

Concentration and Bioavailability of Heavy Metals in Sediments in Lake Yojoa (Honduras)

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A large fraction of heavy metal loads resulting from human activities is ultimately incorporated into aquatic sediments. The bioavailability of sediment-bound metals is of importance from an ecotoxicological viewpoint (Warren 1981). Microelements in soils and sediments may be subdivided into 5 pools which include 1) water soluble, 2) exchangeable, 3) adsorbed, chelated and precipitated, 4) metal oxides and 5) primary minerals (Viets 1962). It has been argued that the first two fractions represent the metal concentration in the soil (or sediment) solution and are closely related to bioavailability to plants (Haeni and Gupta 1986). The extractant often used for the water soluble and exchangeable pools is 0.1 M NaNO₃, which simulates well the availability of heavy metals to plants (Haeni and Gupta 1984; 1986). Soil extraction with NaNO₃ has been adopted by the Swiss Environmental Protection Agency (Office Fédéral de l'Environnement 1987). Toxicity bioassays for sediments determine the impact of whole sediments on invertebrates or the toxic effect of sediment extracts or interstitial water on invertebrates and microorganisms (Dutka et al. 1988; Giesy et al. 1988; Kwan and Dutka 1990; Ross and Henebry 1989; Schiewe et al. 1985; True and Hayward 1990).

The objective of this study was to determine the heavy metal (lead, zinc, copper and cadmium) content and bioavailability in sediments from Lake Yojoa, Honduras. Located at the west center of Honduras, Lake Yojoa, with an area of 89 km², is an important natural reservoir for drinking water and irrigation. Until recently, wastewater from the mining operations of El Mochito mine located in the northwest side of the lake were discharged into streams (e.g., El Raices) which flowed towards Lake Yojoa. Metal content of sediment extract was determined by atomic absorption spectroscopy and metal toxicity was assessed with MetPAD (patent pending), a bioassay kit which is specific for heavy metal toxicity.

MATERIAL AND METHODS

The median depth of Lake Yojoa is 16.4 m and the maximum depth is between 27 and 29 m (Castañeda 1983). Minerals, mainly galena (lead sulfide) and sphalerite (zinc sulfide), are mined in the El Mochito mine. The ore contains several heavy metals, mainly lead, zinc, copper and cadmium. Sixty-two surface sediment (top few centimeters) samples were taken with an Eckman dredge at 31 stations in Lake Yojoa, from December 1988 to May 1989 (Fig. 1). All samples were analyzed

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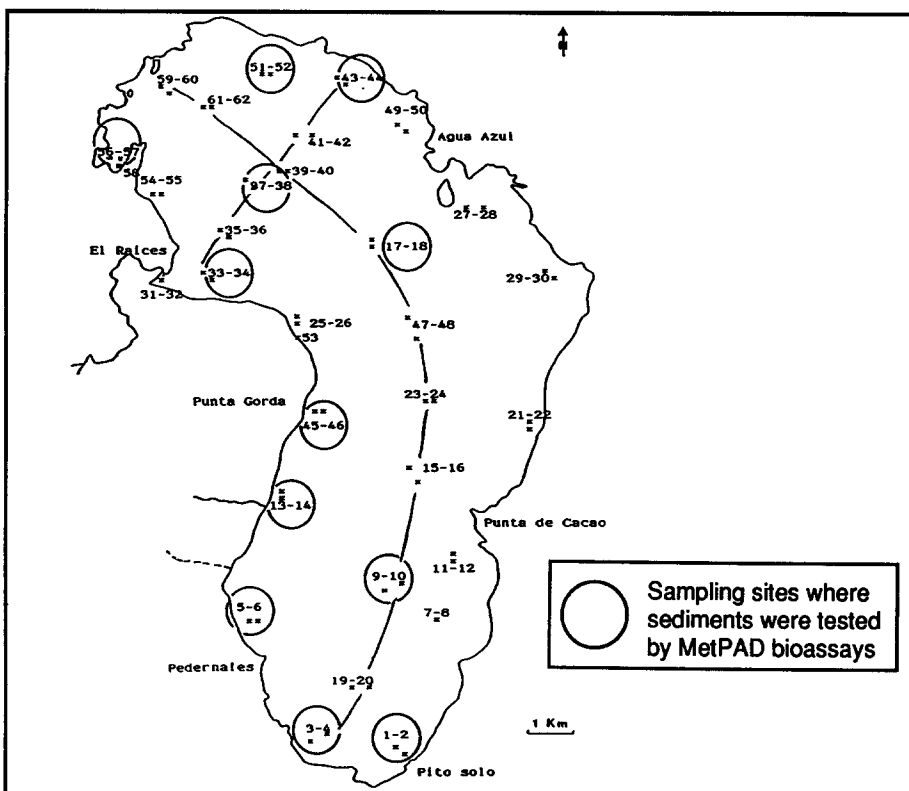


Figure 1. Distribution of sampling sites for sediments in Lake Yojoa.

for heavy metal content. To assess the bioavailability of the heavy metals in sediments, 12 of which were extracted with mineral water or sodium nitrate, they were assayed with a toxicity test (sampling locations in Fig. 1). Twenty six adult fish, mainly black bass (*Micropterus salmoides*) were collected at the sites 5-6, 21-22, 31-32 and 43-44 (Fig. 1) and analyzed. All samples were packed and brought back, inside alumina boxes, to the laboratory of CESCO in Tegucigalpa.

Wet sediments were sieved at 2 mm and dried at 85°C for 24 hours. They were then ground with a mortar and extracted overnight with a nitric acid - hydrochloric acid mixture (1:3) (De Groot et al. 1982). The extract was filtered and analyzed for Pb, Zn, Cu and Cd with a Varian Spectra 10 flame atomic absorption spectrometer. Heavy metal content is expressed as mg/kg of dry sediment. Fish analysis was performed on the edible part. Samples were homogenized, calcinated and the resulting ash solubilized in HCl, 1N, and then analyzed as the sediment extract. Levels of detection ranged from 20 µg/l for Cd to 50 µg/l for Pb in the extract. No reference material was used. Five samples of sediments, randomly selected, were also analyzed in Switzerland by the Soil Science Laboratory of the EPFL and the relative differences between results were always less than 10%.

For toxicity testing two extractions were performed. For water extraction, 5 g of dried sediments were suspended in 20 ml of distilled water and shaken at 200 strokes per minute for 2 hr at room temperature. The sediment was centrifuged at 3000 RPM for 30 minutes and the supernatant, thereafter called water elutriate, was tested for heavy metal toxicity. Sodium nitrate extraction was carried out by

shaking 5 g of dried sediment suspended in 20 ml of 0.1M NaNO₃ at 200 strokes per minute for 2 hr (Office Fédéral de la Protection de l'Environnement 1987). The sediment was centrifuged at 3000 RPM for 30 minutes and the supernatant, thereafter called NaNO₃ elutriate, was tested for heavy metal toxicity.

In a previous study (Bitton et al. in press), a bioassay kit called MetPAD was used to specifically detect heavy metal toxicity. The MetPAD kit includes a freeze-dried mutant strain of *E.Coli* (bacterial reagent), diluent (deionized, activated carbon filtered water), phosphate buffer and assay pads saturated with beta-galactosidase substrate. The assay is thus based on inhibition of enzyme activity specifically by heavy metals. The freeze-dried bacteria supplied in the kit were rehydrated and, after thorough mixing, 0.1 ml of the bacterial suspension was added to 0.9 ml of the water or NaNO₃ sediment elutriates. Following incubation for 90 minutes at 35°C, 0.1 ml of a buffer reagent was added to each assay tube. Ten ml drops of the sample were dispensed on an assay filter pad containing an enzyme substrate. The filter pad was incubated for 30 minutes at 35°C for purple color development. Each assay pad could accomodate up to 10 µl drops. The intensity of the purple color on the pad was compared to that of a control sample, consisting of MilliQ water instead of sediment elutriate. Absence of color development or a reduction in color intensity indicates heavy metal toxicity.

RESULTS AND DISCUSSION

From the results obtained with the 31 sampling sites, the distributions of heavy metal concentrations in surface sediments of Lake Yojoa were plotted at the Joint Research Centre of the European Communities at Ispra (Italy) by computer means (Davies 1973) (Fig. 2). Sediments from 12 sites were selected (Fig. 1), extracted as previously described and assayed for metal toxicity using the MetPAD bioassay kit. Most sediment samples contained relatively high concentrations of copper, zinc and lead (Table 1).

Table 1. Heavy metal content and extract toxicity of sediments from Lake Yojoa.

| SAMPLE | Chemical analysis (mg/kg) | | | | Toxicity testing (MetPAD)* | |
|--------|---------------------------|--------|--------|------|----------------------------|----------------------------------|
| | Cu | Zn | Pb | Cd | H2O extract | NaNO ₃ , 0.1M extract |
| 1 | 253.5 | 382.0 | 371.0 | 6.0 | NT | NT |
| 3 | 142.5 | 148.0 | 94.0 | 4.0 | NT | NT |
| 6 | 277.5 | 837.5 | 1264.5 | 10.0 | NT | NT |
| 9 | 294.0 | 741.0 | 852.5 | 8.0 | NT | NT |
| 13 | 52.5 | 372.5 | 544.5 | 3.0 | NT | NT |
| 18 | 356.5 | 2259.0 | 4195.0 | 22.7 | NT | NT |
| 34 | 438.0 | 3406.0 | 2837.5 | 28.5 | NT | ++ |
| 37 | 542.0 | 2605.0 | 4495.0 | 28.0 | NT | NT |
| 44 | 155.5 | 304.5 | 394.0 | 6.0 | +++ | NT |
| 46 | 130.0 | 333.0 | 461.5 | 5.5 | NT | NT |
| 51 | 138.0 | 191.5 | 317.0 | 9.0 | NT | NT |
| 58 | 22.5 | 121.5 | 42.0 | 0.2 | NT | NT |

*: Degree of toxicity for MetPAD: +++++ = 100% toxic (no purple color development); + = slightly toxic; NT = non toxic (purple spot of similar intensity as the control)

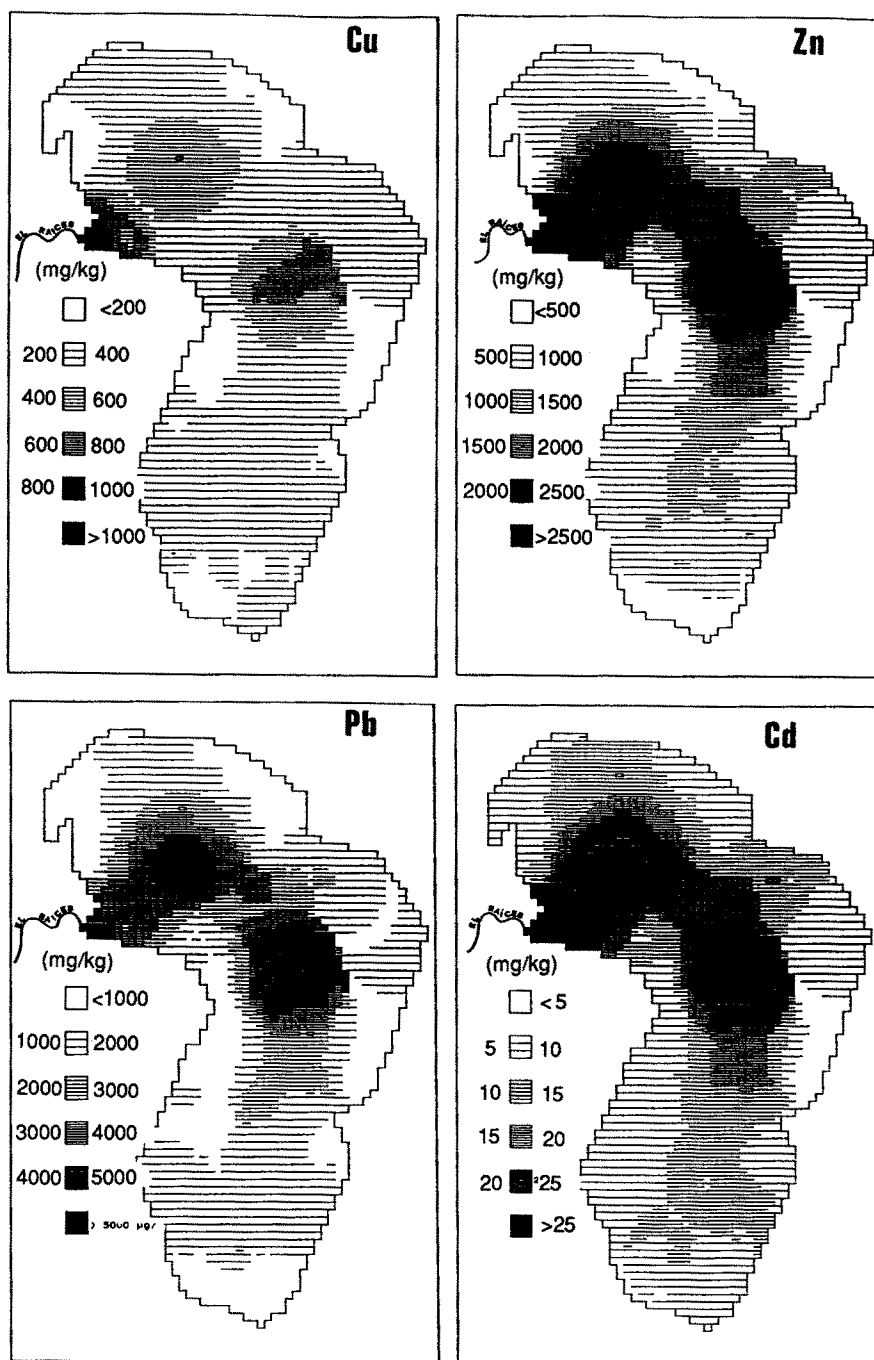


Figure 2. Copper, zinc, lead and cadmium concentrations in Lake Yojoa sediments.

Metal concentrations in the sediments selected for bioassays ranged from 22 to 542 mg/kg for copper, 121.5 to 3406 mg/kg for zinc, 42 to 4495 mg/kg for lead and 0.2 to 28.5 mg/kg for cadmium. As shown in Fig. 2 the metal concentrations detected in Lake Yojoa appear to be similar to those found in Coeur d'Alene Lake, USA, which is also near a mine (Maxfield et al. 1974) or much higher than those found in other lakes such as Lake Geneva, Switzerland (Vernet and Davaud 1977) and Alvarado Lagoon, Mexico (Rosales et al. 1990).

Heavy metal concentrations in black bass flesh (concentrations found in males and females were similar) appear in Table 2.

Table 2. Heavy metals concentration (mg/kg, fresh weight) in the edible part of Lake Yojoa adult black bass (*Micropterus salmoides*).

| | females N=9 | | males N=17 | | mean concentration | |
|-----------|-------------|-------|------------|-------|--------------------|-------|
| | \bar{x} | s | \bar{x} | s | \bar{x} | s |
| Cu | 1.082 | 1.146 | 0.919 | 0.557 | 1.014 | 0.771 |
| Zn | 6.422 | 3.121 | 6.565 | 2.072 | 6.516 | 2.422 |
| Pb | 0.298 | 0.060 | 0.296 | 0.163 | 0.296 | 0.134 |
| Cd | 0.065 | 0.051 | 0.068 | 0.038 | 0.067 | 0.042 |

Testing via MetPAD showed no toxicity except for the water extract of sample N.44 and the NaNO₃ extract of sample N.34 which had nearly the highest heavy metal load (Table 1). This shows that in most of the samples tested, heavy metals are not bioavailable and little would be released into the water column. This is confirmed by the results of Castañeda (1983) who reported relatively low heavy metal levels in water samples from Lake Yojoa (Pb: non detected to 79.4 µg/L; Zn: 217.8 - 846.2 µg/L; Cd: non detected to 0.0017 µg/L). This is also confirmed by the heavy metal concentrations found in fish (Table 2). The levels of heavy metals in fish are significant but do not reflect the extremely high heavy metal concentration detected in sediments by chemical analysis. Considering the heavy metal concentrations found in the edible part of fishes from Lake Yojoa and FAO/WHO, ADI recommendations (FAO/OMS 1984), health risks due to lead, cadmium and zinc may occur following the consumption of about, respectively, 1.5 kg, 1 kg and 3 kg of fish / day, a level much higher than the actual diet of fishermen living around Lake Yojoa.

However toxicity for borrowing animals (e.g., worms, bivalves) and other benthic organisms, has been reported due to ingestion of sediments particles with high heavy metal contents (Bryan and Hummerstone 1978; Ireland 1977; Warren 1981). In addition, changes in physico-chemical conditions of the water sediment interface could cause a higher solubilization of the immobilized heavy metals.

The total amount of heavy metals in soils and sediments, as obtained via extraction with strong acids, does not give any indication of metal bioavailability. Sediment and soil samples must be extracted with water or NaNO₃ to release soluble and exchangeable metals from the solid matrices and the extracts can then be tested for

toxicity. Extraction of soils and sediments with NaNO_3 simulate well the bioavailability of heavy metals to terrestrial and, probably, aquatic plants (Haeni and Gupta 1984; 1986). However, the soluble and exchangeable pools may represent only a small fraction of the total metals associated with a solid matrix. For example, in a soil containing 1212 ppm of zinc, only 0.15 ppm was detected in NaNO_3 extract. Similarly, the total Cd content of ten soils varied between 0.14 to 6.1 ppm but the Cd content of NaNO_3 extract was always lower than 0.06 ppm (Haeni and Gupta 1986).

MetPAD, a bioassay kit was found to be useful for the rapid monitoring of heavy metal toxicity in sediment elutriates (i.e., water extract) from hazardous waste sites in Florida (Bitton et al. in press). In the case of Lake Yojoa the use of MetPAD bioassay in sediments was shown to be useful to predict the low bioavailability of heavy metals, as confirmed by the analysis of water and fish samples. This shows that, in most of the samples tested, heavy metals, as extracted with distilled water or sodium nitrate, are not bioavailable and little would be released into the water column.

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