

GEOPHYSICAL STUDY IN A DIESEL CONTAMINATED AREA DUE TO A RAILWAY ACCIDENT IN CERQUILHO (SP, BRAZIL)

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ABSTRACT. In São Paulo State, Brazil, there are hundreds of contaminated areas due to leakage of hydrocarbons in gas stations, and industry or during transportation. Chemical compounds transportation is a high-risk activity in function of the unpredictability of accidents. The integration between geophysical data and soil/groundwater chemical analyzes provides a comprehensive and appropriate view to the management and monitoring of contaminated areas. This paper brings a set of geochemical data and geophysical diagnosis acquired in a diesel contaminated area due to a railroad accident in 2002, during the transport of fuels in Cerquillo, São Paulo State. Furthermore, the site was still affected by the contamination when the geophysical acquisition was performed. DC Resistivity and Induced Polarization were performed, using electrical tomography technique. High chargeability values (2.97 mV/V) were associated with the neoformation of sulfides and hydroxides minerals in the unsaturated zone due to hydrocarbon degradation. Furthermore, the resistivity data indicated the presence of residual phase in the unsaturated zone by a heterogeneous pattern of anomalies. In addition, low resistivity values (<12 Ω .m) in the saturated zone indicated a dissolved phase of the contaminant. The geophysical diagnosis of residual phases in hydrocarbon contamination are used as a subsidy to the proper planning of remediation techniques in aquifer systems.

Keywords: leakage, hydrocarbon, residual phase, DC resistivity, induced polarization, remediation.

RESUMO. No Estado de São Paulo existem centenas de áreas contaminadas por vazamento de hidrocarbonetos em postos de combustíveis, e indústrias ou durante o transporte, esta última de alto risco devido à imprevisibilidade dos acidentes. A integração de dados geofísicos com análises químicas proporciona uma visão abrangente e adequada ao estudo e monitoramento de áreas contaminadas. Este trabalho reúne um conjunto de dados geoquímicos e de diagnóstico geofísico, adquiridos numa área contaminada por diesel resultante de acidente ferroviário em 2002, no município de Cerquillo/SP, cuja contaminação ainda estava presente no período da investigação geofísica. Foram realizados levantamentos de Eletroresistividade e Polarização Induzida, por meio da técnica de tomografia elétrica. Altos valores de cargaabilidade (2,97 mV/V) foram relacionados à neoformação de sulfetos e hidróxidos em ambiente insaturado, produtos da degradação dos hidrocarbonetos. Por outro lado, os dados de resistividade indicaram a presença de fase residual em zona insaturada através de um padrão heterogêneo, além de baixos valores de resistividade (<12 Ω .m) em zona saturada do aquífero, o que indica uma fase dissolvida do contaminante. O diagnóstico geofísico de fases residuais em contaminações por hidrocarbonetos pode servir de subsídio a planejamento adequado de técnicas de remediação em sistemas aquíferos.

Palavras-chave: vazamento, hidrocarboneto, fase residual, eletroresistividade, polarização induzida, remediação.

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INTRODUCTION

In the Brazilian state of São Paulo, the environmental agency CETESB listed thousands of areas classified as contaminated or rehabilitated sites in the year of 2017. The contamination caused by accidents, agriculture or unknown sources corresponds to 46 out of those occurrences. The four main groups of the identified contaminants comprise liquid fuels, aromatic solvents (benzene, toluene, ethylbenzene, and xylene) and polycyclic aromatic hydrocarbons (PAHs) (CETESB, 2015, 2017).

The oil refining process generates many products like combustible, chemical compounds, gases and paraffin. Diesel is one of the most important fuels, with toxic hydrocarbon compounds as benzene. This organic substance is classified as a light non-aqueous phase liquid (LNAPL), which also includes, benzene, toluene, ethylbenzene and xylene (BTEX), all hydrophobic aromatic hydrocarbons that occupy voids around fine grain size particles as a coating. Thus, the BTEX compounds fill small pores in the non-saturated zones of soils (Newell et al., 1995; USEPA, 1999; König & Weiss, 2009).

According to the CETESB manual for management of contaminated sites, geophysics is indicated as a non-invasive and non-destructive investigation method applied to the diagnosis and monitoring. Their application can be performed in all the different steps of the recovery process of contaminated areas: confirmatory investigation, detailed investigation and remediation. The application of this geophysical tool allied to the remediation planning is capable to generate effective results in a short period of time. Geophysical studies also support the targeting of treatment and location of wells for areas where the impregnation in soil is observed (residual phase), which eventually might act as a secondary source of contamination for the aquifer (CETESB, 1999a, 1999b; Shevvin et al., 2005; Blondel et al., 2014; Mao et al., 2016).

Many studies integrate geophysical methods and chemical analysis of soil and groundwater to diagnose impacted areas. This combination allows a proper management for the study and monitoring of contaminated sites.

The geophysical methods as Ground Penetrating Radar, Inductive Electromagnetic, DC Resistivity, and Induced Polarization are frequently used for the characterization of impacted environments regarding to contamination occurrences, in addition to geochemical analysis, frequently associated to the geophysical data in order to establish an adequate perspective of the contamination (Benson et al., 1997; Bermejo et al., 1997; Moreira & Braga, 2009; Belmonte-Jiménez et al., 2012;

Delgado-Rodríguez et al., 2014; Veloso et al., 2015; Moreira et al., 2017).

The contaminant plume characterization and the identification of its peculiarities are the major goals of a chemical analysis combined to a geophysical acquisition. High values of resistivity are commonly associated to zones with high concentration of contaminant substances. On the other hand, low values of the same electrical parameter indicate dissolved contamination plumes or even low concentrations of the substance. In addition, high chargeability anomalies might be linked to low resistivity values of the extremities of contaminant plumes and high resistivity anomalies of the inner part of the same structure (Benson et al., 1997; Moreira et al., 2006; Moreira & Braga, 2009; Vaudelet et al., 2011; Veloso et al., 2015). Besides petroleum derivative products, another example of organic contaminant substance frequently characterized by geophysical methods is the leachate generated by landfill sites and cemeteries (Silva et al., 2009; Moreira et al., 2015).

LOCATION AND HISTORICAL EVENTS

The study area is situated in Cerquillo, a town in São Paulo State (Fig. 1). According to drilling investigations, the local geological profile is constituted by soils of Tatuí Formation with planar bedding at the top of the geological section. Silt and clay grains are predominant in deeper layers (CETESB, 2006).

In the local aquifer system, the non-saturated zone occurs in the two first layers composed by unconsolidated material and siltstone. Under this level, in the saturated zone, mudstone is observed. In addition, the groundwater level varies between 8 and 10 meters deep in higher altitudes (corresponding to the railway area) and 4 and 5 meters deep associated to lower level terrains.

The hydraulic characterization experiments were performed near the railway, where the obtained results of hydraulic conductivity showed values ranging from 1.47×10^{-4} cm.s⁻¹ to 7.267×10^{-4} cm.s⁻¹. The groundwater flows in the direction of Figueira Velha Creek (SW), which is also occurs to be the recharge zone of the local aquifer, from the higher terrains around the railway following the slope in the topography to southeast. The hydraulic gradients indicate extreme values: 0.032 m.m⁻¹ at the center and north and 0.029 m.m⁻¹ observed at southern portion of the area. In general, the locality is an open valley with topographic variations of 5 and 30 meters in east and south directions, respectively. The ground is practically flat along the railway (CETESB, 2006).

The information regarding to the accident is available in CETESB PA 06/00204/06 process, a free access material



Figure 1 – Location of the study area. Source: Google Earth.

requested at the regional CETESB office in Itu, São Paulo (CETESB, 2006; 2014). The event occurred in 28th April 2002 between the kilometers 164/14 and 166/15 of the Cerquillo-Laranjal railway, operated by Ferrobán – Ferrovias Bandeirantes S.A. The train, transporting fuel oil, derailed and fell over, releasing about 240,000 liters of diesel in the environment (Fig. 2A).

The impacted area is located on a watershed between two drainage basins. On north, there are the springs that originate the Taquaral River, an affluent of Tietê River. The surface run-off of diesel followed the terrain topography and the structure of the railway, but any water springs or drainages were directly reached by the oil. The entire volume of contaminant infiltrated into the soil according to its indication along the railway. The soil occupation is basically sugar cane farms in southeast and northeast and residential/business in the northern portion of the locality.

The emergency recovery of the area took place thirteen days after the accident with the removal of the free-phase by pumping procedures. In 2005 occurred the application of the monitoring system of Free-phase Extraction and implementation of other remediation systems (Dual-phase Extraction – DPE and Soil Vapor Extraction – SVE). Over 2007 the remediation systems were modified in order to optimize the degradation of residual phase of the product. Then, the Multi-phase Extraction – MPE substituted the DPE system and the SVE was modified to include an in situ bio-aeration system.

In 2008, the remediation systems were uninstalled due to absence of contaminant free-phase. However, the monitoring of the impacted has continued over time and identified seasonal and intermittent free-phase. In November 2011, a new procedure composed by a simple pumping method combined with an in situ soil washing system began to operate for the removal of

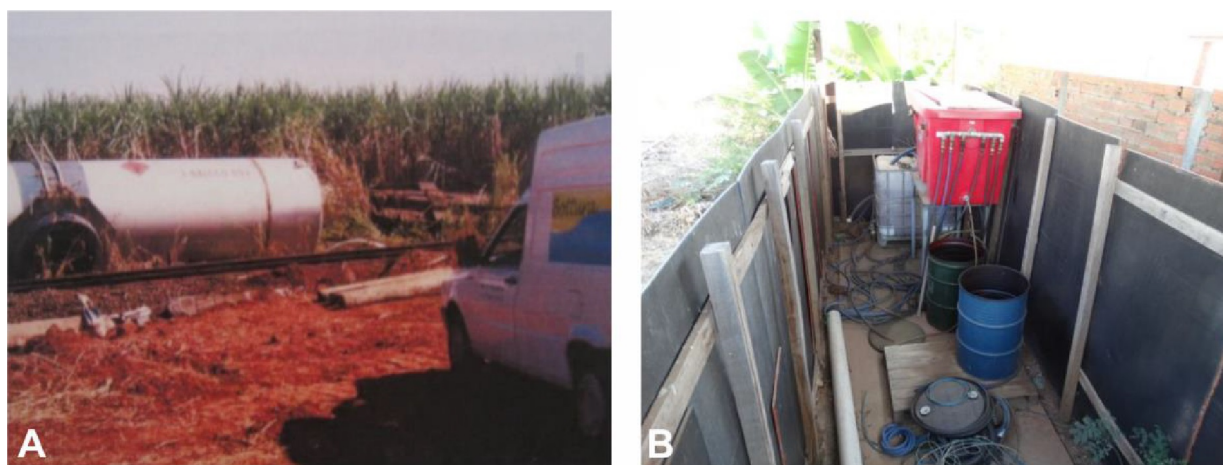


Figure 2 – A) Photo taken right after the accident (CETESB, 2006). B) Remediation system (Junqueira, 2017).

Table 1 – BTEX concentrations analyzed from PM-01 – PM-10 in the years 2002 – 2010. Source: CETESB (2014).

Sampling Date	Substance	Monitoring Wells (concentrations in $\mu\text{g.L}^{-1}$)										I.V.
		PM-01	PM-02	PM-03	PM-04	PM-05	PM-06	PM-07	PM-08	PM-09	PM-10	
June 2002	Benzene	<250	450	500	280	200	<1	<1	320	<1	300	5
	Toluene	950	1425	1200	1240	1140	17	<1	760	9	840	700
	Ethylbenzene	525	550	450	300	380	<1	<1	340	<1	260	300
	Xylene	2550	2325	2125	1540	1740	<1	<1	1560	<1	1380	500
January 2010	Benzene	<L.D.	7.1	-	15.4	13.7	<L.D.	<L.D.	<L.D.	<L.D.	15.8	5
	Toluene	<L.D.	<L.D.	-	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	700
	Ethylbenzene	<L.D.	<L.D.	-	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	300
	Xylene	2.2	45.0	-	2.3	3.4	<L.D.	<L.D.	<L.D.	<L.D.	4.1	500

L.D. = Analytical detection limit (0.1), I.V. = investigation values for groundwater ($\mu\text{g.L}^{-1}$)

the residual free-phase. Some years ago, during the geophysics acquisition procedures in 2014, the pumping and free-phase extraction systems were active (Fig. 2B).

CHEMICAL ANALYSIS DATA AND CONCEPTUAL CONTAMINATION MODEL

Geochemical data presented in the CETESB PA 06/00204/06 process was compiled and indicated in Figure 3 as a comparative of contamination plumes over the period from 2011 to 2014, according to the values of apparent thickness of the free-phase.

From 2011 to 2014, a reduction of the thicker portions of free-phase in the contaminated area was observed and followed by the retraction of the plume. In 2011 the contamination plume

had a “U” shape and the measurements of the thickness of the free-phase showed values up to 1.5 meters. In the following years of 2012 and 2013, this thickness decreased to values between 0 and 0.5 meters. Thereafter, the shape of the contamination plume experienced another alteration, resulting in the reduction of its area in subsurface.

According to Table 1, in 2002 the measurements regarding to BTEX compounds exceeded the investigation values for groundwater in all the monitoring wells, except for PM-06, PM-07, and PM-09. The same thing was observed for ethylbenzene in PM-10 well. During 2010, the BTEX concentration values experienced a reduction on those same sampling points. Only the benzene concentration values sampled



Figure 3 – Evolution of the contamination plume according to free-phase thickness 2011 – 2014 and monitoring wells (red dots). Source: CETESB (2014).

from PM-02, PM-04, PM-05, and PM-10 overcame the investigation reference values for groundwater. Moreover, the PM-03 was disabled in the year of 2010 (BRASIL, 2009).

The dispersion and dilution tendency of hydrocarbon compounds in the geological environment recognized in the chemical data must be analyzed based on the behavior of that specific substance in the soil.

When petroleum-derived hydrocarbons are released in the environment, LNAPL type contaminants migrate vertically by the action of the gravitational force, resulting in four different phases in subsurface: a) residual phase, sorbed in the soil due to the hydrophobic characteristic of hydrocarbon molecules; b) the free-phase, expelling water from pores; c) dissolved; and d) gas-phase (Fig. 4). Under favorable conditions, a contaminant compound might experience degradation process through the reduction of its mass, volume, mobility, toxicity or even concentration in the aquifer system (Newell et al., 1995; USEPA, 1999; Carey et al., 2000; Speight, 2017). Those changes in saturated and/or unsaturated zones can be carried by physical,

chemical or biological processes, which include biodegradation, dispersion, dilution, volatilization and adsorption mechanisms (USEPA, 1998; Speight, 2017). Biodegradation comprises the main mechanism of natural attenuation with the generation of organic acids by the microbial action over petroleum-derived hydrocarbons in underground environment (Bennett & Siegel, 1987; Das & Chandran, 2011). The presence of such compounds might affect the equilibrium of many minerals in soil, causing changes in the aquifer geochemistry. This involves the alteration of ionic concentration in pores caused by the increasing in salinity because of mineral weathering carried by products of the microbial metabolism (Harter, 1977; Bennet et al., 1996).

These physical alterations generate a more suitable and less toxic environment for microorganisms, especially when the oxygen levels increase. The residual phase occurs as impregnations covering mineral grains and is less mobile than the dissolved contaminant, which has a mobility equivalent to the associated groundwater and moves according to the local flux (Wilson & Jones, 1993; Rabus & Heider, 1998).

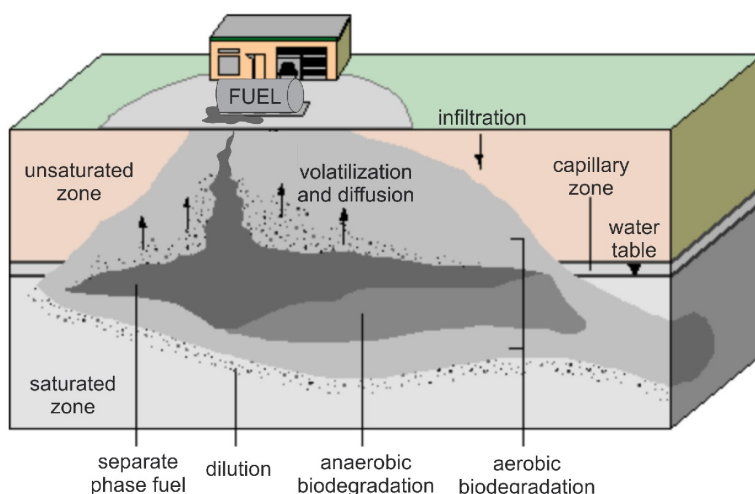


Figure 4 – Scheme showing the relationship between the different hydrocarbon phases in subsurface and natural attenuation processes in aquifers (modified from Bekins et al., 2001).

The presence of electrical receptors (O_2 , SO_4^{2-} , Mn^{4+} , Fe^{3+} , NO_3^-), specific pH values, temperature, redox potential and low and adequate contamination levels are some of the factors that guarantee the efficiency of this biological process, which may lead to complete degradation to non-toxic products such as carbon dioxide, methane and water (USEPA, 1998; Gan et al., 2009). Furthermore, the physical characteristics of the local aquifer system are also very important factor, whose hydraulic conductivity is a fundamental parameter for the dispersion and dilution of the contaminant in subsurface, including the extent of contamination.

METHODOLOGY

DC Resistivity (ER) and Induced Polarization (IP) were the geoelectric methods used in this geophysical acquisition, which was planned based on the chemical behavior of hydrocarbon contaminant in the geological setting over the years. They were combined with tomography technique based on Wenner-Schlumberger array.

The geophysical method of DC Resistivity relies on the determination of the electrical resistivity in different materials in the geological environment. The difficulty propagation of electrical current varies according to the nature of the target material and its physical state, defining the resistivity (ρ) parameter. Thus, the resistivity measures this difficulty of electrical current propagation through a specific material (Musset & Khan, 2000; Milson, 2003).

The method consists in the injection of an artificial electrical current (I) into the ground by the use of a pair of electrodes. An electric potential difference (ΔV) will be generated in subsurface and measured by another pair of electrodes, making possible the calculation of the apparent electrical resistivity and, hence, the real electrical resistivity through the inversion processing (Musset & Khan, 2000). The DC Resistivity method can be applied in different studies: hydrogeological characterization, determination of geological strata, identification of buried residues and mapping of contamination plumes (Knödel et al., 2007).

The Induced Polarization method is based on the delayed response of voltage in geological materials after the application of an electrical current in subsurface followed by its interruption. When this current is established in the soil, the electrical polarization of ions takes place in the underground environment. Once the electrical current is ceased, those polarized cells are slowly discharged. Thus, the potential difference caused by the application of the electrical current experiences a drastic drop right after this current is interrupted, followed by a gradual decrease until zero. Two mechanisms that explain these phenomena are widely described: membrane and electrode polarizations (Kearey et al., 2002; Milson, 2003).

The two possible variations for the use of Induced Polarization method rely on time and frequency domains. The first one consists in the measurement of the voltage decay in function of time. The second one is based on the determination of the

apparent electrical resistivity in two or more low frequencies of alternating currents (Kearey et al., 2002).

Nonpolarizable electrodes were used during the geophysical acquisition with the intent to reduce external electrical interferences that might affect chargeability measurements. Those electrodes are constituted by a porous base and a copper beam, filled with a supersaturated copper sulfate (CuSO_4) solution.

Electrical Tomography technique was chosen for the application of these methods. It consists of measurements performed along a pre-defined acquisition line by the described potential and current electrodes, separated by the same distance. The investigation of the subsurface lateral discontinuities is done by moving those pairs of electrodes, resulting in two-dimensional investigations.

The present study proposes the use of a Wenner-Schlumberger array, which is sensitive to horizontal and vertical structures. Its geometry disposition is characterized by a pair of potential electrodes in the middle and a pair of current electrodes in the extremities of the array, keeping a constant spacing (Milson, 2003; Knödel et al., 2007).

The acquisition of the geophysical data was performed through a total of 7 lines, each one 114 meters long and 6 meters away from each other, the same distance between electrodes. The imaging was performed from northwest to southeast with a theoretical investigation depth of 25 meters (Fig. 5).

The lines 1 and 2 were positioned aside the railway according to its orientation. On the same way, the lines number 3, 4, 5, and 6 were located parallel to the first two geophysical lines, southwest direction based on a sugar cane field, which was harvested at the moment of the acquisition.

In order to establish a reference for the data, the line number 7 was located on the non-affected side of the railway, along the paved road and parallel to the local sugar cane farm.

The equipment used in the geophysical acquisition was a Terrameter LS resistivity meter produced by ABEM Instrument (Sweden) and provided by the Geophysics Laboratory maintained by Applied Geology Department, Universidade Estadual Paulista (UNESP) at Rio Claro, São Paulo. The equipment operates with a previous programming: 250 W, 1 μV resolution and a maximum current of 2.5 A. This equipment allows the acquisition of the following physical parameters: electrical resistivity, chargeability in time domain, and natural electrical potential (ABEM, 2012).

Aiming to obtain a wide range of current injection options in the field acquisition, the equipment was programmed with the

following configuration parameter values: maximum current of 500 mA, a transmission time of 1 second, a delay time of 0.4 seconds and two fixed and consecutive reading intervals of 100 ms as IP windows in time domain procedure.

Then, the geophysical data were processed by RES2DINV software to obtain two-dimensional inversion models. They are used for the qualitative analysis of geophysical data, presented in the form of electrical resistivity and chargeability sections in terms of distance versus depth, for each one of the acquisition lines, using graphic logarithmic scale (GEOTOMO, 2010). The direction of those lines is represented above the models, which were also labelled according to the number and physical parameter that they represent.

The two-dimensional numerical inversion product data from each section was unified in a single spreadsheet which reunites the positions of the readings along the lines ("x" variable), spacing between lines ("y" variable), depth modeled by inversion ("z" variable) and the electrical resistivity value ("R" variable) or chargeability ("M" variable).

This spreadsheet is used for the 3D visualization models generation, in a basic steps routine commonly adopted in mineral prospection research. In this case, the sampling plan is often defined from statistical and structural criteria, mineral accumulation spatial disposition, among others (Moon et al. 2006). A simple procedure consists in sampling a boreholes set, perpendicular to the structure main axis, succeeded by a parallel borehole lines set.

The resolution of the sampling grid is conditioned to the spacing between boreholes, lines and the samples collected quantity on each borehole. The analytical results of the samples are organized in a spreadsheet and then modeled two-dimensionally, so as to interpolate the information in a 3D model. Each point of the final 3D model is transformed in a block, with dimensions conditioned upon statistical and sampling grid criteria, to which a grade (concentration) is attributed and a mean density value relative to the rock holding the ore. The relationship between grade and volume allows the calculation of reserves and economic feasibility of the entrepreneur (Moon et al., 2006).

The resistivity and chargeability 3D visualization models were generated in the Oasis Montaj (Geosoft) platform from the method of minimal curvature, for smoothing of the central values in relation to the limits of the investigated area.

The 3D visualization models generated from geophysical data are great to help understanding complex geological structures and hydrological problems, like the pollutants flow and

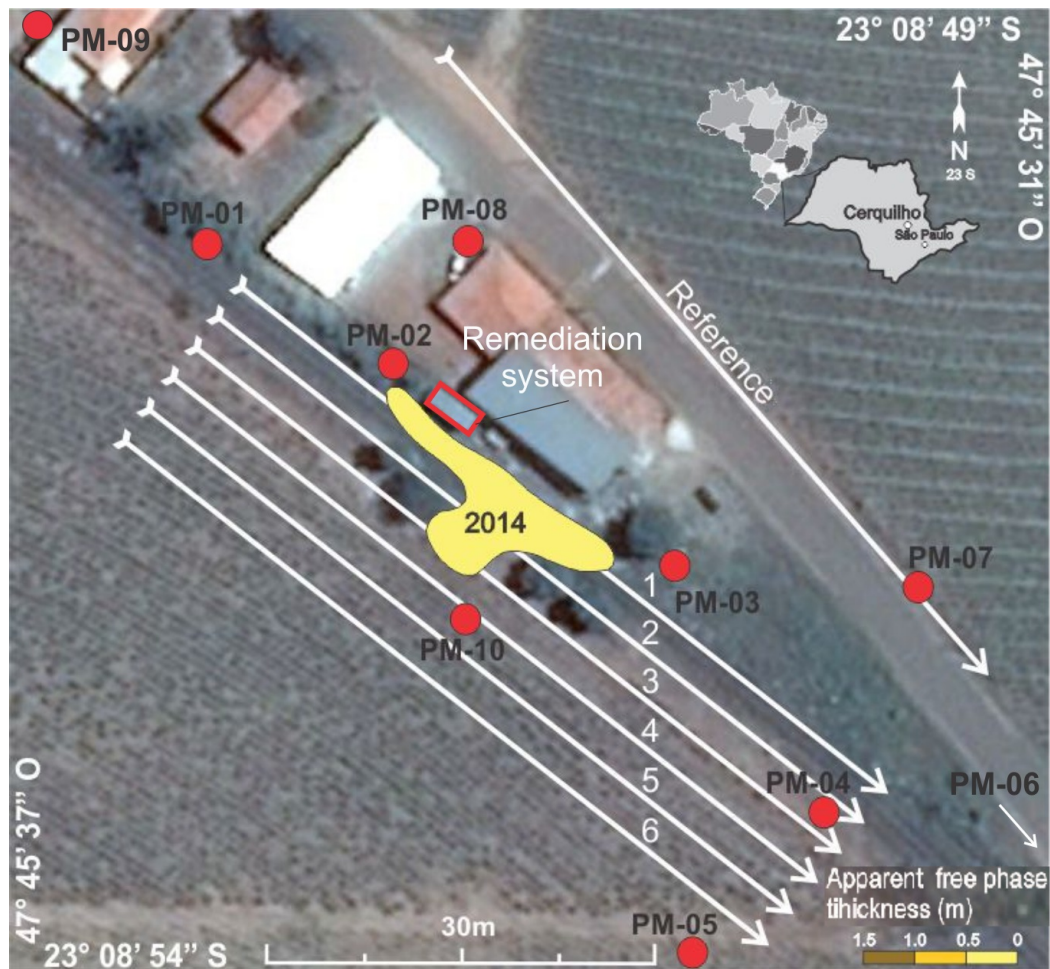


Figure 5 – Contamination plume characterized in 2014 compared to the location of acquisition lines, monitoring wells and remediation system. Source: CETESB (2006, 2014).

modeling ore deposits (Chambers et al., 2006; Aizebeokhai et al., 2011; Moreira et al., 2016; Moreira et al., 2018).

RESULTS AND DISCUSSIONS

The visual analysis of the 1C and 6C chargeability inversion models, compared to the reference acquisition (RC), resulted in two feature patterns: extreme chargeability values above 2 mV/V and under 0.905 mV/V. The inversion models 3C, 4C, 5C, and 6C showed a pattern very similar to RC, with the prevalence of intermediate chargeability values ranging from 0.905 to 2 mV/V (Fig. 6).

Values lower than 1 mV/V as seen on models 1C and 2C represent low chargeability anomalies. These zones might be related to a slightly altered contaminated environment in both saturated and unsaturated levels. Then, the same levels are

represented by intermediate chargeability values ranging from 1 mV/V to 1.22 mV/V in inversion model 3C and associated with a lower degree of contamination. A homogeneous feature with chargeability values ranging from 1.22 mV/V to 1.30 mV/V can be seen from the top to 11 meters deep level of model 4C. This anomaly can be explained by a non-contaminated unsaturated zone, especially because this is a region here no oil infiltration was reported. Under this chargeability feature, a saturated zone is observed and correlated with intermediate values between 1 mV/V and 1.22 mV/V and associated with the evolution of the plume following the general flux direction of the groundwater (Fig. 6).

Finally, sections 5C and 6C do not present values lower than 1 mV/V or even higher than 1.64 mV/V with no possible correlation with saturated or unsaturated zones. These are the

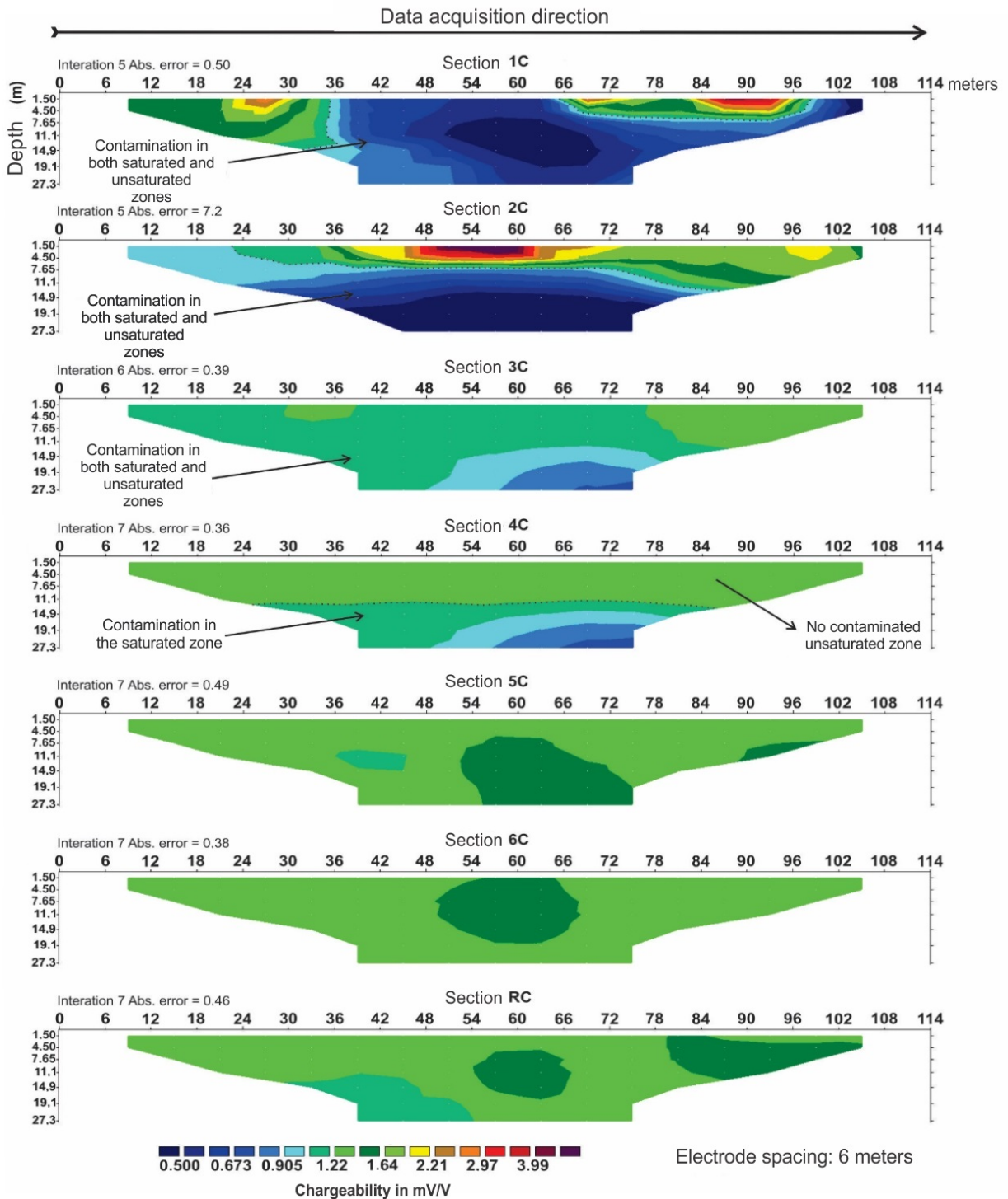


Figure 6 – Chargeability inversion models of acquisition lines 1C, 2C, 3C, 4C, 5C, 6C, and the reference RC. Each one represents a depth of 27.3 m, including the delimitation of interest anomalies.

sections with the greatest similarity with the reference acquisition RC.

Following the same pattern observed in the chargeability data, the electrical resistivity inversion models resulted in a very clear contrast when comparing 1R and 2R sections to the reference RR acquisition. After that, a gradual approximation of the electrical resistivity features observed in 3R, 4R, 5R and 6R to the ones represented by RR was also reported. Values higher than 60 $\Omega\cdot\text{m}$ from the surface to approximately 11 meters deep are present in the two first sections, resulting in a heterogeneous distribution of color shades in the inversion models (Fig. 7).

Models 3R - 6R show a homogeneous pattern of electrical resistivity values as high as 100 $\Omega\cdot\text{m}$ in depths not lower than 11 meters, which configure a homogeneous horizon quite similar to the reference line.

All sections describe a thin horizon that does not exceed 10 meters in depth, whose layer is related to electrical resistivity values ranging from 45 $\Omega\cdot\text{m}$ to 51.9 $\Omega\cdot\text{m}$. This area indicates the groundwater level, defined by the transition from a more resistive unsaturated zone to a less resistive saturated region. This interpretation regarding to the water level is corroborated by direct measurements performed in the area (CETESB, 2006).

The study of Moreira & Braga (2009) has investigated an industrial area affected by benzene, toluene, xylene and other compounds based on DC Resistivity and Induced Polarization methods, identifying high resistivity anomalies associated to a non-degraded residual phase. On the other hand, low resistivity values represent dissolved phase contaminant in the presence of oxygen and low contaminant concentrations, regarded as changes in physical properties of the investigated contaminated site. Braga et al. (2008), in the same way, performed an experiment based on the variability of the geoelectrical response of organic compounds in the hydrogeological environment in function of time. The results showed a decreasing in the resistivity values for older contaminations.

The residual phase occurs in the unsaturated zone through the impregnation on mineral grains. This phase presents a low mobility and high concentrations of contaminants, producing a high toxicity environment that prevents microbial biodegradation (Wilson & Jones, 1993; Rabus & Heider, 1998).

Inversion models 1R and 2R indicated the presence of contaminants related to unsaturated zone. Values around 52 $\Omega\cdot\text{m}$ describe a heterogeneous pattern in the section correlating to high levels of toxicity in an unfavorable environment for biodegradation. Sections 3R - 6R, relatively far from the railway

where the diesel was released, showed a very homogeneous purple colored horizon ($> 100 \Omega\cdot\text{m}$) that reaches about 8 meters deep. This horizon was interpreted as an unsaturated zone without contaminant residual (Fig. 7).

The interpolation of all 2D inversion models resulted in the generation of a pseudo-3D model for both resistivity and chargeability parameters. For a better visualization and understanding of the local aquifer affected by the hydrocarbon contamination, the tridimensional model was divided into separated layers defined by their associated quota. The area with mineral neoformation (iron oxides, sulfides and hydroxides) (Moreira & Braga, 2009), according to the chargeability layers maps, corresponds to the pinky shades portions that represent values higher than 2.97 mV/V, right above the slightly contaminated saturated zone indicated by low chargeability anomalies ($< 1 \text{ mV/V}$). Those anomalies decrease in terms of area in function of depth, reaching 13 m. The overall shape of this occurrence resembles a cone and seems to be restricted to the unsaturated zone of soil (Fig. 8).

On the other hand, low chargeability values can be observed near the railway. It is represented, as seen on the inversion models, by blue shades in all depth levels and related to values lower than 0.7 mV/V.

The resistivity layers show anomalies that comprise three different physical systems: the vadose zone (with and without the presence of residual phase); the transition zone between unsaturated and saturated environment; and the saturated zone affected by the contamination. Along the lines 3 - 6 it is possible to observe again the expressive high resistivity anomaly that extends deep, reaching the -7 m level quota. As mentioned, this occurrence represents the unsaturated zone without the presence residual phase. However, parallel to them, it is possible to observe an orange anomaly ($\sim 45 \Omega\cdot\text{m}$) along acquisition lines 1 and 2, which was considered as the contamination present in the unsaturated zone and directly associated with the higher chargeability values.

The -9m layer is the level of transition from the unsaturated to saturated zone and it is indicated by the absence of a predominant anomaly color. The blue color under this quota was associated with a more permeable area, but higher resistivity values (orange) can still be observed, especially along lines 1 and 2. Those two anomalies represent the transition between the residual phase (orange) to a less resistive blue anomaly ($< 12 \Omega\cdot\text{m}$) in the saturated zone, considered as the region with a higher degree of pollutant degradation.

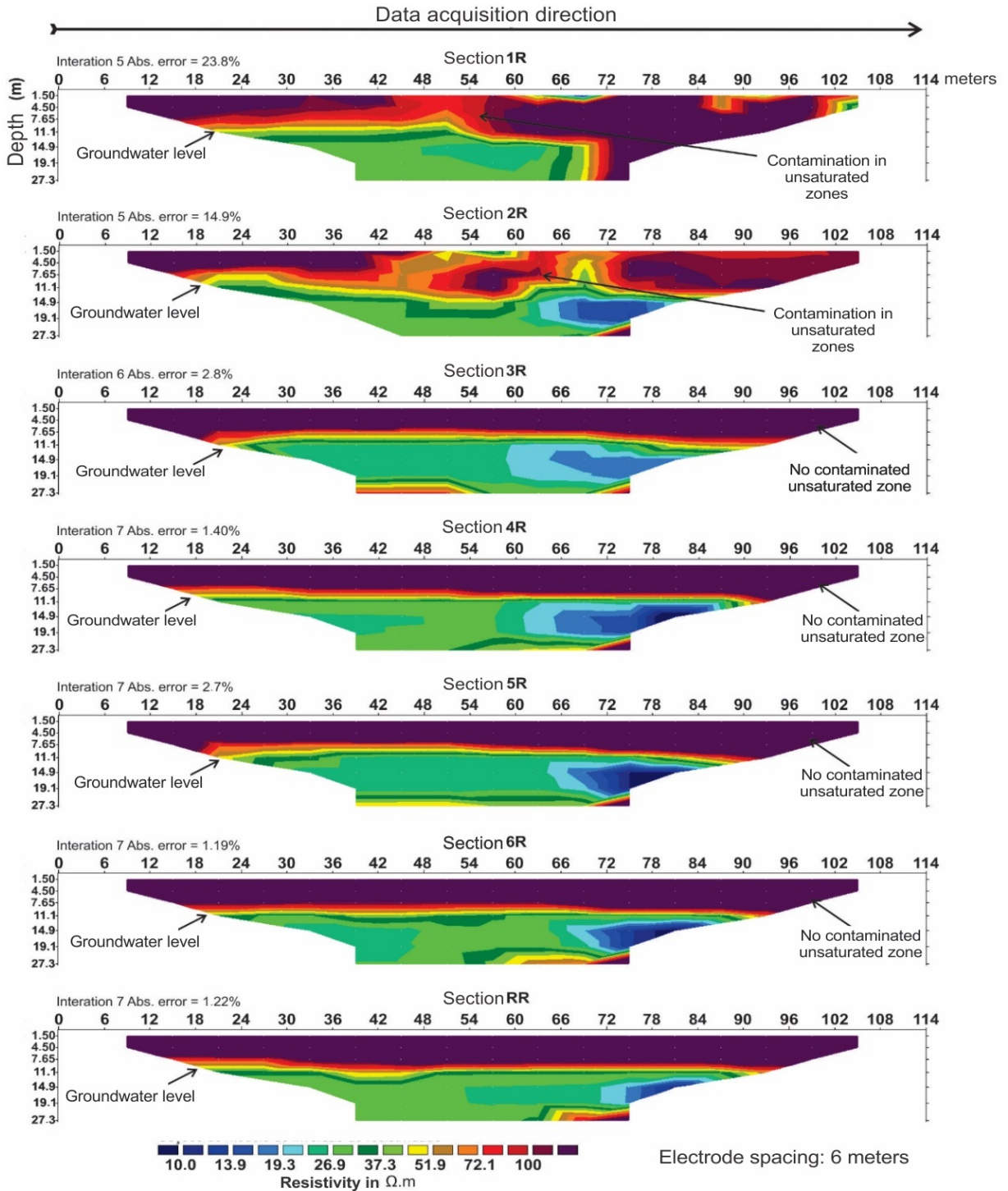


Figure 7 – Resistivity inversion models of acquisition lines 1R, 2R, 3R, 4R, 5R, 6R, and the reference RR. Each one represents a depth of 27.3 m, including the indication of interest anomalies.

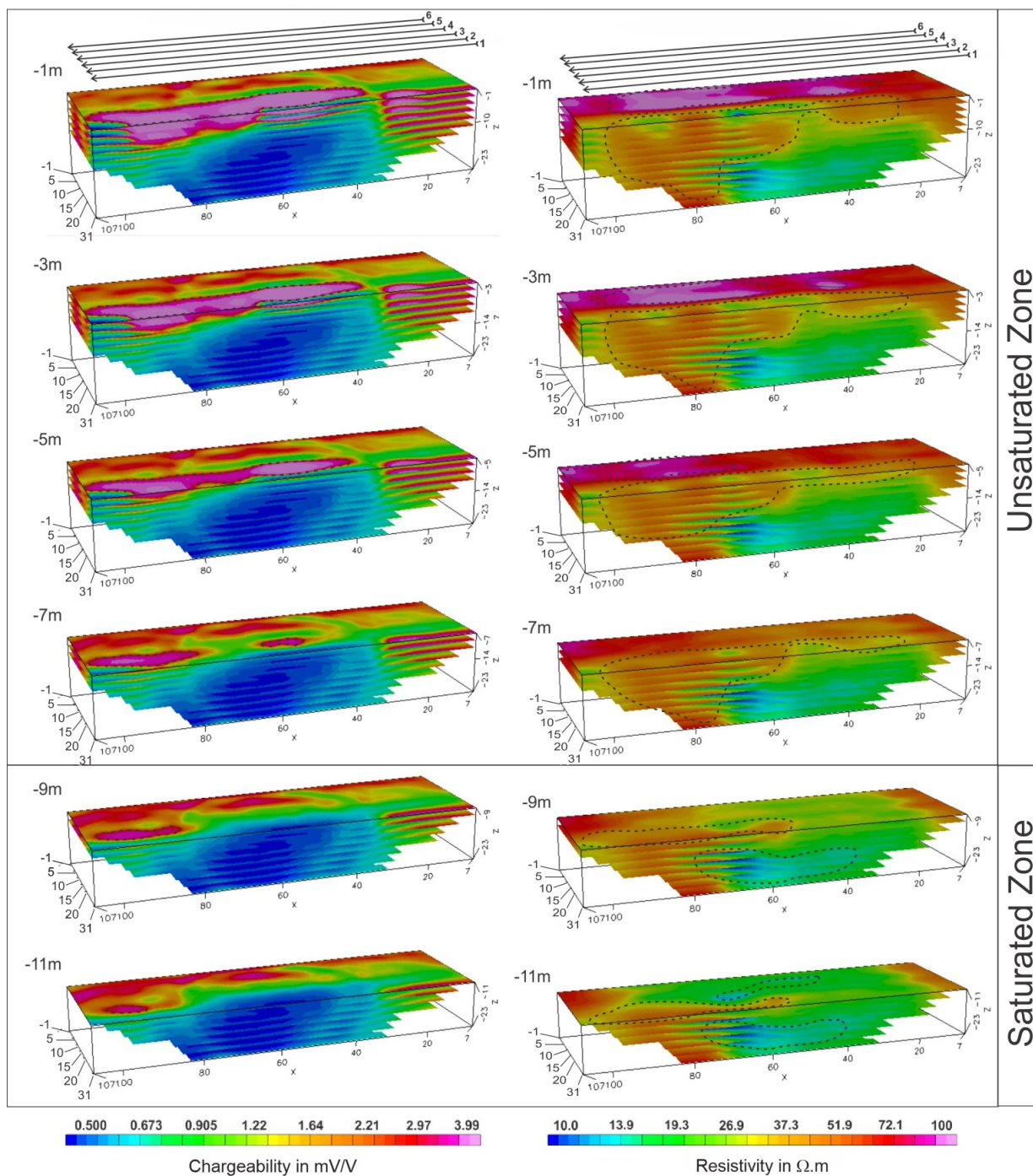


Figure 8 – Chargeability and resistivity layers with the indication of anomalous zones of interest.

CONCLUSIONS

The contamination plumes characterized in the years 2011 and 2014 and the BTEX compounds concentrations analyzed from the monitoring wells PM-01 and PM-10 in 2002 and 2010 indicate a reduction of contaminants in the study area and the efficiency of the applied remediation system, especially regarding to the reduction of free-phase or even in the decreasing of contaminant levels.

The interpretation of geophysical data allowed the identification of the current contamination and the generation of a model for the local plume. The acquired data based on the geophysical methods of DC Resistivity and Induced Polarization were sensitive enough in the detection of products generated by the degradation process taking place in the area.

Geophysics was suitable to identify both residual and dissolved phases, with the possibility to define the boundaries between those two systems according to the chargeability and electrical resistivity models. In addition, the chargeability and electrical resistivity anomalies tent to intermediate values with the decreasing of contamination levels and the tendency to a natural and unaffected geological environment.

The residual phase was neglected many times during the remediation process performed in the locality, once the focus of the operations and chemical analysis was on the free-phase alone. The geophysics acquisition was also successful applied in the detection of the residual phase as an auxiliary tool for the remediation process in the local in many ways: measuring the efficiency of the remediation system, assisting in the location of monitoring wells and in the diagnosis of the contaminated site.

A geophysical acquisition in the local could have provided a proper diagnosis of the contamination with the indication of the residual phase. Neglecting the residual phase can cause future problems due to interaction between infiltration of meteoric water and residual hydrocarbons that remain in the unsaturated zone, which produces a dissolved phase and new contamination to the aquifer. Furthermore, the geophysical study could indicate the best areas for soil sampling and characterization of the unsaturated zone. Nowadays geophysics is a very useful tool for monitoring studies of residual phase and also as an effective way to determine the efficiency of remediation systems.

REFERENCES

ABEM. 2012. Terrameter LS – Instruction Manual. ABEM Instrument AB, Sundbyberg, 122 pp.

AIZEBEOKHAI AP, OLAYINKA AI, SINGH VS & UHUEGBU CC. 2011. Effectiveness of 3D geoelectrical resistivity imaging using parallel 2D profiles. *International Journal of the Physical Sciences*, 6: 5623-5647.

BEKINS BA, RITTMANN BE & MacDONALD JA. 2001. Natural attenuation strategy for groundwater cleanup focuses on demonstrating cause and effect. *Eos, Transactions, AGU*, 82(5): 57-58.

BELMONTE-JIMÉNEZ SI, JIMÉNEZ-CASTAÑEDA ME, PÉREZ-FLORES MA, CAMPOS-ENRÍQUEZ JO, REYES-LÓPEZ JA & SALAZAR-PEÑA L. 2012. Characterization of a leachate contaminated site integrating geophysical and hydrogeological information. *Geofísica Internacional*, 51(4): 309–321.

BENNETT P & SIEGEL DI. 1987. Increased solubility of quartz in water due to complexing by organic compounds. *Nature*, 326: 684-686.

BENNET P, HIEBERT FK & CHOI WJ. 1996. Microbial colonization and weathering of silicates in a petroleum-contaminated groundwater. *Chemical Geology*, 132: 45-53.

BENSON AK, PAYNE KL & STUBBEN MA. 1997. Mapping groundwater contamination using DC Resistivity and VLF geophysical methods. *Geophysics*, 62(1): 80-86.

BERMEJO JL, SAUCK WA & ATEKWANA EA. 1997. Geophysical discovery of a new LNAPL plume at the former Wurtsmith AFB, Oscoda, Michigan. *Groundwater Monitoring & Remediation*, 17(4): 131-137.

BLONDEL A, SCHMUTZ M, FRANCESCHI M, TICHANÉ F & CARLES M. 2014. Temporal evolution of the geoelectrical response on a hydrocarbon contaminated site. *Journal of Applied Geophysics*, 103: 161-171.

BRAGA ACO, MOREIRA CA & CARDINALLI MT. 2008. Variação temporal da resistividade elétrica em contaminação por gasolina. *Geociências*, São Paulo, 27(4): 517-525.

BRASIL. 2009. Resolução no 420, de 28 de dezembro de 2009. Dispõe sobre critérios e valores orientadores de qualidade do solo quanto à presença de substâncias químicas... Available at: <<http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=620>>. Access on: December 13th, 2018.

CAREY MA, FINNAMORE JR, MORREY MJ & MARSLAND PA. 2000. Guidance on the Assessment and Monitoring of Natural Attenuation of Contaminants in Groundwater. Swindon: R&D Publication, 131 pp.

CHAMBERS JE, KURAS O, MELDRUM PI, OGILVY RD & HOLLANDS J. 2006. Electrical resistivity tomography applied to geologic, hydrogeologic, and engineering investigations at a former waste-disposal site. *Geophysics*, 71: 231-239.

CETESB - COMPANHIA AMBIENTAL DO ESTADO DE SÃO PAULO. 1999a. O gerenciamento de áreas contaminadas. In: Manual de Gerenciamento de Áreas Contaminadas. SP, Brazil. chapter I, 1100.

- CETESB - COMPANHIA AMBIENTAL DO ESTADO DE SÃO PAULO. 1999b. Métodos Geofísicos. In: Manual de Gerenciamento de Áreas Contaminadas. SP, Brazil. chapter VI, 6200.
- CETESB - COMPANHIA AMBIENTAL DO ESTADO DE SÃO PAULO. 2006. Process no. PA 06/00204/06. FERROBAN – Ferrovias Bandeirantes S.A., Itu, SP, Brazil.
- CETESB - COMPANHIA AMBIENTAL DO ESTADO DE SÃO PAULO. 2014. Process no. PA 06/00204/06. FERROBAN – Ferrovias Bandeirantes S.A., Itu, SP, Brazil.
- CETESB - COMPANHIA AMBIENTAL DO ESTADO DE SÃO PAULO. 2015. Texto Explicativo: Relação de Áreas Contaminadas e Reabilitadas no Estado de São Paulo, Brazil. 14 pp.
- CETESB - COMPANHIA AMBIENTAL DO ESTADO DE SÃO PAULO. 2017. Áreas Contaminadas e Reabilitadas no Estado de São Paulo: dezembro de 2017, Ordem Alfabética, Brazil. 5942 pp.
- DAS N & CHANDRAN P. 2011. Microbial degradation of petroleum hydrocarbon contaminants: an overview. *Biotechnol Res Int*, 2011: 13 pp.
- DELGADO-RODRIGUEZ O, FLOREZ-HERNANDEZ D, AMEZCUA-ALLIERI MA, SHEVNIN V, ROSAS-MOLINA A & MARIN-CORDOVA S. 2014. Joint interpretation of geoelectrical and volatile organic compounds data: A case study in a hydrocarbons contaminated urban site. *Geofísica Internacional*, 53(2): 183-198.
- GEOTOMO SOFTWARE. 2010. RES2DINV ver. 3.59: for Windows XP/Vista/7. Malaysia: 148 pp.
- GAN S, LAU EV & NG HK. 2009. Remediation of soils contaminated with polycyclic aromatic hydrocarbons (PAHs). *Journal of Hazardous Materials*, 172: 532-549.
- HARTER RD. 1977. Reactions of minerals with organic compounds in soil. In: DIXON JB & WEED SB (Eds.). *Minerals in the soil environment* Madison, p. 709-739.
- JUNQUEIRA PG. 2017. Estudo Geofísico em área contaminada por diesel no município de Cerquilha (SP). Master's dissertation, Universidade Estadual Paulista. Bauru, SP, Brazil. 63 pp.
- KEAREY P, BROOKS M & HILL I. 2002. *An Introduction to Geophysical Exploration*. 3rd ed., Oxford: Blackwell Science Ltd., 268 pp.
- KNÖDEL K, LANGE G & VOIGT HJ. 2007. *Environmental Geology - Handbook of Field Methods and Case Studies*. Berlin: Springer-Verlag, 1374 pp.
- KÖNIG LF & WEISS JL. 2009. *Groundwater: Modelling, Management and Contamination*. New York: Nova Science, 404 pp.
- MAO D, LU L, REVIL A, ZUO Y, HINTON J & REN Z. 2016. Geophysical Monitoring of Hydrocarbon-Contaminated Soils Remediated with a Bioelectrochemical System. *Environmental Science and Technology*, 50(15): 8205-8213.
- MILSON J. 2003. *Field Geophysics*. England: Wiley, 232 pp.
- MOON CJ, WHATELEY MKG & EVANS AM. 2006. *Introduction to Mineral Exploration*. Blackwell Publishing, Oxford. 481 pp.
- MOREIRA CA, DOURADO JC & BRAGA ACO. 2006. Aplicação da técnica de caminhamento elétrico em área contaminada por derivados de petróleo. *Revista Brasileira de Geofísica*, 24(3): 383-392.
- MOREIRA CA & BRAGA ACO. 2009. Aplicação de métodos geofísicos no monitoramento de área contaminada sob atenuação natural. *Revista Brasileira de Engenharia Sanitária e Ambiental*, 14(2): 257-264.
- MOREIRA CA, ALVES DE CASTRO MCA, CARRAZZA LP, CAVALLARI F, HELENE LPI & MACHADO FB. 2015. Relationship between biogas production and variations in electric resistivity in landfill of Rio Claro City, Brazil. *Revista Brasileira de Geofísica*, 33(2): 217-224.
- MOREIRA CA, LAPOLA MM & CARRARA A. 2016. Comparative analyzes among electrical resistivity tomography arrays in the characterization of flow structure in free aquifer. *Geofísica Internacional*, 55(2): 119-129.
- MOREIRA CA, CARRARA A, HELENE LPI, HANSEN MAF, MALAGUTTI FILHO W & DOURADO JC. 2017. Electrical Resistivity Tomography (ERT) applied in the detection of inorganic contaminants in suspended aquifer in Leme City (Brazil). *Revista Brasileira de Geofísica*, 35(3): 213-225.
- MOREIRA CA, HELENE LPI, NOGARA P & ILHA LM. 2018. Analysis of leaks from geomembrane in a sanitary landfill through models of electrical resistivity tomography in South Brazil. *Environmental Earth Sciences*, 77: 7.
- MUSSETT AE & KHAN MA. 2000. *Looking into the Earth: an introduction to geological geophysics*. New York: Cambridge University Press, 470 pp.
- NEWELL CJ, ACREE SD, ROSS RR & HULING SG. 1995. *Light Nonaqueous Phase Liquids*. Oklahoma, US, EPA Ground Water Issue, EPA/540/S-95/500. 28 pp.
- RABUS R & HEIDER J. 1998. Initial reactions of anaerobic metabolism of alkylbenzenes in denitrifying and sulfate-reducing bacteria. *Archives of Microbiology*, 170: 377-384.
- SHEVNIN V, DELGADO-RODRÍGUEZ O, FERNANDEZ-LINARES L, MARTÍNEZ HZ, MOUSATOV A & RYJOV A. 2005. Geoelectrical characterization of an oil-contaminated site in Tabasco, Mexico. *Geofísica Internacional*, 44(3): 251-263.
- SILVA RWC, MALAGUTTI FILHO W & MOREIRA CA. 2009. Emprego do método da eletrorresistividade no estudo da contaminação subterrânea do cemitério municipal de Vila Rezende, Piracicaba – SP. *Revista Brasileira de Geofísica*, 27(3): 389-399.
- SPEIGHT JG. 2017. Removal of Organic Compounds From the Environment. In: SPEIGHT JG. *Environmental Organic Chemistry for Engineers*. Oxford: Butterworth-Heinemann, 2017, 387-432.

- USEPA - UNITED STATES ENVIRONMENTAL PROTECTION AGENCY. 1998. Technical Protocol for evaluating natural attenuation of chlorinated solvents in ground water. Washington, US. 248 pp.
- USEPA - UNITED STATES ENVIRONMENTAL PROTECTION AGENCY. 1999. Microbial processes affecting monitored natural attenuation of contaminants in the subsurface. Ada, US. 20 pp.
- VAUDELET P, SCHMUTZ M, PESSEL M, FRANCESCHI M, GUÉRIN R, ATTEIA O, BLONDEL A, KGOMSEU C, GALAUP S, REJIBA F & BÉGASSAT P. 2011. Mapping of contaminant plumes with geoelectrical methods: a case study in urban context. *Journal of Applied Geophysics*, 75: 738–751.
- VELOSO DIK, MOREIRA CA & CÔRTEZ ARP. 2015. Integration of geoelectrical methods in the diagnostic of a diesel contaminated site in Santa Ernestina (SP, Brazil). *Revista Brasileira de Geofísica*, 33(4): 667-676.
- WILSON SC & JONES KC. 1993. Bioremediation of soils contaminated with Polynuclear Aromatic Hydrocarbons (PAHs): a review. *Environmental Pollution*, 81(3): 229-249.

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