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# Environmental Consequences of Metal Concentrations in Stream Sediments of Atoyac River Basin, Central Mexico: Natural and Industrial Influences

V. C. Shruti, P. F. Rodríguez-Espinosa, D. C. Escobedo-Urías, Estefanía Martinez Tavera, M. P. Jonathan

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***Abstract*—**Atoyac River, a major south-central river flowing through the states of Puebla and Tlaxcala in Mexico is significantly impacted by the natural volcanic inputs in addition with wastewater discharges from urban, agriculture and industrial zones. In the present study, core samples were collected from R. Atoyac and analyzed for sediment granularity, major (Al, Fe, Ca, Mg, K, P and S) and trace elemental concentrations (Ba, Cr, Cd, Mn, Pb, Sr, V, Zn, Zr). The textural studies reveal that the sediments are mostly sand sized particles exceeding 99% and with very few to no presence of mud fractions. It is observed that most of the metals like (avg: all values in $\mu g\ g^{-1}$) Ca (35,528), Mg (10,789), K (7453), S (1394), Ba (203), Cr (30), Cd (4), Pb (11), Sr (435), Zn (76) and Zr (88) are enriched throughout the sediments mainly sourced from volcanic inputs, source rock composition of Atoyac River basin and industrial influences from the Puebla city region. Contamination indices, such as anthropogenic factor (AF), enrichment factor (EF) and geoaccumulation index ($I_{geo}$), were used to investigate the level of contamination and toxicity as well as quantitatively assess the influences of human activities on metal concentrations. The AF values (>1) for Ba, Ca, Mg, Na, K, P and S suggested volcanic inputs from the study region, where as Cd and Zn are attributed to the impacts of industrial inputs in this zone. The EF and $I_{geo}$ values revealed an extreme enrichment of S and Cd. The ecological risks were evaluated using potential ecological risk index (RI) and the results indicate that the metals Cd and V pose a major hazard for the biological community.

***Keywords*—**Atoyac River, contamination indices, metal concentrations, Mexico, textural studies.

## I. Introduction

IN developing countries, river environments are under pronounced pressure due to rapid urbanization and industrial development. The river networks form an important carrier of sediments from terrigenous land to the ocean. These sediments act as a major sink for trace metals in aquatic environments, which are of great concern due to their abundance, persistence, toxicity and bioaccumulating nature [1], [2]. The trace metals are introduced into the aquatic environments by natural ways through weathering processes and human activities along the rivers [3], [4]. The trace metals from river sediments may be released into the water column through hydrological disturbance, chemical and biological processes under variable sedimentary conditions causing potential threat to aquatic biota and human health [5], [6]. Thus, the trace metal assessment in river sediments are essential to evaluate the quality status as well as develop pollution control strategies and approaches to water quality management in hydrological basins.

Trace metal geochemistry in sediments is important as they form the reservoir of contaminants and have a long residence time than compared to water which aids in predicting the pollution history as well as the potential environmental and ecotoxicological impacts [7], [8]. The analysis of trace metals in surface sediments only determines the extent, distribution, origin and possible risks due to the presence of these metals whereas the sediment core studies provides the historical sequence of pollution and record of the events that occurred in the past up to the present [9]. They prove to be an excellent tool in identifying the effects of both the natural and human induced influences over accumulation of metals for an extended period of time.

Atoyac River is a part of Balsas River, a major south–central river flowing through the states of Puebla and Tlaxcala in Mexico finally draining into the Manuel Avila Camacho Dam after the city limits. The striking feature of this river basin is the presence of volcanoes (extinct & active) in eastern and western sides. This region has been experiencing a tremendous industrial and demographic growth potentially influencing the Atoyac river basin. In Mexico, R. Atoyac is stated as one of the most contaminated rivers of the country [10] and it is extremely impacted by the wastewater discharges from urban, agriculture and industrial sources pronouncing the urge for its evaluation. The present study aimed to investigate the state of metal pollution in core sediments of Atoyac River and specifically the objectives of this research were to: (i) determine the concentration of metals in core sediments, (ii) evaluate the level of contamination using pollution indices such as AF, EF, $I_{geo}$, the ecological risk posed by these metals in sediments through potential ecological RI, and (iii) to

V. C. Shruti is with the Centro Interdisciplinario de Investigaciones y Estudios sobre Medio Ambiente y Desarrollo (CIIEMAD), Instituto Politécnico Nacional (IPN), Calle 30 de Junio de 1520, Barrio la Laguna Ticomán, Del. Gustavo A. Madero, C.P.07340, México D.F., México (phone: +52-5557296000 Ext.52708 e-mail: shrutifrnd@gmail.com).

P. F. Rodríguez-Espinosa, Estefanía Martinez Tavera, and M. P. Jonathan are with the CIIEMAD, IPN, Calle 30 de Junio de 1520, Barrio la Laguna Ticomán, Del. Gustavo A. Madero, C.P.07340, México D.F., México (e-mail: pedrof44@hotmail.com, estefmtzt@hotmail.com, mpjonathan7@gmail.com).

D. C. Escobedo-Urías is with the CIIDIR, IPN, Bulevar Juan de Dios Bátiz Paredes #250, Colonia San Joachin Guasave, C.P.81101, Sinaloa, México (e-mail: durais@hotmail.com).

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delineate the natural and/or anthropogenic sources metals using multivariate statistical techniques.

## II. Materials and Methods

### A. Study Area Description

The Atoyac River basin covering an area of 4395. 61 km$^2$ located on the volcanic highlands of Puebla State, Mexico, constitutes R. Zahuapan and R. Atoyac draining into the Manual Avila Camacho (Valsequillo) Dam beyond the city limits (Fig. 1). This river basin is flanked by volcanoes such as Iztaccíhuatl volcano (extinct), Popocatépetl (active) in the west and northwest respectively. The Atoyac River crisscrosses the urban, agricultural and industrial corridor of Puebla-Tlaxcala, thus forming major grounds for effluent discharges from these regions into the riverine environment. The Valsequillo dam was mainly built for irrigation purposes in Tecamachalco-Tehuacan and the main crops irrigated with this 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-September and winter during October-February [11].

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 [12]. The Valsequillo basin is underlined by the bedrock of Balsas group constituting coarse Cretaceous limestone conglomerate cemented together by a matrix of red mudstone [13]. The deposits also include thin layers of volcanic ash, rhyolitic and basaltic with pumice lapilli.

The industrial set up of this basin encompasses numerous 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%) [14].

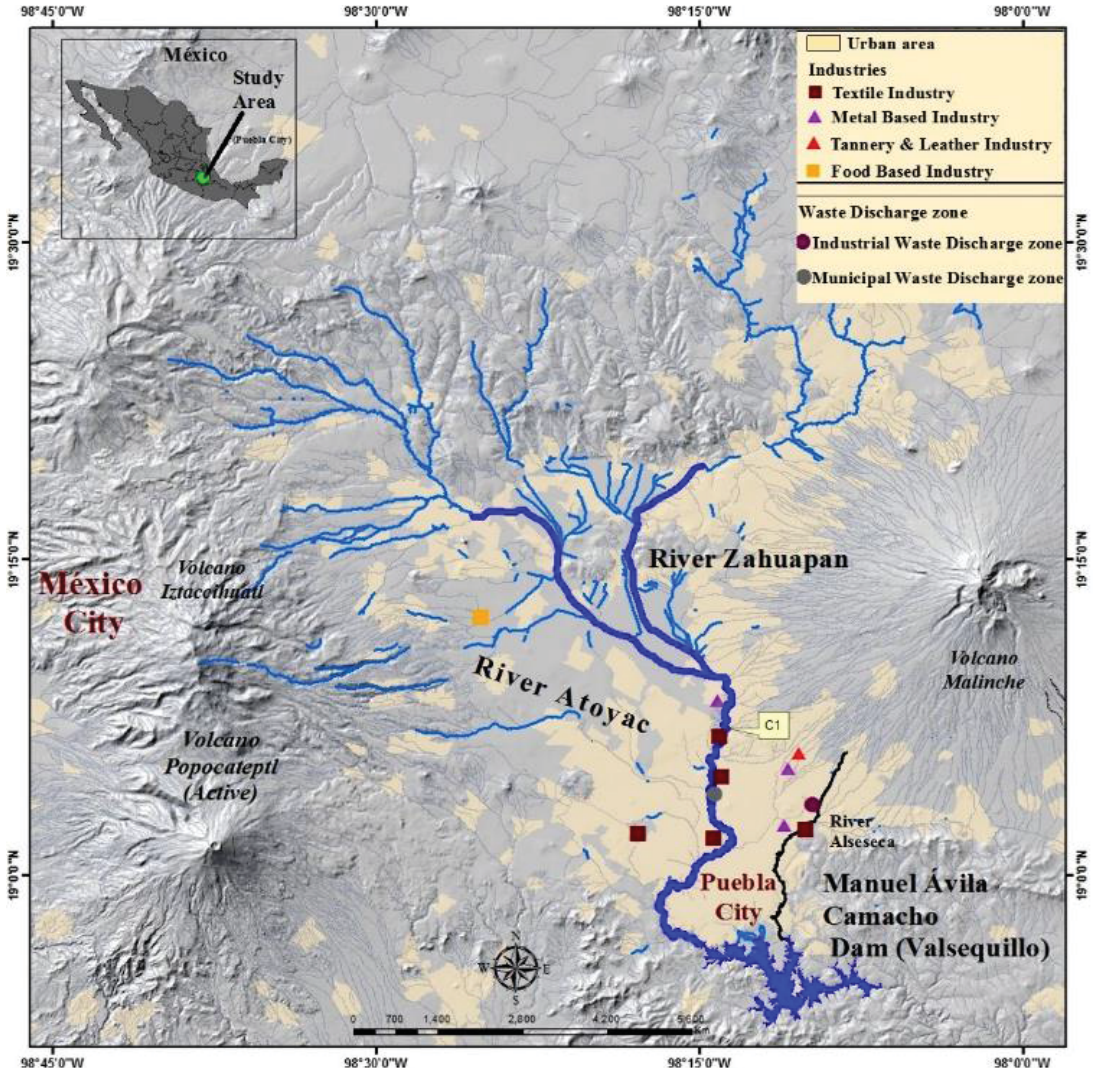



Fig. 1 Study area map showing Atoyac River Basin in Mexico

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### B. Sample Collection

One sediment core (C1) was retrieved from the confluence zone of R. Atoyac and R. Zahuapan during September 2015. The sampling site was selected based on the influence of urban, industrial and agricultural effluents draining into this area and also having a significant impact of volcanoes surrounding the river basin. The sediment core of depth 70 cm (C1) was collected using acid-washed PVC pipes (6.3 in diameter and 2.5 m length). The core was sliced using a plastic cutter and the sub-samples were made at 2cm intervals. The sediment samples obtained were oven dried below 40°C and used for further analysis.

### C. Analytical Procedure

Grain size analysis was conducted by the dry sieving technique [15]. Samples containing more than 5% fine fraction (finer than 4ϕ) were analyzed using the pipette method as described by Griffith [16] and Carver [17]. Sediment textural classes were deduced according to Folk [15]. Analysis of Al, Fe, Ca, Mg, K, P, S, Ba, Cr, Cd, Mn, Pb, Sr, V, Zn and Zr in sediment core samples C1 of Atoyac River basin were determined by x-ray fluorescence method. The dried sediment samples were hand grinded using agate motor and around 4g of sample was pressed into a pellet for metal analysis. The samples were introduced in Thermo Scientific Niton FXL for metals. Standard reference material like NIST (SRM 2702-Inorganics in Marine Sediment) and USGS (SdAR-M2) were run concurrently with the samples.

## III. Results and Discussion

### A. Textural Studies

The sediment textural studies assists in understanding the history of the depositional environment. The grain size distributions along the core showed the presence of relatively sand content exceeding more than 99%. The texture of sediments is closely related to the hydrodynamics of the river [18]. The higher sand content (>99%) in the core sediments indicates a relatively high energy regime that prevents sedimentation of fine-grained particles [19], [20]. Thus the textural studies clearly reflects the high energy environment of the Atoyac River in the confluence zone flowing through the Puebla city, Mexico.

### B. Down Core Variations of Metals

Major Elements

The down core variations (all values in μg $g^{-1}$) of Al (28634 to 34160), K (5757 to 8155), P (39.9 to 66) and S (1143 to 1800) were consistent with no major variations in the core sediments of Atoyac River basin. The higher concentration of Ca (28959 μg $g^{-1}$ to 50416 μg $g^{-1}$) down core suggests that it has been contributed from altered carbonates from volcanic and pyroclastic lithic fragments and bioclasts in addition to mafic igneous minerals rather than limestones or calcareous minerals. The average Fe and Mn concentrations in core sediments are 13,385 μg $g^{-1}$ and 45.14 μg $g^{-1}$ respectively. The C1 core sediments are characterized with a consistent trend in distributions of Fe and Mn concentrations. The down core distribution profiles of Fe and Mn reveals that top 0-5 cm has higher concentrations than compared to the lower sections of the core (Figs. 2 (a)-(h)). These variations are controlled by early diagenetic processes where suboxic conditions results in reduction of Fe and Mn which migrate upward in the sediment column where they get reprecipitated as oxides or hydroxides [21], [22]. The enrichment of Fe and Mn is observed in the lower sections of the core at the depth of 20-25 cm and 55-60 cm which is mainly due to the reducing conditions in this region resulting in higher stability of Fe-Mn oxyhydroxides and precipitation of these elements as metaliferous sulfides [23]-[25]. The Mg concentrations (6104 μg $g^{-1}$ to 18490 μg $g^{-1}$) in the core sediments showed a vertical distribution similar to the Fe-Mn profiles. High Mg values indicate their source from mafic rock forming minerals and pyroclastic deposits of andesitic to dacitic composition present in the study area [26], [27].

Trace Elements

The down core distributions of Cr in C1 core sediments showed higher concentrations in the top 0-5 cm layers. The higher values of Cr (30.02 μg $g^{-1}$ to 44.31 μg $g^{-1}$) in the top layers suggest that it is present as Cr (VI) which is readily adsorbed by Fe-Mn oxyhydroxides [28], [29]. The vertical distribution of Cr in the core samples indicates a similar pattern to Fe and Mn (Figs. 2 (i)-(p)). Diagenetic modifications, however, play a major role in the vertical distribution of Cr indicating a peak at subsurface and greater depth in most core samples [25]. Cr, as one of the redox sensitive metals co-precipitated with authigenic Mn-oxyhydroxide and is supported strong positive correlation between Cr and Mn ($r^2$ = 0.65). In general the concentration of Pb increases down core due to prevailing reducing conditions which have greater affinity to Pb resulting in subsequent higher concentrations in the sediments. The Cd range value (2.1 μg $g^{-1}$ to 6.4 μg $g^{-1}$) in the collected core sediments represented high concentrations. This indicates an anthropogenic source of this metal into sediments which may include discharge of refining wastes and untreated sewage effluents [30]. The vertical distribution pattern of Cd did not show a similar pattern to that of Fe and Mn suggesting that an anthropogenic signal of Cd was relatively high in the core sediments. V and Zn concentrations in the core sediments showed a linear trend with no significant variations. Ba and Sr showed similar trend to Ca concentrations shows their association with plagioclase feldspars and Ca bearing pyroxenes from the volcanic source region. Overall the metal concentrations in the core sediments of Atoyac River basin suggests the enrichment due to natural source rock weathering in addition with industrial influences from the Puebla city region.

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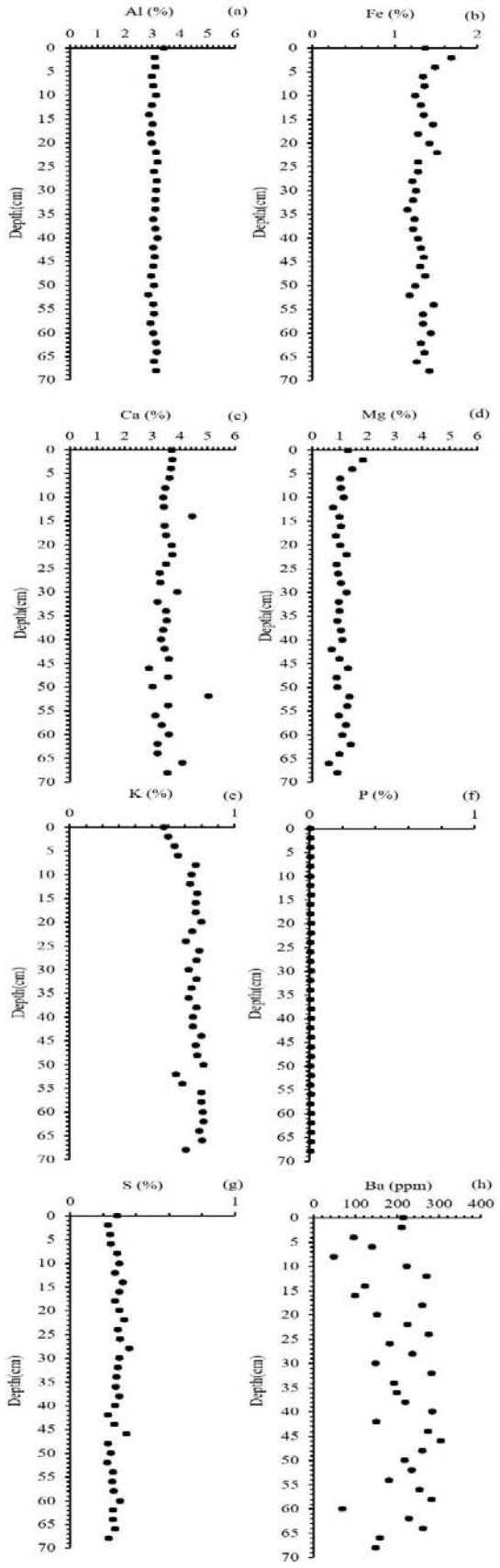



Fig. 2 (a)-(h) Down core variations of metals

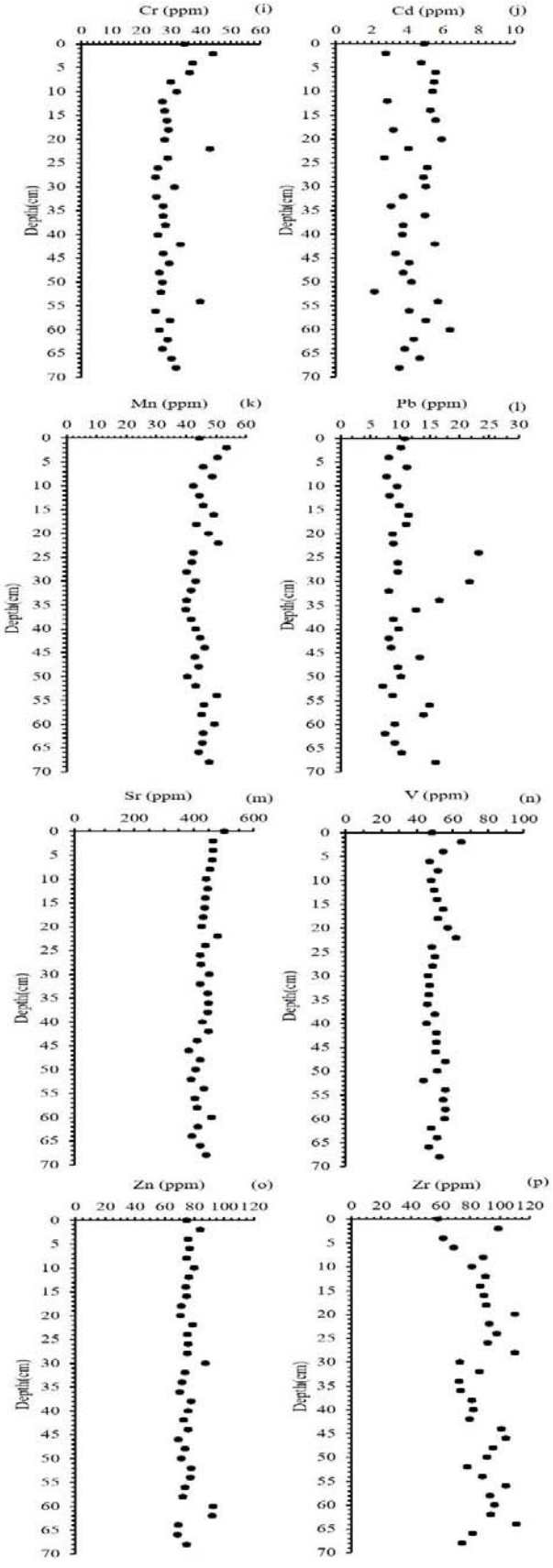



Fig. 2 (i)-(p) Down core variations of metals

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*C. Assessment of Sediment Contamination Levels*

Anthropogenic Factor (AF)

AF is used to identify the metal enrichment of anthropogenic origin in sediment core samples [31]. It is expressed as:

$$AF = C_s / C_d$$

where $C_s$ and $C_d$ are the metal concentrations in surface sediments and at the depth of the sediment column in the core respectively. AF > 1 indicates metal enrichment due to anthropogenic influences and AF > 1 suggests no metal enrichment of anthropogenic origin [32], [33]. In C1 core sediments AF > 1 for metals Ca, Mg, S, Ba, Cd and Zn indicating significant anthropogenic influences over these metals.

Enrichment Factor

EF is a normalization technique to investigate the influence and extent of human activities on metals. In the present study aluminum was used as the reference element for geochemical normalization as it is one of the main components of Earth's crust and a major constituent of the fine fraction (clay and fine silt) of sediments that are generally the predominant carrier phase for metals [2]. The EF is calculated using:

$$EF = [(Me)s / (Al)s / (Me)b / (Al)b]$$

where (Me)s/(Al)s is the metal to Al ratio in the sample and (Me)b/(Al)b is the natural background value of metal to Al ratio. The EF value in the range of $0.5 \leq EF \leq 1.5$ suggests that metals may be entirely from crustal materials or natural weathering processes but EF > 1.5 a significant portion of metals is provided by sources other than natural weathering processes [34]. Seven tiers of contamination were categorized based on EF values: 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 [35]. Severe enrichment of S and Cd exists in C1 core sediments (Fig. 3 (a)). S is significantly enriched, which is derived from active volcano and its recent volcanic deposits.

Cd being a chalcophile element reacts with sulfide and form insoluble precipitates leading to elevated concentrations in sediments. In addition, other major external source of Cd pollution are municipal wastewater discharges, agricultural, mining, incineration and discharges of industrial wastewater [36], [37]. The metals Ca, K and Sr exhibited moderately severe enrichment whereas Mg, Pb and Zr were moderately enriched. The enrichment of these metals indicate their association with plagioclase feldspars and Ca bearing pyroxenes from the volcanic source region.

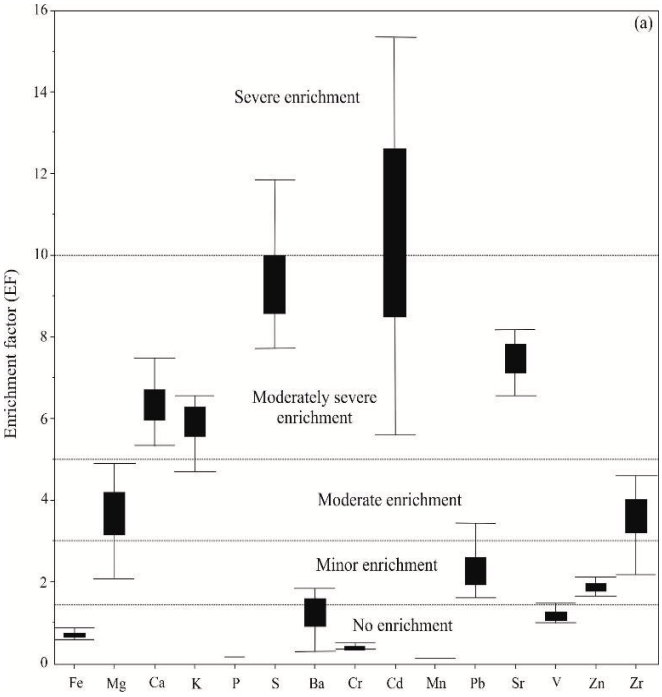



Fig. 3 (a) EF

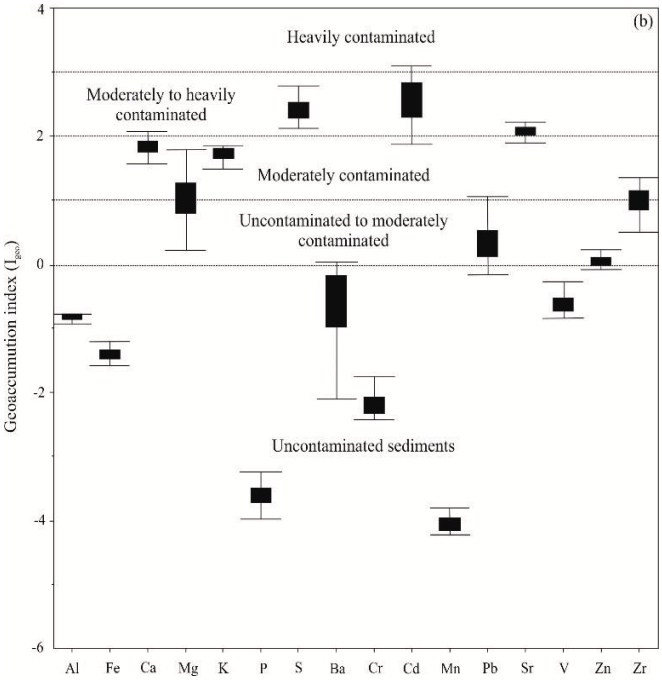



Fig. 3 (b) $I_{geo}$

Geoaccumulation Index ($I_{geo}$)

The $I_{geo}$ proposed by Muller [38] permits to assess the degree of metal contamination in sediments and calculated using the following mathematical relation:

$$I_{geo} = \text{Log}_2 (C_n) / 1.5 (B_n)$$

where $C_n$ is the metal concentration in sediment sample and $B_n$ is the geochemical background concentration of the metal (n).

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Factor 1.5 is the background matrix correction factor used in order to allow content fluctuations of a given substance in the environment. The $I_{geo}$ ranges from class 0 ($I_{geo} \leq 0$, unpolluted) to class 6 ($I_{geo} > 5$, extremely polluted and at least 100 fold enrichment above background). As presented in Fig. 3 (b), the metals Al, Fe, P, Cr, Mn and V falls in Class 0 indicating practically no contamination. Zn is uncontaminated to moderately contaminate in the core sediments falling under Class 1. The metals Ca (Class 2, 3), Mg, K (Class 2), S (Class 3), Cd (Class 3, 4), Pb (Class 2), Sr (Class2, 3) and Zr (Class 2) suggesting moderately to heavily contamination. The $I_{geo}$ values are similar to the EF values suggesting a dual origin of metals: natural source rock weathering, volcanic and external inputs in the confluence zone of the Atoyac River basin.

Potential Ecological RI

The potential ecological risk method proposed by Hakanson [39] is used to evaluate the potential ecological risk of individual metals in sediments. The RI is calculated as:

$$RI \sum_f^i ER_f^i$$

$$ER_f^i = Tr^i \times C_f^i = Tr^i \times (\frac{C_s^i}{C_n^i})$$

where $ER_f^i$ is the potential ecological risk factor for a given element *i*; $Tr^i$ is the biological toxicity factor for element *i*; which is defined as Cr = V = 2, Pb = 5, Zn = Mn = 1, Cd = 30; $C_f^i, C_s^i$ and $C_n^i$ are the contamination factor, the concentration in the sediment and the background reference value for element *i* respectively. The ecological risk of the metals in the core sediments of Atoyac River basin are ranked in the following order Cd > V > Zn > Cr > Pb > Mn (Fig. 4). The calculated RI values indicated that Cd and V contributed the majority of ecological risk in the core sediments.

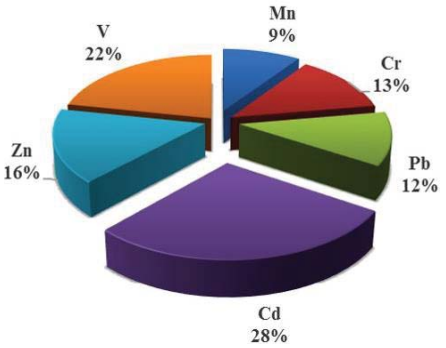



Fig. 4 Potential ecological RI

TABLE I
CORRELATION MATRIX ANALYSIS OF ATOYAC RIVER BASIN SEDIMENTS

| | Sand | Mud | Al | Fe | Ca | Mg | K | P | S |
|---|---|---|---|---|---|---|---|---|---|
| Sand | 1.00 | | | | | | | | |
| Mud | -1.00$^{*\dagger\ddagger}$ | 1.00 | | | | | | | |
| Al | -0.58$^{*\dagger\ddagger}$ | 0.58$^{*\dagger\ddagger}$ | 1.00 | | | | | | |
| Fe | - | - | - | 1.00 | | | | | |
| Ca | - | - | -0.35$^{*}$ | - | 1.00 | | | | |
| Mg | - | - | - | 0.50$^{*\dagger}$ | - | 1.00 | | | |
| K | 0.54$^{*\dagger\ddagger}$ | -0.54$^{*\dagger\ddagger}$ | - | - | -0.39$^{*}$ | -0.52$^{*\dagger}$ | 1.00 | | |
| P | - | - | - | - | - | - | 0.42$^{*}$ | 1.00 | |
| S | - | - | - | - | - | - | - | - | 1.00 |
| Ba | - | - | - | - | - | - | - | - | - |
| Cr | - | - | - | 0.69$^{*\dagger\ddagger}$ | - | 0.55$^{*\dagger\ddagger}$ | -0.62$^{*\dagger\ddagger}$ | - | - |
| Cd | - | - | - | - | - | - | - | - | - |
| Mn | - | - | - | 0.93$^{*\dagger\ddagger}$ | - | 0.47$^{*\dagger}$ | - | - | - |
| Pb | - | - | - | - | - | - | - | - | - |
| Sr | -0.49$^{*\dagger}$ | 0.49$^{*\dagger}$ | 0.38$^{*}$ | 0.38$^{*}$ | - | - | -0.56$^{*\dagger\ddagger}$ | - | - |
| V | - | - | - | 0.86$^{*\dagger\ddagger}$ | - | 0.37$^{*}$ | - | - | - |
| Zn | - | - | - | - | - | 0.51$^{*\dagger}$ | - | - | - |
| Zr | 0.37$^{*}$ | -0.37$^{*}$ | - | - | -0.34$^{*}$ | - | 0.59$^{*\dagger\ddagger}$ | 0.35$^{*}$ | - |

p>0.05$^{*}$; 0.01$^{\dagger}$; 0.001$^{\ddagger}$

TABLE II
CORRELATION MATRIX ANALYSIS OF ATOYAC RIVER BASIN SEDIMENTS

| | Ba | Cr | Cd | Mn | Pb | Sr | V | Zn | Zr |
|---|---|---|---|---|---|---|---|---|---|
| Sand | | | | | | | | | |
| Mud | | | | | | | | | |
| Al | | | | | | | | | |
| Fe | | | | | | | | | |
| Ca | | | | | | | | | |
| Mg | | | | | | | | | |
| K | | | | | | | | | |
| P | | | | | | | | | |
| S | | | | | | | | | |
| Ba | 1.00 | | | | | | | | |
| Cr | - | 1.00 | | | | | | | |
| Cd | -0.64$^{*\dagger\ddagger}$ | - | 1.00 | | | | | | |
| Mn | -0.45$^{*\dagger}$ | 0.65$^{*\dagger\ddagger}$ | - | 1.00 | | | | | |
| Pb | - | - | - | - | 1.00 | | | | |
| Sr | -0.47$^{*\dagger}$ | 0.58$^{*\dagger\ddagger}$ | - | 0.34$^{*}$ | - | 1.00 | | | |
| V | - | 0.53$^{*\dagger}$ | - | 0.77$^{*\dagger\ddagger}$ | - | - | 1.00 | | |
| Zn | - | - | - | - | - | - | - | 1.00 | |
| Zr | 0.35$^{*}$ | - | - | - | - | -0.57$^{*\dagger\ddagger}$ | 0.41$^{*}$ | - | 1.00 |

p>0.05$^{*}$; 0.01$^{\dagger}$; 0.001$^{\ddagger}$

*D. Source Delineation*

Correlation Analysis

In order to establish relationship among metals and determine the common source of metals in Atoyac River basin sediments, a correlation matrix was performed and are represented in Tables I, II. A strong positive correlation of Fe with Mg ($r^2$ = 0.50), Cr ($r^2$ = 0.69), Mn ($r^2$ = 0.93), Sr ($r^2$ = 0.38) and V ($r^2$ =0.86) exists, indicating some common geochemical process controlling their spatial variability and their bonding to Fe oxides. The negative relationship of Ca, K, P, Cd, V and Zr with detrital element like Al (relatively immobile) suggests that they are are associated with volcanic lithic fragments (carbonates and sulphates) and anthropogenic inputs [40]. Mn showed significant correlations with Sr ($r^2$ =

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0.34) and V ($r^2$ = 0.77) revealing that these elements are scavenged by Mn oxides [41]. The significant correlation of Mud with Al ($r^2$ = 0.58) suggests Al has high affinity to fine sediments and the negative correlation of Sand with Al ($r^2$ = -0.58) is due to dilution effect of aluminum by coarser sediments and its concentration becomes lower in the areas of high hydrodynamic energy [42].

## IV. Conclusion

The present study in core sediments of Atoyac River basin from Mexico, allows us to understand the historical record of metal concentrations and their distributions. The higher enrichment of Ca, Mg, K, S, Ba, Cr, Cd, Pb, Sr, Zn and Zr are mainly attributed to the mafic volcanic inputs from active volcano (Popocatépetl) in the western side of the study region and the vast development of industrial complexes in the Puebla City in Central Mexico. The degree of metal contamination obtained using several indexes revealed the extreme enrichments of Cd and S. The metal concentrations in core sediments are mainly regulated by the Fe-Mn oxides. The presence of Cd and V in the study region poses threat to the biological community. Thus the present study reveals the impact of both natural (volcanic) as well as anthropogenic (industries) influences over the metal concentrations in the core sediments of Atoyac River Basin.

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