

Original Research

Changes in the Concentration of Trace Elements and Heavy Metals in El Chichón Crater Lake Active Volcano

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Abstract

The crater lake of El Chichón active volcano represents one of the most important extreme ecosystems in the world due to its high temperatures, low pH and the appearance of high concentrations of heavy metals because of volcanic activity. The latter is of great importance in nearby volcano sites due to heavy metal pollution, which is one of the worst types of environmental problems in the world. In this study, the concentration of heavy metals was evaluated in soils and sediments from different sections in the crater lake of El Chichón volcano. Representative samples were collected from four sediments and soils in 2015 and 2017. These samples were analyzed for 20 metals by inductively coupled plasma-optical emission spectrometry (ICP-OES). The most abundant elements in sediments of the crater lake of “El Chichón” volcano were Fe, Na, Si, Ca, K and Al and not found in soil samples. Be and Tl were more abundant in the soil, but the concentration of Se was higher in soil without showing statistically significant differences. Principal component analysis (PCA) showed that the abundance of metals was influenced by sample type. That is, a higher concentration of heavy metals and trace elements was found in volcanic sediments as compared to soil samples. This difference may be related to metals originating from the magma, which is partially transported in the water stream that gives way to the volcano lake. The most toxic heavy metals identified and quantified in high concentrations in crater soils and sediments were As and Cd. This study suggests that sediments and soils of El Chichón crater lake could be an important source of heavy metals and toxic elements such as As and Cd.

Keywords: active volcano, heavy metal toxicity, ICP-OES, extreme environmental, El Chichón volcano

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Introduction

Volcanoes are a natural source of gases that gives shape to our atmosphere, and they are also extreme environments on Earth. They also emit gases (water, sulfur, and carbon), non-metallic elements, and volatile metals. These play an important role in volcanic activity, in the atmosphere and in microorganisms present in these geothermal systems [1]. The abundance of Heavy Metals (HM), high temperatures, and low nutrient bioavailability favor the development of microorganisms extremophiles [2].

The soil and sediments found in volcanic environments are basic components of biogeochemical systems. Microbial communities have been influenced by geochemical parameters in volcanic lakes, due to microorganisms interacting with the water and sediments [3, 4]. Consequently, toxic components (e.g., heavy metals) can present levels of ecotoxicity and environmental hazards. In addition, these components interact in dissolution, absorption and desorption processes, causing an impact on the surrounding biological components, such as microorganisms and plants [3].

Mexico is one of the countries with the highest volcanic presence in the world, highlighting the presence of the Chiapanecan Volcanic Belt (CVB) [5-7]. El Chichón is an active volcano that belongs to the CVB. In 1982, El Chichón volcano presented the most important eruptive process in Mexican history [8], an eruption that resulted in the formation of a crater lake of $1.4 \times 10^5 \text{ m}^2$ [9]. For this reason, El Chichón has been the most studied volcano of the CVB in terms of hydrology, geothermal potential, geophysics and geological evolution [10-16].

It is known that metals in crater lakes are related to volcanic emissions, as there is a high presence of heavy metals, such as Fe, Pb, Cu, Zn, Cd, Hg and Al, as well as non-metallic elements such as As, Li, and B [17-20]. These metals can be related to the metabolic activity of the microorganisms present in these extreme environments [2, 21]. Recently, the diversity and abundance of bacteria present in the sediments of El Chichón volcano lake was reported [21]. However, there are no reports on the variation in heavy metal content in sediment and soil in and around the crater lake. Thus, the objective of this study was to analyze the changes in levels of heavy metal in sediment and soil in El Chichón crater lake volcano in the years 2015 and 2017.

Materials and Methods

El Chichón volcano is located in the mountainous region northeast of the state of Chiapas, Mexico, with coordinates $17^{\circ}21'31.0''\text{N}$ - $93^{\circ}13'39.9''\text{W}$. This system forms part of the CVB. El Chichón is a stratified volcano with a maximum elevation of 1100 m a.s.l. [16, 21]. After the eruptive process in 1982, a crater lake was formed in its interior, with an estimated area

of approximately $1.4 \times 10^5 \text{ m}^2$ [22, 23]. The geochemical composition, shape and depth of the crater lake have been changing continuously since its formation [10]. Temperatures ranges between 43 and 95°C and pH values are between 2 and 6 [21].

Sampling of Volcanic Sediments and Soil

Samples of volcanic sediment, crater lake and soil were collected from the periphery of the lake in 2015 and 2017 (Fig. 2). The samples were collected in triplicates and were placed in 50 mL sterile conical tubes. In order to preserve the sample integrity, samples were flash-frozen in liquid nitrogen. These were later stored and transported to the Molecular Biology laboratory, where they were kept at -80°C until use [21].

Physicochemical Characterization and Heavy Metals Determination

Temperature and pH were measured *in situ* with the HACH multiparameter model HI-98128 (Merck, Kenilworth, NJ, U.S.A.), according to the procedure described by Rincón-Molina et al. (2019) [21].

Heavy Metals Determination

Sediment and soil samples were dried under vacuum for 24 hours at 40°C at a pressure of 0.05 MPa in a JEIO-TECH oven. Subsequently, the samples were crushed to a particle diameter of 0.049 mm. After size homogenization, acid digestion of soils and sediments were carried out by using Method 3050B reported by the EPA (Environmental Protection Agency). Briefly, 300 mg of each sample were treated with 9 mL of HNO_3 , 1 mL of H_2O_2 and 1 mL of HCl, then heated to reflux at 180°C for 2 hours in order to achieve total oxidation of organic matter. Heavy and total metals were measured by inductively coupled plasma-optical emission spectrometry (ICP-OES) on an Optima 7000 PerkinElmer spectrometer [24, 25]. All metallic element analyses were recorded as averages of triplicate measurements.

Statistical Analysis

The significant differences between the physicochemical characteristics of the sediments were determined by means of Analysis of Variance (ANOVA), which was performed with the software StatGraphic Centurion (version 16.1.18). For the multifactorial analysis of heavy metals, the Rstudio statistical development environment was used [26].

Results and Discussion

El Chichón volcano is a mountain with a well-defined geomorphological structure with variable

Table 1. Description and characteristics of the study samples.

Name	Sampling date	Geographic Localization	Temperature	pH
Sediment 1	Feb. 15	17° 21' 32.79'' N 93° 13' 40.30'' O	50°C	5.8
Sediment 2	Feb. 15	17° 21' 34.28'' N 93° 13' 39.26'' O	65°C	5.5
Sediment 3	Feb. 15	17°21'36.81''N 93°13'39.03''O	90°C	5.1
Sediment 4	Feb. 15	17°21'39.23''N 93°13'39.34''O	92°C	2.9
Sediment 1	Feb. 17	17°21'33.77''N 93°13'39.50''O	65°C	5.1
Soil 1	Feb. 15	17°21'30.14''N 93°13'38.70''O	28°C	6.1
Soil 2	Feb. 15	17°21'30.64''N 93°13'38.76''O	30°C	6.5
Soil 1	Feb. 17	17°21'31.86''N 93°13'37.89''O	28°C	6.0

hydrothermal manifestations over time, which are dependent on natural climatic and magmatic activities. This study surveys the current scenario of changes presented in physicochemical characteristics, which highlights the importance in establishing good safety practices and environmental impact monitoring.

Samples and *in situ* Parameters

In 2015, four sediment samples and two soil samples were collected. Two years later (2017), one sediment sample and one soil sample were collected from the same study site. The main physicochemical parameters of these samples are shown in Table 1.

The temperature values in the soil ranged from 28 to 30°C between study years. The highest temperatures were found in sediment samples, which ranged between 50-92°C for 2015 and with a mean value of 65°C for 2017. The volcanic activity at El Chichón volcano in

1985 gave rise to the formation of a hydrothermal lake [9, 16, 22], rich in sulfur [10, 27]. Sediment 1 had an increase of 15°C, as compared to previous years. This may be due to an increase in volcanic activity and greater abundance of sulfur species, which are widely related to the pH values of this study, which were slightly more acidic [10, 16, 22].

The temperature in the soil remained constant. However, the temperature corresponding to sediments presented variability. The changes are related to volcanic and hydrothermal manifestations of El Chichón volcano, which may be related to temperature variations, depending on the study year. It was observed that there is no difference among pH values in soil according to the year of study. However, there are slight variations in the pH of soils 1 and 2 studied in 2015. This may be due to the presence of metals and ions in these soils that are found in different geographical locations of the El Chichón volcano.

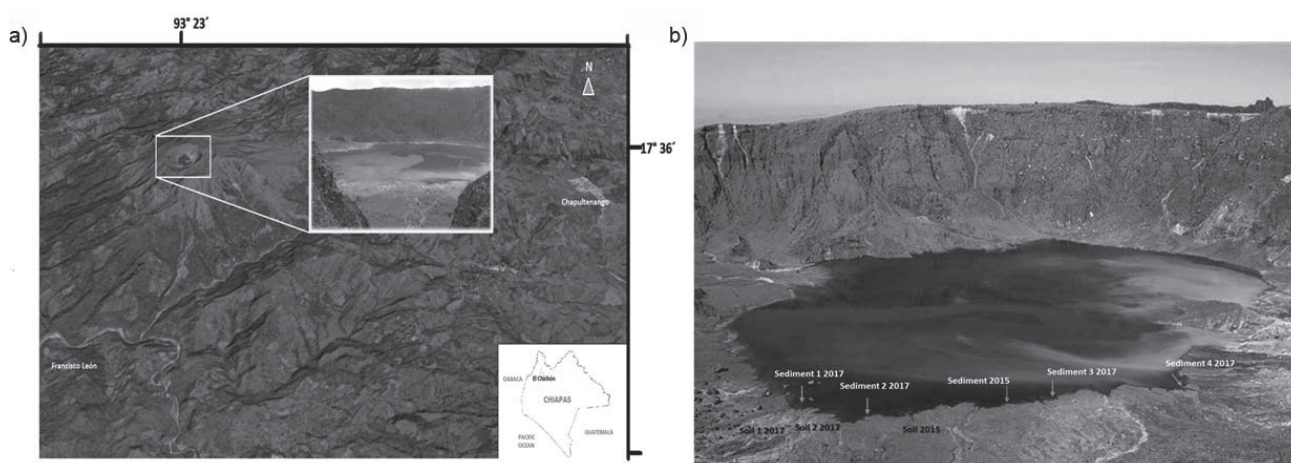


Fig. 1. Geographic localization of study site. a) El Chichón active volcano. b) Samples collected in 2015 and 2017.

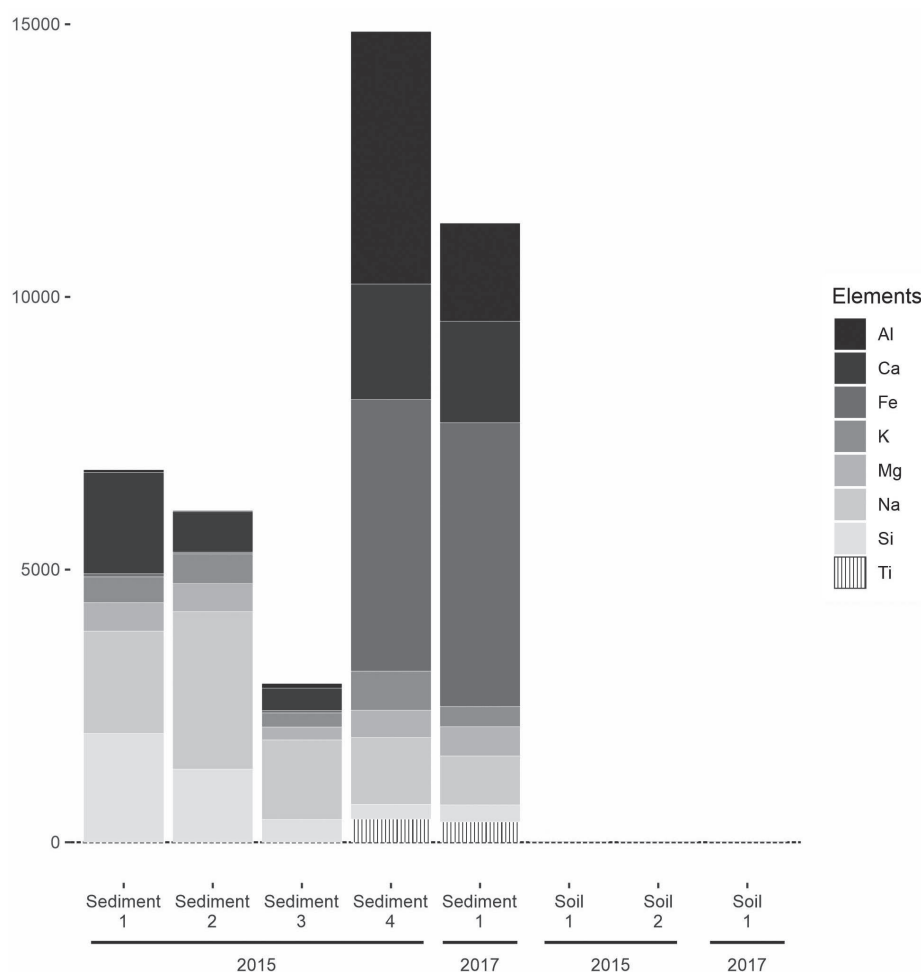


Fig. 2. Heavy metals more abundant in samples of the active volcano the El Chichón.

The sediments of El Chichón crater lake showed the lowest pH values, due to redox transformations of sulfur compounds. The difference found in sediment 4 was evident, as it has a greater amount of dissolved metals in addition to S ions. This sediment also showed the highest temperature determined in this study, as it is located near the area of greatest volcanic activity (Fig. 1). Thus, this is one of the samples originating from a most extreme location.

Lakes that are related to active volcanoes provide information about changes in volcanic activity. Consequently, these have been used as a monitoring system for water chemistry and sediment composition [9, 10]. Such lakes are acidic by nature and have high concentrations of metals [9, 10].

Heavy Metals of El Chichón Volcano

The chemical composition of crater lakes can be determined by volcanic activity (mainly by the entrance of volcanic gas). These studies can take place either before or after the eruptions occur [9]. The chemical composition is a key point for evaluating the contamination of acidic soils found within the crater lake and near the agricultural and livestock soils of the region

in Chiapas, Mexico. The results of HM concentrations in the sediments from El Chichón volcano are shown in Table 2 and Figs 3-4. The concentrations of heavy metals did not show statistically significant differences between 2015 and 2017. However, for most results, this helps in demonstrating that the HM concentration is related to the type of sample, either sediment or soil.

The most abundant metals were Al, Ca, Fe, Na, which were found in concentrations higher than 5000 ppm in sediments (Fig. 2). This contrasted with results pertaining to soil samples, where lower heavy metal concentrations values were found. On the other hand, the less abundant heavy metals were Ba, Li, Tl, whereby a congruent difference between volcanic sediments of the crater lake and the soil of El Chichón volcano was found (Fig. 3). In this study, the most abundant elements were Fe, Na, Si, Ca, K and Al, which have been found in similar concentrations since the formation of the crater lake [16]. The concentrations of Ca, Si, and Fe are controlled by the solubility of some minerals such as anhydrite, cristobalite or tridymite [22]. Na, Ca, K and Mg have been reported in high concentrations, mainly in ionic form [9, 11, 27]. A spring called "Soap Pool" strongly influences the chemistry of the lake [11].

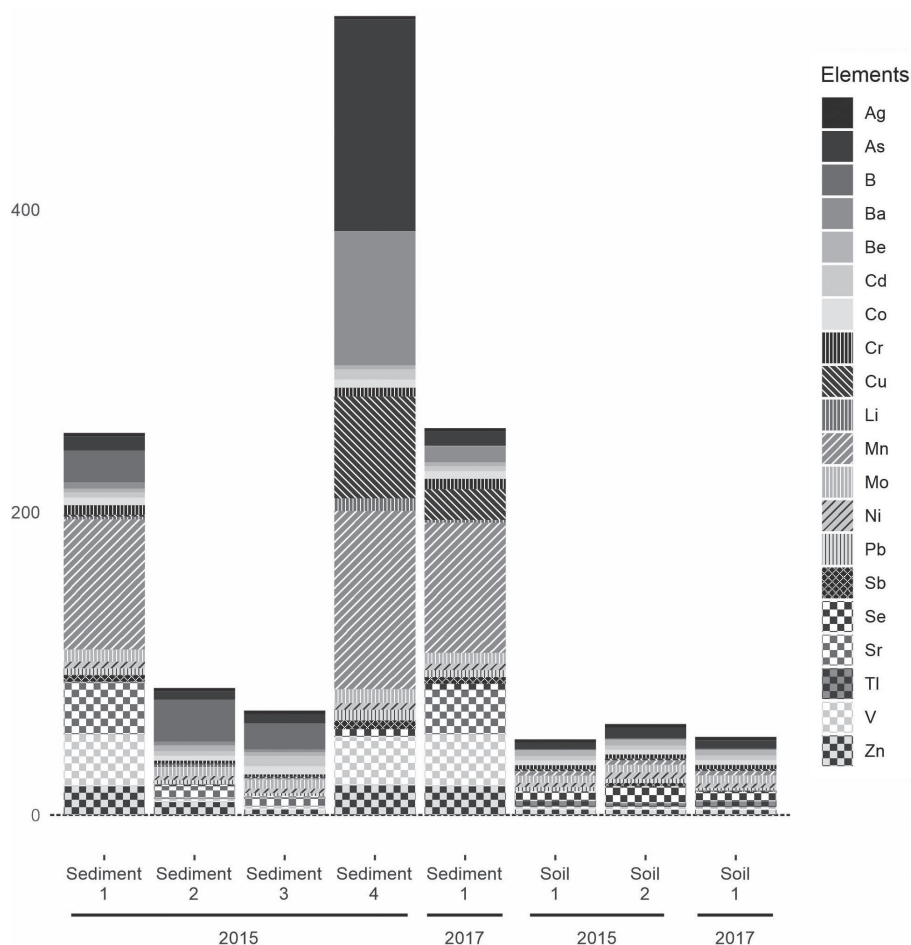


Fig. 3. Heavy metals less abundant in samples of the active volcano the El Chichón.

On the other hand, concentrations of Na, K, Li and B are strongly related to hydrothermal contributions to the lake, as found in other acidic crater lakes, such as Mount Pinatubo [28]. According to Cuoco et al. (2013) [11], mineral saturation could play a key role in the spread of some element concentrations, such as boron, aluminum, strontium and barium. Thus, water–rock interactions (igneous rocks, mainly) have been reported in El Chichón crater lake [9, 11, 27]. This process may leach silica and metal cations such as Mg^{2+} , Sr and Ba, which have been usually detected in high concentrations in this system [11]. Moreover, this interaction involves an oversaturation of magnesium and magnesium silicate minerals [9].

According to the variance in all samples the PCA, the proportion of variance was explained by the first two principal components (PC), which was approximately 80%. Variables such as Ag, Be, Ca, Co, Cr, Cd, Li, Pb, Ni, Sb, Mn, Mo, V, Zn have the highest loading in PC1, which accounts for about 60.3% of the total variance. On the other hand, Al, B, Na, Se, Si, Sr have the highest loading values for PC2, and explain 19.7% of variance (Fig. 4). In high-temperature spots, higher concentrations of metals such as Al, As, Ba, Ca, Cr, Cu, Fe, Li, Mn, Mo were found. Contrary to this finding,

metals such as Be, Se, Tl, Ag, Na, Si, Sr were more dominant in low temperature conditions. All metals are grouped by temperature.

Iron is an abundant element ever since the formation of the crater lake [22]. The Fe concentrations are controlled by dissolution–precipitation reactions, because of oversaturation of goethite. Because of this, the mineral has been obtained in many samples after 1983. This reaction is pH-dependent, as seen in Eq. 1 [29]:



Silicon is a characteristic element of volcanic environments. In the crater lake of El Chichón volcano, it has been mostly found in the form of silica minerals [9, 11, 22]. The high concentrations of Si as an element are related to the degree of saturation of SiO_2 as amorphous silica, quartz and chalcedony. Water–rock interactions, such as silica mineral hydrolysis, play a key role in Si concentration. This phenomenon buffers the acidity derived from dissolution of hydrothermal gases [11].

The chemical characterization of El Chichón crater lake has occurred mainly in water samples. However,

Table 2. Heavy Metal concentration in the crater-lake of El Chichón active volcano (mg/kg).

	Ag	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Li
Sediment 1 (2015)	2.17 a	49.50 a	9.50 a	20.92 a	4.21 ac	2.63 a	1857.92 a	3.25 a	5.04 a	6.38 ac	1.33 a	55.542 a	472.04 a	1.71 a
Sediment 2 (2015)	2.25 b	17.92 a	5.54 b	27.75 b	2.46 a	3.92 b	743.96 b	2.92 bd	3.17 b	2.00 bd	0.54 a	28.58 a	548.54 a	1.79 a
Sediment 3 (2015)	2.25 b	84.54 a	6.25 b	17.25 c	1.71 a	2.58 a	412.75 c	6.75 c	5.38 c	1.54 b	0.75 a	40.58 a	258.67 b	0.33 b
Sediment 4 (2015)	2.17 c	4627.92 b	140.08 c	0.00 d	88.67 b	2.58 a	2120.42 a	6.75 c	5.38 c	5.83 a	67.38 b	4978.33 b	718.88 c	8.33 c
Sediment 1 (2017)	ND	2499.09 ^a	0.78 ^a	ND	28.83a	ND	2045.05a	0.88ab	2.70a	3.3a	9.97 ^a	6899.00a	578.38a	4.68a
Sediment 2 (2017)	ND	7010.70a	18.76b	ND	74.47b	ND	2038.43a	0.53a	2.11a	4.12a	16.69 ^a	4175.65a	832.13a	7.89a
Sediment 3 (2017)	ND	7627.34a	2.72a	ND	85.18b	ND	1022.78b	1.06b	4.49b	5.22a	35.71b	8136.61a	1186.23a	5.86a
Sediment 1 (Rincón-Molina et al., 2019)	1.8 a	144 a	6.33a	17.7 a	7.9 a	1.76 a	2049 a	3.26 b	5.13 a	6.73 a	2.76 a	126 a	424 a	1.8 a
Sediment 2 (Rincón-Molina et al., 2019)	2.3 a	113 a	4.16a	44.5 a	2.0 a	2.56 a	440 b	7.06 a	5.50 a	1.60 b	0.83 a	52 a	270 a	0.4 b
LSD	0.00	159.37	3.20	2.46	7.02	0.07	282.66	0.20	0.15	0.79	6.29	137.09	87.54	0.49
	Mg	Mn	Mo	Na	Ni	Pb	Sb	Se	Si	Sr	Ti	Tl	V	Zn
Sediment 1 (2015)	523.92 a	86.00 a	8.08 ac	1875.84 ab	4.42 a	4.29 a	4.42 a	0.96 a	1994.17 a	33.83 a	1.54 a	0.00 a	34.42 a	19.00 a
Sediment 2 (2015)	514.75 a	0.21 b	5.54 bd	2884.58 b	2.71 a	2.79 b	0.33 b	1.50 ab	1341.67 b	7.58 b	0.83 a	0.38 a	2.00 b	8.58 b
Sediment 3 (2015)	237.92 b	0.75 b	6.08 be	1457.50 a	2.88 a	1.92 b	0.21 b	1.50 ab	418.13 c	5.29 b	3.17 a	0.04 a	2.00 b	3.58 c
Sediment 4 (2015)	499.13 a	117.75 c	9.21 a	1226.67 a	4.38 a	7.04 c	5.75 a	5.04 bc	270.21 d	0.00 c	425.79 b	0.13 a	32.08 a	19.58 a
Sediment 1 (2017)	695.84a	117.31a	1.92a	891.10ab	2.13a	1.80a	ND	ND	339.08a	60.77 ^a	589.82a	ND	32.04a	12.54a
Sediment 2 (2017)	484.99a	77.43ab	3.37a	1936.88a	2.50a	2.60a	ND	ND	457.59a	127.84a	509.35ab	ND	29.54a	10.33a
Sediment 3 (2017)	677.97a	53.97b	0.77a	619.71b	4.12a	2.49a	ND	ND	345.95a	164.47a	414.78b	ND	26.35a	9.81a
Sediment 1 (Rincón-Molina et al., 2019)	239 a	89.2 a	7.6 a	9967 a	4.3 a	4.5 a	3.8 a	0.8 b	1752 a	31.2 a	4.5 a	0.03 a	23 a	17 a
Sediment 2 (Rincón-Molina et al., 2019)	232 a	1.3 b	5.9 b	1399 a	3.2 a	3.2 a	0.2 b	1.8 a	469 b	5.6 b	4.2 b	0.3 a	10.3 a	3.5 b
LSD	50.43	4.45	1.17	1038.43	1.75	1.10	1.59	3.77	140.17	4.10	17.74	1.88	3.84	1.10

a,b,c and d Mean values of three replicates. Means followed by the same letter do not show any significant differences (p<0.05).

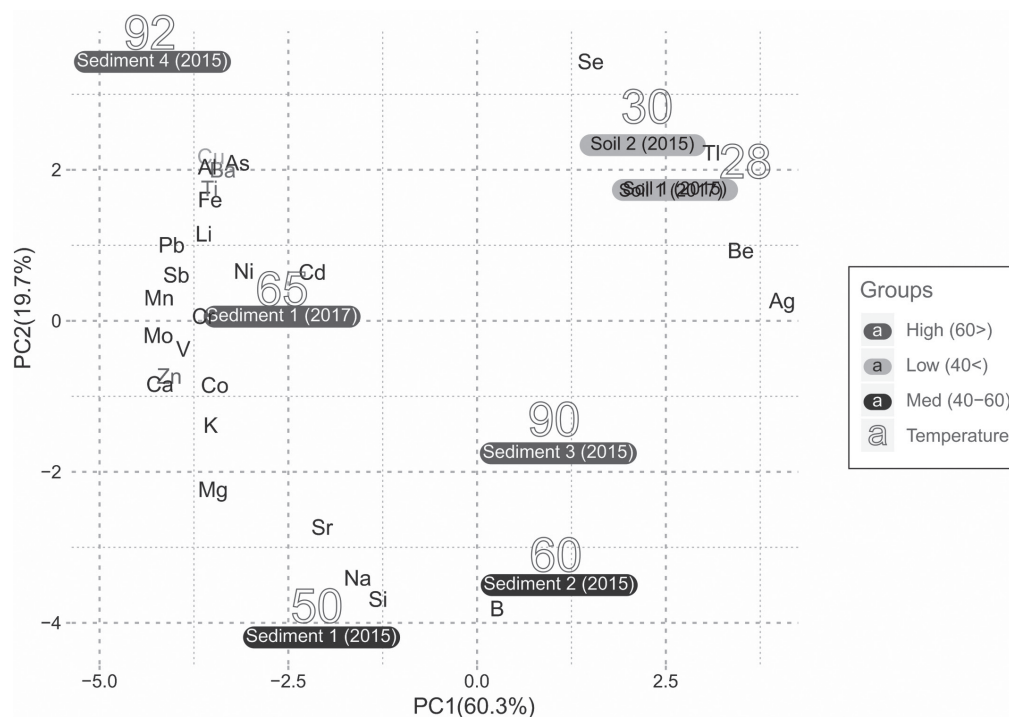


Fig. 4. Principal Component Analysis (PCA) of heavy metals more abundant in samples of the active volcano El Chichón samples.

after the eruption, the sediments from the lake contained the same silicate minerals as the rocks from the 1982 pyroclastic deposits [22].

All processes deriving from volcanic activity, such as rock-water interactions, are involved in the formation of a broad range of chemical elements, including toxic elements such as heavy metals [9, 11, 21, 30]. Thus, the toxicity would be restricted to the lake if water remains inside the crater [30]. However, the distribution of heavy metals and other toxic components occurs via other processes such as water seepage into surface or groundwater. This way, acidic crater-lakes can become a source of environmental pollution [31, 32]. This phenomenon may be occurring in El Chichón crater lake, as seepage through the crater floor has been detected, and multiple orifices or seepages from walls of altered rocks have been found. In this study, As and Cd were the most toxic heavy metals. Toxicity for human health and plant growth could be potentially expected from these metals. Geothermal fluids have high concentrations of arsenic. For instance, there is evidence of concentration of As in volcanic fluids and geothermal systems in some places in Latin America. Common sources of As in volcanic environments are arsenic-rich reservoir rocks (including the rocks of the volcanic edifices) and volcanic gases emitted in plumes and fumaroles [33]. Likewise, Northern Chile has presented arsenic pollution from volcanic sources because the release of As from rocks into geothermal fluids occurs predominantly along the boundaries of active tectonic plates [34]. It is common to find high levels of this element in volcanic environments. The presence of arsenic in this system

could be a source of pollution due to water seepage, as described earlier.

Arsenic (As) has been widely studied due to its high toxicity [20, 35]. According to the World Health Organization (WHO), this element is linked to toxicity for human health due to the formation of dermal lesions, peripheral neuropathy, skin cancer, bladder and lung cancers and peripheral vascular disease. Recently, several studies have shown that there is a closer relationship between exposure to arsenic and the risk of developing diseases such as cancer, cardiovascular events, diabetes and metabolic disorders [36]. There is also evidence that water intake containing 0.06-0.86 mg/L can cause respiratory and pulmonary diseases [37].

El Chichón active volcano has concentrations of As ranging from 4.21 to 140 mg/L. In other lakes of volcanic origin, concentrations of As and B are highly correlated. This correlation, along with high CO₂ emissions (evidenced in "El Chichón" crater lake) suggest the leaching of sediments. This phenomenon has been proposed as a mechanism for increasing arsenic concentration in waters [38].

All of these concentrations of As have been evaluated in other studies, which is alarming due to the risk of toxicity and harmful effects to health [36, 37, 39].

On the other hand, Cadmium (Cd) is a toxic transition metal, which is considered as one of the five most hazardous environmental contaminants by the Agency for Toxic Substances and Disease Registry. Cadmium is considered highly toxic and bioaccumulates progressively in the organism [40]. Exposure to Cd

in animals and humans has toxic effects on various organs and tissues, such as liver, kidney, lung, gut, central nervous system, ovaries, testes, and pancreas [41]. Regarding plants, Cd can produce a toxic effect with amounts as low as 0.2 nM [42]. Because of the above, the exposure and propagation of cadmium can be a factor of environmental risk and serious health issues.

This study suggests that El Chichón crater lake could be an important source of toxic elements. However, it would be important to carry out a study about element speciation and evaluate if water seepage could contaminate water bodies outside of the crater lake. Geothermal fluids with high concentrations of trace and toxic elements may have surface manifestations which can pollute rivers and groundwater near these sites. Sites with a direct connection to these effluents can also be potentially contaminated [43]. Hydrographic studies from El Chichón volcano confirm that the hydrographic system is not isolated and is interconnected with different rivers around the volcano, as reported by Taran and Peiffer (2008). These results indicated that Río Magdalena is the only drainage of all thermal waters discharged from the slopes of the volcano.

Conclusions

The concentrations of heavy metals did not show statistically significant differences between 2015 and 2017. However, in most results they allow us to demonstrate that the concentration of heavy metals was related to the type of sample, either sediment or soil. Also, this study suggests that El Chichón crater lake could be an important source of toxic elements, such as As and Cd. Thus, it would be important to carry out a study on the distribution and speciation of elements and to assess whether water seepage could contaminate water bodies, such as rivers and lagoons outside of the crater lake. Studies regarding concentrations of heavy metals in agricultural soils of the region would be of equal importance.

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Conflict of Interest

The authors declare no conflict of interest.

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