Integration of geoelectric and geochemical data in the evaluation of natural attenuation in a diesel contaminated site in São Manuel (Brazil)

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Resumen

La geofísica es de gran importancia en relación con los análisis químicos en el proceso de diagnóstico de la contaminación en el medio geológico. En este trabajo se presentan los resultados de los métodos geofísicos de Resistividad Eléctrica y Polarización Inducida en un área contaminada por diesel debido a un accidente ferroviario ocurrido en 1999 en el que no se implementaron sistemas de remediación. Los procesos de atenuación natural prevalecientes en la zona resultaron en una reducción gradual de los niveles de hidrocarburos en las aguas subterráneas, como lo demuestra una serie histórica de análisis. La disolución y neoformación mineral son productos de este proceso que en la disponibilidad de elementos como Fe y Mn en suelos tropicales, a menudo resultan en la cristalización de sulfuro. Perfiles 2D y los modelos geofísicos 3D revelan una zona central de alta resistividad y alta capacidad de carga en un área con remanentes de contaminación cuantificados en 2008, asociados a hidrocarburos residuales. Además, los datos de carga elevada proporcionan una visión general de la mineralización del hidrocarburo como resultado de su degradación. Los datos indican la posibilidad de utilizar estos métodos como herramienta en sistemas de remediación de contaminación por hidrocarburos, por la posibilidad de realizar investigaciones sobre suelos secos y subterráneos, además de monitorear la mineralización de metales, productos relacionados con la degradación de hidrocarburos en el entorno geológico.

Key words: hidrocarburos, atenuación natural, resistividad eléctrica, cargabilidad.

Abstract

Geophysics is a very relevant investigation tool in conjunction with chemical analysis, during the diagnosis and monitoring of contamination in the geological environment. This paper presents the results of DCdefine resistivity and Induced Polarization geophysical methods in an area contaminated by diesel due to a railway accident that occurred in 1999 in which no remediation systems were implemented. The processes of natural attenuation prevailing in the area resulted in gradual reduction of the levels of hydrocarbons in groundwater, as demonstrated by a historic series of analyses. The dissolution and neoformation mineral are products of this process that in the availability of elements such as Fe and Mn in tropical soils, often result in the crystallization of sulphide. 2D profiles and 3D geophysical models reveal a central zone of high resistivity and high chargeability in an area with remnants of contamination quantified in 2008, associated to residual hydrocarbons. Besides, the high chargeability data provides an overview of the mineralization of the hydrocarbon as a result from its degradation. The data indicates the possibility of using these methods as an auxiliary tool in systems for remediation of contamination by hydrocarbons, by the possibility of investigations into dry soil and groundwater, and in monitoring metal mineralization, products related to the degradation of hydrocarbons in the geological environment.

Palabras clave: hydrocarbon, natural attenuation, resistivity, chargeability.

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Introduction

Contemporaneous with the process of economic development, contamination of the environment occurs as a result of lack of planning and inadequate management of raw materials, products and hazardous waste which, at concentrations above the recommended values, pose risks to health, to the quality of life and to the environment.

The logistics of hydrocarbons transportation in southeastern Brazil involves oil pipelines linking production fields to refining plants, which subsequently make use of highways for short distances and railroads for long distances. Rail transport is particularly relevant due to the possibility to move large volumes at relatively low cost. In this context, railway accidents often result in the contamination of great extent and significant environmental impact. Brazilian railways belong to the Brazilian Federal Government and are operated by private companies through a concession system.

The origin of the contamination of soil and water environments by hydrocarbons usually occurs due to transport accidents, breakage of pipes or improper storage. The main groups of contaminants found in these areas are the aromatic solvents, represented by BTEX compounds (benzene, toluene, ethylbenzene and xylenes), polycyclic aromatic hydrocarbons (PAH), chlorinate solvents and metals.

The groundwater contamination by organic chemical products is a recurring issue. Given the variability in terms of density and solubility in water, leakage from the surface may form contamination plumes and turn the groundwater a non-potable resource for human consumption.

For a long time the contamination of soil and groundwater has been neglected due to the difficulty of it characterization. When in contact with the physical environment, the transport of organic contaminants can be modeled according to two stages. The first comprises all those that occur entirely above the water level in the vadose zone; the second considers the transport processes inside the aquifer, soluble/dissolved or insoluble/supernatant, characterized by means of chemical analysis of water samples from monitoring wells (Sara, 2003; Berkowitz et al., 2008).

Investigation techniques through direct methods such as physical and chemical analysis of samples are common in the diagnosis of these areas, given the possibility of quantifying the levels (Redd and Adams, 2015). The main disadvantage of this procedure is its sparse sampling and poor representation in spatial terms, in a condition where the analyzed object is mobile and dynamic.

Particularly in the context of contamination by hydrocarbons that occurred several years ago, changes in terms of content, with dispersion, dilution and degradation of the compounds by the action of various agents present in the geological environment are expected. In many cases of areas contaminated by hydrocarbons, reduction of levels occurs without remedial actions. This natural attenuation comprises a set of remediation processes of contamination by hydrocarbons in the geological environment, through the action of physical, chemical and biological processes (Alvarez and Illman, 2006).

The degradation of contaminants by the action of microorganisms, is one of the main mechanisms responsible for the consumption of contaminants with long periods of residence in the environment. The efficiency of this process depends on a combination of factors such as the presence of electrical receptors (O_2, SO_2^{-4}, Fe^{+3}, Mn^{+4}, NO^{-3}), adequate conditions of pH, Eh, temperature and low levels of contamination (Suthersan and Paine, 2005; Twardowska et al., 2006; Romero-Zerón, 2012).

This process is specifically important in the degradation of hydrocarbons, which may be converted by organisms found in nearly all environments. Various BTEX compounds can be biodegraded under environmental conditions (Alvarez and Illman, 2006, Bhandari et al., 2007). The generation of organic acids, dissolution and mineral neoformation are consequences of this process.

The use of geophysics as a noninvasive investigation tool, with low cost and wide coverage in spatial and temporal terms, is used increasingly in recent years by supervisory agencies as a diagnostic tool in the management of contaminated sites (Sara, 2003; Knödel et al, 2007). Electrical and electromagnetic geophysical methods are particularly relevant in this type of investigation due to the frequent contrast in physical properties between contaminated and uncontaminated soil or rock

Several studies demonstrate the effectiveness, benefits and limitations when applied in the diagnosis and geophysical monitoring of

contamination by hydrocarbons (Sauck, 2000; Batayneh, 2005; Shevnin *et al*. 2005; Delgado-Rodriguez *et al*., 2014).

Facing the possibility of delimitation of contaminants in soil and groundwater, geophysical methods allow the analysis of the evolution and persistence of hydrocarbon as a technique for monitoring the natural attenuation of the contaminant.

This paper performs an analysis of geochemical and geophysical data (DC Resistivity and Induced Polarization, IP, methods) over a benzene-contaminated area from a railway accident, which is currently being monitored for natural attenuation processes.

Study area

The area of study is located on a farm named Ribeirão do Paraíso, near São Manuel city, São Paulo State, southern Brazil. The area can be accessed by the highway Marechal Rondon (SP 300) (Figure 1).

In December 1999 a rail accident occurred involving the railway company Ferroban - Ferrovias Bandeirantes - which resulted in the derailment and overturning of three tank cars carrying fuel oil between the segment from Rubião Junior to Bauru with spilling and leakage of about 240,000 liters of diesel (CETESB, 2011).

The property where the accident occurred received from Ferroban the first responses for recovery and containment of the material retained on the surface. The scattering of large quantities of oil impacted the groundwater and surface waters, with contamination of Igualdade creek, which has its course near the accident site.

The contaminated area was approximately 30,000 m². Furthermore, Ferroban was made responsible for the environmental impact report, the risk assessment of the area and also for the delivery of such documents to the supervision of the Environmental Agency of the São Paulo State – Companhia de Tecnologia de Saneamento Ambiental (CETESB), responsible
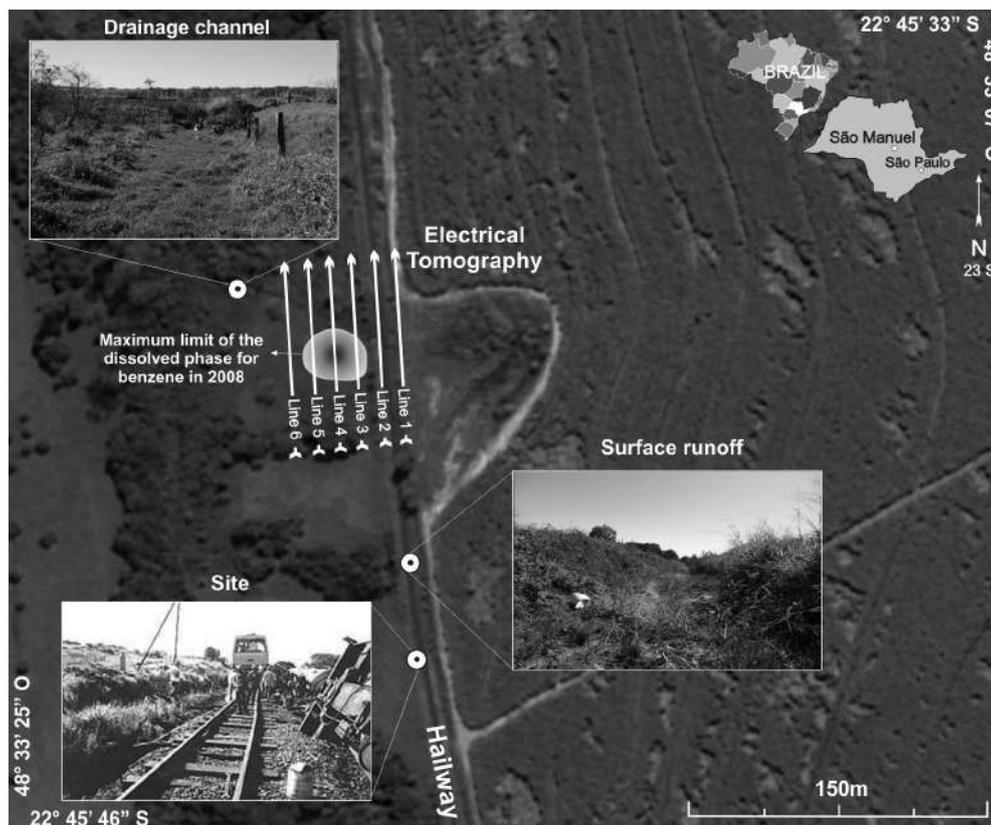
Figure 1. Study area, with site, surface runoff, drainage channel under railway, lines of geophysical investigation and maximum limit of the dissolved phase for benzene in 2008.

for this type of occurrence (CETESB, 2011). Probing carried out on site and the installation of monitoring wells allowed for a geological and hydrogeological characterization of the area. In the profiles surveyed sandy-clay soils were identified, with the presence of organic matter, having a thickness of 0.3 to 1.0 m, superimposed on fine sandstones belonging to the Adamantina Formation, Bauru Group, sequence of the Paraná Sedimentary Basin.

Near the drainage, there are outcrops of Quaternary Age alluvial sediments consisting of medium to coarse quartz sand. The hydrogeological data show that the level of the water table is shallow, with a maximum depth of 4.2m in the highest region of the topography, and sub-cropping near the drainage The results of permeability measurements indicate maximum hydraulic conductivity of 7.663 x 10^{-4}cm/s and minimum of 5.783 x10^{-5}cm/s. The maximum speed of flow calculated was 0.135m/d (CETESB, 2011). The groundwater flow follows the local topography, from southeast to northwest, towards Igualdade creek (Figure 2).

The analytical results of the historical series of groundwater monitoring (at the accident) indicate the presence of BTEX compounds (Benzene, Toluene, Ethylbenzene and Xylene), especially benzene with greater temporal persistence (Table 1).

Natural attenuation processes

Once the petroleum-derived hydrocarbons reach the ground, they can undergo evaporation or penetrate and reach the groundwater. When in contact with these waters, they are subject to dissolution or remain in the residual free phase, named non-aqueous phase liquids (NAPL), which can fill the pores of the soil so that they become a continuous source for the contamination of the aquifer (Suthersan and Paine, 2005; Haritash and Kaushik, 2009).

Reaching the aquifer, the NAPLs are divided according to their relative density to water in light phase LNAPL (Light Non-Aqueous Phase Liquids) represented by compounds BTEX (Benzene, Toluene, Ethylbenzene and Xylenes) and dense phase DNAPL (Dense Non-Aqueous Phase Liquids), consisting of the group of polyaromatic hydrocarbons (PAH). The NAPLs compounds have great potential for contamination in soils and groundwater.

Without human intervention and under favorable environmental conditions, organic compounds undergo a reduction in their mass, toxicity, volume and concentration through physical, chemical and biological processes (Samanta et al., 2002). This process of natural attenuation occurs both in the saturated and unsaturated zone. These processes include, beside biodegradation, mechanisms of dispersion, dilution, evaporation and adsorption.
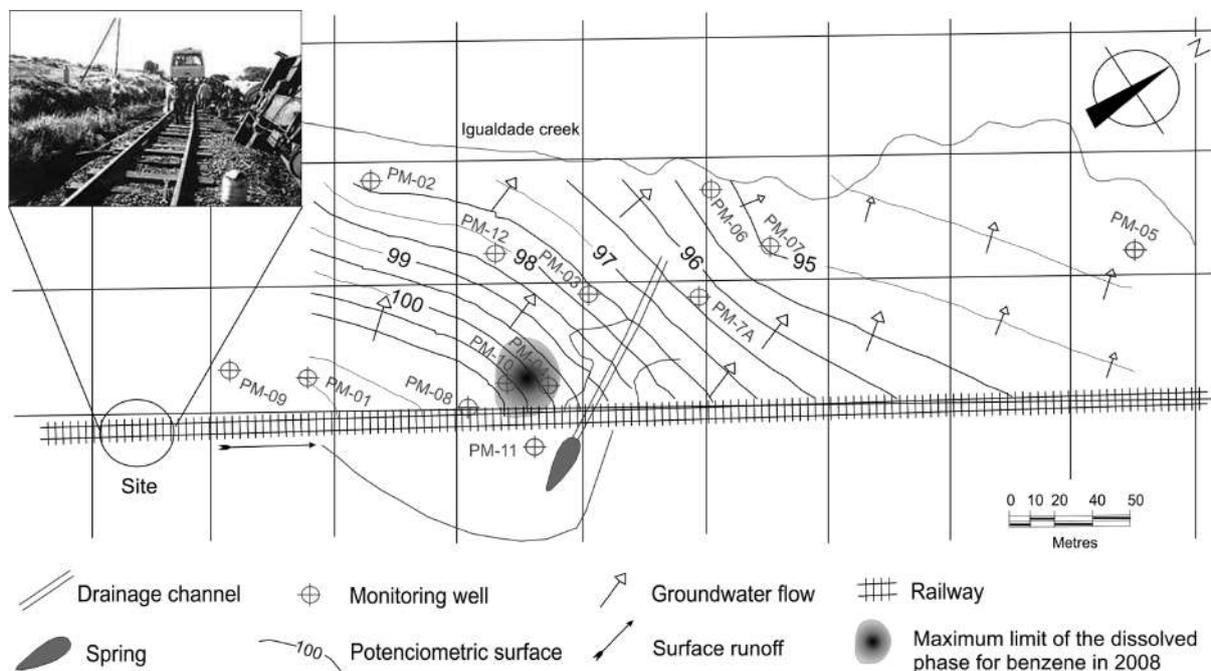
Figure 2. Groundwater flow with electrical resistivity tomography lines.

Table 1. Evolution of the benzene in aquifer (in µg/l) (CETESB, 2011).

Well	Date								
	11/2000	12/2003	08/2006	03/2008	10/2008	06/2009	11/2009	10/2010	03/2011
PM-01	<L.D	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	*	<5,0
PM-02	<L.D	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<5,0	*
PM-03	<L.D	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<5,0	<5,0
PM-04	420	76	55,1	15	2,81	5,7	4,1	<5,0	5,8
PM-05	<L.D	<L.D.	<L.D.	*	*	*	*	*	*
PM-06	-	<L.D.	<L.D.	*	<L.D.	<L.D.	<L.D.	<5,0	<5,0
PM-07	-	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<5,0	<5,0
PM-08	-	-	24,3	<L.D.	<L.D.	<L.D.	<L.D.	<5,0	<5,0
PM-09	-	-	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<5,0	<5,0
PM-10	-	350	20,1	28,3	5,3	3	<L.D.	<5,0	<5,0
PM-11	-	-	<L.D.	<L.D.	<L.D.	*	*	*	*
PM-12	-	-	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<5,0	<5,0

L.D.: Limit of detection   * Destroyed well.

Dispersion and dilution of contaminants depend almost exclusively on the physical characteristics of the aquifer, such as hydraulic conductivity, which influences the transport of groundwater. This conductivity, when high, increases the extent of contamination, but decreases the average concentration due to dilution. Thus, at lower concentrations, microorganisms meet the most favorable environments for the performance of the natural degradation processes (Wilson and Jones, 1993).

Volatilization of compounds is relatively low, because the surface area between the contaminant on residual or dissolved phase with the atmosphere is small, often neglected in diagnostics. Several studies showed that less than 5% of the dissolved phase of BTEX is converted into gas by volatilization (Romero-Zerón, 2015).

Another common destiny for contaminants are the pores present in the soil. Due to the hydrophobicity of the hydrocarbon molecules and to the mechanisms of sorption caused mainly by clay minerals, organic matter and oxides and sulfites of iron and manganese from the soil, these compounds tend to be trapped in these pores or in fractures of rocks at the surface (Thomas and Ward, 1989).

The affinity of the contaminant with the soil matrix may not be sufficient to isolate the contaminant from the permanent groundwater. Sorption does not remove the mass of contaminant, only retards its migration, and depending on the rate of desorption, it can reach the groundwater (Wilson and Jones, 1993; Thomas and Ward, 1989).

The main mechanism of natural attenuation of hydrocarbons in soil and groundwater is biodegradation, where microorganisms convert hydrocarbons to organic acids or promote the complete oxidation and mineralization (Hiebert and Bennett, 1992; Bezalel et al., 1996a; Bezalel et al., 1996b; Hofrichter et al., 1999). The generation of these acids in large amounts results in mineral dissolution and ion release to the saturated zone of the aquifer (Hiebert and Bennett, 1992). In this manner the electrical conductivity of the impacted zone can be greatly increased.

This transformation is mainly limited by the availability of electron receptors and hydrocarbons that assume the role of electron donors to the degradation, and therefore need to be biochemically accessible to microorganisms. Additionally, other parameters such as pH, temperature, salinity and redox potential are also important for biodegradation. Under aerobic conditions, where dissolved oxygen is the electron acceptor, biodegradation is more effective and allows complete conversion of hydrocarbons into non-toxic products such as CO_2, CH_4 and H_2O (Haritash and Kaushik, 2009).

Method

The geophysical methods applied were DC Resistivity and Induced Polarization through six lines of Electrical Resistivity Tomography (ERT) in a Wenner-Schlumberger arrangement with 104m length for each row, placed parallel to the railway with 12.5m spacing, and 2m spacing between electrodes (Figure 1). Due to a greater induction on potential electrodes, this arrangement presents a great signal to noise ratio and satisfactory sensitivity to analyze

structures for vertical flow in the geological environment (Furman *et al.*, 2003; Okpoli, 2013; Moreira *et al.*, 2016).

The geophysical equipment used was the Terrameter LS resistivity meter, manufactured by ABEM Instrument (Sweden), which consists in a single module of transmission and reception of signals. During the acquisition, non-polarizable electrodes based on copper sulfate solution (Cu-CuSO4) were used, characterized by a copper wire inside and a porous base, which allows solution percolation in the soil. This procedure reduces contact resistance and minimizes the generation of parasitic currents generated by the use of metal electrodes during readings.

The equipment has an automatic acquisition through previous programming in a multi-cable system, with 250 W, resolution of 1 µV and maximum current of 2.5 A. It enables the performance of spontaneous potential (SP), DC resistivity (R) and induced polarization (IP) by means of periodic cycles of transmission and reception of signals, automated calculation of the contact resistivity and standard deviation from the measurement set (ABEM, 2012). This equipment was calibrated with the following parameters to the IP time domain method: transmission of 400mA for 1.0s in each measure; two window lectures with 100 ms each and a delay time of 0.4 s.

The positioning of the lines was based on the latest geochemical data available relating to the monitoring of groundwater required by the environmental agency (Figure 1). These data describe the presence of benzene with maximum values of 2.8 µg/l for the dissolved phase in well PM-04 and 5.3 µg/l for PM-08 in 2008 (Table 1).

The field measurements were processed with the software Res2dinv and resulted in profile sections, with logarithmic graphical scale and intervals of interpolation of values in colors. This is a software that determines automatically a two-dimensional model of the subsurface (Griffths and Barker, 1993). It divides the pseudo-section into rectangular blocks, which models the pseudo-section by the adjustment of data until the model produces values that match the field measurements. This optimization aims to reduce the difference between the apparent resistivity/chargeability values, calculated from the model and the one measured in the field, with the combined differences expressed in RMS (root-mean-square) (Loke and Barker, 1996).

The data generated after the 2D inversion were gathered into a single file, which unites the position of the readings along the lines (variable "x"), spacing among lines (variable "y"), depth modeled by the inversion (variable "z") and the value of resistivity/chargeability (variable "M"), later used as a database for generating 3D pseudo-modeling maps.

This spreadsheet was used for the generation of 3D pseudo-models, in a routine of basic steps adopted in mineral research. In this case, the sampling plan is frequently defined from statistic, structural criteria, spatial placement of a mineral accumulation, among other (Moon et al, 2006). A simple procedure consists in sampling by a set of perforations perpendicular to the main axis of the structure, followed by a parallel set of perforation lines.

This process was developed in the Oasis Montaj platform where 2D inversion results obtained from the Res2Dinv were interpolated and modeled using the kriging method, for enhancement of extreme values in a model of three-dimensional blocks, where electrical tomography lines were positioned. Geophysical 3D pseudo-models generated from 2D sections provide a very wide comprehension of the complexity of geological and hydrogeological structures (Chambers *et al.*, 2006; Aizebeokhai *et al.*, 2011, Moreira *et al.*, 2016; Vieira *et al.*, 2016; Côrtez et al., 2016).

Results and discussion

The processed data reveal a range of values for resistivity between 17 Ω.m and 1965 Ω.m, with a predominance of high values in the near-surface portions and gradual reduction on values with increasing depth. The portion of high resistivity in lines 3, 4 and 5 coincides with the delimitation of benzene plume carried out in 2008 based on chemical analysis of groundwater collection from wells. The same occurred for the chargeability data, which ranged from 0.01 mV/V to 21.6 mV/V, and has a zone of high chargeability in the middle of lines 3 and 4 (Figure 3 and 4).

The field work occurred during summer, after long periods of rain; which conditioned a low contact resistance between the electrodes and the soil. In this way the data quality enabled a favorable processing with low RMS to the tomography profiles.

The high resistivity values in the proximity to the area with higher concentrations of hydrocarbons in the aquifer may be an indicative of the presence of residual phase in
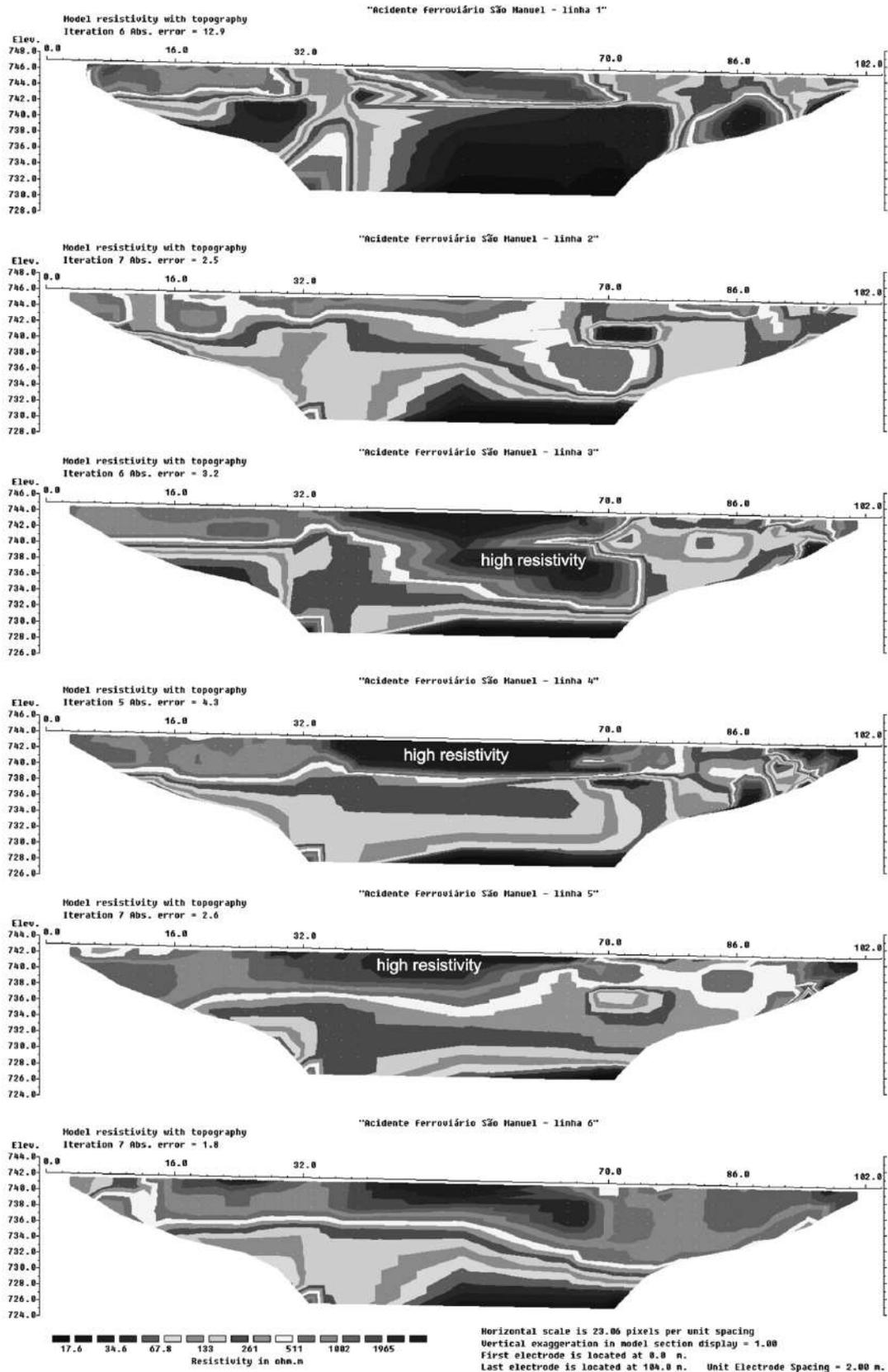
Figure 3. 2D resistivity sections with featuring to high resistivity values.
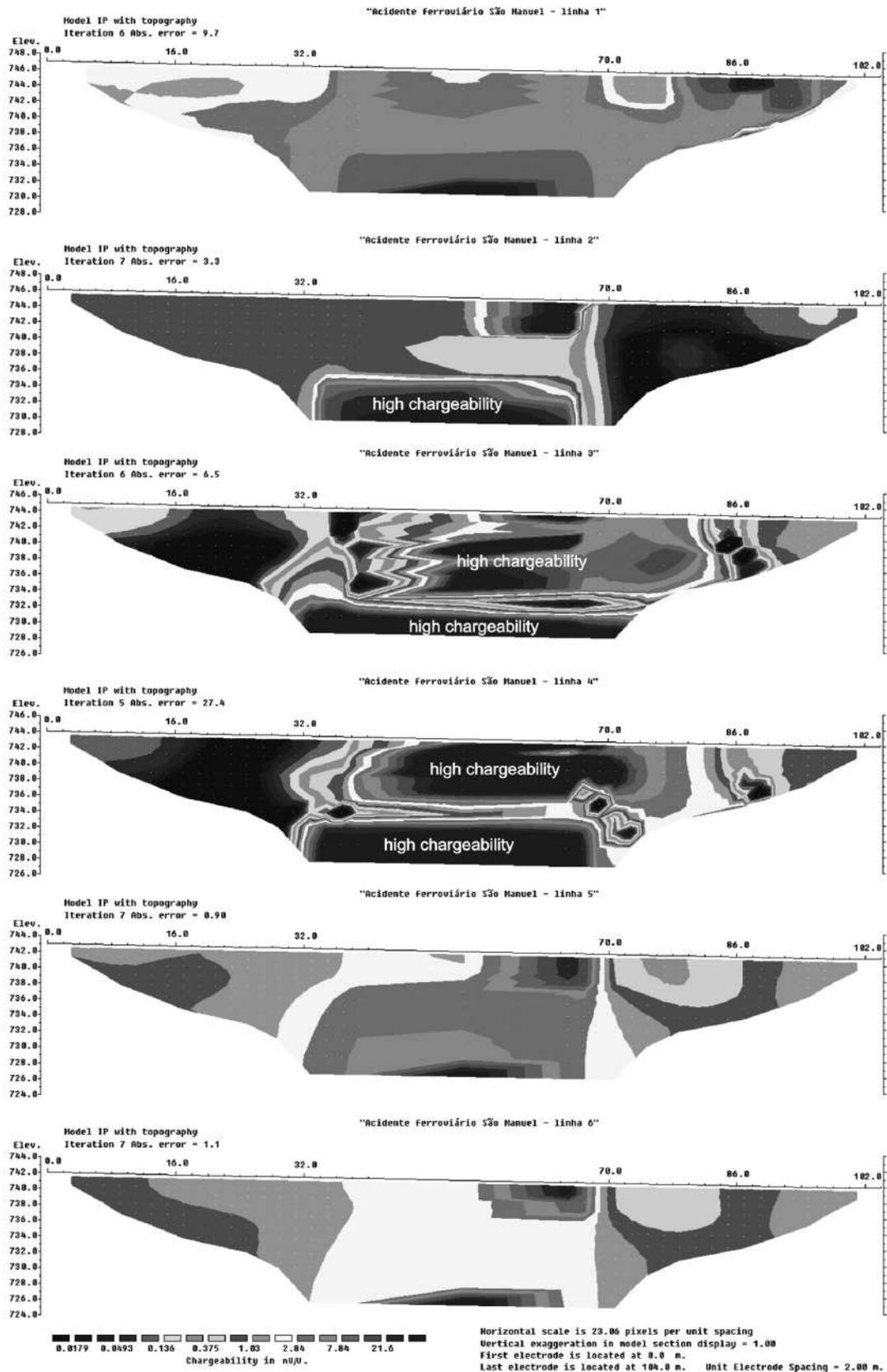
Figure 4. 2D chargeability sections with featuring to high chargeability values.

intermediate conditions of degradation. The gradual decrease in resistivity of lines 5 and 6 may indicate the more effective conversion of residual phase to the dissolved phase, besides the gradual return to the natural conditions of the area through the complete consumption of hydrocarbons by the action of natural attenuation processes.

Chargeability data points out to the residual contamination, however, there are anomalies of high chargeability that do not have the high resistivity corresponding values. Once a large volume of diesel spilled (240.000 litters), it contaminated great areas, hence, the high chargeability values indicates zones that correspond to the dissolved phase and the potential subproducts of biodegradation.

In sequence, the initial data were modeled from the minimum curvature method, for smoothing the core values in relation to the limits of the investigated area, and the range of 1800 Ω.m to resistivity and 20 mV/V for chargeability values was modeled as a 3D surface in an attempt to assess the shape of the high chargeability zone, where the water level and the ground/saprolite contact were also shown (Figure 5).

The 3D surface generated for values of 1800 Ω.m provides a perspective view and the chargeability surface for 20 mV/V allows for an integrated vision of the data and the shape of an elongated body in the direction of the local groundwater flow that crosses the lines of electrical imaging. This chargeability body has a double-conical shape, with reversed and opposite larger bases and smaller overlapping ends, whereas the resistivity body has a large format in the unsaturated zone and a conical shape in the aquifer (Figure 5).

The site is at a sandy aquifer with saprolite clay matrix that increase with depth, and consists of a water column of about 6 m thickness.

The intervals in the unsaturated zone, mainly between depths of 2 and 4 m are characterized by a horizon enhanced in clay, originating from weathering processes and surface conduction for this depth interval, by dissolution and rainfall infiltration into the soil. In the zone of quartz sandstone with clay matrix, the high polarization values obtained in a center of residual contamination in soil/saprolite may reflect products related to the degradation of the leaked hydrocarbons, formed by the action of natural attenuation processes.

The action of organic acids on mineral grains can cause the dissolution and availability of chemical elements in the dissolved phase, due to conditions of pH and Eh artificially generated in the region of the hydrocarbon degradation processes. The mineralization is one of the final steps in this process, which involves the conversion of cations and anions initially dissolved, into forms of higher chemical stability, as secondary minerals (Hiebert and Bennett, 1992; Bezalel et al., 1996a; Bezalel et al., 1996b; Hofrichter et al., 1999).

In this context, the clay minerals can make a decisive contribution as a source of chemical elements. The Fe and Mn are the main cations of low mobility present in clay minerals of tropical soils. These elements tend to remain in the alteration profile and often form structures named laterites, which in many places serve as guides to prospecting for mineral deposits of oxides and sulfides (Moon et al., 2006; Taylor, 2011; Moreira et al., 2014).

Some of these minerals are electrically polarizable based on the phenomenon of electronic polarization, which involves the accumulation of electric charges in metallic materials by artificially induced electric current (Keller and Frishknecht, 1966), the accumulation of which allows the generation of distinguishable contrast in IP surveys.

In the zone above the water table there is a bottleneck in the high chargeability body with an increase in depth, possibly due to the increased water content. In this case, a gradual reduction in aerobic conditions due to the unavailability of atmospheric oxygen and a concomitant increase in anaerobic conditions, i.e., decrease in Eh with depth occurs. It is probable that sulphide predominate in unsaturated locations, gradually converted to hydroxides with the increase in moisture (Govett, 2000).

In the aquifer zone, the body of high chargeability presents the smallest lateral thickness, where sulphide probably predominate in the most reducing locations. The continuous supply of water by lateral groundwater flow in an aquifer of high permeability should oxygenate this horizon and cause changes in the physicochemical conditions that are likely to result in instability of mineral and dissolution, preserving only the most reduced central zone.

The saprolite interval is characterized by a relatively low permeability and decreasing oxygenation with an increase in depth, present
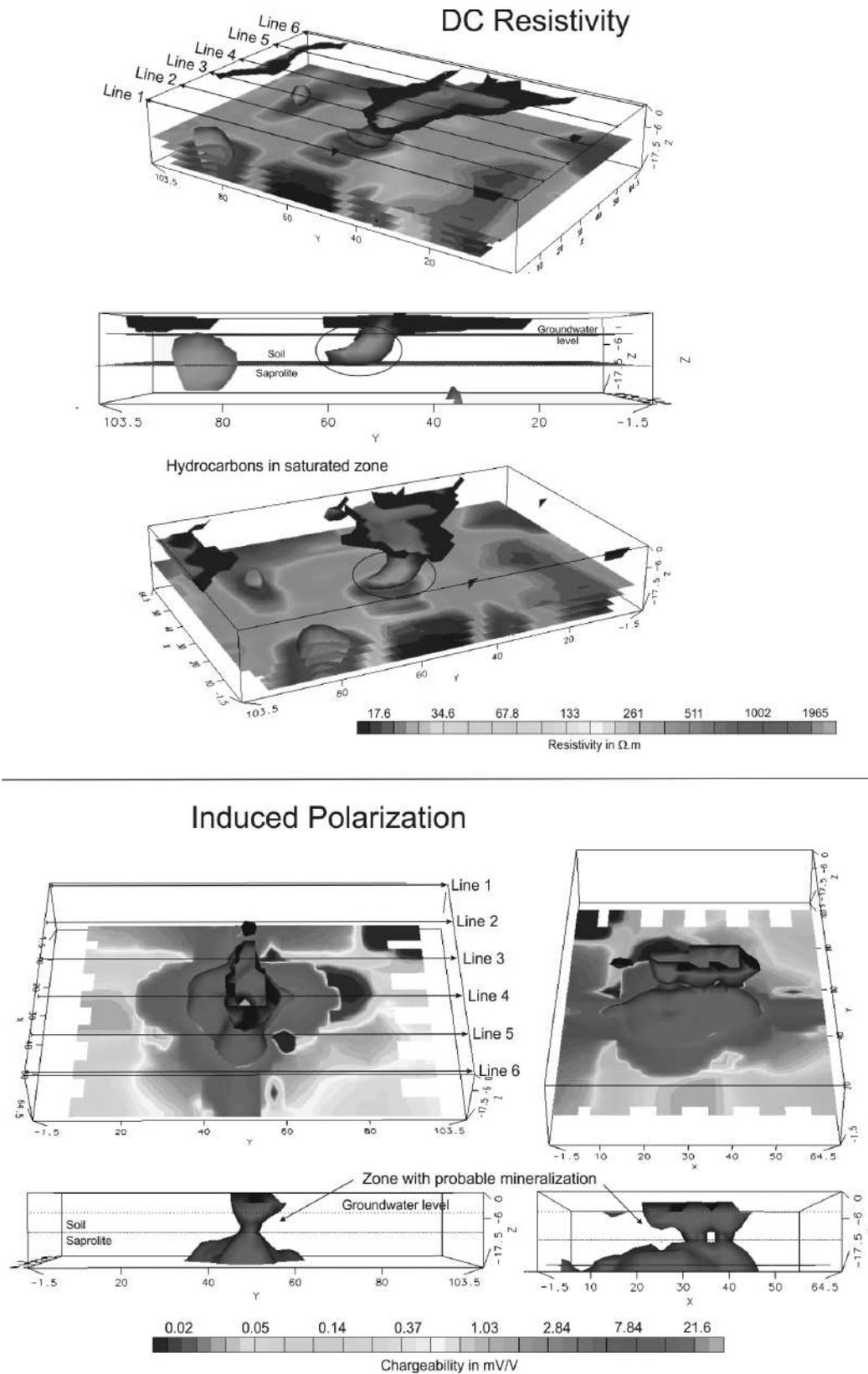
Figure 5. Geophysical integration data. a) Resistivity 3D isosurface modeling of 1800 Ω.m b) Chargeability 3D isosurface modeling of 20 mV/V, with groundwater level and the soil/saprolite contact.

favorable conditions for the preservation of potential sulphide e residual hydrocarbons.

Within this set of processes, the zone of high chargeability associated with the central area of residual contamination must reflect the presence of oxides/sulphide and eventually disseminated sulphide, having available sulfur, crystallized by recombination of chemical elements originated from the mineral dissolution by the attack of organic acids produced during the degradation of hydrocarbons.

Conclusions

The history of events in the area points to a leakage of a large volume of diesel in the railway right-of-way, with surface runoff and impoundment in a drainage channel under the railway, where infiltration occurred for part of the leaked volume, which resulted in the contamination of soil and groundwater. The monitoring of groundwater by chemical analysis indicates a downward trend in the levels over the subsequent years, with moments of slight increase with sporadic input of hydrocarbons into the aquifer.

In the absence of systems for treatment and remediation of the area by invasive techniques, dispersion, dilution and consumption of contaminants occur in the area by the action of natural attenuation processes that act on the physical structure of hydrocarbons and cause their fragmentation and final reduction to methane and water. The generation of organic acids, dissolution and mineral neoformation are consequences of these processes.

Both phases of hydrocarbons were subject to recognition by means of the DC resistivity method, contrasting with the uncontaminated environment. The region with the highest levels of dissolved phase was characterized by high resistivity values (> 1000 Ω.m), indicative of the presence of high concentrations of residual phase, in face of the typical high resistivity of low degraded hydrocarbons.

The signature of high chargeability in the areas contaminated by hydrocarbons is a clear indication of the accumulation of metallic minerals, in contrast with the native materials, suggesting their origin from the natural attenuation processes occurring in the area. Thus, the induced polarization method allows the detection of contrasts in physical properties caused indirectly by the presence of hydrocarbons in soil and groundwater.

Low values of chargeability in areas with signs of contamination do not necessarily indicate the absence of contaminants, whereas high values of chargeability also do not necessarily indicate the presence of these compounds. In many cases, the hydrocarbon may have been completely consumed in old contaminations, and only the by-products of the process remained in the environment, as mineral neoformations subjected to polarizability.

The application of this geophysical method in conjunction with direct techniques for remediation of hydrocarbon contaminated areas can contribute in increasing the efficiency of the site characterization process, especially giving the possibility of geophysical scans in the unsaturated zone and the monitoring of areas of accumulation of metallic minerals, indicative of the effective remediation of contaminant hydrocarbons.

Another important aspect is the great geochemical affinity that sulphides have for a number of metal elements during the crystalli-zation of secondary minerals. This feature is exploited in studies of prospecting and exploration of mineral deposits, as laterites which eventually cover a non-outcropping mineral deposit can incorporate metallic elements directly associated with the deposit (Moon *et al*., 2006; Taylor, 2011; Aal *et al*., 2014).

In this regard, in complex contamination events involving hydrocarbons and metals, the detection of metallic mineralization originated by the presence of hydrocarbons is something desirable and should be considered in decontamination activities, taking into account the high capacity for retention of metals during the crystallization of sulphide in soils and groundwater.

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