PAK Publishing Group
Growing Knowledge for Future

Proceedings Book of ICETSR, 2014, Malaysia
Handbook on the Emerging Trends in Scientific Research
ISBN: 978-969-9347-16-0

Multivariate Treatments Applied to Mineral Composition and Size Data Analysis in Sediments of Urban Rivers as an Emerging Tool for Cleaning Basin of Alto Atoyac, Tlaxcala, Puebla, Mexico

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Abstract

Currently the state government of Puebla, Mexico is investing financial resources to clean up the urban Atoyac River (one of the most polluted in Mexico). A strategy to assist in the cleanup actions state government is the measurement of water quality parameters in real-time monitoring and sampling stations. The location of the stations and mathematical treatment of the results to be generated here are definitely influenced by two aspects: 1) The rural, residential and industrial discharges which have primary treatment; and 2) the geo-environmental condition in the river course route. This paper presents the results of geo-environmental parameters of size and mineral composition of sediments of Atoyac River. The interpretation of the results presented here reflects the conditions of generation, transport and deposit sediment and environmental susceptibility to retain metals or contaminants in those sediments. The present study reports the results of 47 sampling sites in the Basin of Alto Atoyac, which included from its source of sediments in the mountains to reach the Valsequillo Dam (down stream). The sediment sampling sites are located before and after the urban area where the monitoring and sampling stations in real-time (physicochemical parameters of water quality) are located. The emphasis on geo-environmental interpretation of the results of the multivariate treatments, established a scientific tool applied to emerging trends. Plotted multifactor values and their polynomial fits suggested the environmentally sensitive areas or Geoenvironmental Susceptibility Zones (GSZ). The GSZ that were detected are: generation, transport, transport-deposit and deposit sediment. The GSZ ranging from coarse sediments sizes in generation zone with low surface areas and low weathered minerals, to very fine sizes sediments with high surface areas and weathered minerals in the deposit

zone. These sedimentological characteristics (geo) induces or not the incorporation of heavy metals and pollutants (environmental) in sediments of the Atoyac River.

Keywords: Sediments size, Mineral composition, Geoenvironment, Multivariate analysis.

1. Introduction

This project is part of the study "Studies Network Monitoring Stations for the Preservation, Conservation and Improving Water Quality in the Upper Basin Atoyac, which provides the analytical support of the information generated in a future network automatic monitoring and for which essentially the correlation of information generated in different seasons with the characterization of the different areas of the Upper Basin Atoyac, to identify the origin of the different pollutants in time and space.

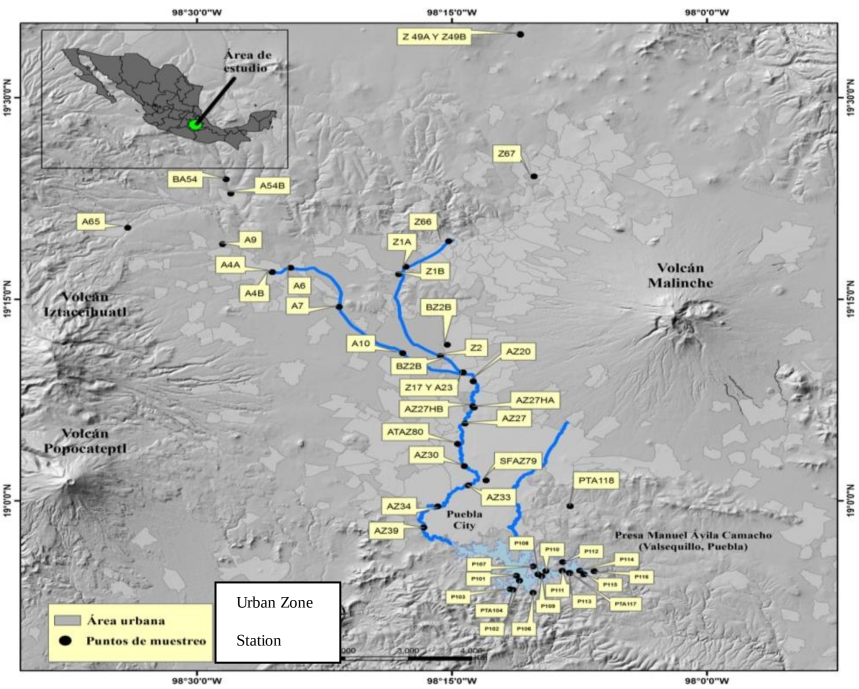
The Atoyac River in the Upper Atoyac contains contaminants in waters and sediments, and organic and inorganic matter, oils, detergents, nitrogen and phosphorus compounds, metals and toxic compounds such as cyanides and phenols, and organic compounds including aromatic hydrocarbons and herbicides are, among others (Declaratoria de Clasificación de los Ríos Atoyac y Xochiac o Hueyapan, y sus afluentes, Diario Oficial de la Federación del 6 de julio de 2011).

Among the pollutants studied, indicating the Declaratoria de Clasificación de los ríos Atoyac y Xochiac o Hueyapan y sus afluentes, include indicators such as nickel (7.86 kg / day), manganese (6.56 kg / day), zinc (5.59 kg / day) , copper (2.75 kg / day), chromium (2 kg / day), lead (1.22 kg / day), nitrobenzene (1.22 kg / day) and xylenes (1177 kg / day). In the case of metals, recent studies in the Valsequillo Puebla and have demonstrated a dual power sources: natural and anthropogenic.

Puebla's government has focused resources to solve the problem of pollution Atoyac Alto, undertaking different actions in order to clean up the river water. Including the construction of new treatment plants wastewater. The current program of modernization of macroplants of wastewater treatment in the Metropolitan Zone of the City of Puebla. The efforts made so far have been insufficient so far, because although the load of biodegradable pollutants (BOD) has declined since 1992, the concentration of chemically degradable pollutants (COD) has increased (Rodriguez-Espinosa, PF et al., 2011) .

Therefore this paper presents correlate geoenvironmental, parameters of the sediment size, metal content in partial digestion and index some metals studied, in order to determine the sites of generation of contaminants in the sediments of the Upper basin of High Atoyac.

Figure-1. Study Area, Metropolitan Area of Puebla, Tlaxcala, Mexico.



2. Study Area

Atoyac river basin belongs to the Alto Balsas basin in Hydrologic Region No. 18. The Atoyac River is one of the most important rivers in the state of Puebla and Tlaxcala (see map 1), its main tributaries are the Atoyac River (3,250 m) and Zahuapan River (2,200 m): both have come together once downloaded Valsequillo dam "Manuel Avila Camacho" (2,000 m). The annual rainfall is 800 mm.

Atoyac River Basin is part of the Central Volcanic Belt (volcanic range) in which various igneous rocks are associated with large faults and fractures. The region of Alto Balsas Atoyac have a geological formations are mainly composed of igneous rocks of the Upper Pliocene to recent, predominantly lavas, breccias and andesitic and rhyolitic tuff. Figure 1 shows the network of monitoring stations that were made for the development of this work (see Figure 1).

3. Method

3.1. Sediments Sampling

The technique used for sampling of sediments was either directly using a dredge Ponar 9x 9 ", this device is made of stainless steel 316, consists of two semicylindrical spoons each provided with a metal articulated arm and coupled together by a shaft. This dredge was appropriate to collect fine to coarse sediments. Sediment Sampling Procedure 45muestras total soil and sediment were collected in three sampling campaigns (January, April and September 2013). According to the following procedure:

Once identified the sampling proceeded to drive the Ponar dredge. Once the sediment taken with the dredge, it was brought to the surface. The collected sediment was homogenized. Samples were refrigerated until arrival at the laboratory in a cooler.

3.2. Analysis of Sediments

The sample pretreatment consisted of drying on the laboratory drying oven Lab-line brand, model 3481M. Crystallizers entering the drying oven at 39 Celsius degrees. Once dry the sample was removed from the oven and placed in a polyethylene bag with seal, later to be homogenized and pulverized. The residence time of each sample in the drying oven was dependent on the amount of moisture and the components of the sample, lasted 10-13 days. This procedure was performed for all samples.

All samples were ground for a nominal mesh of less than 10 (1.7 mm), mechanically separated to obtain a representative sample and then is pulverized below 95% of 150 mesh (105 microns).

Samples were sent to the laboratory Actlabs in Canada, where out partial digestion of the samples (Bettinelli et al, 2000. Hseu et al, 2002) were carried. For partial digestion aqua regia (3:1, v / v, HNO_3 and HCl, respectively) were used. The aqua regia digestion method (USEPA method 3050) was developed for the determination of heavy metals in the soils of the U.S. (USEPA 1986). The accuracy and precision of the measurements were checked by using appropriate reference materials and repetitions.

Following extractions the samples were analyzed on a equipment of Elemental Analysis by Atomic Emission Spectroscopy Inductively Coupled Plasma (ICP / OES). This ionization technique consisted of nebulized sample in an Ar plasma. The metals Selected were Cr, Mo, Ti Ni, Ag, Co, Cu, P, Pb, Te, Zn and Zr.

3.3. Sediment Size Determination

The size of sediments performed by two techniques: pipetting a fine fraction of the sediment and by mechanical separation technique (sieves), Folk (1980).

4. Geoenvironmental Index

The proposed by Müller (1979) Index geoaccumulation (Igeo) has been widely used to evaluate the degree of metal contamination in terrestrial, freshwater and marine environments, compared to the metal content of natural and anthropogenic origin. The I'geo is obtained by using the following equation::

$$Igeo = Log_2 (Cn/1.5Bn)$$

Where: Cn is the concentration of metals in the samples examined sediment and Bn is the geochemical background concentration of metal (n). Factor 1.5 is the correction factor matrix background due to the effects of the lithosphere. The I'geo consists of six classes (Müller, 1981):

≤ 0	Class 0	Uncontaminated
0-1	Clase 1	Uncontaminated to moderately contaminated
1=2	Clase 2	Moderately polluted
2=3	Clase 3	Moderate to heavily polluted
3=4	Clase 4	Heavily contaminated
4=5	Clase 5	Very to extremely contaminated
5=6	Clase 6	Highly contaminated

4.1. Factorial analysis

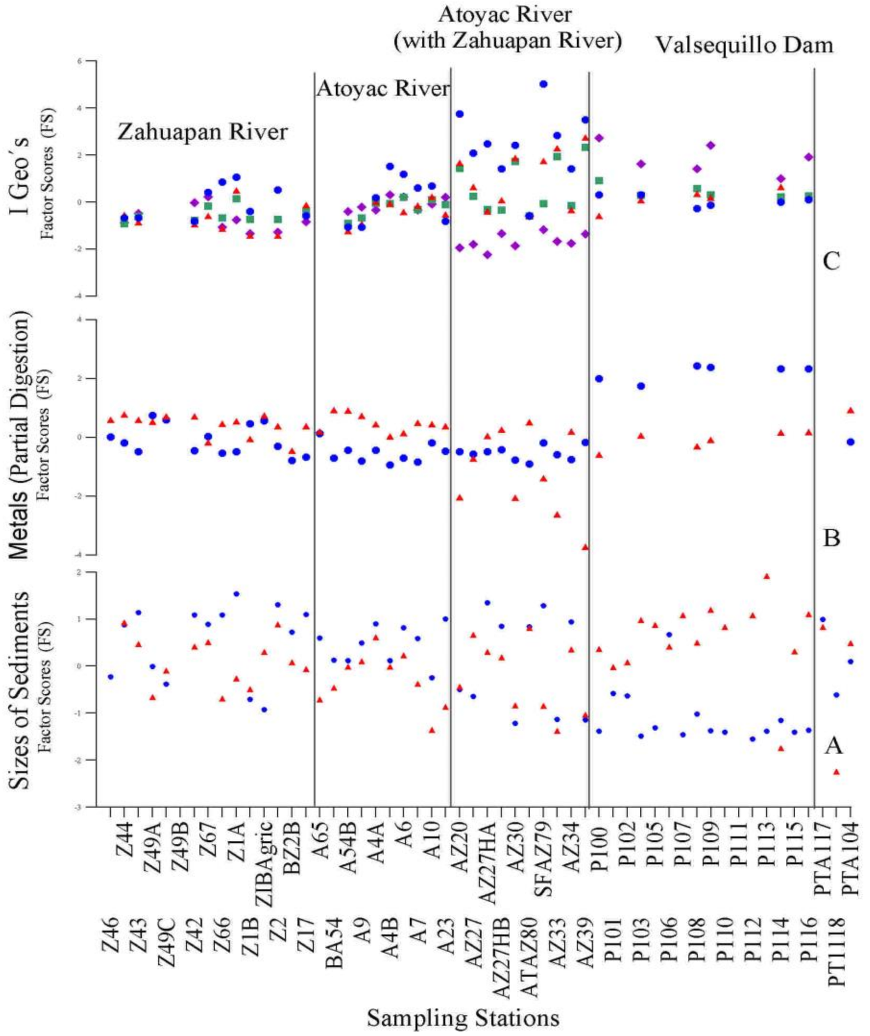
Multivariate statistical methods are used, as they help us identify multicorrelations a number of variables that are in the sample. Each sample can be represented by a vector of measured concentrations of elements or as a point in space of measured variables. The purpose of factor analysis (FA) is the identification of associations observed in different sites through which passes the river. The process is the search for the factors that describe the associations are causally explainable. Reflect factors extracted main part of the data set information. Davis (1986)

5. Results

The information presented here correlated in space and time the correlations major variables studied in the sampling sites of sediments in rivers Zahuapan, Atoyac before and after confluence and Manuel Avila Camacho Dam (Valsequillo). The relationship of the variables correspond to multi-correlations of: sediment size; metals (partial extraction), including some heavy metals, major and trace metals; Geoenvironmental Index of sediments. Calculated by metal and for each sample site. The integration of the information presented here provides an overview of the origin and transport of pollutants, using the sediment like tracers of pollutants responsible for transporting, discharging rural populations and urban areas that sit on the banks and catchment. Studies allow multivariate integration discern conditions of natural and anthropogenic metals provenance; approach also allows the generation sites determined routes, transport and effects tracers, locating areas of environmental sensitivity , namely generating areas , transit , deposition and accumulation of contaminants.

The results are presented in Figure 2 which is a graph composed of three multi-correlations of sediment properties studied and presented as follows: A) sediment size, B) Metals (partial digestion); and C) Geoenvironmental Index of Sediments. The X axis corresponds to the representation of the location of the 74 sequenced sampling sites in the following order, sites Zahuapan the Upper Rio, Rio Atoyac, The Atoyac once Zahuapan river joins the river and already in downstream to reach the dam Vasequillo where the sampling sites is shown (see Figure 1). The regions represented correspond to the sampled sites for Zahuapan River, Atoyac River (upstream of the confluence with the Rio Zahuapan) Atoyac River (after the confluence with the Rio Zahuapan) and Valsequillo Dam. Different regions are represented in the graphs by four vertical lines.

Figura-2. Size sediments, Metals (partial extraction) and Geo Index.



Each individual graphical form Figure 1, which in turn contains graph of two representative factors for each sampling, which are presented by their values obtained in the multivariate mathematical treatments (AF).

5.1. Sediments Size

The size of sediments is shown in Figure 2A, the results are reported in units of factor that integrates the multi-correlations of 11 textural classes for 54 sampling sites for each site or sampling station. The main associations are presented correlation between textural classes : first and second components or load factors corresponding to textural class size analysis of sediments showing the regionalization of this parameter (see Figure 2) Figure 2 Correlation of the first and second load factor ϕ textural classes (-log2 D / Do) units in 54 sediment sampling sites Atoyac, Zahuapan Valsequillo Dam and rivers. As can be seen by the association are presented textural classes or sizes , in thicknesses of -2 to 0 ϕ ϕ 2 to 4 , and finally the region corresponding to the fine fraction of 5 to 9 ϕ .2A comprises two factors describing two trends along its route by Atoyac Zahuapan and rivers to reach the Valsequillo Dam and here the curtain of the dam. Size sediments in the 1st can observe a proportion of the coarse and fine fractions, with a positive predominance of coarse fraction on the fraction of negative media and fine. The graphs of the two factors are inversely proportional representation denoting two characteristics for each of the two factors in the Zahuapan Atoyac River and River before flowing. The interpretation of such behavior indicates that populations are thick materials and resources correspond to the field of gravel and sand which coexist at the study sites , this area is generating thick sedimentary materials and resources, due to the proximity to the source rocks. This represents the general trends of these two sediment size multi-associations denote a crossing on their way to the centroid of the region Atoyac River after the confluence with the Rio Zahuapan and

before it flows into the Valsequillo Dam. The intersection highlights that this region is an area of mixed sedimentary materials of different sizes and supplied by the Atoyac Zahuapan Rivers converge before. This area is mixing; sediment transport and transition of coarse, medium and fine sizes coexist. Finally, the Valsequillo Dam region both load factors in the sampling sites have a separation of the two trends described now in reverse to that presented before the transition, in this region, separation of the two load factors by station size, highlight an environment dominated by deposit the fine fraction where the two factorial components represent two sample populations separated by low energy conditional loss of the slope. So that this region is an area receiving sediments where not only water but also sediment dammed, is a custodian and storage area of fine and very fine fractions of sediments.
Each individual graphical form in Figure 2 which in turn contains graph two factors contained in sediment Metals Partial leaching metals sediment displayed in graph 2B, the results are reported in units of factor that integrates multi-correlations 25 elements including metals metalloids include major and trace elements for 45 or sampling station sites. The main associations of correlation between the variables studied metals that are represented in the graphs of the first three components or factors are presented in Table 1 are presented. Load factors and corresponding metal elements for each sampling site are depicted in the graph in Figure 2B. Now, referring to Figure 2, the two factors that describe two trends along its route by Atoyac Zahuapan Valsequillo Rivers to reach the dam and here the curtain of the dam are represented by the 1st and 2nd factor. We can see the composition of these two plotted factors , we refer to the 1st and 2nd load factor of the composition of metals, in the 1st we can observe an association with metals, and naturally occurring elements such as Al , Co , Cu, Fe, Ga , K, Li , Mo , Ni, K, Pb, Ti, and Zn, how can see in the graph 2B blue represents this factor described above, with a poor presence in areas associated with high mountains and mountain valleys inter basin Tlaxco, Malinche, as well as runoff from Ixtazihuatl volcano, the first factor denotes increased its presence in the area where the river ends Zahuapan Atoyac and to be maximum in the Valsequillo dam . It is noteworthy that the effects of weathering and anthropogenic activities are responsible for this combination of elements of natural and anthropogenic origin. The effects of weathering correspond to elements which are transformed by the effects of weathering and erosion in the path of sediment downstream. The characteristics described above are reversed in the second factor represents a combination of elements and also naturally occurring predominantly metals , the factor is depicted in Figure 2B with red. The elements and metals are present here Pb, Sc, Sr, Ti and Zn is a component represented by elements and metals proportion with a positive influence over the trend presented two-factor until the confluence of the rivers Atoyac and Zahuapan . The graphs of the two factors are inversely proportional representation denoting two characteristics for each of the two factors in the Zahuapan Atoyac River and River before flowing. The interpretation of such behavior indicates that they are locations of these elements and metals which coexist at the study sites; this area is then generating elements and metals, due to its proximity to two major power source rocks and the contribution via industrial discharges. Importantly, the results presented here are the result of the analysis of partial acid digestion, indicating that the items reported herein are environmentally available and not in the matrix of the sediments but in its surface and that are capable of being exchanged. However, polynomials, representing the general trends of these two multi-associations denote a crossing on their way in, and exactly in the region of Atoyac River after the confluence with the Rio Zahuapan and before it flows into the Valsequillo Dam. The intersection highlights that this region is an area of mixed elements and metals, just after the confluence of the contributions of Atoyac and Zahuapan Rivers converge before. As this area is mixing, transportation and transition metals and elements coexist. Finally, in the amount of the Valsequillo Dam region both load factors in the sampling sites have the following separation of the two trends described now in reverse to that presented before the mixing zone to downstream from the confluence, in this region, the separation of the two loading factors highlighted elements and metals deposit an environment dominated by associations of the second factor. So that this region is an area receiving elements and metals were transported and processed .Geoenvironmental IndexIgeo values were calculated for the study area to identify sources and extent of contamination. Concrete graphs Igeo values were obtained for the mountains, the river Atoyac the Zahuapan river confluence and Atoyac - Zahauapan Valsequillo Dam. In the mountains the most values were under class 0 indicates no pollution. Very few were in Class 2 only infer moderately polluted and molybdenum found in class 3, which is moderately to heavily polluted.

Igeo River Zahuapan index shows elements in class 0 and class 1 elements compared to the mountains. Copper is found to be present in class 2. This indicates that it is not polluted river Zahuapan further. Was moderately polluted river. Igeo Atoyac river values indicates a majority if the elements of the class 0 and class 1. Chromium and copper comes in Class 2, wherein the molybdenum belongs to Class 3. Atoyac River is more polluted than compared to Zahuapan river. At sites of confluence of the Igeo Zhauapan Atoyac and values are dispersive and the presence of cobalt, molybdenum and arsenic in class 1 and class 2. Zinc and copper are found in all three classes and a significant presence of lead is observed in class 1, 2, 3.4 and 6. Class 6 indicates extremely contaminated and therefore the confluence site is highly contaminated with lead. Igeo values Valsequillo Dam has little pollution compared to others. Most items are under class 0, elements of class 1 and cadmium, copper and lead in Class 2. The two plotted factors , we refer to the 1st and 2nd load factor of Geoenvironmental indices in the 1st can observe an association with metals, and elements of natural and anthropogenic such as Fe , Al, Ba, Cr, Mn, Ni, V, Y and Zr. In order to present the trend for the metals were the highest geo-environmental indices, the behavior of four typical metals geoenvironmental contamination found in the study area is presented. The blue graph 1C represents the behavior of Pb Geoenvironmental Index, with a significant presence from the region corresponding to Atoyac river after the confluence with the Rio Zahuapan industries area where you see the river receives industrial discharges and settle. This metal denotes a steady increase with advancing the river as it passes through the urban area of Puebla, Atoyac River after the confluence with the river Zahuapan. In this area the highest values observed factor before reaching Valsequillo dam, where its presence is minor. The interpretation of this behavior is due to a significant association of fine sediments and weathered minerals described above and the generation region of different metals and anthropogenic elements, also described above. The behavior described above is similar to that observed for the metals Cu and Zn are plotted in red and green (see graph 2C). Two metals which have an inverse to the trend shown by the Pb , Cu and Zn are the Cr and Ni, which is plotted here in purple colored Ni (see graph 1C) . The reverse trend of these two metals is due to the affinity for minerals and metals and potentiates associated with meeting areas and low energy loss as is pending Valsequillo Dam and increased surface area presented by native sediments that depositional environment. The metal contained in the formulation of Geoenvironmental Index contains the property to distinguish the different contributions of natural and anthropogenic origin. By representing a predominance of an association of metal elements and anthropogenic origin, the set of trends shown in graphical 1C denotes a general tendency to increase their potential to retain geoenvironmental sedimentary strata more and different metals that make abstract in sediments of the Valsequillo dam . The interpretation of such behavior indicates that they are groups of elements , metals and metalloid of natural and anthropogenic origin anthropogenic dominance , which coexist at the study sites , this area of generation and movement of elements, metals and metalloid , due to the proximity two main sources of discharge of residential and industrial areas . The graphics representing the general trends of these two multi-associations denote a crossing on their way in, and exactly in the region of Atoyac River after the confluence with the Rio Zahuapan and before it flows into the Valsequillo Dam. Principal for each sampling site, which are presented by their values obtained in the multivariate mathematical treatments (AF).

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7. Conclusions

- Statistical analysis of main components through variances and major associations can display stations where there is similarity in the behavior of pollutants and which again corresponds to Barranca Honda is no similarity to any other point in the basin.
- The results of the geochemical properties and geoenvironmental determinations allow sediment elucidate the role of the effects of these variables in combination with the different characteristics of water quality and geo-environmental effects in the regions through which passes the river system high Atoyac, giving light to areas of generation of pollutants, transformation zones thereof and transit areas and deposition of the major pollutants that occur in the study area .In the study of origin of metals in sediments was concluded that most of the elements have a natural origin, highlighting a natural double - anthropogenic origin for Cr,

Mo, Ni and Ti elements. While Ag, Co, Cu, P, Pb, Te, Zn and Zr, have a strong anthropogenic origin due to various industrial, urban and agricultural activities are conducted throughout the study area.

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