

METAL CONTENT AND ELEMENTAL COMPOSITION OF PARTICLES IN COHESIVE SEDIMENTS OF THE LERMA RIVER, MÉXICO

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Keys words: heavy metals, X-ray fluorescence, scanning electronic microscopy, river sediments

ABSTRACT

The concentration of Cr, Mn, Fe, Cu, Zn and Pb, enrichment factors and the elemental composition, morphology and relative abundance of particles were evaluated in cohesive sediments of the upper course of the Lerma River, México. The heavy metal concentration in the cohesive sediments decreased in the following sequence: Fe > Mn > Zn > Cr > Cu > Pb. The results of enrichment factors show that Fe and Mn are conservative, Cu, Cr and Pb are lightly enriched and Zn is moderately enriched. Generally, the particle groups decrease in the follow sequence: aluminosilicate > silica > iron > sulfur > metals > calcium carbonate > calcium/phosphorus > manganese. The Fe and Mn concentrations in cohesive sediments are produced principally by natural contributions, whereas Cr, Cu, Zn and Pb concentrations are produced mainly by anthropic contributions.

Palabras clave: metales pesados, fluorescencia de rayos X, microscopía electrónica de barrido, sedimentos de río

RESUMEN

En el presente trabajo se evaluó la concentración de los metales Cr, Mn, Fe, Cu, Zn y Pb, los factores de enriquecimiento y la composición elemental, morfología y abundancia relativa de las partículas presentes en los sedimentos cohesivos del curso alto del río Lerma (CARL), México. La concentración de los metales analizados presentó el siguiente comportamiento: Fe > Mn > Zn > Cr > Cu > Pb. Los resultados de los factores de enriquecimiento indican que, en estos sedimentos, Fe y Mn pueden considerarse como conservadores, Cu, Cr y Pb ligeramente enriquecidos y Zn moderadamente enriquecido. En general los grupos de partículas analizadas presentan la siguiente tendencia: aluminosilicatos > silicio > hierro > azufre > metales > carbonatos de calcio > calcio/fósforo > manganeso. La presencia de Fe y Mn en los sedimentos cohesivos del CARL se debe mayormente a contribuciones naturales, mientras que el origen del Cr, Cu, Zn y Pb es principalmente antrópico.

INTRODUCTION

The determination of trace metals in recently deposited sediments is a useful tool in the assessment of the status of environmental pollution as the cohesive sediments are potentially good indicators of the quality of overlaying waters (Berrow 1991). Once trace elements are discharged into body waters, they rapidly become associated with particles and are incorporated in bottom sediments (Förstner and Wittmann 1979, Hansen *et al.* 1995). The trace metals associated with sediments are not essentially sheltered permanently, and under changing conditions, pH, dissolved oxygen, oxidation-reduction potential, etc., they may be released to the water column by various processes of remobilization (Vaithiyanathan *et al.* 1993, Buffle and De Vitre 1994). Thus, in the aquatic system, cohesive sediments can be a carrier and a possible source of metals (Förstner and Wittmann 1979, Droppo and Jaskot 1995, Hansen *et al.* 1995).

The upper course of the Lerma River (UCLR) (Fig.1) giving rise to the Upper Basin of the Lerma River is located in the State of México, comprising approximately 50 km from the Almoloya lagoons to 9 km downstream from the J. A. Alzate Dam (GEM 2000). This area is the lifeline of the Toluca city, the capital of the State of México, with approximately 1.5 million inhabitants living in the metropolitan zone.

The Lerma River originates from the Lerma lagoons near Almoloya del Río, on a plateau more

than 2600 meters above sea level, and 24 km south-east of Toluca city. The river flows northwestward through the State of México. This water body is not navigable by water craft, but it is critical to regional agricultural irrigation and it is also receptor of residual waters from 30 towns, 10 industrial zones, 12 industrial parks and 4 water treatment plants of the municipal water supply in the Toluca metropolitan zone (GEM 2000). The present research focuses on the determination and relative abundance of trace metals (Cr, Mn, Fe, Cu, Zn and Pb) in the superficial cohesive sediments of the UCLR. The results are very important in order to identify the origin of metals and the main point sources of pollution of the Lerma River.

MATERIALS AND METHODS

Experimental

Eight sampling sites were selected along the UCLR considering the impact of anthropogenic wastewaters and its tributaries, based on the monitoring network of the Comisión Nacional del Agua (National Water Commission) (Fig. 1). Four sampling campaigns were carried out every three months during one hydrological cycle, two sampling campaigns in the dry season, February and May, another one during the rainy season in August and finally, at the end of the rainy season, in November.

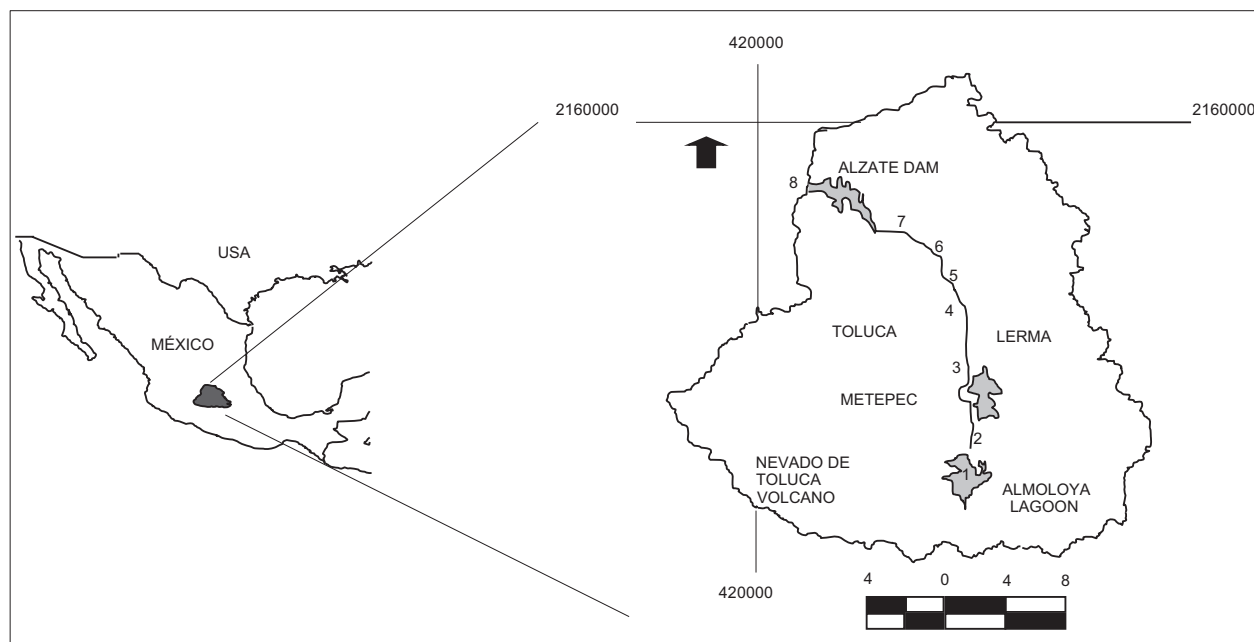


Fig. 1. Location of the upper course of the Lerma River, México, and the sampling sites

Bottom river bed sediments were sampled by a Ponar dredge. Three sediment samples were obtained on each site in the banks and in the center of the river, less than 15 cm of depth. Approximately a 5 kg sample (each) was placed inside a polyethylene bag and was transported at 4 °C to the laboratory for processing (Ávila-Pérez *et al.* 1999).

X-ray fluorescence analysis

Each sample was carefully mixed and dried at room temperature for 120 hours. Clay/silt sediment fraction was separated by wet sieving (63 µm, 300 mesh). Subsamples of the clay/silt sediment fraction (1 g) were homogenized and 1 cm diameter pellets were prepared for elemental analysis (Vaithiyathan *et al.* 1993, Dekov *et al.* 1997, 1998). The solid samples (pellets) were analyzed in triplicate by means of an Ital Structures X-ray Fluorescence Spectrometer TX 2000 with a Si(Li) detector and a resolution of 140 eV (Mn-K α). The analysis was carried out using energy dispersive mode (EDXRF), molybdenum tube (40 kV - 30 mA) and an acquisition time of 1000 seconds.

The analysis of the spectra was performed using the EDXRF32[®] program; the quantification of the metals was carried out using the Compton correction method with external standard, Soil-5 (SL-5, Certified Reference Material IAEA). The certified standard Lake Sediment SL-1 (Certified Reference Material IAEA) was processed and analyzed, under the same conditions as the samples for internal quality assurance.

Sediment enrichment factors (SEF) were also investigated. This factor estimates the enrichment of Cr, Mn, Fe, Cu, Zn and Pb by cultural effects using equation 1. Aluminum is commonly chosen as a “conservative” element. However, this element has a high detection limit by EDXRF. For convenience, rubidium was selected as conservative element (Dekov *et al.* 1998, Enguix *et al.* 2000, Vasallo *et al.* 2001). Values of sediments coming from igneous rocks were considered as reference values (Turekian and Wedepohl 1961, Salomons and Förstner 1984).

$$SEF = \frac{(M_s / Rb_s)_{\text{sample values}}}{(M_o / Rb_o)_{\text{reference values}}} \quad (1)$$

Where, SEF: sediment enrichment factor; M_s : concentration of metal “x” in the sample; Rb_s : concentration of conservative reference element (Rb) in the sample; M_o : concentration of metal “x” in sediments coming from igneous rocks and Rb_o : con-

centration of conservative reference element (Rb) in sediments coming from igneous rocks.

In order to know the enrichment level by metals, several criteria were considered, as it appears in **table I**. (Sinex and Wright 1988, Grant and Middleton 1990, Hansen *et al.* 1995, Soto and Pérez 2001).

TABLE I. ENRICHMENT LEVEL CRITERIA*

Sediment enrichment factor	Enrichment level
≤ 2	Conservative
3 – 5	Slightly enriched
6 – 9	Moderately enriched
≥ 10	Highly enriched

* Sinex and Wright 1988, Grant and Middleton 1990, Hansen *et al.* 1995, Soto and Pérez 2001

Scanning electron microscopy analysis

In order to obtain an homogenous and uniform sample for its analysis by SEM, an aliquot of 0.5 g of each solid sediment sample was mixed with 20 mL of water; it was later filtered using a 0.45 µm Millipore system, then the filter was dried at room temperature. 1 cm² was cut out and mounted on an aluminium holder stage with carbon tape for observation and analysis; the sample was then coated with gold by sputtering for 40 s at 25 µA.

A Philips scanning electron microscope (SEM) XL-30 was used to observe 1 mm² areas of the surface on each of the samples at a magnification between 500x and 10000x and 25 kV acceleration voltage; in addition a coupled EDAX probe was used for elemental chemical analysis by energy dispersive X-ray spectrometry (EDS) at a resolution of 140 eV. A random analysis of 100 particles was carried out at 1500 cps and counting times of 60 seconds. The DX-4i (ZAF) software was used to determine the elemental chemical content as a percentage in weight for the corresponding oxide forms, except for sulfur and phosphorus, which were determined as element. Finally the relative abundance of the particles was estimated on the basis of the Dekov *et al.* (1997) criteria, classifying the data into eight groups (**Table II**) (Ávila-Pérez *et al.* 2007, Zarazúa 2008).

RESULTS AND DISCUSSION

Maximum, minimum and medians of the analyzed metals in the cohesive sediments are given in **table III**. Fe and Mn are elements considered as terrigenous, which showed concentrations ranging

TABLE II. GROUPS USED TO DETERMINE THE RELATIVE ABUNDANCE OF PARTICLES IN THE COHESIVE SEDIMENTS OF THE UPPER COURSE OF THE LERMA RIVER*

Group	Criteria
Aluminosilicates (Al-Si)	Aluminosilicate particles, where $\sum \text{SiO} + \text{Al}_2\text{O}_3 \geq 50\%$
Silicon (Si)	Particles $\text{SiO} \geq 70\%$ or $\geq 50\%$ do not have Al and they do not fulfill other criteria
Sulfur (S)	Particles are composed mainly of sulfur compounds $\sum \text{S} + \text{CaO}, \text{Fe}_2\text{O}_3 \text{ or } \text{BaO} \geq 70\%$
Calcium carbonate (CO_3)	Particles are composed mainly of calcium carbonate $\text{CaO} \geq 90\%$
Calcium/Phosphorus (Ca/P)	Particles where the presence of Ca and/or P is the most important CaO or $\text{P} \geq 40\%$
Iron (Fe)	Particles of iron oxides and/or oxyhydroxides $\text{Fe}_2\text{O}_3 \geq 40\%$
Manganese (Mn)	Particles rich in manganese $\text{MnO} \geq 40\%$
Metals (Metals)	Particles rich in transition metals, except Fe and $\text{Mn} \geq 40\%$

*Basis of the Dekov *et al.* (1997) criteria

TABLE III. pH VALUES IN WATER AND COHESIVE SEDIMENTS OF THE UPPER COURSE OF THE LERMA RIVER

Sample site	Median water pH	Median sediment pH
1	8.6	8.0
2	7.1	7.1
3	7.3	7.2
4	7.5	7.3
5	7.5	7.7
6	7.5	7.2
7	7.6	7.3
8	7.7	7.2

from 19 443 to 84 771 mg/kg and from 278 to 2020 mg/kg, respectively.

Concentrations of Cr, Cu, Zn and Pb, considered as toxic metals in aquatic environments, varied between 13 and 3384 mg/kg, Zn being the highest and Pb the lowest.

Figure 2 shows the distribution of Cr, Mn, Fe, Cu, Zn and Pb in cohesive sediments along the different sampling sites. Statistical differences ($\alpha \leq 0.05$) in the

metal concentrations, between samples taken among the course river (spatial variation) were observed. However, it was not observed, between samples taken in the different sampling periods (seasonal variation).

This spatial variation is due to changes in the contributions of the different discharges and the hydrological conditions in the sampling sites. The first section of the river, where sites 2 to 5 are dominated by industrial discharges and the average annual flow are between 2.2 and 5.4 m³/s presents important sedimentation zones, while the second section, sites 6 to 8, where the mainly contributions are coming from rivers and the average annual flow are between 4.5 and 10.5 m³/s (Hinojosa 2006). The pH seems not to play an important role in this behavior since values in both water and sediment were similar, close to neutrality (**Table III**) (Förstner and Wittmann 1979, GEM 2000, Tejeda 2006).

The concentrations of Fe and Mn show significant statistical differences ($\alpha \leq 0.05$) among all sites. The highest concentrations can be observed toward the end of the section of the river, sites 6 to 8. This

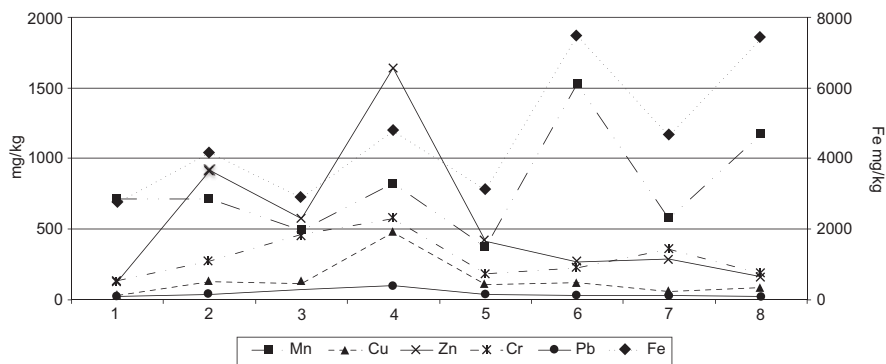
**Fig. 2.** Downstream distribution of Cr, Mn, Fe, Cu, Zn and Pb in the cohesive sediments of the upper course of the Lerma River. Median concentrations in mg/kg

TABLE IV. CONTENT OF Cr, Mn, Fe, Cu, Zn AND Pb IN THE COHESIVE SEDIMENTS OF THE UPPER COURSE OF THE LERMA RIVER AND THEIR COMPARISON WITH INTERNATIONAL CRITERIA. CONCENTRATION IN mg/kg

	Cr		Mn		Fe		Cu		Zn		Pb	
Minimum value	103		278		19443		23		78		13	
Maximum value	661		2020		84771		905		3384		116	
Median	250		711		44045		109		350		33	
USACE	75		500		25000		50		200		60	
OME ¹ (dredged disposal)	25		1625		10000		25		100		50	
OME ² (aquatic live protection)	26*	>110+	460*	>1100+	20000*	40000+	16*	>110+	120*	>820+	31*	250+
Ratio: Median value/USACE value	3.3		1.4		1.7		2.2		1.7		0.5	
Ratio: Median value/OME ¹ value	10.0		0.4		4.6		4.3		3.5		0.6	
Ratio: Median value/OME ² value	9.6*	2.3+	1.5*	0.6+	2.2*	1.1+	6.8*	0.9+	3.0*	0.4+	1.0*	0.1+

USACE: U.S. Army Corps of Engineers (USACE 1976); OME: Ontario Ministry of the Environment and Energy (OME 1976); * LE: Lowest effect; + SE: Severe effect

increase can be due to fluvial dragging of soil and sediments from the tributaries Zolotepec, Ocoyoacac, Xonacatlán, Santa Catarina, Verdiguél and San Lorenzo. This would lead to believe that the observed concentrations of iron and manganese in the surveyed area are mainly due to natural causes (Dekov *et al.* 1998).

In general the highest concentrations of Cu, Zn, Cr and Pb were found at sites 3 and 4, which receive the greatest industrial and urban runoffs, including wastewaters from thirty towns, ten industrial zones, twelve industrial parks and four water treatment plants (Ávila-Pérez *et al.* 1999, GEM 2000). This fact clearly shows the presence of anthropic sources of these contaminants, domestic sewage and industrial effluents, in the surrounding area of the sampling sites, causing the Cu, Zn, Cr and Pb accumulation in the sediments (Hansen *et al.* 1995, Antón and Díaz-Delgado 2002).

In addition, the concentration of these metals in site 4 presented significantly higher values ($\alpha \leq 0.05$), which could be related to the presence in this site of aquatic hyacinth (*Eichhornia crassipes*). The aquatic hyacinth may work as a physical barrier, producing the reduction in the water flow and favoring the sedimentation processes; thus, this site can be considered as the main zone of Cu, Zn, Cr and Pb accumulation.

Cu, Zn, Cr and Pb presented similar behavioural trend with location (positive correlation $r \geq 0.7$, $\alpha \leq 0.05$); Fe and Mn also had a significant positive correlation ($r = 0.9$, $\alpha \leq 0.05$). The significant and separate correlations between: a) iron and manganese and

b) copper, zinc, chromium and lead in the cohesive sediments show that they were associated to material of different origin, probably parental and anthropic material, respectively.

Table IV shows the reference or guide values for river sediments given by the U.S. Army Corps of Engineers (USACE 1976) and Ontario Ministry of the Environment (OME 1976). For both reference values, in the Lerma River sediments Cr exceeds them by up to ten times, followed by $Fe \approx Cu > Zn > Mn > Pb$. Considering the criteria for the aquatic life protection (OME 1976), only Cr could cause severe effects and Cu, Zn, Fe and Mn slight effects on the aquatic biota.

Table V shows the cohesive sediment enrichment factors for Cr, Mn, Fe, Cu, Zn and Pb.

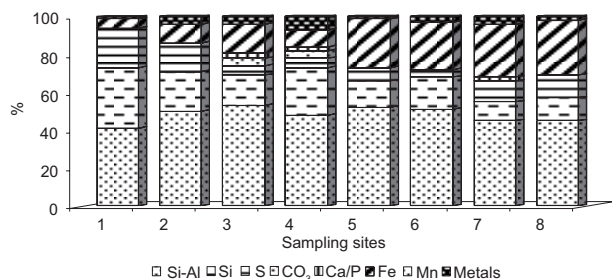
Applying the criteria of Soto and Páez (2001) (**Table I**), sediments can be considered conservative ($SEF \leq 2$) for Mn and Fe; slightly enriched ($SEF = 3-5$) for Cr, Cu and Pb and moderately enriched ($SEF = 6-9$) for Zn. These results support that the main source of Fe and Mn is natural or terrigenous and for the other metals is mainly anthropic.

The predominant groups in all sites are aluminosilicates (49 %) and silica (19 %) (**Fig. 3**). In general, the particle groups in the cohesive sediments of the UCLR are present in the following order: aluminosilicates > silica > iron > sulfur > metals > calcium carbonates > calcium/phosphorus > manganese. The metals group was the highest in site 4 (9 %); this analysis by SEM-EDS concurs with the analytical results obtained by EDXRF.

Grain size analysis of the UCLR sediments indi-

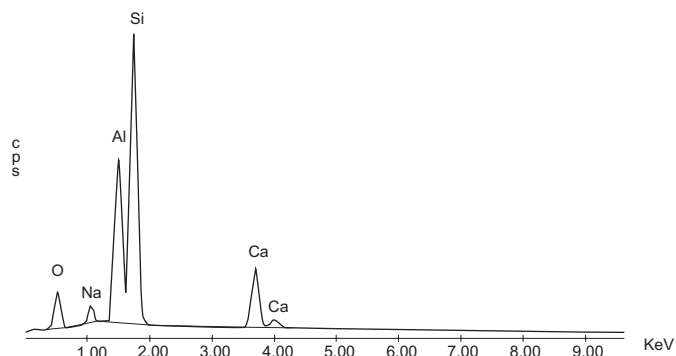
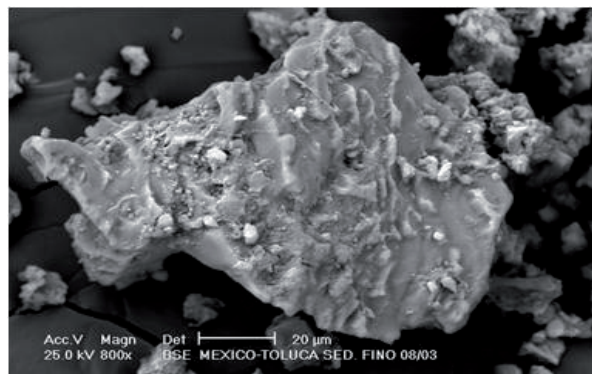
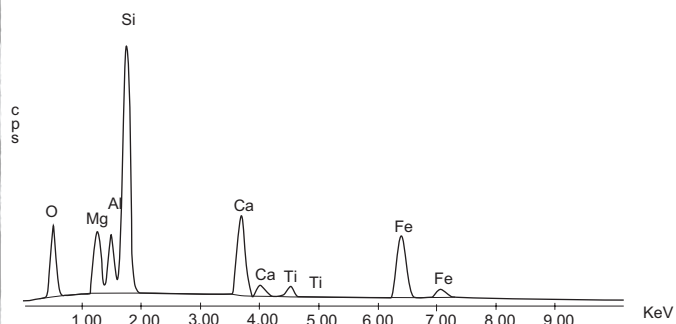
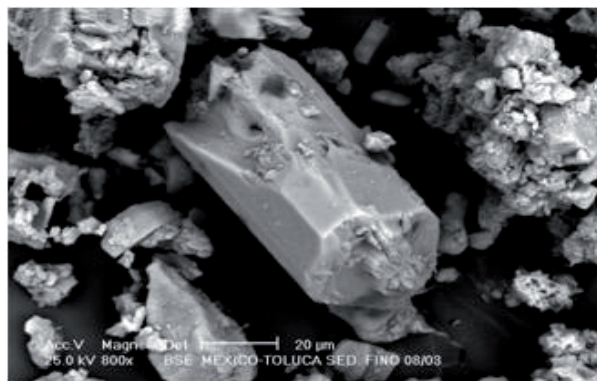
TABLE V. SEDIMENT ENRICHMENT FACTORS FOR Cr, Mn, Fe, Cu, Zn AND Pb IN THE COHESIVE SEDIMENTS OF THE UPPER COURSE OF THE LERMA RIVER. CONCENTRATION IN mg/kg

	Cr	Mn	Fe	Cu	Zn	Pb	Rb
Median	250	711	44045	109	350	33	52
Reference value igneous rocks	100	950	50000	55	70	13	90
Sample ratio Metal/Rubidium	4.8	13.67	847.02	2.10	4.8	0.63	
Reference ratio Metal/Rubidium	1.1	10.55	555.55	0.61	0.77	0.14	
Sediment enrichment factor	4.3	1.3	1.5	3.4	6.2	4.5	

**Fig. 3.** Relative abundance by groups in the cohesive sediments from the upper course of the Lerma River as determined by SEM-EDS analysis. Classification according to Dekov *et al.* (1997)

cates that the clay/silt fraction ($<63 \mu\text{m}$) is as large as 28 %. The aluminosilicates belong to the groups of quartz, feldspars, kaolinites and amphiboles (Tejeda 2006). These groups of particles were observed by scanning electron microscopy (**Figs. 4 and 5**) and their analysis showed content of O, Al, Si, Ca, Na, Fe, Mg, K and Ti, among others.

In site 1, Almoloya lagoon, the groups that displayed the highest relative abundance were aluminosilicates (41 %), silicon (32 %) and sulfur (21 %). The particles of the Almoloya lagoon showed the highest sulfur abundance relative to those of the other seven

**Fig. 4.** Scanning electron micrograph at 800x of an irregular particle composed of Al, Si, O, Na and Ca (feldspar group: albite or anortite)**Fig. 5.** Scanning electron micrograph at 800x, of a cylindrical particle composed of Al, Si, O, Mg, Ca, Fe and Ti (amphibole group: magnesiohornblende)

sampling sites (**Fig. 3**). This difference is caused by the abundance of phytoplankton and aquatic plants in the area, which contribute with significant amounts of iron sulphides of biological origin (**Fig. 6**) (Dekov *et al.* 1997, Sullivan *et al.* 2001, Huerta 2005, Laluraj and Nair 2006).

Scanning electron microscopy analysis shows that in all sampling sites, particles with a high metal content (>40 %) of Ag, Al, Bi, Cu, Hg, Pb, Sn, Zn and Zr were observed (**Fig. 7**). In all the sites, particles

rich in Cr, Fe and Ni, with similar composition to steel (ASTM 2001), were also observed (**Fig. 8**). Although elements as Ag, Al, Ni, Hg, etc., were detected by SEM in sediment particles, their concentration were below to the detection limit by XRF. The presence of elements of typically anthropic origin in the intermediate sites of the testing zone is probably due to industrial and urban discharges from the surrounding area (Fuhrer *et al.* 1996, Vasallo *et al.* 2001, Casper *et al.* 2004, Tejeda 2006).

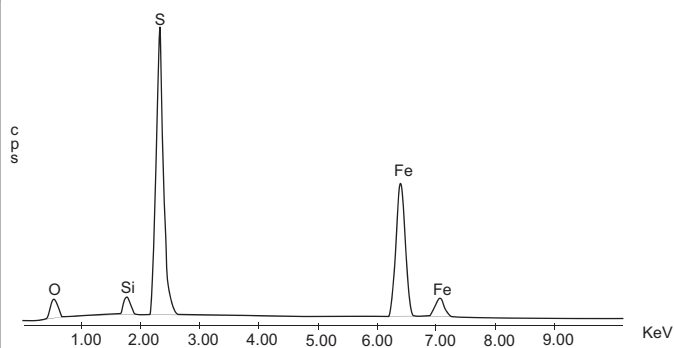


Fig. 6. Scanning electron micrograph at 4000x of polygonal particles in an agglomerate array composed mainly of S and Fe

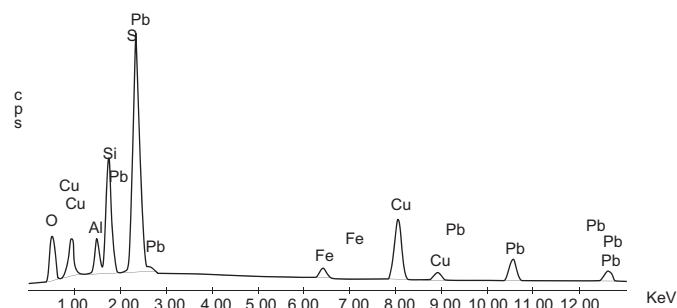
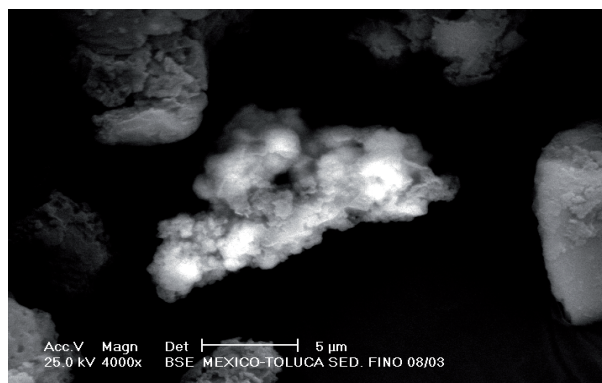


Fig. 7. Scanning electron micrograph at 4000x of a particle composed of S, Fe, Cu, Pb and O

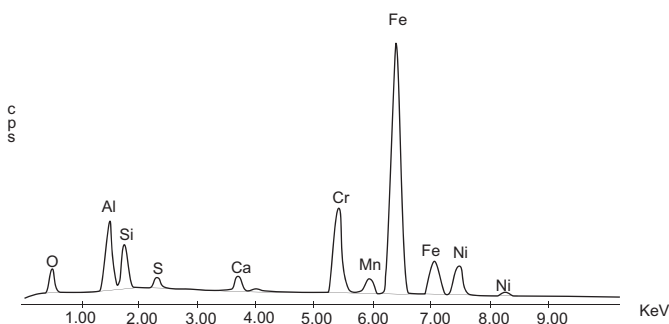
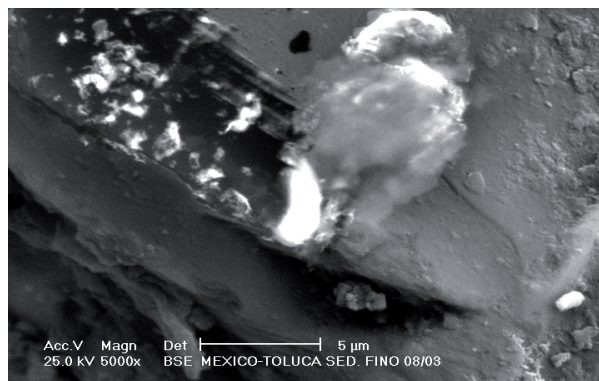


Fig. 8. Scanning electron micrograph at 5000x of several irregular particles composed mainly of Fe, Cr and Ni

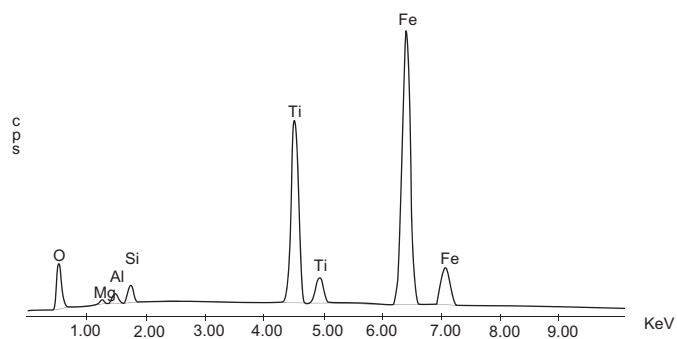
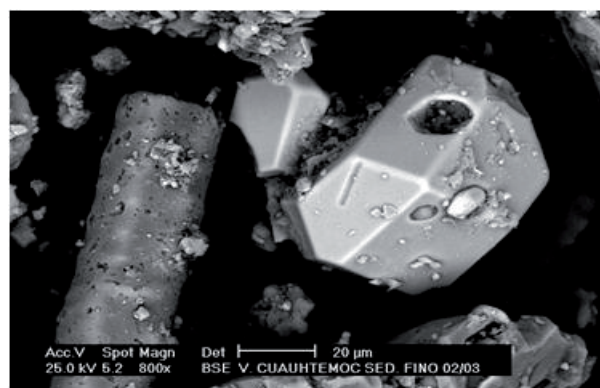


Fig. 9. Scanning electron micrograph at 800x of a particle composed of Fe, Ti and O

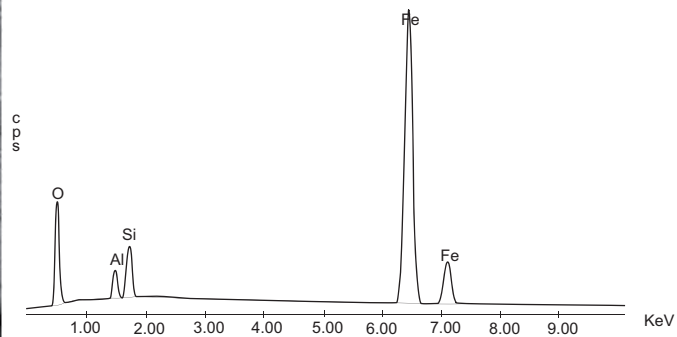
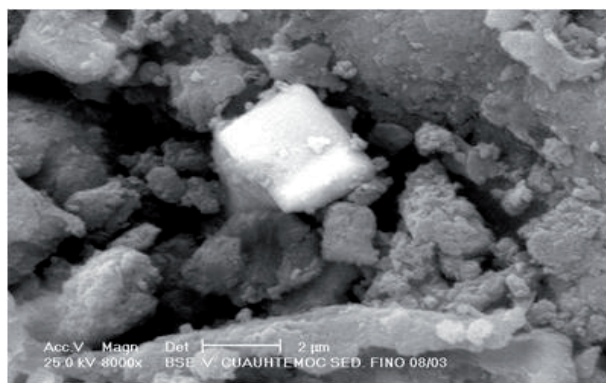


Fig. 10. Scanning electron micrograph at 8000x of a rectangular particle composed mainly of Fe and O

Particles of the Fe group were associated with Ti-O (Fig. 9) and O (Fig. 10). Fe-TiO particles were more abundant in the sites 5-8 of the river. This behavior must be due to the discharges of the tributary rivers of the second section of the river, which introduce iron particles associated to Ti and O coming from the soils of the surrounding area (Dekov *et al.* 1997, Huerta 2005).

CONCLUSIONS

The heavy metal concentration in the cohesive sediments decreased in the following sequence: Fe > Mn > Zn > Cr > Cu > Pb.

With the exception of lead, metal concentrations in sediments exceeded the guide or reference values given by USACE and MOE for dredged sediments.

Bed sediments in the upper course of the Lerma River can be considered enriched with Cr, Cu, Zn and Pb.

Iron and manganese present in the cohesive sediments of the upper course of the Lerma River come mainly from natural sources, while chromium, cop-

per, zinc and lead are associated with anthropic contributions (domestic sewage and industrial effluents).

Sampling site 6, was the main accumulation zone for Mn and Fe, influenced by tributary rivers whereas sampling site 4, was the main accumulation zone for the other metals, corresponding to the main industrial area.

The particle groups in the cohesive sediments of the upper course of the Lerma River were present in the following order: aluminosilicates > silica > iron > sulfur > metals > calcium carbonates > calcium/phosphorus > manganese.

It is important to work continuously in studies that contribute to the control and regulation of the sources of pollution. In the near future, research on speciation could be useful in the evaluation of risk when sediments are applied to agricultural soils.

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