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Research paper

# **Presence of heavy metals in the Jalpan de Serra reservoir, Querétaro, México**

# **Presencia de metales pesados en el embalse Jalpan de Serra, Querétaro, México.**

**Patricia Trejo Reséndiz1 , Marcela Susana Duhne Ramírez2** 

<sup>1</sup> Civil Engineer, Graduate School of Engineering, Universidad Autónoma de Querétaro, Querétaro, Mexico.∣<mark>©</mark> 0009-0005-6267-163X

<sup>2</sup> M.C. Environmental Hydrology, Graduate School of Engineering, Universidad Autónoma de Querétaro, Querétaro, Mexico. | @ 0000-0002-5332-5648 \* Patricia Trejo Reséndiz (paty\_uaq@hotmail.com)

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### *ABSTRACT*

*The study was conducted at the Jalpan de Serra dam, Querétaro, Mexico. In a mountain watershed with a history of artisanal mining activity in the upper part, runoff feeds the reservoir, transporting mining tailings. The Jalpan dam has been used for drinking water supply, agricultural irrigation activities and recreational purposes as a Ramsar site. The reason for the study has been the relevance and social impact of the reservoir sediments as a source of diffuse pollution. The objective was to determine the concentration of arsenic, cadmium and lead in the sediment and to evaluate the level of risk to human health and the environment. The methodology consists of the analysis by atomic absorption carried out in three sites sampled in the superficial layer of 10 cm depth, samples obtained with a PVC tube of 7 cm diameter, identified, preserved for transfer and digested with nitric acid. The results show mean arsenic concentrations of 4.278 mg/kg, cadmium 0.323 mg/ kg and lead 4.873 mg/kg. In conclusion, the sediment analyzed does not represent a risk to human health or the environment of the reservoir according to NOM-147-SE-MARNAT/SSA1-2004. This investigation demonstrates the lack of a policy or standard that establishes permissible limits for heavy metals in sediment.* 

*Keywords: Heavy metal, polluted sediments, mining tailings transport, water erosion.*

### **RESUMEN**

El estudio ha sido realizado en la presa Jalpan de Serra, Querétaro, México. En una cuenca de montaña con antecedentes de actividad minera artesanal en la parte alta, la escorrentía alimenta el embalse, transportando relaves mineros. La presa Jalpan se ha empleado para abastecimiento de agua de consumo humano, actividades de riego agrícola y fines recreativos como sitio Ramsar. El motivo de estudio ha sido la relevancia e impacto social que tienen los sedimentos del embalse como fuente de contaminación difusa. El objetivo ha sido conocer la concentración de arsénico, cadmio y plomo en el sedimento y evaluar el nivel de riesgo para la salud humana y del ambiente. La metodología consiste en el análisis por absorción atómica realizada en tres sitios muestreados en la capa superficial de 10 cm de profundidad, muestras obtenidas con un tubo de PVC de 7 cm de diámetro, identificadas, conservadas para su traslado y digeridas con ácido nítrico. Los resultados muestran concentraciones medias en arsénico de 4.278 mg/kg, cadmio 0.323 mg/kg y plomo 4.873 mg/kg. En conclusión, el sedimento analizado no representa riesgo para la salud humana o entorno del embalse según la norma NOM-147-SEMARNAT/SSA1-2004. Esta investigación evidencia la falta de una política o norma que establezca los límites permisibles de metales pesados en sedimentos.

**Palabras clave:** Metales pesados, sedimentos contaminados, embalse, erosión hídrica.

### **INTRODUCTION**

### **Water erosion**

Water erosion is the process by which soil is lost under the action of water, affecting soil fertility, and consists of three stages; soil detachment, transport and sedimentation (Ares & Varni, 2016). Erosion begins at the moment of contact of the water drop on the soil and the magnitude of the phenomenon depends on the size and speed of precipitation (Pizarro et al., 2010).

The variables that make erosion possible are: climate, vegetation, leaf litter, soil type, topography, flow velocity and land use. Water fall factors, precipitation temperature and storm intensity influence the main climate variable, and in the case of land use, the most problematic human activity in sediments is mining, due to its contribution of toxic elements to water bodies (Brea & Balocchi, 2010).

### **Heavy metals commonly found in reservoirs**

A study of metal and arsenic contamination in sediment has been carried out in three different dams; La Boquilla, Las Virgenes and El Granero in Chihuahua, Mexico, in each of the dams two samples have been extracted, randomly, in the four seasons of the year, using a PVC tube of 7 cm in diameter and one meter long, and each sample with 1. 5 kg of surface sediment (0-10 cm), for which one kilogram was used to obtain organic matter, measure pH, salinity and clay, and the remaining 0.5 kg was digested with concentrated nitric acid and hydrochloric acid in a 1:3 ratio, dried, crushed and homogenized, and analyzed for metals, As by atomic absorption spectrophotometer and Cu, Pb and Zn by optical plasma spectrophotometer. The concentrations observed for As and Pb did not change from one dam to another (P>0.05), Cu and Zn varied between dams (P<0.05), and for Cu and Pb they varied between seasons. The concentration ranges for each of the metals were for As from 13.25 to 18.05 mg kg-1, for Cu from 3.36 to 5.64 mg kg-1, for Zn from 105.54 to 130.66 mg kg-1, in the three dams the parameters were below the permissible limit, however, Pb exceeded the limit of 50 mg kg-1 recommended by the regulations (Hernandez et al., 2008).

Sepúlveda, (2015) conducted a biochemical study in the Suata reservoir, Venezuela, to determine heavy metals in sediment, water and fish. He extracted two sediment samples; one at the dam and the other at the tail of the reservoir, with a separation of 3,270 m distance, using the surface layer of the sediment (0-10cm) were identified with date, coordinates and depth. The sediment was sieved, dried and pulverized, then digested with nitric acid and hydrofluoric acid, entered twice in the microwave oven, and at the end of the digestion, it was neutralized with 20 ml of 5% boric acid, The metals Ca, Mg, Al and Si were analyzed by Atomic Absorption Spectrophotometer, and Cd, Cr, Cu, Ni, Pb, Zn, Co, V, Mn, Fe and Ti were analyzed by Atomic Emission Spectroscopy with Inductively Coupled Plasma. The results indicated that Mn and Zn with very high risk in contamination, Ni, Cd and Cr with medium risk, range obtained through the Risk Assessment Code (RAC).

The analysis of heavy metals in the Cerrillos de Ponce reservoir, Puerto Rico (Ortiz, 2019) was performed to know the presence and concentration of heavy metals, through a simple sampling in water from three sites within the reservoir. The sampled points were at the beginning, in the middle and at the outlet (zone A, B and C) during nine months, by means of the plasma induction method coupled by optical spectroscopy emission, where, silver (Ag), arsenic (As), chromium (Cr), lead (Pb), vanadium (V), cadmium (Cd) and zinc (Zn), exceeded the limit of permissible values established by the World Health Organization (WHO) and the U.S. Agency for Toxic Substances and Disease Registry. This study proved that the water level of the reservoir does have an impact on the concentration of heavy metals that exceed the limits of the applied standards.

### **Toxicology of heavy metals**

Arsenic (As) is naturally present in the air, water and soil, and by anthropogenic action in some foods, in dyes used in glass and ceramics, in metallurgy, mining, in the manufacture and use of insecticides, herbicides and fungicides. It is of grayish color of soft metallic aspect and it is easy to dissolve, by its characteristic without flavor, in the antiquity, it was used as a powerful poison, added in the drinks or foods of the victim; in small but constant doses, they cause weakness of the living being that consumes them. To measure the level of arsenic intoxication, four clinical forms are established; 1. Over-acute intoxication (evolves in hours).2. Acute intoxication (weeks): abundant vomiting, diarrhea, abdominal pain, burning sensation in the stomach, odor in breath and mouth fluids, headache, weakness and dizziness; if not treated in time, it causes renal, hepatic and cardiac damage.3. Subacute intoxication and 4. Chronic intoxication: constant intake of arsenic: digestive and nutritional disorders; (thinning, fatigue, lack of appetite, nausea, vomiting, diarrhea), catarrhal disorders (runny nose, headache and bronchial secretion), skin disorders (tanned tone with white spots, palmar and plantar hyperkeratosis that can evolve to epidermoid carcinoma, appearance of white lines on the nails) and neurological disorders (signs of "foot drop" and "claw hand") (Hernandez, 2018).

Lead (Pb) is a gray, soft heavy metal found in the earth's crust, mainly, in galena ores in the form of sulfide associated with other metals such as silver, copper, zinc, iron and antimony. It can be found in gasoline, manufacture and use of paints, pesticides, lead-soldered packaging, tableware and ceramics.

Long-term low-dose exposure through air, water or food causes chronic poisoning. The non-toxic blood concentration for an adult can be up to 10 µg/dl and in children measures should be taken when the concentration is 10 -14 µg/dl.

Ingestion may be by the respiratory route where metal fume or dust is absorbed by the lungs and concentrations retained in the body vary depending on particle size. Dietary intake: adults can absorb up to 30% of the proportion ingested, in the case of children, they absorb up to 50%.

Lead present in the blood is distributed to bones, teeth, liver, lungs, brain, spleen, kidney and has the capacity to cross the placenta. The means of disposal of some of the ingested lead is through feces and urine. Due to its similarity with calcium, lead interferes in several metabolic pathways in the mitochondria and interference with calcium in endothelial cells in brain capillaries produces a disruption in the intercellular junctions of the blood-brain barrier leading to brain edema. Renal alterations, intestinal alterations such as anorexia, constipation, vomiting and colicky pain may also occur. Reproductive health is affected by infertility in both sexes, spontaneous abortions, premature births and congenital anomalies (Ferrer, 2003).

Cadmium (Cd) has the characteristic of corrosion resistance and is therefore used for electroplating and coating of other metals, such as screws, locknuts, various aircraft parts and motor vehicles. Cadmium compounds can also be used as plastic stabilizers and pigments. In cell phones and other small devices it is present in rechargeable batteries.

Other uses of the compounds are: yellow and red pigments in plastics and dyes, colorants in pyrotechnics, photographic films, textile dyes and printing, manufacture of private mirrors, coating of electronic vacuum tubes, electroplating, glass hardening, among others.

Cadmium can be metabolized and accumulated through intestinal absorption. People with low iron reserves have the capacity to absorb up to 20% of the administered dose. By the pulmonary route through inhalation of tobacco smoke or exposure to cadmium in the environment. Metallothionein is a low molecular weight protein resulting from the ingestion of cadmium that has been lodged in the liver, this protein contributes to prevent cadmium ions from exerting their toxic effect, however, it is thought that renal failure is related to the decrease in the production of metallothionein. Importantly, some of the cadmium that enters the human body is excreted in the urine; however, the process of cadmium excretion is slow. The retention period of Cd varies from 7 to 30 years, allowing its accumulation and health effects.

Two levels of cadmium toxicity are considered; Acute: in concentrations higher than 1 mg/m3 in air, with symptoms of chemical pneumonitis and/or pulmonary edema, starting with flu or fever in a period of 1 to 8 hours after exposure. Food poisoning at concentrations greater than 15 mg/L with symptoms of nausea, vomiting, abdominal pain, diarrhea. The main sources of contamination in food are pots or pans with cadmium-based coatings or welds in hot or cold beverage machines. Chronic toxicity: mainly in occupational exposure to cadmium fumes or dust, affecting the respiratory tract, renal lesions and anemia. In very high concentrations, yellow stains on teeth and loss of sense of smell may be observed. In 1993 the International Agency for Research on Cancer (IARC) determined that cadmium should be considered carcinogenic to humans. (Nordberg, 2017).

### **Characteristics of the Jalpan de Serra Dam, Queretaro, Mexico.**

The Jalpan de Serra dam, Querétaro, Mexico, was built in the Jalpan riverbed in the 1970s, with a capacity of eight million cubic meters, in an area of 68 ha. Since its construction it has served as the main source of supply for agricultural, domestic, small-scale fishing, and recreational activities (Ramsar, 2003). The reservoir is fed by runoff from the upper parts of the basin, which is considered a mountain basin. The upper part of the basin has been used for years for artisanal mining, where tailings dams are usually located near the main riverbeds, and sediments have been exposed to transport by precipitation runoff. The average slope of the basin is 30%, which indicates that sediments are easily transported. Given the morphological characteristics, land use, and anthropogenic activities, it is possible that sediments with heavy metals are deposited in the Jalpan dam reservoir. The contaminating elements present in the sediments can be incorporated into the water chain and, consequently, into the trophic chain and bioaccumulation in living beings can cause irreversible damage due to intoxication. From the above, the present work aims to analyze the sediment of the reservoir to know the quality of water and soil in relation to the presence of heavy metals. Under this objective, a biochemical study is carried out in sediments to determine the concentrations of heavy metals in the Jalpan Dam reservoir, characterization of the basin and graphic representation of the pollutants in the reservoir.

### **METHODOLOGY**

Based on the bibliography consulted, three sampling points were defined, one at the beginning of the dam, the middle point and at the end of the dam, near the curtain as shown in Figure 1 and their respective geographic locations in Table 1. Samples were extracted at a depth of 10 cm, using a 7 cm diameter PVC pipe (Figure 2). The samples were extracted during the dry season in order to reach points of greater depth.

### **Figure 1: Location of sites to be sampled within the reservoir.**



Source: Own elaboration

The characteristics of the sample extraction site were as follows:

Sample 1: at the beginning of the reservoir with abundance of organic matter and vegetation and presence of flowing water (Figure 2). Sample 2: middle point of the reservoir with fine sediment, low presence of vegetation cover and low concentration of organic matter, saturated sediment near the water at rest (Figure 2.1).

Sample 3: very close to the outlet point of the reservoir (curtain) fine sediment and presence of sand in saturation, without organic matter or vegetation (Figure 2.3).

### **Table 1: Geographical location of sampled sites.**



Source: Own elaboration.

### **Figure 2: Sample extraction.**



Source: Own elaboration.



### **Figure 2.1: Sample 2 Figure 2.3: Sample 3**



Source: Own elaboration

Each sample was labeled with its respective geographic location and sample number (Figure 3).

### **Figure 3: Labeling and identification of samples.**



Source: Prepared by the authors.

The samples were placed in a cooler with ice to keep them at a temperature of approximately 4°C for transport and preservation (Figure 4).

**Figure 4: Sample preservation.**



Source: Own elaboration.

The samples were placed in the drying oven, each sample placed in a container and identified at a temperature of 35°C to achieve evaporation of the liquid (Figure 5).

### **Figure 5: Oven drying of samples.**



Source: Own elaboration.

After drying, they were crushed with the help of the mortar and stored in the desiccator to remove all moisture (Figure 6).

**Figure 6: Shredding and moisture extraction.**



Source: Own elaboration.

Once the sample was dry, crushed and homogenized, the quarting method was used to select 2 g of sediment for digestion. The digestion was carried out with nitric acid, hydrochloric acid, and was calibrated to 100 mL with ultrapure water (Figure 7).

**Figure 7: Digestion of samples.**



Source: Own elaboration.

After digestion, the samples were sent to the laboratory for reading in the Atomic Absorption Spectrophotometer (Figure 8).

# **Figure 8: Atomic Absorption Spectrophotometer.** um

Source: Own elaboration.

### **RESULTS:**

Analyzed samples were obtained the values of the concentrations of arsenic, lead and cadmium metals representative of the surface layer of 10 cm depth of the reservoir in the three points sampled in the dry season, is illustrated in Table 2.



**Table 2: As, Pb and Cd concentrations results**

Source: Own elaboration.

It can be observed that arsenic has a homogeneous behavior in the reservoir, with a coincidence of 96.93% between point one and point three, which show the limits of greatest difference of 0.134 mg/kg between them. This indicates that the distribution of arsenic within the reservoir does not have a specific point where the concentration is a red spot or indicative of excess accumulation of the contaminant.

Lead was found in higher concentration in the sample obtained at the midpoint of the reservoir and in lower amount in sample one which was obtained at the beginning of the dam, with a difference of 2,928 mg/kg, that is, sample one represents 53.61% of the concentration of sample two.

In comparison with Cadmium, which was found in lower quantity at point three (outlet) and in the rest of the points it was found in similar concentrations.

## **DISCUSSION**

It is important to mention that, in order to evaluate the permissible limits of metal concentrations in sediments of inland waters, in Mexico there is no specific law that dictates the maximum or minimum concentrations, it can be compared with NOM-147-SEMARNAT/SSA1-2004, Table 3 shows the permissible limits for the metals analyzed.

### **Table 3: Heavy metal concentrations for agricultural land use.**



Source: Own elaboration with information from NOM-147-SEMARNAT/ SSA1-2004

On the other hand, Table 4 shows the limits established in the Canadian Environmental Quality Guidelines (CEQG) for sediments of inland water bodies divided into two: the Interim Sediment Quality Guidelines (ISQG) in which it is expected that there will be no negative biological effects on the environment, otherwise the Probable Effect Level (PEL).

**Table 4. Permissible limits for metals in sediments established by the Mexican (NOM) and Canadian (CEQG) standards.**



Source: own elaboration with information from (LAINO GUANES, AND OTHERS, 2015).

The phytoremediation study by Jara Peña, et al. (2014) found that lead can be absorbed by plant roots, mainly by Fuertesimalva echinata. That is, the presence of plant cover influences the concentration of heavy metals, due to the fact that some plants have the function of bioremediation of the soil where they are found.

### **CONCLUSION**

Finally, it can be concluded that the concentrations of arsenic, cadmium and lead found in the sediment layer at a depth of 10 cm in the Jalpan Dam do not exceed the permissible limits in the applied regulations, that it is safe to use the analyzed layer for agricultural purposes (in case of de-silting) because it does not represent a risk to human health or to the flora and fauna that inhabit it. In future studies, a more exhaustive analysis can be carried out by strata at greater depth. With respect to the vegetation found in the study area, two predominant plant species, Acmella caulirhiza and Phyla lanceolata (Michx.) Greene, were identified, indicating an opportunity to carry out analyses to determine their phytoremediation capacity.

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