Assessment of heavy metals in the muscle of cage-cultured tilapia (*Oreochromis spp*) from ake Güija and its correlation with levels in water and sediment.

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Abstract - Lake Güija, located between El Salvador and Guatemala, is a transboundary exorheic lake, several studies indicate the presence of heavy metals in significant concentrations. This research was conducted with the objective of evaluating the presence and concentration of the heavy metals arsenic, cadmium, chromium, and lead (As, Cd, Cr, Pb) in water, sediment, and tilapia muscle. It also aimed to determine their relationship and the suitability of the fish produced in Lake Güija for consumption. To this end, samples were taken at five production points, and were analyzed in triplicate using atomic absorption spectrophotometry. Additionally, in situ physicochemical parameters were measured in water.

The results indicate that, among the analyzed samples, tilapia muscle only showed detectable concentrations of As and Pb. However, the values are within the safe intake limits, in the water, only chromium and lead were detected. Furthermore, based on data analysis using Eh-pH diagrams, it was possible to identify the present species favored the accumulation of solid species in the sediment. Thus, the species present in the sediments are likely to correspond to arsenate (As^{5+}), cadmium carbonates ($CdCO_3$) and sulfides (CdS), chromium hydroxides ($Cr(OH)_3$), and lead hydroxides ($Pb(OH)_2$).

Keywords: Lake, heavy metals, tilapia, sediment, water.

1 Introduction

Aquaculture in El Salvador began in 1962 with the establishment of freshwater fish farming stations, as part of a government initiative for agricultural diversification supported by the Food and Agriculture Organization of the United Nations (FAO). Over the decades, various tilapia species—including *Oreochromis mossambicus, O. niloticus, O. melanopleura, and O. hornorum*—have been introduced into the country, becoming a key source of animal protein (FAO, 2021).

Due to its adaptability, low production cost, and resilience to adverse environmental conditions, tilapia has driven the growth of aquaculture in developing countries such as El Salvador (CENDEPESCA, 2008). However, as tilapia production has increased, so too have concerns about heavy metal contamination in the aquatic systems where it is farmed—particularly in water bodies like Lake Güija. This ecosystem has been affected by domestic, agricultural, and industrial discharges that have elevated the presence of toxic elements such as arsenic (As), cadmium (Cd), chromium (Cr), and lead (Pb) in both water and sediments. The potential for mining activities in the lake's watershed poses an additional threat, as it could further raise the concentrations of these pollutants, compromising aquatic biodiversity and the food security of populations that rely on fish as a dietary staple (MARN et al., 2008).

One of the main concerns is the bioaccumulation of these heavy metals in tilapia, which could present risks to human health and disrupt the ecological balance of the system. The transfer of these contaminants through the food chain may significantly impact higher organisms and degrade the quality of fishery resources (Espinoza & Falero, 2015). Despite its importance, there remains a knowledge gap in Lake Güija regarding the concentrations of these metals in water, sediments, and tilapia tissues, as well as their interrelationships—making environmental and health risk assessments more difficult.

To address this issue, the present study focused on evaluating the concentrations of As, Cd, Cr, and Pb in water, sediment, and cage-cultured tilapia tissue samples from Lake Güija. Analyses were conducted using atomic absorption spectrophotometry with a graphite furnace for Cd, Cr, and Pb, and a hydride generation module for As.

2 Materials and methods

2.1 Study area

Lake Güija is located within the municipalities of Metapán and San Antonio Pajonal in the department of Santa Ana (El Salvador), and the municipality of Asunción Mita in the department of Jutiapa (Guatemala), between the geographical coordinates 4° 6' 58" N, 89° 4' 54.95" W and 4° 4' 79" N, 89° 8' 5" W, at an elevation of 420 meters above sea level (Figure 1). The lake has a surface area of 42 km², a perimeter of 56 km, and a maximum depth of 25 meters. It receives inflow from three main tributaries: the Angue, Ostúa, and Cusmapa rivers and has one outflow, the El Desagüe river. The following map shows the location of lake Güija in El Salvador, along the border region with Guatemala (PREPAC, OIRSA, 2006).

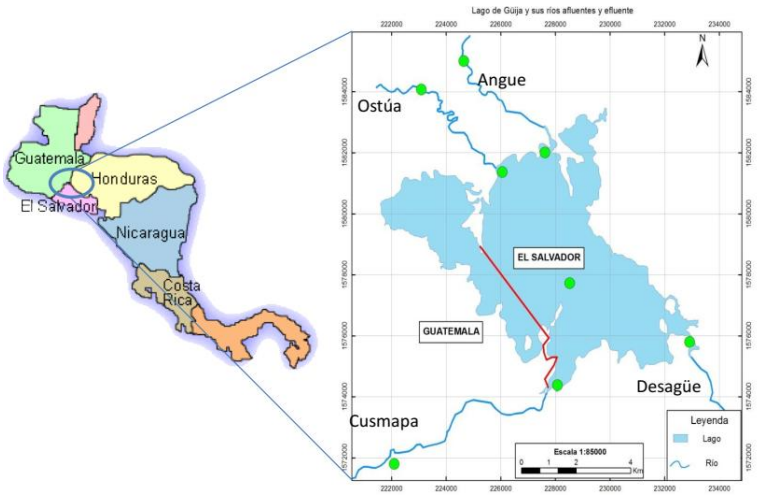

Figure 1. *Location of lake Güija and Its tributary and outflow rivers.*

A reconnaissance visit was conducted at lake Güija, assisted by satellite imagery from Google Earth to observe the clustering of fish cages, complemented by input from local residents. The purpose was to identify the location and arrangement of the tilapia farming cages and to assess their suitability, both in terms of the willingness of locals to allow sampling and the compliance of tilapia sizes with standards for human consumption.

In certain sites, sampling was not permitted due to conditions such as empty cages, denial of access by cage administrators, or the presence of undersized tilapia.

This study employed a convenience sampling method—a non-probabilistic technique—in which site selection was based on criteria such as the number of producers, the quantity of cages, and the availability of producers to provide samples, similar to the approaches used by Hernández Orellana (2022) and Picado Pavón et al. (2024). A total of five sampling points were established, with a single sampling campaign carried out on May 15, 2024.

Figure 2 shows the five sampling sites where the highest concentration of cages meeting the sampling criteria were located. Two sites were selected from the southwestern side and three from the northeastern side of Lake Güija. Coordinates for each site were recorded using a GPS device, and Table 1 provides detailed information for each location.

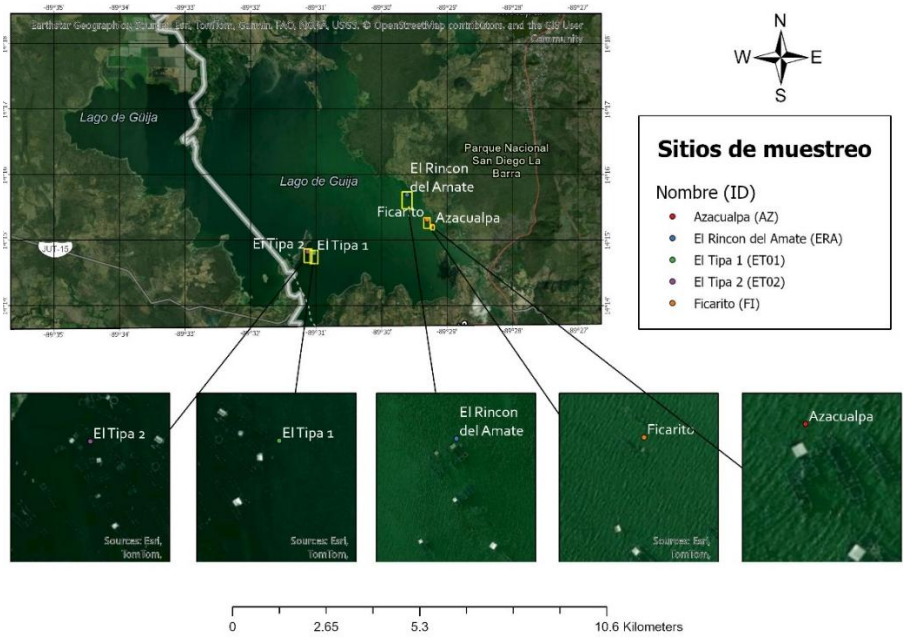

Figure 2. *Map of tilapia cage sampling sites in lake Güija overlaid on satellite imagery (Google Earth).*

Table 1. *Geographic location of sampling sites and designation of tilapia production zones.*

Site Name	Identifier	Coordinate X	Coordinate Y	Elevation (msnm)
El Tipa 1	ET01	14.246791	-89.517157	428
El Tipa 2	ET02	14.247121	-89.518722	430
El Rincón del Amate	ERA	14.261568	-89.493480	435
Azacualpa	AZ	14.253744	-89.487059	433
Ficarito	FI	14.255252	-89.488337	437

2.2 Sample collection

Water Sampling

Water sampling was conducted following the methodology described by (Díaz Vargas et al., 2005; Picado Pavón et al., 2024), which focuses on the determination of heavy metals in both surface and deep lake waters. At each sampling site, two water samples were collected at a point adjacent to the tilapia farming cages: one at a depth of 0.5 meters below the surface and another 0.5 meters above the bottom. These samples were taken in triplicate and adjusted according to the depth of the site, ensuring careful handling to avoid sediment resuspension and potential sample contamination. A high-quality water sampler, made of acrylic glass and 304 stainless steel with a capacity of 2 liters, was used. One liter of each sample was transferred into pre-washed polyethylene bottles for laboratory analysis, while the remaining volume was used for in situ measurement of physicochemical parameters, including temperature, pH, electrical conductivity, total dissolved solids, dissolved oxygen, salinity, and oxidation-reduction potential.

Sediment Sampling

Following the collection of both surface and deep water samples, sediment sampling was carried out in accordance with the methodologies described by (Díaz Vargas et al., 2005; Picado Pavón et al., 2024). For this purpose, a Fieldmaster Mighty Grab dredge (Wildco brand) was used to collect 1 kg of sediment sample.
Excess water retained by the dredge along with the sediment was discarded, and the remaining material was transferred into a plastic tray. Using a stainless steel spatula and forceps, non-sediment debris (such as rocks, shells, and trash) was carefully removed, and the cleaned sample was then placed into a sealed zipper-lock bag and stored in a cooler a temperature of approximately ±4 °C.

Tilapia Sampling

At each sampling site, and with the support of the cage operators, three tilapia specimens were randomly collected that met the appropriate size for human consumption, corresponding to 12 to 16 weeks of their production cycle. This process was performed in triplicate, resulting in a total of nine tilapia per site (Picado Pavón et al., 2024). The specimens were placed in zipper-lock bags and stored in a cooler a temperature of approximately ±4 °C.

2.3 Sample preparation

Digestion of Water Samples (Wet Digestion)

The procedure was carried out following Method 3030 E from the Standard Methods (APHA, AWWA, WEF, 2017). A 100.0 mL aliquot of the water sample was transferred to a 250 mL beaker. Then, 5.0 mL of concentrated nitric acid (HNO_3) was added, and the solution was brought to a boil for 10 minutes. The digest was filtered using Whatman No. 42 filter paper into a 100.0 mL volumetric flask, and the final volume was adjusted with osmotic water.

Preparation of Sediment Samples

The sediment samples were processed following the procedure described by (Picado Pavón et al., 2024). Using a stainless steel spatula, the samples were spread into plastic trays for drying. The trays were then placed in a circulating air oven at 25 °C for three days, ensuring the complete evaporation of moisture.

Once dried, the samples were inspected, and extraneous materials such as snails, stones, wood fragments, or other unrelated debris were removed. The samples were then ground using a mortar and pestle and passed through a 0.50 mm sieve. Finally, the processed sediments were stored in 50 mL plastic tubes and placed in a desiccator until analysis.

Sediment Sample Digestion (Microwave-Assisted Digestion)

This procedure was performed using Method EPA 3051A (USEPA, 2007). A Multiwave GO Plus microwave digestion system (Anton Paar brand) was employed. A 0.50 g portion of each sediment sample was weighed on an analytical balance and placed into microwave-grade Teflon vessels. Then, 10.0 mL of concentrated nitric acid was added, the vessels were sealed, and microwave digestion was carried out under the conditions specified by EPA Method 3051A. After digestion, the samples were transferred to 50.0 mL volumetric flasks and brought to volume with osmotic water.

Preparation of Tialpia Samples

The tilapia samples were processed following the procedure described by (Picado Pavón et al., 2024). The specimens were thoroughly rinsed with distilled water to remove sediment and debris. Using a stainless steel spatula, scales and viscera were removed from each fish, after which the entire muscle tissue was filleted with

stainless steel knives. Each muscle fillet was weighed in glass Petri dishes and then placed in a circulating air oven at 60 °C for 24 hours to obtain partially dried samples.

These samples were subsequently ground and homogenized using an IKA TUBE-MILL 100 at 10,000 rpm for 1 minute. The homogenized material was weighed in Petri dishes and placed in a vacuum oven at 105 °C for 5 hours to achieve complete dryness. Finally, the dried samples were stored in 50 mL plastic tubes and placed in a desiccator until analysis.

Tilapia Sample Digestion (Microwave-Assisted Digestion)

The digestion process was performed following EPA Method 3051A (USEPA, 2007), using a Multiwave GO Plus microwave digestion system (Anton Paar brand). A 0.50 g portion of each sample was weighed on an analytical balance into microwave-grade teflon vessels. Then, 10.0 mL of concentrated nitric acid was added, and the digestion was carried out under the conditions specified by EPA 3051A. After the digestion period, the digests were transferred into 50.0 mL volumetric flasks and brought to volume with osmotic water.

2.4 Atomic Absorption Spectroscopy

To determine the concentrations of cadmium (Cd), chromium (Cr), and lead (Pb), atomic absorption spectrophotometry was used with a graphite furnace module. For arsenic (As), a hydride generation system (HVG-1, Shimadzu brand) was employed. These analyses were conducted on water samples (surface and depth), sediment, and tilapia tissue. Concentrations of As, Cd, Cr, and Pb were identified for each matrix: Tp (Tilapia muscle), Sd (Sediment), AgS (Surface Water), and AgP (Bottom Water). Finally, the obtained results were compared against national and international reference standards for water, sediment, and tilapia muscle tissue to assess compliance with permissible limits.

3 Results

Physicochemical field parameters

The water temperature values measured at the surface and bottom indicate stratification within the water column. Surface temperatures ranged from 31.3 °C to 31.7 °C, with an average of 32.6 °C, while bottom water temperatures varied between 29 °C and 30.1 °C, averaging 33 °C, resulting in a mean reduction of 0.4 °C.

The pH values across all sampling sites indicate that the lake water is alkaline. This parameter shows a similar trend to temperature, decreasing with depth. Surface pH values ranged from 8.92 to 9.02, suggesting a slightly

more alkaline environment, whereas bottom pH values ranged from 8.54 to 8.73. Dissolved oxygen (DO) levels showed surface concentrations between 7.3 mg/L and 8.4 mg/L, while bottom concentrations ranged from 5.49 mg/L to 6.24 mg/L, reflecting reduced oxygen availability with increasing depth. Total dissolved solids (TDS) in surface water were slightly lower than in bottom water, generally ranging between 126.2 and 129.5 mg/L. Exceptions were noted at sites ET01 and ERA, where surface values marginally exceeded those at depth (126.5–129.6 mg/L). Unlike temperature, pH, and DO, TDS did not exhibit a consistent trend between surface and bottom layers.

Surface salinity remained at 0.13 % across all sites except FI, which measured 0.17 %. At depth, salinity ranged from 0.13 % to 0.18 %, with site AZ showing the highest concentration. Electrical conductivity (EC) varied between surface and bottom layers across different sampling points. Surface EC ranged from 280 to 408 µS/cm, with the northeastern sites (ERA, AZ, FI) registering higher values compared to the southeastern sites (ET01, ET02), except for ET01 due to inflow of dissolved materials. In contrast, bottom EC values were more stable, ranging between 295 and 319 µS/cm. Surface oxidation-reduction potential (ORP) values ranged from 113 to 201 mV, while bottom values ranged from 119 to 256 mV, indicating higher redox activity in deeper waters—likely due to decomposing organic matter and other active chemical processes. The corresponding data are presented in Table 2.

Table 2. *Physicochemical characterization of surface and bottom waters in lake Güija, El Salvador.*

		Parameter							
	Sampling Site	Temperature (°C)	pH	EC (µS/cm)	TDS (mg/L)	DO (mg/L)	DO (%)	Salinity (%)	ORP (mV)
Surface water	ET01	31.6	8.96	1280	554	7.44	107.5	0.54	201
	ET02	31.5	8.92	302	126.8	7.3	104.8	0.13	113
	ERA	31.7	8.96	982	423	7.75	111.8	0.42	194
	AZ	31.3	9.01	331	149.3	8	114.6	1.52	191
	FI	31.4	9.02	408	126.2	8.4	120.6	0.17	178
	max	31.7	9.02	1280	554	8.4	120.6	1.52	201
	min	31.3	8.92	302	126.2	7.3	104.8	0.13	113
Botton water	ET01	29	8.71	2106	126.5	6.24	88.8	0.93	256
	ET02	29	8.7	292	127.3	6.12	85.5	0.59	119
	ERA	30.1	8.73	304	129.1	6.17	86.8	0.13	201

	AZ	29	8.54	656	129.6	5.49	77.3	0.28	188
	FI	29	8.66	319	129	6.04	85.1	0.14	202
	max	30.1	8.73	2106	129.6	6.24	88.8	0.93	256
	min	29	8.54	292	126.5	5.49	77.3	0.13	119

Heavy metal concentrations in tilapia muscle, sediment, surface water, and bottom water in Lake Güija

Tables 3 and 4 present the concentrations of As, Cd, Cr, and Pb (mg/L) found in both surface and bottom water samples collected near the tilapia production cages in Lake Güija. These tables include average concentrations, standard deviations, and minimum and maximum values.

Table 3. *Heavy metal concentrations in surface water*

Metal	Sampling Site	Sample (mg/L)			Average (mg/L)	Standard Deviation	Extreme Values	
		1	2	3			Min	Max
Arsenic (mg/L)	ET01	<0.001	<0.001	<0.001	-	-	-	-
	ET02	<0.001	<0.001	<0.001	-	-	-	-
	ERA	<0.001	<0.001	<0.001	-	-	-	-
	AZ	<0.001	<0.001	<0.001	-	-	-	-
	FI	<0.001	<0.001	<0.001	-	-	-	-
Cadmium (mg/L)	ET01	<0.001	<0.001	<0.001	-	-	-	-
	ET02	<0.001	<0.001	<0.001	-	-	-	-
	ERA	<0.001	<0.001	<0.001	-	-	-	-
	AZ	<0.001	<0.001	<0.001	-	-	-	-
	FI	<0.001	<0.001	<0.001	-	-	-	-
Cromium (mg/L)	ET01	0.002	0.002	0.002	0.0020	0.0001	0.0019	0.0021
	ET02	0.004	0.004	0.004	0.0041	0.0004	0.0037	0.0045
	ERA	0.003	0.001	0.003	0.0025	0.0012	0.0011	0.0033
	AZ	0.002	0.002	0.002	0.0017	0.0001	0.0017	0.0018
	FI	0.002	0.004	0.004	0.0029	0.0011	0.0016	0.0035
Lead (mg/L)	ET01	0.006	0.006	0.006	0.0058	0.0001	0.0057	0.0059
	ET02	0.004	0.004	0.004	0.0040	0.0004	0.0037	0.0045
	ERA	0.003	0.004	0.004	0.0039	0.0006	0.0032	0.0043
	AZ	0.006	0.005	0.005	0.0053	0.0006	0.0049	0.0060
	FI	0.005	0.005	0.005	0.0050	0.0000	0.0050	0.0051

able 4. *Heavy metal concentrations in bottom water*

Metal	Sampling Site	Sample (mg/L)			Average (mg/L)	Standard Deviation	Extreme Values	
		1	2	3			Min	Max
Arsenic (mg/L)	ET01	<0.001	<0.001	<0.001	-	-	-	-
	ET02	<0.001	<0.001	<0.001	-	-	-	-
	ERA	<0.001	<0.001	<0.001	-	-	-	-
	AZ	<0.001	<0.001	<0.001	-	-	-	-
	FI	<0.001	<0.001	<0.001	-	-	-	-
Cadmium (mg/L)	ET01	<0.001	<0.001	<0.001	-	-	-	-
	ET02	<0.001	<0.001	<0.001	-	-	-	-
	ERA	<0.001	<0.001	<0.001	-	-	-	-
	AZ	<0.001	<0.001	<0.001	-	-	-	-
	FI	<0.001	<0.001	<0.001	-	-	-	-
Cromium (mg/L)	ET01	0.003	0.005	0.004	0.0040	0.0007	0.0032	0.0045
	ET02	0.001	0.004	0.001	0.0016	0.0017	0.0006	0.0035
	ERA	0.003	0.002	0.002	0.0023	0.0003	0.0020	0.0025
	AZ	0.001	0.001	0.001	0.0010	0.0003	0.0006	0.0012
	FI	0.001	0.001	0.001	0.0011	0.0004	0.0006	0.0013
Lead (mg/L)	ET01	0.003	0.004	0.004	0.0038	0.0006	0.0031	0.0044
	ET02	0.004	0.005	0.004	0.0041	0.0006	0.0037	0.0048
	ERA	0.004	0.006	0.004	0.0049	0.0009	0.0044	0.0060
	AZ	0.002	0.002	0.002	0.0022	0.0002	0.0020	0.0025
	FI	0.003	0.004	0.004	0.0036	0.0007	0.0028	0.0041

Table 5 presents the concentrations of As, Cd, Cr, and Pb (in mg/kg) obtained from sediment samples collected near the tilapia production cages in Lake Güija, including average values, standard deviations, and minimum and maximum concentrations.

Table 5. *Heavy metal concentrations in sediments*

Metal	Sampling Site	Sample (mg/L)			Average (mg/L)	Standard Deviation	Extreme Values	
		1	2	3			Min	Max
Arsenic (mg/L)	ET01	4.9782	5.7403	5.0433	5.2539	0.4225	4.9782	5.7403
	ET02	6.3821	5.9988	6.1205	6.1671	0.1959	5.9988	6.3821
	ERA	5.5180	7.3458	5.9092	6.2577	0.9624	5.5180	7.3458
	AZ	6.7134	4.9937	6.5801	6.0957	0.9567	4.9937	6.7134

Cadmium (mg/L)	FI	6.4162	7.2850	6.5756	6.7589	0.4625	6.4162	7.2850
	ET01	1.2190	1.4461	1.4488	1.3713	0.1319	1.2190	1.4488
	ET02	0.6230	0.6192	0.6178	0.6200	0.0027	0.6178	0.6230
	ERA	0.4122	0.3311	0.3330	0.3588	0.0463	0.3311	0.4122
	AZ	0.3122	0.3331	0.3140	0.3197	0.0116	0.3122	0.3331
Cromium (mg/L)	FI	0.5294	0.5220	0.5219	0.5244	0.0043	0.5219	0.5294
	ET01	30.7928	30.9725	30.5193	30.7615	0.2282	30.5193	30.9725
	ET02	28.7639	23.2146	24.6441	25.5409	2.8813	23.2146	28.7639
	ERA	28.2239	26.3491	26.9283	27.1671	0.9600	26.3491	28.2239
	AZ	29.9150	32.3988	31.0559	31.1232	1.2433	29.9150	32.3988
Lead (mg/L)	FI	26.6473	25.5322	26.2067	26.1287	0.5616	25.5322	26.6473
	ET01	12.6271	11.8471	11.8894	12.1212	0.4386	11.8471	12.6271
	ET02	11.1259	11.6600	11.2197	11.3352	0.2852	11.1259	11.6600
	ERA	13.7137	11.9229	13.5496	13.0621	0.9900	11.9229	13.7137
	AZ	14.4377	14.6874	14.6683	14.5978	0.1390	14.4377	14.6874
	FI	12.6077	12.3503	12.5054	12.4878	0.1296	12.3503	12.6077

Table 6 presents the concentrations of As, Cd, Cr, and Pb in tilapia muscle, expressed in mg/kg (wet weight). The table includes average values, standard deviations, and minimum and maximum concentrations. As can be observed, no significant levels of cadmium or chromium were detected at any of the sampling sites, as all recorded concentrations were below the limit of quantification.

Table 6. *Heavy metal concentrations in tilapia muscle*

Metal *d.w.	Sampling Site	Sample (mg/L)			Average (mg/L)	Standard Deviation	Extreme Values	
		1	2	3			Min	Max
Arsenic (mg/L)	ET01	0.0233	0.0233	0.0288	0.0251	0.0032	0.0233	0.0288
	ET02	0.0335	0.0410	0.0310	0.0352	0.0052	0.0310	0.0410
	ERA	0.0306	0.0181	0.0174	0.0220	0.0074	0.0174	0.0306
	AZ	0.1438	0.1117	0.0931	0.1162	0.0257	0.0931	0.1438
	FI	0.1401	0.1546	0.1293	0.1413	0.0127	0.1293	0.1546
Cadmium (mg/L)	ET01	<0.05	<0.05	<0.05	-	-	-	-
	ET02	<0.05	<0.05	<0.05	-	-	-	-
	ERA	<0.05	<0.05	<0.05	-	-	-	-
	AZ	<0.05	<0.05	<0.05	-	-	-	-
	FI	<0.05	<0.05	<0.05	-	-	-	-
	ET01	<0.05	<0.05	<0.05	-	-	-	-

Cromium (mg/L)	ET02	<0.05	<0.05	<0.05	-	-	-	-
	ERA	<0.05	<0.05	<0.05	-	-	-	-
	AZ	<0.05	<0.05	<0.05	-	-	-	-
	FI	<0.05	<0.05	<0.05	-	-	-	-
Lead (mg/L)	ET01	0.0687	0.0731	0.0762	0.0727	0.0037	0.0687	0.0762
	ET02	0.0684	0.0762	0.0753	0.0733	0.0043	0.0684	0.0762
	ERA	0.0704	0.0515	0.0476	0.0565	0.0122	0.0476	0.0704
	AZ	0.0739	0.0653	0.0479	0.0624	0.0133	0.0479	0.0739
	FI	0.0450	0.0460	0.0492	0.0468	0.0022	0.0450	0.0492

*d.w: dry weight

4 Discussion

Evaluation of arsenic concentrations

Arsenic concentrations in both surface and bottom water were below the limit of quantification, in contrast to the sediment and tilapia muscle, which displayed measurable values.

These results are attributed to the oxidizing conditions prevailing in the aquatic system, as evidenced by oxidation-reduction potential (ORP) values ranging from 113 to 201 mV at the surface and 119 to 256 mV at depth (Figure 3). The ORP and pH levels of the water favor the formation of arsenate (As^{5+}), an inorganic species known for its strong affinity to adsorb onto sediment particles (Mandal & Suzuki, 2022).

According to these authors, in aerobic environments with active oxidation processes, arsenates become strongly adsorbed onto clay minerals, iron and manganese oxides/hydroxides, and organic matter. Under these conditions, arsenic tends to accumulate in the sediment and is removed from the water column through a natural "self-purification" mechanism. As noted by Oremland and Stolz (2000), arsenic is eliminated from the water column via adsorption to sediments or precipitation as less mobile compounds.

The influence of pH and redox conditions is critical, as they determine arsenic speciation and mobility in aquatic systems. With surface pH ranging from 8.92 to 9.02 and positive ORP values, the predominant arsenic species is $HAsO_4^{2-}$ (arsenate, inorganic form), as shown in the Eh–pH diagram of arsenic species (Figure 3). This arsenate form, as stated by Mandal & Suzuki (2022), has high affinity for sediment particles, which explains its absence in water and its accumulation in sediments. In bottom waters, although pH is slightly lower (8.54–8.73), it remains alkaline and, combined with higher ORP values (119 to 256 mV), $HAsO_4^{2-}$ also

predominates in this zone (Figure 3). The enhanced oxidation supports the formation and stability of arsenate, promoting its sediment adsorption and limiting its mobility into the water column.

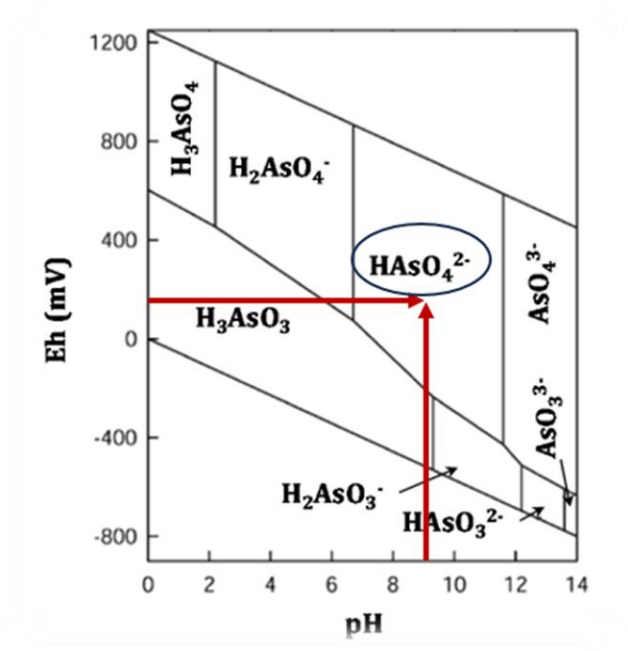

Figure 3. *Pourbaix diagram of arsenic species*
Modified from Smedley and Kinniburgh (2002).

Although arsenate is adsorbed onto sediments, it may be released in small quantities through biological processes or due to changes in lake conditions, such as stratification and mixing. This behavior is influenced by both chemical (pH and redox) and biological factors. According to Acharyya et al. (1999), microbial activity in the sediment can promote arsenic mobility and subsequent adsorption. These inorganic forms may be metabolized by organisms present in the lake, converting into organic compounds such as arsenobetaine, which tends to accumulate in tilapia tissue, primarily in the muscle. According to B´Hymer & Caruso (2004), arsenobetaine is considered non-toxic.

Given that data indicate the presence of arsenic in tilapia muscle, it is possible that the element is present as arsenobetaine (an organic compound), likely formed through the metabolization of arsenic-containing compounds ingested via the diet—though the specific mechanisms were not identified in this study. This suggests that arsenic may be entering the trophic web (Borak & Hosgood, 2007). These observations highlight

the complex interaction among redox conditions, arsenic chemical properties, and biological processes within the aquatic ecosystem.

Evaluation of cadmium concentrations

Cadmium concentrations were only detected in sediment samples, ranging from 0.3122 to 1.4488 mg/kg, with the highest levels recorded at site ET01, exceeding 1 mg/kg. In contrast, cadmium levels in tilapia muscle and in surface and bottom water were below the quantification limits of 0.05 mg/L and 0.001 mg/L, respectively. These findings support the observations reported by Banks et al. (2012), who noted that sediments function both as a sink and a source of Cd in aquatic systems.

Environmental factors such as redox state, pH, and concentrations of acid-volatile sulfides (AVS), iron (Fe), manganese (Mn), and dissolved organic matter (DOM) influence cadmium mobility in sediments. According to Ghavidel et al. (2018), a decrease in pH can lead to the dissolution of Cd from the solid phase and increase its concentration in the pore water. However, based on the pH values recorded in this study—8.92 to 9.02 at the surface and 8.54 to 8.73 at depth—the column of water in Lake Güija presents alkaline conditions that favor cadmium retention in sediments, preventing its release into the aqueous phase.

Stephenson et al. (1996) stated that under reducing conditions, Cd may be released into the water column. However, the lake exhibits oxidizing conditions, with ORP values ranging from 113 to 201 mV at the surface and 119 to 256 mV at depth. These conditions promote cadmium adsorption or co-precipitation with iron and manganese oxides and carbonates, thereby immobilizing Cd within the sediment (Banks et al., 2012; Du et al., 2009).

According to Frohne et al. (2011), a high concentration of sulfide (S^{2-}) in sediments may facilitate the precipitation of cadmium as cadmium sulfide (CdS), which is more likely than for other metals like Fe and Mn. S^{2-} preferentially precipitates Cd due to the extremely low solubility of CdS (8.0×10^{-27}). Under such conditions, and assuming the formation of insoluble compounds, cadmium in Lake Güija is likely to be present in inorganic forms—specifically as iron or manganese oxides, sulfides, or carbonates.

Chemical speciation diagrams of cadmium in freshwater (Figure 4) show that various inorganic forms emerge as pH increases, with cadmium chlorides and carbonates predominating. In oxic systems such as this one, cadmium would exist primarily as a free cation (Cd^{2+}). This explains the absence (i.e., non-quantification) of cadmium in water. Assuming a concentration of 1 mg/L in water, the log of its molar concentration

[8.9×10^{-6} mol/L] equals −5.05, supporting the lack of soluble cadmium in the water column and reinforcing the role of sediments as cadmium sinks under the conditions observed in this study.

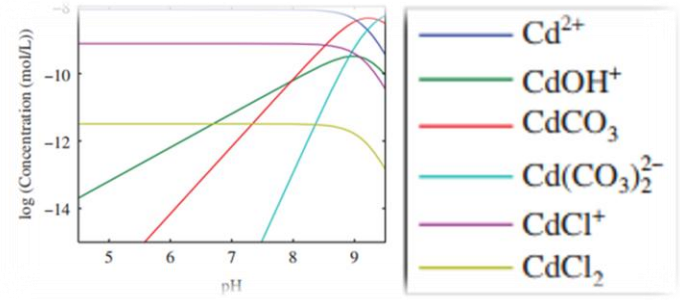

Figure 4. *Chemical speciation distribution diagrams for 1 mg/L of cadmium (Cd) in freshwater. Modified from Mcgeer et al. (2012)*

Under high salinity conditions, cadmium complexation with chloride becomes significant. However, although salinity was detected, the measured values were below 1%, ranging from 0.13% to 0.18% throughout the water column. Therefore, chloride levels are not sufficiently high to promote the formation of cadmium-chloride complexes. On the other hand, carbonate species emerge at elevated pH levels, as illustrated in the Eh–pH speciation diagram for cadmium (Figure 5). Based on the ORP and pH values obtained during sampling, the predominant inorganic cadmium species is likely cadmium carbonate ($CdCO_3$).

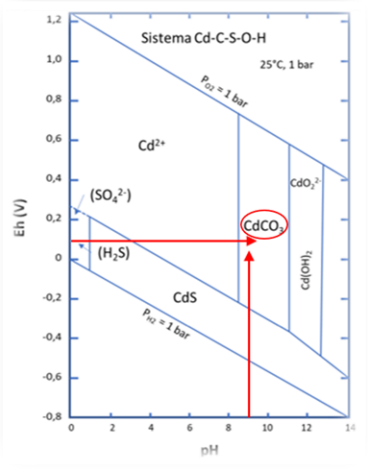

Figure 5. *Pourbaix diagram (Eh–pH) for cadmium Modified from Brookins (1988).*

In a study conducted by Das et al. (2023), cadmium bioaccumulation was induced in fish to improve genetic traits. The researchers found that in tilapia, cadmium accumulation was highest in the liver, followed by the gills and then the muscle tissue. They also observed that water salinity exerted a protective effect against cadmium toxicity in fish species. In the present study, the data indicate that cadmium is not mobilizing, and that the $CdCO_3$ species may persist even under reducing conditions, provided that alkaline pH levels are maintained. However, if cadmium has transformed into a form that can be bioaccumulated by tilapia, this study does not provide sufficient evidence to draw conclusions on that aspect

Evaluation of chromium concentrations

Chromium concentrations in tilapia muscle were below the limit of quantification, whereas sediment samples exhibited the highest levels, ranging from 23.2146 to 32.3988 mg/kg. In contrast, surface and bottom water samples showed much lower concentrations, between 0.0006 and 0.0045 mg/L, highlighting a pronounced difference between sediment and water matrices, with sediments acting as major accumulation zones for chromium. Chromium compounds exist primarily in trivalent (Cr^{3+}) and hexavalent (Cr^{6+}) forms, with Cr^{3+} being the more abundant species. The behavior of Cr^{3+} in aqueous environments is strongly influenced by the formation of oxides and hydroxides, and it tends to form stable complexes with both organic and inorganic ligands (Arauzo et al., 2003). Due to its limited solubility, Cr^{3+} readily precipitates under natural conditions, especially at neutral to alkaline pH. Once precipitated, it adsorbs onto suspended particles and accumulates in bottom sediments, making it less mobile, less soluble, and consequently less bioavailable in aquatic systems (USEPA, 1998). This explains the elevated concentrations observed in sediment compared to the water column in Lake Güija. Based on the measured pH values (8.92–9.02 at the surface and 8.54–8.73 at depth) and ORP values (113–201 mV at the surface and 119–256 mV at depth), speciation analysis using the Eh–pH diagram (Figure 6) indicates that the predominant species under these alkaline and oxidizing conditions is $Cr(OH)_3$ (trivalent chromium). According to Arauzo et al. (2003), this species likely dominates the aquatic system, and its precipitation explains the four orders of magnitude difference between sediment and water concentrations (10^1 in sediment vs. 10^{-3} in water). The predominance of Cr^{3+} is further supported by the non-detectable levels of chromium in tilapia muscle. As noted by Ghosh and Saha (2022), the relevance of studying this metal in tilapia lies in the fact that hexavalent chromium (Cr^{6+}) is bioaccumulative and poses carcinogenic risks to consumers.

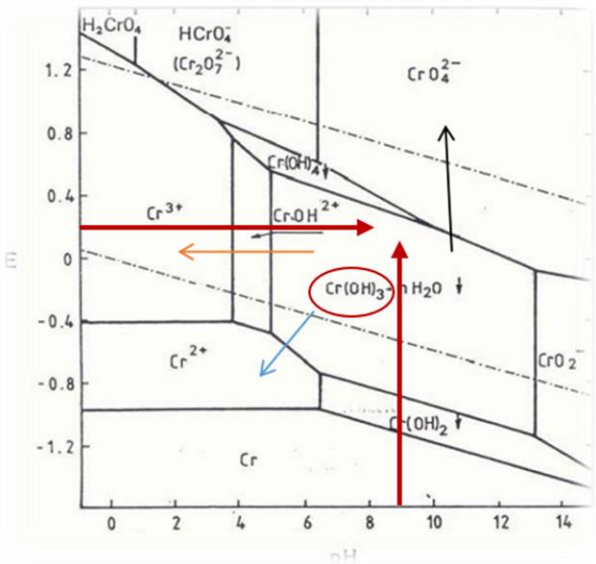

Figure 6. Pourbaix diagram (Eh–pH) for chromium
Modified from Blesa (2020).

Evaluation of lead concentrations

Lead was the only metal among those analyzed that was detected in all matrices—surface water, bottom water, tilapia muscle, and sediment. The lowest concentrations were found in water, while the highest were observed in sediment (10^{1} in sediment versus 10^{-3} in water), where lead tends to accumulate due to deposition and the formation of various metal complexes. Based on the measured pH values (8.92–9.02 at the surface and 8.54–8.73 at depth) and ORP values (113–201 mV at the surface and 119–256 mV at depth), the Eh–pH diagram (Figure 7) indicates that under these alkaline and oxidizing conditions, the predominant lead species is $Pb(OH)_2$, suggesting that Pb^{2+} is incorporated into the molecule.

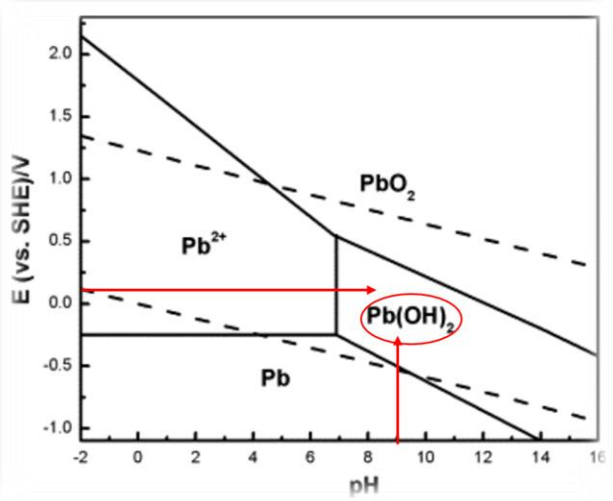

Figure 7. *Pourbaix diagram (Eh–pH) for lead*
Modified from Nikolaychuk (2018).

Figure 8 presents the predominance diagram of Pb^{2+} in aqueous media, showing that, under the pH conditions measured in this study, the predominant chemical species is $Pb(OH)_2$. This finding is consistent with the previously discussed Eh–pH diagram. $Pb(OH)_2$ is poorly soluble and tends to precipitate, which explains its accumulation in sediments and, consequently, the higher lead concentrations observed in that matrix.

Lead(II) hydroxide ($Pb(OH)_2$) is considered practically insoluble in water. Its solubility is governed by its solubility product (Ksp), which has an approximate value of 1.43×10^{-20} at 25 °C. This implies that, under normal conditions, only an extremely small amount of $Pb(OH)_2$ dissolves in water, forming Pb^{2+} and OH^- ions (Dean, 1999).

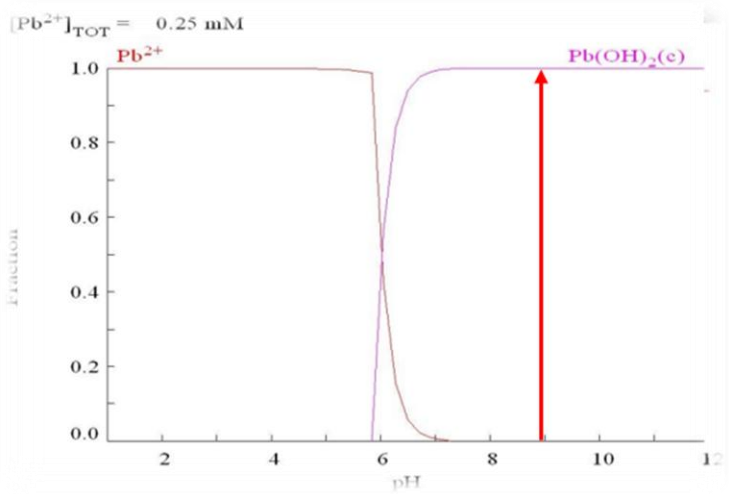

Figure 8. *Predominance diagram of Pb^{2+} species in aqueous media*
Modified from Hidalgo (2004).

According to its solubility product (Ksp), only a minimal fraction of lead becomes soluble in water, which explains the relatively low Pb concentrations in the water column compared to those found in sediment. Nevertheless, Pb^{2+} may still be bioavailable to fish. In addition to Pb^{2+} species that can exist at pH levels above 6, the predominance diagram indicates that at lower pH values (below 7) and under positive ORP conditions (as shown in Figure 57), Pb^{2+} exists as a free ion in water, prevailing over other species.

Under both conditions, fish are capable of absorbing Pb^{2+}, and through bioaccumulation processes, its concentration may increase in tissues—explaining the higher Pb levels observed in tilapia muscle compared to water (10^{-2} in tilapia vs. 10^{-3} in water).

The qualitative insights provided by Gale et al. (2002) may help explain the processes occurring in this system. The author suggests that most Pb found in fish samples originates from organic particles present in sediment, and even from contaminated fish that are subsequently consumed by others. Figure 9 illustrates how Pb^{2+} plays a central role in the generation of other lead species across environmental compartments.

In the atmosphere, Pb^{2+} binds to suspended particles; in water, it forms complexes with organic matter that may enter the trophic web via animals and plants. In soil, the species formed depend on aerobic or anaerobic conditions—resulting in $Pb(OH)_2$, $PbCO_3$, and PbO_2 under oxygenated conditions, and lead sulfides under anoxic conditions.

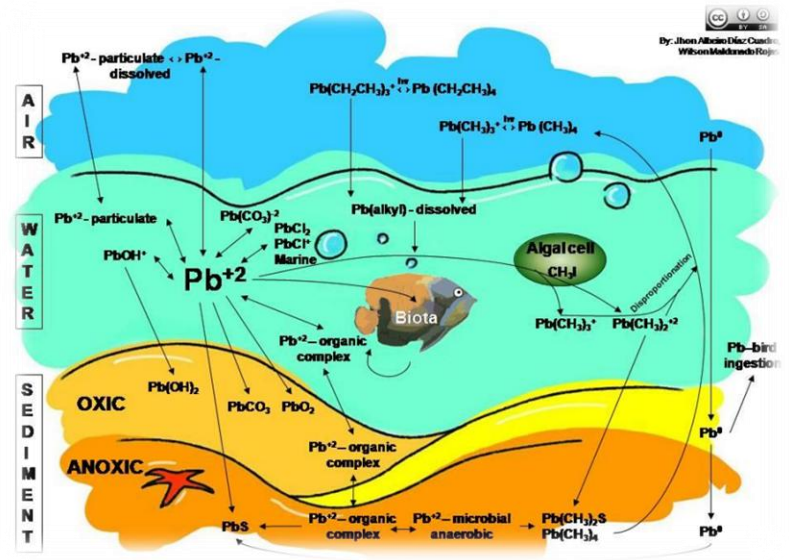

Figure 9. *Environmental dynamics of lead across air, soil, and water matrices, illustrating its transformation and mobility in different compartments.*

Adapted from Grupo de investigación en ciencia, educación, medio ambiente y desarrollo humano (2010).

4.1 Stadistical análisis

Descriptive statistics were performed for the heavy metal results, including mean, maximum and minimum values, and standard deviation. For the physicochemical parameters, data were tabulated and bar graphs were generated to compare surface and bottom water conditions.

Statistical software Infostat was used to conduct linear regressions and principal component analysis (PCA) in order to evaluate the relationships among the different matrices. Linear regression models were used to relate the dependent variable—metal concentration in tilapia muscle—with independent variables—metal concentrations in water and sediment. Additionally, metal concentrations in sediment were compared with those in both surface and bottom water to explore the exchange dynamics between these two phases. Analyses were conducted with a 95% confidence level and a 5% relative error margin.

The linear regression analysis of each variable is presented in Table 7. Results show no statistically significant correlations at the 95% confidence level between heavy metal concentrations in the different matrices analyzed—except for a single case. In particular, only lead (Pb) was evaluated for compartmental correlations, and the highest observed relationship—between muscle tissue and sediment—yielded a determination

coefficient (R^2) of just 0.13, with a statistical significance value of $p = 0.5534$. This indicates that the correlation is not significant and has limited explanatory power.

The only statistically significant correlation was identified between chromium (Cr) concentrations in sediment and surface water ($p = 0.0482$), with an R^2 of 0.78. This suggests a strong association between both matrices and may reflect a shared dynamic of exchange or accumulation between the surface water and sediment. It is important to note that, despite this relationship, the concentration of chromium in sediment is approximately four orders of magnitude higher than that found in surface water, indicating a notable retention or accumulation process in the substrate—similar to the behavior observed with the other metals.

Table 7 Linear regressions for As, Cd, Cr, and Pb concentrations in water, sediment, and tilapia tissue.

Relationship / Metal	p-value
Tp – Sd /As	0.2730
Sd – AgS /Cr	0.0482
Sd – AgP / Cr	0.5363
AgS – AgP / Cr	0.6726
Tp – Sd / Pb	0.5534
Tp – AgS / Pb	0.8709
Tp – AgP / Pb	0.9964
Sd – AgS / Pb	0.6601
Sd – AgP / Pb	0.2611
AgS – AgP / Pb	0.2489

A principal component analysis (PCA) was also performed to reduce the dimensionality of the dataset and identify the variables that significantly contribute to the total variation (Table 8).

Table 81. Eigenvalues for each principal component

Principal Component (PC)	Variance	Proportion	Cumulative Proportion
1	7.11	0.44	0.44
2	5.32	0.33	0.78
3	2.45	0.15	0.93
4	1.12	0.07	1

The eigenvalues represent the proportion of variance explained by each principal component. In this case, PC1 and PC2 account for the majority of variability in the dataset, explaining 44% and 33%, respectively. Together, they capture 78% of the total variance present in the original data.

Table 9. Eigenvectors for each principal component

Variables	e1	e2
AgS_pH	-0.30	0.19
AgS_CE	0.26	0.29
AgS_STD	0.26	0.28
AgS_OD	-0.28	0.07
AgS_Sal	-0.24	0.18
AgS_ORP	-0.06	0.37
AgP_pH	0.35	-0.06
AgP_CE	0.15	0.36
AgP_STD	-0.29	-0.07
AgP_OD	0.34	-0.02
AgP_Sal	0.22	0.15
AgP_ORP	0.05	0.41
AgS_Cr	0.24	-0.30
AgS_Pb	-0.20	0.31
AgP_Cr	0.25	0.29
AgP_Pb	0.29	-0.18

The eigenvectors e_1 and e_2 indicate the direction of each principal component—PC1 and PC2, respectively—and the extent to which they contribute to component variability. Positive values signify that the corresponding variables exert a positive influence on the principal component; as the variable increases, so does the component score. Conversely, negative values indicate a negative influence, meaning that an increase in the variable leads to a decrease in the principal component score. In Table 9, variables with positive influence are highlighted in blue, while those with negative influence are shown in orange.

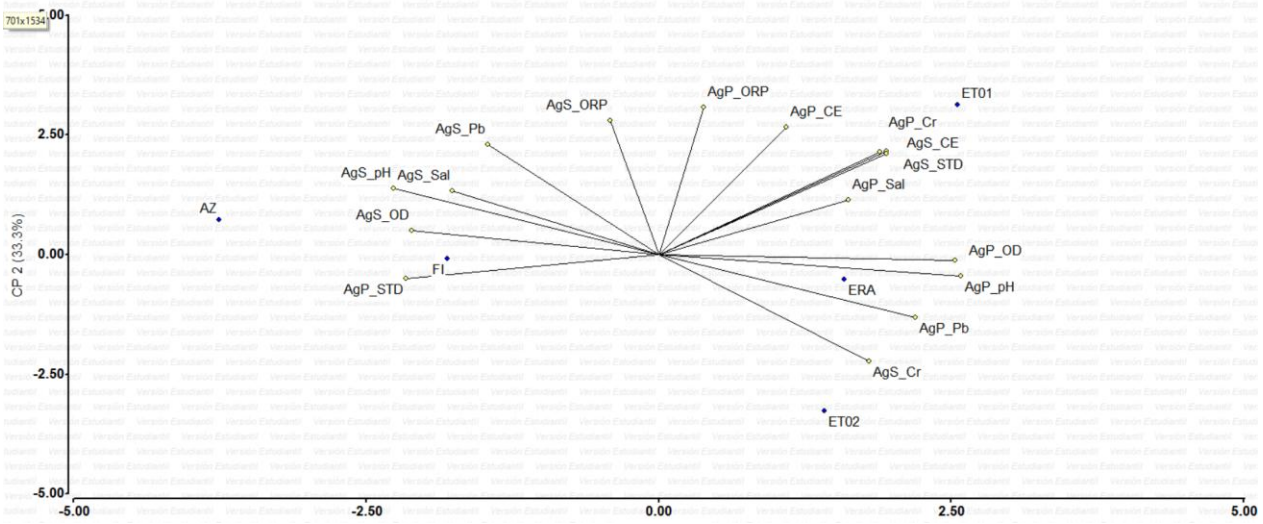

Figure 10. Principal Component Analysis of Heavy Metals and Physicochemical Parameters in Surface and Bottom Water

Under the conditions analyzed, the variables pH, dissolved oxygen (DO), and total dissolved solids (TDS), which comprise PC1, show a stronger correlation with phytoplankton presence (Parinet et al., 2004) and photosynthetic activity in the lentic system. This reflects a clear distinction between surface and bottom parameters and their influence on the principal component. PC2, on the other hand, is more closely associated with allochthonous variables (Cr, Pb) and the lake's self-purification capacity, represented by redox potential and the presence of heavy metals—which, as previously demonstrated, are considerably lower in concentration compared to other matrices.

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