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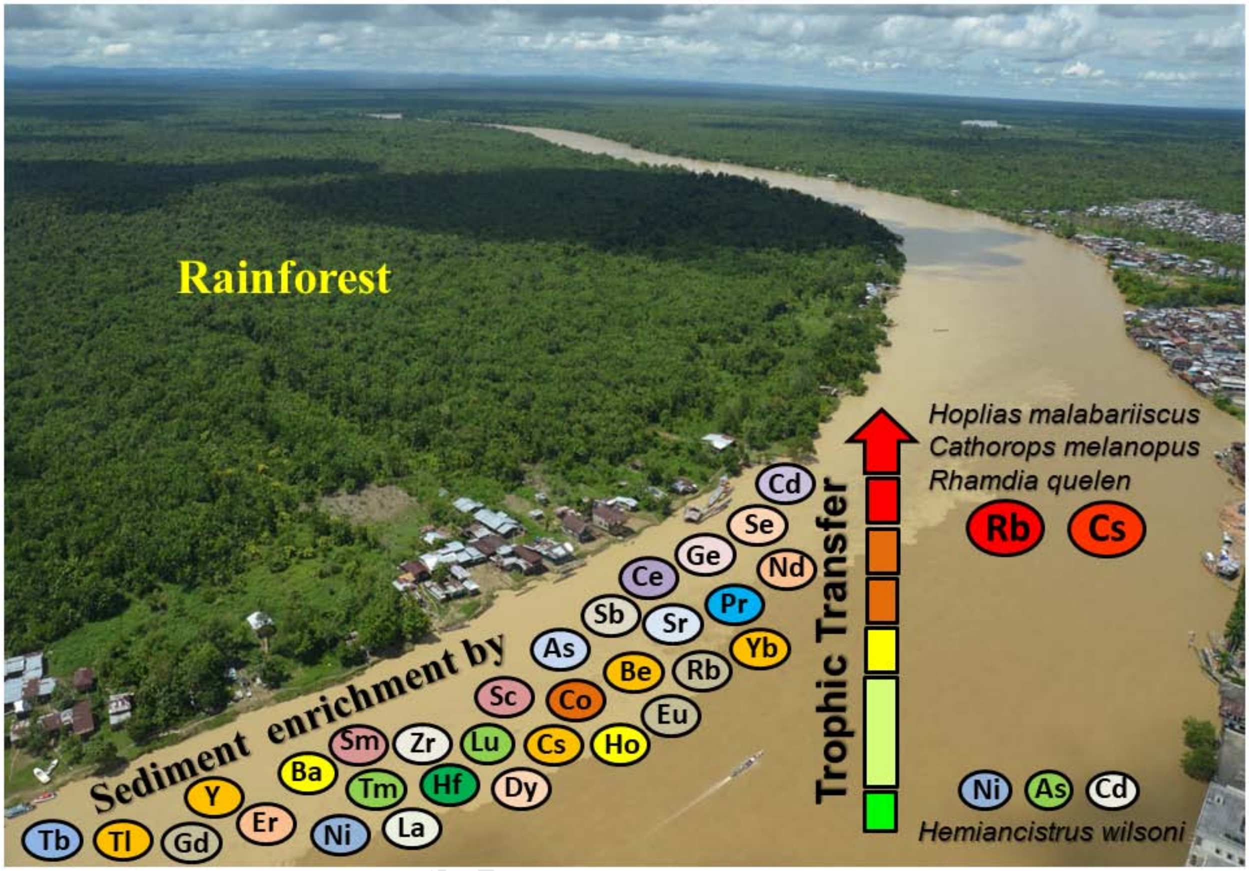
Atrato River polluted by trace elements



Trace elements in sediments and fish from Atrato River: an ecosystem with legal rights impacted by gold mining at the Colombian Pacific

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Abstract

The Atrato watershed is a rainforest that supports exceptional wildlife species and is considered one of the most biodiversity-rich areas on the planet, currently threatened by massive gold mining. Aimed to protect this natural resource, the Constitutional Court of Colombia declared the river subject to rights. The objective of this study was to quantify trace elements in sediments and fish from Atrato watershed, assessing their environmental and human health risk. Forty-two trace elements were quantified using ICP-MS. Thirty-one elements increased their concentration downstream the river. Concentration Factors (CF) suggest sediments were moderately polluted by Cr, Cu, Cd, and strongly polluted by As. Most stations had Cr (98%) and Ni (78%) concentrations greater than the Probable Effect Concentration (PEC) criteria. Together, toxic elements generate a Pollution Load Index (PLI) and a Potential Ecological Risk Index (RI) that categorized 54% of the sediments as polluted, and 90% as moderate polluted, respectively. *Hemiancistrus wilsoni*, a low trophic guild fish species, had the greater average levels for Ni, Cu, As and Cd, among other elements. Rubidium and Cs showed a positive correlation with fish trophic level, suggesting these two metals biomagnify in the food chain. The Hazard Quotient (HQ) for As was greater than 1 for several species, indicating a potential risk to human health. Collectively, data suggest gold mining carried out in this biodiversity hotspot releases toxic elements that have abrogated sediment quality in Atrato River, and their incorporation in the trophic chain constitutes a large threat on environmental and human health due to fish consumption. Urgent legal and civil actions should be implemented to halt massive mining-driven deforestation to enforce Atrato River rights.

Capsule

Trace elements in sediments and fish from Atrato River, an ecosystem with legal rights in a biodiversity hotspot, have the potential to induce environmental and human health risks.

Keywords: Risk assessment, sediment quality guidelines, biodiversity, Choco, Colombia.

1. Introduction

Artisanal and Small Gold Mining (ASGM) activities discharge trace elements into the environment, including heavy metals, that are particularly relevant from an ecotoxicology perspective (Krishna and Govil, 2007). Once in the water column, some of these chemicals are primarily incorporated into sediments (Caballero-Gallardo et al. 2015; Tejeda-Benítez et al. 2016; Torres-Sánchez *et al*. 2017), and from them accumulated by the biota, reaching humans through the trophic chain, where they elicit adverse effects.

The elements released by ASGM are diverse, and each one of them has been associated with aquatic pollution from different sources. For instance, lead (Pb) enters the environment as a result of domestic, industrial and mining discharges, polluting environmental compartments that expose humans by ingestion and inhalation, increasing the risks of central and peripheral nervous system damage, bone weakening, miscarriages and alterations to the sperm-producing system (Martin and Griswold, 2009), among other effects. Cadmium (Cd) is a very toxic metal that has been associated with mining, capable of causing cancer, pulmonary lesions, stomach and brittle bones (Martin and Griswold, 2009). Rubidium (Rb) and Arsenic (As) also are known to inhibit gonadal development (Yamaguchi et al. 2007). The rare earth elements (REE), La, Ce, Pr, Nd, Sm, Pm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y (Liang et al. 2018), are frequently released into the environment by different sources, such as industries and mining. These chemicals are taken up by organisms, and their accumulation may lead to organ damage (Zhuang et al. 2017; Hua et al. 2017; Zhang et al. 2014). In the ecosystem, the biota, including humans, is often exposed to more than one chemical element, therefore experiencing combined or interactive effects (Tao et al. 2012; Alamdar et al. 2017).

Although mining operations usually elicit environmental damage despite of the geographical location, some natural areas are critically vulnerable to these activities, in particular rainforest ecosystems, highly rich in biodiversity (Sonter et al. 2017; Garcia et al. 2017; Murguía et al. 2016). The Atrato River is localized in the state of Choco, northwestern Colombia. It is a highly biodiverse region, with many life forms (Mojica et al. 2004) and considered a hotspot for biodiversity (Marchese, 2015). It is also a region with high rates of poverty (Fisher and Christopher, 2007), where some areas along Atrato River´s main tributaries, for instance, Rio Quito, have been devastated by anthropogenic activities, mostly related to gold mining. In this case, although the mining is considered artisanal and working at small scale, the permanent movement of activities from one place to another makes it a large-scale operation (Figure S1). The river is also a major source of protein for people living on riverside villages located alongside its banks, as well as a pathway of communication and transport for the communities.

As a result of the environmental damage produced by gold mining (Palacios-Torres et al. 2018) along several tributaries of the Atrato River, this ecosystem was declared as a subject of legal rights in order to guarantee its protection (Constitutional Court of Colombia, Judgment T-622-2016), as mining activities have altered its hydrodynamic characteristics, promoting extensive deforestation, sedimentation and fish population decline, among other impacts. The primary aims of this research were (i) to characterize the levels of several trace elements in sediments and fish from Atrato River, and (ii) to examine environmental and human health risks derived from their presence in this fragile and worldwide fundamental ecosystem, as a support to raise international environmental awareness on its protection.

2. Materials and Methods

2.1. Study area

The sediment and fish samples were collected along the Atrato River, covering a total of 295 km (Figure 1). The Atrato River basin is the third largest watershed in Colombia, with 750 Km^2, an approximate flow rate of 5.000 m^3/s, and a sediment load of 11.3 x 10^6 Ton/year (Vélez-Agudelo and Aguirre-Ramirez, 2016). The river stream borns at the Cerro del Plateado at El Carmen de Atrato municipality, on the Western Cordillera of the Andes, and its mouth is located on the Gulf of Uraba, in the Caribbean Sea. The area presents a hydric balance from perhumid to superhumid with an annual rainfall upper 7776 mm, one of the largest in the world, and a megathermal temperature (Poveda et al. 2004). The major threat to the basin is deforestation, mostly derived from gold mining, which in turn deposits sediments and trace elements into the Caribbean Ocean.

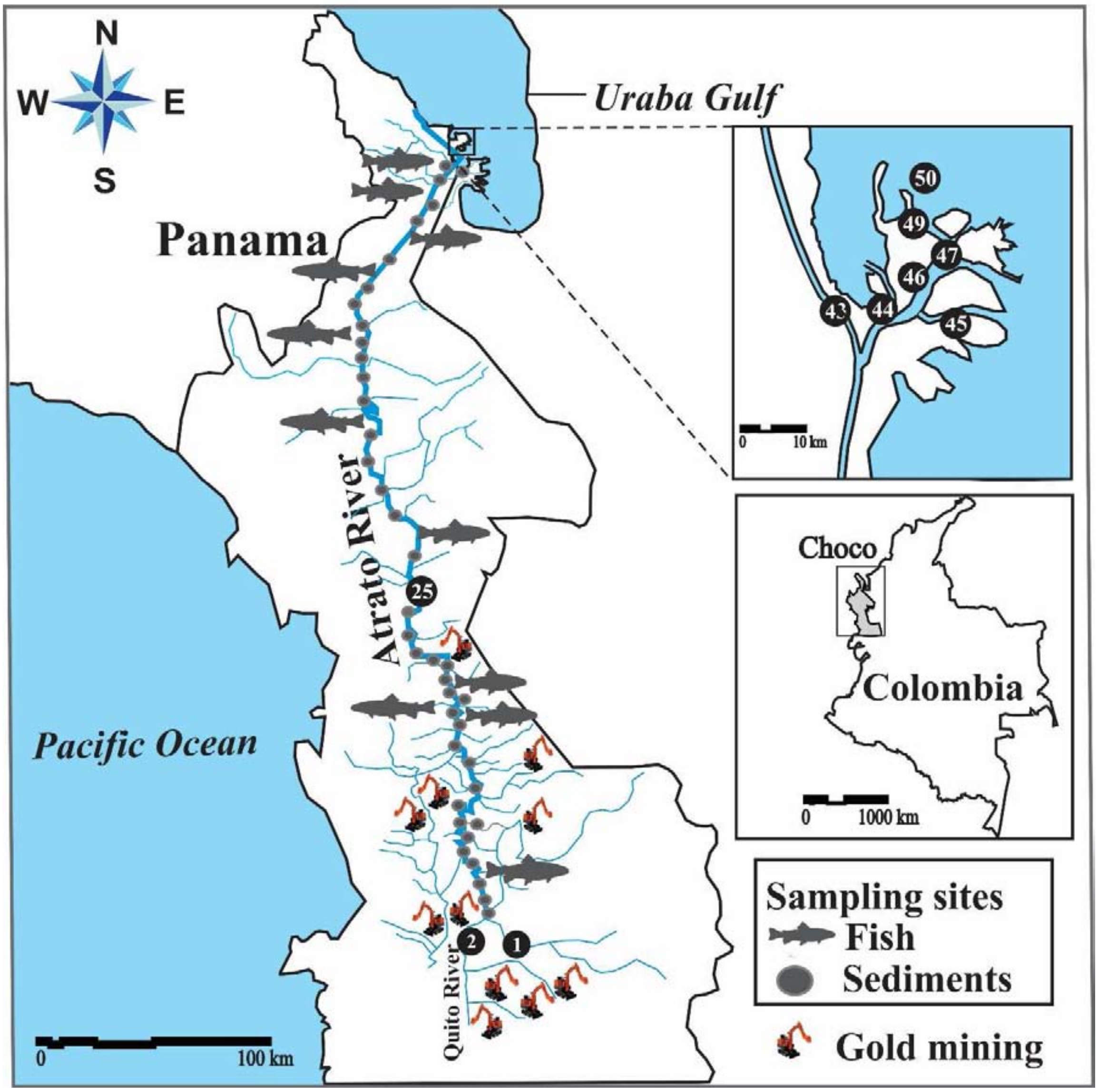

Figure 1. Map of the study area and showing sampling sites at Atrato River watershed.

2.2. Sampling methods

Fifty sediment samples were collected during February 2016 along Atrato River, between 50 to 100 m from the shore. Each location was georeferenced using a GPS. The bottom sediments were removed using an Ekman grab, and at each site, a bulked sample of approximately 500 g was prepared from four sub-samples taken in cardinal directions.

Sediments were placed in plastic bags, labeled, packed on ice, transported to the lab, and stored at -20 °C for their subsequent freeze-drying (Labconco Freezone 2.5) at -50 °C for 20 h. Dried samples were homogenized, sieved to obtain a material with a particle size less than 75 µm, and kept at -20 °C until analysis (Palacios-Torres et al. 2018).

At specific locations along the course of the river (Figure 1), mostly from local fishermen, specimens from 9 fish species were obtained for a total of 104 samples. After morphometric measurements, a subsample of dorsal muscle was removed from each fish using plastic knives, stored in ice and sent to the laboratory (Ashie et al. 1996). Samples were freeze-dried and stored as described for sediments.

2.3. Morphometric measurements

Fish weight (g) and length (cm) were measured using a balance and a ruler, respectively. The condition factor (FC), an indicator of the health status of the fish, was calculated employing the formula: $CF=(W/L^3)\times 100$ (Pauly, 1983; Malik et al. 2010), where W=total weight (g), and L=total length (cm).

2.4. Trace elements analysis in sediments and fish

The analytical procedure for determination of trace elements in sediments and fish was carried out using an Inductively Coupled Plasma–Mass Spectrometry (ICP-MS, AGILENT 7700). About 0.1 g of the lyophilized sediment was mixed with 8 mL hydrofluoric acid (HF) and 3 mL 65% nitric acid (HNO_3), both Suprapur® (Romil Ltd., Cambridge, UK). After evaporation to dryness, 3 mL of HNO_3 and 3 mL of hydrochloric acid (HCl) were added, taken again to dryness, and the residue dissolved in 2 mL of 2% HNO_3. On other hand, 0.1 g of dried fish was weighted in a 5 mL Teflon vessel container and predigested with 0.5 mL of 65% HNO_3 at 90 ºC overnight, allowed cooled to room temperature, and then 3 mL of H_2O_2 were added, and after 1 h the solution was dried at 180 °C. The residue was dissolved in 2 mL of HNO_3 (2%), the solution transferred to a 10 mL volumetric flask and completed with ultrapure water to 10 mL. Multielemental measurements were carried out employing calibration curves constructed using a series of standard solutions containing a mixture of all examined elements (1-250 ppb). The precision for most elements was better than 10%, and the accuracy of the method was assessed using Certified Reference Materials (CRMs: Sediments, SARM-1 and SARM-4; fish, DORM-3, concomitantly with SARM-1 and SARM4). The measured results and the reported values of CRMs are summarized in Tables S1A and S1B, for sediments and fish, respectively. The limits of detection (LOD) and quantification (LOQ) are shown in Table S1C.

2.6. Sediment quality assessment

Sediment quality guideline (SQG) approaches were employed to assess the environmental quality of the sediments. First, the contamination factor (CF), defined as C_i/C_b, was employed to estimate the pollution level by metals, where C_i is the observed sediment metal concentration and C_b its reported background concentration (Lide, 2008). Accordingly, the sediment quality based on CF values was described as follows: unpolluted, if $1 < CF$; moderate polluted, $1 \geq CF < 3$; very strong polluted, $3 \geq CF < 6$; and extremely strong polluted when $CF \geq 6$. This SQG has been widely used by authors such as Hakanson (1980); MacDonald (2000) and Palacios-Torres et al. (2018).

The Pollution Load Index (PLI), a value used to assess the extension of heavy metal pollution in sediments was estimated as the *n*th root of the product of calculated CFs, this is, PLI = $(CF1 \times CF2 \times CF3 \times \cdots \times CFn)^{1/n}$. Based on this index, sediments can be classified as unpolluted when PLI<1, and polluted when PLI ≥ 1 (Priju and Narayana, 2014).

Sediment concentration of environmentally-relevant elements was compared to the threshold effect concentrations (TEC) and the probable effect concentration (PEC) values for freshwater sediments (MacDonald et al. 2000). This method categorizes sediments as not toxic, or that some adverse effects are unlikely to occur when the sediment levels are lower than the TEC value. In contrast, adverse effects are likely to occur when the values are greater than PEC values.

As each heavy metal has unique toxicological features, a common manner to incorporate their intrinsic environmental toxicity in the sediment quality assessment is by using the Potential Ecological Risk Index (RI) (Chandrasekaran et al. 2015) (Equation 1), where $E_{i,}$ is the coefficient of the potential ecological hazard of each heavy metal (Song et al. 2015; Jiao et al. 2015), and $T_{i,}$ is the toxicity coefficient of each heavy metal, adapted from Chandrasekaran et al. (2015). Under this scheme, sediments can be classified as follows: unpolluted if Ei < 30, moderately polluted; 30 ≤ Ei < 60, strongly polluted; 60 ≤ Ei < 120, very strong polluted; 120 ≤ Ei ≤ 240, extremely strong pollution; Ei > 240; whereas Ri values indicate: Unpolluted if Ri < 50; moderately polluted, 50 ≤ Ri < 100; strongly polluted, 100 ≤ Ri < 200; very strong polluted 200 ≤ Ri < 400, and extremely strong pollution when Ri > 400.

Equation 1

$$RI = \sum E_i = \sum T_i * Cf = \sum T_i \frac{C_i}{C_b}$$

2.7. Risk assessment for human health by fish intake

The potential risk for human health derived from fish consumption was calculated using the EDI (µg/kg bw/day) is the Estimated Daily Intake, calculated as follows: EDI = (*Cm**DI*)/*BW*; where *Cm* is the average concentration of metal in fish muscle tissue for a metal (µg/g); DI is the daily intake of fish for children (282.8 g/day) and adult (468.8 g/day); and BW is the average body weight (bw) for children (37.4 Kg) or the adult population (70 kg) (USEPA, 2000). RfD is the Reference Dose (µg/kg bw/day); HQ is the hazard quotient, index that provides a quantitative estimate of the hazard associated with specific chemical elements. The HQ was obtained using the formula: $HQ = EDI/RfD$ (USEPA, 2000; ATSDR, 2000; JECFA, 2015). The RfDs used in this study were 0.3 for As, 1 for Cd, 40 for Cu and 20 for Ni. If HQ is greater than 1, then systemic effects would be evident. In addition, the maximum safe allowed fish consumption limit (CRlim, g/day), considering the non-carcinogenic effect of a specific pollutant, was calculated as follows: CRlim = (RfD*BW)/Cm.

2.5. Statistical analysis

All the data are presented as mean ± standard error. ANOVA was used to evaluate mean differences for chemical element concentrations between fish species, previously checking for normality and homogeneity of variance, using Kolmogorov–Smirnov and Bartlett tests, respectively. When normality was not achieved, Kruskal–Wallis was used instead. As data transformation did not provide normality, Spearman correlation was conducted to evaluate associations between trace elements in sediments and the distance from Station 1, as well as the relationship between trace element levels in fish and trophic status. Principal Component Analysis (PCA) was employed to evaluate the relationship between trophic guild and trace element concentrations in fish. Statistical analyses were performed using IBM SPSS Statistics 21 for Mac. The criterion of significance was set at $p<0.05$.

3. RESULTS

3.1. Trace element contents in sediments

Element concentrations found in bottom sediments at all fifty stations along the course of the Atrato River are shown in Table S2, and the corresponding basic statistics are presented in Table 1. Among examined samples, the median element concentration followed the order: Ba > V > Sr > Cr > Cu > Zr > Ni > Li > Rb > Sc > Ce > Co > Ga > Y > Nd > La > Pb > Nb > Th > Pr > Gd > Sm > Dy > As > Se > Er > Yb > Hf > Cs > U > Ge > Eu > Be > Sn > Ho > Tb > Ta. The rest of the chemical elements, Sb, Tm, Lu, Tl and Cd, had average concentrations lower than 0.50 μg/g (Table 1).

Table 1. Main descriptive statistics of trace element levels analyzed in Atrato River sediments (n=50).

	Statistics (Values in µg/g, dw)				
Element	**Average**	**Median**	**Lower Limit**	**Upper Limit**	**Standard Deviation**
Li	36.3	36.8	21.6	56.8	6.17
Be	1.02	1.06	0.68	1.49	0.17
Sc	31.4	31.0	25.6	45.2	3.20
V	265.3	260.0	207.3	467.3	37.2
Cr	163.2	159.5	90.2	277.1	26.3
Co	25.9	25.4	18. 8	38.0	3.84
Ni	55.2	56.2	30.9	99.6	9.02
Cu	93.4	91.4	47.0	144.6	20.3
Ga	19.8	20.0	17.1	23.4	1.39
Ge	1.27	1.27	1.05	1.56	0.11
As	3.53	3.29	1.68	7.10	0.96
Se	3.12	3.07	2.50	3.88	0.34
Rb	36.4	35.9	21.6	54.2	6.10
Sr	168.9	175.1	58.3	233.0	41.4
Y	19.9	19.9	15.6	24.5	2.27
Zr	61.7	63.5	41.2	77.0	8.07
Nb	5.56	5.61	3.37	7.13	0.64
Cd	0.22	0.21	0.11	0.50	0.06
Sn	0.91	0.92	0.53	1.12	0.12
Sb	0.45	0.42	0.07	1.72	0.22
Cs	1.86	1.92	1.04	2.57	0.32
Ba	**653.1**	621.8	452.0	1300.2	151.5
La*	15.7	15.7	10.3	19.0	1.38
Ce	30.4	30.6	20.0	37.6	2.92
Pr	4.00	3.99	2.88	4.83	0.34
Nd	17.2	17.15	13.1	20.91	1.54
Sm	3.93	3.92	3.17	4.79	0.36
Eu	1.10	1.09	0.85	1.36	0.12
Gd	3.98	3.99	3.15	4.91	0.41
Tb	0.62	0.62	0.49	0.76	0.06
Dy	3.82	3.82	3.03	4.68	0.40
Ho	0.79	0.79	0.63	0.97	0.08
Er	2.34	2.34	1.87	2.87	0.25
Tm	0.34	0.34	0.27	0.41	0.03

Yb	2.25	2.25	1.82	2.73	0.23
Lu	0.33	0.33	0.27	0.40	0.03
Hf	2.06	2.09	1.53	2.49	0.22
Ta	0.54	0.52	0.36	1.08	0.13
Tl	0.26	0.26	0.17	0.35	0.04
Pb	5.62	5.63	1.97	7.41	1.00
Th	4.12	4.01	2.29	10.70	1.07
U	1.61	1.61	1.07	2.24	0.22
ΣLREE			**72.33**		
ΣHREE			**14.47**		
LREE/HREE			**5.00**		

*. Data in yellow and orange correspond to values for LREE (Light rare earth elements) and HREE (Heavy rare earth elements), respectively.

As a way to determine relationships between the concentration of evaluated trace elements at sampling stations and their corresponding distances from Station 1 (Upstream Atrato River, Cabi), a correlation analysis was carried out and the results presented in Figure 2. Interestingly, thirty-one elements increased their sediment concentration downstream the river, with correlation coefficients (Spearman) decreasing in the order: Ba > Yb > Tm > Ho > Er > Y > Lu > Dy > Rb > Tb > Se > Zr > Co > Gd > Sr > Eu > Hf > Cd > Sc > Cs > Sm > Ni > Tl > As > Ge > Pr > Nd > Sb > La > Ce > Be.

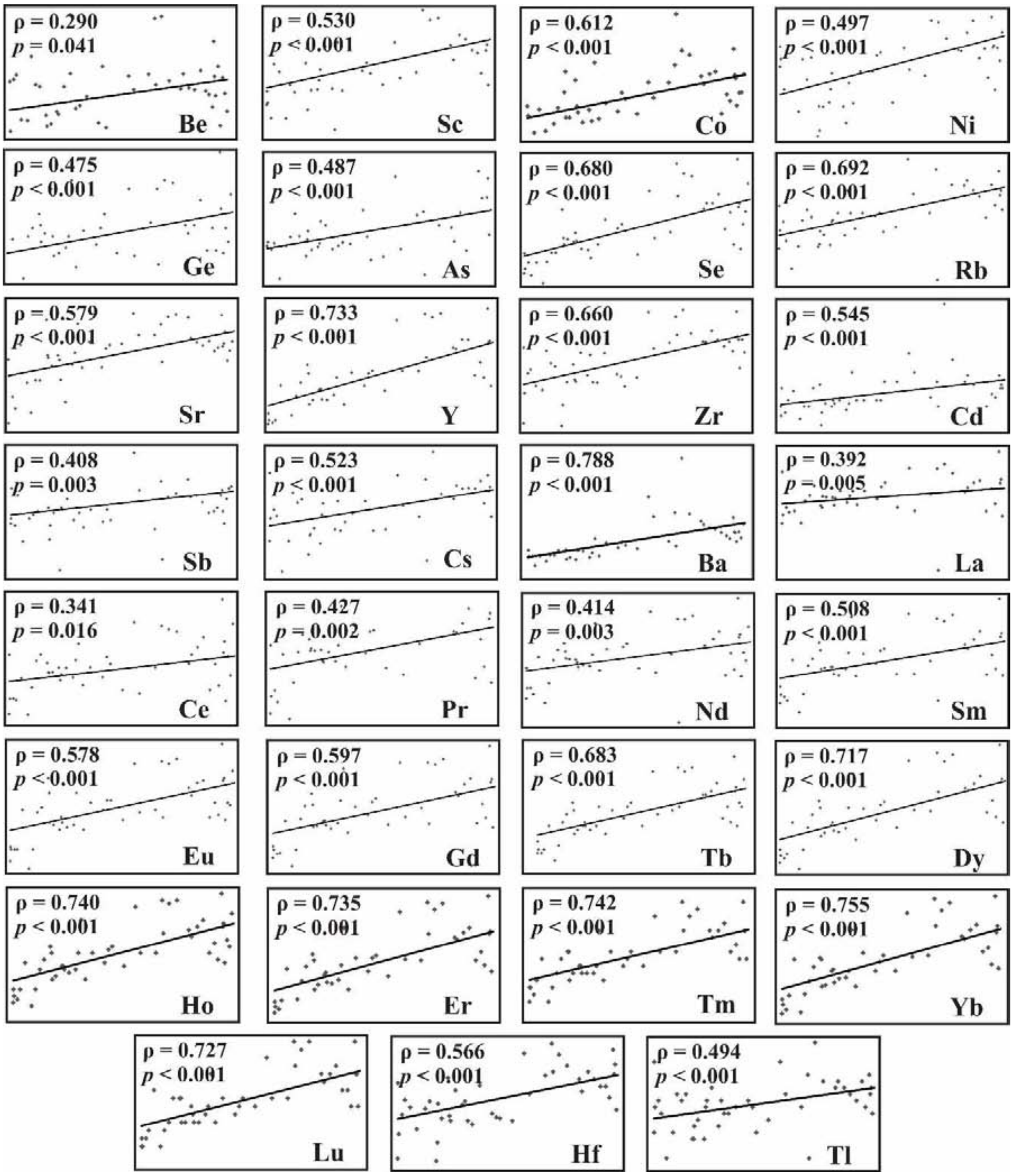

Figure 2. Spearman correlation between trace-element concentration in sediments and distance between the corresponding sampling stations and Station 1. The line appears for illustrative purposes.

3.1. Sediment quality criteria

The frequency distribution for the different evaluated quality criteria on sampled sediments are depicted in Table 2, and the corresponding data for all sampling stations are displayed on Table S3.

Table 2. Frequency of sediment samples categorized according to different sediment quality criteria.

Concentration Factor						
Category / Pollution Level	**Element**					
	Cr	**Ni**	**Cu**	**As**	**Cd**	**Pb**
Unpolluted	2	98	8	2	10	100
Moderate polluted	98	2	92	2	88	0
Strongly polluted	0	0	0	96	2	0
Very strong polluted	0	0	0	0	0	0
Pollution Load Index (PLI)						
Unpolluted			Polluted			
46			54			
TEC and PEC						
< TEC	0	0	0	100	100	100
≥ TEC < PEC	2	22	100	0	0	0
> PEC	98	78	0	0	0	0
Coefficient of the Potential Ecological Hazard (Ei)						
Unpolluted	100	100	100	98	10	100
Moderate Polluted	0	0	0	2	82	0
Strongly polluted	0	0	0	0	8	0

Potential Ecological Risk Index (RI)				
Unpolluted	Moderate Polluted	Strongly polluted	Very strong Polluted	Extremely Strong Polluted
0	90	10	0	0

Findings displayed in Table 2 and Table S3 for Concentration Factor suggest the sediments can be categorized as unpolluted for Ni (98%) and Pb (100%), and moderately polluted for Cr (98%), Cu (92%) and Cd (88%). This sediment quality criterion classified sediments as strongly polluted by As (96%). A different profile seems to emerge when the approach includes mixtures, as represented by PLI. According to this criterion, based on the concentrations of Cr, Ni, Cu, As, Cd and Pb, 54% of the sediment samples are considered polluted. The incorporation of a factor associated with the intrinsic toxicity of these elements in the risk assessment, this is the Ei values, produced RI scores that categorized 90% of sediment samples as moderate polluted and 10% as strongly polluted.

Results showed in Table S3 for As, Cd and Pb levels in sediments were below their respective threshold effect concentration (TEC) in all sampled stations; Cr and Ni were above their probable effect concentration (PEC) in 98 and 78% of samples, respectively; whereas Cu registered concentrations between TEC and PEC in all samples (Table 2).

3.2. Morphometric variables and element content for freshwater fish species

Morphometric characteristics and mean content of toxicologically-relevant elements in muscle tissue for 104 fish specimens gathered from Atrato River are presented in Table 3, whereas data for all elements are shown in Table S4. The largest collected species were *Cathorops melanopus* (1103.3±425.0 g), *Prochilodus magdalenae* (522±73.9 g) and

Hoplias malabaricus (496.9±19.2 g), whereas the most frequently fished were *Hoplias malabaricus*, *Caquetaia kraussii* and *Prochilodus magdalenae*, respectively. The average concentrations (μg/g) of detectable elements in fish decreased in the order: Rb > Sr > Sn > Ba > Cu > Se > Cr > V > As > Ni > Co > Cs > Zr > Cd > Li > Sb > Ce > Ga ≈ La > Tl > Sc > Y ≈ Nd > Be. The rest of the elements were found at levels equal or lower than their LODs (Table S3).

Table 3. Feeding ecology, morphometric parameters and toxicologically-relevant trace element concentrations in fish collected from Atrato River.

Local name	Species	Trophic ecology	n	Weight (g)	Length (cm)	Trace elements (µg/g, fw)				
						Cr	Ni	Cu	As	Cd
Quicharo	*Hoplias malabaricus*	Carnivorous	26	496.9 ± 19.2	34.6 ± 0.4	BDL	0.15 ± 0.02	1.10 ± 0.133	0.07 ± 0.03	BDL
Bagre blanco	*Cathorops melanopus*	Carnivorous	5	1103.3 ± 425.0	46.3 ± 5.7	BDL	BDL	0.96 ± 0.12	0.37 ± 0.09	BDL
Barbudo	*Rhamdia quelen*	Carnivorous	6	221.2 ± 29.8	28.3 ± 1.0	BDL	0.13 ± 0.04	1.19 ± 0.25	BDL	BDL
Doncella	*Ageneiosus pardalis*	Carnivorous	10	221.9 ± 34.3	29.0 ± 1.4	0.53 ± 0.06	0.26 ± 0.05	1.73 ± 0.32	0.38 ± 0.26	BDL
Mojarra amarilla	*Caquetaia kraussii*	Omnivorous	23	187.9 ± 9.4	21.3 ± 0.5	BDL	0.16 ± 0.03	1.15 ± 0.08	BDL	BDL
Charre	*Pimelodus punctatus*	Omnivorous	9	153.5 ± 10.4	27.7 ± 0.7	BDL	0.20 ± 0.05	1.83 ± 0.33	BDL	BDL
Bocachico	*Prochilodus magdalenae*	Detritivores	11	522.2 ± 73.9	32.7 ± 1.2	0.37 ± 0.05	0.22 ± 0.04	1.41 ± 0.13	0.08 ± 0.02	BDL
Guacuco Corroma	*Hemiancistrus wilsoni*	Detritivores	8	269.2 ± 28.5	30.4 ± 1.2	0.41 ± 0.05	0.40 ± 0.06	1.83 ± 0.32	0.43 ± 0.20	0.08 ± 0.03
Boquipompo	*Cyphocharax magdalenae*	Detritivores	6	181.3 ± 29.5	20.0 ± 0.5	BDL	0.12 ± 0.03	1.37 ± 0.30	BDL	BDL

Values are presented as mean ± SEM (adjusted to fresh weight). BDL, Below detection limit. Limits of detection (µg/g, dry weight): Cr, 2.03 µg/g; Ni, 0.60 µg/g; Cu, 0.01 µg/g; As, 0.27 µg/g; Cd, 0.09 µg/g. Pb was assessed but concentrations were below the LOD.

Among well-known toxicologically-relevant elements (Cr, Ni, Cu, As, Cd, and Pb), the largest average concentrations for Ni, As and Cd were observed in *Hemiancistrus wilsoni*, a detritivorous species. This species also depicted high concentrations for about 26% of the analyzed trace elements, indicating it is a direct target from pollution at the Atrato River. The species with the lowest mean levels for these elements, with the exception of As, was *Cathorops melanopus*, a carnivorous species. Largest variation levels in fish muscle were found for Ni and As, with 7.3- and 17.2-fold greater concentrations observed in the species with maximum level compared to that exhibiting the lowest average concentration (Table S4). Moreover, the largest concentrations of Co, Se, Sn and Ni were found for *P. magdalenae* and *H. wilsoni*; whereas *P. punctatus, C. melanopus,* and *P. magdalenae* showed the highest levels of Ba (Table S4).

A correlation analysis was carried out between the trophic level of analyzed fish species and their corresponding trace-element concentrations in fish muscle. The results are presented in Figure 3 (Rubidium, Rb, and Cesium, Cs) and Table 4. Rubidium and Cs showed a positive correlation with trophic level, suggesting these two metals are being biomagnified in the trophic chain. In the case of Rb, *Prochilodus magdalenae*, despite of being a detritivorous species, had the greatest bioaccumulation capacity for this element (Figure 3).

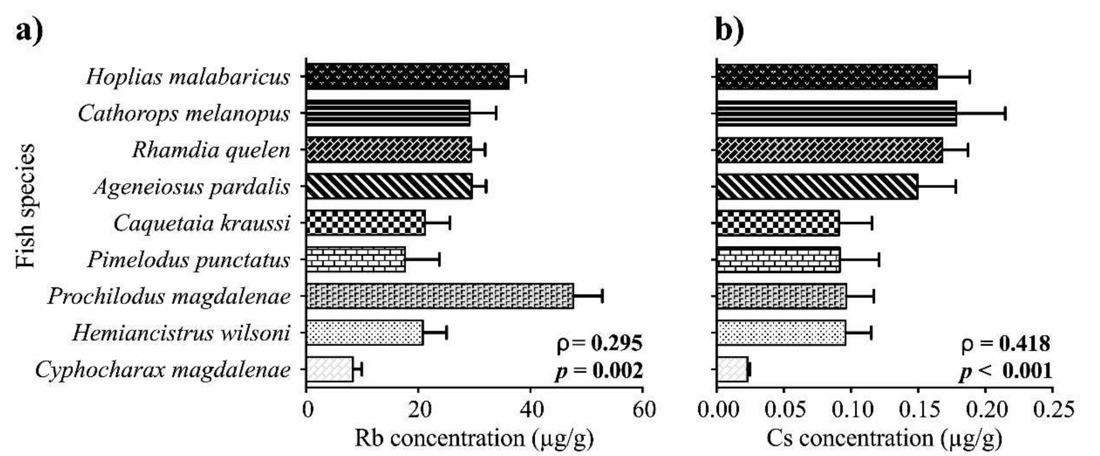

Figure 3. Rubidium and Cs concentrations (fresh weight) in muscle of fish from different trophic levels collected in Atrato River. The spearman correlation (ρ) for trophic level vs. metal concentration, and their respective *p*-values are shown for each metal.

Negative relationships between fish trophic status and tissue concentration were detected for Co, Ni, Cu, Sr and Ba (Table 4), suggesting that element bioaccumulation is not dependent on the food chain but rather on particular fish characteristics.

Table 4. Spearman correlation between element concentration and trophic level in fish (n=104) from Atrato River.

Element	**Spearman Correlation***	***p*-value**
	Positive correlations	
Rb	0.295	**0.002**
Cs	0.418	**< 0.001**

	Negative correlations	
Co	-0,446	**< 0.001**
Ni	-0,208	**0.034**
Cu	-0.359	**<0.001**
Sr	-0.219	**0.026**
Ba	-0.211	**0.032**
Lack of correlations		
Y	0.016	0.874
Ce	0.083	0.402
Nd	0.080	0.418
V	-0.095	0.340
Cr	-0.040	0.690
As	-0.067	0.498
Se	-0.111	0.260
Zr	-0.031	0.755
Nb	-0.052	0.599
Cd	-0.072	0.470
Sn	-0.113	0.257
Sb	-0.074	0.456
Hf	0.021	0.836
Tl	-0.009	0.931
Pb	-0.019	0.846

Th	0.047	0.632
U	-0.113	0.253

*. Elements not shown in this table had at least 50% of all values lower than the LODs.

3.3. Human health risk assessment of heavy metals

The RfDs and diet-based risk indexes derived from toxicologically-relevant trace element values present in fish muscle are show in the Table 5. The highest EDI values were lower than their corresponding RfDs for examined elements, except for As, which reached values 10.8-fold greater than the RfD.

Arsenic in fish muscle generated HQ values between <1 to 10.8, suggesting that consumption of some fish species, in particular *C. melanopus*, *A. pardalis* and *H. wilsoni*, represent a risk for human health in this river (Table S5), as the consumption of a very small piece (26-30 g/day) may represent a risk for As exposure.

Table 5. Estimated Daily Intake (EDI), Hazard Quotient (HQ) and Maximum Safe Allowable Fish Consumption Limit (CRlim, g/day) obtained for some trace-elements present in fish muscle.

Element	Trace Element Concentration	Children			Adults		
RfD		EDI	HQ	CRlim	EDI	HQ	CRlim
As	Lowest	-	-	-	-	-	-
0.3	Highest	3.25	10.8	26.09	2.88	9.60	48.8

Cd	Lowest	-	-	-	-	-	-
1	Highest	0.60	0.60	467.5	0.54	0.54	875
Cu	Lowest	7.26	0.18	1558.33	6.43	0.16	2917
40	Highest	13.84	0.35	817.49	12.26	0.31	1530
Ni	Lowest	-	-	-	-	-	-
20	Highest	3.02	0.15	1870.00	2.68	0.13	3500

RfD. Reference Dose.

4. Discussion

The sediment loads from rivers are considered a global source of pollution to the sea. These discharges cause negative impacts on the marine ecosystems and have been linked to coral reef destruction and reduction abundance of seagrass beds (Dikou and Woesik, 2006; Restrepo et al. 2006), among other impacts. Massive gold mining operations and deforestation in the Atrato River basin incorporates around 11.3 x 10^3 ton/year of sediments in the Caribbean (Vélez-Agudelo and Aguirre-Ramirez, 2016), delivering several pollutants, particularly trace-elements from soil run-off. The evaluation of these pollutants provides valuable information on the impact of this river in the Caribbean Sea.

In this work, forty-two trace elements present in sediments were evaluated, emphasizing on those toxicologically-relevant. Mercury (Hg) was not included in this paper because data regarding this metal was already published (Palacios-Torres et al. 2018). Mean Cr concentration in sediments from Atrato River (163.4 µg/g) were 4.9-fold greater than those found in Magdalena River (33.2 µg/g), the largest in Colombia (Tejeda-Benítez et al. 2018). Moreover, this Cr level was approximately one order of magnitude greater than that found in a typical tropical gulf (17.2-28.4 µg/g) (Norville, 2005), indicating that Atrato River is a likely source for this metal in the Caribbean. Cupper levels were 3.4-fold greater in the Atrato compared to the Magdalena River (Tejeda-Benítez et al. 2016), finding that is not surprising as near the Atrato birth there is an active Cu mine (El Roble Cupper Mine, 5°9.06´37.6” N – 76°14.2´8.64”). In contrast to Cu, average Cd level was 5.9-fold-lower in Atrato than in Magdalena River. This toxic element is a metal commonly found in leachates from landfills where batteries are not properly disposed (Olivero-Verbel et al. 2008), and in urban sewages (Pastor and Hernández, 2012; Noorhosseini et al. 2017), and this may explain its low fingerprint in Atrato River.

Average Pb levels in Atrato River (5.6 µg/g) were lower than those registered in Blanco (32 µg/g) and Tonalá (38 µg/g) Rivers in Mexico (Vázquez-Botello et al., 2004), approximately half those detected in Magdalena River (12.1 µg/g) (Tejeda-Benitez et al. 2018), and similar to those found in the Jamapa-Atoyac fluvial system (5.0 µg/g), one of the most important discharges into the Gulf of Mexico (Cabral-Tena et al., 2019). Lead is a toxic element frequently present in wastewaters from urban cities that is usually associated to economic development (Han et al. 2018), fact that may explain its low levels in Atrato River. In the case of As, sediment levels oscillated from 1.7 to 7.1 µg/g, with an average of 3.5 µg/g. This last value was similar to that found in sediments from Magdalena River (5.3 µg/g), and both are in agreement with those present in sedimentary rocks (5-10 µg/g) (Smedley and Kinniburgh, 2002).

The pollution by trace-elements in sediments has been associated to near distance sources such as wastewater, storm-generated runoff, and industrial activities (Islam et al. 2015; Mohammad Ali et al. 2016; Cooper and Gillespie, 2001). However, due to the absence of large urban centers or industries in the Atrato watershed, As, Cu and Cd may result incorporated in the sediments likely as a result of deforestation and soil removal during ASGM activities (Figure S1), as has been observed in other mining areas (Kinimo et al. 2018; Obiri et al. 2016; Odumo et al. 2011).

For some of the trace elements measured in sediments, their average concentrations (µg/g) were lower or similar to those found in the earth crust, including Yb (2.3 vs. 2.3), Tm (0.3 vs. 0.4), Er (2.3 vs. 2.3), Lu (0.3 vs. 0.4), Rb (36.4 vs 94), Tl (0.3 vs. 0.6), As (3.5 vs. 5.7), Ge (1.3 vs. 1.3), Sb (0.5 vs. 0.8), Cs (1.9 vs 4.9), Be (1.0 vs. 1.9); however, for elements such as Co (25.9 vs. 15), Cd (0.2 vs. 0.09), Sc (31.4 vs. 14) and Ni (55.2 vs 34), their levels were greater (Hu and Gao, 2008), indicating those could represent a hazard for the aquatic diversity along Atrato River watershed, even marine wildlife in the Caribbean.

Something interesting to highlight was the negative relationship between the ratio of LREE/HREE and the distance from the Station 1 to the rest of sampling sites (Figure S2), clearly indicating the enrichment of LREE upstream the river, where gold mining is extensive (Figure S1). It has been demonstrated that rare earth elements, in particular lanthanides, LREE, diffuse from indigenous rocks to the environment (Romero-Freire et al. 2018), making them important pollutants in mining areas (Liang et al. 2018). Other studies have also pointed out that the input/release of rare elements into sediments may result from geological process (Rudnick and Gao, 2003, Hu and Gao, 2008) and also from alluvial and atmospheric deposition (Gómez and

Almanza, 2015). Once in the environment, these rare elements are able to reach organisms and cause adverse biological effects (Amyot et al. 2017).

In Atrato River, gold mining areas are mostly located upstream sampling site 1, although mineral extractions are also present in the middle Atrato. Therefore, it is quite puzzling the enrichment increase observed for many elements downstream the river. The source of elements in sediments can be monitored using different markers, including element ratios. During mining, rocks are broken and their mineral surface area exposed, a process that is considered physical weathering. The Rb/Sr is commonly associated with weathering intensity (An et al., 2018), and as a consequence, high Rb/Sr ratios can be indicative of mining/deforestation inputs in the river. As presented in this work (Figure 4), high Rb/Sr values are observed in upstream stations, suggesting anthropogenic-derived weathering is taking place at these sites.

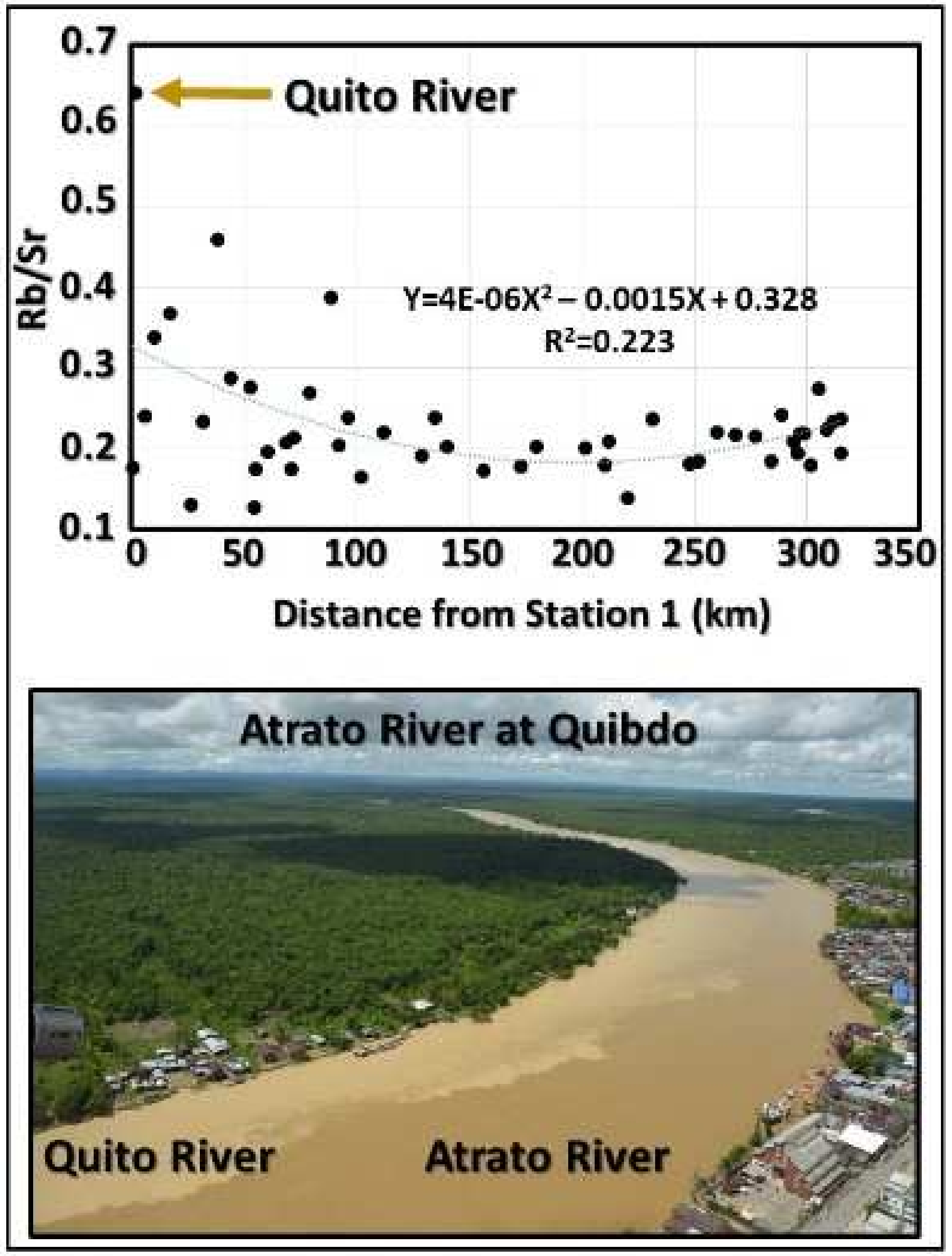

Figure 4. Rubidium - Strontium ratio in sediments from Atrato River (Upper Panel). The impact of mining carried out on Quito River (Station 2) over Atrato River is clearly visible (Lower Panel).

Although evidence presented supports anthropogenic activities are a primary source of trace elements in sediments from Atrato River, still this does not explain the enrichment downstream the current. A plausible explanation may be found in a different trace element ratio, the Zr/Hf. As presented in Figure S3, there is a good correlation between Zr/Hf and distance from Station 1 (ρ=0.626, p<0.001). This ratio is considered a good indicator of the presence of colloidal or very fine sand fractions in the water/sediment that are able to remove Hf faster than Zr (Censi et al., 2018; Li et al., 2016). Smaller particles not only travel farther, they spend longer times in the water before sedimentation, allowing the capture of more water-dissolved elements. Although the presence of colloidal particles in the river could provide some explanation, other factors may be involved in the element enrichment downstream, including element transformation that facilitate its deposition, or even geological factors, among others.

Among trace elements studies here, most of them are being significatively correlated with each other (Figure S4). It is well known that correlations between elements may result from links to common sources or parent minerals (Diami et al., 2016; Wang et al., 2014), suggesting trace elements in Atrato River are likely derived from similar sources. Interestingly, Cr was the element with the lower number of significant correlations with other elements. Although this deserves further research, specific unknown Cr sources or differences in sediment deposition characteristics may be key factor to support this finding.

The sediment quality of Atrato River based on measured trace element concentrations involved both geochemical and biological terms. First, the Concentration Factor based on Cr, Cu and Cd levels characterized most of the sediments samples (88-98%) as moderate polluted, whereas As did it as strongly polluted (96%). Geochemical processes undertaken when the rock is exposed to the air and water during soil removal released different metals from their sinks, and as a consequence, the PLI scores categorized 54% of the sediments as polluted. As these chemicals are enriched in the sediments, most likely as a result of soil and rock leaching (Hadzi et al. 2018; Assawincharoenkij et al. 2018), it is clear that forest destruction during gold mining incorporates these chemicals in the Atrato basin. Results presented here also revealed that sediments from Atrato River contain trace elements at concentrations that may be impacting the biota of this biodiversity hotspot (Reid, 1998). Among analyzed elements, sediment quality guidelines based on TEC/PEC suggest that Cr and Ni are of concern, as most stations are above PEC values, whilst As, Cd and Pb were below their TEC, which indicates that on aquatic organisms potentials effects will be unlikely. This finding for Ni (>PEC) was similar to that observed for Magdalena River in the mining-impacted area of Gamarra (Tejada-Benítez et al. 2016). Moreover, the Ei values also suggested Cd has a moderate potential as an ecological hazard in sediments from Atrato River. Taken together, these toxic chemicals have the potential to generate adverse effects on the environmental and public health in Atrato River (Fashola et al. 2016; Falagán et al. 2017).

The presence of several elements in fish muscle suggests there is a transfer from reservoirs, such as sediments and water, into the trophic chain. In overall, trace elements displayed different patterns of bioaccumulation that did not follow a trend mediated by trophic ecology, suggesting that other factors besides food habits may be determining bioaccumulation, for instance physiological processes, and environmental location, among other processes (Li and Gao, 2014; Velez et al. 2015).

The largest concentrations for Sr, Sn, Ba, Cu, Se, V, As, Ni, Co and Zr were registered in muscle tissue of low trophic level species, as also observed in studies by Kuklina et al. (2014) and Jiang et al. (2018) in fish from South Moravian region and Lake Caizi, China. In this study, *H. wilsoni*, a detritivorous species, displayed the largest average concentrations for Ni, As, Se, Cd, Sn and Sb, whereas for other elements, such as Sr and Co, the greater concentrations were observed also in a detritivore species, *P. magdalenae*. Moreover, greatest levels of Sc, Cr, Y, Nd and Tl were detected in an omnivorous species, *Ageneiosus pardalis.* These last two species are the most popular commercial fish species in the region. This is not an isolated finding, and it may reflect the accumulation of these elements in the sediments, in this case, mainly from extensive mining and deforestation, major anthropogenic activities in Atrato River watershed (Figure S1). These fish species feed on detritus found on bottom sediments, an environmental compartment that at the same time works as a sink for many elements released into the water, leading to their enrichment in biota. A similar accumulation profile for Cd was found in different imported fish of the Prochilodus genus sold in the Colombian Caribbean (Herrera-Herrera et al. 2018).

It is noteworthy to mention that Rb and Cs followed a concentration-dependent relationship with trophic level. Although several reports have shown these two elements can undergo biomagnification processes in the environment (Pinder et al. 2011; Ikemoto et al. 2008), a lack of trophic transfer has also been described (Torres et al. 2014). It should be pointed out that although for several elements trophic transfer may not be a predictor of toxicity (Cardwell et al. 2013), further experiments should be carried out with Rb and Cs to establish their potential hazard in the environment and human diet. The data on Rb is scarce, and the fact that it alters spermatogenesis in *Angilla japonica* (Yamaguchi et al. 2007), should be considered as a starting point to generate evidence linking these chemicals to the decline in some fish populations at Atrato river.

Metals concentration in edible portions of fish tissue can also provide an overview of risk for consumer's health. The HQ values were lower than 1 for Cd, Cu and Ni, but was considerably high for As, with values up to 10.8. According to specific data for fish species (Table S5), carnivorous species such as the *H. malabaricus*, *C. melanopus,* and *A. pardalis,* as well as the detritivorous *P. magdalenae* and *H. wilsoni,* should not be consumed regularly, and As levels should be carefully monitored on these species. This result was similar to that reported for Hg by Palacios-Torres et al. (2018) in fish species such as *H. malabaricus*, *R. quelen, A. pardalis, P. schultzi* and *S. aequilabiatus.* As it has been reported, gold mining constitutes one of the most important anthropogenic forces that impacts the dynamics of Atrato River, especially in terms of Hg pollution (Palacios-Torres et al. 2018). Although it has been a common practice to associate ASGM with Hg pollution in biota (Olivero et al., 1998), this metal cannot be considered the only element of concern, and usually in studies dealing with ASGM, there is very little information available on other trace elements.

Trace elements in fish may have a number of different sources, such as industrial activities, agriculture (Zuliani et al. 2019), natural weathering (Djikanović et al. 2018), and mining (Urien et al. 2018), among many others. Principal Component Analysis (PCA) provides insight into the possible sources of trace-elements in environmental matrices. Based on the PCA analysis (Figure S5), trace elements in fish muscle could be grouped into a three-component model, which accounted for 48.1% of the total variance.

The first PC (26%) correlated with Sn, Ni, Cr, Cu, Co and Se. In this group, Ni, Cu and Co correlated negatively with fish trophic level, as greater bioaccumulation of these elements occurred in fist species corresponding to low trophic level. The second PC explained 11.5% of the data variability, and included Sc, Ce, V, Li and Zr. Among these elements, Sc and Ce correlated positively with trophic status, and V and Li did it negatively, although in all cases correlations were not significant and close to zero. The third PC (10.6%) depended on Rb, Cs and Tl, where both Rb and Cs displayed a trophic-level dependent increase in concentration. These PCA results suggest trace-element distribution in fish is primarily dependent on trophic status, rather than on particular sources of pollutants. As the Atrato River does not have major anthropogenic activities different from gold mining, it is likely that the close proximity between trace-element clusters is highlighting a rainforest soil origin for trace-elements in fish.

This is the first report of multiple trace elements in sediments and fish from Atrato River, and therefore they represent a valuable baseline for future studies. However, the data clearly evidence the large impact of mining practices in sediment quality and human health risks derived from fish consumption. The challenges ahead to guarantee the legal rights of the Atrato River are gigantic, and those include a critical and closer follow up of the mandatory actions given by the Constitutional Court of Colombia to halt destructive operations on the river, to guarantee the protection of civil leaders, and promote a true compromise from government agencies and citizens to guarantee the promulgated rights. The effectiveness of the programs should be monitored on water, sediment quality, as well as on human and fish health, and this requires greater building capacity on the local public university. Finally, the impact of the rushing Atrato River on the Caribbean, should not be underestimated, and this requires further research. At the end, protecting Atrato River is also a guarantee of a longer survival for humans and many living species on this planet.

5. Conclusions

The Atrato River is one of the few in the world protected by a constitutional law due to its destruction by gold mining. Thirty-one trace elements are enriched in sediments along the river, and environmental risk indexes suggest sediments are polluted by As, Cr, Cu, Ni and Cd. Greater average concentrations of Cr, Ni, Cu, As and Cd were detected in species with low trophic status, whereas Rb and Cs concentrations in fish muscle correlated with fish trophic level. The Hazard Quotient (HQ) indicated several species should not be eaten due to As content. In short, sediment and fish quality in Atrato River are deteriorating as a result of the releasing of toxic elements in the environment, likely from mining and deforestation.

Conflict of Interest

The authors declare no conflict of interest.

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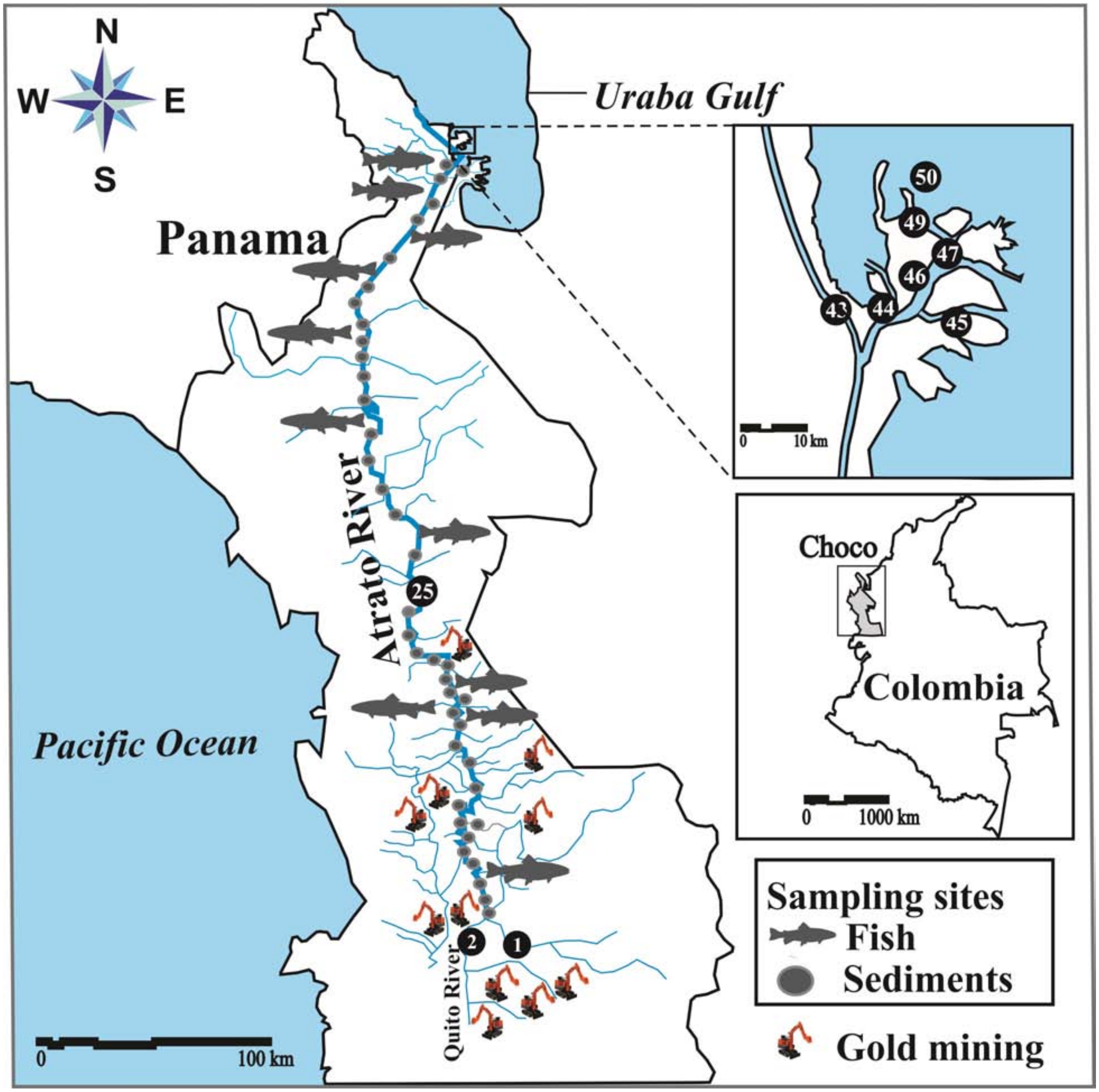
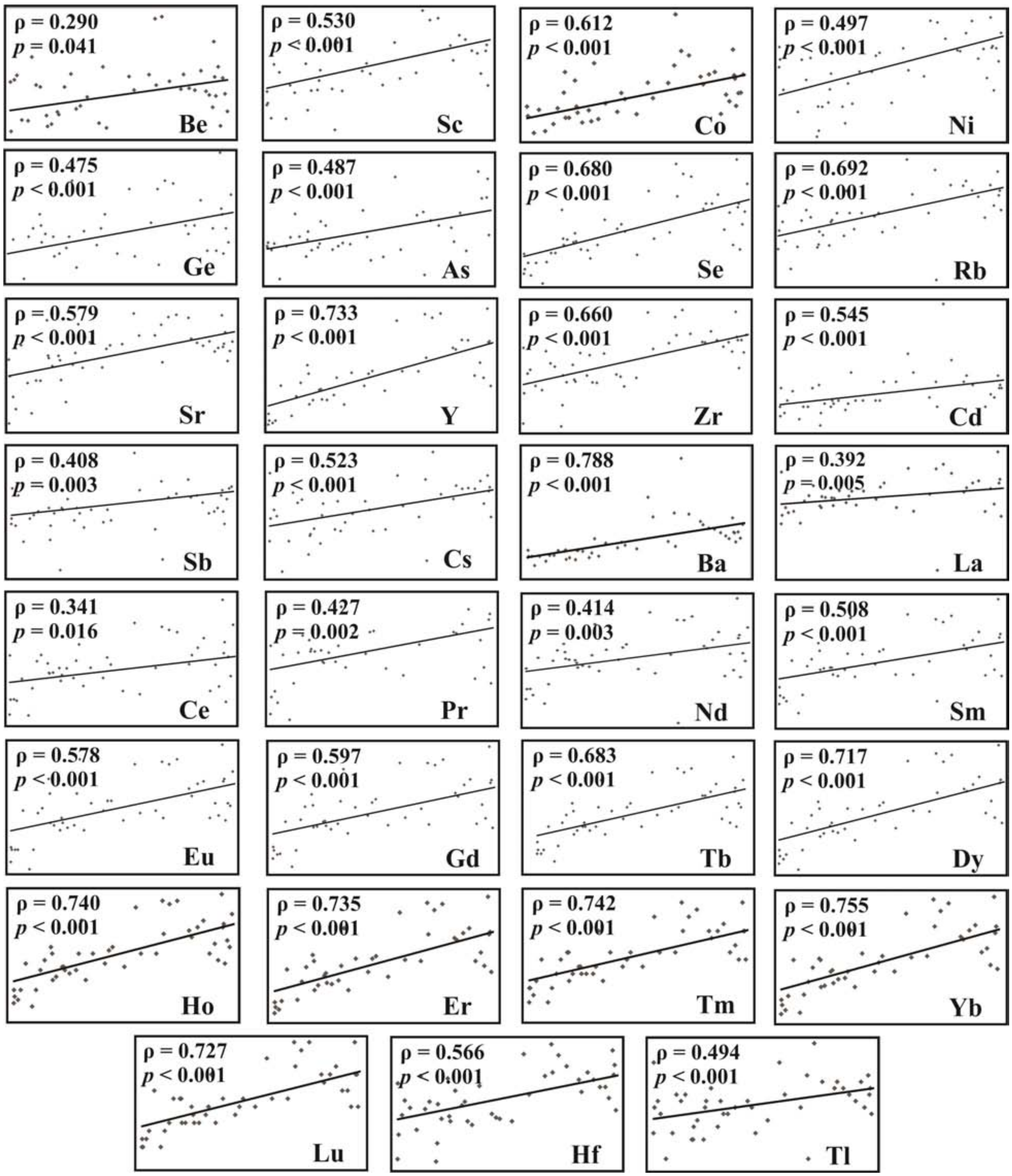
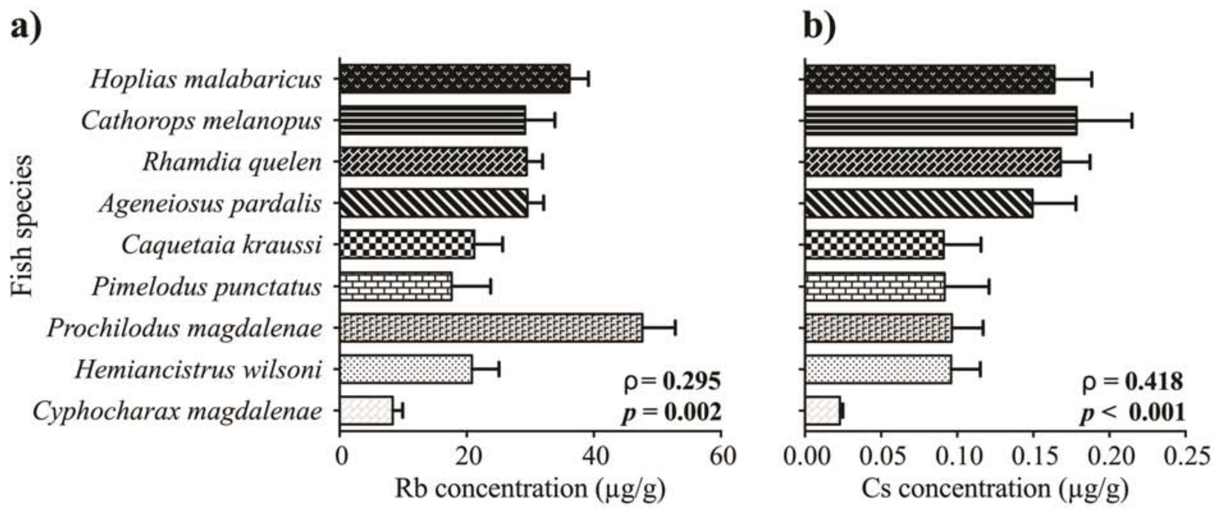
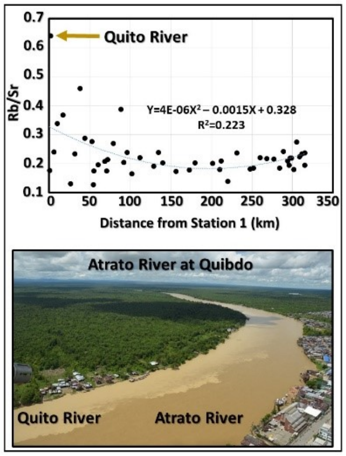

N
W
E
S
Uraba Gulf
Panama
Atrato River
Pacific Ocean
Quito River
25
2
1
0
100 km
50
49
47
46
43
44
45
0
10 km
Choco
Colombia
0
1000 km
Sampling sites
Fish
Sediments
Gold mining


ρ = 0.290
p = 0.041
Be
ρ = 0.530
p < 0.001
Sc
ρ = 0.612
p < 0.001
Co
ρ = 0.497
p < 0.001
Ni
ρ = 0.475
p < 0.001
Ge
ρ = 0.487
p < 0.001
As
ρ = 0.680
p < 0.001
Se
ρ = 0.692
p < 0.001
Rb
ρ = 0.579
p < 0.001
Sr
ρ = 0.733
p < 0.001
Y
ρ = 0.660
p < 0.001
Zr
ρ = 0.545
p < 0.001
Cd
ρ = 0.408
p = 0.003
Sb
ρ = 0.523
p < 0.001
Cs
ρ = 0.788
p < 0.001
Ba
ρ = 0.392
p = 0.005
La
ρ = 0.341
p = 0.016
Ce
ρ = 0.427
p = 0.002
Pr
ρ = 0.414
p = 0.003
Nd
ρ = 0.508
p < 0.001
Sm
ρ = 0.578
p < 0.001
Eu
ρ = 0.597
p < 0.001
Gd
ρ = 0.683
p < 0.001
Tb
ρ = 0.717
p < 0.001
Dy
ρ = 0.740
p < 0.001
Ho
ρ = 0.735
p < 0.001
Er
ρ = 0.742
p < 0.001
Tm
ρ = 0.755
p < 0.001
Yb
ρ = 0.727
p < 0.001
Lu
ρ = 0.566
p < 0.001
Hf
ρ = 0.494
p < 0.001
Tl


a)
b)
Fish species
Hoplias malabaricus
Cathorops melanopus
Rhamdia quelen
Ageneiosus pardalis
Caquetaia kraussi
Pimelodus punctatus
Prochilodus magdalenae
Hemiancistrus wilsoni
Cyphocharax magdalenae
ρ= 0.295
p = 0.002
0
20
40
60
Rb concentration (µg/g)
ρ = 0.418
p < 0.001
0.00
0.05
0.10
0.15
0.20
0.25
Cs concentration (µg/g)


Quito River
Rb/Sr
Y=4E-06X² – 0.0015X + 0.328
R²=0.223
Distance from Station 1 (km)
Atrato River at Quibdo
Quito River
Atrato River

Highlights

Forty six trace elements were evaluated in sediments and fish from Atrato River.

Ninety four percent of sediment samples were polluted by Cr, Ni, Cu, As, Cd and Pb.

Rb and Cs in fish followed a concentration-dependent relationship with trophic level.

H. wilsoni had high values for most elements and its consumption should be avoided.

Gold mining is the most likely source of trace elements in Atrato River

“Trace elements in sediments and fish from Atrato River: an ecosystem with legal rights impacted by gold mining at the Colombian Pacific”

The authors declare no conflict of interest.