

Metal concentrations in aquatic environments of Puebla River basin, Mexico: natural and industrial influences

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Abstract The rapid urban expansion and presence of volcanoes in the premises of Puebla River basin in central Mexico exert significant influences over its aquatic environments. Twenty surface sediment samples from Puebla River basin consisting of R. Alse seca, R. Atoyac, and Valsequillo dam were collected during September 2009 and analyzed for major (Al, Fe, Mg, Ba, Ca, and K) and trace elements (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sr, V, and Zn) in order to identify the metal concentrations and their enrichment. R. Atoyac sediments presented higher concentrations of Ba ($1193.8 \mu\text{g g}^{-1}$) and Pb ($27.1 \mu\text{g g}^{-1}$) in comparison with the local reference sample values. All the metal concentrations except Sr for R. Alse seca sediments were within the range of local reference sample values indicating no significant external influence, whereas Valsequillo dam sediments had elevated concentrations of all the metals suggesting both natural and external influences in the study region. The magnitude of metal contamination was assessed using several indices such as geoaccumulation index (I_{geo}), enrichment factor (EF), degree of contamination (C_d),

and pollution load index (PLI). The results suggest that As, Pb, and Zn were predominantly enriched in the Puebla River basin sediments. Comparing with sediment quality guidelines and ecotoxicological values, it is revealed that Cd, Cr, Cu, and Ni have possible harmful effects on the biological community. The present study provides an outlook of metal enrichment in Puebla River basin sediments, highlighting the necessity to conserve this river ecosystem for the near future.

Keywords Metal concentrations · River and dam sediments · Contamination indices · Puebla · Mexico

Introduction

Trace metal contamination in aquatic systems has elicited a global attention owing to their toxicity, abundance, persistence, and non-biodegradability (Hanif et al. 2016; Fu et al. 2014; Waheed et al. 2013). Rapid industrialization and intensive and uncontrolled urbanization result in excessive release of metals into the riverine system, where they are possibly bioaccumulated and even biomagnified through the food chain posing a potential harmful effects on human health and the entire ecosystem (Mountouris et al. 2002; Rainbow and Luoma 2011). Trace metals in the riverine system are distributed between the aqueous phase and bed sediments, wherein a significant quantity of metals accumulate in sediments via physical, chemical, and biological processes (Suthar et al. 2009; Li et al. 2001). Under changing aquatic conditions, trace metals in sediments can be released into the water column once again, further deteriorating the river quality (Chen et al. 2016; Nemati et al. 2011a; Bartoli et al. 2011). Therefore, river sediments are considered as most important metal repositories to assess pollution in the aquatic environment and possible environmental health risks (Sreekanth et al. 2015; Zahra et al. 2013).

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The discrimination of pollution source of metals and their quantitative determination is mandatory for river eco-environment protection (Varol 2011; Singh et al. 2005). Metals are introduced into the river systems by the following two primary pathways: natural sources (volcanism, erosion, bacterial activity, weathering processes) and exogenous inputs (industrial processing, mining, and other effluent discharge). In order to differentiate the influence of natural and anthropogenic sources of metals, several indices such as enrichment factor (EF), geoaccumulation index (I_{geo}), degree of contamination (C_d), and pollution load index (PLI) are widely applied in environmental studies (Hamdoun et al. 2015; Brady et al. 2014; Armid et al. 2014; Wei et al. 2011). Apart from this, it is equivalently important to evaluate the potential biological risks posed by the presence of these metals in the aquatic environment, which is achieved through comparisons with sediment quality guidelines (SQGs) and ecotoxicological values (Bastami et al. 2015; Merhaby et al. 2015; Wang et al. 2015).

The Puebla River basin in central Mexico constitutes of Atoyac River, a major south–central river flowing through the states of Puebla and Tlaxcala in Mexico, one of the most contaminated rivers of the country (CONAGUA 2010), and the Alseseca River, which forms the receptor of industrial and domestic wastewater, finally draining into the Valsequillo dam located beyond the city limits. The study area is flanked by the volcanoes (extinct and active) in eastern and western sides. This river basin has witnessed an incredible urban and industrial expansion, which led to a substantial demographic growth (154%) during the last two decades (INEGI 2010). Thus, the presence of volcanoes and industrial complexes in the Puebla river basin significantly influence the river environment driving the need for assessment of pollution sources.

The present study aims to (1) evaluate the metal concentrations in the river and dam sediments; (2) quantifying the extent of metal pollution using EF, I_{geo} , the C_d , and PLI; (3) assessing the harmful biological effects by comparing with SQGs and ecotoxicological values; and (4) delineate the metal sources (natural or anthropogenic) by application of multivariate statistical techniques.

Materials and methods

Study area

Regional and hydrological setup

The Puebla River basin covering an area of 4395 km² between the latitude 18° 57' 02" N and longitude 98° 15' 37" W lies on the central part of Mexico over the volcanic highlands, which is flanked by La Malinche volcano in the east, and the Sierra Nevada formed by Iztaccíhuatl and Popocatepétl (active) volcanoes in the west and northwest. The hydrological system of

this basin consists of two main rivers Atoyac and Alseseca draining into the Valsequillo dam (Fig. 1). The Atoyac River is fed by the snowmelt and runoff from Iztaccíhuatl volcano, whereas the Alseseca River on the western side of La Malinche volcano is fed by the runoff from Sierra de Tlaxco (Tlaxcala Plateau). The Atoyac River is joined by Zahuapan River which flows through the Tlaxcala state and connects the Atoyac River before entering the Puebla City. The average annual flows of Atoyac and Alseseca Rivers before draining into the Valsequillo dam are 6.7 and 0.8 m³/s, respectively (Saldaña et al. 2008). The calculated total suspended solids (mg/L) for R. Atoyac and Valsequillo dam were 792.18 and 481.43, respectively (Martínez-Tavera 2016).

The Valsequillo or Manuel Ávila Camacho dam built between 1941 and 1946 located at 22 km south of the city of Puebla receives the runoff from R. Atoyac and R. Alseseca. It is 15 km long with an area of 237.9 km² and 405 million m³ of water storage capacity (CNA 2005). The principal land use of this river basin is attributed for agricultural activities accounting for 63.6% and relatively less for forest cover (22%), pastureland (4.95%), and lastly occupied by urban zone which accounts for 7.6% (IMTA 2005; Martínez-Tavera 2016). The main crops irrigated with this river water are corn, sugarcane, potato, beans, chili, alfalfa, coffee, and tomatoes. The river basin experiences sub-humid climate with an average annual precipitation of 800 mm and temperature of 22 °C. The dry season corresponds to the months of March–May, the rainy season from June to September, and winter during October–February (National Meteorological Service 2010).

Geological setting

Geologically, Puebla basin is surrounded by Neogene-Quaternary stratovolcanoes and mountain ridges of Upper Cretaceous limestone filled with volcanic tuffs, lahars, lava flows, cinder cones, lacustrine fluvial deposits, and reworked glacial-fluvial materials (Morales-Ramírez et al. 2003). The Paleozoic metamorphic rocks of the Acatlan complex and Mesozoic terrigenous and calcareous rocks form the basement of this basin (Von Erfa et al. 1977; Ortega-Gutiérrez 1978 1993; Mooser et al. 1996). The northern limits of the valley are characterized with Pliocene lacustrine deposits composed of shales, sandstones, and continental limestones (Flores-Márquez et al. 2006). The Valsequillo basin is underlined by the bedrock of Balsas group constituting coarse Cretaceous limestone conglomerate cemented together by a matrix of red mudstone. The deposits also include thin layers of volcanic ash, rhyolitic, and basaltic with pumice lapilli (Malde 1968).

Anthropogenic setup

The Puebla River basin has an extension of 2320 km² in the state of Puebla and 2075 km² in Tlaxcala. During the period of

1990 to 2010, there was an increment of population in the states of Puebla (64.55%) and Tlaxcala (64.98%), respectively (INEGI 2010). On the industrial front, the Puebla City hosts a number of industries related to metals (43%), machinery, heavy equipment, food sector (25%), textiles (14%), clothing, leather, chemicals (10%), oil, rubber, plastics, timber products (3%), and other industries (1%) (INEGI 2010). The presence of these industrial complexes close to the river network forms an easy access for discharge of effluents into the river system.

Sample collection

Twenty surface sediment samples were collected during September 2009 from the river channels in the central part of R. Alseseca (sample nos. 1–3), R. Atoyac (sample nos. 4–9), and Valsequillo dam (sample nos. 10–20) (Fig. 1). The surface sediment samples were collected using a plastic spatula, and Van Veen grab sampler was used, where the depth of water column was about 0.5 to 2.3 m. Two local reference samples (sediments) were collected from the mountainous region of San Miguel Canoa (BS1) and San Marcos Jilotepec (BS2) of similar source rock composition to that of the riverine sediments and considered to have no external influence. These samples were used as background values for calculating the different environmental indices used in the present study. The samples were immediately packed, oven dried below 40 °C, and grinded using agate mortar for further analyses.

Analytical procedure

Major geochemical elements (Al, Fe, Mg, Ba, Ca, and K) and trace elements (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sr, V, and Zn) were analyzed based on modified microwave digestion technique of EPA 3051A (2007). Dry powdered sample (0.5 g) were mixed with 10 ml of HNO₃, 3 ml of HCl, and 1 ml of deionized water and enclosed in a polytetrafluoroethylene (PFA) vessel. They were heated to 120 °C for 40 min, and the solutions were filtered and made up to 50 ml. The final solutions were analyzed in ICP-OES (Varian 720 ES) for metal concentrations. Standard Reference Material Loam Soil B (SRM no. 691029) was introduced in every fifth sample to check the accuracy of the analysis. Recoveries of the elements were in the following order: Al (109%), Fe (112%), Mn (81%), Zn (101%), Cr (102%), V (112%), Ni (96%), Cu (100%), Co (88%), Pb (99%), and Cd (92%). The uncertainty values for the analyzed elements were as follows: Al ±23,695; Fe ±6015; Mn ±274; Mg ±571; Ba ±477; Ca ±542; K ± 1430; As ±1.29; Cd ±3.37; Co ±6.32; Cr ±22.76; Cu ±14.35; Ni ±16.36; Pb ±29.91; Sr ±29.03; V ± 1881; and Zn ±38.04.

The degree/level of metal enrichment in the study region was assessed using several contamination indices such as I_{geo} (Müller 1979), EF (Buat-Ménard and Chesselet 1979), C_d (Hakanson 1980), and PLI (Tomilson 1980). The possible harmful

ecological effects due to the presence of these metals were identified through sediment quality guidelines (threshold effect concentration (TEC), probable effect concentration (PEC)) (MacDonald et al. 2000) and ecotoxicological values (lowest effect level (LEL), severe effect level (SEL), effect range low (ERL), effect range medium (ERM)) (USEPA 2001; Long et al. 1995).

Statistical analysis

In the present study, bivariate statistical processing and multivariate analysis (principal component analysis (PCA)) were conducted using Statistics software version 8 to evaluate correlations among different elements and to find the groups of elements with similar behaviors for the identification of possible sources. The whole data set was varimax normalized, and correlation matrices with $p < 0.5$, 0.01, and 0.001 values were obtained. Three distinct factors were generated based on the eigenvalues for river and dam sediments.

Results and discussion

Metal concentrations in river and dam sediments

The concentration patterns of elements (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Sr, V, and Zn) for R. Alseseca, R. Atoyac, and Valsequillo dam are represented in Fig. 2a–q. The average metal concentrations ($\mu\text{g g}^{-1}$) for all the three regions were obtained as follows: Al (4969; 10,861; 53,019), As (0.05, 0.16, 1.90), Ba (44, 1194, 229), Ca (1182, 78, 1239), Cd (2.35, 2.58, 8.73), Co (5.79, 8.42, 17), Cr (16, 25, 60), Cu (8.22, 10.2, 35), Fe (7779; 8267; 19,180), K (505, 897, 3371), Mg (1108, 1336, 2259), Mn (99, 138, 542), Ni (7.0, 14.4, 40), Pb (3.90, 2.71, 16), Sr (29, 46, 85), V (29, 31, 60), and Zn (31, 32, 97), respectively. The Puebla region that consists of cinder cones, maars, shield volcanoes, and stratovolcanoes of Late Tertiary and Quaternary age often has pyroclastic deposits of andesitic to dacitic composition (Robin 1984; Robin and Boudal 1988; Kolisnik 1990; Schaaf et al. 2005). The average metal concentrations were compared with the values of local reference sample values from Puebla region in order to identify the enriched metal concentrations (Table 1). It is observed that Ba concentrations in R. Atoyac ($1193.8 \mu\text{g g}^{-1}$) showed an eightfold increase than compared to the reference sample values ($145.5 \mu\text{g g}^{-1}$). The high concentrations of Ba could be attributed to the barite assemblages of Popocatepetl volcano (active) situated on the western side of the study area (Larocque et al. 2008), and they are hosted generally in K-feldspars, where Ba substitutes K in many K-bearing minerals (Prinz 1967; Wedepohl 1972). The strong positive correlation of Ba vs K ($r^2 = 0.99$) in the river sediments further justifies that they are mainly controlled by the K-feldspars. The concentrations of Pb ($27.1 \mu\text{g g}^{-1}$) were also

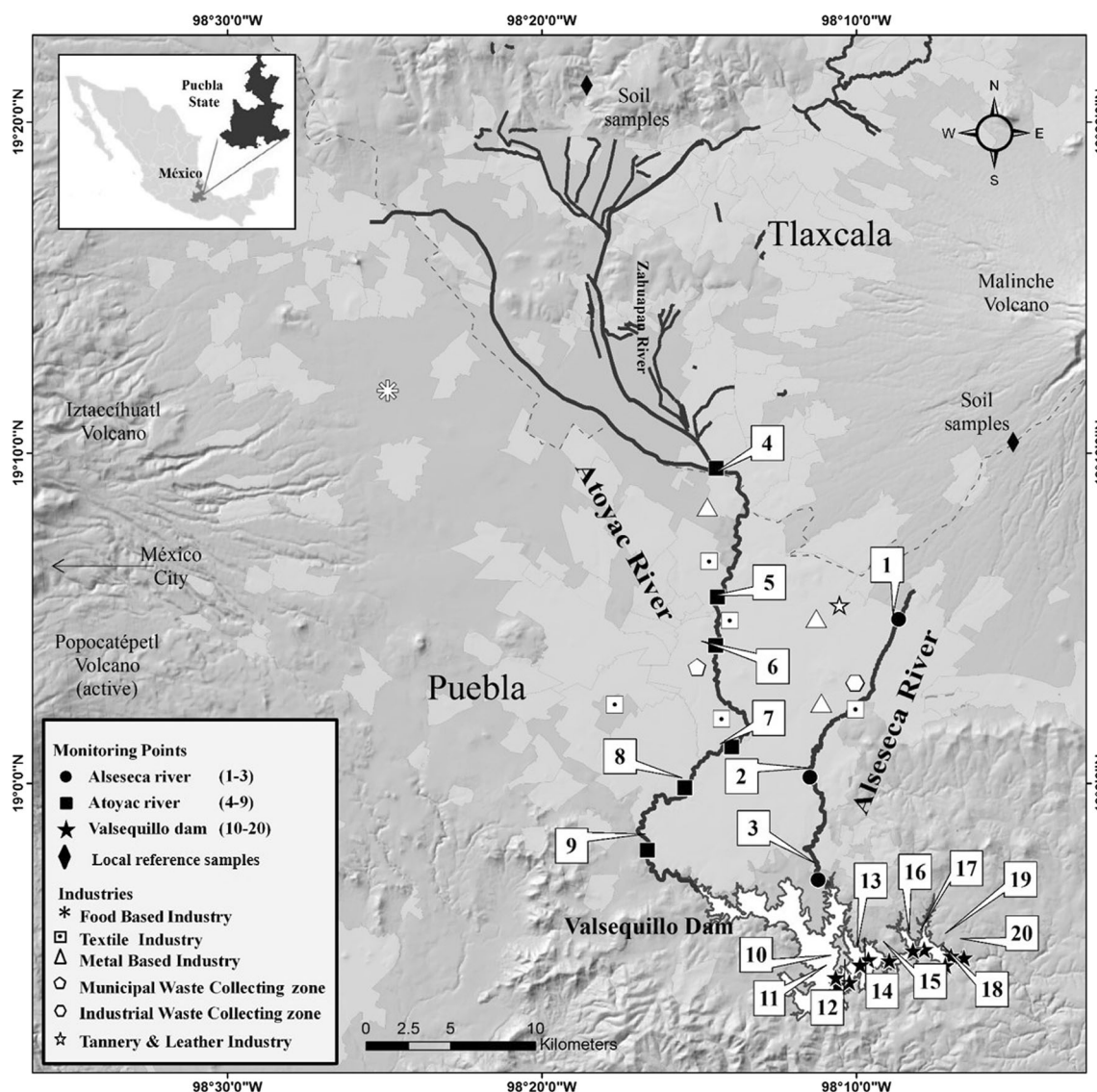


Fig. 1 Study area map illustrating the sediment sampling locations from R. Alseseca (sample nos. 1–3), R. Atoyac (sample nos. 4–9), and Valsequillo dam (sample nos. 10–20) in Puebla River basin, Mexico

observed to be higher in R. Atoyac sediments. Apart from the volcanic input, the permanent local road traffic present in the roads that crosses the river basin would probably add to the increased concentrations of Pb in the sediments by surface runoff (Zaborska 2014). In case of R. Alseseca sediments, all the metal concentrations except Sr were within the background values, suggesting that there is no significant external influence. Higher concentrations of Sr are observed in all the three regions due to the presence of Ca-rich minerals, such as plagioclase, which are the primary hosts of Sr (Davidson et al. 2007; Deniel 2009; Gao et al. 2015).

The Valsequillo dam sediments presented higher concentrations for almost all the metals, wherein Cu ($35 \mu\text{g g}^{-1}$), Pb ($16 \mu\text{g g}^{-1}$), and Zn ($97 \mu\text{g g}^{-1}$) are mainly attributed to the external influences such as agricultural wastes and automotive exhausts entering via R. Atoyac crisscrossing the Puebla City

(Sun et al. 2010; Neşer et al. 2012). The higher values ($\mu\text{g g}^{-1}$) of Sr in the dam sediments (3371) than river sediments (R. Alseseca = 505; R. Atoyac = 897) are from fresh rocks in the region and high chemical weathering nature and, it also suggests the dominating role of chemical weathering in the catchment region (Xu et al. 2010). It is further supported by strong positive correlation ($p > 0.5$ and 0.01) between Ca vs Sr ($r^2 = 0.74$) in the Valsequillo dam sediments (Das and Krishnaswami 2007). The high positive relationship of Al vs Sr ($r^2 = 0.95$) infers that it is mainly due to the presence of plutonic sediments in the river sediments and Ca-rich carbonate rocks, which shows depletion of Sr concentration compared to Al. The non-existence of Al/Sr correlation also suggests progressive intermediate weathering during transportation process (Young et al. 2013).

The overall observation on the concentration pattern suggests that considerable input is from the river sediments as the

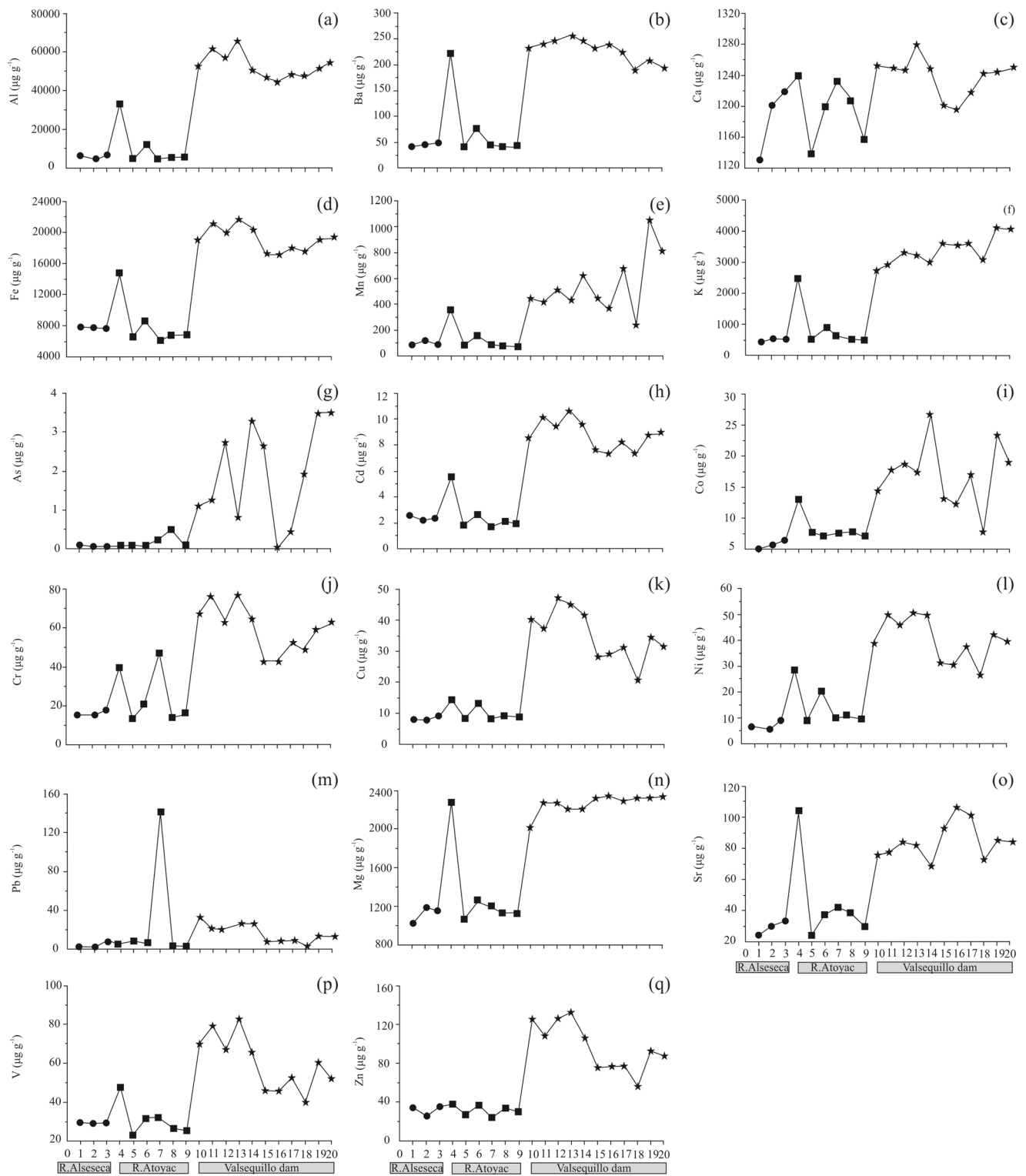


Fig. 2 a–q Distribution of metals in R. Alseseca, R. Atoyac, and Valsequillo dam sediments from Puebla River basin, Mexico

Fe/Al ratio indicates very high values in rivers (1.5; 0.76), and in the dam site, it is very less (0.04) due to mixing of sediments (e.g., Emelyanov 1994; Krom et al. 1999; Sandler and Herut 2000). The higher ratios

of Mg/Ca in all the three zones (0.93, 17.12, 1.82) infers that considerable amount of biogenic carbonates are present in the region (especially in R. Atoyac) (e.g., Morse and Mackenzie 1990).

Table 1 Comparison of metal concentrations with other riverine environments worldwide

Elements/locations	Metal concentrations ($\mu\text{g g}^{-1}$)								
	Al	Ba	Ca	Fe	Mn	K	As	Cd	Co
Similar studies in México									
Valsequillo dam, Puebla									
PV-entrance	19,769	–	–	10,621	337	–	0.373	ND	–
PV-middle part	34,294	–	–	22,242	11,087	–	0.679	ND	–
PV-curtain	34,997	–	–	24,565	19,582	–	0.541	ND	–
Pánuco River, Tamaulipas	–	–	–	14,448	674	–	–	1.76	–
Worldwide									
Geyik dam, Turkey	–	–	–	1,120	190	–	–	2	80
Narmada River, India	–	–	–	89,577	–	–	–	–	–
Sarikay Creek, Turkey	–	–	–	11,120	2,613	–	–	6	476
Hussainsagar River, India	–	–	–	139,700	173,400	–	2.80	1.21	0.58
Tigris River, Turkey	–	–	–	–	1,682	–	–	7.9	516
Chenab River, Pakistan	–	–	–	–	494	–	–	1.67	7.95
Sallum Sidi-Kreer, Egypt	–	–	–	1,122.9	57.9	–	–	0.721	–
Rimac River, Peru	–	–	–	–	–	–	–	31	24
Tinto River, Spain	–	–	–	–	–	–	–	0.13–12	6.8–42
Present study									
Alseseca River	4,969	44.4	1,181.5	7,779	98.7	29.0	0.05	2.35	5.79
Atoyac River	10,861	1,193.8	78	8,266.5	138.4	45.7	0.16	2.58	8.42
Valsequillo dam	53,019	229	1,239	19,180	542	85	1.90	8.73	17
Sediment quality guidelines									
TEC	–	–	–	–	–	–	9.79	0.99	–
PEC	–	–	–	–	–	–	33	4.98	–
Ecotoxicological values									
LEL	–	–	–	20,000	460	–	–	–	–
SEL	–	–	–	40,000	1,100	–	–	–	–
ERL	–	–	–	–	–	–	8.2	1.2	–
ERM	–	–	–	–	–	–	70	9.6	–
Local reference sample values	24,978	146	1,118	13,933	334	1,136	0.51	4.72	10.83

Elements/locations	Metal concentrations ($\mu\text{g g}^{-1}$)								
	Cr	Cu	Ni	Pb	Mg	Sr	V	Zn	References
Similar studies in México									
Valsequillo dam, Puebla									
PV-entrance	11.9	21.3	29.4	14	–	–	–	48	CONAGUA México (CNA 2005)
PV-middle part	34.4	39.5	52	35	–	–	–	102	
PV-curtain	32.7	27.6	42	31	–	–	–	61	
Pánuco River, Tamaulipas	21.7	34.1	17.6	47.9	–	–	–	122.8	Jonathan et al. (2013)
Worldwide									
Geyik dam, Turkey	239	120	104	28	–	–	–	104	Tuna et al. (2007)
Narmada River, India	199.3	188.8	200.3	13.9	–	–	–	196.2	Sharma et al. (2010)
Sarikay Creek, Turkey	1,308	128	304	29	–	–	–	304	Tuna et al. (2007)
Hussainsagar River, India	0.91	3.91	1.87	12.73	–	–	–	25.68	Vikram et al. (2010)
Tigris River, Turkey	–	2,860	–	66	–	–	–	1,061	Varol and Sen (2012)
Chenab River, Pakistan	–	8.16	–	18.1	–	–	–	33.7	Hanif et al. (2016)
Sallum Sidi-Kreer, Egypt	24.1	30.3	38.7	27.8	–	–	–	59.7	Hoda et al. (2009)
Rimac River, Peru	–	796	–	2,281	–	–	–	8,076	Mendez (2005)
Tinto River, Spain	11–151	22–2,700	1.6–36	17–13,400	–	–	–	68–5,280	García et al. (2012)
Present study									
Alseseca River	15.8	8.22	7.0	3.90	1,107.7	505	29	31.4	
Atoyac River	24.5	10.2	14.4	27.1	1,336	897	30.9	31.5	

Table 1 (continued)

	Metal concentrations ($\mu\text{g g}^{-1}$)								
Valsequillo dam	60	35	40	16	2,259	3,371	60	97	
Sediment quality guidelines									
TEC	43.4	31.6	22.7	35.8	–	–	–	121	MacDonald et al. (2000)
PEC	111	149	48.6	128	–	–	–	459	MacDonald et al. (2000)
Ecotoxicological values									
LEL	26	16	16	31	–	–	–	120	USEPA (2001)
SEL	110	110	75	250	–	–	–	820	USEPA (2001)
ERL	81	34	20.9	46.7	–	–	–	150	Long et al. (1995)
ERM	370	270	51.6	218	–	–	–	410	Long et al. (1995)
Local reference sample values	38	15.5	21.43	3.69	1,501	36.5	45.5	38.5	

TEC threshold effect concentration, PEC probable effect concentration, LEL lowest effect level, SEL severe effect level, ERL effect range low, ERM effect range medium, NASC North American shale composite

Worldwide comparison

The metal concentrations of the present study were compared with those from other river environments worldwide (Table 1). The Valsequillo dam presented elevated concentrations of As, Cr, Cu, and Ni in duration of 4 years (2005–2009). The worldwide comparison of metal concentrations in Puebla River basin suggests that the Al (average 22,949.50) and Fe (average 11,741.83) concentrations were higher among all the other river environments. The Cd concentrations in the present study were observed to be higher than compared to Geyik dam (Turkey), Hussainsagar River (India), Chenab River (Pakistan), and Sallum Sidi-Kreer (Egypt). Overall comparison results reveal that the average metal concentrations in Puebla River basin are less compared to other riverine environments globally.

Degree/level of metal contamination

In order to assess the level of metal contamination, I_{geo} , EF, C_d , and PLI were used.

I_{geo}

The I_{geo} (Muller 1979) permits to assess the extent of sediment contamination and is calculated by $I_{geo} = \log_2 (C_n/1.5 \times B_n)$, where C_n is the concentration of metal in studied sediment sample and B_n is the geochemical background concentration of the metal (n). The factor 1.5 is used to account the possible variations in the background values due to lithospheric effects. The geoaccumulation index consists of seven classes. The I_{geo} ranges from class 0 ($I_{geo} \leq 0$, uncontaminated) to class 6 ($I_{geo} > 5$, extremely contaminated and at least 100-fold enrichment above background) (Bhuiyan et al. 2010; Kalender et al. 2013).

The calculated I_{geo} values are plotted as box and whisker graph and are represented in Fig. 3a. The negative I_{geo} values

indicate that no contamination exists with reference to the background value in the study region. It is observed that the metals K, As, Cu, Mn, Pb, and Zn fall under class 2, indicating moderate contamination which includes natural enrichment of elements. The metals Cu, Mn, and Zn are mainly attained from the non-crystallized particles often discharged from active volcano Popocatepetl, which is situated on the western side of the study area consisting mainly of andesite, dacite, and minor amounts of basaltic andesite (Obenholzner et al. 2003). In the study area, As falls under class 3, suggesting moderately to heavy contamination, whereas Pb falls under class 3 and class 5, signifying heavily to extreme contamination. The input sources of As and Pb are both natural as well as anthropogenic. The trace metals such as As and Pb are fractioned in the vapor phase during volcanic eruption, and the deposition of volcanic ash leads to dissolution of these adsorbed metals leading to higher concentrations in sediments (Stimac et al. 1996; Jones et al. 2008). The other external sources of As are mainly from the agricultural runoff consisting of pesticides and fertilizers (Wang et al. 2014; Bhattacharya et al. 2007; Bulut and Aksoy 2008), while Pb is mainly attributed to the automobile exhausts and direct discharges from industries (Neşer et al. 2012; Townsend and Snape 2008).

EF

EF is widely used to differentiate the natural and anthropogenic sources of metal in sediments (Buat-Ménard and Chesselet 1979).

It is calculated as follows:

$$EF = (\text{Me}/\text{Al})_{\text{sample}} / (\text{Me}/\text{Al})_{\text{baseline}}$$

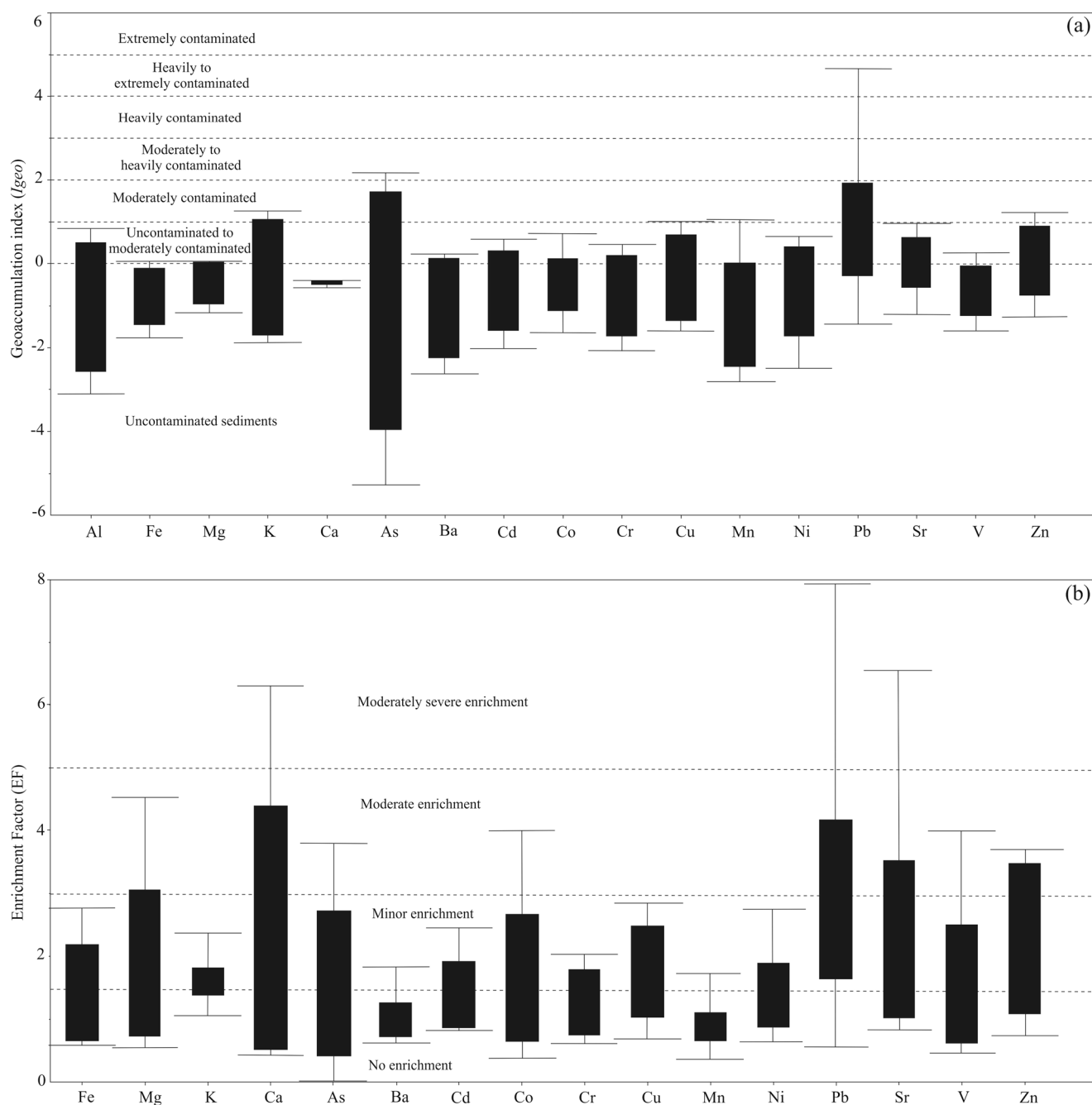


Fig. 3 a, b Results of I_{geo} and EF values for the river and dam sediments from Puebla River basin, Mexico

where $(Me/Al)_{sample}$ and $(Me/Al)_{baseline}$ represent the ratio of metal to Al concentrations in the studied samples and in the background sample, respectively. The EF values less than 1.5 suggest that the metals originate entirely from natural weathering processes of crustal contribution, whereas the values greater than 1.5 indicate a significant proportion of non-crustal materials due to anthropogenic influences (Zhang and Liu 2002; Li et al. 2013). The enrichment is evaluated as follows: $EF < 1$ indicates no enrichment, < 3 is minor enrichment, $3-5$ is moderate enrichment, $5-10$ is moderately

severe enrichment, $10-25$ is severe enrichment, $25-30$ is very severe enrichment, and > 50 is extremely severe enrichment (Sakan et al. 2009). The EF values for the present study are represented in Fig. 3b. The results indicate that all the metals (Fe, Mg, K, Ca, As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sr, V, and Zn) have EF values greater than 1.5, suggesting a significant anthropogenic influence. Moderately severe enrichment of Ca, Pb, and Sr exists, and the metals Mg, Ca, As, Co, Pb, V, and Zn fall in between the range of $3-5$, inferring moderate enrichment. The Ca is mainly sourced from the source rock

composition with the presence of limestone and calcareous minerals (Von Erfa et al. 1977; Ortega-Gutierrez 1978, 1993; Mooser et al. 1996; Morales-Ramírez et al. 2003) as well as from the altered carbonates from volcanic and pyroclastic lithic fragments and bioclasts, in addition to mafic igneous minerals.

C_d

The degree of contamination provides an overall assessment of sediment pollution (Hakanson 1980) and is determined using the following equation:

$$C_d = \sum_{i=0}^n C_f$$

where $C_f = M_s/M_b$, in which M_s is the metal concentration in the sediment and M_b is the background value of the same metal. It is evaluated as $C_d < 8$ is low degree of contamination, $8 \leq C_d < 16$ is moderate degree of contamination, $16 \leq C_d < 32$ is considerable degree of contamination, and $C_d \geq 32$ is very high degree of contamination (Pejman et al. 2015; El-Sayed et al. 2015). The degree of contamination in the R. Alseseca and R. Atoyac sediments ranges from 8.55 to 47.48, while in the Valsequillo dam, it ranges from 25.85 to 43.28, inferring higher values in the dam site (Fig. 4a). The higher values in

the dam site compared to upstream sediments are primarily attributed to the dense cover of halophytes present in this region. Halophytes efficiently extract metals from the overlying water column, and as they decay, the export of these dead plant materials that are highly enriched in metals are subsequently added to the sediments (Weis and Weis 2004; Van Oosten and Maggio 2015).

PLI

The pollution load index (Tomilson et al. 1980) is calculated as the contamination factor of each metal with respect to its background value in the sediment using the following equation:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n}$$

PLI value >1 represents the polluted conditions and <1 indicates no pollution. The PLI values for all the river sediments were below 1 (Fig. 4b), suggesting no pollution except for station no. 4 (R. Atoyac) dotted with numerous textile industries, and the PLI values of Valsequillo dam range from 1.42 to 2.18, indicating significant pollution.

Fig. 4 a, b Results of C_d and PLI values for the river and dam sediments from Puebla River basin, Mexico

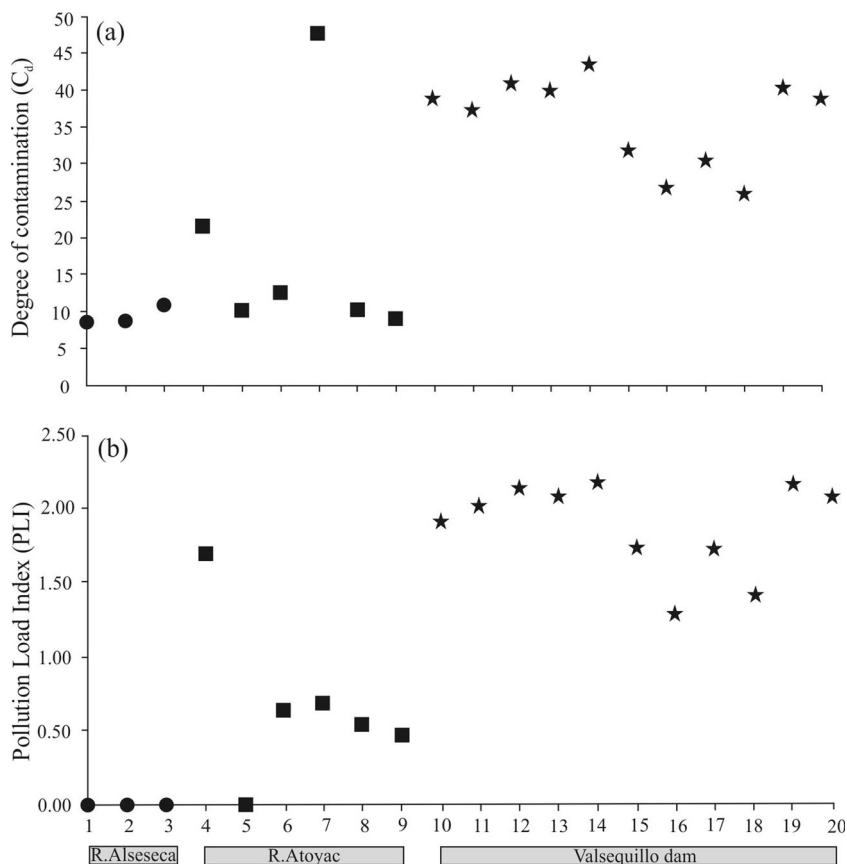


Table 2 Correlation matrix of R. Alseseca, R. Atoyac, and Valsequillo dam in Puebla, México

	Al	As	Ba	Ca	Cd	Co	Cr	Cu
Alseseca and Atoyac Rivers (<i>N</i> = 9)								
Al	1.00							
As	–	1.00						
Ba	0.99*, **, ***	–	1.00					
Ca	–	–	–	1.00				
Cd	0.98*, **, ***	–	0.97*, **, ***	–	1.00			
Co	0.87*, **	–	0.88*, **	–	0.80*, **	1.00		
Cr	–	–	–	0.68*	–	–	1.00	
Cu	0.84*, **	–	0.84*, **	–	0.78*	0.70*	–	1.00
Fe	0.98*, **, ***	–	0.97*, **, ***	–	1.00*, **, ***	0.77*	–	0.82*, **
Mn	0.99*, **, ***	–	0.99*, **, ***	–	0.98*, **, ***	0.84*, **	–	0.83*, **
Mg	0.97*, **, ***	–	0.98*, **, ***	–	0.96*, **, ***	0.91*, **, ***	–	0.78*
Ni	0.92*, **, ***	–	0.93*, **, ***	–	0.85*, **	0.84*, **	–	0.95*, **, ***
Pb	–	–	–	–	–	–	0.76*	–
K	0.99*, **, ***	–	0.99*, **, ***	–	0.97*, **, ***	0.90*, **, ***	–	0.80*
Sr	0.95*, **, ***	–	0.96*, **, ***	–	0.93*, **, ***	0.92*, **, ***	–	0.75*
V	0.92*, **, ***	–	0.94*, **, ***	0.68*	0.93*, **, ***	0.75*	0.69*	0.76*
Zn	–	–	–	–	–	–	–	0.75*
Valsequillo dam (<i>N</i> = 11)								
Al	1.00							
As	–	1.00						
Ba	–	–	1.00					
Ca	0.81*, **	–	–	1.00				
Cd	0.93*, **, ***	–	–	0.80*, **	1.00			
Co	–	–	–	–	0.61*	1.00		
Cr	0.92*, **, ***	–	–	0.88*, **, ***	0.95*, **, ***	–	1.00	
Cu	0.73*	–	0.74*, **	–	0.83*, **	0.61*	0.78*, **	1.00
Fe	0.91*, **, ***	–	–	0.83*, **	0.99*, **, ***	–	0.96*, **, ***	0.82*, **
Mn	–	–	–	–	–	0.72*	–	–
Mg	–	–	–	–	–	–	–	–
Ni	0.81*, **	–	–	0.70*	0.96*, **, ***	0.77*, **	0.89*, **, ***	0.88*, **, ***
Pb	0.60*	–	–	0.66*	0.72*	–	0.79*, **	0.86*, **, ***
K	–	–	–	–	–	–	–	–
Sr	–	–	–	0.74*, **	–	–	–	–
V	0.90*, **, ***	–	0.65*	0.74*, **	0.93*, **, ***	–	0.95*, **, ***	0.87*, **, ***
Zn	0.78*, **	–	0.70*	0.67*	0.82*, **	–	0.83*, **	0.97*, **, ***
Fe	Mn	Mg	Ni	Pb	K	Sr	V	Zn
Alseseca and Atoyac Rivers (<i>N</i> = 9)								
Al								
As								
Ba								
Ca								
Cd								
Co								
Cr								
Cu								
Fe	1.00							
Mn	0.98*, **, ***	1.00						
Mg	0.94*, **, ***	0.97*, **, ***	1.00					
Ni	0.86*, **	0.90*, **, ***	0.88*, **	1.00				
Pb	–	–	–	–	1.00			
K	0.96*, **, ***	0.99*, **, ***	0.99*, **, ***	0.90*, **, ***	–	1.00		
Sr	0.91*, **, ***	0.95*, **, ***	0.99*, **, ***	0.87*, **	–	0.98*, **, ***	1.00	
V	0.92*, **, ***	0.94*, **, ***	0.93*, **, ***	0.86*, **	–	0.94*, **, ***	–	1.00

Table 2 (continued)

	Fe	Mn	Mg	Ni	Pb	K	Sr	V	Zn
Zn	–	–	–	–	–	–	–	–	1.00
Valsequillo dam (<i>N</i> = 11)									
Al									
As									
Ba									
Ca									
Cd									
Co									
Cr									
Cu									
Fe	1.00								
Mn	–	1.00							
Mg	–	–	1.00						
Ni	0.96*, **, ***	–	–	1.00					
Pb	0.75*, **	–	0.86*, **	0.75*, **	1.00				
K	–	0.72*	0.68*	–	–	1.00			
Sr	–	–	–	–	–	–	1.00		
V	0.93*, **, ***	–	–	0.91*, **, ***	0.83*, **	–	–	1.00	
Zn	0.82*, **	–	0.67*	0.83*, **	0.91*, **, ***	–	–	0.91*, **, ***	1.00

**p* > 0.05

***p* > 0.01

****p* > 0.001

Ecological risk indices

The possible ecological risks posed by these metals were assessed through comparison with SQGs and ecotoxicological values (Table 1). The SQGs include a TEC and PEC. If the concentrations of metals are below TEC, harmful effects are unlikely to be observed, while if the values are above PEC, harmful effects are likely to be observed (MacDonald et al. 2000). The ecotoxicological values include LEL, SEL, ERL, and ERM. The values below LEL and ERL suggest no biological effects, whereas values above SEL and ERM indicate harmful effects on the biological community (USEPA 2001; Long et al. 1995).

In comparison to SQGs, Cd (2.35 µg g⁻¹) is observed to be exceeding TEC values in R. Alseseca and R. Atoyac (Cd = 2.58 µg g⁻¹), whereas in Valsequillo region (Cd = 8.73 µg g⁻¹), it also exceeds the PEC values indicating harmful effects. The values of all the other metals (As, Cr, Cu, Ni, and Pb) in both R. Alseseca and R. Atoyac were below TEC, suggesting no harmful effects. In case of Valsequillo dam site, the values for metals Cr (60 µg g⁻¹), Cu (35 µg g⁻¹), and Ni (40 µg g⁻¹) were between TEC and PEC values, suggesting that the presence of these metals has

a significant harmful effect in the study area. In ecotoxicological sense, the presence of Cd (2.35, 2.58, 8.73 µg g⁻¹) in all the three regions were above LEL and ERL, resulting in harmful biological effects. In Valsequillo dam sediments, Cu (35 µg g⁻¹), Mn (542 µg g⁻¹), and Ni (40 µg g⁻¹) were above LEL and ERL values, suggesting harmful effects on the biological community.

Metal source identification

Correlation matrix

In order to determine the source of metals and identify their inter-relationship, a correlation matrix for the metals in Puebla River basin sediments was calculated and is represented in Table 2. In the river sediments, the strong positive correlations of Al and Fe with Ba (*r*² = 0.99; 0.97), Cd (*r*² = 0.98; 1.00), Mn (*r*² = 0.99; 0.98), Mg (*r*² = 0.97; 0.94), Ni (*r*² = 0.92; 0.86), K (*r*² = 0.99; 0.96), Sr (*r*² = 0.95; 0.91), and V (*r*² = 0.92; 0.92) indicated that the inputs of these metals are from lithogenic origin, since Al and Fe are the petrogenic elements forming major components of aluminosilicates. The significant correlations of these metals with Al and Fe

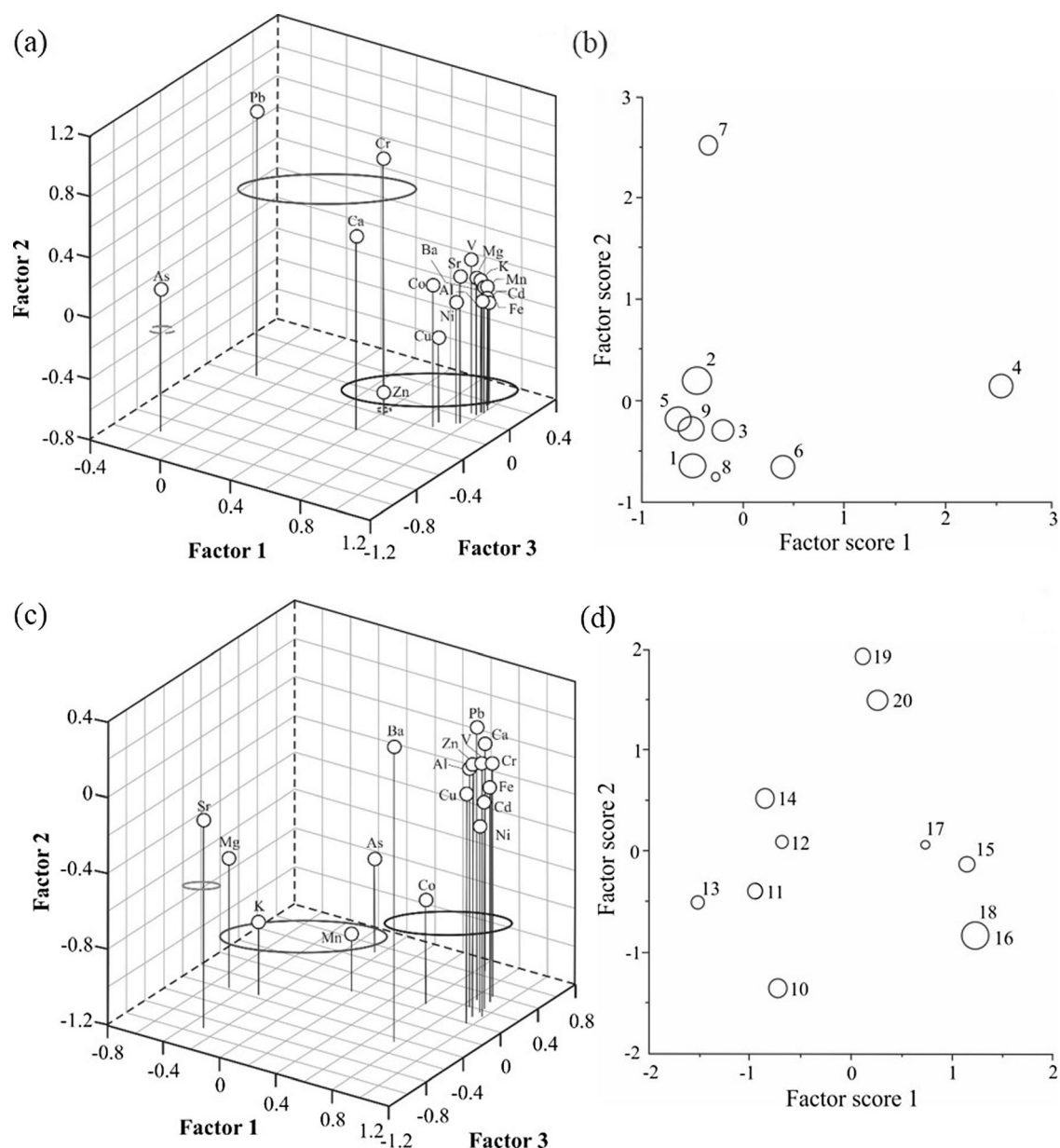


Fig. 5 a–d Factor loadings and score of metals in sediments of Puebla River basin

suggest that Al and Fe oxides are important binding phases for metal precipitation (Turner 2000; Yuan et al. 2004). There was no significant correlation between Al with As, Ca, Cr, Pb, and Zn, suggesting a different source of origin. The correlation of Ca vs Cr ($r^2 = 0.68$) and V ($r^2 = 0.68$) indicated that they are associated to plagioclase feldspars present in the study region (Sergio Raúl Rodríguez 2005). The As, Pb, and Zn have a dual origin of natural volcanic input, wherein they get fractionated in magmatic vapor phase (Ruggieri et al. 2012) and external inputs from industrial activities in the Puebla River basin (Wang et al. 2014).

In Valsequillo dam sediments, majority of the trace metals such as Cd, Cr, Cu, Ni, Pb, V, and Zn are associated with

aluminosilicates, which is evident through strong positive correlations of Al and Fe with Cd ($r^2 = 0.93$; 0.99), Cr ($r^2 = 0.92$; 0.96), Cu ($r^2 = 0.73$; 0.82), Ni ($r^2 = 0.81$; 0.96), Pb ($r^2 = 0.60$; 0.75), V ($r^2 = 0.90$; 0.93), and Zn ($r^2 = 0.78$; 0.82) inferring their lithogenic origin. The elements Ba and K have no significant correlation with Al, and the concentrations of these elements are affected by natural weathering processes due to their mobile nature (Nesbitt et al. 1980; Roy et al. 2008). The positive correlation of Ca vs Sr ($r^2 = 0.74$) suggests their association with source rock composition of Balsas group (Malde 1968). The As has no significant correlation with other elements suggesting a specific source of origin from volcanic ash deposition in the dam site (Juncos et al. 2016).

Factor analysis

Three distinct factors for R. Alseseca, R. Atoyac, and Valsequillo dam were obtained representing 92.29% of the total variance of the system. The spatial distributions of elements between the factor loadings are plotted in Fig. 5a. The results show that the associations identified in the correlation matrix originate from the following three main sources: source 1 (factor 1) shares a common origin of elements, Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mg, Ni, K, Sr, and V; source 2 (factor 2) shares a common origin of Cr and Pb; and source 3 (factor 3) consists of As alone. These groups support the associations of metals shown by the correlation matrix. The strong positive associations of Al and Fe with Ba, Cd, Co, Cr, Cu, Mn, Mg, Ni, K, Sr, and V in factor 1 suggest their lithogenic origin, whereas the origin of Cr and Pb in factor 2 and As in factor 3 could originate both through natural and anthropogenic sources.

The behaviors between the sampling stations of R. Alseseca and R. Atoyac are shown in Fig. 5b. It is clearly evident from the Fig. 5b that the sampling stations 4, 6, and 7 behave differently, showing abnormal values of metal concentrations in comparison to other sampling stations. Reviewing the behavior of the elemental concentrations discussed in these stations, it is observed that stations 4 and 6 had higher concentrations of Ba, Cd, Co, Cu, Fe, Mn, Mg, Ni, Sr, K, and V. These two stations are situated immediately after the confluence of Rabanillo River with R. Atoyac, which carries the urban and industrial wastewaters from the municipal of San Pedro Cholula. In station 7, higher concentrations of Cr, Pb, and As were observed, where numerous textile, fabric, plastic, and metal-based industries are located.

Similarly, three factor loadings for Valsequillo dam site were obtained with a total variance of 86.72%. The associations in Fig. 5c reveal the following three sources: source 1 (factor 1) which share a common origin of elements, Al, Cd, Cr, Cu, Fe, Ni, Pb, V, and Zn; source 2 (factor 2) consists of As, Mn, and K with a common origin; and source 3 (factor 3) consisting of Ca and Sr. Figure 5d shows the associations between sampling stations in Valsequillo dam, and three associations are observed with the stations 10–14 grouped in the western end of the dam with higher average concentrations of Cu (42.25), Pb (25.28), and Zn (119.78) due to the presence of halophytes in this region, which leads to absorption from the water column and subsequent precipitation in the sediments. The stations 15–17 and 18 after the ferry point of San Baltasar, wherein the metal concentrations were within the background values, and stations 19 and 20 near the wall of the Valsequillo dam have higher average metal concentrations of Cu (33), Mn (913), and Zn (90) due to precipitation of oxides from the above water column.

The correlation matrix and factor analysis revealed that the sources and associations of metals in the river and dam

sediments were mainly from natural weathering processes of source rock, volcanic inputs, and influence of industrial discharges from the Puebla City.

Conclusion

The Puebla River basin sediments were analyzed for the metals Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mn, Mg, Ni, Pb, K, Sr, V, and Zn. The geochemical concentration pattern suggests that these metals are mainly controlled by aluminosilicates (clay minerals). The higher concentrations of Ba and Pb in R. Atoyac sediments and Cu, Pb, and Sr in the Valsequillo dam sediments are due to the contributions from source rock weathering along with volcanic input. The degree/level of contamination assessed through several indices suggests a significant proportion of external influence over the metals As, Pb, and Zn in the study area. The presence of Cd, Cr, Cu, and Ni in the study region poses a threat to the biological community. The metal concentrations and their enrichment in the sediments of Puebla River basin is primarily due to source rock weathering, inputs from the active Popocatepetl volcano situated in the western side of the study area, and industrial sources set up close to this river network.

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