



## **Distribution and assessment of the environmental risk of heavy metals in Aguada Blanca reservoir, Peru**

**ARTICLES** doi:10.4136/ambi-agua.2838

**Received: 22 Feb. 2022; Accepted: 06 Jun. 2022**

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### **ABSTRACT**

Sediments containing high concentrations of heavy metals in reservoirs, lakes and rivers, can resuspend into aquatic environments and negatively impact water quality. The concentrations of 10 elements were studied in surface sediments and water from the Aguada Blanca Reservoir, Peru, an important water source to 1,080,000 people in the arid province of Arequipa. Sediment and water samples were collected from nine points in 2019. The enrichment, accumulation, ecological risk and distribution of metals in sediment were determined, and the information on heavy metals in water was used to assess the quality of the aquatic system. Spatially, heavy metals showed variations throughout the study area, with an increase for most elements near the deepest part of the reservoir. The average concentration of Cd in sediment was 4 times higher than the natural background. In water, As was the only element that exceeded Peruvian regulations ( $As > 10 \mu\text{g L}^{-1}$ ). The Enrichment Factor (EF) and Geoaccumulation Index (Igeo) of metals in sediment presented the following order: Cd > As > Pb > Zn > Cu > Ni > Cr, with Ni and Cr being the only elements that did not present enrichment. The most considerable Igeo was Cd ( $1.21 \pm 1.45$ ), presenting a classification of moderately to heavily contaminated. The integrated potential ecological risk (RI) of Cd presented high values in 5 points of the reservoir. The information developed will assist in establishing effective control strategies for the quality of the aquatic system.

**Keywords:** heavy metals, reservoir, sediments, water quality.

### **Distribuição e avaliação do risco ambiental de metais pesados no reservatório Aguada Blanca, Peru**

#### **RESUMO**

Sedimentos contendo altas concentrações de metais pesados em reservatórios, lagos e rios, podem ressuspender no ambiente aquático e impactar negativamente na qualidade da água. A concentração de 10 elementos foi estudada em sedimentos superficiais e na água do reservatório Aguada Blanca, Peru, uma importante fonte de água para 1.080.000 pessoas na árida província de Arequipa. Foram determinados o enriquecimento, acúmulo, risco ecológico e distribuição de metais no sedimento, enquanto as informações de metais pesados na água foram utilizadas para corroborar a qualidade do sistema aquático. Amostras de sedimentos e água foram



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coletadas em nove pontos em 2019. Espacialmente, os metais pesados apresentaram variações ao longo da área de estudo com aumento para a maioria dos elementos próximos à parte mais profunda do reservatório. A concentração média de Cd no sedimento foi 4 vezes maior do que o fundo natural. Na água, o As foi o único elemento que ultrapassou as regulamentações peruanas ( $As > 10 \mu\text{g L}^{-1}$ ). O Fator de Enriquecimento (EF) e Índice de Geoacumulação ( $I_{\text{geo}}$ ) dos metais no sedimento apresentaram a seguinte ordem:  $Cd > As > Pb > Zn > Cu > Ni > Cr$ , sendo Ni e Cr os únicos elementos que não apresentaram enriquecimento. O  $I_{\text{geo}}$  mais expressivo foi o Cd ( $1.21 \pm 1.45$ ), apresentando uma classificação de moderada a fortemente contaminada. O risco ecológico potencial integrado (RI) do Cd apresentou valores elevados em 5 pontos do reservatório. Os resultados encontrados fornecem informações necessárias para estabelecer estratégias de controle sobre a qualidade do sistema aquático.

**Palavras-chave:** metais pesados, qualidade da água, reservatório, sedimentos.

## 1. INTRODUCTION

Reservoirs often present problems of heavy metal accumulation due to sediment retention behind reservoirs (Hahn *et al.*, 2018; Kondolf *et al.*, 2014; Vukovic *et al.*, 2014), which results in contamination or reduction of the quality of the water (Varol, 2013). The accumulation of heavy metals in aquatic systems can lead to human health risks and deterioration of aquatic ecology (Hahn *et al.*, 2018; Hou *et al.*, 2013). Therefore, the accumulation of metals in sediments is the subject of environmental studies in much of the world by environmental researchers (Hou *et al.*, 2013; Marziali *et al.*, 2017).

Reservoirs are of great economic importance because they supply water to the population, agricultural and industrial activities, among others (Schleiss *et al.*, 2016; Yasarer and Sturm, 2016). Therefore, water quality must be monitored because heavy metals are non-biodegradable, persistent, bio accumulative elements and with a tendency to enter the food chain (Keshavarzi and Kumar, 2019). The existence of heavy metals in water bodies is the result of anthropogenic activities and natural processes such as rock weathering and volcanic activities, with aquatic environments being the most susceptible to the negative effects of heavy metal pollution (Hahn *et al.*, 2018; Hou *et al.*, 2013; Keshavarzi and Kumar, 2019).

Sediments are important reservoirs of trace elements and could exchange cations with the aquatic environment, and over time contribute pollutants into the water column due to their constant contact (Yahaya *et al.*, 2012). Trace element concentrations in sediments become a problem when they are enriched above natural background levels due to contamination, which may create a threat to the aquatic environment (Olatunde *et al.*, 2014).

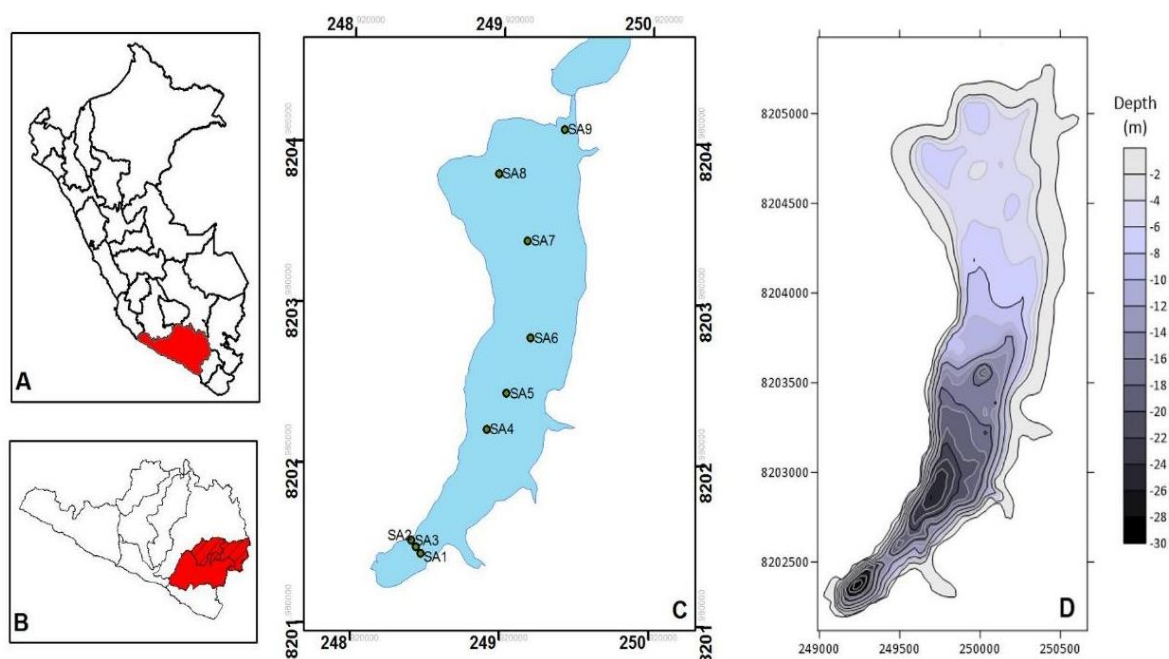
Knowing the concentrations and distribution of heavy metals are very useful to determine the degree of contamination of aquatic environments and provide the necessary information for environmental health risk assessment (Li *et al.*, 2019). The indices commonly used to assess heavy metal contamination in sediments are the Enrichment Factor (EF), the Geoaccumulation Index ( $I_{\text{geo}}$ ) and Integrated Potential Ecological Risk Index (RI) (Barbieri, 2016; Decena *et al.*, 2018).

The present study was carried out in the Aguada Blanca Reservoir, located at 3650 m.a.s.l in the Arequipa region of southern Peru. An important water source to 1,080,000 people in the arid Arequipa province. This reservoir has had sediment removal problems since 1989 due to the inoperability of the discharge gate, promoting sediment accumulation until today (ANA, 2016), which could generate a problem for water quality. This research evaluated the enrichment, geoaccumulation, potential ecological risk, distribution of metals in the reservoir and the relationship between the concentration of metals in sediment and reservoir water.

## 2. MATERIAL AND METHODS

### 2.1. Study area

The Aguada Blanca Reservoir is located in the south of the Republic of Peru, in the Arequipa region (Figure 1, A-B), on the slopes of the Misti and Chachani volcanoes about 27 km from the city of Arequipa (19K, 248920 E, 820498 S and 250920 E, 8204980 S). The reservoir is 3.2 km long with an average width of 0.5 km and a maximum depth of 30 m (Figure 1, C-D). The surface of the reservoir is 1.73 km<sup>2</sup> and accumulates approximately 30 million m<sup>3</sup> of water. The function of Aguada Blanca Reservoir is to receive, regulate and distribute the water from six other reservoirs (the Chalchuanca, the Dique de los Españoles, the Bamputañe, the El Pañe, the El Frayle and the Pillones), which feeds the Chili River Basin and supplies water to 1,080,000 people in the city of Arequipa.



**Figure 1.** Study area: A). Republic of Peru, B) Arequipa Region, C) Aguada Blanca Reservoir with sampling points, D) Depth of the reservoir.

### 2.2. Sampling collections and analysis

Sediment and water samples were collected at 9 points in the reservoir (water entry zones, middle zone and reservoir zone), in the months of April, July and October 2019, which were averaged. The water samples were taken with a 250 mL Niskin bottle between 0.5 to 1 meter above the sediment (CCME, 2011), then surface sediment sampling was performed using a Lamotte model dredger (Cavanagh *et al.*, 1997). Sampling depth was determined using an Eagle Cuda 168 graphic echo sounder. The water samples were preserved with analytical grade nitric acid (1%) and deposited in bottles (0.25 L) and sediment samples were placed in polyethylene bags (1 Kg) to be transported to the laboratory in a cooler box with ice.

For the determination of heavy metals in sediment, we used the EPA 200.7 method (Inductively Coupled Plasma Optical Emission Spectrometry, ICP-OES, Perkin Elmer) and the EPA 200.8 method in water (Inductively Coupled Plasma Mass Spectrometry; ICP-MS, Agilent) (APHA *et al.*, 2005), for totals metals. Organic matter was determined using the ASTM D 2974-87 method (ASTM International, 2014), and the pH was determined by the APHA 4500-H + B electrometric method (APHA *et al.*, 2005) using an EXO 2 multiparameter probe (Xylem, USA).

### 2.3. Reagents and standards

All reagents were of analytical grade or Suprapure quality (Merck, Germany). Double deionized water was used for the preparation of all solutions. Standard solutions of elements used for calibration were prepared by diluting stock solutions of 1000 mg L<sup>-1</sup> of each element. The stock standard solutions were Merck Certificate standard. All glasswares used were cleaned by soaking in dilute nitric acid for at least 24 hours and were rinsed thoroughly in deionized water before use.

### 2.4. Quality control

The quality of the analytical data was assured through the application of quality methods and laboratory control. Method precision and quality control were verified by triplicate analysis of proficiency test material. Good agreement was observed between analytical results and certified values, with recovery percentages ranging from 97% (As) to 106% (Cd).

### 2.5. Sediment contamination assessment

#### 2.5.1. Enrichment factor

The enrichment factor (EF) is used to determine metal enrichment factors in sediments and soils, as well as to assess the presence and intensity of anthropogenic contaminant deposition on the land surface (Barbieri, 2016). The reference values used were those defined by Turekian and Wedopohl (1961), values widely used by different researchers worldwide. The EF calculation reflects the enrichment of metals in sediments in relation to iron (Fe), which was chosen as a stationary reference element to perform this calculation (Ekengele *et al.*, 2017), as seen in Equation 1.

$$EF = \frac{\left(\frac{M}{Fe}\right)_{sample}}{\left(\frac{M}{Fe}\right)_{Background}} \quad (1)$$

Where EF = Enrichment Factor;  $\left(\frac{M}{Fe}\right)_{sample}$  Is the ratio of metal/Fe in the sample; and  $\left(\frac{M}{Fe}\right)_{Background}$  is the metal/Fe ratio of the reference value. EF values are classified as follows: When EF <1 indicates no enrichment; 1 <EF <3 is low; 3 <EF <5 is moderate; 5 <EF <10 is moderately severe; 10 <EF <25 is severe; 25 <EF <50 is very serious; and EF > 50 is extremely severe (Acevedo-Figueroa *et al.*, 2006; Decena *et al.*, 2018).

#### 2.5.2. Geoaccumulation index (I<sub>geo</sub>)

The geo-accumulation index (I<sub>geo</sub>) was used to assess heavy metal contamination in sediments and is defined as follows (Equation 2) (Li *et al.*, 2019).

$$I_{geo} = \text{Log}_2 \frac{C}{kB} \quad (2)$$

Where: C: is the concentration of the sample; B: is the reference value; k: is the geoaccumulation constant (1.5). The I<sub>geo</sub> value of each heavy metal is classified into seven classes, from uncontaminated to extremely contaminated. Classification of heavy metal contamination according to I<sub>geo</sub> value: Class 0 (I<sub>geo</sub> <0), uncontaminated; Class 1 (0 < I<sub>geo</sub> ≤ 1), uncontaminated to moderately contaminated; Class 2 (1 < I<sub>geo</sub> ≤ 2), moderately contaminated; Class 3 (2 < I<sub>geo</sub> ≤ 3), Moderately to heavily polluted; Class 4 (3 < I<sub>geo</sub> ≤ 4), heavily contaminated; Class 5 (4 < I<sub>geo</sub> ≤ 5), strong to extremely contaminated; Class 6 (5 < I<sub>geo</sub> ≤ 10), extremely contaminated (Li *et al.*, 2019).

### 2.5.3. Ecological risk index

The potential ecological risk index (RI) is commonly used as a diagnostic tool to determine contamination in sediments, soils and waters due to the presence of metals in the environment. The RI is defined as the sum of the ecological risk index (RE) of each heavy metal, for which Equations 3 and 4 are shown (Hakanson, 1980; Miranzadeh Mahabadi *et al.*, 2020; Sun, 2017).

$$RE = T_r^i \times C_f^i \quad (3)$$

$$RI = \sum_{i=1}^N RE = \sum_{i=1}^N T_r^i \times C_f^i \quad (4)$$

Where:  $T_r^i$  is the toxic response factor of different heavy metals, the ecological values of Cd, Pb, Cu, Cr and Zn are 30, 5, 5, 2, 1.  $C_f^i = C_i/C_r^i$ : is the pollution coefficient of each heavy metal.  $C_r^i$ : is the concentration of each heavy metal.  $C_i$ : is the recommended value for heavy metal concentration in sediments and soils (Sun, 2017), Table 1.

**Table 1.** Potential ecological risk classification.

Level	Ecological Risk	
	RE	RI
Low	RE < 40	RI < 150
Moderate	40 < RE ≤ 80	150 < RI ≤ 300
Considerable	80 < RE ≤ 160	300 < RI ≤ 600
High	160 < RE ≤ 320	300 < RI ≤ 600
Very High	RE > 320	> 600

**Source:** Hakanson (1980); Sun (2017).

### 2.6. Analysis of data

A mean and standard deviation (SD) were determined for the entire reservoir for all parameters analyzed. Statistical analyses were performed with SPSS statistics v24 software; Pearson correlation analysis ( $p < 0.05$ ) was applied to assess the association between the concentration of metals in sediment and water. Spatial distribution graphs were made with the software Surfer Golden 16.

## 3. RESULTS AND DISCUSSION

### 3.1. Heavy metals, pH and organic matter

The heavy metal concentrations found for ten elements analyzed in sediments (mg d.w. Kg<sup>-1</sup>) are shown in Table 2, where the mean concentration of Cd ( $1.46 \pm 0.94$ ) and the concentrations of As ( $12.54 \pm 5.70$ ) and Pb ( $16.35 \pm 5.59$ ) in some points was higher in relation to values of study by Turekian and Wedepohl (1961), while Cr ( $7.73 \pm 2.16$ ), Sb ( $1.03 \pm 0.92$ ), Ni ( $7.96 \pm 2.86$ ), Cu ( $35.02 \pm 12.36$ ), Zn ( $45.63 \pm 13.60$ ) and Fe ( $12.984 \pm 4.195$ ) presented low values. Cd is characterized by presenting high concentrations in sediments from various parts of the world (Cáceres Choque *et al.*, 2013; El-Radaideh *et al.*, 2017; Vrhovnik *et al.*, 2013; Yahaya *et al.*, 2012), A source of entry of Cd into the environment is anthropogenic; however, the study area is far from the urban area and industrial activities. These high concentrations would be attributed to the geological characteristics of the area (Vargas, 1970), volcanic material and volcanic emissions (Hutton, 1983), since the reservoir is close to two volcanoes (Misti and Chachani). Another source could be atmospheric deposition (Cai *et al.*, 2019). The dynamics of sedimentation and the entry of pollutants is little known for the reservoir.



**Table 2.** Concentration of heavy metals in sediment (mg d.w. Kg<sup>-1</sup>), water (µg L<sup>-1</sup>), pH, organic matter (%) and depth (m) in Aguada Blanca Reservoir, Peru.

Matrix	Points	As	Cr	Cd	Pb	Sb	Ni	Cu	Zn	P	Fe	pH	OM	Depth
Sediment	SA1	20.60	11.05	1.64	22.96	2.80	12.06	48.40	58.80	1773	20000	6.22	5.30	28
	SA2	10.50	6.47	2.53	18.16	1.00	6.62	35.50	43.20	1016	14104	5.96	6.30	24
	SA3	19.50	8.67	0.33	20.76	0.30	10.14	44.30	61.40	408	13289	5.95	6.27	22
	SA4	18.30	8.72	0.34	20.41	0.30	10.34	44.70	63.10	416	12514	5.90	6.15	16
	SA5	13.80	10.68	1.42	18.72	2.30	10.61	46.40	49.70	1492	18255	6.47	4.75	16
	SA6	8.20	5.93	2.20	15.00	0.70	5.73	30.20	38.60	1008	12297	6.02	5.17	10
	SA7	8.80	6.21	2.16	16.28	1.00	5.93	32.50	37.70	954	11275	6.01	5.54	5
	SA8	8.00	6.90	0.20	7.93	0.20	6.53	20.20	35.10	255	7461	5.93	3.44	5
	SA9	5.20	4.91	2.28	6.91	0.70	3.69	13.00	23.10	287	7662	5.86	-	4
	Min	5.20	4.91	0.20	6.91	0.20	3.69	13.00	23.10	255	7461	5.86	3.44	-
	Max	20.60	11.05	2.53	22.96	2.80	12.06	48.40	63.10	1733	20000	6.47	6.30	-
	Mean	12.54	7.73	1.46	16.35	1.03	7.96	35.02	45.63	841	12984	6.04	5.37	-
	SD	5.70	2.16	0.94	5.59	0.92	2.86	12.36	13.60	537	4195	0.19	2.00	-
Water	SA1	9.44	0.30	0.03	0.20	0.20	0.56	1.70	16.65	-	220.80	8.41	-	28
	SA2	11.79	LOD	0.03	0.20	0.20	0.70	2.00	9.67	-	136.10	8.23	-	24
	SA3	10.92	LOD	LOD	LOD	0.20	0.39	1.90	19.83	-	102.90	8.36	-	22
	SA4	11.21	LOD	LOD	LOD	LOD	0.43	1.80	19.12	-	139.30	7.96	-	16
	SA5	7.37	0.50	0.21	0.60	0.20	0.55	1.60	15.98	-	302.00	8.55	-	16
	SA6	12.42	LOD	0.05	0.60	0.20	0.73	2.20	9.85	-	121.70	8.53	-	10
	SA7	120.70	LOD	LOD	0.20	0.20	0.60	1.70	212.50	-	115.60	8.48	-	5
	SA8	11.30	0.20	LOD	0.30	0.20	0.45	2.70	52.29	-	128.50	8.66	-	5
	SA9	138.30	LOD	LOD	0.20	0.20	0.58	1.80	11.92	-	106.40	8.43	-	4
	Min	7.37	0.20	0.03	0.20	0.20	0.39	1.60	9.67	-	102.90	7.96	-	-
	Max	138.30	0.50	0.21	0.60	0.20	0.73	2.70	212.50	-	302.00	8.66	-	-
	Mean	37.05	0.33	0.08	0.33	0.20	0.55	1.93	40.87	-	152.60	8.40	-	-
	SD	52.62	0.18	0.07	0.22	0.07	0.12	0.34	65.65	-	66.08	0.21	-	-

LOD: Limit of Detection – in water; LOD<sub>Cr</sub>=<0.20; LOD<sub>Cd</sub>=<0.03; LOD<sub>Pb</sub>=<0.10; LOD<sub>Sb</sub>=<0.10.

The sediments had a slightly acidic to neutral pH (5.86 to 6.47). This slight acidity would be explained by the geology of the study area, which is composed of volcanic rocks (Vargas, 1970). Low pH values prevent the adsorption of metals, since under acid conditions there are enough H<sup>+</sup> ions to bind to the surface of clay and organic matter (Adeniyi *et al.*, 2011), leaving metals available in the water; however, the slightly acidic to neutral pH (5.86 to 6.47) and the basic pH of the deep zone water (7.96 - 8.66) (Table 2), would promote the adsorption of metals.

Other factors influencing heavy metal adsorption are organic matter, anoxic conditions, high Fe and Mn concentrations and low temperatures (Li *et al.*, 2014). The study area presented a considerable percentage of organic matter in the sediments (3.44 - 6.30%), as well as low water temperatures of 7°C to 12°C, which makes these factors reduce the release of metals into water (Li *et al.*, 2014). The adsorption of metals by the sediment is corroborated by the low concentrations found in the water, with the exception of As (Table 2), which presents values above that established in Peruvian regulations, As > 10 µg L<sup>-1</sup> (ANA, 2016).

Heavy metal concentrations in water samples (µg L<sup>-1</sup>) presented the following order: Fe (152 ± 66.08) > Zn (40.87 ± 65.65) > As (37.05 ± 52.62) > Cu (1.93 ± 0.34) > Ni (0.55 ± 0.12) > Pb (0.33 ± 0.22) > Cr (0.33 ± 0.18) > Sb (0.20 ± 0.07) > Cd (0.08 ± 0.07). The results of this study show that the concentrations are high in comparison with the study of two lakes in the central region of Peru where As values were found: 4.2±0.9 µg L<sup>-1</sup>, for Lake Paca and 4.2±0.9 µg L<sup>-1</sup>, for Tragadero Lake (Custodio *et al.*, 2021). While in comparison with other international studies, the values of metals were notably high for As, in the case of Cr, Cu, Ni and Pb present low concentrations, while Cd is compatible with other results (see Table 3).

The high concentration of As in the water could be due to the weathering processes of the rocks, which would incorporate As into the aquatic system. This would be reflected in the considerable concentrations of As in the Aguada Blanca Reservoir (Prieto *et al.*, 2016). The concentrations of phosphorus (P) in the sediment would have two effects: it would make As highly available in the aquatic system due to its low adsorption by the sediment (Prieto *et al.*, 2016; Zhang and Selim, 2008), and it would reduce the availability of Cd in the water, as phosphorus works as an adsorption system avoiding its release into the water (Wang and Xing, 2004). This is reflected in the values in Table 2.

Table 4 shows the analyzed data, where a significant positive correlation is observed between the As in the sediment and the other elements in the sediment: Cr, Pb, Ni, Cu, Zn, Sb, and Fe.

The strong correlation of As with the other elements explains its high content in the study area and, consequently, said element would be available in the water. Statistically, no correlation is observed between the concentration of elements in sediment and in the water, possibly the low resuspension of elements in water influences the results.

### 3.2. Evaluation of sediment contamination

#### 3.2.1. Enrichment factor

The EF of each sampling point was calculated to determine the degree of enrichment in the reservoir sediment. The results are shown in Table 5. We observe that the degree of enrichment presents the following order: Cd (18.78 ± 14.89) > As (3.46 ± 1.14) > Pb (2.93 ± 0.58) > Zn (2.49 ± 0.62) > Cu (2.78 ± 0.57) > Ni (0.43 ± 0.11) > Cr (0.32 ± 0.07), where Ni and Cr, are elements that do not present enrichment, Cd presents different degrees of enrichment from moderate to very severe, while As, Pb, Zn and Cu had a low to moderate degree. An EF value between 0.5 - 1.5 (0.5 < EF < 1.5) indicate natural enrichment and values above 1.5 (EF > 1.5) are characterized by an anthropogenic enrichment (Zhang and Liu, 2002). The EF values in our study are low in relation to the EF values found by Cáceres Choque *et al.* (2013) from Lake Titicaca, which presents the following order Cd (14 - 519) > Pb (32 - 233) > Zn (10 - 162) > Co (6 - 71) > Cu (5 - 15) > Mn (3 - 10) > Ni (1 - 18), where we observe the predominance of Cd, Pb, Zn, Cu in presenting the higher enrichment values. The difference between EF values lies in low Fe values in Lake Titicaca in relation to our Fe concentration.

**Table 3.** Concentration of heavy metals ( $\mu\text{g L}^{-1}$ ) in water in other studies.

		As	Cd	Cr	Cu	Fe	Ni	Pb	Zn	Reference
Aguada Blanca Reservoir, Peru	Min	7.37	0.03	0.2	1.6	102.9	0.39	0.2	9.67	Present study
	Max	138.3	0.21	0.5	2.7	302	0.73	0.6	212.5	
	Mean	37.05	0.08	0.33	1.93	152.59	0.55	0.33	40.87	
Kralkızı Dam Reservoir	Mean	2.39	0.036	20.06	2.83	58.63	15.75	2.56	5.02	(Varol, 2013)
	Median	0.70	0.018	16.77	nd	51.28	9.78	0.59	4.01	
	Max	22.61	0.25	90.12	9.18	189.24	52.12	26.48	19.6	
Dicle Dam Reservoir	Mean	1.61	0.03	18.58	2.12	62.07	15.86	1.84	4.12	(Varol, 2013)
	Median	0.40	0.014	14.27	nd	55.73	9.99	0.34	2.72	
	Max	14.14	0.322	46.63	9.63	251.62	54.23	14.73	19.32	
Batman Dam Reservoir	Mean	0.71	0.044	16.5	nd	57.66	15.96	1.56	4.09	(Karadede and Ünlü, 2000)
	Median	0.36	nd	12.11	nd	63.11	12.01	0.38	3.45	
	Max	6.11	0.428	40.89	9.08	119.12	36.46	11.12	24.57	
Atatürk Dam Reservoir, Turkey		-	nd	-	25	62	15.4	nd	64	(Karadede and Ünlü, 2000)
Tigris River, Turkey		12.32	nd	48.58	4.52	159.46	17.32	22.03	3.62	(Varol, 2013)
Danjiangkou Reservoir, China		11.08	1.17	6.29	13.32	19.14	1.73	10.59	2.02	(Li <i>et al.</i> , 2008)
Alzate Reservoir, Mexico		-	-	79	70	6923	34	61	68	(Avila-Pérez <i>et al.</i> , 1999)
Reference values		13	0.3	90	45	46700	68	20	95	(Turekian and Wedepohl, 1961)

nd: not detected.



**Table 4.** Pearson correlation coefficients for elements in sediment and water in Aguada Blanca Reservoir, Peru.

Elements / matrix	As_S	As_W	Cr_S	Cr_W	Cd_S	Cd_W	Pb_S	Pb_W	Sb_S	Sb_W	Ni_S	Ni_W	Cu_S	Cu_W	Zn_S	Zn_W	Fe_S	Fe_W	
As_S	1																		
As_W	-0.572	1																	
Cr_S	0.845**	-0.598	1																
Cr_W	0.256	-0.366	0.728*	1															
Cd_S	-0.498	0.466	-0.414	-0.156	1														
Cd_W	0.073	-0.316	0.504	0.786*	0.133	1													
Pb_S	0.864**	-0.522	0.734*	0.181	-0.112	0.225	1												
Pb_W	-0.425	-0.151	-0.002	0.513	0.37	0.725*	-0.217	1											
Sb_S	0.344	-0.141	0.663	0.741*	0.348	0.604	0.464	0.364	1										
Sb_W	-0.379	0.184	-0.172	0.227	0.447	0.196	-0.272	0.438	0.300	1									
Ni_S	0.945**	-0.654	0.968**	0.541	-0.5	0.339	0.826**	-0.177	0.512	-0.312	1								
Ni_W	-0.522	0.175	-0.411	-0.126	0.915**	0.196	-0.104	0.569	0.269	0.401	-0.482	1							
Cu_S	0.889**	-0.606	0.854**	0.372	-0.255	0.381	0.969**	-0.123	0.502	-0.294	0.915**	-0.227	1						
Cu_W	-0.403	-0.283	-0.408	-0.168	-0.32	-0.334	-0.556	0.141	-0.559	0.147	-0.382	-0.049	-0.525	1					
Zn_S	0.968**	-0.661	0.799**	0.194	-0.528	0.111	0.894**	-0.374	0.231	-0.481	0.922**	-0.485	0.924**	-0.34	1				
Zn_W	-0.261	0.55	-0.254	-0.181	0.143	-0.236	-0.085	-0.11	-0.077	0.124	-0.262	0.033	-0.13	-0.114	-0.233	1			
Fe_S	0.700*	-0.508	0.837**	0.591	0.106	0.577	0.842**	0.179	0.839**	0.042	0.796*	0.11	0.866**	-0.578	0.666	-0.233	1		
Fe_W	0.355	-0.383	0.779*	0.932**	0.007	0.873**	0.401	0.498	0.833**	0.075	0.617	0.022	0.556	-0.42	0.325	-0.226	0.767*	1	

S: Sediment, W: Water.

\*\* . The correlation is significant at the 0.01 level (bilateral); \* . The correlation is significant at the 0.05 level (bilateral).

### 3.2.2. Geoaccumulation index evaluation ( $I_{geo}$ )

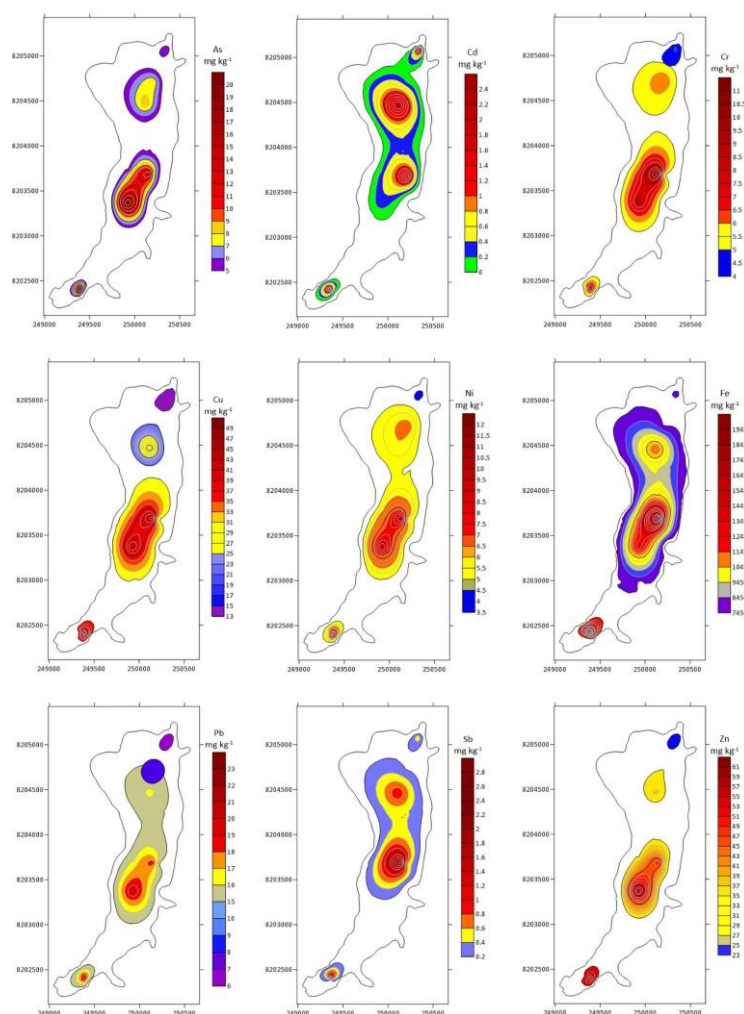
$I_{geo}$  values were calculated to determine contamination in the sediments of Aguada Blanca Reservoir. The results are shown in Table 5, where the Cd value ( $1.21 \pm 1.45$ ) presents values greater than 0 ( $I_{geo} > 0$ ), and presented a degree of contamination from moderately to heavily contaminated, while As ( $-0.78 \pm 0.69$ ), Pb ( $-0.98 \pm 0.62$ ), Cu ( $-1.05 \pm 0.64$ ), Zn ( $-1.71 \pm 0.47$ ) and Cr ( $-4.18 \pm 0.40$ ) do not present contamination for the reservoir. The high EF and  $I_{geo}$  of Cd would be a risk in the reservoir in relation to other evaluated elements, and compared to other studies, our Cd  $I_{geo}$  would be slightly higher (Abata, 2013; Ekengele *et al.*, 2017; Li *et al.*, 2018; Marziali *et al.*, 2017; Zhang *et al.*, 2017) and less equal to studies where the concentration of Cd is described as a strong anthropogenic effect (Cáceres Choque *et al.*, 2013; Çevik *et al.*, 2009; Li, 2014; Nowrouzi and Pour Khabbaz, 2014).

### 3.2.3. Ecological risk index

Table 5 shows the RI values of the sediment samples, and they present the following order of risk  $Cd > Cu > Pb > Zn > Cr$ . The RI value of Points SA3, SA4 and SA8 were less than 150, indicating that these points present a low ecological risk ( $<150$ ). While Points SA1, SA2, SA5, SA6, SA7 and SA9 presented values higher than 600, which means a high ecological risk due to the presence of heavy metals (see Table 5). The ER value of Cd is the one that most contributes to the ecological risk of the water body; an element that is characterized by increasing the risk in different investigations (Li, 2014; Mohamaden *et al.*, 2017).

### 3.3. Spatial distribution of metals

The Aguada Blanca Reservoir presents the highest concentrations of As, Sb, Cu, Ni, Zn, Fe, Cr and Pb in the narrow zone of the reservoir (dam - water outlet) and middle zone (Figure 2), zones characterized by greater depths and where the accumulation of sediments is greater. Therefore, there is a higher concentration of heavy metals (Colman *et al.*, 2011). High concentrations of heavy metals would be the result of deposition and low water flow velocities and where fine particles act as sinks (Palanques *et al.*, 2014). Figure 2 shows the spatial distribution of Cd, As, Pb, Cu, Ni, Zn, Cu, Fe and Sb along the Aguada Blanca Reservoir. According to the maps in Figure 2, it is observed that most of the elements present an increase in their concentrations as they approach the narrow zone of the reservoir (dam - water outlet) and the middle zone of the reservoir, with the exception of Cd, which does not present uniformity in its distribution.



**Figure 2.** Spatial distribution of heavy metals in sediments of Aguada Blanca Reservoir, Peru.

**Table 5.** EF,  $I_{geo}$ , RE and RI values in Aguada Blanca Reservoir.

Points	EF							$I_{geo}$							RE				RI	
	As	Cr	Cd	Pb	Ni	Cu	Zn	As	Cr	Cd	Pb	Ni	Cu	Zn	Cd	Cu	Pb	Zn		Cr
SA1	3.7	0.29	12.76	2.68	0.41	2.51	2.02	0.08	-3.61	1.87	-0.39	-3.08	-0.48	-1.28	586	10.08	4.45	0.93	0.33	601.5
SA2	2.72	0.3	12.11	2.39	0.4	2.64	1.87	-0.89	-4.38	2.49	-0.72	-3.95	-0.93	-1.72	904	7.4	3.52	0.68	0.2	915.4
SA3	2.67	0.24	27.92	3.01	0.32	2.61	2.1	0	-3.96	-0.45	-0.53	-3.33	-0.61	-1.21	118	9.23	4.02	0.97	0.26	132.3
SA4	2.4	0.25	27.85	2.85	0.32	2.55	2.16	-0.09	-3.95	-0.4	-0.56	-3.3	-0.59	-1.18	121	9.31	3.96	0.99	0.26	136
SA5	2.8	0.29	29.82	3.37	0.36	2.99	2.3	-0.5	-3.66	1.66	-0.68	-3.27	-0.54	-1.52	507	9.67	3.63	0.78	0.32	521.5
SA6	2.44	0.33	46.32	2.11	0.33	1.76	2.07	-1.25	-4.51	2.29	-1	-4.15	-1.16	-1.88	786	6.29	2.91	0.61	0.18	795.7
SA7	5.27	0.34	3.87	3.65	0.52	3.46	3.17	-1.15	-4.44	2.26	-0.88	-4.1	-1.05	-1.92	771	6.77	3.16	0.59	0.19	782.1
SA8	5.25	0.36	4.23	3.81	0.57	3.71	3.46	-1.29	-4.29	-1.17	-1.92	-3.97	-1.74	-2.02	50	4.21	1.54	0.55	0.21	56.51
SA9	3.85	0.48	4.17	2.48	0.6	2.81	3.23	-1.91	-4.78	2.34	-2.12	-4.79	-2.38	-2.62	814	2.71	1.34	0.36	0.15	818.9
Min	2.4	0.24	3.87	2.11	0.32	1.76	1.87	-1.91	-4.78	-1.17	-2.12	-4.79	-2.38	-2.62	50	2.71	1.34	0.36	0.15	56.51
Max	5.27	0.48	46.32	3.81	0.6	3.71	3.46	0.08	-3.61	2.49	-0.39	-3.08	-0.48	-1.18	904	10.08	4.45	0.99	0.33	915.4
Mean	3.46	0.32	18.78	2.93	0.43	2.78	2.49	-0.78	-4.18	1.21	-0.98	-3.77	-1.05	-1.71	517	7.3	3.17	0.72	0.23	528.9
SD	1.14	0.07	14.89	0.58	0.11	0.57	0.62	0.69	0.4	1.45	0.62	0.56	0.64	0.47	338	2.57	1.08	0.22	0.06	337.1

## 4. CONCLUSIONS

Sediment quality often reflects the current state of aquatic systems. This study used sediment quality indices to characterize the status of the Aguada Blanca Reservoir in relation to heavy metal concentrations.

According to the quality indices, the reservoir sediments are enriched by Cd, As and Pb, which present concentrations higher than background concentrations and the highest concentrations are distributed in the deeper areas of the reservoir. The high EF and  $I_{geo}$  values in Cd would make it a promoter of ecological risks for the aquatic system, if appropriate conditions are given for its availability and mobilization within the system, conditions that would not be currently present due to the low concentration of Cd in the water ( $0.08 \pm 0.07 \mu\text{g L}^{-1}$ ). As concentrations exceed Peruvian regulations and present high values in relation to other aquatic systems.

The results of this study underline that it is important to carry out further studies on the dynamics of mobilization of Cd and As to determine the possible risks to water quality under environmental and hydrological changes.

## 5. ACKNOWLEDGMENTS

The authors wish to thank Universidad Nacional de San Agustín de Arequipa. This research was funded by Universidad Nacional de San Agustín de Arequipa. Financing Contract N° TIM-002-2018-UNSA.

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