

Joint interpretation of geoelectrical and volatile organic compounds data: a case study in a hydrocarbons contaminated urban site

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Resumen

Debido a la ocurrencia de un derrame de gasolina en un área urbana, los métodos de Tomografía de Resistividad Eléctrica (TRE), Perfilaje Electromagnético (PEM) y de medición de Compuestos Orgánicos Volátiles (COV) fueron utilizados para definir la pluma de contaminación y dirigir los trabajos de muestreo de suelo. Las anomalías COV (contaminación reciente) indicaron que una gasolinera localizada en el área de estudio es una fuente de contaminación activa. Las zonas con contaminación madura definidas con los métodos TRE y PEM correspondieron con anomalías de baja resistividad debido a los procesos de degradación de los hidrocarburos contaminantes. Los resultados alcanzados con los métodos TRE, PEM y VOC fueron integrados en un mapa, permitiendo la configuración final de las plumas de contaminación y la optimización de las perforaciones y el muestreo de suelo y producto libre. Análisis de laboratorio de las muestras de producto libre sugieren la existencia de más de un evento de contaminación en el sitio, con la presencia de contaminantes hidrocarburos frescos y degradados, clasificados en el rango de gasolina. Este estudio demuestra las ventajas de la aplicación conjunta de TRE, PEM y COV en sitios con fuentes de contaminación activa, donde se asume la existencia de hidrocarburos contaminantes recientes y maduros en el subsuelo.

Palabras claves: Benceno, Tolueno, Etilbenceno, Xilenos (BTEX), compuestos orgánicos volátiles (COV), contaminación por hidrocarburos, fuga de gasolina, tomografía de resistividad eléctrica (TRE), perfilaje electromagnético (PEM).

Abstract

As a result of a gasoline spill in an urban area, Electrical Resistivity Tomography (ERT), Electromagnetic Profiling (EMP) and Volatile Organic Compounds (VOC) methods were used in order to define the contamination plume and to optimize the drilling and soil sampling activities. The VOC anomalies (recent contamination) indicated that a gas station located at the study site is an active contamination source. The mature contaminated zones defined by ERT and EMP methods corresponded with low resistivity anomalies due to degradation process of the hydrocarbons contaminants. The ERT, EMP and VOC results were integrated on a map, allowing the final configuration of contamination plumes and the optimization of drilling and soil/free-product sampling. Laboratory analyses of free-product samples suggest the existence of more than one contamination event in the site, with the presence of recent and degraded-hydrocarbon contaminants classified in the gasoline range. This study shows the advantages of joint application of ERT, EMP and VOC methods in sites with active contamination source, where the existence of recent and mature contaminants in subsoil is assumed.

Keywords: Benzene, Toluene, Ethylbenzene, Xylenes (BTEX), hydrocarbons contamination, volatile organic compounds (VOC), gasoline spill, electrical resistivity tomography (ERT), electromagnetic profiling (EMP).

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Introduction

Hydrocarbons are among the main factors of geological medium contamination. The effectiveness of electrical methods for the characterization, on surface and depth, of oil contaminated plumes has been reported by several authors (Vanhala, 1997; Modin *et al.*, 1997; Atekwana *et al.*, 2001; Osella *et al.*, 2002; Delgado-Rodríguez *et al.*, 2006; 2006a). Just after contamination, a high resistivity anomaly delimits the contaminated zone. Oil contaminants cause changes in physical, chemical and biological properties of soil (Sauck, 2000; Atekwana *et al.*, 2001), mainly during the first four to six months after contamination. Abdel-Aal *et al.* (2004) found some important details on biodegradation process and changes in the electrical properties of contaminated zones. They demonstrated that the decrease of resistivity in soil contaminated by degraded hydrocarbons is mainly related to high surface conductivity in the pores of the affected rocks. Thus, the low resistivity anomalies are associated to the existence of mature hydrocarbon contamination. Electrical Resistivity Tomography (ERT) and Electromagnetic Profiling (EMP) are effective tools to mapping low resistivity anomalies caused by hydrocarbon contamination (Shevlin *et al.*, 2005).

ERT is applied in order to obtain a geoelectrical image of the sub-surface using electrical measurements made along profile at the surface. The application of ERT method is based on apparent resistivity determination with the help of linear array (e.g. Dipole-Dipole, Wenner-Schlumberger) of many electrodes connected to resistivity equipment. Resistivity data are then processed to obtain a resistivity cross-section (Loke, 2013). As a result of interpretation, true layers resistivity and their thickness are estimated.

The application of EMP method involves measuring the response of the subsurface to an electromagnetic field. An electromagnetic field is generated by a transmitter antenna, inducing eddy currents within the ground. These induced current generate a secondary magnetic field. Both primary and secondary magnetic fields are measured in a receiver antenna. The ground conductivity due to geological characteristics, conductive materials (metal objects) and contaminants can be calculated from the ratio of the secondary and primary magnetic fields (Keller and Frischknecht, 1966). The EMP results, although not providing detailed lithology (layers and their thicknesses) information, can

quickly determine the horizontal changes in soil apparent conductivity (e.g. hydrocarbon contamination plume) at different study depths. The electromagnetic measurements are sensitive to buried elongated conductors such as metallic pipes, electric lines, sanitary sewer, etc. These are usually recognized by the large meter fluctuations which occur in short distance. When the antennas are oriented perpendicular to the elongated conductor's axis, a minimum conductivity value will be registered (reaching negative values). When the antennas are parallel and close to the conductor's axis, conductivity values will have a maximum (Geonics Limited, 2010). In this work, as part of the survey technique, to evaluate the magnitude of electromagnetic interference from metal objects in EMP measurements, soil conductivity measurements were performed to two orthogonal directions of the antennas.

Volatile organic compounds (VOC) are the most common contaminants encountered at hydrocarbon contaminated sites. VOC survey is applicable under a variety of geological setting. Accurate VOC determinations are needed to assess the extent of contamination to make decisions for appropriate remedial action. The evaluation of subsurface organic vapors is based on the physical phenomena of hydrocarbons volatilization given by the Henry law (Lin and Chou, 2006), as well as the site characteristics. It has been demonstrated that the analysis of gases or vapors is a good screening technique in hydrocarbon contaminated sites, with GWT depths between 2 to 10 m (API, 1991; Ochoa *et al.*, 2007). Determination of VOC is usually performed in situ using a photoionization detector. Using this equipment, it is possible to detect a wide range of compounds in the gasoline to diesel range.

As a result of digging for a water cistern in a basement of an apartment building, a gasoline spill was detected. ERT and EMP methods were applied, as well as VOC measurements, in order to define the contamination plume and to guide the sampling activities. Through the application of the VOC, ERT and EMP methods, it was possible to calculate the dimensions of the affected area. Laboratory analyses of free-product samples suggest the existence of several contamination events with the presence of recent and mature hydrocarbon contaminants.

Site background

The site is located in a popular neighborhood of Mexico City between 2,240 and 2,244 m.a.s.l. The geological composition of the site belongs

to the sedimentary Mexico City basin and Texcoco ex-lake's west shore (Marín-Córdova *et al.*, 1986). The stratification sequence showed low permeability clay and silt within fine and medium sand lenses. The groundwater table (GWT) was between 3.75 and 5.00 m in the central and northern portions of the site, meanwhile, in the southern portion, near to gas station, the GWT can reach up to 9.00 m depth. The permeability coefficient rate was 1.0×10^{-6} to 1.0×10^{-7} cm/s (low permeability).

A paved (main) street runs from southwest to northeast along 350 m (Figure 1). As a result of digging for a water cistern in a basement of an apartment building, a hydrocarbon spill with gasoline-like odor from a thin layer at an approximate depth of 5 m was detected. The spill point is about 100 m from a gas station, and about 50 m from small factories with solvents and fuel storage tanks, indicating the probable existence of active contamination sources (Figure 1). Indirect methods were applied to map the contaminated zones and to select the soil boring locations, defining a study area of 5.3 ha.

Application of geoelectrical and VOC methods: configuration of the contamination plume

Application of VOC measurements

Subsurface vapors were measured in situ to assess the content of VOC. The methodology to measure VOC has been tested and improved since 1992 to allow a rapid measurement (screening) of the most likely occurrence and distribution of hydrocarbons in the subsurface and thus select the sites to perform the drilling and soil sampling. Sampling equipment including a specialized hammer and a hammer sampler probe, allows by vacuum, the extraction of vapor from subsoil. VOC content in subsoil can then be determined using a portable photoionization detector (PID), which can measure concentrations from ppb to up to 10,000 ppm. Since the presence of VOC in the subsurface originated from the hydrocarbons contaminants are quantified, this method could be considered as semi-indirect. VOC were measured at 91 selected points.

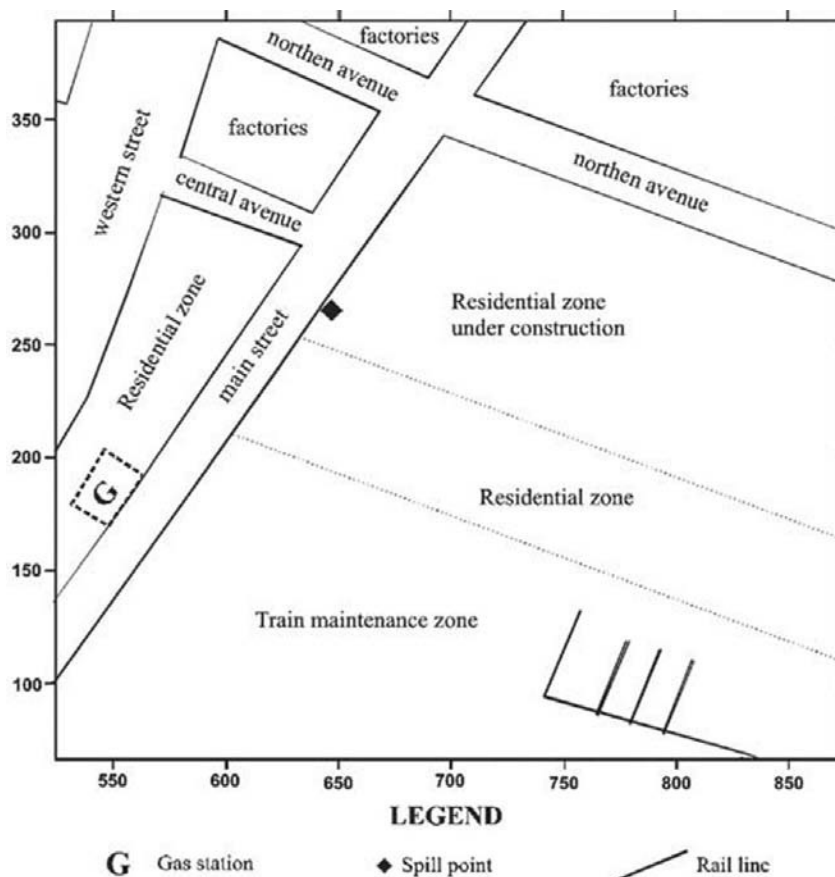


Figure 1. Scheme of the site.

Application of ERT method

Three ERT parallel profiles were performed on Main Street (Figure 1) in order to obtain resistivity anomalies associated with the presence of hydrocarbon-contaminated soils. A total of 64 ERT measurements points were settled. ERT survey was carried out using a great number (~ 50) of electrodes placed along each profile with a constant interval of 4 m, using AB/2 spacing of a Wenner-Schlumberger array from 6 to 42 m, ensuring a maximal study depth of 15 m. Spacing between sounding centers was 8 m.

Application of EMP method

Using the EM31-MK2 equipment (Geonics Limited, 2010), the horizontal changes in soil apparent conductivity for maximal study depth of 6 m is determined. Taking into account that in the most of the site the local GWT depth varies between 3.75 m – 5.00 m, it is feasible to use the EM31-MK2 equipment to detect the hydrocarbon contamination zones in soil, subsoil and groundwater, while in the southern end of the site (GWT depth = 9.00 m), EMP is feasible to detect the contamination in soil and subsoil, but not in the groundwater. The EMP survey was carried out considering the electromagnetic interference of the buried elongated conductors. According to our work experience using EM31-MK2 in urban and industrial sites (IMP 2006; 2006a; 2008; 2013; Mendez-Velarde *et al.*, 2012), when the difference between conductivity values recorded to two orthogonal directions of the antennas is more than 10%, the EMP station is rejected and a new measuring point is selected, otherwise the average value can be used for the data reduction. In this way, we ensured that variations in the electromagnetic field are given only by variations in soil conductivity. After removing the measurement points affected by electromagnetic noise, 306 EMP data were recorded and an apparent resistivity map was made.

Results and discussion

The results of the application of ERT, EMP and VOC methods were processed using software SURFER 8 (Golden Software Inc., 2002) with minimum curvature algorithm. The minimum curvature gridding provides reasonable maps with satisfactory smoothing of the field lines (Briggs, 1974), widely used in the earth sciences (Ontario Geological Survey, 2003; Orfanos and Apostolopoulos, 2012), including geoelectric methods (Korhonen *et al.*, 2005; Siemon, 2009).

VOC data interpretation

There are no national or international normative values that include normal or natural conditions of VOC for hydrocarbon contaminated soils. However, it has been observed that an anomalous value (greater than background) is evidence of contamination phenomena (Arpel, 1992). Fischer *et al.* (1996) studied a gasoline-contaminated site and they considered that VOC = 21 ± 2 ppm correspond to low contamination levels. Based on our experience (Ochoa *et al.*, 2002; Delgado-Rodríguez *et al.*, 2006, Mendez-Velarde *et al.*, 2012), we had determined that in hydrocarbons contaminated sites VOC values greater than 20 ppm are associated with presence of hydrocarbons, either as free product, absorbed in the subsurface or dissolved in groundwater.

Fresh gasoline contamination presents high VOC (> 20 ppm) concentration. Low VOC (< 20 ppm) values could indicate the presence of clean soil or soil contaminated by mature hydrocarbons. Figure 2 shows some plumes with high VOC concentrations (dark zones, Figure 2), indicating the presence of fresh contaminants in the subsoil; one of them possibly related to the gas station.

In sites with an active contamination source it is possible to have both degraded contaminants (low VOC values) and fresh contaminants (high VOC values). In the spill point, such as in zone with clean soil, low VOC values are observed, indicating the possible existence of degraded hydrocarbon contaminants in the subsoil in zones with low values of VOC. Because of this, ERT and EMP methods are applied since they are effective for mapping mature contamination plumes.

Statistical analysis of ERT data

Figure 3 shows the statistical distribution (apparent resistivity vs. AB/2 distances) from 64 ERT measurements points. The legend represents the occurrence frequency values. In general, the apparent resistivity values are below of 20 Ohm.m, even in the vadose zone (minimal depth of GWT is 3.75 m), which means the clay content in soil is significant at different study depths. The mean curve (curve H, Figure 3) characterizes the subsurface up to 15 m depth by a three layer curve (type H) with low resistivity contrast. In most of the SEV, the resistivity decreases from 10 to 7.8 Ohm.m (first and second layer) which marks the transition from a semi-saturated to saturated clayey sediments, respectively, followed by a third layer (AB/2 > 30 m) with

Figure 2. VOC map. The dark zones indicate the presence of recent hydrocarbon contamination.

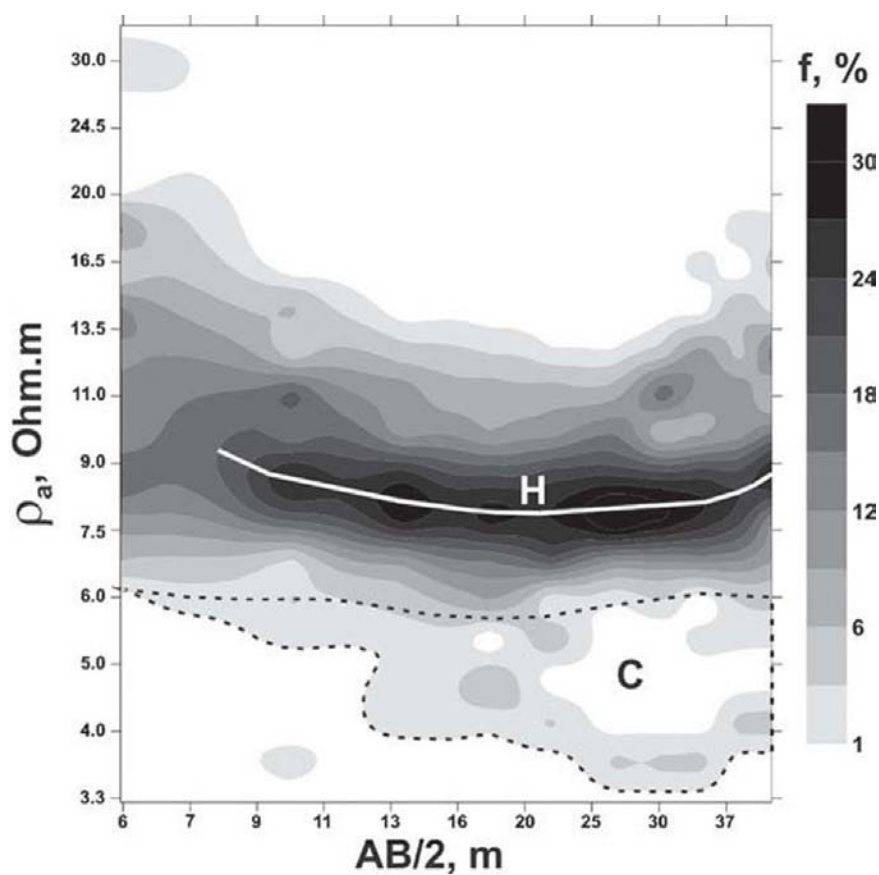
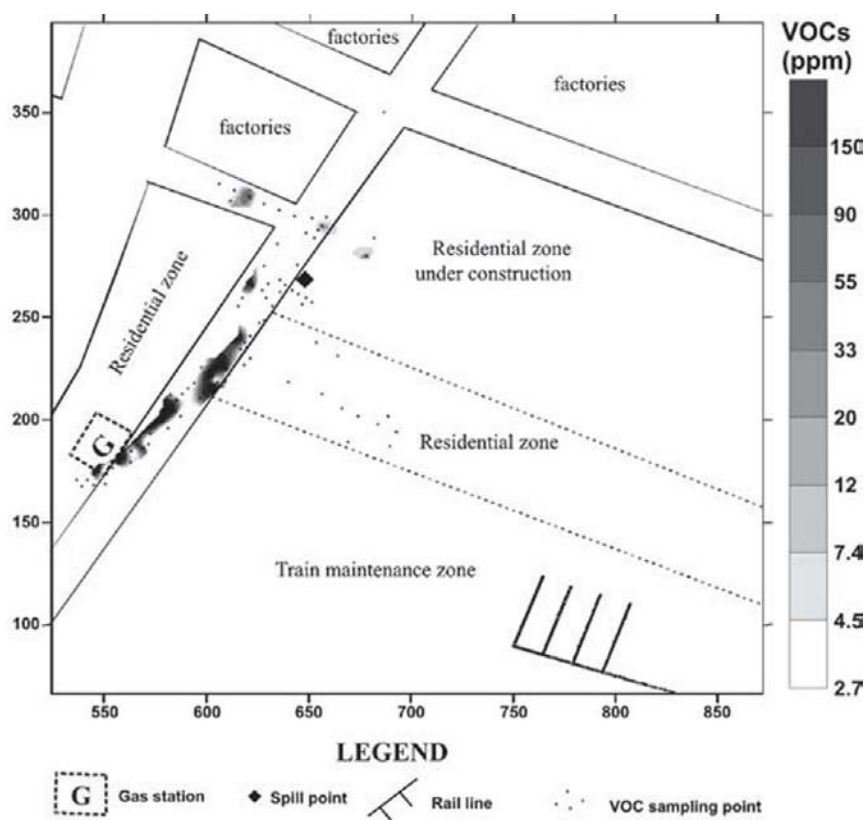


Figure 3. Statistical distribution of ERT data. (H) Mean resistivity curve for the study site. (C) Cloud of low apparent resistivity values separated from mean curve.

lower clay content ($\rho_a \sim 9 \text{ Ohm.m}$). Apparent resistivity values below 6.4 Ohm.m are outlined in a cloud of data (dashed line contour, zone C, Figure 3), indicating the presence of low resistivity anomalies (mature contamination) for some ERT points, mainly for $AB/2 > 10 \text{ m}$ or study depth $\geq 5 \text{ m}$ (second layer).

ERT data interpretation. Defining the geoelectric boundary between clean and contaminated soil

The RES2DInv software was used for the interpretation process and an interpreted geoelectrical section was obtained for each profile. The RES2DInv software uses the smoothness-constrained least-squares method inversion technique to produce a 2D model of the subsurface. Two different variations of the smoothness constrained least-squares method are provided; one optimized for areas where the subsurface resistivity varies in a smooth manner, and another optimized for areas with sharp boundaries (Loke and Barker, 1996). The obtained geoelectrical sections have the same number of layers with same thicknesses along each profile, giving great advantage to make interpreted resistivity maps for different study depths (e.g. groundwater table depth, contamination plume, etc).

Figure 4 shows the interpreted resistivity sections for ERT₁, ERT₂ and ERT₃ profiles with three main layers: a superficial resistive layer consisting of sandy-clayey deposits with resistivity range from 8 to 20 Ohm.m , a second layer where clay content increases with

resistivity ranging from 1.5 to 9 Ohm.m and a resistive third layer given by the decrease in clay content with resistivity ranging from 8 to 35 Ohm.m .

Taking into account the existence of high clay content in the subsoil and the characterization of mature hydrocarbon contamination as low resistivity anomaly, we need to define the geoelectric boundary between clean and contaminated soil. For this purpose, we used in the present work a conductivity model for unconsolidated formations and the "PetroWin" software for calculation of the soil resistivity developed by Ryjov and Shevnin (2002). This model considers the geometrical microstructure of the components as well as electrochemical processes occurring in the soil for a wide range of the pore-water salinity and clay content. Once groundwater (or salinity) and soil resistivity are known, clay content and porosity are estimated for clean soil, and the geoelectric boundary is defined. The characteristics of the conductivity model, the procedure to determine the groundwater (from in-field measurements) and soil (from lab measurements) resistivity, and the equations for calculate the soil petrophysical parameters (including clay content and porosity) are explained in detail in Shevnin *et al.* (2006; 2007) and Delgado-Rodríguez *et al.* (2012).

In order to define the geoelectric boundary, four wells located far enough from the spill point (Figure 7B) were drilled in the residential zone under construction using a Geoprobe System (Figure 5). Four soil samples (one per

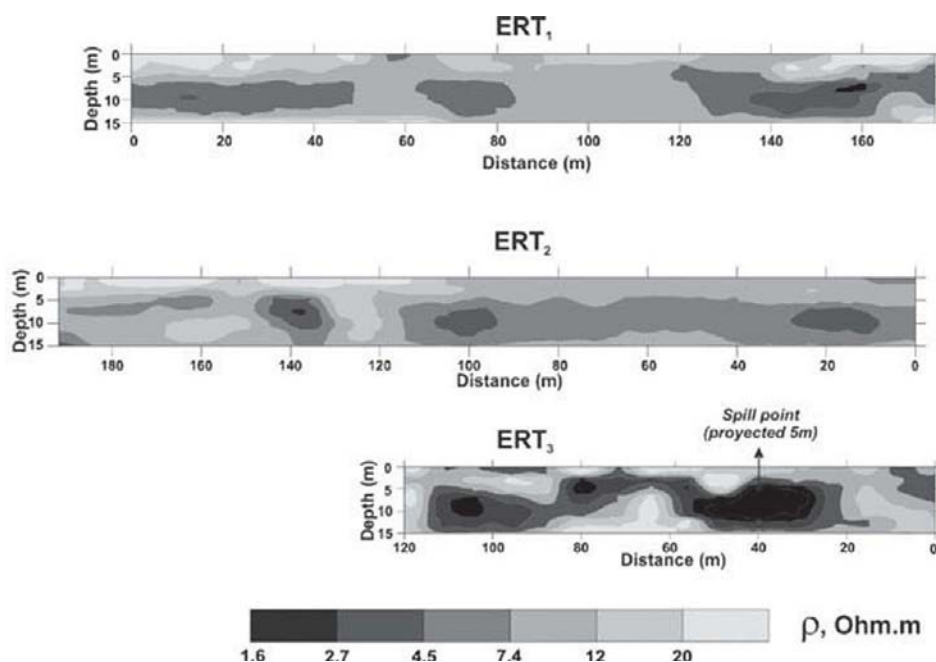


Figure 4. Interpreted resistivity section from ERT profiles with three layers. Low resistivity anomalies in the second layer indicate the presence of mature contamination.

Figure 5. Geoprobe System used to collect soil and ground-water samples



well) were collected from the layer noticeably more argillaceous, at depths of 6 to 7 m (second layer, Figure 4) and then analyzed in the laboratory, resulting in a clay content range between 37% and 50% (Table 1). Likewise, groundwater samples were collected from local aquifer, resulting in a mean resistivity values of 5.9 Ohm.m at 20 °C, which means a salinity of 1 g/l.

In Figure 6 the results of theoretical calculations with the "PetroWin" software are shown. Soil resistivity is considered as a function of water salinity (NaCl content at 20°C). Soil resistivity curves for different sand and clay proportions are displayed: curve for

sand (in the upper part of Figure 3A, 0% clay, and 25% porosity) and curve for pure clay (in the lower part of Figure 3A, 100% clay, and 55% porosity). Water curve (dashed curve) gives us the relation between water resistivity and water salinity; while the vertical dotted line represent the groundwater salinity mean value of 1 g/l for the study area. Two horizontal dotted lines show the resistivity range 4.5 Ohm.m to 6.1 Ohm.m for soils with clay content between 37% -50% and pore-water salinity 1 g/l, being 4.5 Ohm.m the geoelectric boundary between clean and contaminated soil. Resistivity values less than 4.5 Ohm.m correspond to mature oil contaminated soils; however, low levels of hydrocarbons contamination may be present

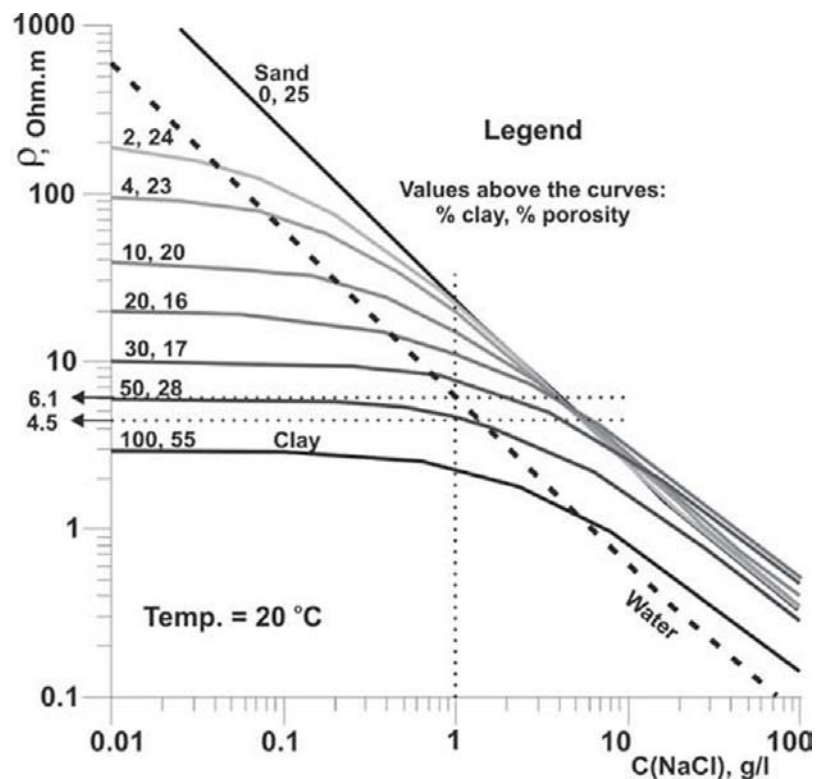


Figure 6. Experimental results and theoretical dependence of soil resistivity versus pore water salinity for different clay content in soils. Theoretical model: clay porosity = 55%, sand porosity = 25%.

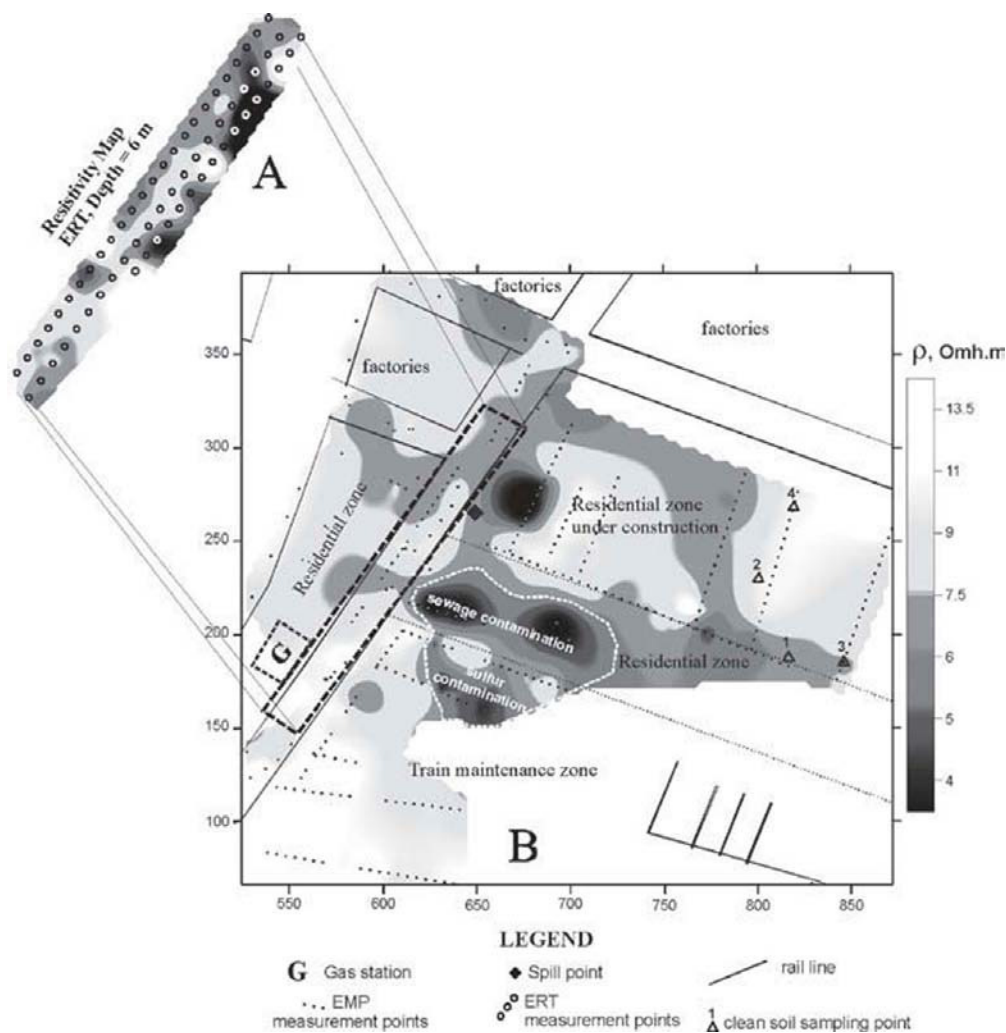
Table 1. Clay content and sampling depth values of the clean soil samples. Clay content values were used to define the geoelectric boundary between clean and contaminated soils.

Clean soil sample	Clay content (%)	Sampling depth (m)
1	49	6.6
2	38	6.3
3	50	6.0
4	37	7.0

in soils with resistivity values within the aforementioned resistivity interval. Resistivity values greater than 6.1 Ohm.m indicate that there is no mature contamination.

The second layer presents low resistivity zones associated with the presence of mature hydrocarbons contamination. Using

the interpreted information from Figure 4, the behavior of the resistivity on the second layer (local aquifer) can be mapped with high resolution. A map of interpreted resistivity for the second layer is shown in Figure 7A where the dark zones may indicate the presence of mature contamination.

**Figure 7.** Resistivity maps. Interpreted resistivity map from ERT for depth= 6m. (B) Apparent resistivity map from EMP.

EMP data interpretation

The maximum study depth with EM31-MK2 is 6 m. Considering the conductive sediments of the site, the maximum study depth corresponding, in Figure 3 to $AB/2 = 12$ to 13 m, and higher values of the occurrence frequency, the ρ range from 7.5 to 9.5 Ohm.m is defined as representative of the lithological variations in the study site for study depth equal to 6 m.

Figure 7B shows the apparent resistivity map given by the EMP method. Three main (southern, central, and northern) low resistivity anomalies (dark zones, Figure 7B) are observed. The southern anomalous zone includes the railroad maintenance area (Figure 7B) where sulfur powder can be seen dispersed on the ground surface. Due to biodegradation processes, sulfur can cause an acidic environment, which generates salts in the subsoil and the consequent low resistivity anomaly. Therefore, the existence of chemical contamination is possible due to the presence of sulfur, therefore railroad maintenance area will be considered as contaminated by sulfur. The central anomalous zone is located within a residential zone (Figure 7B), coinciding with the drainage system. Due to land subsidence in the Valley of Mexico, frequently the drainage system, consisting of concrete pipelines, is broken and sewage leakages occur. In this case, we observed part of the sewage emerging on the terrain surface, resulting in low resistivity anomaly. Furthermore, the VOC values in this zone are almost zero (Figure 2), ensuring the absence of recent hydrocarbon contamination. Therefore, we propose that sewage is causing this low resistivity anomalies inside residential zone (Figure 7B). These two areas contaminated (by sulfur and sewage) should not be considered in the setting of hydrocarbon contamination plumes (see zone framed with dashed white line in Figure 7B).

The northern anomaly zone is located in the area where a new residential zone is being built, including the spill point (black diamond, Figure 7B). The cause of this anomaly zone is the presence of degraded hydrocarbons (mature contamination).

Zones with high apparent resistivity values indicate the absence of degraded hydrocarbon contaminants in the subsurface and the possible presence of recent hydrocarbons contamination. However, these high values are influenced by the superficial layer of subsoil. The superficial soil resistivity is determined not only by the clay content but also by its

moisture, depending on the topographical elevations changes, masking the recent contaminants effect. This is why EMP method, as well as ERT, has low resolution in detecting fresh hydrocarbons contamination plumes.

In general, there is a good correspondence between ERT and EMP resistivity maps (Figure 7), showing possible migration routes of the contaminants in the subsurface.

Integrated data map from EMP, ERT, and VOC results.

High VOC values (high level of volatiles) indicate the presence fresh contamination in the subsurface. In contaminated zones (e.g. around of the spill point), where low VOC values ($VOC \leq 1.2$ ppm) such as clean soil are observed, low resistivity anomalies ($\rho \leq 4.5$ Ohm.m) confirm the existence degraded contamination. Due to this, it is necessary to integrate the geoelectric (ERT and EMP) and VOC methods results in order to define and to map all contamination plumes at the site and to focus the drilling and soil/free-product sampling.

To make the integral map, a grid of 5×5 m for the study site was created, and values (rather the logarithm of the values) obtained by each method were interpolated. The grid size is equal to the study area, with an approximate value of 5.3 ha. At each grid point, the applied methods receive a weight according to the interval wherein their values are (Table 2).

The parameters or variables that integrate the map are: gas concentration (VOC) in ppm, true resistivity (ERT) in Ohm.m and apparent resistivity (EMP) in Ohm.m. Each variable, depending on the values range, generates a weight (or degree of reliability, X_{ij}) of the anomalous zone. The obtained values of the indirect methods (ERT and EMP) receive weights between 0 and 5, while VOC, considered as semi-indirect method, their values receive a weight range between 0 and 7 (Table 2). Based on the petrophysical modeling performed in clean soil samples (Table 1, Figure 6), the ERT interval $6.1 \text{ Ohm.m} \leq \rho < 14 \text{ Ohm.m}$ gets weight 0 since it is not related to the presence of neither fresh or mature contaminant but rather is the sediments resistivity range of the site, while the other weights values are distributed as follows: 3 to 5 and 1 to 2, for low (high resolution) and high (lower resolution) resistivity anomalies, respectively. In a similar manner, based on the correspondence between apparent resistivity

Table 2. Weight assigned to each value range obtained from application of the EMP, ERT and VOC methods.

EMP		ERT		VOC	
ρ interval (Ohm.m)	Weight (X_{ERT})	ρ interval (Ohm.m)	Weight (X_{EMP})	VOC interval (ppm)	Weight (X_{VOC})
$\rho_a < 4.3$	5	$\rho < 3.2$	5	$VOC < 20$	0
$4.3 \leq \rho_a < 5.9$	4	$3.2 \leq \rho < 4.5$	4	$20 \leq VOC < 28$	1
$5.9 \leq \rho_a < 7.5$	3	$4.5 \leq \rho < 6.1$	3	$28 \leq VOC < 37$	2
$7.5 \leq \rho_a < 9.5$	0	$6.1 \leq \rho < 14.0$	0	$37 \leq VOC < 49$	3
$9.5 \leq \rho_a < 13.0$	1	$14.0 \leq \rho < 19.0$	1	$49 \leq VOC < 67$	4
$\rho_a \geq 13.0$	2	$\rho \geq 19.0$	2	$67 \leq VOC < 90$	5
				$90 \leq VOC < 120$	6
				$VOC \geq 120$	7

and interpreted resistivity maps (Figure 7), EMP (apparent resistivity) values receive weights 1 and 2 to high resistivity anomalies and 3 to 5 to low resistivity anomalies. Taking into account the statistical distribution of the apparent resistivity values of the Figure 3, the interval $7.5 \text{ Ohm.m} \leq \rho_a < 9.5 \text{ Ohm.m}$ receives weight 0. The index for VOC varies between 1 and 7 depending on the increase of VOC value from 20 to 179 ppm. VOC values less than 20 ppm will have weight 0 (Table 2).

The X_{ij} calculated for each method i , in each grid point j is multiplied by a coefficient MC_i ($MC_{VOC} = 5$ for VOC, $MC_{ERT} = 4$ for ERT and $MC_{EMP} = 3$ for EMP). Finally, the average of all the values resulting from the multiplication (integral parameter, IP) is calculated by the expression:

$$IP_j = \frac{\sum_{i=1}^{N_j} (X_{ij} * MC_i)}{N_j} \quad (1)$$

Where: IP_j -integral parameter value of the grid point j .

X_{ij} -weight value calculated from field value of the method i in grid point j .

MC_i -multiplication coefficient for method i .

N_j -Total number of methods applied in grid point j ($N_j = 1, 2$ or 3).

It should be noted that the ranges and weights in Table (2) are valid for the site studied in the present study. New sites require a particular analysis of the obtained data, defining new ranges and assigned weights.

Tables 3 and 4 show the calculation procedure using equation (1) in grid portions corresponding to two small zones predominantly contaminated with fresh and mature hydrocarbons, respectively. Near to well S_1 , the zone with fresh contaminants shows high VOC values (Table 3), while low resistivity and VOC values highlight in the zone with degraded contaminants located close to the spill point (Table 4).

The IP_j values are mapped and shown in Figure 8. Three contamination plumes are observed in the integrated map.

The first plume starts at the southwestern corner of the study area and extends down Main Street to the center of the site. Taking into account its connection with gas station and the high values of VOC in this plume (presence of fresh hydrocarbons), we can affirm that the gas station is an active contamination source. Four months after the completion of this work, as a result of an integrity testing of the underground storage tank, a gasoline leaking point was found and repaired in the gas station. The second plume, located in the residential zone under construction, is related with spill point, where medium and low values of VOC and low resistivity anomalies indicate the existence de mature hydrocarbon contamination. A third contaminated zone located in the central avenue is characterized by medium values of VOC and high resistivity values. This zone was related to the basement of a furniture factory, which uses solvents and white gas for painting and cleaning activities. The factory owner recognized that oil-based paints and solvents are poured directly on the soil (personal communication).

Table 3. Calculation of IP in a portion of the grid around the well S1, where the recent contamination is mainly characterized by high VOC values.

X	Y	EMP data	ERT data	VOC data	$X_{MC_{EMP}}^{*}$	$X_{MC_{ERT}}^{*}$	$X_{MC_{VOC}}^{*}$	N	IP
580	190	12.0	7.1	---	3	0	0	2	1.5
580	195	10.2	7.2	1.8	3	0	0	3	1.0
580	200	8.6	7.1	98.9	0	0	30	3	10.0
580	205	7.6	4.4	170.0	0	8	35	3	14.3
580	210	7.6	2.8	26.8	0	16	5	3	7.0
580	215	7.5	4.5	---	9	8	0	2	4.0

Table 4. Calculation of IP in a portion of the grid around the spill point, where mature contamination is characterized by low resistivity and VOC values.

X	Y	EMP data	ERT data	VOC data	$X_{MC_{EMP}}^{*}$	$X_{MC_{ERT}}^{*}$	$X_{MC_{VOC}}^{*}$	N	IP
640	250	8.1	---	0.5	0	0	0	2	0.0
640	255	8.1	6.1	0.7	0	12	0	3	4.0
640	260	8.1	4.8	0.9	0	16	0	3	5.3
640	265	8.1	3.2	1.0	0	20	0	3	6.7
640	270	8.2	3.3	1.2	0	20	0	3	6.7
640	275	8.2	4.0	1.1	0	16	0	3	5.3

Verifying indirect results

Since benzene, toluene, ethylbenzene, and xylenes (BTEX) are some of the main VOC found in petroleum derivatives such as gasoline; we performed a measurement of the concentrations of each of their constituents in order to verify the anomalies. BTEX compounds are notorious due to the contamination of soil and groundwater by gasoline (EEA, 2010). Contamination typically occurs near petroleum and natural gas production sites, petrol stations, and other areas with underground or above-ground storage tanks, containing gasoline (EEA, 2010). Therefore, these compounds might be good indicator of recent contamination by gasoline. Although BTEX ratio were obtained to this purpose, it is acknowledge that inferring the age of a release based on BTEX ratios alone could be a valid approach only in well constrained situations, due to the rate of change of the gasoline BTEX ratio is affected by many site-specific variables. Another reason to measure BTEX in a gasoline contamination event was to comply with the current Mexican regulation (SEMARNAT, 2005).

In addition to BTEX, light oil fraction (LOF) was measured. LOF term refers to all volatile

compounds which cover the range of carbon atoms from C_5 to C_{10} . The measurement of this fraction was performed to complement the measurement of all volatile compounds that may be present on the site, complying with current Mexican regulation on soil contamination.

Soil LOF Analysis

Using the integrated map (Figure 8), the drilling activities were conducted to the specific contaminated areas. Using a Geoprobe System (Figure 5), six monitoring wells were drilled up to 10 m of depth in strategic and topographic relevant points, taking into account the urban infrastructure and the access level to each point. Twenty two soil samples (Table 5) were collected in monitoring wells S_1 - S_5 and S_x , (Figure 8). The analytical results revealed an irregular distribution of LOF depending on the depth ranges from bellow the detection limit to 11312 mg/kg. The maximal concentration (11312 mg/kg) of the site was detected in S_4 in the interval of depth 3 to 4 m. In well S_1 , a concentration value of 1338 mg/kg was determinate for interval of depth 9.5 to 10 m, corresponding to the GWT depth in the southern end of the site. Other noticeable concentration

Table 5. Soil LOF concentration and sampling depth values. Grey rows show the maximal LOF concentrations for each well.

Well	X	Y	LOF (ppm)	Sampling Depth
S ₁	589	208	678	5.50 - 6.00 m
			1338	9.50 - 10.00 m
			50	0.0 - 2.00 m
			834	2.00 - 3.00 m
S ₂	620	267	306	3.00 - 4.00 m
			141	4.00 - 5.00 m
			62	5.20 - 5.80 m
			65	6.00 - 6.30 m
S ₃	654	281	BDL	6.80 - 7.00 m
			50	0.0 - 3.80 m
			51	6.00 - 7.00 m
			38	1.50 a 1.90 m
S ₄	621	245	BDL	2.00 - 3.00 m
			11312	3.00 - 4.00 m
			330	4.00 - 5.00 m
			86	5.00 - 6.00 m
S ₅	630.9	253.8	44	3.00 - 4.00 m
			55	4.00 - 5.00 m
			33	5.00 - 6.80 m
			2071	3.15 - 4.00 m
S _x	616	294	301	4.00 - 4.40 m
			279	4.40 - 5.00 m

value (834 mg/kg) was determinate in well S₂ (Table 5). On the other hand, the well S_x shows significant value (2071 mg/kg) of LOF in sample of soil collected near to ground surface (depth ~1.2 m), as evidence of contamination by hydrocarbons poured on the terrain. LOF was very low in wells S₃ and S₅ (Table 5).

BTEX analysis in FP samples

One of the age-dating methods uses benzene plus toluene to ethylbenzene plus xylenes ratios (B+T/E+X). Use of this ratio minimizes uncertainties related to historical variations in BTEX composition of manufactured gasoline and provides a valuable tool for monitoring environmental changes in a dissolved gasoline plume with time (Stout *et al.*, 2002). Although the rate of change of the gasoline BTEX ratio is affected by many site-specific variables, inferring the age of a release based on BTEX ratios alone could be a valid approach only in well constrained situations.

The samples of free product FP₁ and FP₂ collected in well S₁ and recollection trench, respectively (Figure 8), did not present significant changes in the B+T/E+X ratio (Figure 9). Observations revealed that fuels collected in monitoring S₁ were freshly released products by continuous leaking, as noted above. This could confirm that the free product fluid rapidly migrated to the GWT. Further work is needed to analyse if chemical substantial alteration occurred during its vertical migration into the soil or it may have remained in a relatively unaltered state.

BTEX ratio of free-phase gasoline sample FP₃, collected in the spill point (Figure 8) reached a value of 0.32, as shown in Figure 9. The significant decrease of BTEX ratio on free-phase in sample FP₃ implies a weathering by solubilisation, water washing or biodegradation process. Weathering and BTEX ratios imply that gasoline was transported to the water table and did not undergo substantial alteration during its vertical migration in the soil. Hence, a thin layer of free product was carried through sand lenses to the impermeable clay stratum. Therefore, when advanced alteration of the pattern has occurred due to environmental exposure, it is difficult to estimate, by composition of the free-phase, when the fuel was released. Lead and lead alkyls were absent in the free-phase sample, and is worth noting that regular unleaded gasoline was introduced in 1992.

Based on the results obtained from integral map (Figure 8) and BTEX analysis of FP samples (Figure 9), three contaminated plumes are characterized and showed in Figure 10.

Plume I. "Recent Infiltration Zone", corresponds to the most recent leakage of regular unleaded gasoline. The characteristics of the weathering processes (evaporation and solubilization) are not significant in the soil and FP samples. The contaminated plume I area is 1280 m², with a thickness according on sand layer thickness.

Plume II. Defined as "soil confined gasoline zone". It was contaminated by regular unleaded gasoline released within the last one to five years, based on the BTEX ratio analysis in FP samples. It showed a weathering process including evaporation, solubilisation, and biodegradation for a long time in a low permeability soil layer. Hydrogeology field analysis identified sand lenses confined in low permeability soil layers, the released gasoline could be trapped in a confined sand lens for years. However, site assessment work did not provide hydrogeochemical information from which reliable estimations about spill age could

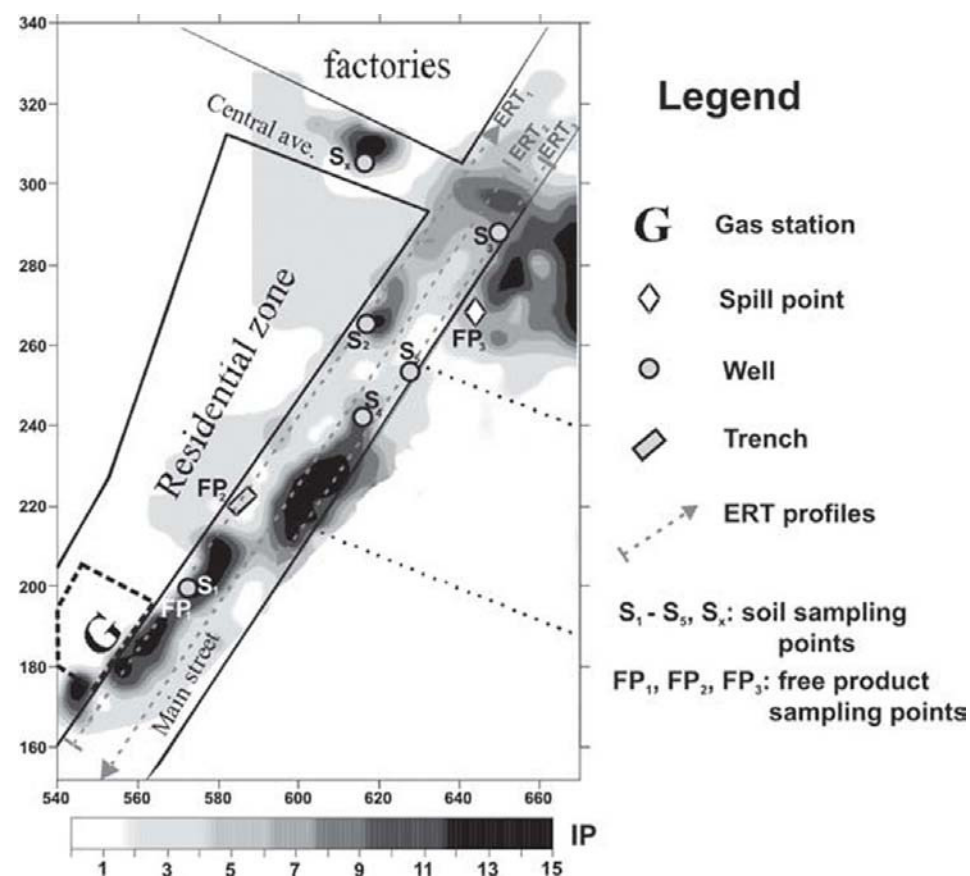


Figure 8. Integrated data map from indirect methods.

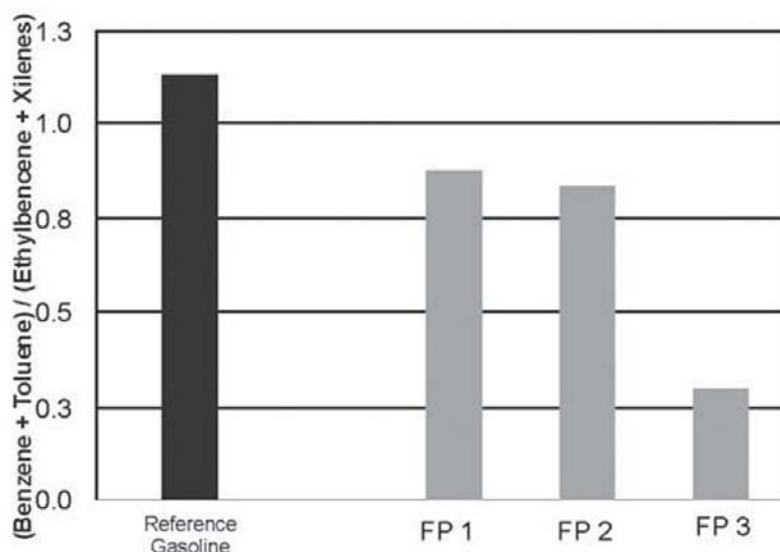


Figure 9. BTEX ratio of free-phase gasoline samples.

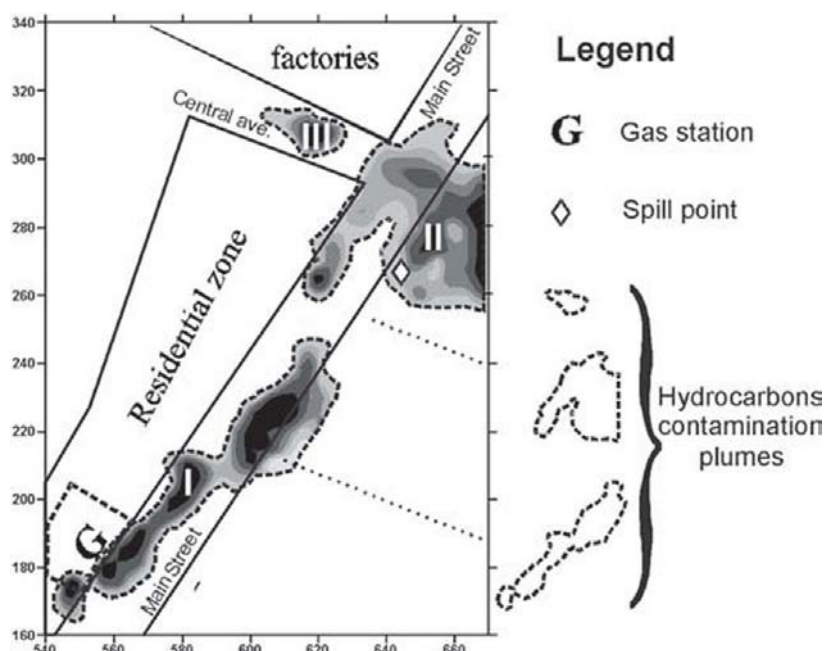


Figure 10. Map of hydrocarbons contamination plumes.

be drawn based on the BTEX ratios. The plume II area is 1152 m², with a volume according to sand lens thickness (~ 0.5 m).

Plume III. Zone characterized by a type of hydrocarbon different to the regular gasoline founded in plumes I and II. The composition of gasoline found in the shallower part of the subsurface (depth ~ 1.2 m) was similar to "white gas". Because of the chemical composition, weathering characteristics, contaminant transport, and hydrocarbons concentration in soils along the monitoring well S_x, plume III was considered an isolated event, not related with the other two plumes, covering a 160 m² area.

The sum of the areas of each contamination plumes is 2592 m², which almost represent 5% of the study area (5.3 ha), demonstrating the benefit of using indirect methods for the optimized selection of drilling points and soil sampling depths.

Conclusions

The indirect (ERT, EMP and VOC) methods are efficient tools for studying the hydrocarbons contaminated sites, reducing the number of drilling and soil samples. The high values of VOC mapped the presence of fresh gasoline in the subsoil and suggested that the gas station located at the study site is an active contamination source. Later, from an integrity testing, a gasoline leaking point was found in the underground storage tank of the gas station. However, the considerable degradation of the

regular gasoline founded in the surrounding construction area indicates, at least, the existence of a previous contamination event.

The gas station is topographically located at an up gradient from the spill present in the nearby apartment construction. Therefore, gasoline released from buried pipeline would migrate toward the apartment construction area. Mature contaminated zones were defined by ERT and EMP methods as low resistivity anomalies. The ERT, EMP and VOC results were integrated on a map, allowing the final configuration of contamination plumes and the optimization of drilling and soil/free-product sampling.

The affected area by hydrocarbons can be separated in three plumes with different type of contaminants: Plume I, with recent release of regular gasoline, which is connected with the gas station as active contamination source; Plume II corresponds, according to geoelectrical and BTEX analysis results, to mature (weathering and biodegradation) hydrocarbons contamination due to regular unleaded gasoline released within the last one to five years; and a small Plume III, not related with the other two plumes mentioned above, caused by pouring of solvents and white gas on soil.

This study shows the advantages of joint application of ERT, EMP and VOC methods in sites with an active contamination source, where the existence of recent and mature contaminants in subsoil is suspected.

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