

APPLIED GEOPHYSICS ON A SOIL CONTAMINATED SITE BY CHROMIUM OF A TANNERY IN MOTUCA (SP, BRAZIL)

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ABSTRACT. The management of contaminated sites includes the purchase of a data set ranging from the historical information of the occurrence, preliminary and detail diagnostic, monitoring and remediation. The settlement Monte Alegre located in Motuca (SP, Brazil) received an irregular disposal of waste of tannery leather on the soil surface in 2001 by the industries of the region. The tanning process involves the use of chromium salts, considered a carcinogen element in its hexavalent form. Based on preliminary evidence, the Environmental Agency of São Paulo State (CETESB – Companhia Ambiental do Estado de São Paulo) performed chemical analysis and recognized soil contamination in some lots. This study conducted geophysical surveys at one of these lots, the one that received the higher amount of leather (40 tons). The geophysical methods of resistivity and induced polarization conducted by 10 parallel lines of electrical tomography of Schlumberger array were used. The analysis of the environmental history of the field and geophysical results to characterize the presence of metal contaminants (Cr) in soil, which receive leather, indicated high chargeability (above 0.67 mV/V). More than one decade from the end of the disposal, it is still recognized clear indications of contamination in the soil by chromium, possibly due to its dissolution in rainwater, infiltration into the soil and complexation/retention by clay minerals.

Keywords: contamination, leather, resistivity, chargeability, 3D modeling.

RESUMO. O gerenciamento das áreas contaminadas prevê o levantamento de um conjunto de dados que variam desde informações do histórico da ocorrência, diagnóstico preliminar e de detalhe, monitoramento e remediação. O assentamento Monte Alegre localizado no município de Motuca – SP foi alvo de disposição irregular de aparas de couro de curtume no solo em 2001. O processo de curtimento envolve o uso de sais de cromo, considerado cancerígeno em sua forma hexavalente. Baseado em indícios prévios, a Companhia Ambiental do Estado de São Paulo (CETESB) realizou análises químicas no local e reconheceu a contaminação do solo em alguns lotes. O presente estudo realizou levantamentos geofísicos em um destes lotes, que recebeu a maior quantidade de aparas (40 toneladas). Foram utilizados os métodos da eletrorresistividade e da polarização induzida, por meio de 10 linhas paralelas de tomografia elétrica em arranjo Schlumberger. A análise conjunta do histórico ambiental da área e dos resultados geofísicos permite caracterizar a presença de contaminantes metálicos (Cr) em faixas de solo que recebem leiras de aparas de couro, cuja presença de metal é indicada pela alta cargabilidade (acima de 0,67 mV/V). Decorridos mais de uma década, ainda são reconhecidos indícios de contaminação no solo por cromo, possivelmente devido à dissolução em águas de chuva, infiltração no solo e complexação/retenção por argilominerais.

Palavras-chave: contaminação, couro, resistividade, cargabilidade, modelamento 3D.

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INTRODUCTION

The distribution of chemical elements and minerals in the subsurface is a result of several geological processes that can cause a dispersion or accumulation of elements in certain areas. Areas where the main process occurring was the concentration of minerals can be defined as geochemical anomalies, which can feature mineral deposits with potential economic value. However, anthropogenic activities such as mining and industrial processes that manage some chemical elements can create these geochemical accumulations. Those unnatural anomalies can cause potential damage in the environment such as soil and water contamination (Bell, 1998).

Chromium is one of the metals that can reach the soil and groundwater and cause several environmental impacts due to its large use in industrial activities such as ore refining, metal corrosion inhibitors, ferrous and nonferrous alloys, leather tanning and others (Papp, 1994; Bielicka et al., 2005; USEPA, 2010).

Leather tanneries use chromium salts in the tanning process so it can transform animal's skins into leather. About 90% of manufacture leather is made by tanning using chromium, which gives the skin a blue coloration from the salts (wet-blue) (ABDI, 2011).

During the process of tannery, a large generation of wastewater and solid waste contains chromium. Metals such as chromium cannot be removed from the effluents only by conventional treatment; and the amounts of solid waste are classified as dangerous and should have a correct destination (Moreira & Teixeira, 2003). According to studies on the mass balance in tanneries, for each ton of skin entering the process, only 250 kilograms are transformed into premium leather, the remainder are crust and waste (CETESB, 2005). Usually these waste ends up being in the environment for a long time, since they are not biodegradable and are disposed in irregular places without the proper treatment.

In this way, without the correct management, treatment and destination, the tannery can cause environmental impacts creating contaminated sites.

The management of contaminated sites provides a protocol of steps that involves the previous record of the site, preliminary and detail investigation, succeeded by planning the remediation efforts and the monitoring program (CETESB, 2001). In soil and groundwater, chromium can be identified by quantitative data from the direct methods such as samples, or by indirect methods, that provides qualitative data from the contamination such as geophysics.

Applied geophysics investigate structures, materials and elements in the subsurface through indirect measurements of physical properties of underground, with no invasion to the environment. Metals can change the natural electrical properties in the

environment under contamination, and can be detected by geophysical survey. Some studies show the use of electrical geophysics methods in sites with soil and groundwater contaminated by chromium (Elis & Zuquette 2001; Nunes & Luiz, 2006; Fachin et al., 2006; Sankaram et al., 2009; Cunha & Shiraiwa, 2010; Ye et al., 2011).

The following study presents a geophysical survey from a site with residual chromium of an improper release of leather crust in a rural settlement in Motuca (SP). The study takes the environmental history of the location as reference to plan the geophysical survey. In this way, it was conducted an electrical tomography using the resistivity and chargeability parameters to produce 2D profiles and 3D models.

LOCATION AND HISTORY

The study area is located in a rural settlement named Monte Alegre in Motuca, a city on the countryside of the State of São Paulo, 313 km away from its capital (Fig. 1). The settlement received an irregular disposal of tannery waste consisted in leather crust with blue aspects, which suggests that the crust has residual chromium. It was registered complaint at the environmental agency CETESB (Environmental Agency of São Paulo State) in 2002 and the monitoring program began (CETESB, 2013).

The disposal occurred in several areas of the settlement, in about 15 properties (reaching 1200 farmers from 19 families). With lack of information, the farmers used the waste as a growth organic compound to their crops. Once the farmers grew food, such as mango, lemon, orange, tangerine, sugar cane, corn and other vegetables with the organic compound and used to consume and sell it in groceries markets nearby, the situation became a potential public health problem.

The remediation work consisted only on the removal of the material in the soil surface; about 150 ton of waste removed between the years of 2002 and 2003 were designated to a regular landfill. CETESB sampled groundwater from wells used for irrigation and consumption of the farmers. The results showed that none of the well had a chromium concentration above $50\mu\text{g/L}$, reference value to total chromium in water proper to consume.

Soil samples from some properties were analyzed in 2002 to detect the presence of total chromium. Some results presented concentrations above the limit allowed by CETESB, which classifies the samples according to a reference value of 40 mg of chromium/kg. When the concentration reaches a level beyond 75 mg/kg the samples are considered in an alert value, and by the time it gets higher than 150 mg/kg, it is classified as an agriculture intervention (CETESB, 2014).

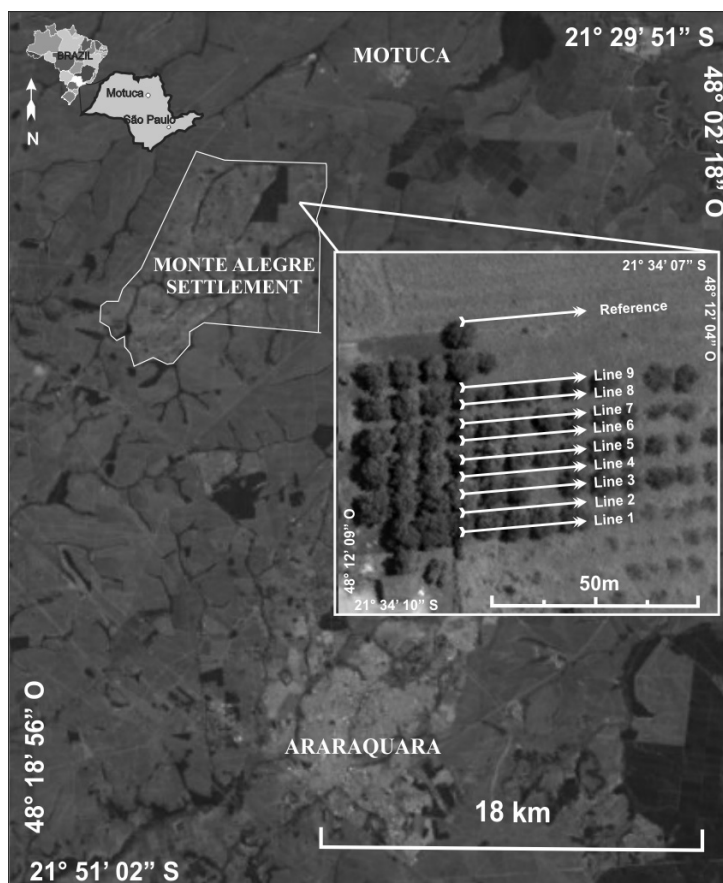


Figure 1 – Location of Monte Alegre Settlement with detail of geophysical survey.

The illegal disposal caused a change in soil quality regarding chromium concentration. In this way, the farmers received a notification about the contamination state of their lands and a formal request to stop the activities until the concentrations were normalized and did not represent a threat to them and the consumers.

The property studied in this work was the number 20. The concentration of chromium in the soil sampled by CETESB in 2002 presented the value of 85,3 mg Cr/kg soil, considered therefore as a state of alert. In the year of 2004, however, a new sample collected presented a value of 187 mg Cr/kg soil, which characterized the area as an agricultural intervention. The analytical monitoring continued and the area remained in a state of alert according to the 2007 samples, which showed a chromium concentration of 85,88 mg Cr/Kg of soil in the first layers of soil (0-5 cm) and 54,26 mg Cr/Kg soil in depth (5-20 cm) (CETESB, 2013).

Once the concentration of total chromium decreased throughout the years; the waste was completely removed from the settlement, and no new sources of contamination occurred, the

monitoring work ended in 2012, giving back the farmers the possibility to continue their activities regularly.

METHODS

The use of applied geophysics in environmental problems is a very important and widely recommended tool, once it supports the characterization of contaminated sites, and the identification of geological materials with environmental interest. In addition is a very efficient instrument for monitoring plans (Knödel et al., 2007).

The electric current methods make use of the electrical properties from the subsurface materials and add geometric parameters like thickness, depth and direction to produce an electric profile capable of distinguish the different materials from the distinct electrical responses (Telford et al., 1990). The contaminants that reach the environment can change the electrical response when in soil and groundwater; therefore, the use of methods such as Resistivity and Induced Polarization, used in this work, can detect contaminants in subsurface.

Both methods use a pair of electrodes on the ground that send an specific electrical current, then the equipment can read the response of underground materials such as resistance and residual voltage to calculate the parameters of resistivity and chargeability in the time domain.

The geophysical survey occurred in the property number 20 of the Monte Alegre settlement. This land received the larger quantities of waste from all the contaminated areas, around 40 ton (CETESB, 2013). According to the owner, the disposal occurred for a year in his mango trees, in which were build parallel waste windrows of 1 meter high and 2 meters long over the base of the mango trees.

In field, were conducted 9 parallel lines of electrical tomography with 30 meters each, with an 3,75 meters of space between lines, positioned alternately along and between the lines of crop. To compare the results and have a better understanding of the situation, it was conducted a reference line, located in a northern area that did not receive the waste (Fig. 1). During the acquisition, some residual crust waste over the ground was found even when the environmental report claimed for the total removal of all the crust waste (Fig. 2).

The acquisition of the geophysical data by the equipment Terrameter LS made by ABEM with cable and electrodes happened in July, 2015. Is was used the Schlumberger array and spacing between electrodes of 1,5 m. The instrument was programmed to use a maximum electric current of 100 mA and a minimum of 50 mA, the current was sent during 1 second, the delay time was 0,4 second and the readings occurred in 2 intervals of 100 miliseconds each.

The data acquired in field was processed and labored on in order to obtain as a result a bidimensional electrical profile and tridimensional models to resistivity ($\Omega.m$) and chargeability (mV/V) parameters. The measures in field were processed by the software Res2dinv (version 3.53) and resulted in an inversion model in terms of distance \times depth, and an interpolation with a logarithmic scale. The profiles have presented the contrast from the measures after the interpolation in a color scale, where the cold colors are attributed to low values and hot colors to the high ones. This software determines automatically a bidimensional model of the subsurface from resistivity or chargeability obtained in the electrical tomography survey (Griffiths & Barker, 1993).

The numeric values of the bidimensional inversion profile from each section (field line) were reunited in a spreadsheet that contains the position of the values along the lines (variable x), the space between the lines (variable y), the depth (variable z)

and the resistivity or chargeability values (variable R). Each point from the 3D modeling is transformed in a block with conditional dimensions from a statistic criterion by the minimum curve method in the software Oasis Montaj, Geosolft plataforma (version 6.4). The works of Moreira et al. (2013, 2015, 2016); Vieira et al. (2016); and Cort ez et al. (2016) describe in detail the elaboration of 3D visualization models used in this work.

DISCUSSION AND RESULTS

The analysis of the inversion models indicates an evident value variation between the alternate lines, with respect to the reference line positioned at north. The odd lines (1, 3, 5, 7, and 9) presented great contrast. On the other hand, the even lines (2, 4, 6, and 8) presented similar patterns to the reference line. In the field, the tomography lines 1, 3, 5, 7 and 9 were placed under the line of mango trees, where the waste disposal occurred, and the tomography lines, 2, 4, 6 and 8 were placed parallel and between the line of the mango tress (with no disposal waste) (Fig. 2).

The resistivity and chargeability measures were processed in a joint way, on logarithmic scale to highlight the extremes values. The same scale were applied to all resistivity profiles and the values ranged from 200 $\Omega.m$ to 2568 $\Omega.m$, and the same procedure to chargeability showed values that ranged from 0,5 mV/V to 0,99 mV/V (Fig. 3).

In terms of resistivity, it was expected that the profiles of the lines that received the waste had lower values than the natural pattern of the area (200-288 $\Omega.m$) due to the presence of chromium, however, the parameter was not enough to detect the contaminant. The high resistivity (1238-1783 $\Omega.m$) may be linked to a higher presence of roots or the presence of Fe in the oxidized form.

Comparing the geophysical lines in the contaminated area with the reference one, it indicates that the limit of natural chargeability for the area is 0,67 mV/V, in that way, values above this limit indicate a contamination by residual chromium.

The 3D modeling through the interpolation of the 2D sections allowed the generation of depth visualization models at several levels (Fig. 4). In processing, the color scale was the same as the 2D inversion values.

The depth maps allow a reaffirmation of the disparity between the areas below the trees where the waste were added to the areas between the trees that were not impacted, demonstrating that the presence of residues modified the natural physical parameters of the site.

In the beginning of the first lines, the chargeability shows a value of 0,99 mV/V, which can indicates that the area are



Figure 2 – Detailed acquisition of geophysical data and residual crust.

contaminated. In those areas, there is a depression of the local relief that can accumulate water during the rainy seasons and become saturated with water for long periods, indicating the presence of mud cracks only in this particular area (Fig. 5).

In addition to characterizing the area, environmental contamination studies should understand how the contaminants, once inserted in the environment, present themselves. What determines the expression of the contamination depends on the chemical form or speciation of the element, since it affects the distribution, mobility and toxicity. Speciation can be understood as the form that an element in the environment presents itself: free, complexed, adsorbed or precipitated. Many agents control speciation, the most relevant ones are pH and Eh (Rai et al., 1989; Plant et al., 1996; Kotas & Stasicka, 2000).

Therefore, the physical-chemical conditions in the mud cracks allow a period of chemical reduction, a process favorable to the persistence of Cr (III) on soil. The accumulation and persistence of chromium in this area can be attributed to the occurrence of soils with their origins in igneous basaltic extrusion, with high levels of clay's minerals and a characteristic red coloration from the oxidation of magnetite. This soil are rich in this type of oxides and is a possible important agent to fix the chromium in the superficial levels of the soil.

To understand what happened to the chromium in the rest of the area, it is important to know that the reduction of Mn e Fe

oxides is a common process that is used to convert Cr (III) to Cr (VI) (Bartlett & James, 1979; USEPA, 1994). This last one is highly mobile and soluble in water, in this way, in rainy periods; the pluvial waters can lixiviate the element completely. Probably this is the main process occurring in the study area.

In this way, the geophysical survey indicates that the physical and chemical conditions allowed the process of lixiviation occurred in almost the entire contaminated area, however, a small area still have the presence of chromium in soil, but it is not in a form that is available for the mango trees. It is possible that the chromium will be found in an oxides or hydroxides form, complexed in the soil.

CONCLUSION

The results of the joint application of electrical current methods in an area with amounts of chromium from an irregular disposal of leather crust, showed a contrast in the physical properties of the area. Among the processes, that involves a concentration or dispersion of chromium in the environment, the lixiviation and complexation processes probably were crucial to the initial mobility and posterior retention of the chromium in the first soils layers.

The chromium on soil has its origins in the lixiviation of the leather crust that were disposed in windrows along the mango trees. The interconnection between the geophysical data and

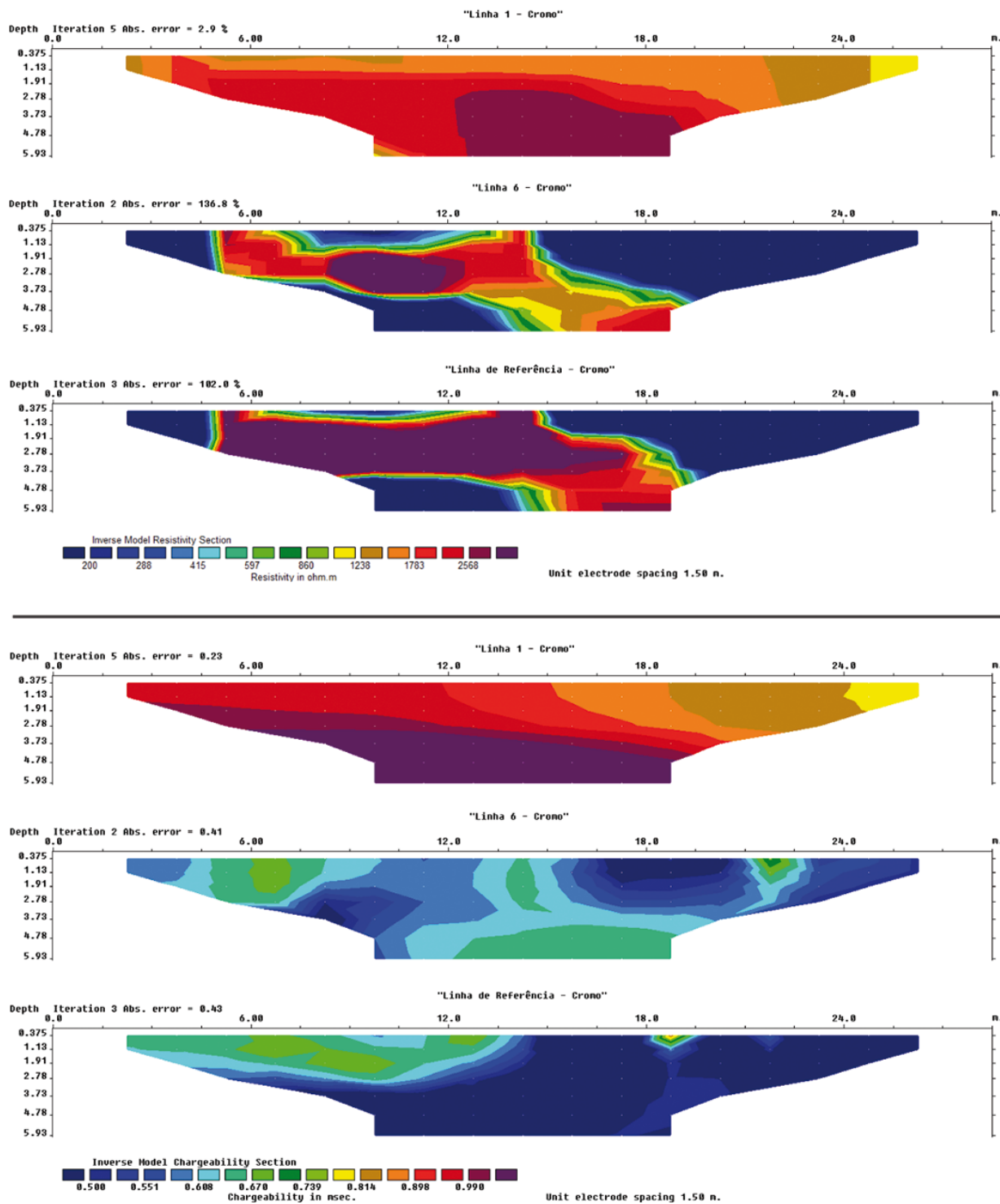


Figure 3 – Geophysical data of lines with and without waste.

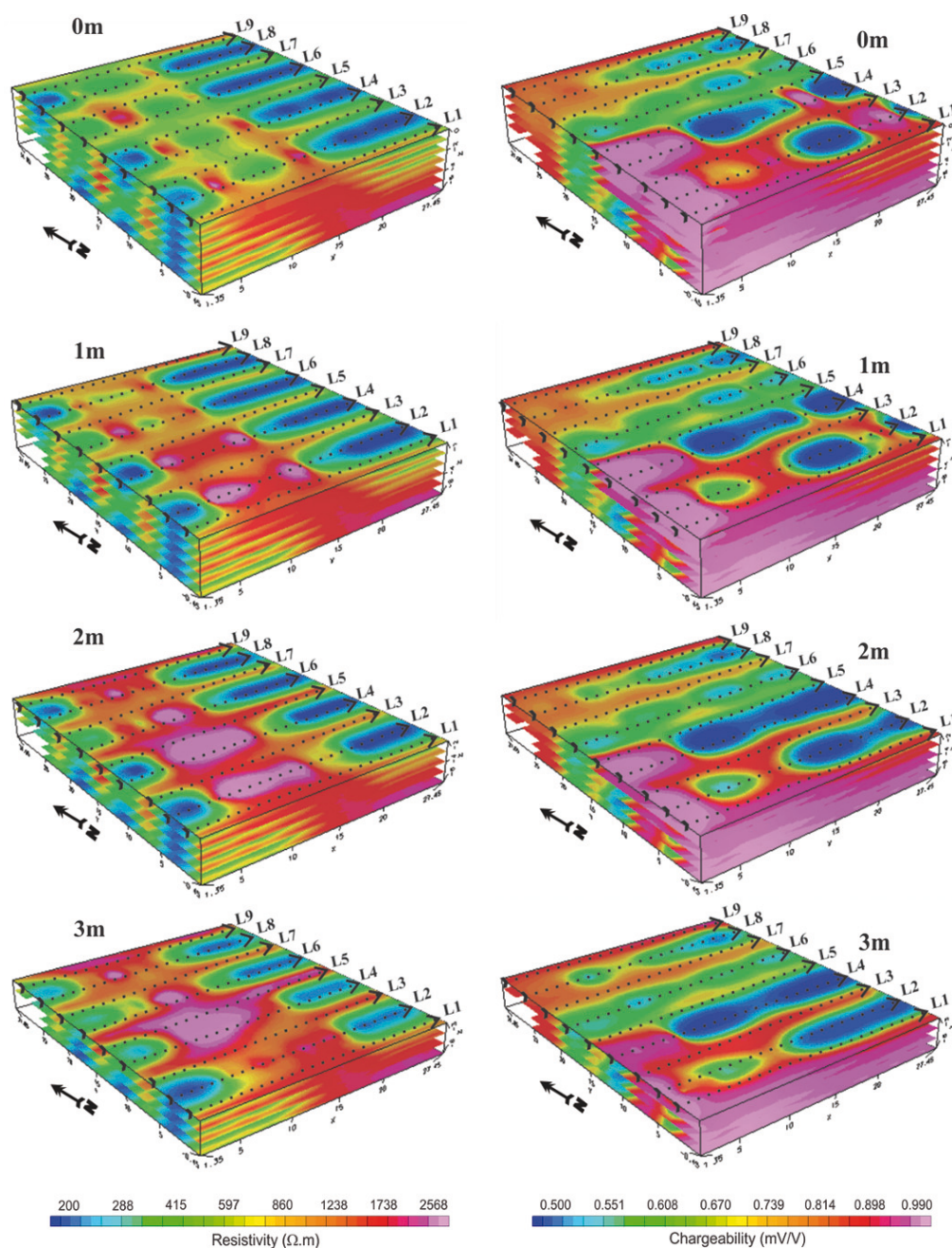


Figure 4 – 3D models for the resistivity and chargeability for several depths.

the record of the contaminated area, allows the definition of a geophysical signature to the compound in soil that contains chromium, differently from the natural electrical pattern.

Chargeability data are essential to identify the residual contamination, once only by this method it is possible to set out the situation of the contaminated site. For metals such as chromium, it is possible that occur the phenomenon of electronic polarization, with accumulation of charges under the presence of an elec-

trical current. Even with the high concentration of metallic minerals such as iron in the soil, only when the minerals were complexed to the chromium ions, forming oxides, it was possible for the chargeability measures to obtain a higher value that distinguishes itself from the rest of the area.

Among the alternatives of remediation of contaminated sites by chromium, the natural attenuation is a very common one. The diversity of elements that are capable of reduce the Cr (VI) to Cr

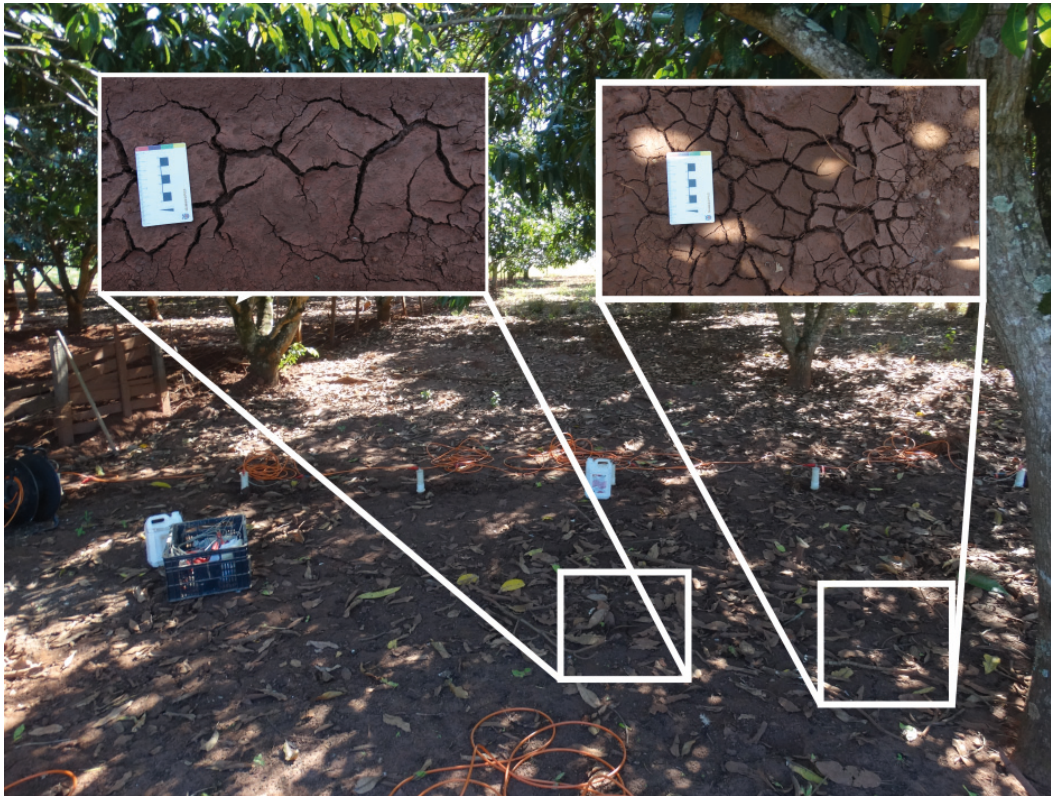


Figure 5 – Presence of mud cracks in field.

(III) in normal environmental conditions and posteriorly precipitate the element, gives this technic an important viability on reducing the toxicity and even the concentration of the element.

In this way, with the soil analyses that had a reduction in the total chromium concentration throughout the years; the geophysical response that indicates a restrict area of residual contamination in an area with less than 100 square meters; the assumption that the chromium occur in his less toxic speciation (Cr (III)), it is possible to conclude that the natural attenuation phenomenon occurred well in the study area.

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