at 80°C until obtaining a constant weight. Then, they were pulverized and homogenized in a porcelain mortar; they were placed in hermetically closed glass vials with lids, Bakelite. The chemical attack was carried out with concentrated nitric acid, hydrochloric acid, and hydrogen peroxide. Calibration standards and blanks received the same treatment and were read by inductively coupled plasma mass spectrometry (ICP-MS, NexION 2000B, PerkinElmer, USA). The samples were digested with nitric acid, hydrochloric acid, and potassium permanganate for the Hg analysis following the USEPA 7471 B Rev. 2 methodology [30].

The mean concentrations of heavy metals in *T. chocolata* tissues were compared with the Swiss, Brazilian, Codex Alimentarius, European Community, and Australian-New Zealand Food Standards [31 - 33].

2.7 Bioconcentration Factor (BCF)

The BCF is a constant of proportionality that corresponds to the ratio between the concentration of the substance in the organism and its concentration in the water or the soil: BCF = (concentration of the heavy metal in the muscle of *T. chocolata* / concentration of the metal heavy in water or sediment) [34 - 35].

2.8 Statistic analysis

The statistical analyses for the inferential statistic did not consider heavy metals without variability in their concentrations. Therefore, the concentrations that were lower than the detection limits were used as absolute values. The Analysis of Variance (ANOVA) was used to evaluate significant differences between the mean concentrations of metals between the sampling areas, between the seasons of the year, between the mollusc-water BCF and the mollusc-sediment BCF. Additionally, the Spearman correlation coefficient was used to determine the dependency relationship between the metals in *T. chocolata*, sediment and water and the physicochemical parameters of the water. For all statistical analyzes, the criterion of significance was established at $p < 0.05$. The data were analyzed with the statistical package SPSS version 25.0.

3. Results

3.1 Water Characteristics

The following annual averages of the water characteristics of Callao bay were observed: T ° (20.18°C), pH (8.21), CE (53.56 $mS.cm^{-2}$), salinity (35.04 $g.L^{-1}$), TDS (32673.33 $mg.L^{-1}$), DO (2.00 $mg.L^{-1}$), transparency (3.58 m), turbidity (3.52 FTU), chlorophyll (0.69 $ug.L^{-1}$), ORP (190.17 mV), ammonia (51.86 $mg.L^{-1}$), ammonia (2.03 $mg.L^{-1}$) and nitrates (392.12 $mg.L^{-1}$); likewise, there was no presence of phycocyanins in the water of the Callao bay. The most variable water characteristics (SD>10) were the TDS ($mg.L^{-1}$) with values from 32673.33 to 38500, the nitrates from 73.98 to 957.67, and the ORP (mV) from 164 to 234.4 (Table 1).

Table 1. Physicochemical parameters of the surface water of the Callao's Bay, Perú.

A	E	T° (°C)	pH	EC ($mS.cm^{-2}$)	Sal ($g.L^{-1}$)	TSD ($mg.L^{-1}$)	DO ($mg.L^{-1}$)	Trans (m)	Turbidity (FTU)	BGA_PC ($ug.L^{-1}$)	CLOR ($ug.L^{-1}$)	ORP (mV)	ammonium ($mg.L^{-1}$)	ammonia ($mg.L^{-1}$)	nitrates ($mg.L^{-1}$)
P1	Autumn	24.6	8.2	53.9	35	38500	3.61	7.5	ND	ND	ND	ND	ND	ND	ND
	Winter	18.4	8.1	53.7	35.1	34702	3.11	4.75	2.4	0	2	234.4	33.57	0.29	114.75
	Spring	19.9	8.6	53.3	34.9	34011	2.4	5	-	0	0.48	170.8	53.71	4.42	562.84
	Summer	23	9.1	53.6	35.3	34104	4.32	2.75	-	0	0	164	48.37	2.2	304.01
EQS	C1						≥4							…	16.00
P2	Autumn	20.4	7.9	53.7	35.2	38357	1.35	3.12	2.3	0	0.2	ND	ND	ND	ND
	Winter	16.9	8	53.9	35.1	34773	2.21	2.75	2.7	0	1.6	225.3	55.43	0.3	73.98
	Spring	20.1	8.1	53	34.8	33808	0.9	2.25	7	0	0.68	182.7	54.89	4.25	957.67
	Summer	20.8	8.1	53.2	34.8	34010	1.33	3.75	-	0	0	176	51.39	1.35	365.58
EQS	B1		6 a 9				≥5		100						10
P3	Autumn	20.1	8	53.8	35.2	38428	1.74	2.87	2.9	0	0.7	ND	ND	ND	ND
	Winter	17.2	8	53.7	34.9	34180	1.44	3	7.6	0	1.1	211.2	64.52	0.45	156.22
	Spring	19.6	8.2	53.5	34.9	33893	0.89	3	2.5	0	0.88	176.2	54.61	3.77	672.19
	Summer	21.2	8.2	53.4	35.3	34076	0.65	2.25	0.73	0	0	170.9	50.22	1.26	321.85
EQS	C3						≥2.5							…	..
	$\bar{X}$	20.18	8.21	53.56	35.04	35236.83	2.00	3.58	14.24	0	0.69	190.17	51.86	2.03	354.51

A = Area, P1 = between the San Lorenzo Islands and the Frontón (12 ° 5'16.57 "S; 77 ° 11'52.03" W) and it was located in C1, space destined to the extraction and cultivation of molluscs , P2 = in front of IMARPE (Instituto del Mar del Perú) (12 ° 3'56.20 "S; 77 ° 9'30.70" W) and it was located in B1 space destined to the recreation of primary contact, P3 = area of influence of the Callao

Wharf (12 ° 2'34.10 "S; 77 ° 9'15.40" W), and it was located in C3, space destined to marine port, industrial or sanitation activities. S = Season of the year, EQS = Environmental Quality Standard for water in Perú, T = Sea Surface Temperature, EC = Electrical Conductivity, Salt = Salinity, TDS = Total Dissolved Solids, DO = Dissolved Oxygen, TRANS = Transparency, TURB = Turbidity, BGA_PC = Phycocyanins, CHLOR = Chlorophyll, ORP = Reduction oxide potential. ND = Not determined.

According to the EQS (Environmental Quality Standard) for water, low DO levels were found in all areas, except P1 in summer. Nitrates in P1 and P2 were much higher at their limit concentrations.

3.2 Metals in water and sediment from the bay of Callao

The concentrations of all the metals analyzed were higher in water compared to the residue; in addition, the concentrations of Na in water and sediment were similar (1.13 and 0.88, respectively) (Table 2).

Table 2. Metal concentration in water and sediment of Callao's Bay, Perú. A = autumn, Wi = Winter, Sp = Spring, Su = Summer. P1 to P3 = Area of evaluations.

	Water							**Sediment**						
	Zones			**Season**				**Zones**			**Season**			
	P1	**P2**	**P3**	**A**	**Wi**	**Sp**	**Su**	**P1**	**P2**	**P3**	**A**	**Wi**	**Sp**	**Su**
Al	0.10	0.12	0.15	0.12	0.09	0.12	0.16	9592.25	13275.50	13572.00	11504.33	9599.67	13441.33	14041.00
As	0.01	0.01	0.01	0.01	0.02	0.01	0.01	13.38	37.73	179.15	77.30	69.27	116.40	44.03
Ba	0.01	0.01	0.01	0.01	0.01	0.01	0.01	38.90	127.18	139.53	120.13	92.50	99.33	95.50
B	5.08	4.87	4.91	4.29	4.31	5.55	5.44	23.06	33.82	23.15	25.54	21.46	31.02	28.67
Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.43	8.01	5.96	5.47	4.36	7.24	6.13
Ca	472.35	457.40	462.93	435.10	416.87	502.07	502.87	43632.50	43510.50	16166.50	41838.00	33031.33	33698.33	29178.33
Co	0.00	0.00	0.01	0.00	0.00	0.01	0.00	4.23	7.28	10.27	7.66	6.52	7.69	7.16
Cu	0.01	0.01	0.01	0.01	0.00	0.01	0.01	24.58	147.30	177.05	114.40	86.07	113.90	150.87
Cr	0.00	0.01	0.00	0.00	0.00	0.01	0.01	18.53	27.38	18.15	21.83	17.63	23.93	22.00
Sr	7.77	7.29	7.40	7.03	6.76	7.98	7.84	287.25	258.25	72.78	230.23	209.63	200.67	183.83
P	0.09	0.15	0.16	0.13	0.10	0.12	0.18	2056.75	1608.00	1292.25	1558.00	1808.67	1468.67	1774.00
Fe	0.04	0.11	0.12	0.08	0.04	0.11	0.12	13380.25	22351.75	26116.50	19720.00	17371.67	23872.33	21500.67
Li	0.22	0.21	0.21	0.20	0.20	0.23	0.23	16.00	21.50	20.00	17.67	14.67	21.67	22.67
Mg	1442.00	1401.00	1415.75	1339.00	1299.00	1550.00	1490.33	6198.50	9173.25	8341.25	7901.67	6497.67	8489.67	8728.33
Mn	0.00	0.00	0.01	0.00	0.00	0.01	0.01	171.80	268.28	426.35	286.80	238.70	341.97	287.77
Hg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.27	0.99	0.45	0.35	0.48	0.80	0.64
Ni	0.02	0.02	0.02	0.02	0.01	0.03	0.02	6.44	12.28	8.88	9.26	7.13	10.37	10.03
Ag	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48	1.45	3.03	1.73	1.10	2.40	1.37
Pb	0.04	0.05	0.05	0.04	0.04	0.05	0.07	26.18	251.70	232.40	215.60	110.17	200.83	153.77
K	477.93	457.70	464.60	432.83	418.00	507.50	508.63	1871.75	2794.25	2471.50	2227.33	1865.33	2572.67	2851.33
Se	0.04	0.03	0.02	0.01	0.01	0.05	0.04	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Na	11581.25	10003.50	8531.19	6645.91	10146.00	12160.50	12880.00	11424.25	18876.00	8223.50	11427.33	9835.33	15219.67	14882.67
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	450.63	577.03	752.40	517.47	498.73	659.70	697.50
Va	0.01	0.01	0.01	0.01	0.01	0.01	0.01	34.98	55.61	65.75	44.14	45.73	63.64	54.95
Zn	0.05	0.03	0.02	0.01	0.01	0.01	0.09	87.33	460.93	987.20	488.00	386.37	629.97	542.93

P1 = between the San Lorenzo Islands and the Frontón (12 ° 5'16.57 "S; 77 ° 11'52.03" W) and it was located in C1, space destined to the extraction and cultivation of molluscs , P2 = in front of IMARPE (Instituto del Mar del Perú) (12 ° 3'56.20 "S; 77 ° 9'30.70" W) and it was located in B1 space destined to the recreation of primary contact, P3 = area of influence of the Callao Wharf (12 ° 2'34.10 "S; 77 ° 9'15.40" W), and it was located in C3, space destined to marine port, industrial or sanitation activities.

3.3 Heavy metals in the muscle of T. chocolata

During the autumn season in zone P3, there was no presence of individuals of *T. chocolata*. The elements with the highest average concentrations in the *T. chocolata* muscle presented the following relationship: Mg> Na> Ca> K> P> Fe> Zn (Table 3). The average concentrations of As, Cd, Cu, Cr, Hg, Pb, and Se in all zones and stations exceeded the minimum concentration among the consulted regulations, except for Cu in P1. Likewise, the average concentrations of Cd in P1 (10.1 mg.kg-1), Autumn (14.39 $mg.kg^{-1}$), Winter (5.26 $mg.kg^{-1}$) and the annual (4.79 $mg.kg^{-1}$) exceed that established by the Codex Alimentarus (2 $mg.kg^{-1}$) (Table 3).

There were significant differences by sampling area in the concentrations of Ca ($p = 0.02$), Cu ($p = 0.02$), Sr ($p = 0.02$), Mg ($p = 0.02$) and Ag ($p = 0.02$) in the muscle of *T. chocolata*. Regarding the significant differences by season of the year, the Li concentration presented significant differences between the winter and summer seasons ($p = 0.04$), the Ni between the winter season with spring ($p = 0.004$) and summer (0.013), while in Se between the autumn season with the winter, spring and summer seasons ($p = 0.001$, 0.001 and 0.018, respectively).

Table 3. Comparison between metal concentrations in *Thaisella chocolata* muscle from Callao's Bay, Perú, with food regulations. Bold = Metal concentrations that exceed the minimum allowable limit. Italics = Minimum standard concentration.

	P1	P2	P3	autumn	Winter	Spring	Summer	$\bar{X}$	Switzerland	Brazil	Codex FAO	European Commission	Australia N. Zeland
Al	10.97	29.84	9.35	17.29	10.30	13.13	28.81	17.39					
As	**48.82**	**65.05**	**60.22**	**54.67**	**53.85**	**60.58**	**61.17**	**57.83**		1			1
Ba	0.45	1.03	0.18	0.89	0.25	0.20	1.11	0.59					
B	8.52	15.27	12.45	12.39	16.14	10.73	9.03	12.04					
Cd	**10.7**	**1.24**	**1.66**	**14.39**	**5.26**	**0.80**	**1.92**	**4.79**	0,5	1	2	1	2
Ca	4654.5	15192	10603.67	12085.00	15642.00	6635.33	6731.67	10108.82					
Co	0.3	0.36	0.46	0.43	0.29	0.37	0.38	0.36					
Cu	25.51	**58.47**	**84.75**	**42.03**	**52.39**	**71.98**	**44.34**	**53.65**		30			
Cr	**0.42**	**0.26**	**0.17**	**0.40**	**0.29**	**0.34**	**0.17**	**0.29**		0,1			
Sr	35.18	93.2	65.05	78.37	90.66	48.02	45.30	64.43					
P	4838.25	4027.25	4055	4551.50	3989.67	4206.67	4645.00	4329.73					
Fe	167.59	233.09	104.02	297.20	105.89	79.48	254.76	174.07					
Li	0.65	0.65	0.8	0.20	0.20	1.00	1.20	0.69					
Mg	12928.25	45423.75	30425.33	33495.50	43657.67	24817.00	17423.00	29516.73					
Mn	5.22	12.43	5.66	6.76	6.11	5.55	13.02	7.96					
Hg	**0.26**	**0.26**	**0.12**	**0.59**	**0.38**	**0.03**	**0.02**	**0.22**	0,2	0,01		0,5	0,5
Ni	1.05	1.79	1.57	1.47	2.89	0.51	0.98	1.46		5			
Ag	4.18	0.14	0.12	3.29	1.36	1.29	1.04	1.6					
Pb	**2.25**	**4.29**	**2.91**	**4.33**	**2.99**	**1.52**	**4.25**	**3.17**	*0,5*	0,8		1,5	2
K	8924.25	8296.5	8170.33	7994.00	7885.67	8724.67	9191.67	8490.36					
Se	**2.22**	**2.29**	**1.95**	**4.52**	**1.21**	**2.61**	**1.12**	**2.17**		0,3			
Na	10168.25	12032	11982.67	10324.00	12663.33	10168.33	11868.67	11340.82					
Ti	1.5	3.38	2.02	4.34	1.50	1.75	2.39	2.32					
Va	0.15	0.4	0.11	0.37	0.18	0.09	0.33	0.23					XA
Zn	177.72	70.78	78.99	220.48	118.20	73.95	71.18	111.9					

Swiss, Brazilian and European Commission food standards taken from MICT (2017). FAO Codex extracted from CA (1995). Australian and New Zealand standard taken from FSANZ (2011). P1 to P3 = Zones of evaluations. P1 = between the San Lorenzo Islands and the Frontón (12 ° 5'16.57 "S; 77 ° 11'52.03" W) and it was located in C1, space destined to the extraction and cultivation of molluscs , P2 = in front of IMARPE (Instituto del Mar del Perú) (12 ° 3'56.20 "S; 77 ° 9'30.70" W) and it was located in B1 space destined to the recreation of primary contact, P3 = area of influence of the Callao Wharf (12 ° 2'34.10 "S; 77 ° 9'15.40" W), and it was located in C3, space destined to marine port, industrial or sanitation activities.

3.4. Bioconcentration Factor (BCF)

The water BCFs were always higher than the sediment BCFs. In addition, the water BCF with the highest average values were: P> Cu> As> Zn> Cd> Fe> Ti, while the sediment BCF with the highest average values were: Mg> Se> K> P> Ag> Na> Cd. Likewise, the BCFs of P, Mg, K, and Se in all zones and stations were greater than 1 (Table 4).

Table 4. Bioconcentration factors of *Thaisella chocolata* in relation to surface water and surface sediment of the Callao's Bay, Perú. A = Autumn, Wi = Winter, Sp = Spring, Su = Summer. Wa = water. Se = Sediment.

	Zones						Seasons								TOTAL	
	P1		P2		P3		A		Wi		Sp		Su			
	Wa	Se	Wa	Se	Wa	Se	Wa	Se	Wa	Se	Wa	Se	Wa	Se	Wa	Se
Al	110.31	0.00	253.98	0.00	61.90	0.00	139.02	0.00	119.02	0.00	106.23	0.00	184.46	0.00	141.76	0.00
As	3493.02	3.65	6956.95	1.72	6546.01	0.34	5941.85	0.71	3459.10	0.78	6445.04	0.52	6648.55	1.39	5333.97	0.76
Ba	82.79	0.01	158.85	0.01	22.51	0.00	117.48	0.01	43.27	0.00	30.65	0.00	172.02	0.01	89.04	0.01
Bo	1.68	0.37	3.14	0.45	2.53	0.54	2.89	0.48	3.74	0.75	1.93	0.35	1.66	0.31	2.43	0.45
Cd	4552.13	3.12	588.10	0.15	1023.59	0.28	8634.00	2.63	3508.89	1.21	311.69	0.11	809.86	0.31	2366.78	0.81
Ca	9.85	0.11	33.21	0.35	22.91	0.66	27.78	0.29	37.52	0.47	13.22	0.20	13.39	0.23	21.78	0.29
Co	71.95	0.07	84.52	0.05	65.71	0.04	111.21	0.06	78.90	0.04	44.62	0.05	83.82	0.05	70.94	0.05
Cu	4049.60	1.04	7495.83	0.40	11188.56	0.48	4347.41	0.37	14159.46	0.61	7968.63	0.63	6821.03	0.29	7425.98	0.49
Cr	118.57	0.02	47.00	0.01	44.73	0.01	112.86	0.02	129.41	0.02	66.01	0.01	27.96	0.01	68.18	0.01
Sr	4.53	0.12	12.79	0.36	8.79	0.89	11.15	0.34	13.42	0.43	6.02	0.24	5.78	0.25	8.64	0.30
P	54347.09	2.35	27124.09	2.50	24755.80	3.14	34178.97	2.92	39830.28	2.21	34641.78	2.86	25762.62	2.62	32367.76	2.62
Fe	4070.13	0.01	2129.67	0.01	898.05	0.00	3633.25	0.02	2535.20	0.01	726.07	0.00	2084.18	0.01	1959.88	0.01
Li	2.95	0.04	3.10	0.03	3.76	0.04	0.98	0.01	1.01	0.01	4.41	0.05	5.26	0.05	3.22	0.04
Mg	8.97	2.09	32.42	4.95	21.49	3.65	25.02	4.24	33.61	6.72	16.01	2.92	11.69	2.00	20.79	3.73
Mn	1491.43	0.03	4518.18	0.05	906.13	0.01	1448.57	0.02	6106.67	0.03	1110.67	0.02	2170.56	0.05	1910.62	0.03
Hg	1050.00	0.98	700.00	0.27	246.67	0.28	923.68	1.69	600.00	0.80	300.00	0.04	175.00	0.04	598.79	0.35
Ni	50.73	0.16	91.22	0.15	77.98	0.18	84.68	0.16	240.56	0.40	16.35	0.05	49.00	0.10	72.53	0.16
Ag	1193.57	8.79	45.83	0.09	27.41	0.04	758.08	1.90	681.67	1.24	296.92	0.54	259.17	0.76	437.11	0.99
Pb	55.96	0.09	83.35	0.02	58.49	0.01	116.89	0.02	85.33	0.03	30.81	0.01	63.07	0.03	67.29	0.02
K	18.67	4.77	18.13	2.97	17.59	3.31	18.47	3.59	18.87	4.23	17.19	3.39	18.07	3.22	18.19	3.57
Se	59.13	2.22	91.50	2.29	97.67	1.95	452.00	4.52	121.00	1.21	49.00	2.61	30.64	1.12	78.94	2.17
Na	0.88	0.89	1.20	0.64	1.40	1.46	1.55	0.90	1.25	1.29	0.84	0.67	0.92	0.80	1.13	0.88
Ti	1666.67	0.00	2291.53	0.01	1680.56	0.00	2477.14	0.01	1666.67	0.00	1806.90	0.00	1790.00	0.00	1951.91	0.00
Va	12.47	0.00	31.69	0.01	9.87	0.00	32.69	0.01	15.38	0.00	6.91	0.00	28.29	0.01	19.34	0.00
Zn	3524.44	2.04	2264.80	0.15	4999.37	0.08	17315.18	0.45	11329.07	0.31	4941.20	0.12	775.06	0.13	3444.10	0.22

P1 = between the San Lorenzo Islands and the Frontón (12 ° 5'16.57 "S; 77 ° 11'52.03" W) and it was located in C1, space destined to the extraction and cultivation of molluscs , P2 = in front of IMARPE (Instituto del Mar del Perú) (12 ° 3'56.20 "S; 77 ° 9'30.70" W) and it was located in B1 space destined to the recreation of primary contact, P3 = area of influence of the Callao Wharf (12 ° 2'34.10 "S; 77 ° 9'15.40" W), and it was located in C3, space destined to marine port, industrial or sanitation activities.

The As and Zn BCFsediment showed significant differences in P1 ($p = 0.009$, $p = 0.01$; respectively), the Ba sediment in P3 ($p = 0.04$). The Ni sediment BCF presented significant differences in P2 ($p = 0.02$) and its water BCF in P3 ($p = 0.010$), while the Se sediment BCF presented significant differences in zone 1 ($p < 0.05$).

3.5. Integrated correlation analysis

Cu in *T. chocolata* was positively correlated with Sb, As, Co, Cu, Mg, Ag, and V of the sediment; on the other hand, the Hg in *T. chocolata* was negatively correlated with Na, K, Mo, Mg, Ca, Sr and Li of the surface water. By season, Ni, Li, Hg, and Se in marine snails showed significant differences.

The Cd in *T. chocolata* was positively correlated with TDS ($r = 0.75$, $p < 0.01$) and negatively with turbidity ($r = - 0.85$, $p < 0.05$) and ammonium (r = - 0, 90, $p < 0.05$). As in *T. chocolata* was positively correlated with sediment Cd ($r = 0.84$; $p < 0.01$).

EC was positively correlated with Hg in *T. chocolata* ($r = 0.78$; $p < 0.01$) and with Hg in water ($r = 0.82$; <0.01), while Hg in water was negatively correlated with Ni in water ($r = - 0.85$; $p < 0.01$), ammonia ($r = -0.83$; <0.01) and nitrates (r = -0.81; p <0, 01). Sediment As was positively correlated with Cu ($r = 0.75$; $p < 0.01$), Ba ($r = 0.96$; $p < 0.01$) and sediment Zn ($r = 0.73$; $p < 0.01$) and negatively with dissolved oxygen ($r = -0.85$; $p < 0.01$). In the sediment, Cu was positively correlated with Pb ($r = 0.83$, $p < 0.01$), Zn ($r = 0.80$; $p < 0.01$) and Ba of the sediment ($r = 0.74$; $p < 0.01$).

4. Discussion

4.1 Water Characteristics

The lowest pH and temperature values in the water of Callao Bay were found during the winter season. The pH values are related to temperature, decomposition of organic matter, the influence of the influx of water, among others [36]. Ammonia concentrations only during this season did not exceed the recommended standard concentration. They represent a low risk of acute or chronic toxic effects in slightly or moderately disturbed systems ($0.46\ mg.L^{-1}$) [37]. Because the water quality in P1, P2, and P3 mainly presented low concentrations of DO and since P3 does not have regulations for ammonia, but it presented higher values than in P1 and P2 than if they exceed their standard concentrations [38], There is low quality of the water in the Bay of Callao due to DO, nitrates and ammonia.

In the estuary's surface waters that comprise the mouth of the Chillón River and Márquez Beach, high concentrations of ammonia (21 $mg.L^{-1}$) were found. In the study, Ammonia values in P3, the evaluation zone closest to the mouth of the Chillón River, ranged from 0.45 to 3.77. Likewise, in an evaluation of the concentration of metals in a space located in the zone of mineral concentrates warehouses that adjoin the port of Callao, it was found that all concentrations of As (179 to 500) and Pb (956 to 2695) are higher than the EQS (140 and 800, respectively), while the Cd concentrations (6.63 to 62.41) were higher than the EQS [22] in most of the areas evaluated. These concentrations reinforce the theory that the contamination in Callao Bay comes from the discharge of the Chillón River and mineral concentrates [1].

4.2. Heavy metals in the muscle of T. chocolata

In the *T. chocolata* muscle from the Bay of Callao, high concentrations of macroelements (> 3400 $mg.kg^{-1}$) were found, such as Na, Ca, K, Mg, and P; and microelements (> 35 $mg.Kg^{-1}$), such as Fe and Zn, which are essential elements [39]. Gastropod molluscs have strategies for regulating and accumulating metals; Cu and Zn are stored in granules, making them necessary to monitor these metals in the marine environment [39]. The present study found mean concentrations of Cu and Zn in *T. chocolata* muscle (53.6 $mg.Kg^{-1}$ and 111.9 $mg.Kg^{-1}$, respectively). Additionally, only P1 presented Cu values below the permissible limits of the Brazilian quality standard for molluscs, which indicates less contamination of this element and highlights the importance of T. chocolata for monitoring this metal.

Compared to studies of metal concentration in Argopecten purpuratus and Aulacomya ater on the coast of Perú, Cd, Hg, and Pb in *T. chocolata* in Callao Bay were always higher [16]. The average concentrations of Cu, Pb, and Zn in *T. chocolata* from the Bahía de San Jorge in Chile were lower than those reported in the present study [22]. Regarding other studies of metal concentration in *T. chocolata* carried out in Huarmey, Paracas and Moquegua and Tacna, the average concentrations of Cd, Cu, Pb and Zn in *T. chocolata* from the Bay of Callao were consistently higher, except Cu in Moquegua and Tacna [19-20, 24].

Additionally, the mean As, Cd, Cr, Hg, Pb, and Se concentrations in *T. chocolata* muscle in P1 exceeded different environmental quality standards [31-33). Because P1 is an area destined for the extraction and cultivation of molluscs, *T. chocolata* is a species consumed in the country, and the high concentrations of heavy metals in food represent a severe problem to people's health; the consumption of This mollusc from Callao bay would be a severe health problem for people [18, 25, 40].

4.3 Bioconcentration Factors

Most of the sediment BCF in *T. chocolata* from Callao Bay resulted <1, as did Cu and Zn sediment BCF in various benthic organisms from San Jorge Bay, Chile [21). Likewise, it was observed that the highest concentration of Cd in *T. chocolata* muscle (10.77 $mg.kg^{-1}$) occurred in the area with the lowest concentration of this metal in the sediment (3.43 $mg.kg^{-1}$) and reaching a sediment BCF = 3.12, demonstrating a relationship of inverse proportionality sediment - *T. chocolata*. Some species of molluscs can accumulate Cd from water in the form of binding peptides until reaching concentration values of 100 to 1000 ug kg^{-1}, likewise, it has been observed that the bivalve *Ostrea edulis* presents a lower permeability that restricts the entry of pollutants in specimens of environments contaminated against samples from clean environments [40 -41]. Therefore, the high accumulation of Cd in *T. chocolata* in P1 could be due to strategies of collecting Cd in water added to a possible high permeability of the specimens that inhabit this area, allowing a more significant accumulation of Cd in their tissues.

The high correlation values between metals both in the sediment and in the water in our study area suggest that familiar sources and/or similar processes could govern the behavior of these metals [42]. One of the pairs of metals that presented a high and significant correlation ($r = 0.80$, <0.01) were Cu and Zn and this may be due to the use of anti-fouling paints for boats based on Cu/Zn that are They have been used since the prohibition of antifouling paints based on organotin in the late 1980s [43]. These antifouling paints typically contain Zn and Cu in the range of 15-30% [43]. On the other hand, the Pb/Zn pair also presented a high and significant correlation ($r = 0.76$) in this study; the literature records that the presence of these two metals in marine sediments is related to vehicle emissions associated with high traffic conditions [43].

The grouping between the Pb, Cd of water and the Pb and Cd of the sediment indicate that the sources of contamination of these metals to the bay of Callao are closely linked. Studies suggest that Cd and Pb contamination can come from industrial activity and mining [44]; Furthermore, high concentrations of these metals have been found in an area of mineral concentrates warehouses located very close to the study area. Therefore, various sources of anthropic contamination would determine the contamination by Cd and Pb in the sediment and water of the Callao bay.

5. Conclusions

The bay of Callao presents low quality for DO and nitrates. The elements with the highest average concentrations in the muscle of *T. chocolata* showed the following relationship: Mg> Na> Ca> K> P> Fe> Zn. In addition, the average concentrations of As, Cd, Cu, Cr, Hg, Pb, and Se in all zones and stations exceeded the minimum limit concentration among the regulations consulted, except for the average of Cu in P1. Likewise, the water BCF and sediment BCF of As (5333.97 and 0.76) and Cd (2366.78 and 0.81) were found among the highest values. It is concluded that the consumption of *T. chocolata* from the bay of Callao would be a severe problem for people's health.

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References

[1] APROCALLAO. Calidad del agua de mar en la Bahía del Callao. Informe anual del monitoreo de efluentes y cuerpo marino receptor. Callao, 2006.

[2] GRC (Gobierno Regional del Callao). Plan de Desarrollo Concertado 2011-2021. Callao, 2011.

[3] F.A. Tejada, A.M. Fernández and C. M. Mejía. Big Bang Faustiniano, 5, 10 (2016).

[4] J. Rosas and J. Iannacone. Cienc. del Suelo. 38, 343 (2020).

[5] M.S. Islam, M.K. Ahmed, M. Habibullah-Al-Mamun and M. F. Hoque. Environ. Earth Sci. 73, 1837 (2015).

[6] M.K. Ahmed, M.A. Baki, M.S. Islam, G.K. Kundu, S.K. Sarkar and M.M. Hossain. Environ. Sci. Pollut. Res. 22, 20 (2015)

[7] MINAGRI. Protocolo Nacional para el Monitoreo de la Calidad de los Recursos Hídricos Superficiales, Lima, 2016.

[8] M. K. Ahmed, N. Shaheen, M. S. Islam, M. Habibullah-Al-Mamun, S. Islam and C. P. Banu. Environ. Monit. Assess. 187, 6 (2015).

[9] Z. Peñafiel-Sandoval and J. Iannacone. Agron. Colomb. 38, 251 (2020).

[10] K. Sekabira, H. Oryem-Origa, T. A. Basamba, G. Mutumba and Kakudidi, E. Int. J. Environ. Sci. Technol. 7, 435 (2010).

[11] C. Zhang, Q. Qiao, J. D. A. Piper and B. Huang. Environ. Pollut. 159, 3057 (2011).

[12] J. Bai, R. Xiao, B. Cui, K. Zhang, Q. Wang, X. Liu, H. Gao and L. Huang. Environ. Pollut. 159, 817 (2011).

[13] T. Grigoratos, C. Samara, D. Voutsa, E. Manoli and A. Kouras. Environ. Sci. Pollut. Res. 21, 7708 (2014).

[14] J. A. R. Martin, C. D. Arana, J. J. Ramos-Miras, C. Gil and R. Bluda. Environ. Pollut. 196: 156 (2015).

[15] T. G. Krupnova, I.V. Mashkova, A. M. Kostryukova, E.E. Schelkanova and S.V. Gavrilkina. Ecol. Indic. 95, 1001 (2018).

[16] F. Baroudi, J. A. Alam, Z. Fajloun and M. Millet. Ecol. Indic.113, 106240 (2020).

[17] M. Barriga-Sánchez and D. Aranda-Pariasca. Ecol. Apl. 17, 56 (2018).

[18] Í, Braga-Castro and G. Fillmann. Environ. Toxicol. Chem. 31, 955 (2012).

[19] S. Alfaro. Bol Inst Mar Perú. 35, 19 (2016).

[20] M. Guzmán, J. Chávez, O. Morón, S. Sánchez and Flores, G. Inf. Progr. Inst. Mar Perú, 54, 3 (1997).

[21] M. E Jacinto and S. Aguilar. Rev. Perú. Biol. 14, 307 (2007).

[22] C. Calderón and J. Valdés. Rev. Biol. Mar. Oceanogr. 47, 121 (2012).

[23] J. Valdés, M. Guiñez, A. Castillo and S. E. Vega. Cienc Mar, 40, 45 (2014).

[24] S. Enrique, A. Guabloche, E. Tuesta, J. Iannacone and I.B. Castro. Reg. Stud. Mar. Sci. 26, 100510 (2019).

[25] F. Cárdenas, R. Pastor, D. Baldárrago, V. Castañeda and Y. Romucho. Inf. Inst. Mar. 42, 122 (2015).

[26] USEPA. Method 200.7: Determination of metals and trace elements in water and wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry. Revision 4.4. USEPA, Cincinnati, 1994.

[27] INVEMAR. Manual de técnicas analíticas para la determinación de parámetros fisicoquímicos y contaminantes marinos (aguas, sedimentos y organismos), Cargraphics, Santa Marta, 2003.

[28] USEPA. Method 245.1: Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry. Revision 3.0. USEPA, Cincinnati, 1994.

[29] H. Karadede and E. Ünlü. Environmental Monitoring Assessment, 131, 323 (2007).

[30] USEPA. Method 7471B (SW-846): Mercury in solid or semisolid wastes (Manual Cold-Vapor Technique). Revision 2. USEPA, Cincinnati, 2007.

[31] CA (Codex Alimentarius). Norma general para los contaminantes y las toxinas presentes en los alimentos y piensos. Codex Stan 193-1995. [Revisada en 1997, 2006, 2008, 2009 Enmendada en 2010, 2012, 2013,2014, 2015, 2016, 2017, 2018, 2019], 1995.

[32] FSANZ. Standard 1.4. 1-Contaminants and Natural Toxicants, 2011.

[33] MICT (Ministerio de Industria, Comercio y Turismo). Contenidos máximos en metales pesados en productos alimenticios, Unión Europea, 2017.

[34] W. Fu, A. Franco and S. Trapp. Environ. Toxicol. Chem. 28, 1372 (2009).

[35] H. Kim and J. G. Kim. Sci. Total Environ. 610–611, 1210 (2018).
[36] A. Sundaraman, T. Sivakumar, R. Kumaran, V. Ammaiappan and R. Velappan. Int. J. Environ. Sci. Technol. 1, 1 (2007).
[37] G. E. Batley and S. L. Simpson. Mar. Pollut. Bull. 58, 1472 (2009).
[38] MINAM. D.S. N° 003-2017-MINAM. Aprueban Estándares de Calidad Ambiental (ECA) para Aire, 2017.
[39] G. Bonanno, J. Brg and V. Di Martino. Sci. Total Environ, 576: 796 (2017).
[40] Y. C. Reyes, I. Vergara, O. E. Torres, M. Díaz and E. E. Gonzáles. Ing. Investig. Desarro. 16, 66 (2016).
[41] E. R. Baqueiro-Cárdenas, L. Borabe, C.G. Goldaracena-Islas and J. Rodríguez-Navarro. Rev. Mex. Biodivers. 78, 1 (2007).
[42] J. Gibert, D. C. Culver, M. J. Dole-Olivier, F. Malard, M. C. Christman and L. Deharveng. Freshw. Biol. 54, 930 (2009).
[43] J. M. Guerra-García and J.C. García-Gómez. J. Environ. Manage. 77, 1 (2005).
[44] U. Aleksander-Kwaterczak and E. Helios-Rybicka. J. Soils Sediments. 9, 13 (2009).