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Geochemical Characterization of Soils in the Playa Lake Environment of Laguna de Encinillas, Chihuahua, Mexico

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Abstract

Laguna de Encinillas, located in Chihuahua, Mexico, is an ephemeral lake situated within a playa lake sedimentary depositional environment. This region plays a significant role in the aquifer supplying water to Chihuahua City. A surficial soil sampling campaign was conducted in 2017, 2018, and 2021 to assess the potential impact of surface soil composition on groundwater quality. The collected soil samples were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) following microwave-assisted digestion. The analytical results were employed to generate spatial distribution maps of elemental concentrations using QGIS, applying interpolation methods such as inverse distance weighting (IDW) and Kriging. The analysis revealed elevated concentrations of beryllium (Be), calcium (Ca), cadmium (Cd), chromium (Cr), magnesium (Mg), and strontium (Sr) in the eastern part of the study area. In contrast, arsenic (As) and iron (Fe) were more prevalent in the western sector. Notably, high levels of barium (Ba), silver (Ag), cobalt (Co), potassium (K), and scandium (Sc) were identified in the northeastern region. At the same time, nickel (Ni), titanium (Ti), and vanadium (V) were concentrated in the northern portion. Manganese (Mn) was particularly prominent in the southern area. The geogenic source of these elements is likely linked to the volcanic rocks from the surrounding mountain ranges.

Keywords

Groundwater Quality, Soils, El Sauz-Encinillas Aquifer, Chihuahua, GIS

1. Introduction

Soil contamination is nowadays one of the most significant global socio-environmental concerns, with deep implications for groundwater quality. The characterization, assessment, and remediation of contaminated soils represent a key environmental challenge that must be addressed shortly. The risk posed by soil contaminants extends beyond their total concentration; it is particularly critical due to their potential mobility and bioavailability, which can lead to the contamination of groundwater resources.

Heavy metals are considered environmental contaminants subject to greater research and concern, primarily due to their mobility and the low concentrations at which they start to manifest their toxic effects [1]. Metals come into the soil through natural processes (geogenic and air-borne) and human-induced actions like agricultural, industrial, and mining [2]. The soil serves as a repository for numerous substances potentially considered contaminants, some of which may infiltrate the food chain through crop uptake and subsequently accumulate in the human body via biomagnification [3].

Given its role as an interface between the geosphere (rocks, sediments), hydrosphere (both freshwater and saltwater), biosphere (including all living organisms, humans), and atmosphere, soil functions are both a transit station and a reservoir for pollutants. These pollutants can be retained for extended periods, which increases the likelihood of their degradation and diminishment of their toxic properties, or they may disperse throughout the environment, potentially causing detrimental effects on ecosystems [1]. Additionally, toxic heavy metals (THMs), organic pollutants (OPs), emerging contaminants (ECs), and other biotic and abiotic stressors can adversely impact nutrient availability, plant metabolic processes, agricultural productivity, soil fertility, and groundwater quality [4].

This study aims to expand the existing dataset on soil composition in different regions within, or close to, the ephemeral lake known as Laguna de Encinillas. Evaluating possible contaminant levels, their fate, and transport is relevant to academia, government agencies, and the area's inhabitants. This required performing a geochemical characterization of soil samples and developing a spatial distribution model for the analyzed elements. Identifying areas with high concentrations of elements that negatively impact groundwater quality—such as arsenic (As) and fluoride (F)—is crucial, particularly given the issues previously reported [5]-[8]. Accurate measurement of the degree of heavy metal contamination and soil mapping are important for identifying high-risk areas and developing effective remediation strategies [9]. The surficial-soil sampling included areas to the east and west of the Laguna de Encinillas, located in the central-western portion of the Chihuahua state, northern Mexico, specifically in the 368,396 m E and 362,049 m N coordinates (**Figure 1**).

The study area is located approximately 92 km north of Chihuahua City in northern Mexico. Groundwater represents ca. 60% of the drinking water usage throughout the state for any activity [10]. This percentage is even larger for counties with large cities, such as Juarez and Chihuahua, since their surficial water bodies are small, almost depleted, and experiencing severe drought conditions.

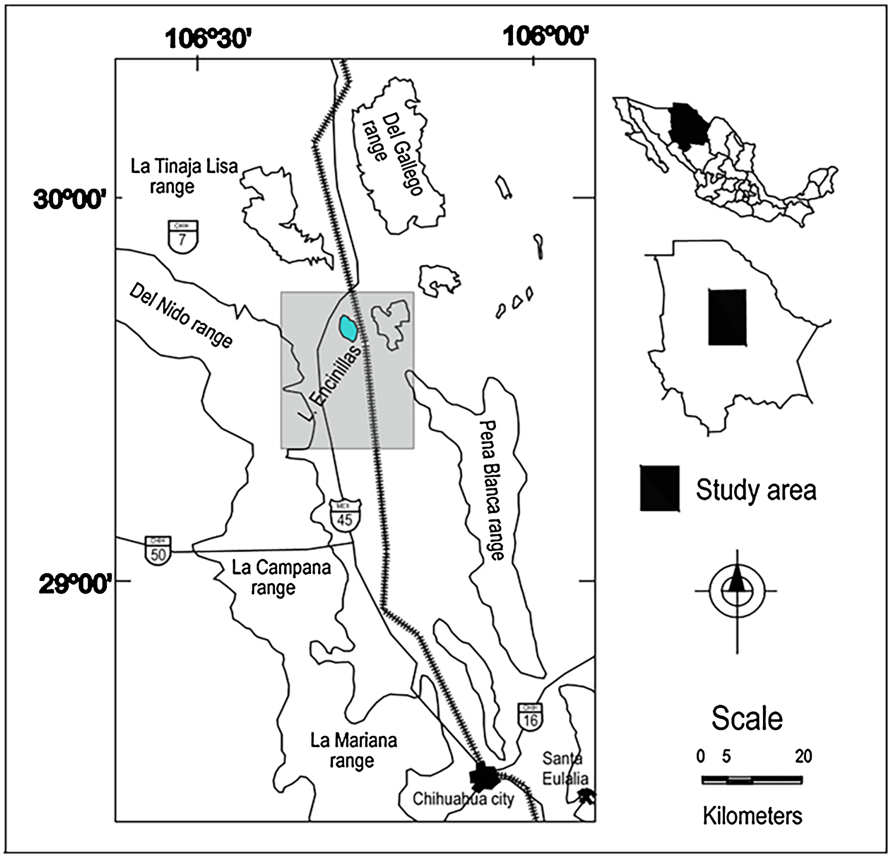

Figure 1. Location map of the study area Laguna de Encinillas, Chihuahua México [7].

Officially, the state of Chihuahua has 61 aquifers supplying drinking water for its population, but 42 are overexploited (El Sauz-Encinillas, one of them) and 9 have no reported availability [11].

Laguna de Encinillas, or as it is commonly known in the area: "Ojo Laguna", is an endorheic (or closed) basin, and is considered a seasonal (or ephemeral) body of water since only in monsoon seasons has water [12]-[14], but lately is experiencing a severe drought period and coupled with drawdowns caused by wells nearby remains dry throughout the whole year. The lake is part of the El Sauz-Encinillas aquifer that supplies water to Chihuahua City, thus making this soil characterization relevant to decision-makers and government agencies involved in groundwater, agricultural, and environmental issues.

Geological Setting

This closed basin was created due to specific tectonic conditions during its geologic past. The related structures, mainly normal faults (**Figure 2**), observed in the aquifer on a regional scale, are attributed to events that occurred at the end of the Cretaceous and the beginning of the Paleogene when the maximum compressive stress of the Laramide orogeny took place. This event lifted and folded the whole pre-existing sedimentary sequence, causing thrusting and reverse faulting of the carbonated rocks east of the valley [15]. At the end of the compressional

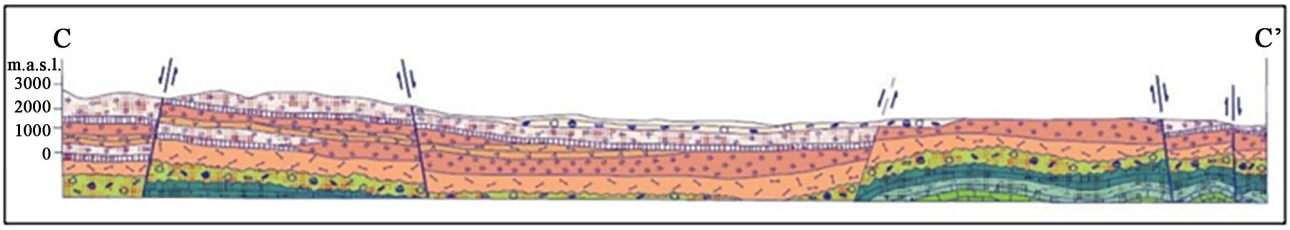

Figure 2. Geologic cross-section of the central part of the El Sauz-Encinillas aquifer (Geological-Mining Chart H13-7 Buenaventura, Chihuahua) [19].

setting, during the Oligocene-Miocene, a major tectonic distension event (Basin and Range tectonics) caused a notable tilting of the volcanic sections through a system of normal faults, wide distribution and extension that produced a series of horsts and grabens where the dominant structures of the aquifer lie [16]. Finally, another recent tectonic event has affected the area and is currently active, corresponding to a distensive stress that allowed the formation of the Rio Grande Rift, and which has caused mafic volcanism associated with normal faulting [17] [18].

To the West side of the valley that contains the ephemeral lake, a mountain range called Sierra Majalca-El Nido-Paporin rises and is composed of a more than 1000 m thick section of Tertiary felsic volcanic rocks that includes tuffs, domes, and rhyolitic ignimbritic flows. Younger basaltic flows from the Paleogene-Neogene are also exposed to the top of the felsic volcanic sequence, however, Eocene andesitic rocks crop out in the lower part of the volcanic section [20] [21]. The Peña Blanca Mountain range, which forms the eastern boundary, exhibits a comparable volcanic sequence with slight variations in lithology, age, and thickness. The volcanic sequence rests unconformably on Cretaceous limestones [12] [22].

According to the Geological-Mining Chart H13-7 Buenaventura, Chihuahua [19], the El Sauz-Encinillas aquifer area features several distinct types of rock (**Figure 3**). The Rhyolite-Rhyolitic Tuff Tom (R-Ta), located mainly in the western part of the study area, is characterized by an irregular sequence of spherulitic rhyolites, lava flows, ignimbrite layers, rhyolitic tuff, and felsic volcanic breccia. In the northwestern part of the aquifer, the Conglomerate Q (cg) is present, featuring a sandy clay matrix. The Conglomerate Ts (cg), found in the northern and some southern regions, consists of continental deposits of conglomerates and minor conglomeratic sands with a calcareous cementitious matrix, and fragments originating from volcanic and intrusive rocks. The Limestone Ki (cz), located in a portion of the southwestern area, is notable for its strata with variable textures. The Felsic Tuff (sic) Tom (Ta), observed in the northern section of the aquifer, is a Cenozoic formation composed of lithic tuffs and breccias with compositions ranging from rhyolitic to rhyodacitic, a small portion of the aquifer to the south features Monzonite T (Mz). Lastly, the Alluvium Q (al) is widely distributed across the eastern part of the aquifer, consisting of Cenozoic alluvial deposits of gravel, sand, silt, and unconsolidated clay.

The El Sauz-Encinillas aquifer is emplaced in Quaternary alluvial deposits, is

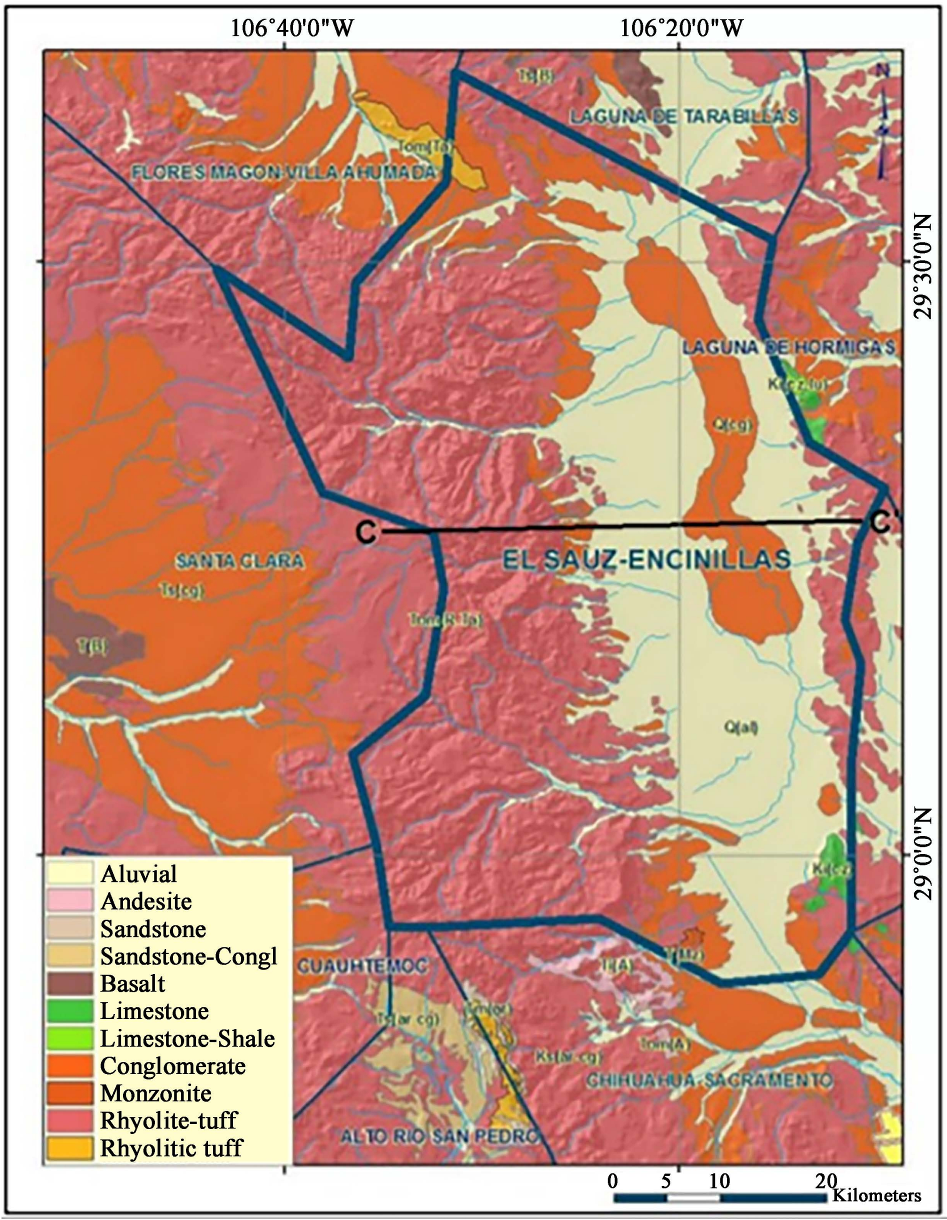

Figure 3. Geology of the study area, Laguna de Encinillas (Geological-Mining Chart H13-7 Buenaventura, Chihuahua) [19].

heterogeneous and anisotropic, with local semi-confinement conditions due to the interdigitation of low permeability strata. The deposits are part of a graben, which includes different granulometry and reaches a thickness of approx. 800 m at its center and decreases towards the sides of the mountain ranges, where alluvial fans and bajadas lie [12]. As previously mentioned, mountain ranges to both sides of the aquifer valley are composed mostly of Cretaceous limestones to the base and Tertiary volcanic rocks to the top, which in deeper environments present fracturing and allow a secondary permeability [12], this part is considered the recharge area of the aquifer.

In 1985, total dissolved solids (TDS) values from 150 to 1375 mg/l were reported at El Sauz-Encinillas aquifer, and water was classified as being fresh to tolerable. Water families were cataloged as calcium-bicarbonate, sodium-bicarbonate, and calcium-sodic-bicarbonate waters [23]. However, high fluoride concentrations have been found in several wells [24]-[27]. It is considered that this high level of fluorine detected is due to the water-rock interaction [6] [12]. To the central-eastern portion of the aquifer, nitrates concentration is 7.4 mg/l with a maximum of 38.5 mg/l. Fluoride exceeds the Mexican norm (NOM 127 SSA 2021) values for drinking water (1 mg/l) [28], having an average value of 3.1 mg/l and a maximum value of 10.6 mg/l in a well northeast of the aquifer. Other elements exceeding the Mexican drinking water standards are iron and arsenic [8]. In other studies, from 1996, 2008, and 2010, fluorine content increased mainly in the northern and central parts of the aquifer, while in the southern zone of the aquifer, the fluoride levels were similar, but, in some cases, they decreased [8]. Arsenic content data also exceeds the amount of 0.01 mg/l established by the Mexican norm NOM-127-SSA1-2021 [28].

2. Methodology

The research began with a review of previous studies conducted in the area [5] [14] [29]-[31] to establish an understanding of the existing findings and reports. Once the area was explored, sampling points were identified (**Figure 4**). Soil sampling was performed in the field using shovels up to a depth of 30 cm, and samples were collected and stored in 20-liter plastic recipients. The samples were sieved and analyzed using the unified soil classification system (USCS). The unified soil classification system (USCS) is governed by ASTM D-2487 and is the most widely used in geotechnical practice [32]. Initially proposed by Arthur Casagrande in 1932, it is based on grain size analysis and Atterberg limits (liquid and plastic limits) of soils [32].

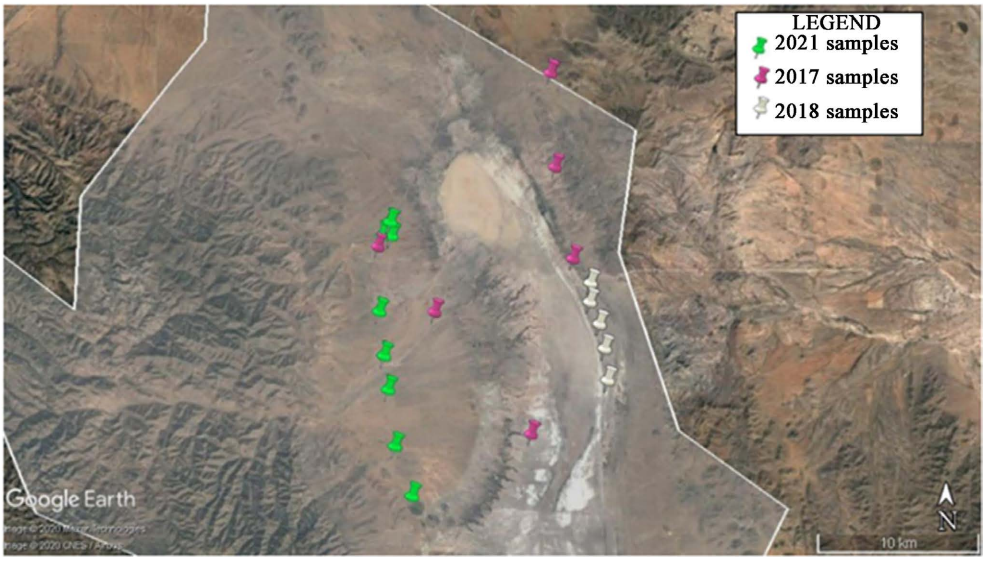

Figure 4. Samples' location within the study area surrounding Laguna de Encinillas [33].

Portions of the samples were chemically analyzed in the Mexican Geological Survey Laboratories, where the soil samples were digested with 4 acids (HCl, HNO_3, $HClO_4$, and HF), and later analyzed for 33 elements (Ag, Al, As, Au, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Sc, Se, Sn, Sr, Te, Ti, Tl, U, V, W, and Zn) via the Inductively coupled plasma optical emission spectroscopy (ICP-OES) technique, except Au, that was analyzed via the atomic absorption spectroscopy (AAS) technique.

With the geochemical data, distribution maps were drawn using the QGIS software, using the inverse distance weighting (IDW) and Kriging methods as interpolators. The IDW tool is also known as a deterministic interpolation method since it is based directly on measured values or specific formulas that determine the smoothness of the resulting surface. The inverse distance weighting (IDW) method is a non-geostatistical interpolation technique. IDW operates on the premise that a point with an unknown value is more influenced by nearby control points than those farther away. However, this method does not inherently provide a way to verify the accuracy of its predictions. As a result, the quality of the generated map can only be assessed by using validated sample points [34]. Whereas Kriging is a geostatistical tool using autocorrelation, that is, statistical relationships between the measured points [35]. Kriging uses nearby points weighted by distance from the interpolate location and the degree of autocorrelation or spatial structure for those distances and calculates optimum weights at each sampling distance [36].

To generate the distribution maps, an initial dataset was first prepared in Excel, consisting of tables for each analyzed element, which included coordinates and corresponding concentration values. First, to understand and relate the anomalies with the area, a satellite image was added to the bottom of the map, to serve as a base map. The study area was then georeferenced using QGIS software, allowing us to measure distances and orientation of the element concentration within this ephemeral lake environment. Later, the dataset was imported to create anomaly maps for each element. Interpolation methods, such as inverse distance weighting (IDW) and Kriging, were applied to develop these maps. With the help of a reference color bar, the blue tones refer to low values, while the red tones refer to higher values.

3. Results

The soils at Laguna de Encinillas, according to the USCS method, were classified as sandy soils, since more than 50% of the material passed through sieve No. 4, which represents the sand particle size (**Figure 5**).

Table 1 shows the Chemical analyses for the soil samples, along with the values for 11 (plus Fe) elements considered major contaminants for soils, part of the Mexican Official Norm for soils (NOM-147-SEMARNAT/SSA1-2004) [37]. None of the element's concentrations go beyond the maximum allowable limits of the norm NOM-147, so the area can be acknowledged as free of agricultural, residential,

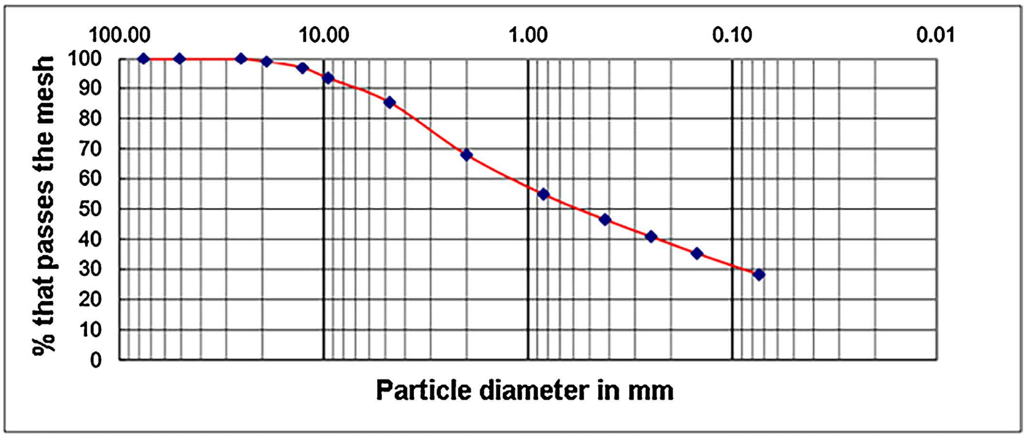

Figure 5. Representative sample of soil classification, using the USCS method.

Table 1. Chemical analyses, location, and reference values (CRT) NOM-147-SEMARNAT/SSA1-2004.

Element			Ag	As	Ba	Be	Cd	Cr	Fe	Ni	Pb	Se	Tl	V
Detection Limit			1.0	1.0	1.0	1.0	1.0	1.0	0.001	1.0	1.0	1.0	1.0	1.0
Units			mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
NOM-147-SEMARNAT/ SSA1-2004			**390**	**22**	**5400**	**150**	**37**	**280**	**-**	**1600**	**400**	**390**	**5.2**	**78**
Sample	East	North	**2017**											
17M1	374687	3257528	2	14	311	5	<1	23	2.37	12	44	<1	<1	70
17M2	374361	3257542	1	8	391	5	<1	23	1.81	6	41	<1	<1	27
17M3	373104	3269023	2	11	484	5	<1	26	2.19	10	44	<1	<1	37
17M4	371646	3246810	2	8	388	5	<1	29	2.70	9	44	<1	<1	51
17M5	365771	3254371	2	13	420	7	<1	32	3.11	13	49	<1	<1	59
17M6	373333	3263252	1	13	514	5	<1	26	2.56	12	33	<1	<1	51
17M7	362310	3258432	2	16	756	4	<1	29	2.72	11	41	<1	<1	55
Sample	East	North	**2018**											
18M1	375456	3256066	<1	14	112	5	1	56	1.84	9	45	<1	<1	25
18M2	375395	3254897	<1	<1	103	5	1	61	1.65	8	36	<1	<1	20
18M3	375973	3253536	<1	<1	109	5	1	46	1.59	8	34	<1	<1	21
18M4	376280	3252025	<1	11	134	8	1	27	2.27	12	34	<1	<1	36
18M5	376448	3250083	<1	11	137	8	1	22	2.06	13	30	<1	<1	35
Sample	East	North	**2021**											
21M1	363114	3259940	<1	13	442	2	<1	28	3.88	14	37	<10	<10	47
21M2	362586	3259097	<1	14	121	2	<1	29	3.71	12	27	<10	<10	59
21M3	363158	3259096	2	14	152	2	<1	25	3.37	12	33	<10	<10	41
21M4	362368	3254442	<1	2.26	163	2	<1	22	2.89	11	17	<10	<10	35

Continued

21M5	362629	3251726	<1	2.62	166	3	<1	21	3.33	13	36	<10	<10	34
21M6	362863	3249648	<1	2.94	124	3	<1	20	3.52	11	52	<10	<10	40
21M7	363241	3246165	<1	1.78	60	6	<1	7	2.19	4	59	<10	<10	7
21M8	364257	3243090	<1	2.73	94	5	<1	13	2.6	6	52	<10	<10	15

and/or commercial contaminants.

The distribution maps were made using QGIS. First, sampling points were georeferenced, and then, after generating a database, maps were drawn using the IDW and kriging methods. Mapping the concentrations of contaminants in soils is essential for grasping their spatial distribution and the processes influencing them. Detailed contaminant maps allow to pinpoint areas of high pollution and recognize patterns, which aids in evaluating the severity of contamination and its potential effects on both the environment and public health. This spatial analysis also sheds light on how contaminants move over time and how different environmental factors, such as water movement or changes in land use, affect their spread. These insights are crucial for designing effective remediation plans and managing soil health effectively.

After comparing both interpolators' results, the Kriging maps were selected, since they were more consistent. Looking at quantity levels, arsenic (As), manganese (Mn), nickel (Ni), phosphorous (P), and scandium (Sc) are showing major concentrations. In the northern part, elements with high concentrations are Ni, titanium (Ti), and vanadium (V) (**Figure 6**). While at the NE portion, silver (Ag), barium (Ba), cobalt (Co), potassium (K), and Sc (**Figure 7**) display high values.

Only manganese (Mn) appears in high concentrations in the southern part (**Figure 8**); while in the western portion, only arsenic (As), and iron (Fe) showed high amounts (**Figure 9**). Finally, to the East, beryllium (Be), calcium (Ca), cadmium (Cd), chromium (Cr), magnesium (Mg), and strontium (Sr) are found in higher values (**Figure 10**).

Summarizing the previous statements, elements showing high concentration values are grouped according to their location within the valley (see **Table 2**).

The high arsenic levels found in the western portion can be attributed to the weathering of igneous rocks (mostly felsic and few mafic lava flows) and the transport of these elements through the deposits in the area. The main elements in the northern zone seem to be due to the weathering of basaltic rocks (El Milagro basalt) that outcrop in the area.

The abundant elements in the eastern portion are elements of groups 1A and 2A of the periodic table and have a certain affinity to the presence of limestone and fine sediments of the Laguna de Encinillas, except for Cr and Mg, which are usually associated with ultramafic rocks but could also be due to weathering of ballast used on the train tracks that cross the area of study and is composed of mafic rocks and/or smelter slags.

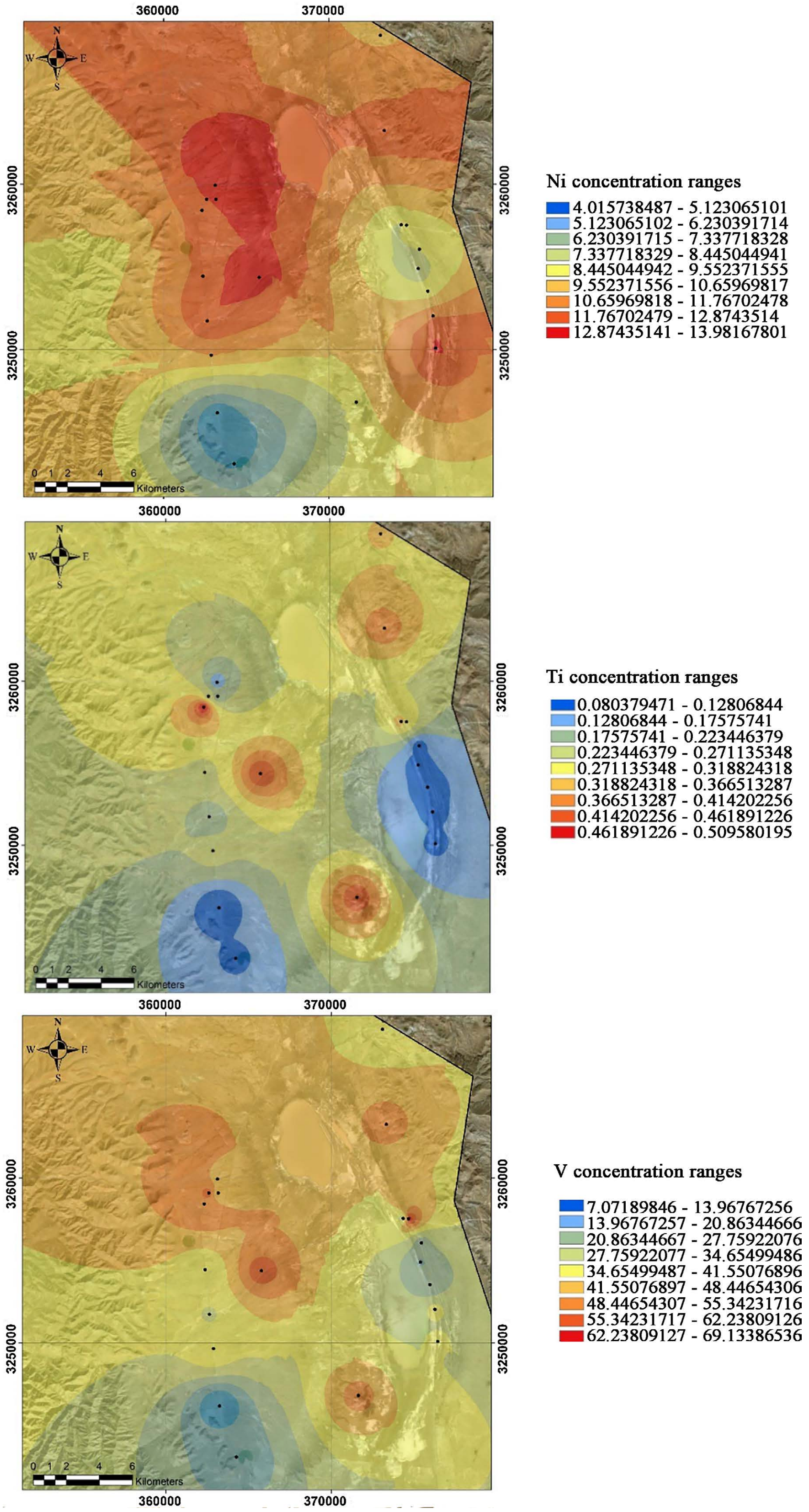

Figure 6. Ni, Ti, and V show high concentration levels in the northern portion of the study area, as shown in the as shown in the Kriging distribution maps.

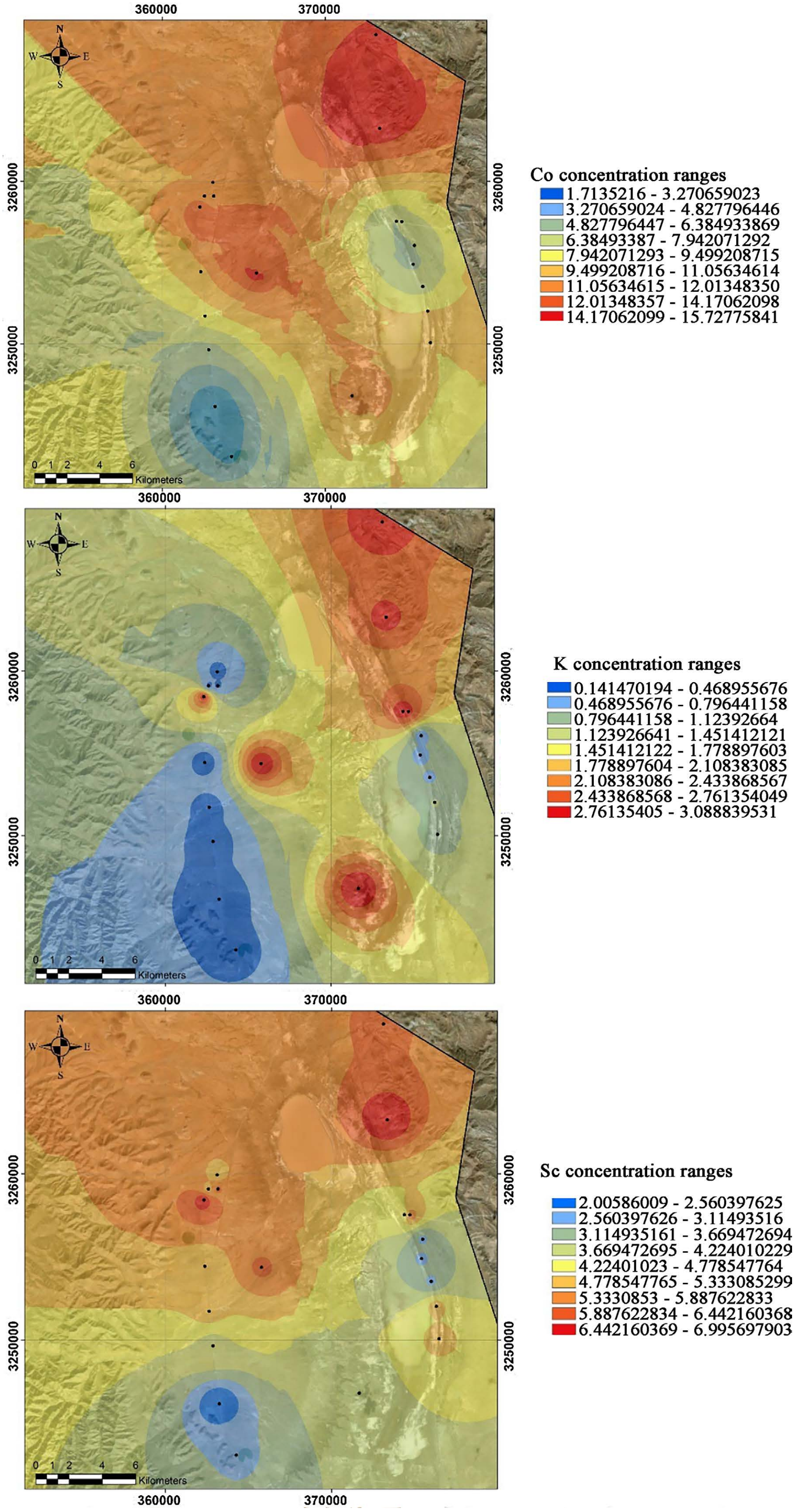

Figure 7. Co, K, and Sc are the elements displaying high concentration levels in the northeastern portion of the study area, as shown in the Kriging distribution maps.

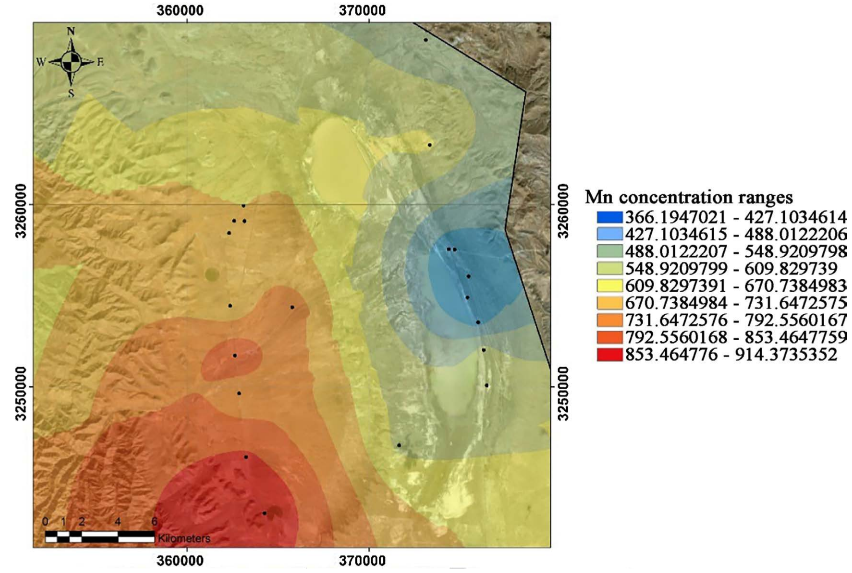

Figure 8. Only Mn appears as the major element in the southern portion of the study area, as shown in the Kriging distribution map.

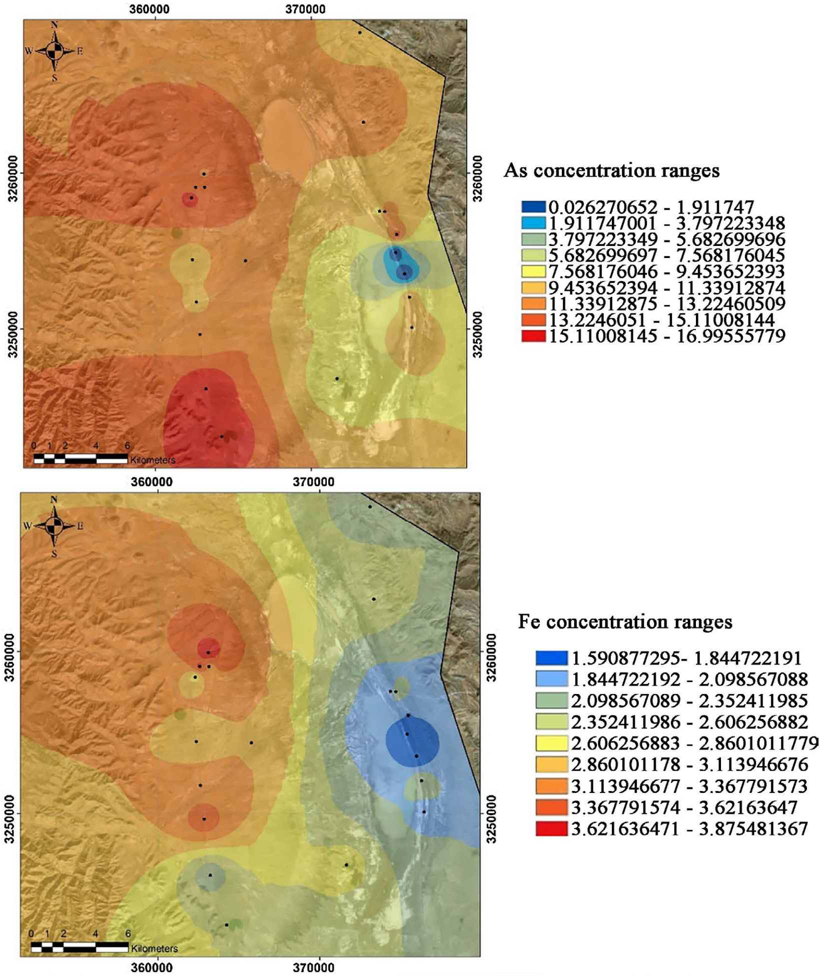

Figure 9. As and Fe display high concentration values in the northwestern portion of the study area, as shown in the Kriging distribution map.

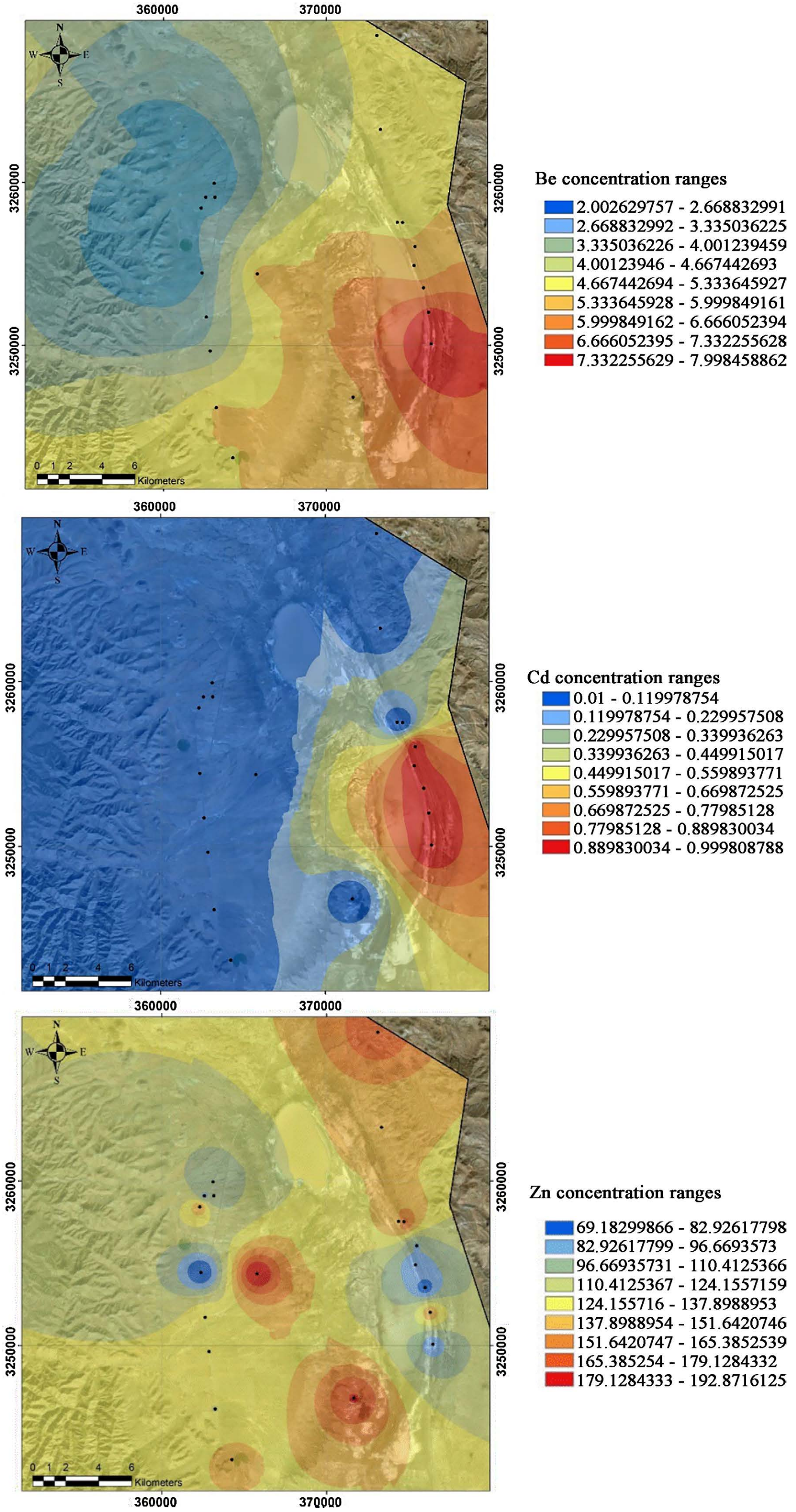

Figure 10. Be, Cd and Zn Mn show high concentration values in the eastern portion of the study area, as shown in the Kriging distribution map.

Table 2. High concentration levels of elements in different portions of the study area.

Zone	North	South	East	West	NE	NW	SW
Elements	Ni, Ti, Va	Mn	Be, Ca, Cd, Cr, Mg, Sr	As & Fe	Ag, Ba, Co, K, Sc	Ag, As, Ba, Fe, Ni, P, Sc, Ti, V	Mn & Ni

4. Conclusions and Future Work

Concentrations above the normative values (NOM 127-SSA 2021) of fluorides, iron, and arsenic in well waters in the El Sauz-Encinillas aquifer have been previously reported [8] [24] [25] [27] [31] [38]-[47]. Previous work has proposed that the presence of these elements in groundwater is due to the existence of sulfides, evaporites, and clays in the ephemeral lake (Laguna de Encinillas) area [40] [48].

It also has been considered that the rocks that interact with the aquifer are the main source of the elements dissolved in the water of the aquifer system [48] [49]. However, a complete geochemical characterization of minerals present in rocks and sediments has not yet been attained, partly because research has been focused mostly on measuring concentrations in water, but also the small number of wells that are found in the northern portion of the aquifer, due to the presence of clays and evaporites that compromises the quality and quantity of the water extracted. It must also be mentioned that drilling in the area has not been able to reach the basement.

In previous research [5], leaching experiments were performed in columns, using surface soil material from near the wells with high concentrations of As and fluorides. That material was classified as silt and clayey sands. After the experiments, it was observed that both elements leach with water, suggesting that these contaminants occur in the granular portion of the aquifer.

This research sought to determine the presence of elements with high concentrations in the surface sediments of the study area. It was concluded that in the eastern portion of the study area, the highest concentrations are found in Be, Ca, Cd, Cr, Mg, and Sr. In the W portion, the elements that show higher concentrations are As, and Fe. For the NE portion, they are Ba, Ag, Co, K, and Sc. In the northern part, Ni, Ti, and V, and finally, for the southern portion, Mn. The high concentrations of arsenic and fluorides are probably due to the chemical reactions caused by the water-rock and/or water-soil interactions. Based on the elements' behavior and the directions of groundwater flow, the possible source is the rocks of the Calera-El Nido Block, located east of the ephemeral lake. According to the representation scheme of recharge and discharge zones from Laguna de Encinillas [31] [50], one of the flows comes from the NW towards the lake, which could confirm that, indeed, the arsenic content in the lake comes from that area, as shown in the distribution maps.

It is important to note that none of the elements analyzed in the soil samples exceed the permissible limits set by Mexican regulations, indicating that the material in the area is free from contaminants typically associated with agricultural, residential, or commercial use. Arsenic (As) and iron (Fe) are the two elements that may exhibit elevated concentrations in the western part of the ephemeral lake. These anomalies are likely due to the weathering of felsic volcanic rocks (such as rhyolites and rhyolitic tuffs) and mafic rocks (such as basalt), as well as the transport of ions through the region's alluvial fans. In the northern area, the presence of nickel (Ni), titanium (Ti), and vanadium (V) could be attributed to the weathering of basaltic rocks, specifically the El Milagro basalt, which is prevalent in this region. In the eastern portion, elements such as beryllium (Be), calcium (Ca), cadmium (Cd), chromium (Cr), magnesium (Mg), and strontium (Sr) are associated with limestone and fine sediments of the ephemeral lake. Since no ultramafic rocks have been reported in this region, chromium and magnesium, which are typically linked to weathering these rocks, could be derived from the weathering and leaching of ballast used on the railway tracks that cross the area as found in previous tank leaching experiments [51].

For future research, conducting soil sampling at various depths and characterizing the rock minerals interacting directly with the aquifer water via XRD (X-ray diffraction) and EMPA (Electron Microprobe Analyses) is recommended. It is also crucial to investigate whether the lithology near the lake is a source of elevated ion concentrations in the groundwater. Additionally, an evaluation of the pH and Eh conditions in the area is necessary to understand their role in the mobility of specific ions. A thorough assessment of the current levels of heavy metal contamination in the soil is essential to develop a theoretical framework and provide technical guidance for soil environmental protection, pollution control, and sustainable land use.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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