

Contamination and risk assessment of heavy metals in bottom sediments from Lake Valencia, Venezuela

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Abstract. The contamination and risk assessment of heavy metals in the bottom sediments of the Lake Valencia, Venezuela, was performed by determining the Enrichment Factor (EF), the Geoaccumulation Factor (*Igeo*), the availability of metals and the Risk Index Code (RAC). The sediments were anthropogenic ally enriched with Pb, Zn, Cu and Cr and classified as uncontaminated to moderately contaminated, with a medium risk of Zn, Co, Ni and Cr, and low risk of Cu, Pb and Cd. Analysis of correlations and PCA showed temporal variations in the concentration of metals in the sediments during the rainy season, and spatial variations, where the depth and anthropogenic inputs are the main variables. The contamination of sediments was located on the axis connecting the mouths of the river Guayos, which crosses the city of Valencia, and the river Güey which crosses the city of Maracay, both highly industrialized. Although the concentration of dissolved heavy metals into the waters was within the regulations, important concentrations of Pb and Hg and the bioaccumulation of Hg and Cr, determined by the Bioconcentration Factor (BCF), were found in the fish tissues which indicate that the metal enrichment of the lake sediments is affecting the biota.

Keywords: Heavy metals, available fraction, risk assessment, sediments, contamination, Lake of Valencia.

Introduction

The Lake Valencia, Venezuela, is the biggest natural fresh water lake in the country. It is located between the cities of Valencia and Maracay, important industrial, agricultural and urban centers, with high growth during the last decades. Sewage and waste from antropic activities are introduced into the lake by the tributaries and runoff affecting its environmental status. Studies in the area have reported the enrichment of bottom sediments of the lake (Mogollon and Bifano, 1993, 1996) as well as its waters and biota (MARN-JICA, 2001) with heavy metals. The information on the environmental condition of the lake has not been updated in the last decade.

Materials and Methods

Studied area

Lake Valencia is located in north-central Venezuela (Fig. 1), between 67° 07' and 68° 12' west longitude, and 09° 57' and 10° 26' N north latitude. Currently, the lake covers an area

of 344 km², an average depth of 19 meters and a maximum depth of 39 meters (González de Juana, 1980).

Sampling

Sampling was conducted at five stations (E1, E2, E3, E4 and E5), selected considering the industrial, urban and agricultural activities around the lake (Fig. 1). The sediments were collected from June to October, 2009, using an Ekman dredge. Water samples, at the surface and close to the sediment, using a van Dorn bottle, and fish (*Oreochromis mossambicus* and *Hoplias malabaricus*) were also collected from June 2009 to May 2010. The sampling was conducted bimonthly.

Samples treatment

The sediments were subsequently sieved in wet, dried at room temperature, and brought into solution following the standard procedure EPA 3052 to determine the total concentration of the elements. The sequential extraction procedure BCR-modified (Rauret et al., 1999) was employed to determine the chemical fractionation of the

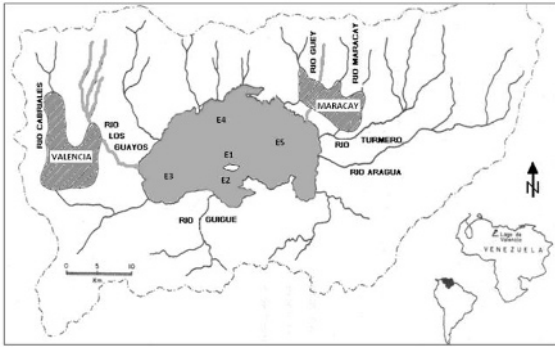


Fig.1 Location map and sampling stations at Lake Valencia

elements in the sediments. Water samples were filtered (0.45 mm) and adjusted to $\text{pH} < 2$ with HNO_3 . The fish were dissected to obtain the muscle and liver samples, which were lyophilized and digested using HNO_3 and H_2O_2 and a microwave digester.

Chemical analysis

In the sediment samples were determined: Al, Si, Ca and Mg by atomic absorption spectrometry (FAAS); Cd, Cr, Cu, Ni, Pb, Zn, Co, V, Fe, Ti and Mn by inductively coupled plasma atomic emission spectrometry (ICP-OES); and TOC using an elemental analyzer. Cd, Cr, Cu, Ni and Pb by electrothermal atomic absorption spectrometry (ET AAS) were determined in water samples and fish tissue. The determination of Hg in all the samples was performed by cold vapor atomic fluorescence spectrometry (CV-AFS). The accuracy and precision of the methodologies applied were determined using certified reference samples of sediment (LKSD-4 and BCR-701), oyster tissue (NIST 1566b) and bovine liver (BCR-185R).

Results and Discussion

Composition of the sediments

The 98% w/w of the sediments collected corresponded to silt and clays ($< 63 \mu\text{m}$). The TOC concentration in the sediments was high ($10 \pm 4\%$ w/w) suggesting a strong anthropic intervention. The concentration of the elements Al, Si, Ca, Mg, Fe, Ni, Co and Cd was comparable to the baseline values for Lake Valencia (Mogollon and Bifano, 1996), considering that these correspond to lithology contribution. In almost all stations, the concentrations of the elements Pb, Zn, Cu, Cr, Ni and Mn were higher than those of baseline. According to the EF (Gonçalves et al., 1992; Sutherland, 2000) and the *I_{geo}* (Muller G., 1969; Loska et al., 2004), determined using baseline values for Lake Valencia, the sediments were anthropogenically enriched with Zn, Pb, Cu and Cr ($\text{EF} > 1.5$) and were classified as moderately contaminated to uncontaminated ($0 < I_{\text{geo}} < 1$). The metallic enrichment showed differences between stations, observing the enrichment with Pb, Zn and Cu in

E1, with Zn and Cr in E2, with Pb and Zn in E3, with Zn in E4, and with Pb, Zn, Cu and Cr in E5.

Distribution of the metallic content of sediments

The multiple correlation analysis showed significant correlations ($p \leq 0.05$) between the elements Al, Ca, Si and Mg, reflecting the mineralogical composition of sediments, carbonates and clays, specifically smectites and chlorites (González de Juana, 1980), and between the elements Ti, Fe, Co, Cr and Cd. In the deeper stations (E1, E4 and E5) significant correlations between TOC and Hg, and between these and the elements Zn, Pb and Cu were found, indicating that the introduction of these elements into the lake sediments could occur together, either with the organic matter and/or by its precipitation due to the reducing conditions found in the bottom of the deeper stations.

Results from principal component analysis (PCA) showed spatial variations in the composition of the sediments, which are determined by the depth, represented by the Component 1 (29.6% of PCA), and the anthropogenic input, represented by the Component 4 (9.5% PCA) (Fig. 2). Depth is the variable determining the reducing and anoxic conditions in the deeper stations (E1 and E5), where together with the high levels of TOC and alkalinity produce the precipitation of the easily reducible elements: Hg, Cu, Zn and Pb.

The Component 4, associated with the anthropogenic input of TOC, Hg, Zn, Pb, Zn and Cu, was attributed to the discharge of the rivers Caño Central and Los Guayos, which cross the city of Valencia, and Guey and Aragua rivers that cross the city of Maracay, and their surroundings, this would explain the contamination of the sediments located on the axis connecting the stations E3, E1 and E5.

Temporal variations, identified by the Component 3 (15.3% of PCA) (Fig. 3), occur during the rainy season when the concentrations of Ca, Mg and Mn increase by its precipitation from the water as carbonates, due to the consequent increase of the pH of the waters by loading of sediment and nutrient to the lake, well as the Cinorg related to the carbonate lithology, represented by the Component 2 (22.4% of PCA) (Fig. 3).

The elements: Fe, Cr, V and Ti were not grouped in any of the seven principal components determined (93,6% of variability), indicating that their concentration in the sediments is mainly due to the lithochemical contribution.

Chemical fractionation, mobility and availability of metals in the sediments

The exchangeable or available fraction of metals (water soluble, inter-changeable and carbonate-associated elements) from the sediments showed elevated levels of Ca, Mg and Mn, reflecting the carbonate lithology nature of the area. According to the concentrations of the metals in this fraction, the mobility and availability of the elements presented the following order: $\text{Zn} > \text{Co} > \text{Ni} > \text{Cr} > \text{Cd} > \text{Pb} > \text{Cu}$. The available concentration of the elements varied

between stations, being the highest values of Zn, Ni, Cd and Co in the stations E1 and E5, and that of Cr in the E3, while that of Pb was fairly homogeneous between stations.

As stated by the Risk Index Code (RAC) (Perin et al., 1985), determined by the available fraction of the element, the sediments from the west of the lake (E3) showed a high risk of Cr ($31 < \text{RAC} < 50$); those from the south (E2) and east (E5) showed a medium risk of Zn, Co and Ni ($11 < \text{RAC} < 30$); and in the center of the lake (E1) the sediments showed a medium risk of Co and Zn. A low risk of Cu, Pb and Cd ($1 < \text{RAC} < 10$) was determined in the sediments from all the sampling stations.

Given the significant correlations determined between the elements ($p \leq 0.05$), the source of the enrichment of Cu, Cr, Pb, Ni and Zn may be associated with the runoffs of chemical pesticides and fertilizers from agricultural zones, as well as wastes from industries involved in paper, pigments, dyes and different foods industries, including beer; Cd, Pb and Ni would be associated to waste power battery (Forstner et Wittmann, 1981).

Recent studies in the Suata reservoir, which receives water from the Rio Aragua before emptying into Lake Valencia, have also shown contamination of its bottom sediments with Ni, Cd, Cr and Co and signs of bioaccumulation of Hg and Ni in the liver of fish caught (Alvarez et al., 2012).

The metallic enrichment found in the bottom sediments from Lake Valencia is consistent with previous results (Mogollon and Bifano, 1993, 1996; MARN, 2001). Unfortunately, it was not possible to determine the variation of the enrichment over time, due to the use of non-standard methods to determine the levels of metal enrichment and the exchangeable fraction in the work of these authors.

Waters

According to the values of: pH: 8.4-9.6; T: 26.2-32.4 °C; dissolved oxygen: 0-17.5 mg L⁻¹; conductivity: 1874-1942 µS cm⁻¹; ammonium: 33-1308 mg L⁻¹; hardness: 444-470 mg L⁻¹; and phosphates: 263-1052 mg L⁻¹, the lake is classified as hypertrophic.

Results obtained by multiple correlation analysis showed seasonal variations on the concentration of the dissolved metals in the waters of the lake, observing a decrease in the concentration during the rainy season, which is attributed to the increase in pH that occurs at this time. Throughout the year, the content of dissolved metals in the waters of Lake Valencia did not exceed the maximum values specified in the national and international regulations (Decreto 3219, 1999; EPA, 2006). Spatial homogeneity of the concentration of the dissolved metals in the waters of the lake were also found, both among sampling stations and within the water column, which is attributed to the continuous mixing of waters by the wind.

The annual average concentration of dissolved metals in the waters of Lake Valencia was: Cd 0.06 µg L⁻¹; Cr 0.86 µg L⁻¹; Cu 0.57 µg L⁻¹; Hg 0.08 µg L⁻¹; Ni 1.96 µg L⁻¹; and Pb 1.18 µg L⁻¹.

Fish Tissues

The average concentration of metals in the liver of *Oreochromis mossambicus* and *Hoplias malabaricus* was higher than in the muscle. The concentrations of Cd and Cu in the muscle of fish were within the national regulation (COVENIN, 1998), while those of Pb (0.2 to 1.7 mg kg⁻¹) and Hg (0.02 - 0.39 mg kg⁻¹) were higher. Considering the Bioconcentration Factor (BCF) (OEHHA, 2000), there are indications of Hg bioaccumulation (BCF = 14) and Cr (BCF = 12) in some specimens of fish caught, which would indicate that anthropogenic enrichment of the lake sediments could be affecting the biota.

Conclusions

The bottom sediments of Lake Valencia are enriched with TOC, Zn, Pb, Cu, Ni, Cr and Cd. The metal contamination would be reaching the lake through the discharge of its tributaries, rivers Guey and Los Guayos, which carries the urban and industrial wastes from the large cities and industrial centers of Valencia and Maracay, as well as from the runoffs from agriculture activities. The metal contamination is retained in the bottom sediments and its desorption is not favored due to the alkaline pH of the water. Thus, the concentration of dissolved metals into the waters of the lake is within the regulations. However, evidence of bioaccumulation of Hg and Cr determined in fish tissues, show that metal enrichment of the sediments is reaching to the biota.

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