Geochemical composition and geophysical characterization of "Brunita" mining silt pond, Cartagena, SE Spain

Aracil E.[1], Faz A.[2], Martínez-Pagán P.[2], Martínez-Martínez S.[2], Acosta J.A.[2], Fisher T.[3], Maruri U.[1]

[1] Análisis y Gestión del Subsuelo. Madrid. Spain.
[2] Technical University of Cartagena. Spain.
[3] University of Oregon, Eugene. Oregon. USA.
E-mail: earacil@ubu.es
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ABSTRACT

In the Murcia Province, there are 85 mining silt ponds resulting from the treatment and exploitation of the metallic sulphur. These silt ponds are the potential focus of environmental pollution. The Technical University of Cartagena has been carrying out an integral study of these structures from the year 2003 to the present.

In this work, studies from the "Brunita" mining silt pond (La Union-Murcia) are described. These have allowed the characterization of different horizons, combining the results obtained through geochemical analysis with data derived from electric tomography 2D/3D technique.

Geochemistry has demonstrated that oxidation and salinization processes are more active in the sediment surface layers than in subsurface layers. Acidification has also been found to be more active in surface layers, with analyses of the poll showing pH's slightly less acidic, combined with high concentrations of Zn. The results were analyzed with the different geoelectric profiles, and corroborated with the geochemical sampling and analysis; where different layers can be differenced.

INTRODUCTION

In the Murcia Province, there are 85 mining silt ponds due to intensive mining activities that occurred during last century, especially in the Sierra de Cartagena-Union. Mining activity was abandoned several decades ago.

The silt ponds, due to their composition and location, may create environmental risks of geochemical pollution, negatively affecting soil, water, plant, animal, and human populations, as well as infrastructure.

The Ministry of Economy, through the "Dirección General de Política Energética y Minas" has compiled an inventory of these abandoned silt ponds in 2003.

The major purpose of this inventory was to establish a classification of the existing silt ponds in the Province, according to their potential risk for the environment, human population, and infrastructure. The inventory offers an evaluation describing the potentially affected receptors. Based on these evaluations, an action plan can be established.

To deepen the knowledge of the current state of silt ponds with the most potential risk, detailed studies were conducted, following the recommendations of the inventory. These studies were carried out with the application of geophysical and geochemical techniques, which allowed the establishment of an analysis and quantitative evaluation of the contamination risks. This work shows the results of the studies corresponding to the silt pond called "Brunita".

MATERIAL AND METHODS

Study area

The "Brunita" silt pond is located in the southern part of the La Union-Cartagena mining district. The mine from which this silt pond originated was active from 1940 to 1952, and "Brunita", as a sedimentary structure, was finally consolidated in 1956. The pond is a differential flotation pond formed from the exploitation of an area characterized mainly by sulfide compositions such as pyrite, sphalerite, galene, marquesiste and pyrrotine, and, secondarily, calcopyrite, arsenopyrite, tetrahydrite and stannite, with siderite as the main carbonate (López *et al.*, 1986). In 1981, the mining company closed and, consequently, the pouring of residual materials into the pond ended (Bautista y Egea, 1991).

Geochemical technique

For the geochemical characterization of the silt pond, a poll located in a representative area was carried out (Figure 1), which was driven down into the substrate (14.8 meters depth). Samples were taken every meter from 0 to 14 m, while 3 punctual samples (13.8; 14 and 14.8 meters) were taken in the substrate.

Samples were air dried, passed through a 2 mm sieve, and ground. For soil moisture determination, the samples were weighed and oven dried at 105 °C for 24 h. Soil pH was measured with a glass electrode in a 1:1 soil/water suspension using the method of Peech (1965) referred to water and 1M KCl (pH-meter Basic 20 CRISON). Soil electrical conductivity was measured in a 1:5 soil/water suspension (Andrades, 1996). The total amount of metals was determined by acid digestion with nitric/percloric and measured with atomic absorption spectrophotometer (UNICAM 969).

Geophysical technique

Profile	Northwest			Southeast		
	X	Y	Z	X	Y	Z
A	686359.00	4164868.00	145.00	686546.00	4164683.00	228.00
B	686424.02	4164868.90	159.00	686611.00	4164685.28	167.00
C	686486.95	4164944.21	155.00	686664.05	4164747.08	-
	Southwest			Northeast		
	X	Y	Z	X	Y	Z
D	686397.00	4164752.00	160.00	686565.00	4164801.00	158

Table 1.- Coordinates of the geolectric profiles

The geophysical equipment used was a Syscal R1 Bonus resistivimeter (IRIS Instruments), which had a cable multinodo with 72 connections and allows measurements to be taken on each of the electrodes simultaneously. Four profiles of electric tomography with 72 electrodes were taken; three of them were prepared lengthwise in the pond, and one traversing the pond. Coordinates are shown in Table 1.
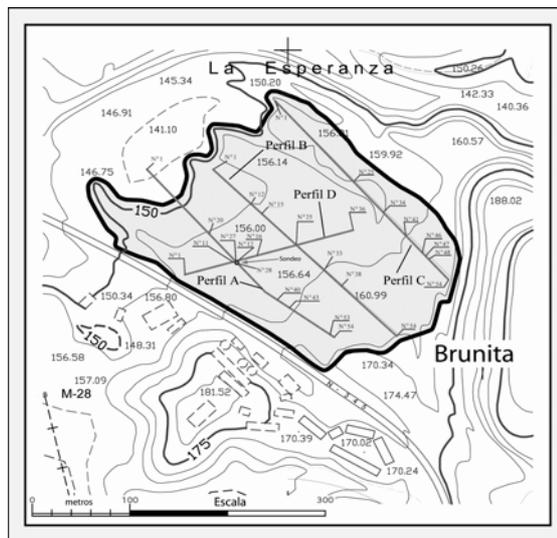

Figure 1.-Situation of the profiles of electric tomography and the geochemical poll at the "Brunita" silt pond.

The electrodes were then located on the map using GPS coordinates (Figure 1) and the measures pre-handing is carried out, using the software Prosys. The software Res2dinv was used for the final data handling, which consisted of statistical algorithms (Edwards, 1977; Loke and Barker, 1996).

After of pre-handling and handling phases comes the interpretation phase where the obtained results are analyzed; everything supported by the geologic information of the area, and the data of the determinations of the samples coming from mechanical poll.

**RESULTS AND DISCUSSION**
Geochemistry
Table 2 and figure 2 show that both pH measured in water and KCl 1M solution follow the same distribution pattern. There is not a clear increase or decrease of the pH with regards to depth.

| Depth (meters)	pH water	pH KCl	E.C. (ds/m)	% Clay	Pb (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Cd (mg/kg)
0-1	4.89	4.84	11.83	5.2	2.240	125.7	6.084	11.72
1-2	6.31	6.16	11.05	3.2	1.705	174.9	8.060	20.16
2-3	6.64	6.35	6.22	3.8	2.434	142.4	9.999	29.25
3-4	6.36	6.04	4.70	7.7	1.934	395.1	4.943	10.26
4-5	6.55	6.29	3.45	2.9	4.558	211.4	7.315	117.2
5-6	6.55	6.30	2.98	3.5	6.874	306.6	8.330	21.16
6-7	6.57	6.31	2.76	2.8	7.687	231.1	7.692	17.80
7-8	5.88	5.63	2.90	27.4	2.265	402.9	4.107	16.53
8-9	5.24	5.21	3.31	3.8	2.439	407.5	2.835	12.52

9-10	4.59	4.50	5.06	3.8	4.555	229.0	13.358	35.71
10-11	5.12	4.78	4.04	1.0	2.963	153.7	12.890	33.67
11-12	5.01	4.90	4.91	2.3	5.884	128.0	10.009	30.98
12-13	4.79	4.69	5.87	2.6	4.242	144.3	16.068	44.38
13-14	6.22	6.26	3.38	5.8	3.761	175.2	14.131	44.01
13.8 (substrate)	6.87	6.85	2.51	11.1	2.440	165.6	29.936	24.09
14.0 (substrate)	7.43	7.32	2.47	11.3	729.9	63.75	5.038	19.89
14.8 (susbtrate)	7.34	7.27	1.83	12.6	670.6	31.05	3.999	9.18

Table 2. pH water and KCl solution; electrical conductivity, clay content, and total heavy metals in the samples of the poll.

pH$_{water}$ from 0 to 1 m presents a value of 4.89, strongly acidic according to Porta *et al*. (1999); from 1 to 2 m, pH increases to 6.31, slightly acidic. The same results occur in the layer between 3-7 m. The pH is neutral from 2 to 3 meters. In Figure 2, a slight decrease in the pH was seem from 9 to 13 m, being slightly acid from 8 to 9 m, and strongly acid to the depth 9-10 m and 11-13 m; while the layer 10-11m is characterized for being strongly acidic.
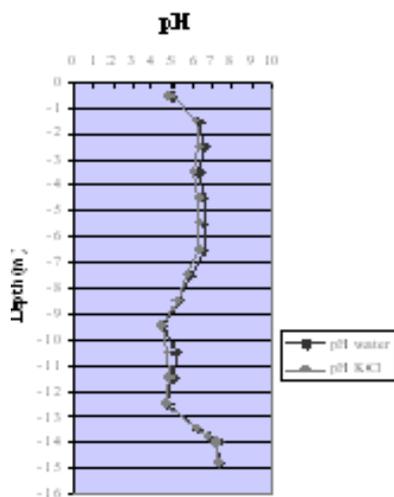
Figure 2.-pH water and KCl solution with depth
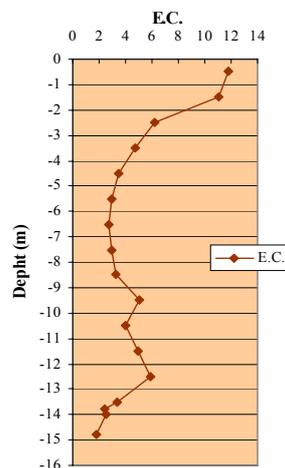
Figure 3.-Electrical conductivity with depth

Finally, the sample located near the substrate (13-14 m) is classified as slightly acid, presenting a value of 6.22. A certain increase of pH in the three samples taken from 13 m to 14 m is seen, passing from slightly acidic to fairly basic silts.

Regarding the electric conductivity, a decrease in the soluble salts concentration with relation to depth occurred, although some variations were observed, as seen in Figure 3. The first decrease of the value of the E.C. occurs from 0 to 7 m, with strongly saline silts (11.83 dS/m) at the surface and slightly saline (2.76 dS/m) in the last depth. Then, a progressive increase in salt concentration reaches 5.06 dS/m (9-10 m) classifying the samples as moderately saline. The layer located between 7 and 9 m is classified as slightly saline with values ranging from 2.1 to 4.0 dS/m. In the interval between 9 and 11 m there is another decrease, with the E.C. changing from 5.06 to 4.04 dS/m (lightly saline); followed by an increase to 5.87 dS/m, down to 13 m, with moderately saline silt. From this depth, the values of the electrical conductivity descend continuously to 14.8 m.

Negative correlation between pH and E.C. can also be clearly determined (Figures 2 and 3). pH values of the surface samples are lower than those from the deeper samples ones. This is due to the fact that the most active weathering occurs in the surface layer, where the different sulphides are oxidized. Table 2 shows that the first poll sample is the most acidic in relation to the subsequently deeper samples. Electrical conductivity values are higher in the surface samples, which indicates that the quantity of some chlorides, sulphates, nitrates, carbonates and phosphates diminish with depth.

The percentage of clay in all the samples of the poll, in general, is low, around 5%. Only in the sample from 7 to 8 meters the clay content is 27.4%. It is also appreciated on Table 2 that a lightly increase of the content of the clay fraction from the 11 m of depth appears, this is because those belong to substrate samples, and therefore, natural soil.

Zinc concentrations surpass 4000 mg/kg in most of the samples, with some of them exceeding 10000 mg/kg (Table 2). In Figure 4, the maximum concentration of Zn registered in the substrate limit (13.80 m) is 29936 mg/kg, while the lowest content, 2835mg/kg, appears from 8 to 9 m.

In relation to the distribution of zinc, the concentration increases from the surface to 3 m, from 6083 to 9999 mg/kg (Figure 4). Then, there are increases and decreases of the concentration of Zn in the remaining layers. From 4 m to 6 m depth the content increases, reaching 8330 mg/kg Zn.

This is followed by a progressive decrease down to 9 m, where the content of the metal is 2835 mg/kg. From 9 to 14 m a series of fluctuations occur, oscillating from 10009 to 16067 mg/kg. An abrupt increase takes place at 13.8 m (limit of the substrate), with the concentration increasing from 14131 to 29936 mg/kg. Finally, these values decrease considerably in the substrate (3999 mg/kg), to the final depth (Figure 4).
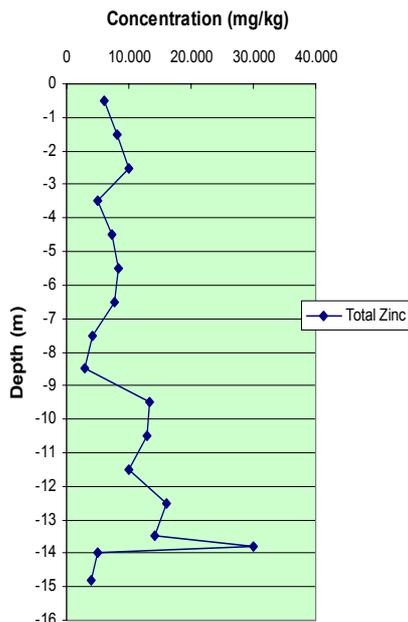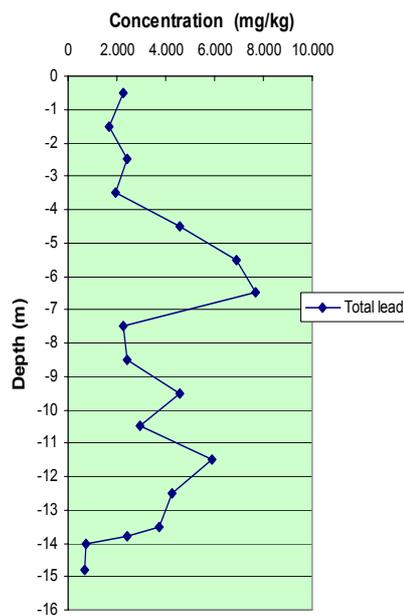

Figure 4.-Total zinc of the poll

Figure 5.-Total lead of the poll

High lead concentration in the residual layers of the pond also appears (Table 2). In this case, the highest Pb content appears from 6 to 7 m, being 7687 mg/kg, while the lowest concentration occurs at 14.8 m. From surface to 4 m, the Pb concentrations range from 1705 to 2434 mg/kg (Figure 5). Then, the values increase, reaching 7687 mg/kg at 7 m. A considerable decrease takes place below 7 m, and then some fluctuations appear down to 11 m; these fluctuations range between 2265 and 4555 mg/kg. It is clearly observed that the concentrations decrease with greater depth, and an important change in the substrate, from 13.8 m and 14 m, should be noted. The nature of this material is different from the material of the residual layers, showing low mobility of the metal.

Regarding copper, the maximum concentration of Cu was reached from 8 to 9 m, (407.5 mg/kg). On the contrary, the lowest contents were obtained in the last two samples of the substrate (as also seen with PB), with concentrations of 63.8 and 31.1 mg/kg. The distribution pattern of Cu is different to Pb and Zn, showing some fluctuations occurring in the first 7 m; from 7 to 9 m the Cu content is nearly the same, about 400 mg/kg. Then, the concentration decreases down to 12 m (128 mg/kg). In the following 2 meters, opposite to what happens with Pb, the content increases to 14 m, where a value of 175.2 mg/kg was indicated. Starting from this depth, the concentrations decrease reaching only 31.1 mg/kg in the substrate.

Finally, the residual layers of this poll and the substrate surpass 9 mg/kg of cadmium. The maximum concentration of Cd was observed from 4 to 5 m, at 117.2 mg/kg, while the lowest content was observed in the substrate at 14.8 m.
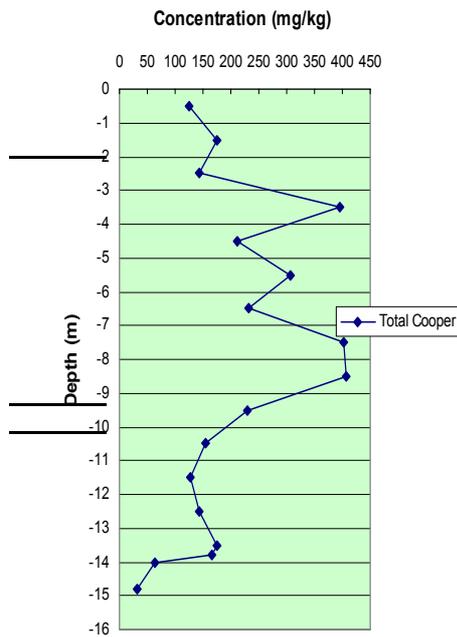
Concentration (mg/kg)

Figure 6.-Total copper in the poll
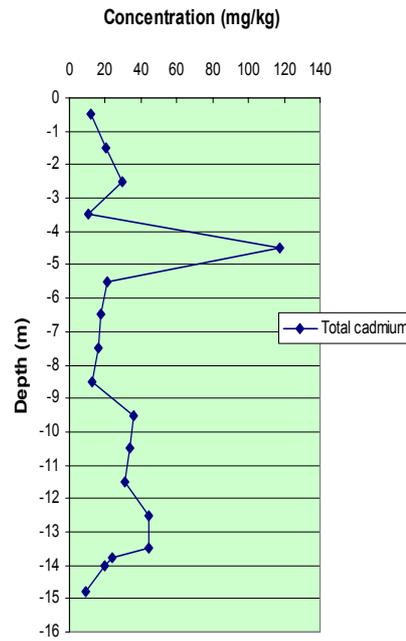
Concentration (mg/kg)

Figure 7.-Total cadmium in the poll

When Figures 4 and 7 are compared, the similarity between the depth distribution of Zn and Cd can be seen. The most significant differences take place at the intervals between 4 and 5 m, and 13 to 14 m. From 4 to 5 m it is due to the increase in the concentration of cadmium, from 10.26 mg/kg at 4 m depth to 117.2 mg/kg at 5 m. In the latter interval, the quantity of Cd progressively decreases to 14.8 m, while in the case of Zn an important increase takes place at 13.8 m (limit with the substrate), and then continues to decrease through the substrate.

Geophysics

Figure 8 represents the geoelectrical pseudosection of profile A. The silt materials are detected in the geophysical section with low values of resistivity, less than 10 Ohm·m.
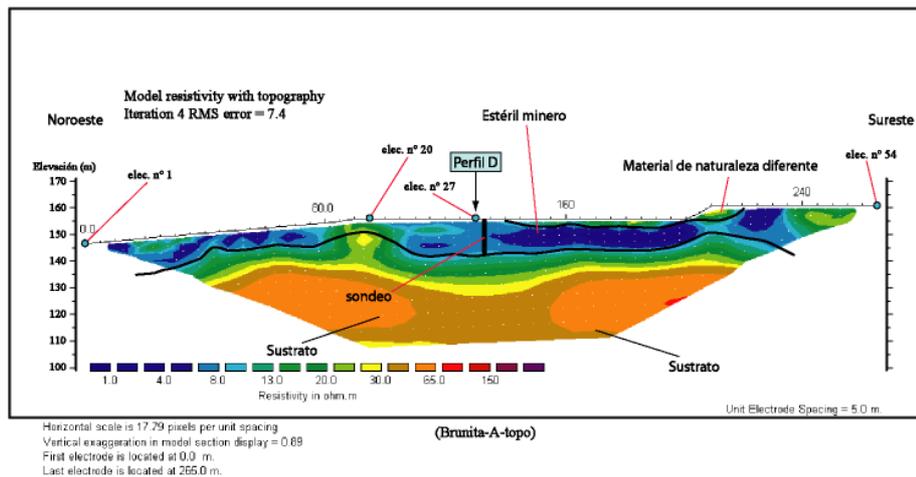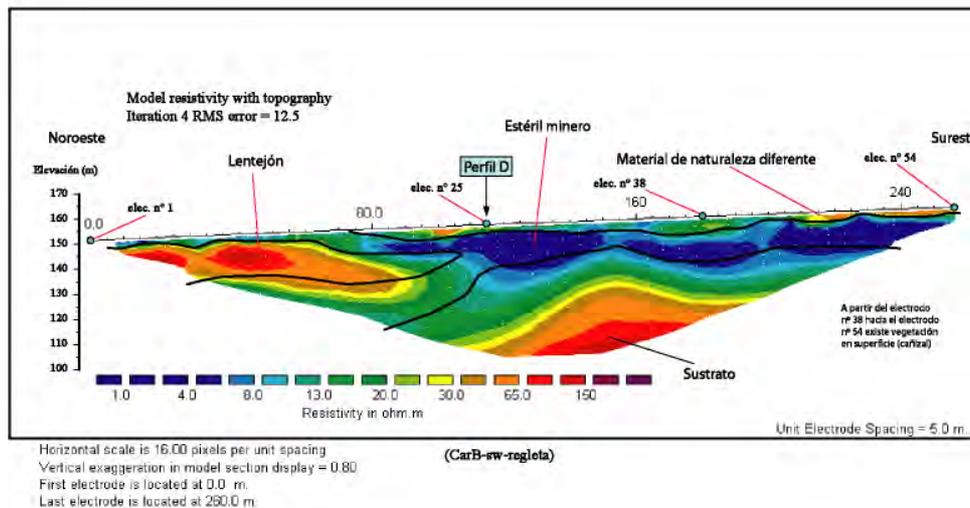
Figure 8.- Electrical Pseudosection of the profile A.

On the right side of the profile, a different resistibility material, with slightly higher values to those described previously, is observed at the surface, varying from 10 Ohm·m to 60 Ohm·m. In this area the predominant surface material has a more compact nature, with a lajose morphology. In other parts of the pond, with presence of the same material, a moderate resistibility has also been detected.

Figure 9 shows the geoelectrical section of profile B. The result of the representation is quite coherent in relation to profiles A and C, which present increase of the thickness of the materials (with a low resistibility) in the central part of the section, with about 15 meters depth, and a decrease of the thickness of this material towards the left side of the section, with an increase in the presence of material with more resistibility (values higher than 50 Ohm·m). This last material forms a fracture and infiltration area.

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In the right part of the section the presence of resistive material can be observed at the surface, the same as in the profile A, coinciding with the presence of more compact material and with the development of vegetation.

Figure 9.- Electrical Seudosection of the profile B.

The geoelectrical pseudosection of the profile C is shown in the figure 10. As in the previous profiles, a material characterized by resistibility low values is presented, lower to 10 Ohm·m. In the left part of the profile, zones of high resistibility are presented, similar to those presented in the previous profile. The profile also detected areas of possible fractures.

In the right part of the profile the presence of more resistive residual material is seen at the surface, indicating the presence of a different material in this area of the section.
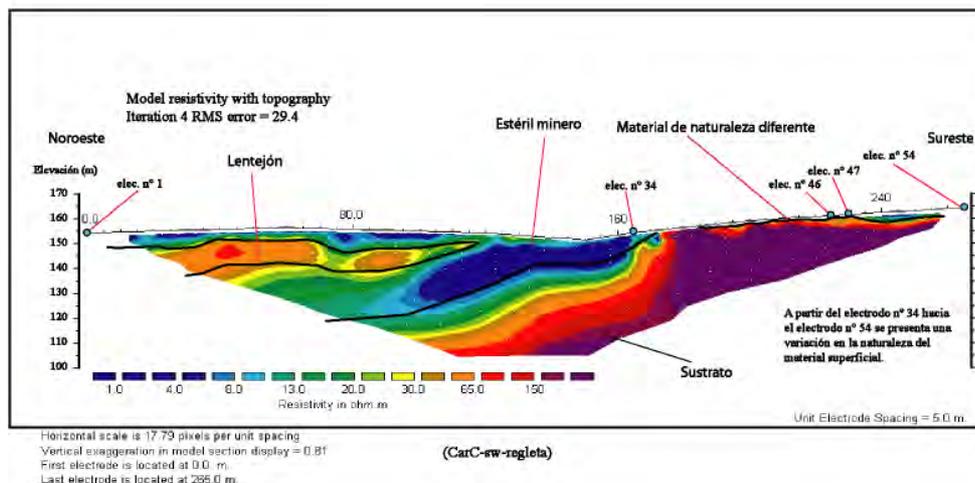
Figure 10.- Electrical Pseudosection of the profile B.

Figure 11 represents the geoelectrical pseudosection of the profile D, showing the mining silt with a value of resistibility down to 10 Ohm·m. The baseboard is presented in the inferior part of the pseudosection through resistibility values higher to 10 Ohm·m, reaching 150 Ohm·m. Profile D crosses profile A and profile B, and when comparing the obtained results of the previous profiles a very precise correlation with these areas of high resistibility is observed, due to compaction of the surface material accompanied by the phenomena of chemical alteration.

The thickness of the material below profile D varies, with its minimum thickness occurring toward the left of the profile and an increase to the right. The pseudosection shows a maximum thickness of 15 m.
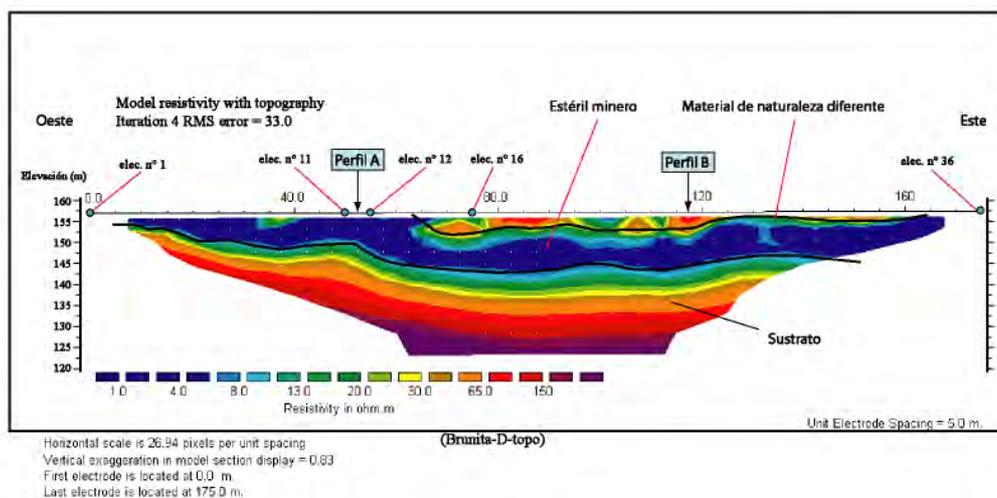
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Figure 11.- Electrical pseudosection of profile D.

CONCLUSIONS

The pH$_{water}$ presents an increase with depth reaching values fairly basic. Regarding the electrical conductivity, a decrease of the concentration of salts takes place with the increase of depth.

Geochemistry has demonstrated that oxidation and salinization processes are more active on the surface than in deep layers. This also occurs in acidification, with the analyses of the poll having showed pH's slightly less acidic together with high concentrations of Zn.

Most of the samples show the concentration of Zn higher than 4,000 mg/kg, with some samples reaching 10,000 mg/kg. The maximum concentration of Zn is 29,936 mg/kg, while the lowest content of this metal is 2,835mg/kg and appears from 8 to 9 m. Lead concentrations are also important in these layers. In this case, the highest lead content is observed from 6 to 7 m depth, at 7,687 mg/kg, while the lowest concentration is at 14.8 m.

With respect to copper, the maximum concentration of 407.5 mg/kg is reached from 8 to 9 m; on the contrary, the lowest contents are presented in the last two samples of the substrate, being 63.8 and 31.1 mg/kg. The pattern of distribution of Cu is also different to Pb and Zn ones. Finally, the residual layers of this pond exceed 10 mg/kg of cadmium. The maximum concentration of Cd is observed from 4 to 5 m, at 117.2 mg/kg, while the lowest content is seen in the substrate at a depth of 14.8 m.

The electrical tomography shows values of electrical resistibility of the mining silt are mainly lower than 10 Ohm·m, indicating that it is a material with high conductivity, normal in substances coming from metallic minerals treatment. The electrical profiles show an increase of the thickness toward the north of the pond, below profile B and profile D. These reflect an area with low mechanical characteristics, showing fracture and infiltration areas.

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