Rev. FCA UNCUYO. 2014. 46(2): 203-221. ISSN impreso 0370-4661. ISSN (en línea) 1853-8665.

Heavy metal contamination in sediments of a riparian area in San Luis Potosi, Mexico

Contaminación por metales pesados en sedimentos de un área ribereña en San Luis Paotosí, México

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Originales: Recepción: 31/12/2013 - Aceptación: 18/10/2014

ABSTRACT

The aim of this study was to determine the presence of heavy metal in sediments of a fragmented riparian area, as an indicator of environmental pollution in San Luis Potosi, Mexico. Eleven sampling points, including four different land uses were established: Pond, Agriculture, Livestock and Rural Settlement. Sediment samples were taken during the seasons of spring, summer and autumn 2010, and winter 2011. The technique of ICP-MS was used to determine Pb, Cd, Cu, and Zn data analysis was performed with Minitab®. Land use has an effect on the accumulation of Cu, Zn and Cd, with the agricultural area containing the highest concentrations. The season was a significant factor for concentrations of Zn, Cd and Pb, emphasizing spring 2010 and autumn 2010, respectively. Significant correlations were found between Cu-Zn (r = 0.746), Pb-Cu (r = 0.635) and Cd-Zn (r = 0.720). The normal limits of Cu, Cd, Zn and Pb in sediments established by the Canadian Environmental Quality Guidelines were exceeded. By using other scientific and technical sources, maximum levels of Cu, Cd and Pb were defined with a condition of high pollution. This condition is attributed to the land

RESUMEN

Se determinó la presencia de metales pesados en sedimentos de un sistema ribereño fragmentado por usos de suelo como indicador de contaminación ambiental en San Luis Potosí, México. Se establecieron once puntos de muestreo considerando los usos de suelo: Estanque, Agrícola, Asentamiento rural y Ganadero. Durante las estaciones de primavera, verano y otoño de 2010 e invierno 2011, se tomaron muestras de sedimentos. Se utilizó la técnica de ICP-MS para determinar Pb, Cd, Cu and Zn y los datos fueron analizados en Minitab®. El uso de suelo incide en la acumulación de Cu, Zn y Cd, siendo la zona agrícola la que cuenta con mayores concentraciones. La estación fue significativa respecto de las concentraciones de Zn, Cd y Pb, destacando primavera 2010 y otoño 2010 respectivamente. Asimismo, fueron encontradas correlaciones significativas entre Cu-Zn (r = 0,746), Pb-Cu (r = 0,635) y Cd-Zn (r = 0,720). Los límites normales de Cu, Cd, Zn y Pb en sedimentos establecidos por la Canadian Environmental Quality Guidelines fueron rebasados. Con otras fuentes se definieron que los niveles máximos de Cu, Cd y Pb presentaron una condición alta de contaminación. Esta condición es atribuida a la

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use change dynamics, to wastewater discharges, and urban, agricultural and livestock wastes. Thus, a further environmental assessment is recomended for the study area.

dinámica de usos de suelo, descargas de aguas residuales, desechos sólidos urbanos, agrícolas y ganaderos, recomendándose continuar su evaluación ambiental.

Keywords

land use • environmental impact • pollution • season

Palabras clave

usos de suelo • impacto ambiental • contaminación • estacionalidad

INTRODUCTION

In the evaluation of environmental pollution, the analysis of coastal systems becomes an alternative for the assessment of the environmental impact of human activities and the physico-chemical processes involved in the biological and ecological functionality.

The term riparian area refers to the transition region where the interactions between the terrestrial and aquatic areas ocurr. It is characterized by a flora and fauna whose composition is strongly influenced by light intensity, water content and soil particle size. These ecosystems have many attributes that enhance their biodiversity: boundaries, patterns of succession, vertical strata and especially microhabitats that can be defined by their physical features.

The current water regime of the river system is linked to rainfall and seasonal changes (21). In riparian systems the influence of vegetable morphology, soil characteristics and the potential impacts of productive activities such as livestock in retaining soil on the banks rivers are associated with erosion and sedimentation (38). Moreover, a greater breadth of functionality can be obtained by including an ecological assessment of pollution in resources such as soil, sediments, flora and fauna and riparian systems (12).

The presence of contaminated sediments in aquatic environments is a situation found worldwide since the twentieth century. This is due to industrial fly-tipping, as well as the use of chemicals such as pesticides that are passed to sediments from agricultural areas (20). Sediment is an integral component of aquatic ecosystem providing habitat, feeding, spawning and rearing areas for many aquatic organisms. Sediments also serve as reservoir for pollutants and therefore represent a potential source of pollutants to the water column, organisms, and ultimately human consumers of those organisms (24).

Heavy metals in aquatic systems and sediments derived from natural and anthropogenic processes are influenced by the mineralogical composition, texture of sediments, adsorption, desorption, redox, among other factors (39). The variety and quantity of sediment-transported pollutants includes construction debris, oil, toxic chemicals from automobiles, nutrients, viruses, bacteria and heavy metals (21).

Therefore, there are no clear criteria for establishing the heavy metal contamination of sediment because the sediment composition can be varied, depending on the rock, the grain size of organic matter content, electric conductivity, potential of hydrogen, among other factors (12). Heavy metal pollution in sediments is a good indicator for assessing coastal areas. This can provide information to assess their impact on the ecological dynamics of populations, because of the possible magnitude of its bioaccumulation, as the cases of Cu, Mn, Fe, Cd, Ni, Cr, Pb and Zn (1, 32). Knowledge of the properties and composition of sediments allows the evaluation of the condition and disturbance resulting from the accumulation of anthropogenic and natural substances that could pose risks to the ecosystem health (39).

In Mexico there are few studies related to the processes that take place in the sediment and water together or independently (16). In this context, the municipalities of San Luis Potosi and Soledad de Graciano Sanchez converge in a microregion with environmental issues related to the impacts of population, industry and large areas of crops under a rainfed irrigation regime.

The climatic characteristics of this area indicate a dry, temperate climate with warm summers. It records an annual rainfall of 400 mm concentrated particularly from May to October (29). It also shares a watershed that integrates a drainage area of 264.6 km ^{2}, including Dams Toll, El Potosi and San Jose Dam located upstream, and their shade.

The latter provides a runoff that supplies Santiago River (31). Additionally, the Santiago River runoff passes the outlet of a pond with wetland features called "Tanque Tenorio" and its hydrological catchment area affects distribution and coastal pathways. This area has been used since the 70' s for the discharge of industrial water, and to a lesser extent for domestic and continuously discharged wastewater (25). In turn, there are problems due to overfishing and pollution of aquifers, erosion, salinization and loss of soil fertility and improper disposal of household and industrial waste (28).

Given this scenario, the study aimed to evaluate the presence of heavy metals associated to various land uses such as agriculture, livestock, rural-urban settlements and natural areas in the Rio Santiago river system and "Tanque Tenorio" pond.

In the past, studies had associated heavy metal concentrations in lands with different uses to the emissions of particles to the atmosphere and releases of residues from industrial, urban, semi-urban and agricultural zones (3). Therefore, it is of great interest to evaluate the environmental issues involving these relationships and the quality of the river system, using the presence of heavy metals in sediments as an indicator of environmental pollution. It is considered that land uses, along with the season of the year, may affect the variation of the presence and concentration of heavy metals.

MATERIALS AND METHODS

Study Area

The study was conducted in the municipalities of Soledad de Graciano Sanchez and San Luis Potosi (San Luis Potosi State, Mexico) (28, 29, 30 ,31). The municipality of Soledad de Graciano Sanchez, lies between 22°27' N and 100°58' W. The municipality of San Luis Potosi is located at coordinates: 22°12'27 "N, 101°01'20" W, with an altitude of 1.883 m (23, 27). Considering the location of the Pond Tenorio System and its influence area converging on the route of Rio Santiago, 11 points were placed randomly according to the land use types: Pond, Agriculture, Urban-rural Settlement and Livestock (figure 1). In the path where samples were taken, crops such as corn and alfalfa were grown. Moreover, inhabitants of the zone used to have cattle and goats, mainly under livestock conditions.

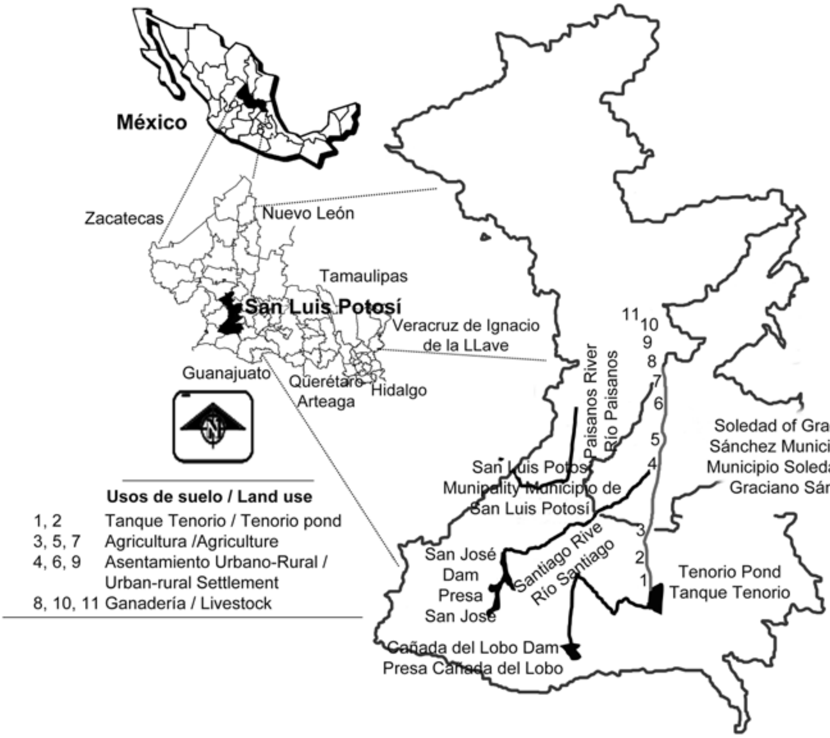

Figure 1. Study area and location of sampling points.
Figura 1. Localización del área de estudio y puntos de muestreo.

Sediment Sampling

Samples were taken at each sampling point during the seasons of spring, summer and autumn 2010 and winter of 2011. Sediment samples correspond to the two banks of the river system and on the channel, which were taken with a maximum depth of 15 cm. In total 132 samples were taken, corresponding to a total of 33 samples per season. According to the Mexican norm NOM-021-REC-NAT-2000 applied to soils as a reference (15) physical and chemical parameters such as pH (AS-02 method), texture (AS-09 method), electrical conductivity (AS-18 method), $CaCO_3$ (AS-29 method) and organic matter (AS-07 method) were determined.

Analysis of Metals in Sediments

To determine the concentration of metals in sediments, samples were prepared by drying them at room temperature for 3 days, and then sieved on a 2 mm mesh, adding 1 g of volume to a mixture of HNO_3 with ultra-high purity. They were left in a vial in a Teflon microwave accelerated reaction system MARS 5 with a ramp control of temperature for ten minutes at 180°C, and the extracted liquid was diluted with distilled water for analysis of Pb, Cd, Cu and Zn concentrations. Some criteria used were based on (2, 34).

Analysis was performed in the laboratory using the technique of atomic absorption spectrophotometry ICP-MS. Given that in Mexico does not exist a specific norm for heavy metals in sediments; metal concentrations in sediments were compared with standard values established by the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (13), referred to as the Canadian Environmental Quality Guidelines (ISQG - Interim Sediment Quality Guideline), and the criteria established by (Garbarino *et al.*, 1995), which classifies maximum levels of heavy metals in sediments according to the criterion: unpolluted, moderately polluted and heavily polluted. The previous was performed due to the absence of specific regulations for heavy metals in sediments in Mexico.

Statistical Analysis

Regarding the statistical analysis, two procedures were used to process the data related to the presence of heavy metals in sediments. A general lineal model (GLM) that included variance analysis ($\alpha \leq 0.05$) and regression analysis. The first analysis considered the four land uses: Pond, Agricultural, Urban-rural settlement and Livestock.

The GLM was adjusted to test the individual effect, the interactions between land use factors, and seasonality with respect to the concentrations of heavy metals. A second analysis was used to eliminate the effects of the Pond land-use.

The previous, analysis was performed to avoid the interference of Pond land-use with the results, given that it is considered a system with significant pollution problems. This analysis only considered agricultural, urban-rural settlement and livestock land use, while applying the same statistical model. In these two criteria, the means and the Pearson correlation coefficient test were determined. To determine the existence of heavy metals that could establish relationships between concentrations and land use and seasonality, principal component analysis (PCA) aimed at grouping the sampling points or sites and stations of higher accumulation of metals (20). Once the variation of the main components was determined, dispersion graphs were created in order to know the influence of the heavy metal accumulation in sediments regarding the land uses and season. A similar study was performed for the four analyzed elements (4, 14, 37, 40).

All analyses were performed in the statistical package MINITAB ®.

RESULTS

From the physical and chemical characterization performed on the sediments. Values of pH, found in the range from 7.66 to 8.05, were considered slightly high, based on the ranges established by NOM-021-RECNAT-2000 (15). In general, the texture was found to be silty in rages from 84 to 90%. The electrical conductivity (EC) presented ranges from 0.479 to 1.395 dS/m, considered in this norm as very low and low, respectively. Regarding the concentration of $CaCO_3$, this component was in the range from 0.78 to 1.79%, interpreted in the norm as low. Finally, and regarding the presence of organic matter, ranges oscillated 0.9 to 3.16%, considered as low and high, respectively.

Analysis of metals in four land uses

There were found significant effects on the analyses of concentrations of Cu, Zn and Cd by the presence of Pb, Zn and Cd in each relation to land use-season; Cd-season interaction was found according to land use.

The mean concentrations were in the order of Zn> Cu> Pb> Cd, corresponding to 108.6, 20.9, 18.5 and 3.2 mg kg^{-1}, respectively. Using Pearson's correlation coefficient, significant relationships were obtained, which emphasised higher Cu-Zn (r = 0.746), Pb-Cu (r = 0.635) and Cd-Zn (r = 0.720) associations. These results are presented in table 1. Moreover, the regression analysis showed a representativeness of 57.6% for Cu-Zn and 73.3% for Cd-Zn (figure 2, page 209).

Table 1. Correlation of heavy metals in sediments considering four land uses.
Tabla 1. Correlación de metales pesados en sedimentos considerando cuatro usos de suelo.

	Elements		
	Cu	**Zn**	**Cd**
Zn	0.746		
	0.000		
Cd	0.495	0.720	
	0.000	0.000	
Pb	0.635	0.388	0.234
	0.000	0.000	0.000

PCA was determined jointly; components PC1 and PC2 explained 86% of the variability of the data. Figure 3 (page 209) shows the dispersion diagram. The PC1 showed positive correlations between Cu (0.546), Zn (0.563), Pb (0.396) and Cd (0.478). PC2 presented negative correlations with respect to Zn (-0.255) and Cd (-0.551) and positive with respect to Cu (0.185) and Pb (0.722). Figure 3 (page 209) shows the variability of the observations determined in PC1 and PC2 in which a set of disperse data of land use near the axis interception of both components was found. An eight point dispersión in land uses of agriculture and livestock was observed and others of six in the land uses of agriculture, livestock and rural settlement.

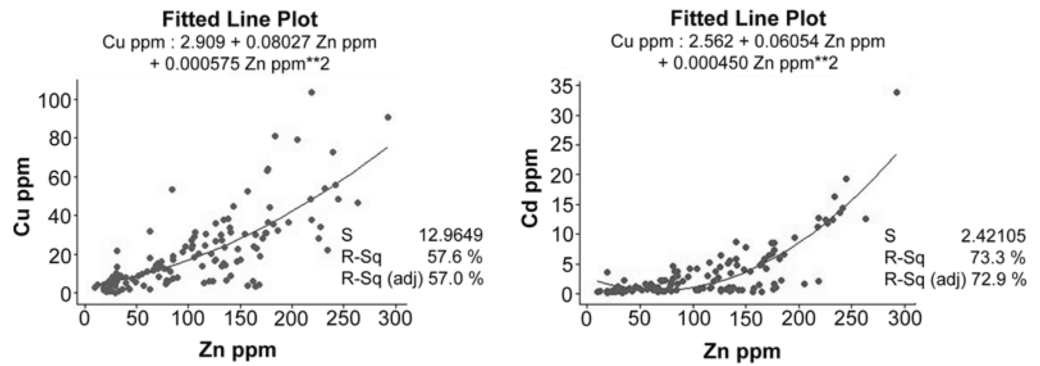

Figure 2. Regression analysis between Cu-Zn and Cd-Zn.
Figura 2. Análisis de regresión entre Cu-Zn y Cd-Zn.

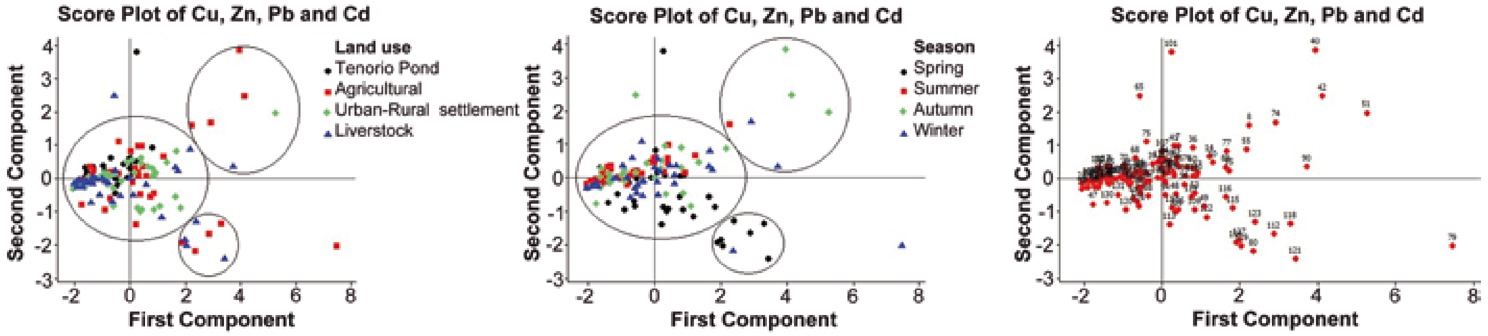

Figure 3. Dispersion of points derived from the main component analysis considering four land uses.
Figura 3. Dispersión de puntos derivado del análisis de componentes principales considerando cuatro usos de suelo.

There are three samples over PC1 away from the intercepted axis between PC1 and PC2 from the sample 79, which presented the highest values of Cu (91.07 mg kg^{-1}), Zn (293.210 mg kg^{-1}), Pb (49.16 mg kg^{-1}) and Cd (33.75mg kg^{-1}). This data belonged to agricultural land use and winter 2011. Along the PC2, there are five sample sediments removed from the shaft 51, which highlight the concentrations of Cu (72.81 mg kg^{-1}), Zn (239.6mg kg^{-1}), Pb (79.42 mg kg^{-1}) and Cd (13.63 mg kg^{-1}). These samples are outside the urban-rural settlement land use type and the autumn season of 2010.

In figure 4 a dendogram derived from the similarity of the analysis is presented in which it shows the Euclidian distance between the studied metals in sediments.

Such analysis, which indicates the degree of affinity, shows a relationship between Cu and Zn with a level of 87%. Cadmium presents a lower degree of affinity associated to Cu and Zn while Pb stays separated from these metallic elements.

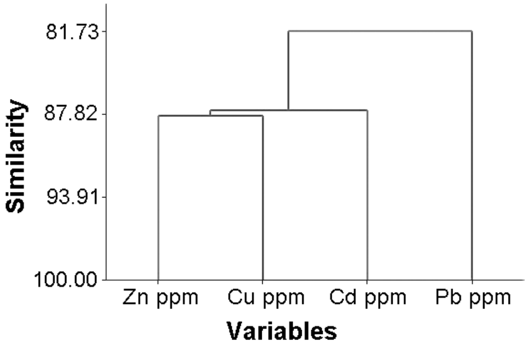

Figure 4. Dendogram of the similarity of the Euclidian distance of studied metals in sediments.
Figura 4. Dendograma de similitud de la distancia Euclidiana de metales estudiados en sedimentos.

a) Effect of land use. The land use factor had an effect on the concentrations of Cu ($p = 0.011$), Zn ($p = 0.023$) and Cd ($p = 0.004$) in the sediments. Trends in concentrations obtained in the three elements are shown in figure 5 (page 211). Regarding Cu, the highest concentration occurred in the use of agricultural land with 28.72±3.2 mg kg^{-1}, while the lowest concentration was found in the livestock land use (15.20±3.20 mg kg^{-1}).

b) Effect of season. The season factors had an effect on the concentrations of Zn ($p = 0.000$), Pb ($p = 0.084$) and Cd ($p = 0.002$). Regarding Zn, the highest concentration occurred in the spring season 2010 with 142.54±10.35 mg kg^{-1}, and the lowest in the summer season with 69±10.35 mg kg^{-1} (figure 6, page 211).

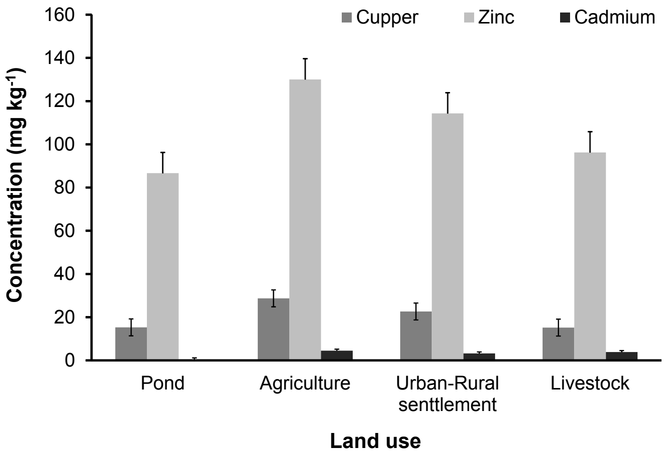

Figure 5. Concentrations of copper, zinc and cadmium affected by land use.
Figura 5. Concentración de cobre, zinc y cadmio bajo el efecto de usos de suelo.

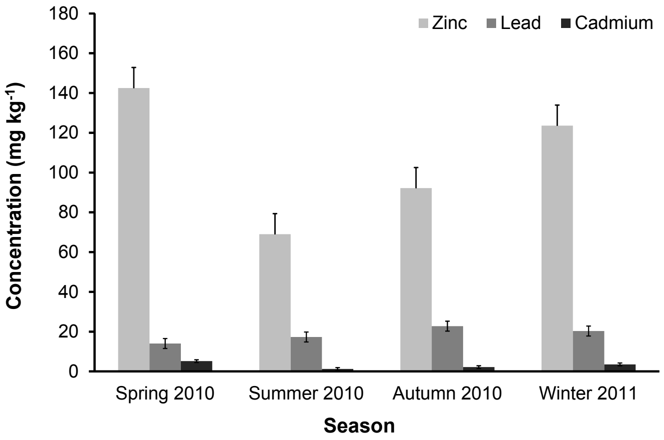

Figure 6. Significant concentrations of zinc, lead and cadmium affected by the season.
Figura 6. Concentración significativa de zinc, plomo y cadmio bajo el efecto de la estación.

c) Effect of season-land use. The analysis of double interaction in the concentrations of heavy metals in sediments (Pb, Cu, Zn and Cd), along with seasonal factors and land use, indicates that this relationship was only significant for Cd concentrations ($p = 0.077$). This description is presented in figure 7 (page 212). The highest concentration of Cd was found in the spring 2010 in the livestock land use (2.8 ± 1.4 mg kg^{-1}), and the lowest concentration was found in winter 2011 in the Pond land use (0.339 ± 1.4 mg kg^{-1}).

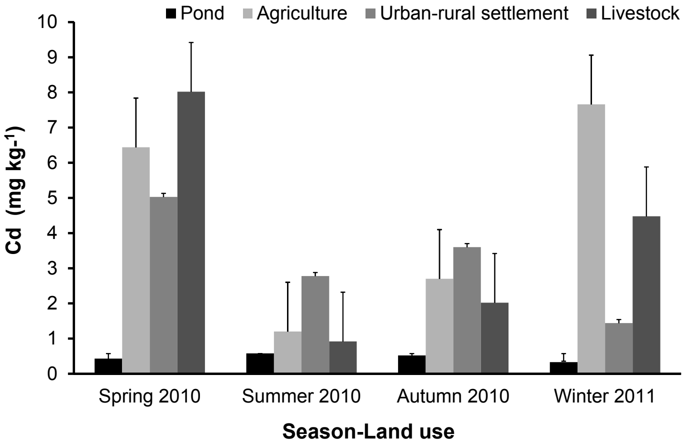

Figure 7. Significant concentrations of cadmium affected by the land use-season.
Figura 7. Concentraciones significativas de cadmio bajo el efecto de usos de suelo-estación.

Analysis of metals in three land use types

According to the analysis of the samples, considering only the agricultural and livestock land uses, together with the rural settlements, without considering the effect of the Pond land use, there were significant relationships between the effects of seasonality and land use on heavy metals on the sediment. Land use significantly influenced concentrations of Cu ($p=0.022$) and Zn ($p = 0.063$).

The highest concentrations of Cu (28.72±3.40 mg kg^{-1}) and Zn (130.04±10.02 mg kg^{-1}) were found in the agricultural land use, highlighting that this factor did not impact significantly on Cu concentrations, compared to the first analysis. In this case, soil-station concentrations of Zn ($p = 0.000$), Pb ($p = 0.015$) and Cd (0.001) matched the results of the first analysis, indicating the significant effect of the season.

Zinc concentrations remained high during spring 2011 with 160.03±11.57 mg kg^{-1}. Pb concentrations were highest in autumn 2010 with 23.661±2.72 mg kg^{-1}, while Cd showed the highest concentration in spring 2010 with 6.50±0.89 mg kg^{-1}. These results are presented in table 2 (page 213).

Using the Pearson's correlation coefficient, significant relationships were obtained for Cu-Zn ($r = 0.759$), Pb-Cu ($r = 0.635$) and Cd-Zn ($r = 0.751$). These results are presented in table 3 (page 213).

Table 2. Significant concentrations of heavy metals in sediments considering only three land uses.
Tabla 2. Concentraciones significativas de metales pesados en sedimentos considerando solo tres usos de suelo.

	Elements (mg kg^{-1})			
Factor	Cu*, **	Zn*	Pb**	Cd**
Land use				
Agriculture	28.72 ± 3.40	130.04 ± 10.02	22.30 ± 2.36	4.51 ± 0.77
Rural Settlement	22.64 ± 3.40	114.31 ± 10.02	17.93 ± 2.36	3.23 ± 0.77
Livestock	15.19 ± 3.40	96.26 ± 10.02	15.02 ± 2.36	3.86 ± 0.77
Season				
Spring 2010	27.50 ± 3.92	160.03 ± 11.57	11.719 ± 2.72	6.50 ± 0.89
Summer 2010	15.58 ± 3.92	71.37 ± 11.57	17.153 ± 2.72	1.65 ± 0.89
Autumn 2010	22.31 ± 3.92	96.55 ± 11.57	23.661 ± 2.72	2.80 ± 0.89
Winter 2011	23.34 ± 3.92	126.19 ± 11.57	21.144 ± 2.72	4.53 ± 0.89

* Significative effect of land use.
** Significative effect of season.

* Efecto significativo del uso de suelo.
** Efecto significativo de la estación.

Table 3. Pearson's correlation coefficient of heavy metal concentrations in sediments resulting from the use of agricultural land and livestock, urban-rural settlement.
Tabla 3. Coeficiente de correlación de Pearson´s de la concentración de metales pesados en sedimentos en los usos de suelo agrícola, ganadero y asentamiento rural.

	Elements		
	Cu	Zn	Cd
Zn	0.759		
	0.000		
Cd	0.490	0.751	
	0.000	0.000	
Pb	0.635	0.471	0.272
	0.000	0.000	0.004

Moreover, the regression analysis showed a ratio between Cu-Zn and Cd-Zn of 63.7% and 59.4%, respectively (figure 8, page 214). Regarding the PCA, it was determined that PC1 and PC2 explained 88% of the variability of the data.

The PC1 showed positive correlations between Cu (0.538), Zn (0.559), Pb (0.426) and Cd (0.466). PC2 presented negative correlations with respect to Zn (-0.252) and Cd (-0.618) and positive with respect to Cu (0.237) and Pb (0.706). Figure 9 (page 214) shows the variability of the observations determined in PC1 and PC2. It shows a core group of soils near the axis intercept of both components. Over nine samples were observed away from the intercepted axis between PC1 and PC2, coming from sample 61 which presented the highest values of Cu (91.07 mg kg^{-1}), Zn (293 mg kg^{-1}), Pb (49.16 mg kg^{-1}) and Cd (33.75 mg kg^{-1}). These data belonged to agricultural land use and winter 2011. Throughout the seven samples, PC2 observed distant land, emphasizing the 39 with high concentrations of Cu (72.81 mg kg^{-1}), Zn (239.6 mg kg^{-1}), Pb (79.42 mg kg^{-1}) and Cd (13.63 mg kg^{-1}). These samples belong to the rural settlement land use type and the autumn season 2010.

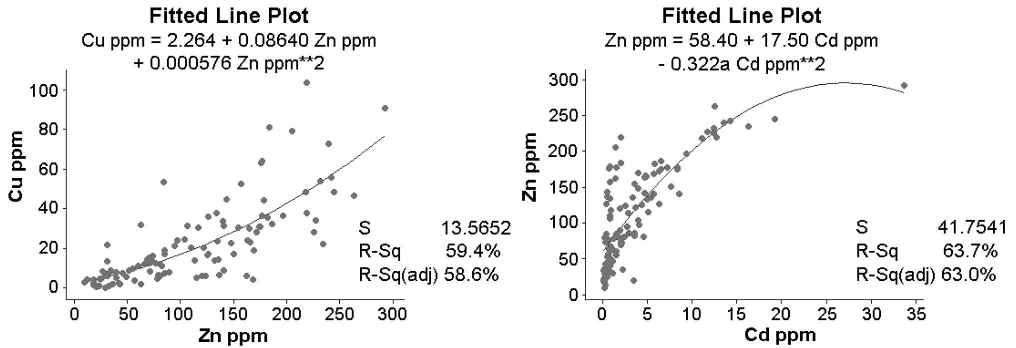

Figure 8. Correlation diagram Cu-Zn and Zn-Cd in three land uses.
Figura 8. Diagrama de correlación Cu-Zn y Zn-Cd en tres usos de suelo.

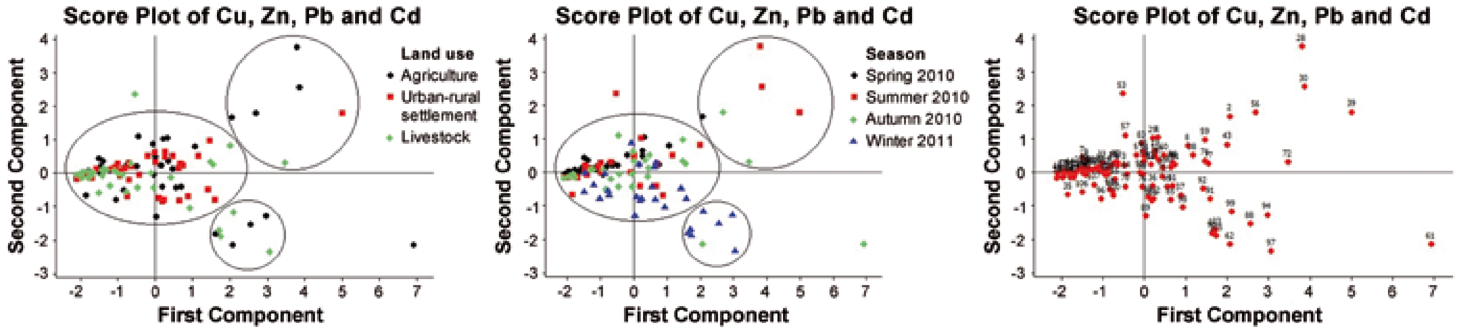

Figure 9. Dispersion of points derived from the main component analysis considering three land uses
Figura 9. Análisis de componentes principales con tres usos de suelo.

DISCUSSION

Regarding the physical-chemical parameters, it is worth to note that the values in the range from 7.66 to 8.05 are considered slightly high in terms of alkalinity. Similar results indicate that it may be related with the accumulation of organic matter and the nature of the carbonate found in the sediment, which favors the fixation of heavy metals (10). The condition of this parameter could affect the solubility of metals and their potential leaching (24). Considering a variation in the organic matter content from low to high (0.9 to 3.16%), there could be a relation of sediments from sample sites, which contain higher content of organic matter and the presence of heavy metals (36, 40). The high content of organic matter found in the sediments is mainly related to the discharge of water residuals from domestic use and the industry (10).

In the first analysis of the four land uses, a significant effect of land use and season was found on the concentrations of components considered as pollutants in some cases. Regarding the effect of land use, and according to the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (13), the permissible limit of Cu in sediments is 35.7 mg kg^{-1}. Also, considering the criteria established by (Garbarino *et al.*, 1995) and those reported by (García-Rico *et al.*, 2004), it indicates that these levels of copper reported a condition of high sediment contamination by this metal, with a value greater than 25-50 mg kg^{-1}. ATSDR (7) attributes that copper is released by the mining industry, agriculture and manufacturing, and the release of wastewater into rivers, producing a decaying in vegetation. Some of the soluble copper compounds enter the groundwater and are eventually deposited in the sediments of rivers, lakes and estuaries. Cooper is linked to the use of various fertilizers and fungicides in agriculture (22).

While the highest concentration of Zn was found in the agricultural land use (130.04±9.87 mg kg^{-1}), the lowest was found in the Pond land use with a value of 86.68±12.08 mg kg^{-1}. According to the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (13) the allowable limit of Zn in sediments is 123 mg kg^{-1}. This means that the level of 7.4 mg kg^{-1} found in the section of the river located in the agricultural land use is above this limit. ATSDR (8) indicates that zinc is in the air, soil and water and that its presence in the environment may be associated with hazardous waste sites, natural processes and human activities, sewage and domestic chemical industry with contents of zinc or other metals and fluxes from land. Agricultural inputs can be a source of contamination in the area. In small quantities, zinc is an essential nutrient required by all animals.

The functions performed by zinc in the plants are varied, the vast majority related to the formation and operation of various enzyme systems involved in life processes of plants. In agricultural soils, the total concentration typically ranges from 10 to 300 mg kg^{-1} (8). This may somehow affect the entry of particles derived from erosion processes, impacting the agricultural zone with the accumulation in the sediments.

Regarding Cd, the highest concentration occurred in the agricultural land use, with 4.51±0.71 mg kg^{-1}, and the lowest in the Pond land use with 0.46±0.87 mg kg^{-1}. According to the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (13), the allowable limit of Cd in sediments is 0.6 mg kg^{-1}, meaning that this exceeded the permissible concentration 6.51 times (3.91 mg kg^{-1}).

Considering the criteria established by (Garbarino *et al*.,1995) and those reported by (García-Rico *et al.*, 2004), it is indicated that these levels of cadmium present a condition of high sediment contamination by this metal, when having a value greater than 6 mg kg^{-1}.

Cadmium enters the air from sources such as mining, industry, and by burning coal and household wastes. In air, cadmium particles can travel long distances before settling to the ground or water when coming from landfills and spills or leaks at hazardous waste sites.

Cadmium remains for a long time in the same place where originally deposited in the environment. Large amounts of Cadmium are naturally released into the environment, about 25,000 tons per year. Half of this Cadmium is released into rivers through the decomposition of rock. Wastewater from metallurgical industries mostly ends up in soils and can be transported long distances before getting absorbed by the mud. This cadmium-rich sludge can contaminate surface water and soil. This metal is strongly absorbed by soil organic matter (6).

The increased activity of suburban, urban and industrial processes, associated with deforestation, agriculture, erosion of topsoil, fertilizer and chemicals, can alter the natural biochemical processes and operation of highly productive ecosystems, because the residues produced can contain large amount of metals (Cd, Cr, Cu, Ni, Pb and Zn) and other pollutants that would cause significant changes in water quality and sediment (17). Also, San Luis Potosi is associated with increased environmental pollution by heavy metals such as copper and zinc due to substantial mining and industrial activities (5).

The Nature Conservation Service and Wildlife Habitat Council (26) states that sediment and erosion processes are often associated with the use of land for development. Some construction sites have inadequate erosion processes and sediment control measures that should begin with the construction, because the remaining riparian areas are unable to mediate the sediment load entering the water. Impervious surfaces like parking lots and roads create a water circulation system quite different to that which occurs in a natural basin. The rain runs off impervious surfaces into river channels.

The runoff in watersheds with significant amounts of impervious surfaces has the potential to lead to an increased load in sediments and other materials such as fertilizers, pesticides, trace metals, and other toxic materials that have been improperly released or removed. The effect of season on the concentrations of Zn, Pb and Cd levels indicates them as contaminants. This concentration exceeds the permissible limit of Zn in sediments, which is 123 mg kg^{-1}, according to the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (13).

For Pb, the highest concentration was in autumn 2010 with 22.77±2.51 mg kg^{-1}, and the lowest in spring 2010 with 14.05±2.51 mg kg^{-1} (figure 6, page 211). According to the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (13), the allowable limit of Pb in sediments is 35 mg kg^{-1}. Based on the criteria established by (Garbarino *et al.*, 1995) and those reported by (García-Rico *et al.*, 2004), these levels of lead indicate a condition of high sediment contamination by this metal when having a value greater than 60 mg kg^{-1}.

ATSDR (9) indicates that high ambient levels of lead are commonly found in soil especially near roads, old houses, old orchards, mining areas, industrial sites near power plants, incinerators, landfills and hazardous waste sites. Small amounts of lead may enter rivers, lakes and streams when soil particles are mobilized by rainwater; lead can also remain attached to soil particles or sediment in the water for many years.

The mobilization of lead in soil depends on the type of lead compound and the physical and chemical characteristics of the soil. Sources of lead in surface water or sediment deposition come from the atmospheric dust, wastewater from industries that handle lead (primarily iron and steel industries that manufacture and lead), water runoff in urban areas, and mining piles. Lead is associated with the use of fertilizers and pesticides in crop areas (22).

In the case of Cd, the highest concentration occurred in spring 2010 with 5.16±0.75 mg kg^{-1} and the lowest in summer 2010 with 1.22±0.75 mg kg^{-1} (figure 6, page 211). According to the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (13) the allowable limit of Cd in sediments is 0.6 ppm, meaning that the permissible concentration was exceeded 7.6 times (4.56 mg kg^{-1}). Based on the criteria established by (Garbarino *et al.*, 1995) and those reported by (García-Rico *et al.*, 2004) these levels of Cd indicate a condition of high sediment contamination by this metal, when having a value greater than 6 mg kg^{-1}.

The average concentration of Zn, Pb and Cd, may be present at higher levels in dry seasons compared to the rainy seasons, probably due to rainwater dilution that influences the concentration and mobility of heavy metals. However, the mobility of heavy metals does not depend only on the concentration in soil and sediment, but also on the metallic properties of soil or sediments, and environmental factors (27).

On the analysis of double interaction in the concentrations of heavy metals, Cd was significant. According to the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (13), the allowable limit of Cd in sediments is 0.6 mg kg^{-1}, indicating the highest level found is 7.42 mg kg^{-1} above this limit, *i. e.*, 12.3 times. Based on the criteria established by (Garbarino *et al.*, 1995) and those reported by (García-Rico *et al.*, 2004), these levels of cadmium indicate a condition of high sediment contamination by this metal when having a value greater than 6 mg kg^{-1}.

A this point, it is worth to note that some of the reasons for not having a clear criteria for establishing heavy metal contamination of sediments is that the sediment composition can be varius types, depending on the rock, the grain size, the organic matter content, among others (10).

Now, for the second analysis, significant variations in the concentrations of Cu, Cd and Pb were mainly found. These variations in the concentration of the metals may be due to increased water flow that allows a process of dilution, as well as variations of dissolved oxygen, and other organic content (35). The significant positive correlations of heavy metals in sediments indicate that these fractions are of the same chemical material that affects the ecosystem (17).

The presence of heavy metals in sediments is attributed to industrial effluents, agricultural runoff, domestic sewage and municipal drainage. It is considered that the presence of Cu, Cd and Pb in sediments is not only due to its presence in the bedrock, but also because of anthropogenic effluents derived from a variety of industrial activities (38).

The erosion of rock and soil leads to the accumulation of sediment from natural and anthropogenic processes (27). The two analysis performed (including four land use types and three land use types, respectively) reflect that the elements evaluated are associated to the agricultural land use and to both the urban and rural settlements zones where the concentration of such elements could be due to wastewater discharges, pesticides applications and solid wastes found along the river banks. Correlations found between the heavy metal concentrations indicate the influence of lithologic sources or the association to antrophogenic activities (24). Moreover, these correlations indicate that contaminants of the sediments could come from the same sources (33).

The PCA allowed defining how these types of land use (agricultural land use and urban and rural settlements) affect the concentrations of these metals along the riparian area (figure 3, page 209; figure 9, page 214) complementing the other developed analysis in this study.

The variation in the dispersion of points may occur by the influence of the antrophogenic dynamism of the uses of soil, associated to natural processes that lead to the presentation of sample groups that may be considered with high or low concentrations, also with temporary or seasonal variation indicating its dispersion with concentrations that exceed normal standards of metals in established sediments (12, 18). Some heavy metals have been associated to groups of origin of contamination determined by main components.

The Pb in sediments has been found to be associated to antrophogenic factors in a higher degree, Zn in natural sources and Cu in the agricultural activity (11). Other studies indicate that sediment sample groups analyzed with main components have been associated to natural processes, including the outdoors and the erosion of the land and the local mother rock and the atmospheric deposition associated to the antrophogenic activity. Moreover, the hidrogeochemistry dynamism of these types of systems is sufficiently high to mobilize and redistribute the sediments (14).

The use of pesticides and fertilizers in these areas might be related to the higher concentrations found on the wastewaters sampled on these points. Distribution and concentrations of these metals could be affected by the amount of organic matter and compounds including Fe and minerals having carbonates, as well as by the contamination load (10, 36). Sediment data can provide information on the impact of human activity on the ecosystem as a whole.

The composition of the sediment sequences offers the best natural archive of past environmental changes. The evaluation of the level of metals in water is useful for the control of heavy metal deposits in sludge and the provision of water used by agriculture and industry. An important factor is the heavy metal content of soils that provide mineral content to water sources, as a result of rain, and the presence of rivers, farms and local industries, indicating a need for control (36).

CONCLUSIONS

In this study, land use (Pond, Agriculture, Livestock and Rural Settlement) and season of the year (spring, summer and autumn, and winter) influenced the presence of heavy metal son the studied riparian area. Considering as a reference the levels established by the Canadian Environmental Quality Guidelines, levels of Cu, Cd, Zn and Pb found in sediments were exceeded. Moreover, when using other scientific and technical sources as reference, levels of Cu, Cd and Pb were considered under a condition of high pollution.

The greatest concentrations of these elements were found in the riparian area with an agricultural land use. Therefore, the presence of heavy metals in sediments could be used as indicators to evaluate the environmental assessment on the riparian ecological systems.

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Acknowledgements

Samuel Storr

This study was supported by the Research Grant / PROMEP/103.5/10/5456 from the "Programa de Mejoramiento al Profesorado", México.