HEAVY METALS SPECIATION IN SEDIMENTS OF A MEXICAN TROPICAL LAKE

ESPECIACIÓN DE METALES PESADOS EN SEDIMENTOS DE UN LAGO TROPICAL MEXICANO

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Abstract

Heavy metals speciation of Mexican Lake Chapala sediments was studied using sequential extraction to assess their mobility. Mineralogical constitution of sediments was studied by XRD. Results show Pb and Cr present in exchangeable and carbonate fractions indicating anthropogenic origin. Risk Assessment Code indicates low risk of pollution for water column. XRD results indicate mineralogy of Lake Chapala sediments present spatial variation. Presence of Pb and Cr in exchangeable and carbonate fractions suggests heavy metals pollution control not effective by corresponding authorities.

Keywords: sediments, toxic metals, speciation, lake pollution.

Resumen

La especiación de metales pesados del lago Mexicano de Chapala fue estudiada usando extracción secuencial para evaluar su movilidad. La constitución mineralógica de sedimentos fue estudiada mediante XRD. Los resultados muestran Pb y Cr presentes en las fracciones intercambiable y de carbonatos indicando un origen antropogénico. El código de evaluación de riesgo indica bajo riesgo de contaminación a la columna de agua. Los resultados de XRD indican que la mineralogía de sedimentos del lago de Chapala presenta variación espacial. La presencia de Pb y Cr en fracciones intercambiable y carbonatos sugiere que el control de contaminación por metales pesados, no es efectiva por autoridades correspondientes.

Palabras clave: sedimentos, metales tóxicos, especiación, contaminación del lago.

1 Introduction

The bioavailability and subsequent toxicity of heavy metals in natural water bodies (e.g. lakes, rivers, estuaries, etc.), is dependent upon the geochemical partitioning to the sediment components (Luoma and Jenne, 1977; Luoma, and Bryan, 1982), referred to as metal speciation. In many instances, biological toxicity is related more closely to the concentrations of some of these particular physico-chemical forms (Tessier, *et al* 1979; Florence, 1982; Batley, 1989; Ure, 1990; Davidson *et al*.,1994; Quevauviller, *et al*., 1994; Thomas *et al*., 1994). Therefore, to assess the potential pollution effects of metal-bearing sediments to biota (e.g., bioavailability and toxicity), the sole criterion of total metal concentration cannot provide data about the extent of pollution due to the assumption that all the species of a particular metal have equal impact on the ecosystem (Quevauviller *et al*.,1994; Franco *et al*., 2007). As a result, other analytical methods must be implemented and that can offer a more realistic estimate of the actual environmental impact. Thus, speciation analysis of heavy metals provides useful information regarding the chemical nature or potential mobility and bioavailability of a particular element, which in turn can offer a more realistic estimate of actual environmental impact.

Since the mobility of a metal and its bioavailability also depend on its speciation, considerable attention has been paid to this aspect in lacustrine systems. For example, Dollar *et al*. (Dollar *et al*., 2001) employed the sequential extraction scheme of Tessier *et al*. (1994) to study the portion of a metal bound to different geochemical groups at Indiana

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Dunes National Lakeshore. A potential risk of pollution was shown by the release of Cd, Pb, and Cr and attributed to anthropogenic sources. In the Mexican Lerma-Chapala Watershed, studies using total metal concentrations have demonstrated that transport vectors of six metals (Cd, Cr, Ni, Cu, Pb, Zn) were the suspended sediments along the Lerma River, with Lake Chapala as the final destination (Hansen and Maya, 1997; Ávila-Pérez *et al*, 2007, Zarazua *et al*, 2011). However, these studies did not identify the sources of pollution of these metals, posing a limitation of the extent of contamination assessment that would be helpful in proposing more effective pollution control procedures.

Shallow tropical Lake Chapala is Mexico?s largest freshwater body and is the final part of the Lerma-Chapala Basin (Figure 1). It is the most important lake in this country, in part because it supplies ~65% of water consumed by the city of Guadalajara (pop. 4.1 million inhabitants). The presence of potentially toxic substances such as heavy metals and other substances in this water body has prompted concern since large quantities of wastes from municipal, industrial, and agricultural activities from the entire Lerma-Chapala basin flow largely untreated into the lake through the Lerma River (the main tributary to the lake, see Figure 1) (Hansen *et al*., 1995). Despite the importance this lake has as water supply for human consumption (Badillo-Camacho *et al*, 2015), only a few studies have being reported concerning the status of the presence of heavy metals and their risk to the water column. Trujillo-Cardenas *et al* (2010), were the first ones who reported the presence of some metals (lead and chromium) in the exchangeable and carbonate fractions of sediments of lake Chapala.

In view of the lack of studies that evaluate the heavy metal pollution risks from sediments to the water column of Lake Chapala, the main objective of the present study was to investigate -using a five-step sequential extraction procedure- the geochemical groups the different trace metals metals (Fe, Cd, Ni, Zn, Cu, Mn, Cr, and Pb) belong to. The procedure was used for the study of the sediments from six sites of this lake and the potential pollution risk they pose to the water column. The source of metals was determined at the six sites, including the depocenter, i.e., the area of maximum sediment deposition and the place where the sedimentary column reaches its thickest value and the sedimentary process is disturbed the least (Neuendorf *et al*., 2005). Mineralogical constitution of sediments was studied by powder X-Ray Diffraction on the six sites sampled.
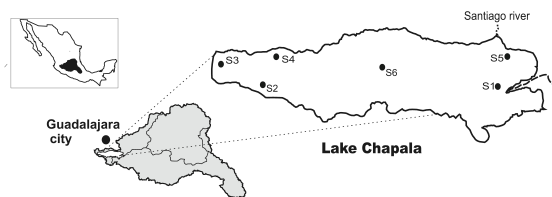

Fig. 1. Location sediment sampling sites along Lake Chapala. S1: Lerma. S3=S2: Soyatlán. S4=S3: Jocotepec. S5=S4, San Juan Cosalá. S8=S5: Jamay. S10=S6: Depocenter.

2 Materials and methods

2.1 Reagents and instruments

All analytical grade reagents were used without further treatment. Metal concentrations were analyzed by Atomic Absorption Spectrometry (AAS, Analytik Jena Model ContrAA 300, Jena, Germany). Certified standard metal ion solutions (Sigma-Aldrich, St. Louis, MO.) were used to obtain concentration versus absorbance calibration curves. Instrument detection limits were (mg L^{-1}): (a) Cd = 0.002, (b) Pb = 0.05, (c) Cr = 0.02, (d) Mn=0.01, (e) Zn = 0.005, (f) Ni =0.02, (g) Cu = 0.01, (h) Fe = 0.02. Blank solutions, i.e., the same composition as the target solution but without metal ions, were used as background for absorption corrections. All the solutions were prepared using deionized water with a resistivity of 18 MΩ (Barnstead, Chicago, Ill). A Thermo Electron (Model Orion 3-Star) pH meter was used for pH measurements.

2.2 Study zone

Lake Chapala is part of the Lerma-Chapala watershed and is located in the western central side of Mexico at about 1515 m above sea level; it covers a surface area of $\sim 80 \times 15$ km^2, and its average depth varies between 4 and 7 m (Figure 1). The lake is the largest freshwater body of Mexico, provides ~7.5 m^3/s of the water consumed in the city of Guadalajara (see Fig. 1) (Scott *et al*., 2001), and has a unique ecosystem. Due to wind action and low depth, lake stratification is reduced, and consequently the lake is oxidized at all depths (Hansen and van Afferden, M, 2001), as reflected by the dissolved oxygen values (6.8-7.0 mgL^{-1}) which represent a saturation level >90%. This phenomenon is attributed to the almost complete water mix and to the low depth of the lake (Limon *et al*.,1989; De Anda and Shear, 2001). The human activities have changed

significantly the original regime of the lake over the last 50 years. These changes (caused by inputs of the Lerma River) were due in part to the industrial development of cities located along this river. The lake acts as a sink for dissolved substances (e.g. heavy metals) and suspended sediments transported from upstream agricultural, urban and industrial areas through the Lerma river and the local watershed (Hansen and van Afferden, M, 2001).

2.3 Sediment sampling

Sediment core samples were obtained during the sampling campaign of May 2009, using a Benthos-type gravity corer, sealed to avoid contact with air, and transferred to the laboratory. Once in the laboratory, the sediment cores were subsectioned to the desired depths; the first 10 cm of homogenized samples were used for both sequential and total metal analysis. All sediment samples were air dried, passed through a 63 μm sieve to obtain the silt/clay fraction, frozen, and stored in sealed plastic bags until analyzed. The analysis of the fraction < 63 μm was performed since silt and clay size particles adsorb the highest concentrations of metals and are more readily transported in suspension in natural waters (Fytianos and Lourantou, 2004).

2.4 Sediment analysis

i) Total metal digestion of sediments was used here to verify the mass balances between sequential extraction and total metal methods. Sediment samples were digested using the USEPA Method 3052: Microwave assisted acid digestion of siliceous and organically based matrices (USEPA, 1996). Briefly, about 0.5 g of dry sediment was digested with 9 mL of concentrated HNO_3 and 3 mL of concentrated HF in a programmable Microwave Oven Model Ethos Touch (Sorisole, Italy). After digestion, the mixture was heated to evaporate the HF and the resulting solution was transferred to a 50 mL volumetric flask and diluted to the mark. Digestion extracts were used to analyze total metal concentrations by AAS. Water blanks containing all the components except sediment digests were analyzed to determine background interferences. All measurements were performed in triplicate and average values are reported. *Inorganic carbon* was determined by the loss on ignition method, LOI (Dean, 1974).

ii) Sequential extraction: the sequential extraction procedure proposed by Tessier *et al*. (1979) was applied to obtain partitioning of trace metals on the lake's sediment samples. The following extractions were obtained: fraction I: exchangeable, fraction II: carbonates, fraction III: Fe/Mn oxides, fraction IV: organic matter, and fraction V: residual. All selective extractions were conducted in centrifuge tubes (polypropylene, 25 mL) to minimize loss of solid material. Suspension separation was performed between each successive extraction by centrifuging at 3000-4000 rpm for 30 min. The supernatant was removed with a pipette; the solid residue was washed with deionized water. Comparison of metal content between the two procedures (i.e., total and sequential) was ≤ 10 % difference for most of the metals. All measurements (total and sequential) were performed in triplicate and average values are reported.

2.5 XRD data for mineralogy of sediments

X-ray diffraction patterns were obtained using a Siemens Diffraktometer D500 X-ray instrument with a CuKα source operated at 30 kV.

2.6 Quality assurance

Glassware and glass fiber filters were solvent rinsed and heated at 450 °C prior to use. Sediment coring equipment was rinsed with hexane and acetone prior to use. The Standard Reference Material (SRM) 2702: Inorganics in Marine Sediment from the National Institute of Standards and Technology (Gaithersburg, MD) was used as the total metals standard for purposes of quality control. Acids used for total metal extractions and analyses were trace-metal grade (Fisher Scientific, Pittsburgh, PA). The metal concentrations measured by AAS for the certified material SRM 2702 shown in Table 1, guarantee the analytical results of this study.

Table 1. Results of the measured metal concentrations and sediment reference material SRM 2702 (mg kg^{-1}, dry basis).

Metal	Certified SRM 2702 (mg kg^{-1})	Measured (mg kg^{-1})	% Recovery
Zn	485.3 ± 4.2	511.5 ± 2.5	105.4
Cr	352 ± 22	343.6 ± 8.6	97.6
Mn	1757 ± 58	2060.5 ± 21.2	117.2
Ni	75.4 ±1.5	86.4 ± 5.2	114.6
Pb	132.8±1.1	123.5 ± 6.8	93.0
Cu	117.7	140.1 + 7.3	119.0

Table 2. Sediment characteristics of six sites of Lake Chapala.

Site	pH	Humidity %	C_{org} %	$C_{carbonate}$, %
S1	7.9	71.3	25.0	6.0
S2	8.5	61.7	25.0	7.0
S3	8.3	75.1	16.0	6.0
S4	8.1	94.4	22.0	7.0
S5	7.1	40.1	34.0	7.0
S6	8.3	82.9	13.0	7.0

3 Results

3.1 Physicochemical properties of Lake Chapala sediments

The physicochemical characteristics of Lake Chapala sediments of six sites are shown in Table 2. Sediment pH ranged between 7.1 and 8.5, indicating their slightly alkaline nature. The high organic matter content (13-34 % as C_{org}) and the presence of carbonates (6 and 7% as $C_{carbonate}$) in sediments of the six sites can explain the relatively low amounts of metals bound to the carbonate fraction and the predominance of some metals present in the organic matter fraction (e.g. Cd, Pb, and Cr), as it will be shown in the fractionation studies (section 2.3). The carbonate contents at the six sites are in agreement with literature reports which indicate that terrigenous particles are the major component of sediments with ca. 6-7% wt. calcite (Trujillo-Cárdenas *et al*., 2010).

3.2 Total metal concentrations in Lake Chapala sediments

The total metal concentrations in sediments of the six sites of Lake Chapala are shown in Table 3 along with the Average Abundance of Metal in Basaltic Rocks (AAMBR) (Krauskopf, 1967), LEL and SEL values. LEL is the Lowest Effect Level; the majority of benthic organisms can tolerate this level whose value is obtained by using field data on the co-occurrence of sediment concentrations and benthic species (Hansen and van Afferden, 2001; Krauskopf, 1967). SEL stands for Severe Effect Level and it represents contaminant concentrations in sediments that could potentially eliminate most of the benthic organisms (Persaud *et al*,1993). AAMBR, LEL and SEL values are taken here as reference points to assess the level of contamination of Lake Chapala sediments. Pb concentrations exceed LEL at sites S1 and S5, with the highest values at site S5. Due to the alkaline nature of water in the lake, metals such as Pb, and to a lesser extent Cd, can be present as precipitates in the sediments and settled as carbonates, oxides and hydroxide-bearing sediments. Cd was not detected at all sites. Cr concentrations exceeded LEL at sites S1, S2, S3, S4, and S6 and SEL at sites S3 and S4. Mn exceeded LEL at all sites except at site S4. Cu, Ni and exceeded LEL values at all sites, whereas Zn exceeded AAMBR and LEL values at all sites; Fe exceeded AAMBR at all sites. In summary, elevated concentrations of Pb, Cr, Cu, Ni and Zn in sediments of Lake Chapala, indicate higher exposure risks to the benthic biota of the lake.

Table 3. Total metal concentrations (mg kg^{-1}; Fe and Mn in g kg^{-1}) in sediments of six sites of Lake Chapala sampled during dry season of 2009.

Site	Metal							
	Pb	Cd	Cr	Mn	Cu	Ni	Zn	Fe
S1	31.5	ND	91.4	0.931	38.2	29.8	151.8	31.6
S2	18.1	ND	81.3	0.879	32.2	33.9	121.6	38.5
S3	16.8	ND	137.4	0.651	38.7	34.8	139.7	44
S4	11.9	ND	122.9	0.574	38.6	41.1	128.1	40.7
S5	59.7	ND	22.8	0.532	18.7	29	140.3	36.7
S6	21.1	ND	53.7	1.01	25.6	42.2	164.4	42.2
AAMBR*	5	0.02	200	1.5	100	150	100	8.6
LEL	31	0.6	26	0.46	16	16	120	N.A.
SEL	250	10	110	1.1	110	75	820	N.A.

*From ref. [34] ND = Not detected. N.A. = Not available

3.3 Sequential extraction results

Singh *et al.* (2005) and Jain (2004) suggested that a large part of metals introduced by human activity are present in the exchangeable and carbonate fractions (fractions I and II). Metals bound to the easily reducible phase (Fe/Mn oxides, fraction III) and to organic matter and sulfides (fraction IV) may be better held by a scavenging effect (i.e., this fraction acts as a sink of metals). Metals in the residual fraction (fraction V), strongly bound to solid matter, originate mainly from natural sources (Salomons and Forstner, 1984). The fraction of exchangeable metals included is held by the electrostatic adsorption as well as those specially adsorbed. The amount of metals in this phase indicated the environmental conditions of the overlying water bodies. The speciation patterns in sediments from six sites of Lake Chapala are shown in Figure 2. The fractionation profile of lead suggests that a major portion is associated with the Fe/Mn oxides at all sites. Moderate contribution is associated with the residual fraction at all sites. A significant portion is associated to organic matter at Site S5, whereas Sites S1, S3 and S6 show small portions associated to carbonates. The fractionation profile for chromium indicates that it is mostly bound to the residual fraction at all sites, and very small portions are bound to the rests of fractions at all sites.
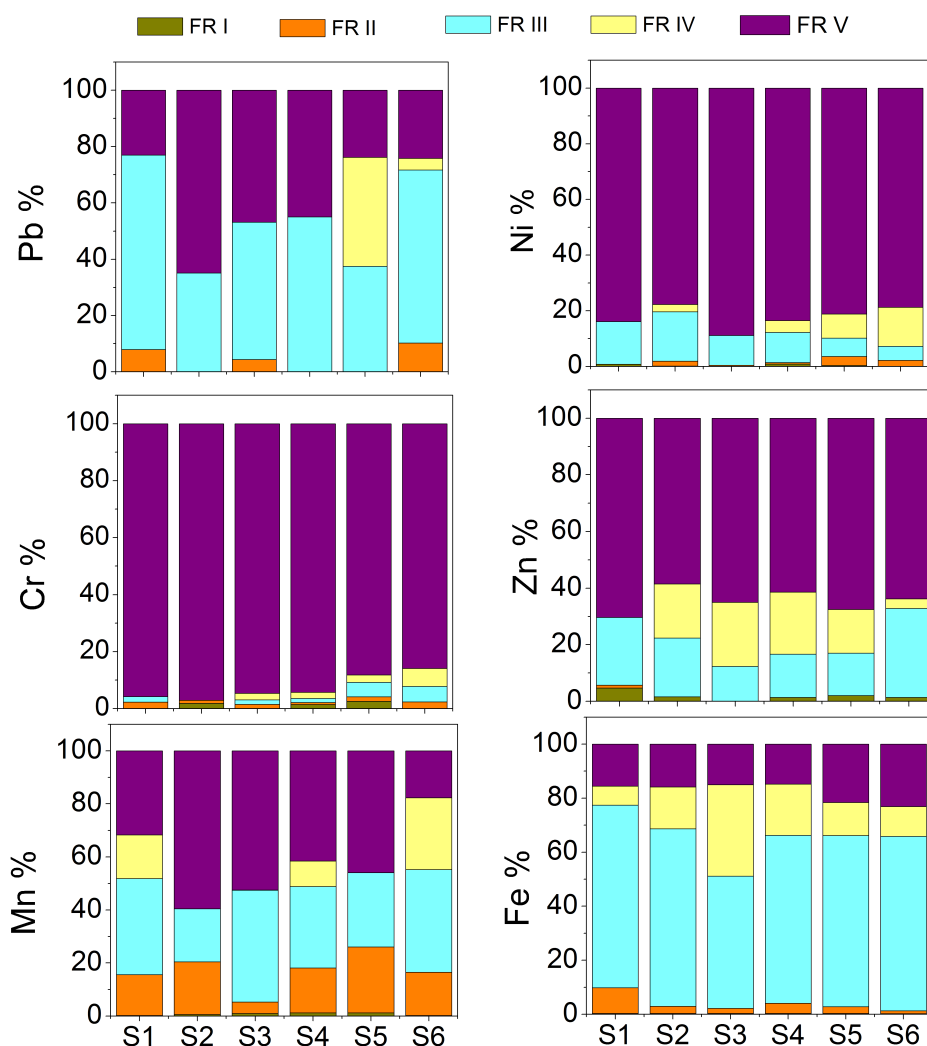

Fig. 2. Speciation of heavy metals in sediments of six sites of Lake Chapala. S1: Lerma; S2: Soyatlán; S3: Jocotepec; S4: San Juan Cosalá; S5: Jamay; S6: Depocenter.

The profiles for zinc and nickel indicate that they are present mostly in the residual fraction. However, these profiles indicate that moderate portions bound to Fe/Mn oxides and organic matter fractions at all sites, being most significant in the case of Zn. In the case of manganese and iron, their fractionation profiles indicate major portions bound to the residual fractions. However, as expected, significant portions of these two metals are present in the Fe/Mn oxides fraction and organic matter. Significant amounts of manganese are present in the carbonates fraction, whereas iron is present in smaller amounts in this fraction at all sites. Copper was mostly present in the residual fraction at all sites (data not shown), whereas cadmium concentrations were below detection limit of the instrument at all sites. It is evident from the results of sequential extraction studies that metals in the sediments of Lake Chapala are bound to different fractions with different portions. The amount of metals bound to a given fraction can, therefore, provide an indication of the reactivity of sediment and, consequently, the risk associated with the presence of metals in this water body, can be assessed.

The reactivity of sediments was evaluated by applying the criterion of the Risk Assessment Code (Perin *et al.*, 1985). The risk assessment code (RAC) has been used to assess environmental risks and estimate possible damage to benthic organisms caused by contaminated sediments (Trujilo-Cardenas *et al.*, 2010; Arcega-Cabrera *et al.*, 2009; Ishikawa *et al*, 2009; Passos *et al*., 2010). This criterion considers that when less than 1% of the total metal content is bound to the exchangeable and carbonate fractions, i.e., liable to be released from the sediment, the latter will be considered safe for the environment; when more than 50% of the total metal content can be released from exchangeable and carbonate fractions, the sediment will be considered of very high risk; the rest of the classification includes low risk (1-10%), medium risk (11-30%) and high risk (31-50%). This code (shown in Table 4), applied to the six sites sampled in Lake Chapala, reveals that only lead presents a low risk at site S6 whereas sites S1 and S3 present no risk. In the case of less toxic metals like iron and manganese, there is a medium risk of leaching from all sites. Manganese is present in carbonate fractions at site S3, followed by sites S1, S4, S5, and S6. In summary, the results of sequential extraction measurements indicate slight anthropogenic pollution at site S6 (Depocenter) due to the presence of lead in the carbonate fraction. These results suggest that heavy metals pollution control is not being effective by the corresponding authorities.
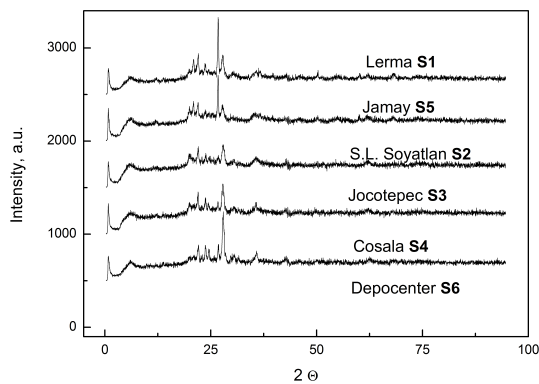

Fig. 3. X-ray pattern diffraction results of sediments from six sites of Lake Chapala. S1: Lerma; S2: Soyatlán; S3: Jocotepec; S4: San Juan Cosalá; S5: Jamay; S6: Depocenter.

Table 4. Results of Risk Assessment Code (RAC) applied to sediments of six sites of Lake Chapala.

Site	No risk	Low risk	Medium risk	High risk
S1	Cu, Ni,	Pb, Cr, Zn, Fe	Mn	—
S2	Ni, Mn	Cu, Cr, Zn, Fe	Mn	—
S3	Ni, Cr	Pb, Cr, Mn, Fe	—	—
S4	Ni	Cr, Zn, Fe, Mn	Mn	—
S5	Cu	Cr, Ni, Zn, Fe, Mn	Mn	—
S6	Mn	Pb, Cr, Ni, Zn, Mn, Fe	Mn	—

The Tessier extraction method of this study and applied in previous works, is relevant compared to other non-conventional extraction techniques such as Chemical Speciation, Screening Speciation, or Group Speciation (Benson *et al*, 2013) in that it involves the determination of the different forms of the same chemical species. The tessier´s technique is more suitable for trace metal analysis, and trace metal analysis of different forms present in soil and sediment after sequential extraction.

3.4 X-ray diffraction results

Figure 3 depicts the results of the X-ray diffraction patterns of Lake Chapala sediments from the six sites sampled in this study. In general, it can be observed that all sites present similar mineral species and these include clays, such as montmorillonite, smectite, chlorite, kaolinite, illite (Ramírez-Sánchez, 2001). Some mineral mixtures can be observed such as quartz-illite. Other mineral species present include pure quartz, feldspars, carbonates and some oxides (Fernex *et al*.,2001; García-Arriola *et al*,

2015). The XRD results also show that mineralogy of Lake Chapala sediments present spatial variation, both granulometric and sedimentary with respect to the most intense peak of the diffraction pattern. For example, at the East side of the lake (sites S1 and S5), the predominant mineralogical species are silts (particle size of 2-63 μ) and fine sands (particle size of 63-250 μ) that are comprised of felspar, quartz and some carbonates, whereas clay materials such as montmorillonite (< 2 μ) are present in small quantities. At the Central part of the lake (site S6), clay material are predominant (montmorillonite and kaolinite), followed by silts and fine sands (quartz, tridimite, feldspars and carbonates). At the West sector (sites S2, S3 and S4), silts predominate over fine sands and clays. In general, it can be observed from the XRD results that most of the materials found are clay minerals as the main components. It is known that these minerals have a layered-type basic structure that confers them a high metal uptake capacity due to the presence of interlayered fixed ions on outer surface of the crystallites which can be easily exchanged by metal ions present in the water column (Salomons and Forstner 1980).

Conclusions

Sequential metal extraction techniques were applied to six sites of Lake Chapala sediments to determine the origin of metal contaminants. At sites S1, S3 and S5, it can be concluded that Cr, and Pb were introduced to the lake via anthropogenic activities. Pb and Cr were introduced via municipal and industrial discharges of untreated wastewaters of cities located along the lakeshore. This is in part due to the fact that Mexican water regulations do not require tertiary treatments to eliminate these toxic metals. By applying the Pollution Assessment Risk Code at sites S1, S3 and S5, these sites show a low contamination risk due to the presence of Cr and Pb in the two more labile fractions of the sediments (i.e., exchangeable and carbonates). Finally, metal concentration data in sediments from Lake Chapala indicate the need for continuous monitoring of the levels of chromium and lead in waters to be used for human consumption.

Acknowledgements

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