

# Heavy Metal Contamination and Ecological Risk Assessment in Fluvial Sediment of San Juan –Taxco River System in Mining Region of Taxco Guerrero, Mexico

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## Research Article

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## Abstract

The hydrological system of San Juan-Taxco Rivers is located inside of one of the oldest and major mining districts in Mexico. Several communities in the area use the rivers water along its flow for domestic water supply and crop irrigation. Sediment is an essential, integral and dynamic part of river basins, in polluted environments these act as sink of heavy metals and as a source of contaminants on the fluvial system. The management and sustainability of sediment should be assessed and secured to achieve good ecological status of the basins, for this task, approaches as ecological risk identification and geochemical indices are being used.

Superficial sediment samples were collected in San Juan-Taxco river system. The results demonstrated that the degree of pollution from thirteen heavy metals and metalloids studied decreases in the following sequence: Cd > Zn > Pb > Cu > As > B > Mn > Ni > Fe > Co > Ba > Al and Cr. Cd made the most dominant contribution. Geochemical indices revealed important external anthropogenic influences in the rivers. The geochemical indices indicated very high enrichment for As, Cu, Pb and Zn, and extremely high for Cd in the three-rivers. The calculation of Pollution Load Index (PLI) showed in Cacalotenago River and in Taxco River are the sites with the highly contaminated sediments. PLI values were very high in all the samples sites due mining tailings erosion, wastewater and agriculture run off. Cd, Zn, Pb, Cu and As were the main potential risk elements that will cause harmful biological effects in the riverine environment.

## 1. Introduction

Heavy metal pollution in the rivers systems is one of the major threats for aquatic life and human population due to the abundance, inherent toxicity, persistence, ubiquity, non-degradability, subsequent bioaccumulation and biomagnification in the food chain (Liu et al., 2016; Malvandi, 2017; Rodriguez et al., 2018). The concentration of heavy metals has increased in the environment due to their anthropogenic inputs. Numerous rivers have been polluted with heavy metals from industrial manufacturing processes and mining activities, especially from the inappropriate disposal of wastewater and mine tailings, resulting in negative effects (Morales et al., 2017; Singh and Kumar 2017).

Heavy metals and metalloids discharged into an aquatic ecosystem by both anthropogenic and natural sources; they are dispersed in the different compartments of these ecosystems, such as water, sediment and biota (Ali et al., 2016; Maanan et al., 2015). Once they enter the aquatic ecosystem, only an insignificant portion of free metal ions stay dissolved in water because of the particularities of heavy metals and metalloids, the rest gets deposited and stored in the sediments (Rodriguez et al., 2018; Hernandez et al., 2019). The sediments are an ecologically component of the aquatic system and play a main role in the transport and storage of potentially hazardous metals since they are a potential secondary source of pollutants in the water body (Zheng et al., 2013; Malvandi, 2017;). Metals confined in the sediments can release dissolved and particulate fractions to the water column via hydrodynamic disturbance, chemical and biological processes (Rodriguez et al., 2018).

The ecological risk assessment of river sediment is a suitable technique to investigate the metal contamination (Zahra et al., 2014; Morales et al., 2017; Siddiqui and Pandey, 2019). A number of geochemical indices have been developed and widely used to assess the metal contamination in sediments (Corami et al., 2020; Rodriguez et al., 2018; Morales et al 2017; Malvandi, 2017; Magesh et al., 2011). Geochemical indices such as geoaccumulation index (Igeo), enrichment factor (EF), pollution load index (PLI) to assess the metal contamination and sediment quality guidelines, ecotoxicological values as well as Potential ecological risk index (RI) had been developed to evaluate the ecological risk modelled by metals in sediments. These indices provide useful data that can be easily communicated to local managers and decision makers (Zhang et al., 2018; Siddiqui and Pandey, 2019).

San Juan-Taxco river system represent key resources in terms of providing water for drinking supply, mining industry and agricultural activities (Dotor et al., 2017). Furthermore, in urban areas the rivers usually receive wastewater and surface runoff discharges whilst maintaining recreational and conservation facilities. Mining has been the main economic activity in Taxco region, for five centuries. Ore extraction and heavy metal processing have created wastes posing an environmental threat to the area (Arcega et al., 2009).

The aim of this study was to assess the contamination status of the site through geochemical indices such as Geoaccumulation Index (Igeo), Enrichment factor (EF), Contamination Factor, Pollution Load Index (PLI) and their the potential ecological risk of these metals through Potential Ecological risk Index (PERI) to identify the possible sources of metals a cluster analysis was developed.

## 2. Study Area

The study area is located in the northern part of the state of Guerrero in the municipalities of Taxco and Iguala (Fig. 1). The study area belongs to the Medio Balsas Basin in the Hydrological Region No. 18 and the administrative region IV Balsas (INEGI, 2020). Within the study area is situated the mining district of Taxco recognized for years of mining and processing of precious metals since pre-Hispanic times. In 1522, Hernán Cortés opened in Taxco the first mine of Latin America called "Socavón del Rey" to exploit silver. Silver mining activities continued through the following centuries (Armienta et al., 2004).

The extraction of silver, the main activity of Taxco region, led its inhabitants to undertake the task of working this metal, and there appeared great artists and artisans that today characterize the oldest mining city in the American continent. Already in the 19th century, the silversmiths of Taxco

specialized in the manufacture of service pieces (such as plates, jugs, dishes and cutlery for the use of families with the highest purchasing power in the country), as well as objects for religious rites until today with the realization of pieces of jewelry of national distribution and exclusive pieces of export. From colonial times to the present day, in Taxco region silver companies have been familiar; this industry has been growing, becoming an artisan tradition in Mexico for more than 200 years (Clausell, 2010).

This has brought negative impacts on natural resources in the region, with rivers being the most affected resources by the waste from these activities (Talavera et al., 2016). The study area is composed by three rivers. The San Juan (length of 10 km), Cacalotenango (length of 11.5 km) and the Taxco (length of 29.3 km) rivers that jointly discharge at the southern portion of the city of Taxco, also in the town of Taxco el Viejo forming the Iguala or Cocula River (length 75 km), and finally discharging into the Infiernillo reservoir (Arcega et al., 2009; Dotor et al., 2014).

The San Juan River receives wastewater from nearby towns, chemical waste from silversmiths for the manufacture of silver crafts and mining tailings (Ramirez, 2013). The Cacalotenango River receives mine waste from La Concha and El Fraile tailings, and urban wastewater without treatment (Romero et al., 2007). The Taxco River receives mine waste from several tailing piles along its flow and receives untreated urban wastewater discharged from the city itself and surrounding localities (Dotor et al., 2014; 2017).

## 3. Materials And Methods

### 3.1. Sediment sample collection and analytical procedure

Seven surface sediment samples were collected in dry season in May of 2019, these samples were taken on San Juan river before its confluence with Taxco River, along the Cacalotenango and Taxco rivers and above and below of their confluence as shown Fig. 1. The samples were collected in plastic bags and kept at 4°C until further analysis. In the laboratory sediment samples were air-dried and ground to a fine powder with an agate mortar and then sieved through a 230 ASTM mesh at the Laboratory of Nutrition and Plant Physiology Campus Tuxpan of the Faculty of Agricultural and Environmental Sciences of the Autonomous University of Guerrero (UAGro).

For determining total metals contents, dry-sediment samples were digested in a 1:1 HCl: HNO<sub>3</sub> mixture inside a CEM MarxXpress microwave oven (Tessier et al. 1979). Metal quantification was conducted using an inductively coupled plasma optical emission Spectrometer Thermo iCAP 6500 Duo in the Environmental Geochemistry Laboratory of the National Autonomous University of Mexico (UNAM).

The grain size analysis was carried out and the sediment textural classes were deduced according to the Unified Soil Classification System (USCS), ASTM D2487-06 (2006). The measured results were classified into gravel, sand, silt and clay according to the sediment composition. The characterization of mineralogical phases in sediment samples was carried out by X-Ray diffraction, in a Bruker AXS D8 Advance diffractometer to identify the major minerals in sediments samples; this analysis was performed at the Geochemistry Laboratory of Regional School of Earth Sciences of the Autonomous University of Guerrero.

### 3.2. Assessment of sediment contamination

The metal concentrations were compared with the sediment quality guidelines of Canada and threshold effect concentration and probable effect concentration (TEC and PEC). These guidelines allowed a simple, comparative mean for assess the potential risk of pollution in a fluvial aquatic ecosystem (Table 1). The Canadian Sediment Quality Guidelines were designed for the assessment of potential risk, and to assist in determination of the relative priority of sediment quality concerns. The probable effect level threshold (PEL) explains the level above which adverse effects are expected to occur frequently (CCME 1999).

The concentrations below the TEC denote a minimal-effect range, which is considered to identify the contaminant concentrations (conditions) where biological effects are not expected; concentrations equal to or greater than the TEC, but less than the PEC indicate a range where biological effects not commonly occur. Concentrations at or above the PEC means a probable effect range where adverse biological effects often occur (MacDonald et al., 2000).

### 3.3. Assessment of metal enrichment in sediments

#### 3.3.1 Geoaccumulation index (Igeo)

The Index of geoaccumulation (Igeo) can be used to evaluate the environmental pollution status compared with geochemical background concentrations (Müller, 1969; Corami et al., 2020). The Igeo index is calculated by the following equation:

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where  $C_n$  is the content of elements in the sediment samples and  $C_{bn}$  is the concentration of geochemical background for the same elements (n). The background values of the studied elements used in the calculation this index is the same as those used in the calculation of the contamination factors (CFs) index. Factor 1.5 is the background matrix correction factor due to lithological variations. The Igeo index includes seven classes: Class

0 (uncontaminated):  $I_{geo} \leq 0$ ; Class 1 (Uncontaminated to moderately contaminated):  $0 \leq I_{geo} \leq 1$ ; Class 2 (moderately contaminated):  $1 \leq I_{geo} \leq 2$ ; Class 3 (moderately to heavily contaminated):  $2 \leq I_{geo} \leq 3$ ; Class 4 (heavily contaminated):  $3 \leq I_{geo} \leq 4$ ; Class 5 (heavily to very contaminated):  $4 \leq I_{geo} \leq 5$ ; Class 6 (extremely contaminated):  $5 < I_{geo}$  (Varol, 2011; Corami et al., 2020).

### 3.2 Enrichment factor ( )

Enrichment factor ( ) is a useful indicator reflecting the degree of anthropogenic heavy metal pollution (Sakan et al., 2009). The is calculated using the relationship below:

$$EF = \frac{C_i}{C_{i0}}$$

In the present study, aluminium (Al) was employed as the reference element for geochemical normalization, this element in sediments is useful to eliminate the effect of grain size, since it is a major element, exhibits relatively small content variations and a large distribution.

Interpretation provided by Malvandi et al. (2017) from the EF values were used for the assay, where:  $EF < 1$  indicates no enrichment;  $< 3$  is minor enrichment;  $3-5$  is moderate enrichment;  $5-10$  is moderately severe enrichment;  $10-25$  is severe enrichment;  $25-50$  is very severe enrichment; and  $N50$  is extremely severe enrichment (Al Rashdi et al., 2015; Malvandi et al., 2017).

#### 3.3.3 Contamination Factor (CF)

The CF index values were obtained by dividing the concentration of each metal in the sediment by baseline or background values (Hakanson, 1980). The background values used were presented in Table 1 and reported by Rudnick and Gao (2014) and Barats (2019).

$$CF = \frac{C_i}{C_{i0}}$$

CF values were explained as follows: low contamination at  $CF < 1$ ; moderate contamination at  $CF < 3$ ; moderate contamination at  $1 < CF < 3$ ; considerable contamination at  $3 < CF < 6$ ; and very high contamination at  $CF > 6$ , according to Hakanson (1980). The background values (initial concentration) used were 92 for Cr, 0.09 for Cd, 628 for Ba, 774 for Mn, 50,400.0 for Fe, 17.3 for Co, 28 for Cu, 47 for Ni, 67 for Zn, 4.8 for As, 17 for B, 17 for Pb, and  $81,500 \text{ mg kg}^{-1}$  for Al, respectively (Rudnick and Gao 2014; Barats et al., 2019).

#### 3.3.4 Pollution Load Index (PLI)

For the entire sampling site, PLI has been estimated by the n-root from the product of n CFs of the studied metals included:

The PLI for the entire study area can be estimated using the same calculation principle for each sampling point, substituting the CF values for the PLI value of each point, it is determined as the nth root of the product of the n CF (Contamination Factors) according to Tomlinson et al. 1980:

The index permits a simple, comparative means for assessing heavy metal pollution levels. PLI index of  $> 1$  is contaminated whereas  $< 1$  indicates no contaminated (Tomlinson et al., 1980).

Corami et al., (2020) use other evaluation criteria, classifying the degree of contamination for PLI index as follows:  $PLI < 1$  Unpolluted;  $1 < PLI < 1$  Moderately polluted,  $2 < PLI < 3$  Heavily polluted,  $PLI > 3$  extremely polluted.

#### 3.3.5 Potential ecological risk index (PERI)

Potential ecological risk index method (PERI) was used to evaluate quantitatively the level of the ecological risk degree of heavy metals in aquatic sediments. This index includes eight elements such as: mercury (Hg), cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn), and chromium (Cr). Polychlorinated biphenyls and arsenic (As). PERI was calculated by using the following formula (Hakanson 1980).

where  $E_r^i$  is the potential ecological risk factor for a given contaminant (i),  $T_r^i$  is the toxic response factor of each element, including Cr = 2, Cu = 5, Cd = 30, As = 10, Pb = 5 (Hakanson, 1980), and CF are the contamination factors, which have already been described before. The  $E_r^i$  values for each metal were interpreted as follows:  $E_r^i < 40$  low ecological risk;  $40 < E_r^i \leq 80$  moderate ecological risk;  $80 < E_r^i \leq 160$  appreciable ecological risk;  $160 < E_r^i \leq 320$  high ecological risk; and  $E_r^i > 320$  serious ecological risk.

The classification according to RI results is as follows:  $RI < 100$ , low ecological risk;  $100 < RI < 200$ , moderate ecological risk;  $200 < RI < 400$ , considerable ecological risk; and  $RI > 400$ , very high ecological risk for the studied area.

### 3.4. Statistical analysis

A cluster analysis was also performed to identify the relationships between the metals in their source. The variables under consideration were thirteen (Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn). The calculations were performed using STADISTICA 10 software (Stat soft Inc., 2011), and considering the Ward's method with Euclidean distances as a measure of similarity (Ward, 1963).

## 4. Results And Discussion

### 4.1. Grain size

According to the grain size analysis results of surface sediments in the study area, sand is the dominant grain size overall. At most sites, the sand content exceeds 80%, the contents of gravel and fine particles (clay and silt) were very small (avg. 6.25 and 2.38%, respectively). Grain size is significantly influenced by the flow rate and flow velocity of the surface water; the textural parameters derived from the grain size analysis reflect the energy conditions in the sedimentation environment. In a low-energy environment, the sediments are fine, although in a high-energy environment, the sediments are coarse (Kim et al. 2017). In this study, the grain size distribution explains the high-energy environment in the stream producing by the dominance of sand size particles, in which the water flux is high and the slope is steep thereby preventing the sedimentation of fine-grained particles. The sedimentation process occurs on the banks of rivers and in backwaters.

### 4.2. Sediment Mineralographic composition

XRD studies revealed the presence of different minerals as: Quartz, Calcite, Sanidine, Albite, Biotite, Wickenburgite, Lipsconmbite, Phengite, Gypsum and Muscovite. In all the samples a predominance of Quartz crystals (36 to 51%) and Calcite (6 to 18%) were shown by XRD; Albite was present in four samples (11.5 to 19.2%), sanidine was present in three samples (11.8 to 13.9%).

The minerals founded in the sediment samples, the presence of aluminosilicate minerals that are minerals composed of aluminum oxide and silicon dioxide such as Albite, Sanidine, Biotite, Muscovite, Wickenburgite stood out. This is related to the aluminosilicate minerals of igneous and metamorphic rocks are generally unstable in earth-surface weathering conditions, these elements transformed to stable end-products (crystalline clay minerals, oxides and hydroxides) that largely conserve aluminum and iron (Farmer, 1986).

### 4.3. Metals concentrations in sediments

Compared with Canadian Sediment Quality Guidelines (CCME, 1999) for aquatic life protection, metal contents were above the probable effect level (PEL) in 87.5 % of samples for As, 75% for Zn, 62.5 % Pb, 50% for Cd and Cu and 25% for Ni (Table 1). The concentrations of heavy metals of sediment samples were contrasted with the TEC, PEC and PEL values, the results are summarized in Table 1 (MacDonald et al., 2000). The concentrations of Ni were below the TEC values for 50% of the samples, indicating that there are no adverse effects in these samples (M1, M2, M3, M7 and M8 samples). The results showed that more than 50% of the samples were found between the TEC and PEC values for As, Cd, Cu and Zn, indicating that concentrations of these metals occasionally could exhibit adverse effects on the ecosystem. All sites exceeded the TEC levels for As, Cd, Cu, Pb, Zn demonstrating high level of pollution only M1 is below of TEC value for Pb; in case of Ni two sites exceeded the TEC values (M4 and M6).

Table 1

Metal concentrations of surface sediments in the study area, background values, Canadian Sediment Quality Guideline values (SQGs), PEL, TEC and PEC used in this study (mg/kg).

Sites/SQGs	Al	As	B	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
	mg kg <sup>-1</sup>												
PEL		17			3.53		90	196.6			75	91.3	314.8
TEC		9.79			0.99		43.4	31.6			22.7	35.8	121
PEC		33			4.98		111	149			48.6	128	459
M1- San Martín	16771	<l.c.	15.8	154	2.10	5.20	5.00	209.0	18637.0	231.0	18.70	35.60	351
M2-R. San Juan	16610.00	39.30	16.80	151.00	1.80	6.10	2.50	68.30	20009.0	362.0	16.60	94.20	144
M3- R.Cacalotenango	18313.00	48.80	12.80	173.0	16.20	7.20	<l.c.	78.40	20526.0	795.0	15.70	265.0	2008
M4-R. Pte Tecapulco	20303.00	25.50	31.20	278.0	50.40	7.80	5.50	393.0	20614.0	2710.0	111.0	244.0	4509
M5-R. Taxco Acolco	19032.00	24.70	15.90	104.0	5.50	7.20	<l.c.	41.80	23223.0	334.00	18.6	160.0	967
M6-El Milagro	22982.00	<l.c.	19.90	143.0	2.00	9.00	9.40	117.0	20930.0	105.00	24.2	13.90	142
M7-R. Campuzano	12086.00	21.30	13.80	88.0	9.40	6.30	<l.c.	55.90	22301.0	660.00	20.00	189.0	1763
M8-R. San Juan Metlapa	22849.00	17.10	21.60	227.0	2.20	5.20	17.10	502.0	15366.0	298.00	15.40	32.60	811
Mean	18618.25	29.45	18.48	164.7	11.20	6.75	7.90	183.1	20200.7	686.88	30.03	129.2	1336.9
Max	22982.0	48.8	31.2	278.0	50.4	9.0	17.1	502.0	23223.0	2710.0	111.0	265.0	4509
Min	12086.0	17.1	12.8	88.0	1.8	5.2	2.5	41.8	15366.0	105.0	15.4	13.9	142
Background values (Rudnick and Gao 2014)	81500	4.8	17	628	0.09	17.3	92	28	50400	774	47	17	67
SQGs-PEL-Probable Effect Level Threshold													
TEC-Threshold Effect Concentration and PEC-Probable Effect Concentration (MacDonald et al., 2000).													

The results also showed values higher than PEC, for Pb, Zn and As in 50%, 37.5%, 25% of the samples respectively indicating that adverse biological effects often can be occur. From all selected sites, sample M6 was below PEC and PEL for all metals. For all other sites, As, Zn and Pb found to be the metals of the highest importance due the PEC and PEL values are exceeded for As and Zn in 6 samples (M2, M3, M4, M5, M7 and M8) and Pb in 5 samples (M2, M3, M4, M5 and M7)

#### 4.4. Degree of metal enrichment and ecological risk assessment

The Index of geoaccumulation (Igeo) values are presented in Table 2. The Igeo values of Al, B, Ba, Co, Cr and Fe at all sampled sites were less than zero, suggesting that these sites were not polluted. The values of Igeo for As were greater than 1 but less than 2 in the sediments of M4, M5, M7, and M8, which were classified as moderately contaminated while the samples M2 and M3 were considered as moderately to heavily contaminated. Cadmium was the metal that presented the highest contamination in all the sampled sites, the sediment samples were grouped in heavily contaminated for M1, M2 and M6, heavily to very contaminated for M8 and extremely contaminated for M3, M4, M5 and M7. Zinc, lead and copper are the three metals that have the greatest influence the contamination of river sediments, since they present the highest contamination values of the accumulation index; In the case of zinc, these Igeo values were classified as uncontaminated to moderately contaminated (M2 and M6), moderately contaminated (M1), moderately to heavily contaminated (M5 and M8), heavily to very contaminated (M3 and M7) and extremely contaminated (M4).

Table 2  
The values of Geoaccumulation indices (Igeo) of heavy metals for sediments in San Juan-Taxco River basin.

Sites	Geoaccumulation indices (Igeo)												
	Al	As	B	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
M1-R. San Martín	-2.87	-	-0.69	-2.61	3.96	-2.32	-4.79	2.32	-2.02	-2.33	-1.91	0.48	1.80
M2-R. San Juan	-2.88	2.45	-0.60	-2.64	3.74	-2.09	-5.79	0.70	-1.92	-1.68	-2.09	1.89	0.52
M3-R. Cacalotenango	-2.74	2.76	-0.99	-2.44	6.91	-1.85	-	0.90	-1.88	-0.55	-2.17	3.38	4.32
M4-R. Pte Tecapulco	-2.59	1.82	0.29	-1.76	8.54	-1.73	-4.65	3.23	-1.87	1.22	0.65	3.26	5.49
M5-R. Taxco Acolco	-2.68	1.78	-0.68	-3.18	5.35	-1.85	-	-0.01	-1.70	-1.80	-1.92	2.65	3.27
M6-El Milagro	-2.41	-	-0.36	-2.72	3.89	-1.53	-3.88	1.48	-1.85	-3.47	-1.54	-0.88	0.50
M7-R. Campuzano	-3.34	1.56	-0.89	-3.42	6.12	-2.04	-	0.41	-1.76	-0.81	-1.82	2.89	4.13
M8-R. San Juan Metlapa	-2.42	1.25	-0.24	-2.05	4.03	-2.32	-3.01	3.58	-2.30	-1.96	-2.19	0.35	3.01
Mean	-2.74	1.94	-0.52	-2.60	5.32	-1.97	-4.42	1.58	-1.91	-1.42	-1.62	1.75	2.88
Max	-2.41	2.76	0.29	-1.76	8.54	-1.53	-3.01	3.58	-1.70	1.22	0.65	3.38	5.49
Min	-3.34	1.25	-0.99	-3.42	3.74	-2.32	-5.79	-0.01	-2.30	-3.47	-2.19	-0.88	0.50

Igeo for lead element were categorized as uncontaminated in sample M6, uncontaminated to moderately contaminated in samples M1 and M8, moderately contaminated for sample M2, moderately to heavily contaminated in samples M5 and M7 and heavily to very contaminated for M3 and M4. For copper Igeo values were classified as uncontaminated in sample M5, uncontaminated to moderately contaminated in samples M3, M4 and M7, moderately contaminated for sample M6, moderately to heavily contaminated in samples M8 and M4. According to the calculation of each sampling point, the order of the metals according to the Igeo evaluated is as follows: Cd > Zn > Pb > Cu > As > Mn > Ni > B > Fe > Co > Ba > Al > Cr. The critical points associated with the geoaccumulation of metals were M3, M4 and M8; the first with four metals in the range of heavily to very heavily contaminated and the rest with three.

The results from this study show that the Cd enrichment factor, EF (Cd), ranges from 78.81 to 2247.94, EF (Zn) from 7.52 to 270.15, EF (Pb) from 2.9 to 74.97, EF (As) from 12.71 to 45.25, EF (Cu) from 6.39 to 63.95, EF (Mn) from 0.48 to 14.05, EF (Ni) from 1.17 to 9.48, EF (Fe) from 1.09 to 2.98, EF (Ba) from 0.71 to 1.78, EF (Co) from 1.07 to 2.46 and EF (Cr) from 0.13 to 0.66 (Table 3). The average enrichment factors of Ba (1.14), Co (1.75) and Fe (1.84) are found to be less than 3 (EF < 3) (Table 3), indicating minor enrichment.

Table 3  
The values of enrichment factor (EF) of studied heavy metals for sediments of all sites studied in San Juan-Taxco River Basin

Sites	Enrichment factor (EF)												
	Al	As	B	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
M1-R. San Martín	1	-	4.52	1.19	113.39	1.46	0.26	36.27	1.80	1.45	1.93	10.18	25.46
M2-R. San Juan	1	40.17	4.85	1.18	98.13	1.73	0.13	11.97	1.95	2.29	1.73	27.19	10.55
M3-R. Cacalotenango	1	45.25	3.35	1.23	801.07	1.85	-	12.46	1.81	4.57	1.49	69.40	133.38
M4-R. Pte Tecapulco	1	21.33	7.37	1.78	2247.94	1.81	0.24	56.34	1.64	14.05	9.48	57.62	270.15
M5-R. Taxco Acolco	1	22.04	4.01	0.71	261.69	1.78	-	6.39	1.97	1.85	1.69	40.30	61.81
M6-El Milagro	1	-	4.15	0.81	78.81	1.84	0.36	14.82	1.47	0.48	1.83	2.90	7.52
M7-R. Campuzano	1	29.92	5.47	0.94	704.30	2.46	-	13.46	2.98	5.75	2.87	74.97	177.44
M8-R. San Juan Metlapa	1	12.71	4.53	1.29	87.19	1.07	0.66	63.95	1.09	1.37	1.17	6.84	43.18
Mean	1	28.57	4.78	1.14	549.07	1.75	0.33	26.96	1.84	3.98	2.77	36.17	91.18
Max	1	45.25	7.37	1.78	2247.94	2.46	0.66	63.95	2.98	14.05	9.48	74.97	270.15
Min	1	12.71	3.35	0.71	78.81	1.07	0.13	6.39	1.09	0.48	1.17	2.90	7.52

Although the average enrichment factors of B (4.78) and Mn (3.98) are found between 3 and 5 (EF = 3 a 5; Table 3), suggesting that these metal contaminations are currently not a major concern although moderate enrichment; Copper, lead and zinc presented very severe enrichment (25 < EF < 50) and extremely severe enrichment (EF > 50), the average enrichment factors for these heavy metals were 26.96, 36.17, and ranged from 6.39 to

639, 2.90 to 74.97 and 7.52 to 270.15 respectively. Arsenic in almost all samples sites presented very severe enrichment except for M8 (San Juan Metlapa), with a minimum 12.71 and a maximum 45.25.

The Cd presents extremely high enrichment in all the points evaluated. The points of attention correspond to the M21, M7, M9, M10 and M17, the first with very severe enrichment with four of the twelve metals and the rest with three of the twelve metals.

The results of contamination factors (CFs) and individual and global pollution load index (PLI) for the sediment from samples sites in the San Juan, Cacalotenango and Taxco Rivers are summarized in Table 4. The CF values for Cd were > 6 in all the studied sediments, indicating "very high contamination" by Cadmium. The CF values for Zn, Pb, Cu and As present "very high contamination" and "considerable contamination". The CF values for Al, Ba, Co, Cr and Fe in all the samples denotes "low contamination" for all the sediments. The critical sites correspond to M3, M4, M5, M7 and M8; the first with four extremely enriched CF values and the rest with three. The level of CF values for each heavy metal in the sediment was in the order: Cd > Zn > Pb > Cu > As > Mn > Ni > Fe > Co > Ba > Cr. These results indicated that the contamination is relatively high; there are serious impacts of pollution related heavy metals in the nearby areas to abandoned mining tailings and where heavy metals processing (jewelry) is done and untreated sewage. Among all metals, contamination by Cd is the highest in all the sediment samples in a range of CF values of 20 to 560.

Table 4  
Metal contamination factors (CFs) and Pollution load indices (PLIs) for sediments of all sites studied in San Juan-Taxco River basin.

Sites	Contamination factors (CFs)													PLI
	Al	As	B	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	
M1-R. San Martín	0.21	-	0.93	0.25	23.33	0.30	0.05	7.46	0.37	0.30	0.40	2.09	5.24	0.796
M2-R. San Juan	0.20	8.19	0.99	0.24	20.00	0.35	0.03	2.44	0.40	0.47	0.35	5.54	2.15	0.862
M3-R. Cacalotenango	0.22	10.17	0.75	0.28	180.00	0.42	-	2.80	0.41	1.03	0.33	15.59	29.97	<b>2.078</b>
M4-R. Pte Tecapulco	0.25	5.31	1.84	0.44	560.00	0.45	0.06	14.04	0.41	3.50	2.36	14.35	67.30	<b>2.829</b>
M5-R. Taxco Acolco	0.23	5.15	0.94	0.17	61.11	0.42	-	1.49	0.46	0.43	0.40	9.41	14.43	1.434
M6-El Milagro	0.28	-	1.17	0.23	22.22	0.52	0.10	4.18	0.42	0.14	0.51	0.82	2.12	0.718
M7-R. Campuzano	0.15	4.44	0.81	0.14	104.44	0.36	-	2.00	0.44	0.85	0.43	11.12	26.31	1.593
M8-R. San Juan Metlapa	0.28	3.56	1.27	0.36	24.44	0.30	0.19	17.93	0.30	0.39	0.33	1.92	12.10	1.194
Mean	0.23	6.14	1.09	0.26	124.44	0.39	0.09	6.54	0.40	0.89	0.64	7.61	19.95	1.44
Max	0.28	10.17	1.84	0.44	560.00	0.52	0.19	17.93	0.46	3.50	2.36	15.59	67.30	2.83
Min	0.15	3.56	0.75	0.14	20.00	0.30	0.03	1.49	0.30	0.14	0.33	0.82	2.12	0.72

The PLI values estimated by sampling points ranged from 0.72 to 2.83 (Table 4); These indicate that samples M1, M2 and M6, where PLI was below 1 were classified as unpolluted, the samples M5, M6 and M8 were considered as Moderately polluted but samples M3 and M4 were reported as heavy polluted. For the estimation of global value it were considering all the samples and making correction for points M1, M3, M5, M6 and M7, which are the points in which they do not have concentrations of As and Cr, therefore n = 12, the global value of PLI for the entire study area was 1.29 which makes it a moderately contaminated area (Fig. 2). This indicates that the San Juan, Taxco and Cacalotenango rivers are in a state of contamination due to the influence of the 13 metals evaluated, being Cd, Zn, Pb and Cu the most influential.

The ecological risk of metals in fluvial sediments of San Juan-Taxco river system were assessed through potential ecological risk indices (ERi and RI) and summarized in Table 5. ERi values for cadmium in all cases indicated low risk, while for As the values were between 35.6 and 101.1 indicating low ecological risk for M8, moderate for M4, M5 and M7 and appreciable for M2 and M3. The ERi values for lead showed low ecological risk in samples M1, M2, M6 and M8, and moderate in samples M3, M4, M5 and M7. In the case of Cu, the values in almost all the samples showed a low ecological risk, but in the M4 a moderate and M8 appreciable ecological risk. In addition, the values of RI at all sites were > 600, which indicated very high ecological risk for the studied area.



Table 5  
Potential ecological risk indices  $E_{ri}$  and  $RI$  for studied metals in the San Juan-Taxco River basin

Sites	$E_{ri}$					$RI$	Risk grade
	As	Cd	Cr	Cu	Pb		
M1-R. San Martín		700.0	0.109	37.32	10.47	747.90	very high
M2-R. San Juan	81.88	600.0	0.054	12.20	27.71	721.83	very high
M3-R. Cacalotenango	101.67	5400.0		14.00	77.94	5593.61	very high
M4-R. Pte Tecapulco	53.13	16800.0	0.120	70.18	71.76	16995.19	very high
M5-R. Taxco Acolco	51.46	1833.3		7.46	47.06	1939.31	very high
M6-El Milagro		666.7	0.204	20.89	4.09	691.85	very high
M7-R. Campuzano	44.38	3133.3		9.98	55.59	3243.28	very high
M8-R. San Juan Metlapa	35.63	733.3	0.372	89.64	9.59	868.56	very high
Mean	61.35	3733.33	0.17	32.71	38.03	3850.19	
Max	101.67	16800.00	0.37	89.64	77.94	16995.19	
Min	35.63	600.00	0.05	7.46	4.09	691.85	

In summary, the  $E_{ri}$  and  $RI$  indices for the studied elements in the surface sediment at all sites showed that San Juan, Cacalotenango and Taxco river pose any potential ecological risk with major contribution of As and Cd (Table 5 and Fig. 3). The results of heavy metal pollution in surface sediments of San Juan – Taxco river system indicated that the contamination is relatively high. There are serious impacts of heavy metal pollution, related to mining tailings, these have been washed down by the rain towards the rivers bed in the areas near these deposits, non-point source release that carries toxic elements (with heavy metals content as phosphate fertilizers, insecticides and fungicides, etc.), municipal wastewater and discharge with wastes from workshops of metal processing for handicraft and jewelry. The major steps in the manufacturing process of handicrafts and handmade jewelry include refining and alloying with other metals, smelting process and framing the metals, soldering, palatinate, polished, or etched of the piece. Each task is generally accomplished by the use of some substances and actives of heavy metals as Cd, Zn, Ni. For example, Cadmium (Cd) traditionally has been used in jewelry solders or galvanized with zinc is used too (Clausell, 2010). Among all metals, contamination by Cd is the highest followed in order of importance by Zn, Pb, Cu and As.

## 4.5. Worldwide comparison of heavy metal concentration

The concentrations of heavy metals of San Juan-Taxco river system were compared with other major polluted rivers in Mexico and worldwide and summarized in the Table 6. The comparison of the heavy metals concentrations with other Mexican rivers showed that, this system presents higher concentrations of As, Cd, Ni, Fe, Cu and Zn than those reported in the Atoyac river; Cd, Cu, and Zn higher than those reported in the Panuco River and exceeds the concentrations of As, Fe, Cu, Ni, Zn measured in the Coatzacoalcos River.

A worldwide comparison of metal concentrations in fluvial sediments of San Juan-Taxco River system with those from other river environments showed higher concentrations, the comparison with Zarrin-Gol River in Iran in As, Ni, Zn and Fe, the sediment concentrations of Cd, Cu, Ni, Pb and Zn in the present study exceed those reported in the Yantze, Yellow, Ganga and Euphrates rivers.

Table 6  
Comparison of metal concentrations with other riverine environments worldwide

	As	Cd	Cr	Cu	Ni	Pb	Zn	Fe
<b>Metal concentrations (mg kg<sup>-1</sup>)</b>								
<b>Present study</b>	17.1–48.8	1.8–50.4	2.5–17.1	4.3–502	15.4–111	2.5–13.9	45.09–142	15,366 – 23,223
<i>Studies in Mexico</i>								
Atoyac River (Morales et al., 2017)	0.16	2.58	24.5	10.2	14.4	27.1	31.5	19,180
Panúco River (Jonathan, et al., 2013)	-	1.79–1.89	17.03–21.69	22.58–34.13	-	39.01–51.35	74.78–122.45	11,331 – 14,575
Coatzacoalcos River (Ruiz-Fernández et al., 2012)	5–10	-	29–92	15–30	18–35	11–30	64–109	-
<i>World wide studies</i>								
Yangtze River (Wang, 2015)	9.1	0.19	79.1	24.7	31.9	23.8	82.9	-
Yellow River (Ma et al., 2015)	-	0.1–0.3	61.3–139.5	14.1–30.3	19.3–34.6	15.5–24.6	39.9–74.6	-
Tinto River (García et al., 2012)	1130	2.75	56	805	17	2230	901	11,500
Tigris River (Varol and Sen, 2012)		7.9	-	2860		66	1061	-
Ganga River (Pandey and Singh, 2017)	-	1.7	69.9	29.8	372	26.7	67.8	31,988.6
Euphrates River (Salah et al. 2012)	-	1.9	58.9	18.9	67.1	22.6	48	2,249.5
Zarrin-Gol River (Mavandi et al., 2017)	21.91	-	37.67	-	12.39	-	32.68	13,751

Concentration of Fe were found higher than the values in Tinto River and Euphrates Rivers (Table 6). The Fe abundance in these sediments has been attributed: weathering, erosion and other natural sources, large-scale human activities (mining release, municipal solid waste and agricultural activities). Cadmium values are considerably high, compared to the other rivers of Mexico and the world as presented in Table 6; the results shown concentrations in all study sites above of the background values and these values is associated with wastes from: mining and handicrafts and jewelry industry, urban and agricultural runoff. Concentration of Pb in this study was found lower than the reported in Atoyac, Panuco, Coatzacoalcos, Yangtze, Yellow, Tinto, Ganga and Euphrates Rivers. This metal is mainly associated with Fe oxide fraction and shows high retention in sediments. Pb and Zn concentrations is attributed that tailings are being washed down by the action of rain towards the riverbed. Zn is one of the most abundant elements in the sediment of San Juan-Taxco system (Table 6). Those values are higher than the values reported in Atoyac, Panuco, Coatzacoalcos, Yangtze, Yellow, Ganga, Euphrates and Zarrin Rivers (Wang et al. 2015; Ma et al., 2015; Pandey and Singh, 2017; Salah et al., 2012).

The rivers in the mining region of Taxco constantly receive trace amount of heavy metals from terrigenous sources weathering of rocks. Continuous or intermittent but relatively higher input of heavy metals to rivers and streams is linked to anthropogenic sources (Armieta et al., 2004; Dotor et al., 2017). The comparison study reveals that globally the average metal concentrations in San Juan-Taxco River system are similar compared to other polluted riverine environments as summarized in Table 6.

## 4.6. Cluster analysis

The cluster analysis was performed to identify the relationship between the heavy metals in sediment samples (Fig. 4). The first of the cluster group includes Al and Fe (cluster 1), As, B, Cd, Co, Ni, Ba, Pb, Cu, Mn and Zn take part of cluster 2. The dendrogram indicates that the first group originates from the minerals present in the study area and group 2 is mainly associated with anthropogenic activities.

## 5. Conclusions

The results revealed that the Cd, Zn, Pb, Cu and As concentrations in contaminated sites might cause hazardous effects to the sediment-dwelling organisms. Most abundant minerals identified by XRD were quartz, calcite, sanidine and albite from igneous and metamorphic rocks.

The degree/level of metal enrichment assessed through various geochemical indices reveal significant external influences over the metals Cd, Zn, Pb, Cu and As. The enrichment of these metals is related to mining tailings erosion, to the land-based point source discharges, heavy metal processing for handicrafts and jewelry, non-point and urbanization.

The areas identified with the highest pollutant load determined with Pollution load index, they were the closest to the mining tailings and areas with a history of metal processing for handicrafts and jewelry (M3 Cacalotenango and M4 Puente Tecapulco respectively). PLI values indicates that the Taxco and Cacalotenango rivers are in a state of contamination due to the influence of the 13 metals evaluated, being Cd, Zn, Pb and Cu the most influential.

The calculated RI values indicate that Cd and As contributed majority of ecological risk in San Juan-Taxco River sediments. The single factor of Potential ecological risk index indicates a very high potential risk. Also, anthropogenic sources have contributed significantly to heavy metals concentrations in the study area, while natural sources have contributed only small amounts. The analyses also indicate that the main processes that controlling the pollution are mining tailings erosion with discharge processes, and proportional dilution related to grain-size distribution processes, metal concentrations tend to accumulate in areas with fine sediments with reduced flow rate and flow velocity.

## Declarations

**Ethics approval and consent to participate:** Not applicable

**Consent for publication:** Not applicable

**Availability of data and materials:** All data generated or analysed during this study are included in this published article.

**Competing interests:** The authors declare that they have no competing interests.

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### Authors' contributions:

Edith R. Salcedo Sánchez: sampling collection, data analysis, geochemical assessment, paper writing and edition.

Manuel Martínez-Morales: Statistical analysis, paper writing and edition.

Juan Manuel Esquivel Martínez: Sampling collection, maps edition and paper edition.

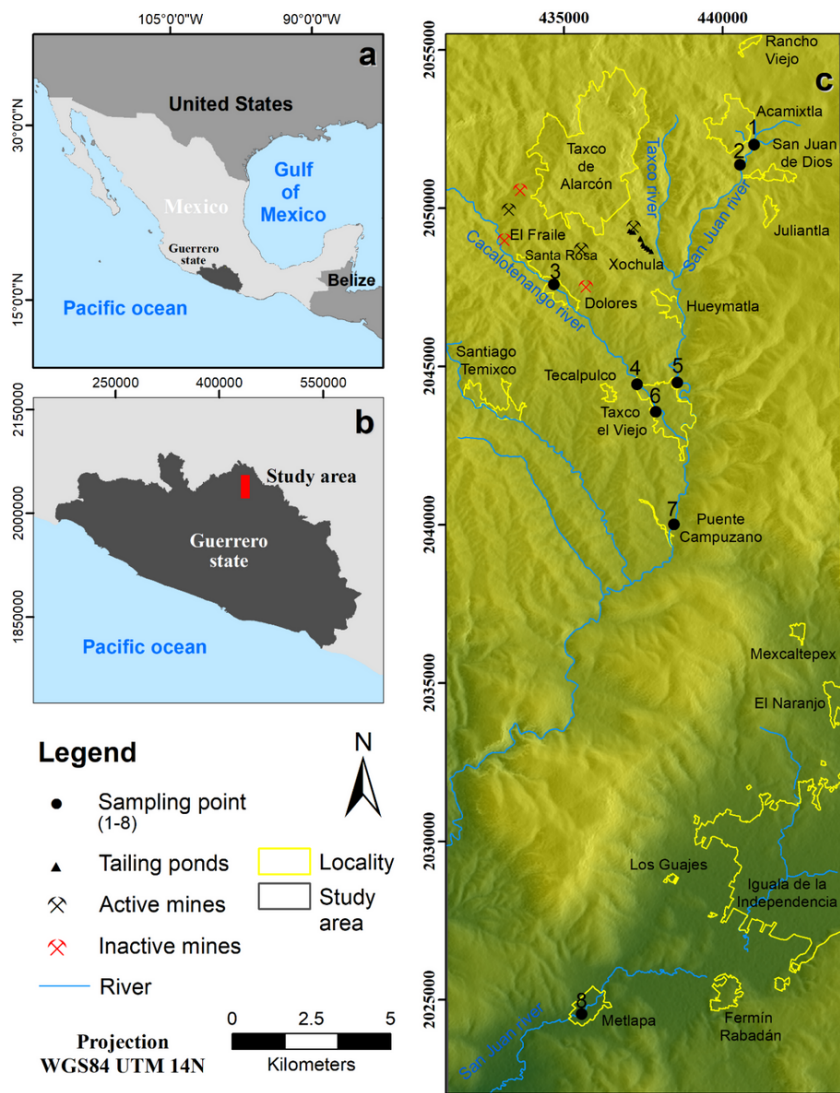
Oscar Talavera-Mendoza: Laboratory analysis and paper edition,

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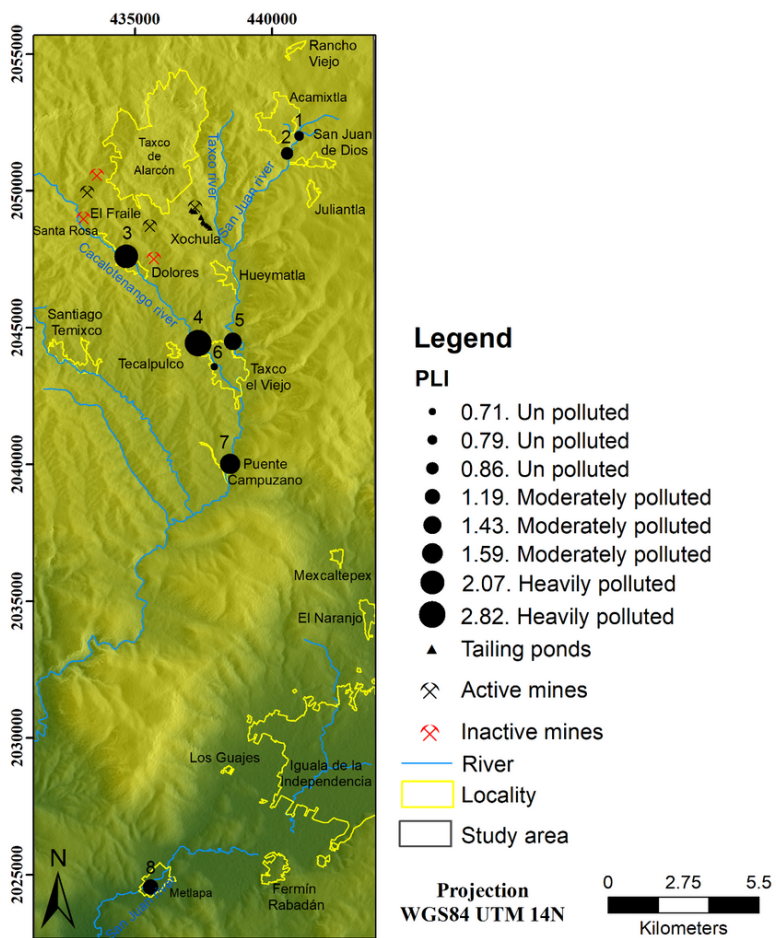
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## Figures



**Figure 1**

The location of the study area and sampling sites in the San Juan-Taxco river system



**Figure 2**

Pollution load index (PLI) for sediments of all sites studied in the San Juan-Taxco River system

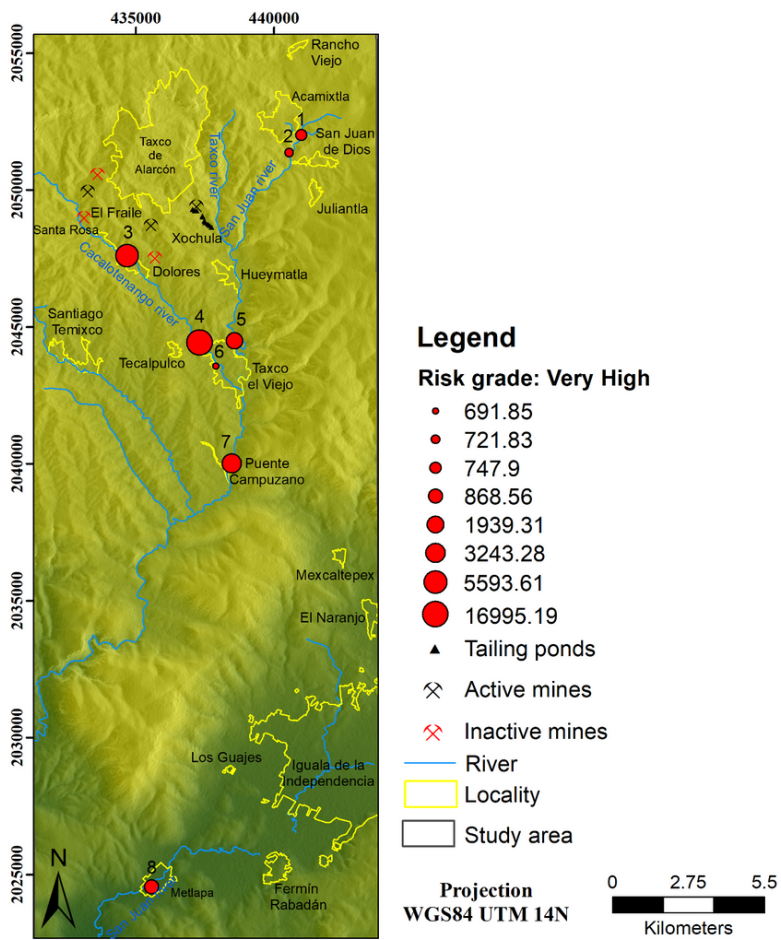
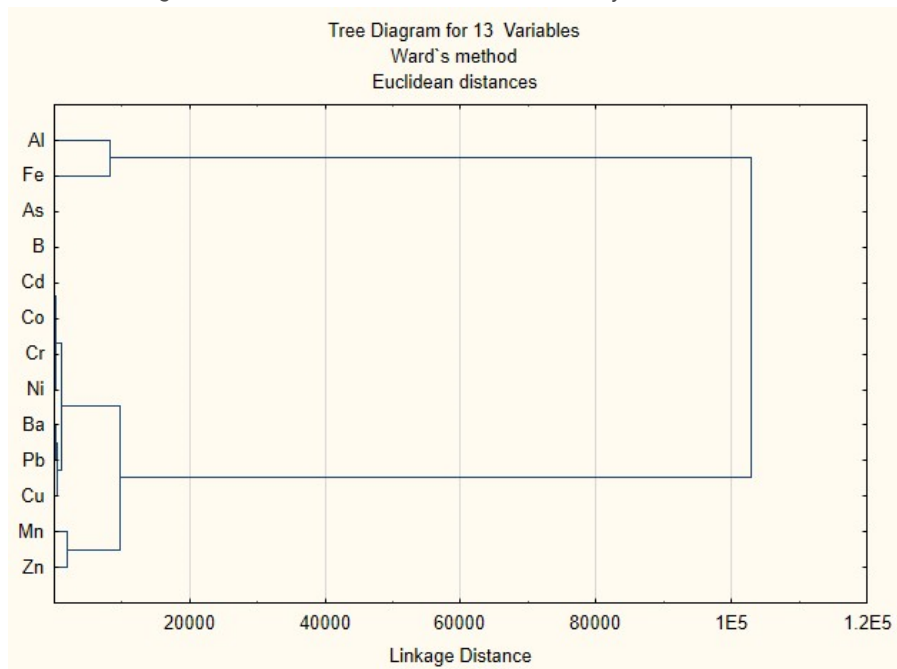


Figure 3

Potential ecological risk index in the San Juan-Taxco River system



**Figure 4**

Dendrograms showing the clustering of the analyzed metals