

ENVIRONMENTAL GEOPHYSICAL DIAGNOSIS OF A CONTAMINATED AREA BY HYDROCARBONS IN A RAILWAY ACCIDENT IN THE MUNICIPALITY OF BOTUCATU-SP, BRAZIL

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ABSTRACT. The diagnosis of contaminated areas is a mandatory procedure to treatment and remediation of soil and groundwater. Complex contaminants like hydrocarbons undergo physical and chemical changes along the dwell time in the geological environment, with changes in dissolution and spread in unsaturated and saturated soil aquifer system. This research describes the application of geophysical methods integrated with a history of chemical data in a contaminated area by leaked hydrocarbon in a railway accident, in 2005, at rural area in Botucatu (SP, Brazil). The geophysical methods Electrical Resistivity and Induced Polarization were used by 5 parallel lines of electrical resistivity tomography in Schlumberger array, programmed and adjusted from a history of chemical analysis of groundwater. The electrical tomography data allowed the generation of 2D inversion models and visualization of 3D models. The data integrated analysis indicated the advanced state of degradation of hydrocarbons, recognized by high values of high chargeability in relation to the natural pattern of the area, concomitantly to areas of medium resistivity. This pattern may be indicative of the advanced state of degradation of the contaminants in the geological environment, with probable formation of sulphides resulting from the stabilization of the sulphur from the hydrocarbons and the iron present commonly found in tropical soils.

Keywords: accident, railway, fuel, contamination, natural attenuation, geochemistry.

RESUMO. O diagnóstico de áreas contaminadas é um procedimento obrigatório ao tratamento e remediação de solo e águas subterrâneas. Contaminantes complexos como hidrocarbonetos passam por transformações físicas e químicas ao longo do tempo de permanência no ambiente geológico, com alterações no seu grau de dissolução. Este trabalho descreve a aplicação de métodos geoeletricos integrados a um histórico de dados geoquímicos, numa área contaminada por hidrocarbonetos provenientes de um vazamento em um acidente ferroviário no ano de 2005 na zona rural do município de Botucatu (SP, Brazil). O trabalho consistiu na aplicação dos métodos da Eletroresistividade e Polarização Induzida por meio de 5 linhas paralelas de tomografia elétrica em arranjo Schlumberger, programadas e posicionadas a partir da interpretação do histórico de análises geoquímicas do solo e água subterrânea. Os dados foram processados em modelos de inversão 2D e modelos de visualização 3D. O resultado integrado da aplicação dos dois métodos indica um avançado estado de degradação dos hidrocarbonetos, reconhecido por elevados valores de cargabilidade em relação ao padrão natural da área, concomitante a zonas de resistividade moderada. Este padrão pode ser um indicativo da neoformação de sulfetos oriundos da estabilização do enxofre proveniente da decomposição dos hidrocarbonetos e do ferro comumente encontrado em solos tropicais.

Palavras-chave: acidente, ferrovia, combustível, contaminação, atenuação natural, geoquímica.

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INTRODUCTION

Current issues of pollution in Brazil reflect a historical past marked by the late industrialization model, the process of capital accumulation, the phenomenon of urban growth, which occur with little or no participation of public social policies or environmental planning (Günther, 2006).

Hydrocarbons are currently one of the main contaminants described in contaminated areas due to their wide distribution network whether they are occasional contaminations in urban areas such as gas stations, or diffuse contamination in industries refineries and transport infrastructures (pipeline leaks and conveyor vehicles) (CETESB, 2015).

The lack of management of areas of environmental liabilities in previous decades, a period lacking environmental legislation in force, refers to social consequences of high magnitude, since the absence of civilian environmental responsables permeated the deprivation of knowledge and concretization of the characteristics of the contaminated areas and, mainly, the definition of more appropriate intervention measures. Thus, a portion of the most vulnerable population tends to occupy these areas and expand their exposure to chemical compounds contained in them, which promote damage and / or risks to the goods to be protected and directly to human health (Sara, 2003).

Recurrent contamination and the accumulation of these risk areas made it necessary to create Contaminated Area Management (GAC) policies that became part of the environmental agenda to mitigate environmental impacts, with the objective of enabling the continuous occupation of contaminated areas by minimizing and controlling the risks (CETESB, 2001; IPT, 2014). Thus, contaminated area can be defined as a site that presents chemical substances in concentrations above the recommended by the environmental agency to maintain the environmental quality and to secure population's health (Sara, 2003).

At the national level, the management of contaminated areas is supported by CONAMA Resolution nº 420/2009, which maintains guidelines and procedures for the management of chemical substances in detriment to anthropic activities, as well as the Associação Brasileira de Normas Técnicas (ABNT) which develops specific norms for the phases of the management of contaminated areas. As a pioneer among state environmental regulators, the Companhia Ambiental do Estado de São Paulo (CETESB) systematically collaborates in the definition of technical procedures, guidelines, norms, standards

and guiding values, with publication of documents (for example the Contaminated Area Management Manual, DD 103/2007 updated by DD 038/2017), besides state laws and decrees such as Law 13.577 of the State of São Paulo and its decree 59.263 of 2013, which are used as a reference not only in the state of São Paulo, but all over Brazil.

Among the taken for the management of contaminated areas, the preliminary diagnosis and a risk assessment to human health help in the decision making regarding the most appropriate forms of intervention. In this way, it is increasing the use of techniques aimed mainly at research and monitoring contaminated areas with greater speed and quality.

Therefore, geophysical methods are an extremely useful alternative, because they indirectly offer a large range of coverage during data collection and with low relative cost, directional information that contributes to the decision making and the creation of plans of activities more concise (Knödel et al., 2007; Redd & Adams, 2015). Besides the Brazilian legislation, in general, not consider geological heterogeneity, geomorphology and climate as a whole occurring in the country, which affect the dynamics of pollutants in subsurface (Ramos et al., 2016).

In addition to the geophysical methods, it is possible to highlight the application of geoelectric methods in the diagnosis of hydrocarbon contamination in soil and groundwater, due to the detection and mapping of the extension of the affected area and information about the depth of the saturated zone, direction of the underground flow and depth of rock substrate unchanged (Benson et al., 1997; Moreira & Braga, 2009; Zogala et al., 2009; Minozzo, 2010; Nwankwo & Emujakorue, 2012; Ayolabi et al., 2013).

On the other hand, understanding the characteristics of the contaminating compounds and their behavior in the geological environment is fundamental. The very low solubility in water, the strong sorption tendency to the solid phase of the soil, and the permanence for long periods in the environment make the presence of the hydrocarbons in the environment a complex situation in terms of remediation (Corseuil & Marins, 1997; Berkowitz et al., 2014).

The petroleum compounds are susceptible to natural degradation by microorganisms, with rates varying with the concentration of the pollutant and the size of the hydrocarbon molecule (Chosson et al., 1991; Kanaly & Harayama, 2000; Seo et al., 2009). However, for biodegradation to occur, specific conditions of the environment are required, besides the availability of microorganisms, and other reagents such as

oxygen, nitrate, iron and sulfides (Alexander, 1994; Samanta et al., 2002; Twardowska et al., 2006).

In face of this scenario, this work combines the evaluation and diagnosis of an area contaminated by hydrocarbons after a spill occurred during a railway accident with the application of geophysical methods of the Resistivity and Induced Polarization, together with a history of geochemical data to understand the aspects conditions of control and monitoring of the impacted area.

DEGRADATION OF HYDROCARBONS IN SOIL

The main fuels derived from petroleum are gasoline and diesel, produced and used all over the world. Petroleum consists of a complex mixture of hydrocarbons, other organic components and some organometallic constituents. From 60% to 90% of the oil can undergo biodegradation and the remainder is considered recalcitrant (Tonini et al., 2010).

In Brazil, the automotive gasoline is a mixture of hydrocarbons ranging from 4 and 12 carbon atoms (C_4 through C_{12}) and its composition mainly contains the aromatic hydrocarbons formed by benzene rings (benzene, toluene, ethylbenzene and xylene - BTEX) (Alvarez & Illman, 2006). On the other hand, diesel oil consists of hydrocarbons ranging from 8 to 38 carbon atoms in its chain (C_8 through C_{38}).

The hydrocarbons are characterized as "non-aqueous phase liquids" whose physical and chemical properties make it immiscible, with occurrence of a physical interface between two fluids that prevents the interaction and mixing of the same. With regard to their density, NAPLs can be classified into LNAPL (Light-NAPL) and DNAPL (Dense-NAPL) (Newell et al., 1995).

Characteristics such as density and viscosity of the hydrocarbons define their ease in remaining adsorbed to the organic matter due to the hydrophobicity of the molecules; in addition, the mobility differences of the compound in the soil are associated with the size of the carbon chains (Berkowitz et al., 2014). Other intrinsic properties to the hydrocarbons that influence the transport of the same in the geological matrix are: concentration, solubility, volatility, cosolvency, polarity and vapor pressure (Powers et al., 2001).

Liquid fuels released into the soil, migrate downwards due to the gravity and capillary forces of the soil matrix. Afterwards, four phenomena control the transport of the hydrocarbons into subsurface, which are: advection, dispersion, adsorption and retardation through chemical and biological transformations (Berkowitz et al., 2014).

When petroleum-based fuels reach the soil, its components are partitioned into three phases: dissolved, liquid and gaseous. A small fraction of the components of the mixture is dissolved in the aquifer, a second portion is retained in the porous spaces of the soil in its pure liquid form as residual saturation and another part of the evaporative contaminants gives rise to atmospheric contamination (Nadim et al., 1999).

In natural environments, most organic matter is aerobically mineralized, but this process can also occur in the absence of oxygen (Smith, 1990; Hopper, 1991). However, according to the microbial degradation of petroleum and its refined products, it is much faster and energy efficient in aerobic conditions than in anaerobic conditions (Díaz, 2004).

For a reason that they are organic molecules, the hydrocarbons are susceptible to biodegradation and their susceptibility to these processes varies according to the concentration of the pollutant and the size of the hydrocarbon molecule (Chosson et al., 1991). In turn, biodegradation rates are influenced mainly by physical-chemical soil parameters such as temperature, nutrient availability, pH and electron acceptors.

Degradation by bioavailable microorganisms is an oxidation-reduction reaction, in which petroleum hydrocarbons are oxidized (donated electrons) in the presence of terminal electron acceptors (TEAP), such as oxygen, nitrate, iron (III), sulfate and carbon dioxide (Alexander, 1994; Twardowska et al., 2006).

Due to the consumption and consequent reduction of the oxygen concentration of the environment, degradation reactions are initiated by facultative and anaerobic microorganisms. In an anoxic environment, the sequence of reactions depends on the microorganisms present, the pH and the redox potential, besides the greater energetic beneficitation for the microorganisms (Table 1) (Bedient et al., 1994; Cruz & Marsaioli, 2012).

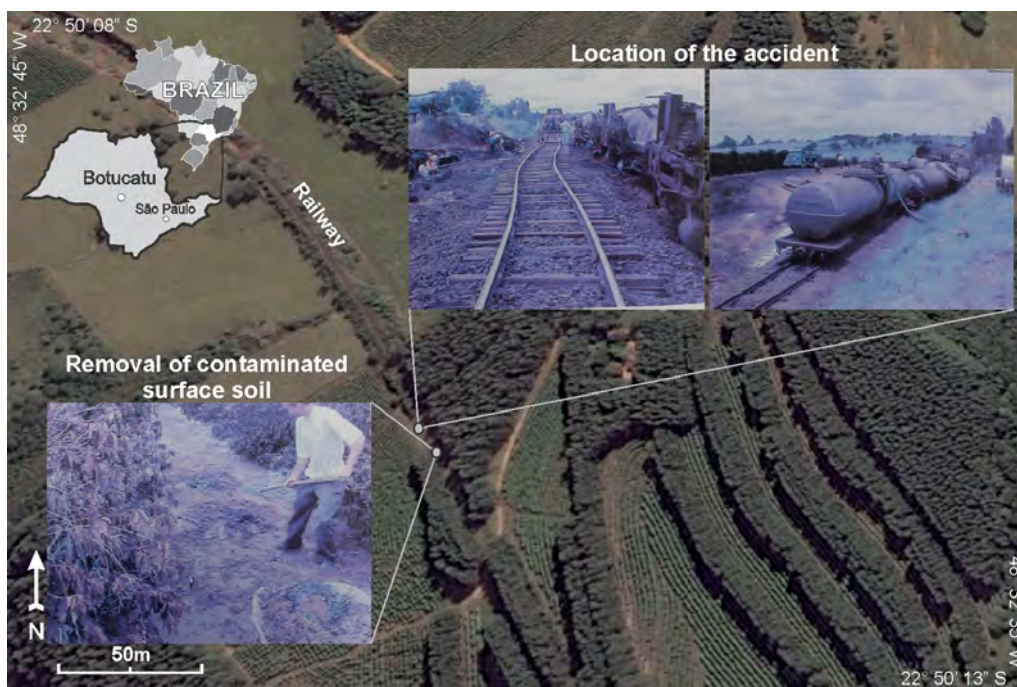
The denitrification process consists of the release of molecular nitrogen (N_2) into the atmosphere after nitrate (NO_3^-) and nitrite (NO_2^-) are reduced in their totality (Winegardner, 1996). The availability of nitrogen, however, is not so significant as to be representative in the processes of hydrocarbon degradation. Because it is a limiting nutrient, nitrogen is consumed by other organisms.

On the other hand, the high availability of Fe^{3+} ions in several subsurface environments allows this reaction to occur more strongly in the natural hydrocarbon attenuation processes.

During Fe^{3+} reduction, the electrons are transferred by reducing Fe^{2+} , making possible the oxidation of organic

Table 1 – Types of aerobic and anaerobic respiration involved in the microbial metabolism of organic matter.

Process	Electrons Acceptor	Metabolized Products	Relative Potential Energy
Aerobic Respiration	O_2	CO_2, H_2O	High
Denitrification	NO_3^-	CO_2, N_2	↑
Iron Reduction	Fe^{3+}	CO_2, Fe^{2+}	
Sulfate Reduction	SO_4^{4+}	CO_2, H_2S	Low
Methanogenesis	CO_2	CO_2, CH_4	

**Figure 1** – Detail of the study area, with photos from the time of the accident (FERROBAN, 2005; adapted from Google Earth, 2016).

compounds and, even, the assimilation of iron as a cellular component, in order to allow the conservation of energy to support the growth of microorganisms (Moreira, 2005; Soriano Junior, 2009). High concentrations of Fe^{2+} are generally found in aquifers contaminated with petroleum hydrocarbons, suggesting the importance of this process for the degradation of these compounds.

As a major degradation process of organic contaminants in anoxic environments, sulfate reduction is less favored in relation to the previously cited processes because the mineralogical composition of the geological matrix is conditioned (Edwards et al., 1992; PETROBRAS, Petróleo Brasileiro S A, 2006). During this phase, H_2S production is favored and, under conditions of low solubility, it can precipitate as iron sulphide minerals.

Finally, the methanogenesis occurs as last resource to biodegradation. During the previous biodegradation processes, where there is the generation of CO_2 as the final product, the generation of by-products such as acetate and hydrogen can also occur (Weiner & Lovley, 1998). The availability of these compounds can serve as a substrate for decomposition with consequent methane generation.

LOCATION AND HISTORIC OF STUDY AREA

A study area is located at Santa Marta Farm, a rural area of the municipality of Botucatu, in the State of São Paulo countryside (235 km from the Capital) (Fig. 1).

In 2005, wagons loaded with fuel (gasoline and diesel), suffered derailment and tipping in kilometer 285 of the railroad

that passes in the Santa Maria Farm area. Part of the leaked cargo was accumulated in the soil, in a trench formed by the drag of the fallen wagons and part was consumed by a spontaneous fire in the area (FERROBAN, 2005).

After that, work began on the recovery of the area, which included pumping actions of the accumulated oil, removal of about 1000 kg of impacted surface soil, disposal of absorbent materials and reconfiguration of the railway.

In order to evaluate the impacted area, three monitoring wells were placed: one upstream of the impacted area (PM 01), one downstream (PM 02) and one in the center of the area with direct influence of the accident (PM 03) (Fig. 2).

The analysis of volatile gas measurement results in the installed drilling points to the presence of volatile gases in the PM 01 profile. On the other hand, PM 02 presents volatile gases throughout the unsaturated soil profile, indicating the vertical migration of hydrocarbons.

In PM 03, significant anomalies of 1140 ppm and 2828 ppm, at levels 0.6 m and 3.0 m depth, respectively, were detected (Table 2). The soil profile shows an increase in concentration up to 3.0 m and then a decrease among depth (CETESB, 2005).

For the determination of BTEX (benzene, toluene, ethylbenzene and xylene) and PAH (polynucleated aromatic hydrocarbons) in the soil, a sample of each soil survey was selected for chemical analysis in the laboratory, based on the highest indication of volatile gases in situ measurement (Table 3) (CETESB, 2005).

Although results of the chemical analyzes in groundwater samples indicate concentrations below the intervention values (CETESB, 2001) for all wells, soil analyzes demonstrate that toluene, xylene and naphthalene occur in concentrations higher than recommended by São Paulo environmental agency, which then characterizes the area as contaminated.

In a monitoring report carried out in 2006, it is described that the contaminants are partitioned in gas phase, adsorbed phase in soil grains and/or phase dissolved in the interstitial water. Thus, the contaminants would be relatively dissociated from the saturated zone and are subject to slow leaching of rainwater (about 1.4 m in 14 months) (CETESB, 2007). Currently the area is considered reclaimed in terms of current legislation.

The analysis of the regional and local geological context aims to support the systemic understanding of the area regarding the vulnerability to contaminating substances. The main lithology of the study area is rich in very fine to fine sandstones, interspersed with silty or sandy lamites. Locally, conglomerate

sandstone lenses with small cross-stratification and containing clay or carbonate intraclasts (IPT, 1981; CPRM, 2006).

The site of study is directly related to dystrophic red latosols, constituted by latosolic B horizon, immediately below any type of horizon A. In the northeast region of the study area there are nitosols and dystrophic red-yellow latosols, respectively associated to the Serra Geral and Botucatu formations (EMBRAPA, 2006).

At the local level, the measurements taken in the monitoring wells indicate that the water level varies between 10.30 m to 10.56 m. The coefficient of hydraulic conductivity presented low variation, between 1.51×10^{-4} cm/s and 2.72×10^{-4} cm/s.

Table 2 – In situ measurements of volatile gases in soil (CETESB, 2005).

Depth	Soil Borings		
	PM 01	PM 02	PM 03
	Concentration (ppm)		
0.00	9.07	144.0	94.3
0.60	13.20	3,720	1,140
1.20	0	210.0	1,509
1.80	0	112.0	2,108
2.40	0	58.1	2,793
3.00	0	33.1	2,828
3.60	–	170.0	53.2
4.20	0	297.0	33.2
4.80	0	133.0	7.2
5.40	0	61.8	8.9
6.00	0	82.7	8.6
6.60	0	39.0	5.8
7.20	0	30.2	6.0
7.80	0	35.8	4.1
8.40	7.30	29.6	14.7
9.00	0	27.3	18.2
9.60	0	49.4	–
10.20	–	51.0	–
	Soil sample selected for chemical analysis		

The values of hydraulic conductivity and transmissivity obtained in hydraulic characterization tests are typical of sandy sediments and sandy silts. The inferred underground flow based on the local topography develops from the impacted area, flowing from northeast (NE) to southwest (SW) toward downstream localized drainage. In relation to the hydraulic gradient calculated for the area was 0.001 m/m and the velocity of displacement of groundwater flow is 0.18 cm/day (CETESB, 2005).

MATERIALS AND METHODS

The understanding of the behavior of the contamination and the physical characterization of the area of studies are of extreme relevance for an interpretation of the values acquired by the geophysical methods, since it is a contaminant complex present in a heterogeneous environment.

The methods used in the acquisition of contaminated area data were the electroresistivity and induced polarization methods.

Both methods consist of the injection of electric current through electrodes arranged on the surface. In the electroresistivity method, the parameter evaluated is the electrical resistivity, that is, the resistivity of the geological material in propagating a electrical current. In turn, the induced polarization performs measurements of the ability of the materials to undergo polarization at the time of interruption of electric current flow. Further information on the theory of methods can be found in Telford et al. (1990), Kearey et al. (2002), Mussett & Khan (2009), Milson & Eriksen (2011).

The acquisition lines were defined according to information obtained through geochemical data, located in the region most affected by the accident, where part of the cargo contained in the wagons was accumulated in the ground.

This way, the set of acquisition lines is composed of 5 lines of electrical tomography containing 220 m of length each, with 44 electrodes spaced each other by 5 m. The spacing between lines is equivalent to 15 m. For comparison with the natural values, a reference line was also made outside the impacted area (Fig. 3).

The acquisition of the geophysical data counted on the resistivity meter Terrameter LS and current transmission cables, both developed by ABEM, besides a set of electrodes made of porous ceramic.

By means of the electrical tomography technique in the arrangement Schlumberger, a data acquisition in time of sending of 1 s, with variation of 50 mA to 100 mA, between minimum and maximum current, beginning of the reading window of 0.4 s after the cut from the current. As the resistivity meter

allows for automatic purchase and storage in its own memory, the data is extracted from spreadsheet format via USB. With the objective of obtaining two-dimensional geoelectric sections and three-dimensional visualization for resistivity ($\Omega.m$) and chargeability (mV/V), extracted data were filtered and modelled.

The data were then processed in the program Res2Dinv version 3.53 (Geotomo, 2004), and are presented as inversion model in sections with distance and depth, with interpolation interval, with values converted in color and graphic scale in logarithmic ratio.

After data processing for the purpose of obtaining 2D inversion models, each file modeled and generated in Res2Dinv is integrated into a table, placed in the sequence. In this way, the spreadsheet files will be finalized and can be uploaded on the Oasis Montaj platform (Geosoft) to generate the 3D visualization models.

The interpolation of the data consists of the sampling plan, constituted and conditioned to the spacing between the electrodes and the quantity of apparent resistivity/chargeability values sampled, often defined from statistical criteria, in this work by means of the kriging method, followed by the application of the method statistic of minimal curvature for smoothing of the central values in relation to the extremities.

RESULTS

The 2D inversion models are designated as the number of the acquisition line infield and are presented in a logarithmic scale of values that could be applied to all tomography lines. They ranged from 15 $\Omega.m$ to 6000 $\Omega.m$ for resistivity values (Fig. 4) and from 0.5 mV/V to 10.1 mV/V for chargeability values (Fig. 5).

The geoelectric signature to contaminated sites with petroleum products suggest results of high and low resistivity/chargeability. The apparent divergence can be explained by the correlation with time of contaminant exposure to the degradation process (Atekwana et al., 2000; Sauck, 2000; Batayneh, 2005; Delgado-Rodríguez et al., 2006).

In the studies of Benson et al. (1997), Zogala et al. (2009), Nwankwo & Emujakporue (2012) and Ayolabi et al. (2013), the changes in the physical properties are influenced by the presence of the hydrocarbons once the degradation process by microorganism generate several reactive subproducts – most of all interact with inorganic solute dissolved and minerals materials, conditions that can modify the resistivity and chargeability response (Moreira & Braga, 2009). In this way, it is possible to attribute high resistivity to the presence of recent

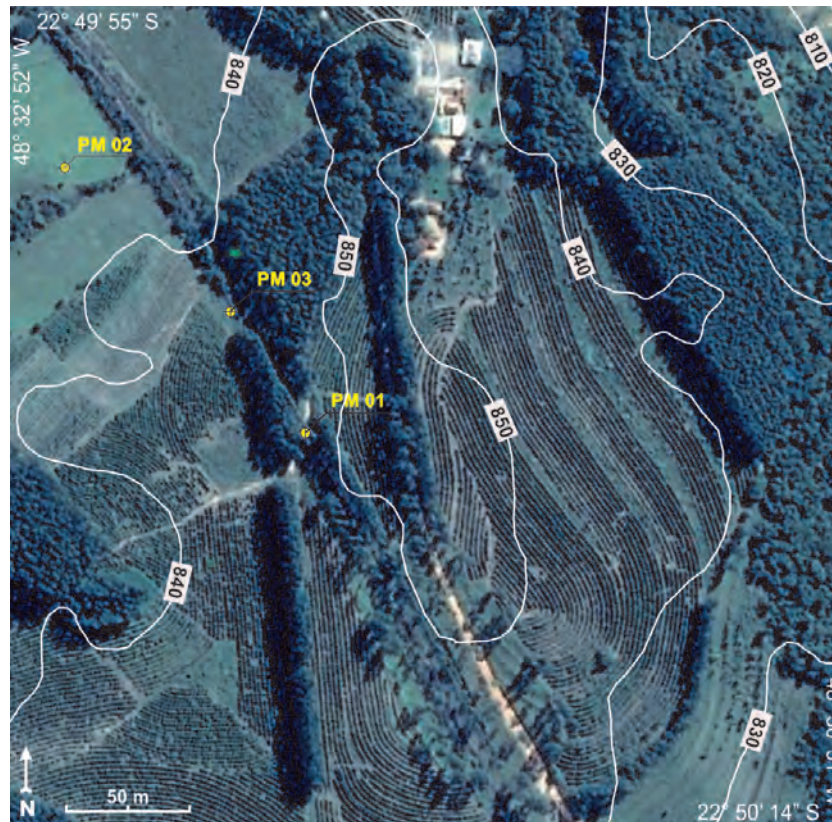


Figure 2 – Location of monitoring wells installed in the study area (FERROBAN, 2005; adapted from Google Earth, 2016).

hydrocarbons in the environment. The chargeability response presented in the literature varies due to local condition of the studied sites, mainly because the relation of the contaminant with the soil pores that can result in high or low chargeability anomalies (Johansson et al., 2015).

The resistivity pattern for the reference line presents the natural values for the area. The natural resistivity profile is typical of unconsolidated sandy sediments and sandstones. Geophysical studies performed for stratigraphic determination of geology, attribute values around $120 \Omega \cdot m$ for sediments of the Botucatu Formation and Bauru Group, the same material that occur in the study area (Braga et al., 2016).

Line 4 has a resistivity profile similar to that of reference, which allows the inference that the changes suffered by the presence of the contaminant are restricted to lines 1, 2 and 3. For chargeability data, natural values around 1 mV/V are persistent in the reference line, in the line 1 and line 4. A small zone of high chargeability is found in the superficial portion at the end of line

3, and a large zone in depth for the beginning and end of line 2 (Fig. 5).

Usually, in areas where the process of natural attenuation occurs, the resistivity values are low during the first phase due to the release of ions during the degradation reaction. In this way, the areas with high resistivity presented in the center of lines 1 and 3 occur in depth of 12 m, below the water table, and might represent the methanogenic zones of degradation, characterized by the intense degradation rate of hydrocarbon in residual phase.

The data carried out in 2007 showed in Table 2 indicates the presence of volatile gases along the entire profile to a depth of 9 m in PM 03, located in the center of the electrical tomography line. This information allied with the high hydraulic conductivity (0.18 cm/day) of the area it is possible that the high resistivity values represent the subproducts of the degradation.

In its turn, the high chargeability in contaminated environments for more than 11 years can be related to the occurrence of metallic mineral neoformed, because of the

Table 3 – Results of chemical analysis in soil samples ($\mu\text{g/kg}$) (CETESB, 2005).

Parameter	Soil Samples ($\mu\text{g/kg}$)			Gridding Values (CETESB, 2001)	
	PM 01 (0.0 - 0.6 m)	PM 02 (0.0 - 0.6 m)	PM 03 (2.4 - 3.0 m)	Reference	Intervention
Benzene	<5.0	31	<6.0	250	600
Toluene	<5.0	493	1,399	250	30,000
Ethylbenzene	<5.0	<6.0	33.5	-	35,000
Xylene (total)	<5.0	2548	455	250	3,000
Naphthalene	<83	51,815	4,179	250	15,000
2- Methylnaphthalene	<83	47,815	16,599	-	-
Fluorene	<83	<1695	1839	-	-
Phenantrene	<83	1,201	4,773	-	15,000
Concentration above the Reference Values					
Concentration above the Intervention Values (maximum protection)					

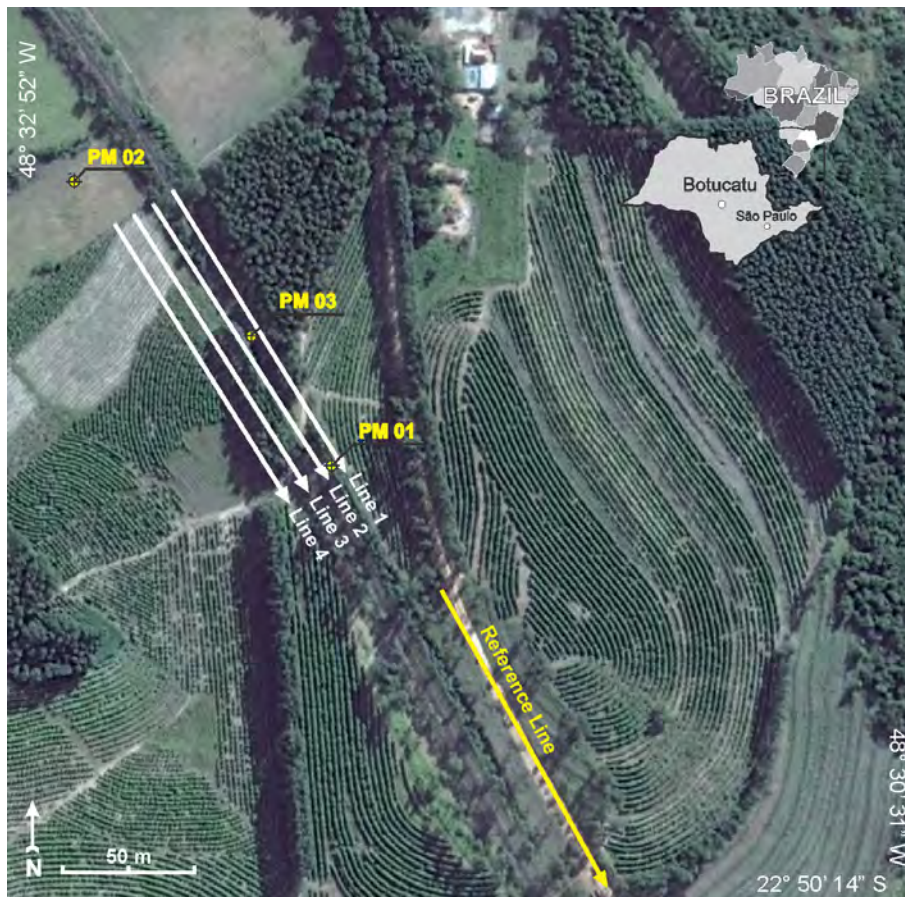


Figure 3 – Location of lines in the field (adapted from Google Earth, 2016).

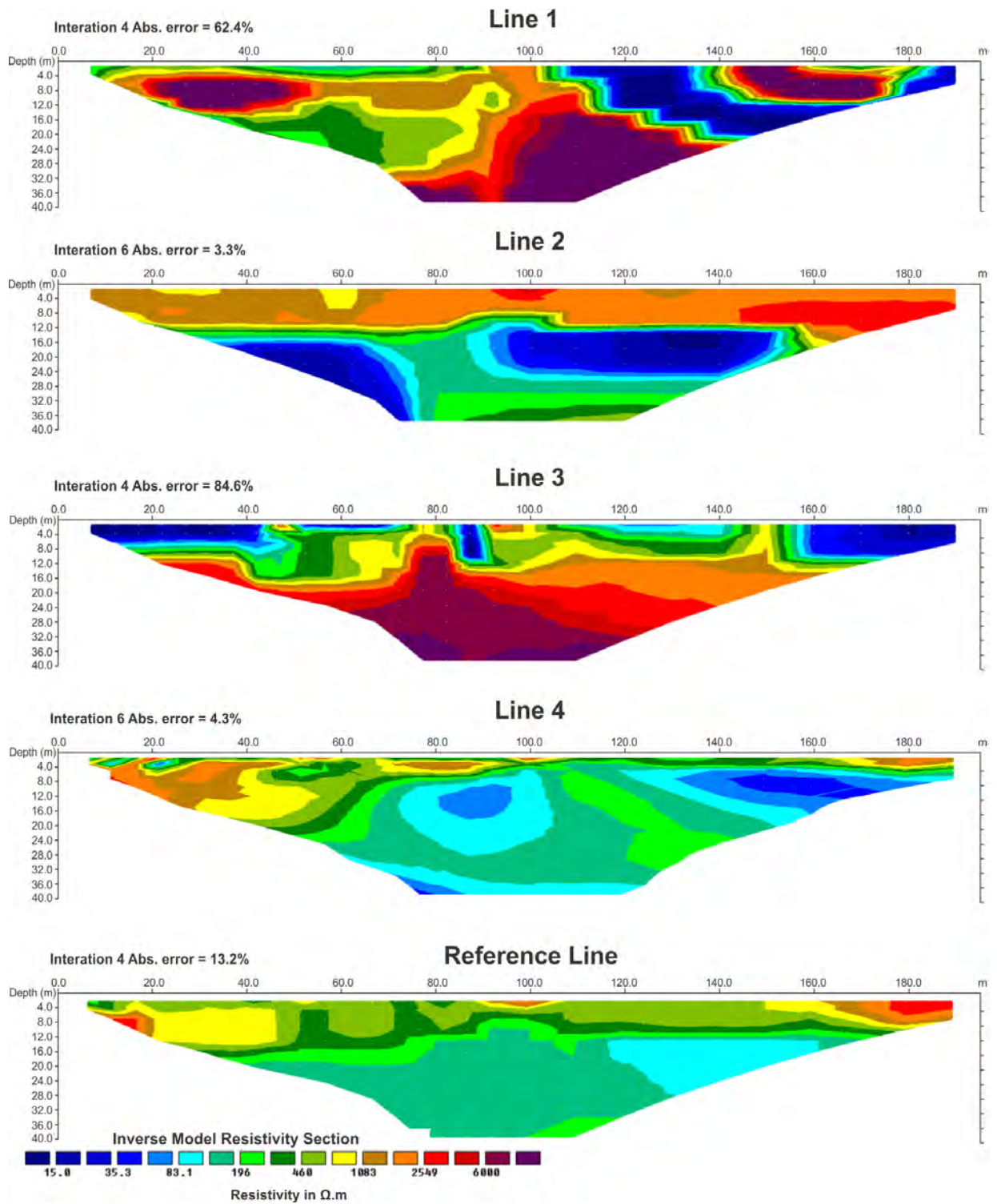


Figure 4 – Inverse models resistivity sections.

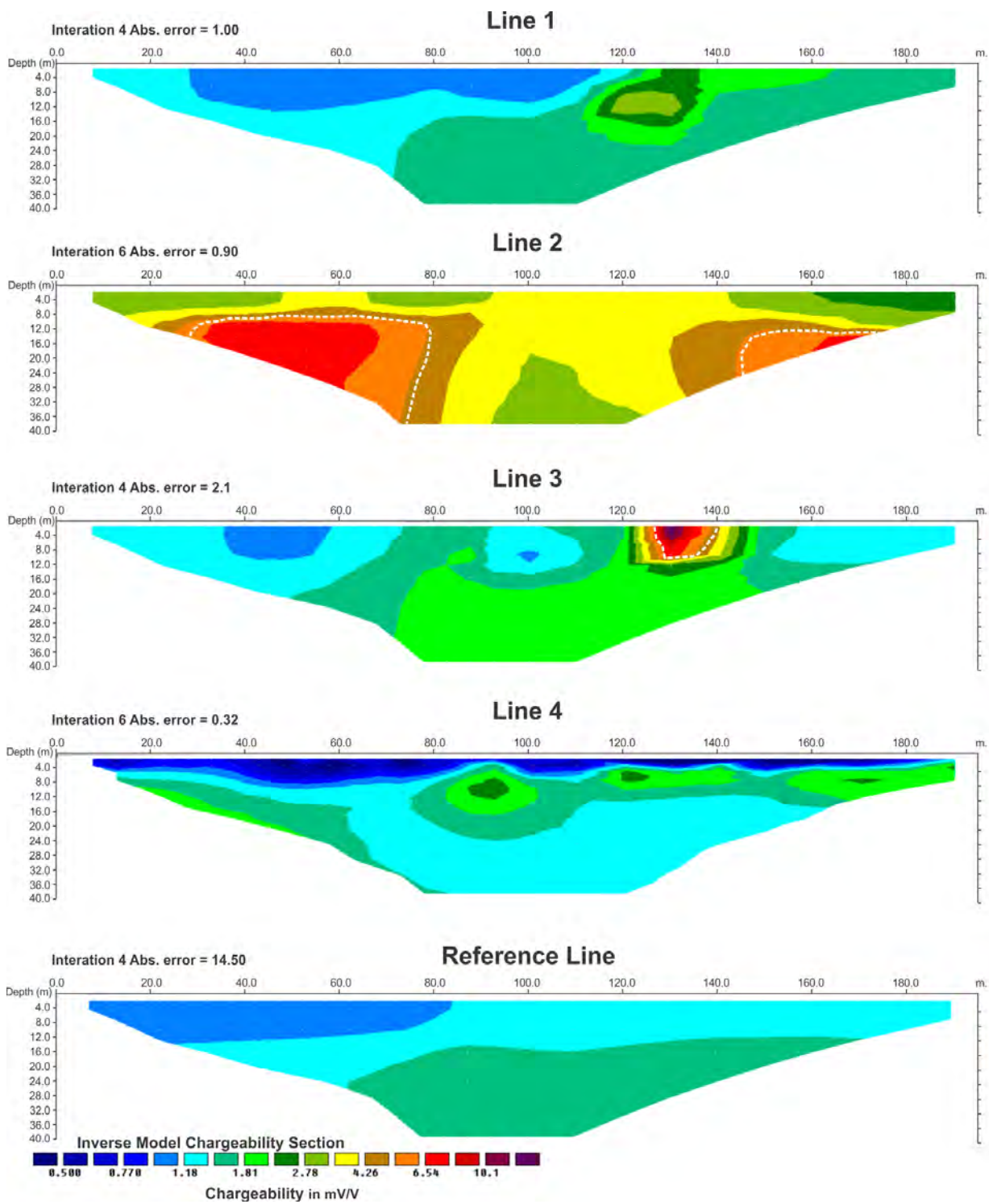


Figure 5 – Inverse models chargeability sections.

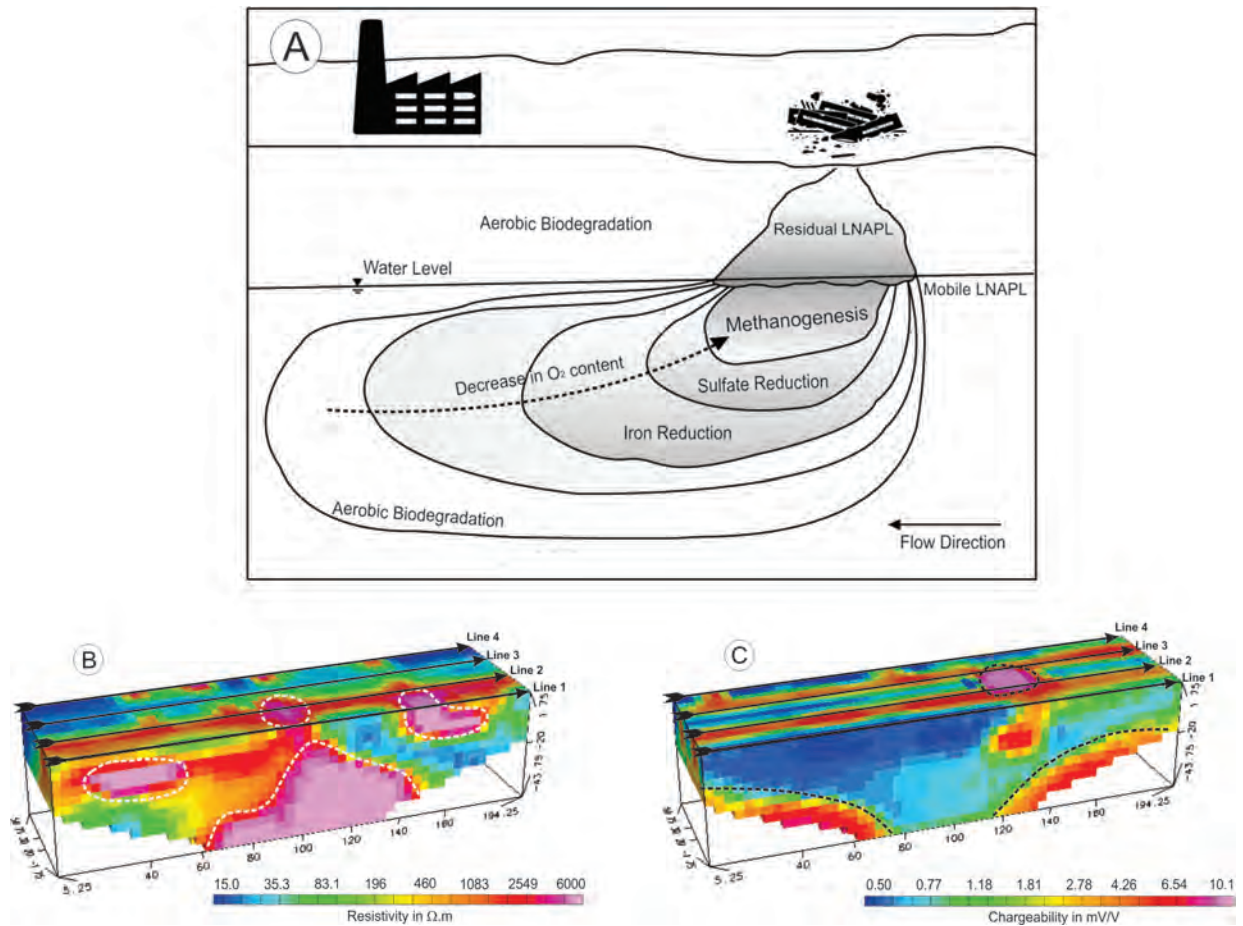


Figure 6 – A) Zones of hydrocarbon biodegradation, Adapted from Rabus & Heider (1998). B) 3D visualization model of high resistivity zones highlighted. C) 3D visualization model of chargeability in a single block with emphasis on high chargeability zones.

changes in the physical-chemical environment. The presence of Fe^{+2} and S^{-2} in contaminated areas enable the formation of metallic minerals such as sulfides, oxides and hydroxides in the degradation process (Lovley, 1991).

The study of Ntarlagiannis et al. (2005), suggest that in the early stages of biomineralization, the quantity of sulphide precipitate dispersed is high, as well as the fixation of microbial cells in soil grains, characteristics that may increase the effective polarization of mineral-fluid interfaces because of increased surface area and/or bulk density. As the biominerals turn compacted at the nutrient source and fill the porous spaces, the chargeability tends to decrease and starts to promote the electronic conduction in the porous media.

The 3D visualization models of resistivity and chargeability performed through the interpolation of the data from the sample of the 2D sections made it possible to create a single block from

the interpolation of 2D inversion models. These data allow an association with zones of biodegradation, possibly related to final phases, due to advanced consumption of organic compounds (Fig. 6).

In the study of Vencelides et al. (2007), Schreiber et al. (2004) and Colombiani et al. (2009), the metabolization of the hydrocarbon can occur in several stages, so that there is at least specific activation energy. Thus, the simultaneous action of two or more biodegradation reactions can occur naturally and concomitantly, as observed in the study area, because the potential redox are practically equivalent for sulfate and carbon dioxide (Wiedemeier et al., 1995).

Since the availability of electrons is limited in an anaerobic environment, the sulfate-reducing bacteria competes with the methanogenesis process in the substrate dispute. In this way, it is possible to associate the presence of the final phase of the

degradation (methanogenic) to the most central region of the impacted area by characterizing an area with greater depletion of the substrates required for the sulfonating biomineralization process. Therefore, the reduction of sulfate acts in the outermost regions and in depth in relation to the center of mass can be evidenced by the accumulation of sulfides and associated with high chargeability zones (Fig. 6).

After 11 years of the accident in the area, the geophysical data suggest the existence of hydrocarbons apparently in residual phase in impregnations of mineral grains. Such weighting can be observed in 2D and 3D models of chargeability, where it can be seen that most of the biodegradation zone is located in the saturated zone below the local water level, approximately 10.5 m. As the degradation is conditioned to physicochemical parameters, the groundwater flow promotes the renewal of electron receptors, and thus contributes to the natural attenuation of the pollutants.

CONCLUSIONS

Contaminations arising from spills of petroleum derivatives are a common occurrence and, in a dependent manner, are in line with the intense technological, industrial and logistic failure of transportation and storage of such products. In this way, the recurrence of contamination and the damage to human health and the environment are justifications for advances in scientific knowledge about diagnostic and monitoring techniques.

The geophysical results reveal zones of high chargeability in the studied area, concomitantly to zones of moderate resistivity, that can reflect the advanced state of natural attenuation of hydrocarbons and indicators of the installation of reducing conditions to the reduction of sulfate in sulfides (intermediate phase of attenuation natural). In this sense, high chargeability zones reflect mineralization in sulfides and a by-product of hydrocarbon degradation.

The contrasts of electrical resistivity observed between contaminated area and natural environment can be a clear indication of the advanced state of natural attenuation and consequent final stage of consumption of these contaminants. Thus, zones with high resistivity, located in the central region of the impacted area can be characterized with methanogenic zones with methane production as the main by-product.

Therefore, the integrated use of geophysical methods of DC resistivity and induced polarization is highly relevant in the diagnosis of areas with very old contaminations, where the action of physical and chemical processes, together with the hydrogeological flow dynamics, makes the pollutant mobile

and with characteristics temporally changeable. Targets defined by the application of geoelectric methods should be used for direct soil and groundwater sampling and to verify the degree of decontamination of the area. In addition to these targets there is probably no residual or dissolved contamination.

The application of the geophysical tools in a joint and collaborative way acts differently and advances the understanding and establishes the importance of the relationship between the use of geophysical methods and environmental studies, especially in the diagnosis of contaminated areas, as an example of this work. The complementation with geochemical analyzes of soil and groundwater in the study area tends to foster the geophysical assumptions made in this study and to guarantee a more informed final diagnosis.

The results suggest the performance of final stage biodegradation as the main mechanism to reduce the mass of contaminants in the studied area. From natural, physical and chemical processes, natural attenuation sets up and ensures the continuous rehabilitation of the area at varying speeds, according to the active processes, but in an acceptable period, without human intervention and the most important, without the characterization of risk to human health.

REFERENCES

- ALEXANDER M. 1994. Biodegradation and bioremediation. San Diego: Academic Press. 453 pp.
- ALVAREZ PJ & ILLMAN WA. 2006. Bioremediation and natural attenuation: process fundamentals and mathematical models. Volume 27. John Wiley & Sons. 614 pp.
- ATEKWANA EA, SAUCK WA & WERKEMA JR DD. 2000. Investigations of geoelectrical signatures at a hydrocarbon contaminated site. *Journal of Applied Geophysics*, 44(2-3): 167-180.
- AYOLABI EA, FOLORUNSO AF & IDEM SS. 2013. Application of electrical resistivity tomography in mapping subsurface hydrocarbon contamination. *Earth Science Research*, 2(1): 93-104.
- BATAYNEH AT. 2005. 2D electrical imaging of an LNAPL contamination, Al Amiriyya fuel station, Jordan. *Journal of Applied Sciences*, 5(1): 52-59.
- BEDIENT PB, RIFAI HS & NEWELL CJ. 1994. Ground water contamination: transport and remediation. Prentice-Hall International, Inc. 624 pp.
- BENSON AK, PAYNE KL & STUBBEN MA. 1997. Mapping groundwater contamination using DC resistivity and VLF geophysical methods—a case study. *Geophysics*, 62(1): 80-86.

- BERKOWITZ B, DROR I & YARON B. 2014. Contaminant Geochemistry – interaction and transport in the subsurface environment. 2nd ed., Heidelberg: Springer. 577 pp.
- BRAGA ACO, DOURADO JC, BIRELLI CA, BLANCO RG & FRANCISCO RF. 2016. Geofísica aplicada no controle estrutural na área do Domo de Piratininga (SP). *Geociências* (São Paulo), 35(4): 598-608.
- CETESB. 2001. Manual de gerenciamento de áreas contaminadas. Technical report. São Paulo, Brazil: CETESB/GTZ.
- CETESB. 2005. Estudo confirmatório do potencial de contaminação dos solos e água subterrânea da área impactada por vazamento de combustíveis decorrente de acidente ferroviário, no distrito de Toledo, Botucatu/SP. Technical report. São Paulo, Brazil: Bottura Consultoria Ltda.
- CETESB. 2007. Estudo complementar do potencial de contaminação dos solos e água subterrânea da área impactada por vazamento de combustíveis decorrente de acidente ferroviário, nos distrito de toledo, Botucatu/SP. Technical report. São Paulo, Brazil: Biotech Ambiental Ltda.
- CETESB. 2015. Texto explicativo. Relação de áreas contaminadas e reabilitadas no Estado de São Paulo. Available on <http://areascontaminadas.cetesb.sp.gov.br/relacao-de-areas-contaminadas>.
- CHOSSON P, LANAU C, CONNAN J & DESSORT D. 1991. Biodegradation of refractory hydrocarbon biomarkers from petroleum under laboratory conditions. *Nature*, 351: 640-642.
- COLOMBIANI N, MASTROCICCO M, GARGINI A, DAVIS G & PROMMER H. 2009. Modelling the fate of styrene in a mixed petroleum hydrocarbon plume. *Journal of Contaminant Hydrology*, 105(1-2): 38-55.
- CORSEUIL H & MARINS M. 1997. Contaminação de águas subterrâneas por derramamentos de gasolina: o problema é grave? *Revista Engenharia Sanitária e Ambiental*, 2(2): 50–54.
- CPRM. 2006. Mapa geológico do estado de São Paulo - Escala 1:750.000. Serviço Geológico do Brasil.
- CRUZ GFD & MARSAIOLI AJ. 2012. Processos naturais de biodegradação do petróleo em reservatórios. *Química Nova*, p. 1628-1634.
- DELGADO-RODRÍGUEZ O, SHEVNIN V, OCHOA-VALDÉS J & RYJOV A. 2006. Geoelectrical characterization of a site with hydrocarbon contamination caused by pipeline leakage. *Geofísica Internacional*, 45(1): 63-72.
- DÍAZ E. 2004. Bacterial degradation of aromatic pollutants: a paradigm of metabolic versatility. *International Microbiology*, 7: 173-180.
- EDWARDS EA, WILLS LE, REINHARD M & GRBIC-GALIC D. 1992. Anaerobic degradation of toluene and xylene by aquifer microorganisms under sulfate-reducing conditions. *Environ. Sci. Technol.*, 58(3): 794-800.
- EMBRAPA. 2006. Centro Nacional de Pesquisa de Solos. Sistema Brasileiro de Classificação de Solos. 2nd ed., Rio de Janeiro, Brazil.
- FERROBAN. 2005. Relatório de atendimento a acidente ferroviário em São Manuel. Ferrovias Bandeirantes S.A. Brazil.
- GEOTOMO S. 2004. RES2DINV and RES3DINV. 3.53 version. 69 pp.
- GÜNTHER WMR. 2006. áreas contaminadas no contexto da gestão urbana. *São Paulo em Perspectiva*, 20(2): 105-117.
- HOPPER DJ. 1991. Aspects of the Degradation of Aromatics by Microorganisms. *Biodegradation: Natural and Synthetic Materials*. London. Spring-Verlang Limited, p. 69-89.
- IPT. 1981. Mapa Geomorfológico do Estado de São Paulo - Escala 1:1000.000. São Paulo, Brazil.
- IPT. 2014. Introdução. In: MORAES SL, TEIXEIRA CE & MAXIMIANO AMS (Eds.). Guia de elaboração de planos de intervenção para o gerenciamento de áreas contaminadas. p. 5-7. São Paulo, Brazil: IPT.
- JOHANSSON S, FIANDACA G & DAHLIN T. 2015. Influence of non-aqueous phase liquid configuration on induced polarization parameters: conceptual models applied to a time-domain field case study. *Journal of Applied Geophysics*, 123: 295-309.
- KANALY RA & HARAYAMA S. 2000. Biodegradation of high-molecular-weight polycyclic aromatic hydrocarbons by bacteria. *Journal of Bacteriology*, 182(8): 2059-2067.
- KEAREY P, BROOKS M & HILL I. 2002. An introduction to geophysical exploration. 3rd ed., London: Blackwell Science. 262 pp.
- KNÖDEL K, LANGE G & VOIGT HJ. 2007. Environmental geology: handbook of field methods and case studies. Springer.
- LOVLEY DR. 1991. Dissimilatory Fe(III) and Mn(IV) reduction. *Microbiological Reviews*, 55(2): 259-287.
- MILSON J & ERIKSEN A. 2011. Field Geophysics, The geological field guide series. 4th ed., John Wiley & Sons Ltd. 297 pp.
- MINOZZO M. 2010. Métodos geofísicos aplicados na avaliação ambiental em uma indústria química na cidade de São Paulo-SP. *Brazilian Journal of Geophysics*, 28(4): 742-742.
- MOREIRA CA. 2005. Aplicação do método eletromagnético transiente em área contaminada sob atenuação natural. Master's dissertation. Instituto de Geociências e Ciências Exatas, Universidade Estadual Paulista (UNESP). Brazil. 161 pp.
- MOREIRA CA & BRAGA ACDO. 2009. Aplicação de métodos geofísicos no monitoramento de área contaminada sob atenuação natural. *Engenharia Sanitária e Ambiental*, 14(2): 257-264.
- MUSSETT AE & KHAN MA. 2009. Looking into the Earth: an introduction to geological geophysics. Cambridge University Press. 493 pp.

- NADIM F, HOAG GE, LIU S, CARLEY RJ & ZACK P. 1999. Detection and remediation of soil and aquifer systems contaminated with petroleum products: an overview. *Journal of Petroleum Science and Engineering*, 26: 169-178.
- NEWELL CJ, ACREE SD, ROSS RR & HULING SG. 1995. Light Nonaqueous Phase Liquids. U.S.EPA. Ground Water Issue, EPA/540/S-95/500.
- NTARLAGIANNIS D, WILLIAMS KH, SLATER L & HUBBARD S. 2005. Low-frequency electrical response to microbially induced sulfide precipitation. *Journal of Geophysical Research*, 110: 1-12.
- NWANKWO C & EMUJAKPORUE G. 2012. Geophysical method of investigating groundwater and sub-soil contamination: A case study. *Environmental Research Journal*, 6: 124-129.
- PETROBRAS, Petróleo Brasileiro S A. 2006. Avaliação de tecnologias in-situ para a remediação de hidrocarbonetos de petróleo na Fazenda Experimental da Ressacada. Florianópolis, Brazil. 386 pp.
- POWERS SE, HUNT CS, HEERMANN SE, CORSEUIL HX, RICE D & ALVAREZ PJ. 2001. The transport and fate of ethanol and BTEX in groundwater contaminated by gasohol. *Critical Reviews in Environmental Science and Technology*, 31(1): 79-123.
- RABUS R & HEIDER J. 1998. Initial reactions of anaerobic metabolism of alkylbenzenes in denitrifying and sulfate-reducing bacteria. *Archives of Microbiology*, 170: 377-384.
- RAMOS SM, GIUSTI DA & ROSA FILHO EF. 2016. Relationship between geological domain and physicochemical parameters in lotic system. *RBRH*, 21(4): 882-893.
- REDD K & ADAMS J. 2015. Sustainable remediation of contaminated sites. New York: Momentum Press. 268 pp.
- SAMANTA SK, SINGH OV & JAIN RK. 2002. Polycyclic aromatic hydrocarbons: environmental pollution and bioremediation. *TRENDS in Biotechnology*, 20(6): 243-248.
- SARA M. 2003. Site assessment and remediation. 2nd ed., Florida: Lewis Publishers. 1109 pp.
- SAUCK WA. 2000. A model for the resistivity structure of LNAPL plumes and their environs in sandy sediments. *Journal of Applied Geophysics*, 44: 151-165.
- SCHREIBER M, CAREY G, FEINSTEIN D & BAHR J. 2004. Mechanisms of electron acceptor utilization: implications for simulating anaerobic biodegradation. *Journal of Contaminant Hydrology*, 73: 99-127.
- SEO JS, KEUM YS & LI Q. 2009. Bacterial degradation of aromatic compounds. *International Journal of Environmental Research and Public Health*, 6: 278-309.
- SMITH MR. 1990. The biodegradation of aromatic hydrocarbons by bacteria. *Biodegradation*, 1: 191-206.
- SORIANO JUNIOR R. 2009. Avaliação da presença de vapores no solo em antiga área industrial contaminada por hidrocarbonetos: concentrações medidas e simuladas. Master's dissertation. Instituto de Geociências e Ciências Exatas, Universidade Estadual Paulista (UNESP). Brazil. 108 pp.
- TELFORD WM, GELDART LP & SHERIFF RE. 1990. *Applied Geophysics*. 2nd ed., London, UK: Cambridge University Press. 792 pp.
- TONINI RMCW, DE REZENDE CE & GRATIVOL AD. 2010. Degradação e biorremediação de compostos do petróleo por bactérias: Revisão. *Oecologia Australis*, 14: 1010-1020.
- TWARDOWSKA I, ALEEN HE & HÄGGBLUM M. 2006. Soil and water pollution: monitoring, protection and remediation. *Nat Science*. Springer, Krakom. 662 pp.
- VENCELIDES Z, SRACEK O & PROMMER H. 2007. Modelling of iron cycling and its impact on the electron balance at a petroleum hydrocarbon contaminated site in Hnevice, Czech Republic. *Journal of Contaminant Hydrology*, 89: 270-294.
- WEINER JM & LOVLEY DR. 1998. Rapid benzene degradation in methanogenic sediments from a petroleum-contaminated aquifer. *Applied and Environmental Microbiology*, 64(5): 1937-1939.
- WIEDEMEIER TH, WILSON JT, KAMPBELL DH, MILLER RN & HANSEN JE. 1995. Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater. Technical report. Brooks AFB. San Antonio, Texas. 130 pp.
- WINEGARDNER DL. 1996. An introduction to soils for environmental professionals. New York: CRC Press. 270 pp.
- ZOGALA B, DUBIEL R, ZUBEREK W, RUSIN-ZOGALA M & STEININGER M. 2009. Geoelectrical investigation of oil contaminated soils in former underground fuel base: Borne Sulnowo, NW Poland. *Environmental Geology*, 58: 1-9.

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