

# Probability of Heavy Metals Mobility from Dumped Sediments in a Quarry

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## ABSTRACT

Dregs from the former Texcoco Lake were used to build the new international Mexico City airport and pumped in a quarry. The dredged sediments could have heavy metals (HMs) capable of polluting water bodies. The study's objective was to evaluate the content of Cu, Zn, Cd, Ni, and Pb of the sediments deposited in the quarry, their transfer to the runoff water and the adsorption of Cu, Zn, Ni, and Pb in the subsoil. Other variables measured were water infiltration rate, HM in sediments, water runoff, and the HM adsorption in the subsoil. The infiltration rate in sediments is low ( $\leq 10\text{-}7$  cm/h). HMs in sediments are within the maximum permissible limits by Mexican regulations, for sewage sludge. The HMs in the runoff from the sediments are in the range of the Mexican regulations for the discharge into rivers and for irrigation purposes of agricultural soils. They are also within safe limits for irrigation use considered by FAO and EPA. The materials adsorption capacity of Pb ( $1250\text{ mg kg}^{-1}$ ), Zn ( $588\text{ mg kg}^{-1}$ ), and Cu ( $1250\text{ mg kg}^{-1}$ ) is higher than the concentration of metals in the runoff water, so the movement of HMs down into the subsoil is unlikely.

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## INTRODUCTION

Mining of materials for construction in open-pit mines is relatively inexpensive, but it causes conspicuous changes in ecosystems. Among its negative effects there is deforestation, habitat destruction, landscape change, rock fracturing from the use of explosives, dust generation, alteration of the site's hydrology, formation of large craters with risk of collapse (Green *et al.*, 2005, Korkmaz *et al.*, 2011).

Performing large civil works involves the removal of the superficial layer of the soil or unstable sediments for the foundation of the structures. For the construction of the new international airport in Mexico City (NAICM, the acronym in Spanish language) in the former Texcoco Lake, it was necessary to drag and transport large volumes of sediment to authorized confinements (GACM, 2014). The confinements are located 10 km away in the middle part of the Sierra Nevada that fed the lake. Due to the origin and management

of the excavation material, the place of its confinement and the concentrated volume, the following question arises: Could the sediments represent a source of heavy metals (HMs) that would contaminate the bodies of water that are used for human consumption and other activities such as agriculture? The confinement site corresponds to an exhausted quarry, adjacent to a tributary of the Texcoco River, of up to 65 m of depth, abandoned without rehabilitation. The appropriate use of these sinkholes as confinement sites could solve two environmental problems of strong impact in the zone, the rehabilitation of the quarry and the confinement of sediments, but could unleash a greater impact in the long term: underground water contamination.

The sediment from the former lake constitutes the superior clay formation (Anónimo, 2014). It has a very alkaline pH (Balderas *et al.*, 2006), deficient drainage, high content of salts and high rate of exchangeable sodium (Segura *et al.*, 2000). This sediment contains Ni, Cu, Mo, Pb (Morales-García *et al.*, 2020), Cr, Zn and V (Morton-Bermea *et al.*, 2009), whose origin is a combination of the open air conditions of the rock from the high parts of the basin, industrial activities and flow transport, among the most notable sources. The Fe, Pb, Cr, As, Cu, Zn, Cd, V, and Hg content was reported in sediments from other lakes (Vowotor *et al.*, 2014; Pejman *et al.*, 2015). The metals can be freed as a result of different processes, among them their physical alteration, which can increase their solubility and impact negatively the environment (Wu *et al.*, 2014). Vowotor *et al.* (2014) suggest the following potential for ecological risk: Cd > Hg > As > Pb > Cu > Cr > Zn.

The HMs of the sediment have low or null potential for lixiviation because they are united to stable mineral fractions in the soil (Balderas *et al.*, 2006). In an alkaline medium the mobility of metals is minimized, and this sediment has poor drainage, characteristic derived from its high content of smectites (Ortiz and Gutiérrez, 2015) and amorphous silica (Balderas *et al.*, 2006), as well as the lack of structure due to its high sodium content (Rowell, 1994).

In the confinement site, the impermeability of the bottom would favor rainfall runoff and cracking could give rise to a preferential flow of HMs towards water table layers, although it is unknown whether the site has cracks formed during the material's extraction. And, depending on its ability to sorb metals, it could continue its migration towards underground waters, since the potential of transference of HM contents in the sediments towards the water medium depends on their concentration and solubility (Kabata-Pendias, 2011).

Soluble HMs in the infiltration water can be adsorbed in the bottom of the confinement (Van der Perk, 2013) and with it, reduce the risk of contamination of underground waters. The adsorption in the soil-water interphase (Sparks, 2003) indicates the capacity of substrates to retain solutes (Appelo and Postma 2005), with which their mobility can be predicted. The best known models to simulate the isotherms are those by Freundlich and Langmuir (Roy *et al.*, 1992). The objective of this study was to evaluate the content of Cu, Zn, Cd, Ni and Pb of the sediments of the former Texcoco Lake and in the runoff water, and the sorption of Cu, Zn, Ni and Pb in the bottom of the confinement.

## MATERIALS AND METHODS

### Localization and Delimitation of the Confinement of Sediments

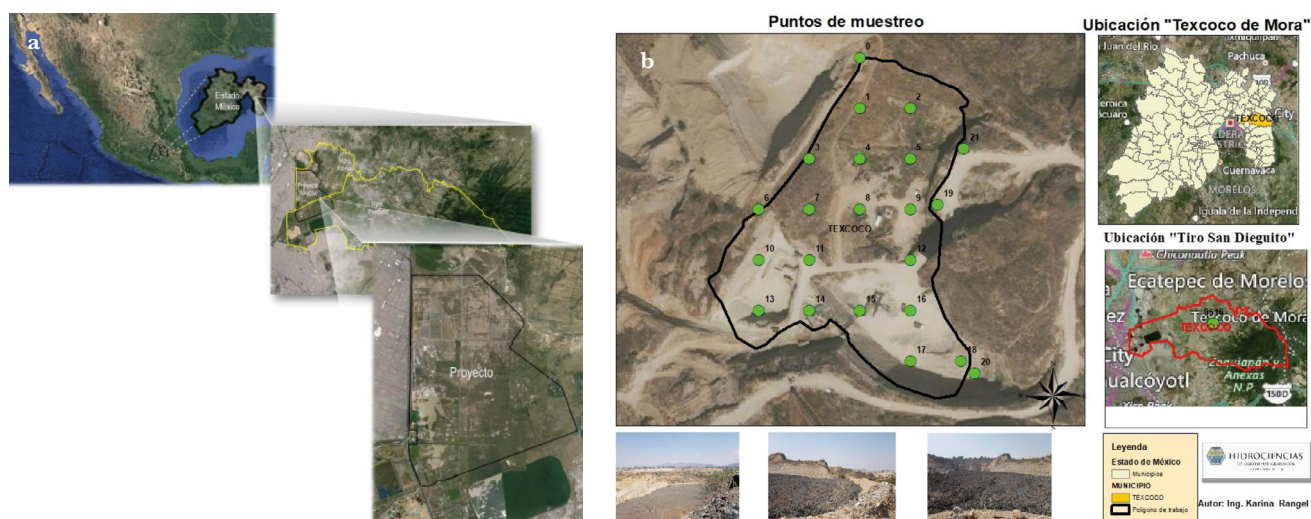
The site for confinement of the sediments is known as Tiro San Dieguito and it is located in San Dieguito Xochimanca, Texcoco, Mexico at 19° 29' 53.08" N and 98° 49' 42.36" W of latitude and longitude, respectively (Figure 1). This is a mine quarry of non-metallic rocky material that was abandoned some years ago. It has a surface of 2.49 ha and down to 66 m in its deepest part. With the help of a total station (Sokkia) and satellite image, the volume of the sediments in the confinement was delimited and obtained, for which the QGIS software was used (QGIS Development Team, 2009). The weight of the confined sediment was determined based on its volume and apparent density ( $D_a$ ) obtained by the procedure described by Rowell (1994).

### Permeability Test in the Sediments

Permeability (as infiltration speed) was measured using the procedure proposed by Siltecho *et al.* (2015). Waterproof PVC tubes were used (5 cm of diameter by 40 cm of length), to obtain unaltered samples in the bottom of the quarry (Figure 1b), 30 cm deep; 2 L of rain water was added to measure the infiltration at 24 and 48 hours.

### Sampling and Cd, Cu, Zn, Ni and Pb analyses in the Sediments

Through random sampling of the confinement area (2.49 ha), 19 samples (2 kg) of sediment were collected from the superficial layer of 0-20 cm. The samples were dried at 35 °C for 72 h and sifted in a size 10 sieve (2 mm) according to the NMX-AA-132-SCFI-2006 (SE, 2017). The HMs were determined through digestion of the sample with nitric acid according to the NOM-004-SEMARNAT-2002 (SEMARNAT, 2003) and reading was made in an inductively coupled plasma spectrophotometer (ICP-OES) Varian 725-ES model (Agilent Technologies, 2012).



**Figure 1.** a) Location of the NIAMC (SCT, 2014) and b) sampling points on the quarry used as disposal area.

### **Sample and Cd, Cu, Zn, Ni and Pb analyses in Runoff Water**

The runoff water of the sediment was sampled in the quarry during the rainfall period (May to August 2018). After each rainfall, simple samples from the surface of the sediment were obtained in the zones flooded, and with these a compound sample was obtained according to the NMX-AA-003-1980 (SECOFI, 1980). The pH was determined from the samples potentiometrically (Rowell, 1994). Later, they were acidified (pH<2) through the addition of nitric acid, kept at 4 °C and filtered (NMX-AA-051-SCFI-2016; SE, 2016a). The quantification of metals was done with ICP-OES. The pH and the EC were determined by the procedures described previously.

### **Sampling and Characterization of the Subsoil of the Quarry**

Previous to removing the sediments, samples were obtained from the subsoil exposed in the mine's sinkhole at a depth of 0-20 cm. The samples were prepared for their characterization according to the NMX-AA-132-SCFI-2006 (SE, 2017), characterized, and the determinations of Cd, Cu, Ni, Pb and Zn were made with the procedures described previously. In the sediments and the material from the bottom of the sinkhole, the pH, electric conductivity (EC), capacity for cationic exchange (CCE), sodium adsorption ratio (RSA), apparent density (Da) and texture following the procedures described by Rowell (1994) were measured.

### **Adsorption of Heavy Metals in the Subsoil**

In balance experiments, the adsorption of HM was estimated (Roy *et al.* 1992). In reactors of 50 mL, 5 g of subsoil were added with increasing concentrations (50, 100, 200, 500, 1000 and 2000 mg/L) of HM with electrolytic solution of CaCl<sub>2</sub> 0.01 M to maintain the ionic strength, in a 1:4 soil-solution rate. The solutions were prepared with the following salts: Ni(NO<sub>3</sub>)<sub>2</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, ZnSO<sub>4</sub>·7H<sub>2</sub>O and CuSO<sub>4</sub>·5H<sub>2</sub>O. The isotherms of Cd were not determined since the concentration of this element in the sediments is very low. The interval of concentrations was chosen in function of the change in the slope of the isotherms, although avoiding for precipitation of the element to take place. The suspension was agitated during 6 h at 120 rpm at 20 °C, until equilibrium concentration. It was centrifuged at 2200 rpm for 10 min and the supernatant was filtered with Whatman 42 paper. The equilibrium concentration of Ni, Pb, Zn and Cu was determined in atomic absorption equipment by the flame technique (SE, 2016a). The pH was measured during equilibrium. The adsorption isotherms were obtained when graphing adsorption in function of the equilibrium concentration. The adjustment of the Freundlich and Langmuir equations was evaluated using the linear form of each equation (Jain *et al.*, 2004). The respective constants and isotherms predicted by each equation with the adjustment constants were calculated, to compare with the experimental isotherms.

$$\text{Freundlich equation } \frac{x}{m} = K_F C^{1/n}$$

Where:  $\frac{x}{m}$  = adsorption per unit of mass.  $K_F$  is Freundlich's distribution coefficient,  $n$  is the correction factor, and  $C$  is the equilibrium concentration of the adsorptive.

$$\text{Langmuir equation } \frac{x}{m} = \frac{K_L M C}{(1 + K_L C)}$$

Where:  $\frac{x}{m}$  = adsorption per unit of mass.  $K_L$  is the constant related with the retention force,  $M$  is the maximum adsorption and  $C$  is the equilibrium concentration of the adsorptive. To ensure the quality control of the data and the repeatability of the analyses, the experiments and analyses were made by triplicate. Certified standards were used (Purity) for the preparation of calibration curves of the equipment.

## RESULTS AND DISCUSSION

### Delimitation of the Confinement of Sediments

In the quarry, andesitic limestone predominates, which are igneous volcanic rock (tephra) fragments solidified at some point of the volcanic eruption, whose mineral composition is similar to the andesitic rock and size smaller than 4 mm (SGM, 2002). Until June 2018, 1 074 960 m<sup>3</sup> of sediments had been deposited in the confinement site, corresponding to 1 096 459 kg of sediment, taking as reference the average apparent density.

### Permeability of the Sediments from the Former Texcoco Lake

The sediment presented null to extremely low hydraulic conductivity (Hazelton and Murphy, 2007) during the trial that lasted 48 hours. In determinations made in situ with sediments of the former Texcoco Lake, López *et al.* (2016) reported very low permeability (of 10<sup>-3</sup> to 10<sup>-6</sup> cm/s) in the hard layer of the sediment, whose thickness varies from 30 to 32 m. Tarín and Velázquez (1986) found that the hydraulic conductivity is <0.1 cm/h, even lower than the one determined in this study. The poor permeability is attributed to the lack of structure (Segura *et al.*, 2000; Carranza, 2018) and the content of smectite, which expands and closes the porous spaces when hydrated (Musso *et al.*, 2017). Therefore, a low probability of metal lixiviation is considered. However, under conditions of cracking, not studied in this study, the transference of metals to greater depths (reaching underground water) would be a potential risk.

### Heavy Metals in the Sediment

Due to the values of pH, EC and SAR, the sediment is classified as strongly alkaline, very strongly saline, and with high sodium concentration compared to calcium and magnesium (Hazelton and Murphy, 2007; SEMARNAT, 2003). This is an impediment for the development of many cultivated plant species (Sparks, 2003) and can induce the degradation of the soil per salinization (Table 1).

In contrast to what was reported for other lake areas (Morales-García *et al.*, 2020), and in sediments from other lakes (Luo *et al.*, 2008), the HM concentrations are compared with the limits established in national and international regulations; the HMs of the sediments are within the maximum permissible limits for their use with agricultural, forestry, and soil improvement purposes, which includes their urban use with direct public contact during their application, and were classified as excellent according to

**Table 1.** Heavy metals, pH, electrical conductivity (EC), cation exchange capacity (CIC) and sodium adsorption ratio (SAR) in the disposed sediment, and maximum permissible limits in the nation regulation for aquatic life protection in North-America.

	Cd	Cu	Ni	Pb	Zn	pH	CE dS/m	CIC cmol <sub>c</sub> /kg	SAR
	mg/kg								
Maximum	0096	1.91	0.31	1.7	0.88	10.4	10.3	16.2	733
Minimum	ND	7.45	1.98	7.29	12.62	10.9	97.3	27.1	16772
average <sup>1</sup>	0.03±0.03	3.66±1.35	0.51±0.36	2.04±1.32	2.47±2.63	10.7±0.15	70.9±23.42	22.6±2.5	4790±4119
NOM-004 <sup>2</sup>	39	1500	420	300	2800				
NOM-147 <sup>3</sup>	37	--	1600	400	--				
GPCS <sup>4</sup>	0.6	35.7		35	123				
NEP <sup>4</sup>	3.5	197		91.3	315				
NF <sup>5</sup>	0.1-0.3	10-25	9.9	4-17	7-38				
CP <sup>6</sup>	0.38	32	15	30	94				

n=19 No. of samples.

<sup>1</sup> Average ± deviation standard.

<sup>2</sup> Mexican Official Regulation 004-SEMARNAT-2002 (SEMARNAT, 2003).

<sup>3</sup> Mexican Official Regulation-147-SEMARNAT/SSA1-2004 (SEMARNAT, 2004).

<sup>4</sup> GPCS=Sediment quality guidelines for the protection of aquatic life (CCME, 2019a).

<sup>5</sup> Background levels for NOAA (Buchman, 2008).

<sup>6</sup> Probable concentration for 20% toxic doses (Field *et al.*, 2002), NOAA screening quick references Tables (Buchman, 2008).

the NOM-004-SEMARNAT-2002 (SEMARNAT, 2003). This implies that the metals have a low risk of entering the trophic chain through the absorption by plants. The concentrations are found below the maximum limits permissible of contaminated soils according to the NOM-147-SEMARNAT/SSA1-2004 (SEMARNAT, 2004) and of metals in sediments to protect the aquatic life of bodies of fresh and marine water established in the Canadian Guide and United States legislation. They are also considered from normal (Cd, Ni and Pb) to adequate (Cu and Zn), according to the NOM-021-SEMARNAT-2000 (SEMARNAT, 2002). In reference to the values compiled by Kabata-Pendias (2011) for natural soils, the Cu and Zn concentrations from the samples are considered normal.

### Heavy Metals in Runoff Water

The pH (9.7) is alkaline and it is not considered adequate for irrigation water (Bastian and Murray 2012). The EC present in the runoff water was 76 dS m<sup>-1</sup>, and exceeds the acceptable value for irrigation water in agriculture (SEMARNAT, 1997) and therefore it is not adequate for the development of crops (Ayers and Westcot, 1985), due to its high content of soluble salts (Table 2). It has been argued that the runoff water quality is of great importance, since the impermeability of the confinement (Ortiz and Gutiérrez, 2015) favors leaching and the leachate could contaminate the intermittent water courses that exist in the zone. The deposits on the margin of a tributary of the Texcoco River can have serious effects for soils downstream.

**Table 2.** Water soluble metal concentrations in leachates and permissible concentrations.

	Cd	Cu	Ni	Pb	Zn
	mg/L				
Average <sup>1</sup>	0.01	0.06	0.09	0.36	0.13
DE <sup>2</sup>	0.009	0.047	0.086	0.254	0.044
NOM-001 <sup>3</sup> soils	0.05	4	2	5	10
NOM-001 <sup>3</sup> rivers	0.2	4	2	0.5	10
FAO <sup>4</sup> irrigation	0.01	0.2	0.2	5.0	2.0
EPA <sup>5</sup> irrigation	0.01	0.2	0.2	5.0	2.0
GCA <sup>6</sup> irrigation	0.005	0.2–1.0	0.2	0.2	1-5

<sup>1</sup> leachate sampling after rain (n=5), April 27, may 21, June 6 and 12 and July 2019.

<sup>2</sup> DE, Standard deviation.

<sup>3</sup> Mexican official regulation-001-SEMARNAT, monthly average (SEMARNAT, 1996).

<sup>4</sup> Maximum concentration in irrigation water (Ayers y Westcot, 1985).

<sup>5</sup> Maximum concentration in irrigation water (Bastian y Murray, 2012).

<sup>6</sup> Water Quality Guidelines for the Protection of Agriculture, Canada (CCME, 2019b).

Cadmium, Cu, Ni, Pb and Zn are lower than the maximum permissible limits of contaminants in residual water discharges in water and soil, and in its use for agricultural irrigation established in the NOM-001-SEMARNAT-1996 (SEMARNAT, 1997). Cadmium and Cu are within the maximum permissible limits to spill residual waters into the urban drainage systems. Likewise, the HM values are within the limits that are considered safe for the protection of agriculture established by the Food and Agriculture Organization of the United Nations (FAO; Ayers and Westcot, 1985); the United States Environmental Protection Agency (EPA; Bastian and Murray, 2012), and the Canadian Council of Ministers of the Environment (CCME, 2019a). Only the levels of Cd and Pb slightly exceed the safe limit (CCME, 2019b), although it should not be forgotten that concentrations in pristine water are of the order of micrograms per liter.

The low values of soluble metals determined in the runoff water are congruent with the concentrations of the sediments from the present study. Balderas *et al.* (2006) reported that Cu, Pb and Zn from an agricultural soil near the extraction zone of the sediments of this study are adsorbed in clays and oxides, so they have low solubility, and this agrees with the reports already mentioned previously for lake sediments.

### Characteristics of subsoil of the Confinement

The rock base where the sediments were deposited is the sinkhole bottom of the mine of rocky materials is a compacted and dense material, alkaline and with high EC (Table 3). According to its C.I.C. it is classified as normal, deficient and low, respectively; due to its strongly alkaline pH, and based on EC and RAS, it is moderately saline and with high rate of sodium absorption (SEMARNAT, 2002). Likewise, it has a low organic matter content (1.96%) and a high proportion of sand (62%) compared to silt (22%) and clay (16%), which is why it is classified as loam-sandy. These characteristics make the quarry unfavorable for good plant development, so in order to rehabilitate it, corrections are required to

**Table 3.** pH, electrical conductivity (EC), cation exchange capacity (CEC), and heavy metals in the subsoil of the disposal facility.

Concentration	Cd	Cu	Ni	Pb	Zn	pH	CE dS/m	C.E.C. cmol <sub>c</sub> /kg
	mg kg <sup>-1</sup>							
Máximo	0.02	0.2	0.23	0.61	0.49	10.1	11.9	2.59
minimum	DL	0.09	0.13	0.18	0.22	9.65	1.21	1.56
Average	0.02	0.14	0.16	0.39	0.35	9.72	5.16	1.96
DE*	0.006	0.081	0.05	0.21	0.26	0.31	5.86	0.54

<sup>a</sup>LD=Below detection limit. <sup>b</sup>DE=Standard desviation. n=4 replicates.

improve its agronomic characteristics. The concentrations of HMs measured are below the maximum permissible limits of contaminated agricultural soils, according to the NOM-147-SEMARNAT/SSA1-2004 (SEMARNAT, 2004).

### Sorption of Ni, Cu, Pb and Zn

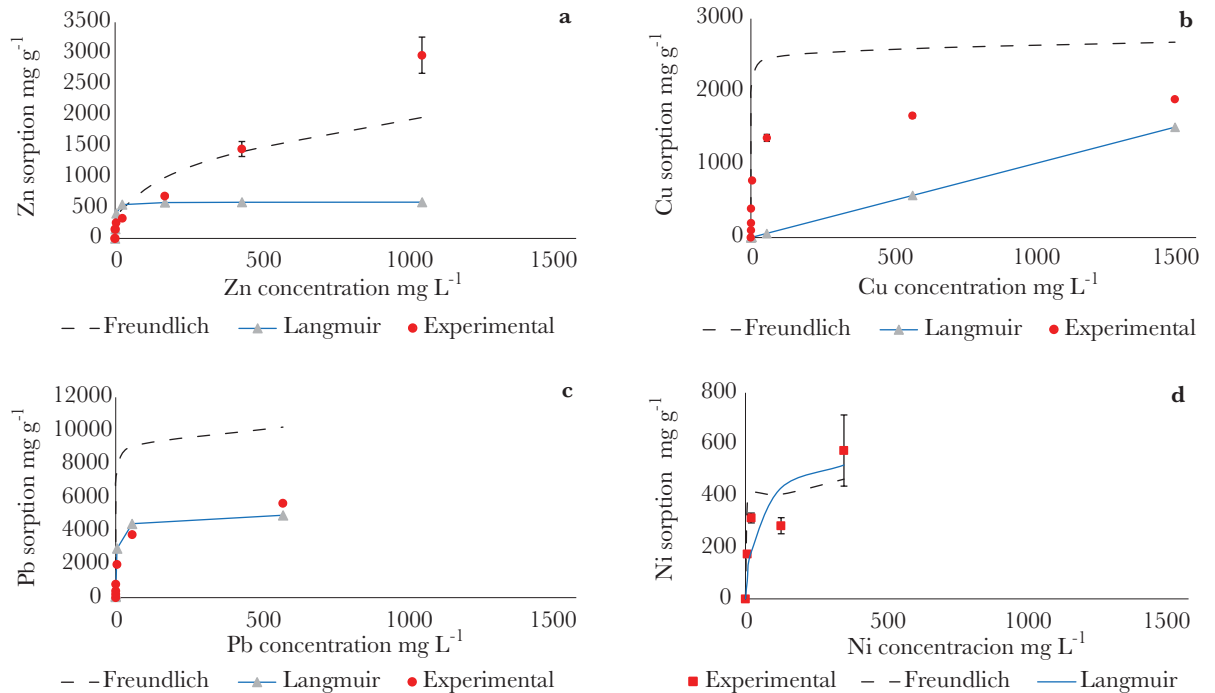
The subsoil from the quarry has low permeability; however, under occasional conditions of cracking and superficial runoff, an extreme situation can be foreseen, in which the percolation water drags high concentrations of HMs, and the possible transference to the base of the confinement and underground waters; this is why the capacity of sorption of HMs was determined in confinement materials, which could be a filtrating barrier for the transport of metals towards the aquifer.

Sorption is very high, as can be observed in the strong slopes of the isotherms at low equilibrium concentrations, to then decrease to high concentrations (L Curve, Sparks, 1995; Figure 3), which indicates a relatively high affinity of the substrate to metals at low concentrations, and decreases as the concentration increases and the specific surface of the adsorbent is saturated.

The slopes of the Zn and Pb isotherms remained high, although they decreased as the concentration increased. The slope of the Cu isotherm was asymptotic since its slope is high at low concentrations and then approximates zero. The slope of the isotherm of Ni decreased when increasing the concentration. The isotherm that best describes the behavior of Zn is that of Freundlich (Figure 2a), and this agrees with Cortés *et al.* (2015) since a good adjustment was observed to the adsorption of Zn in andisols, vertisols and humic acids.

In the case of Cu neither of the two isotherms described appropriately the tendency of the isotherm, but at high concentrations the most proximal was Langmuir's (Figure 2b), which agrees with the report from other authors who reported that the Langmuir (Abdelhamid *et al.*, 2012) and Bourliva *et al.*, 2015) and Redlich-Peterson isotherms provided the best adjustment for Cu (Han *et al.*, 2006). The Langmuir isotherm described well the retention of Pb (Figure 2c). This agrees with Melichová and Hromada (2013), who found that Langmuir's isotherm explains the behavior of Pb and Cu using natural bentonite as adsorbent. Salem and Akbari-Sene (2011) obtained better adjustment with Langmuir for Pb in zeolite-kaolinite-bentonite adsorbent.

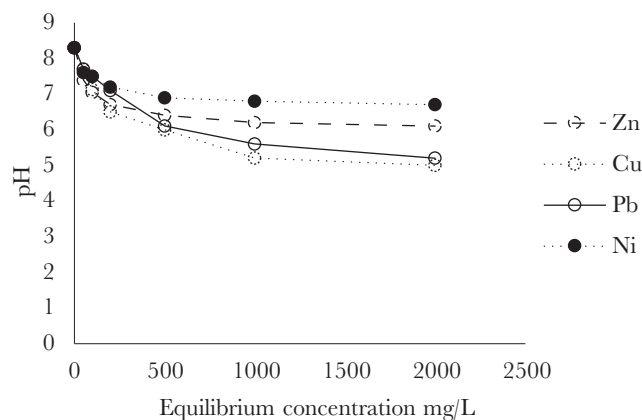




**Figure 2.** Experimental and simulated (using Langmuir and Freundlich equations) sorption isotherms of a) Zn, b) Cu, c) Pb, and d) Ni in the subsoil of the disposal facility.

Nickel adsorption was well fit by Freundlich's equation (Figure 2d). The divergence in the sorption at intermediate concentrations can be the result of joint processes of adsorption, precipitation and change of surface in the adsorbent by the alkaline pH (Wang and Cheng, 2009).

When the equilibrium concentration of metals was increased, there was a decrease of the pH (Figure 3), which implies that chemical sorption took place (chemisorption) in the subsoil, characterized by liberation of hydronium ions (Sparks, 2003). This implies a more stable adsorption. However, Bradl (2004) mentions that the pH in the solution controls the sorption processes, because the hydrogen ions are constituted in an adsorbent, strongly competitive, and affected by the presence of functional groups. The sorption of cations



**Figure 3.** The pH at the equilibrium solution of the Zn, Cu, Pb, and Ni isotherms.

tends to be favored for pH values higher than 4.5, and the sorption of anions prefers a low value of pH between 1.5 and 4 (Tejeda-Tovar *et al.*, 2015). Measuring the pH is important since Chaudhurib *et al.* (2014) mentioned that a reduction in the pH can unleash the transference of HMs from the adsorbent to the equilibrium solution.

Wang *et al.* (1997) concluded that the percentage of  $\text{Cu}^{2+}$  adsorbed, in most of the sediments studied, reached 100% after reaching a pH of 8.5. At a high pH the forms of Cu are more stable and there is higher adsorption in the residual fraction (Balderas *et al.*, 2006). Kaya and Ören (2005) point out a fast removal of Zn in the equilibrium, when the pH was higher than 7 and, according to Jain *et al.* (2004), the degree of adsorption of Zn increased with an increase of the pH. Bourliva *et al.* (2015) point out that the adsorption of Pb, Cu and Ni increases with the pH. It is suggested that it would be necessary to break the buffer capacity of the adsorbent to reduce significantly the pH. It is likely that the adsorption of the HMs reduces the possibilities of their lixiviation to the lower layers.

The maximum Cu, Pb, and Ni absorption could be estimated, since the slope tends to zero when increasing the equilibrium concentration (Table 4). The capacity for adsorption is higher than the concentration observed in the muds deposited in the confinement. A maximum in the sorption of Zn was not observed, for an asymptote curve was not generated in the graphic representations.

The readings of metals in the filtered supernatant were made when reaching the equilibrium, without controlling the pH or any other parameter as is done in some studies about adsorption (Musso *et al.*, 2017). The pH of the adsorptive medium influences the behavior of the metal and its solubility, generally increasing with the rise in the concentration of hydrogen ions and influence of the intensity of the reduction-oxidation reactions (Appelo and Postma 2005). Elbana *et al.* (2018) reported that the soils with high content of organic matter and with alkaline pH show a strong adsorption for Cd, Cu, Ni, Pb and Zn, due to the presence of carbonate; however, in complex systems, as in the present study, it is not possible to differentiate adsorption from precipitation of insoluble forms.

## CONCLUSIONS

The concentrations of Cd, Cu, Ni, Pb and Zn from the sediment of the former Texcoco Lake confined in the quarry were within the maximum permissible limits by the Mexican laws, applicable to residual water muds for use. However, SAR, EC and pH are limiting factors for the development of plant species with low adaptation to salinity and alkalinity.

**Table 4.** Zn, Cu, Pb, and Ni adsorption fitting parameters to the Langmuir and Freundlich equations on the subsoil of the quarry.

Metal	Langmuir			SqMin.	Freundlich			SqMin.
	M (mg/ g)	$K_L$ (L/mg)	$R^2$		$K_F$ (mg/ L /g)	1/n	$R^2$	
Zn	588	0.54	0.76	6.48	141.3	0.37	0.92	1.13
Cu	2000	0.07	0.99	3.87	354.6	0.26	0.89	8.56
Pb	5000	0.133	0.99	2.28	808.5	0.29	0.93	13.51
Ni	580	0.021	0.88	0.05	137	0.191	0.452	0.07

SqMin. Square minimums  $\times 10^6$ .

The concentrations of HMs in the runoff water are within the acceptable limits established by the Mexican laws for the discharge of waters into rivers and the soil for irrigation; they are also within the safe limits for irrigation proposed by FAO and EPA. However, the pH and EC would limit their use in irrigation. Considering Freundlich and Langmuir's adsorption isotherms, the material from the subsoil of the confinement sorbs metals following the decreasing affinity order:  $Pb > Zn > Cu$ . The capacity for adsorption of Pb, Zn, Cu and Ni in the materials from the bottom is higher than its concentration in the runoff water.

The materials from the bottom present low Cd, Cu, Ni, Pb, and Zn concentrations, poor fertility and high pH values. These last characteristics anticipate their low capacity to support wild vegetation or cultivated normally. However, there is still the need to evaluate the capacity to liberate the metals adsorbed, desorption, which could be increased if the pH or the content of salts varies in the system.

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