Eurasian Journal of Soil Science

Journal homepage : http://fesss.org/eurasian_journal_of_soil_science.asp

Methodology for the detection of contamination by hydrocarbons and further soil sampling for volatile and semi-volatile organic enrichment in former petrol stations, SE Spain

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Article Info

Received : 01.12.2011
Accepted : 07.05.2012

Abstract

The optimal detection and quantification of contamination plumes in soil and groundwater by petroleum organic compounds, gasoline and diesel, is critical for the reclamation of hydrocarbons contaminated soil at petrol stations. Through this study it has been achieved a sampling stage optimization in these scenarios by means of the location of potential contamination areas before sampling with the application of the 2D electrical resistivity tomography method, a geophysical non destructive technique based on resistivity measurements in soils. After the detection of hydrocarbons contaminated areas, boreholes with continuous coring were performed in a petrol station located in Murcia Region (Spain). The drillholes reached depths down to 10 m and soil samples were taken from each meter of the drilling. The optimization in the soil samples handling and storage, for both volatile and semi-volatile organic compounds determinations, was achieved by designing a soil sampler to minimize volatilization losses and in order to avoid the manual contact with the environmental samples during the sampling. The preservation of soil samples was performed according to Europe regulations and US Environmental Protection Agency recommendations into two kinds of glass vials. Moreover, it has been taken into account the determination techniques to quantify the hydrocarbon pollution based on Gas Chromatography with different detectors and headspace technique to reach a liquid-gas equilibrium for volatile analyses.

Keywords: petroleum contaminated soils, petrol stations, soil sampling, electrical resistivity tomography method.

Introduction

Soil pollution due to petroleum products: gasoline, diesel and heavy oils as well as the possible scope of the groundwater bodies is one of the major currently environmental issues for great concern due to the toxicity of some volatile organic compounds (VOCs) and semi-volatile organic compounds present in these fuels. A soil contamination could be produced by petroleum products spill and leaks related to activities of refinement and fuel dispensing at petrol stations. Although pipelines and tanks are designed to avoid this kind of accidents, the large amount of fuel dispensed at petrol stations during the years which are operating

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ISSN: 2147-4249

may cause a very important damage in the surrounding area.

Electrical resistivity tomography is increasingly being used at sites contaminated by petroleum organic compounds, as an aid in the characterization and monitoring of these sites (Atekwana et al., 2000). Hydrocarbons are excellent insulators and exhibit very high values of electrical resistivity (Delaney et al., 2001). Geophysical techniques can be also used to monitor remedial actions conducted on the environmental sites (Park, 2001).

Some authors have studied different electric responses in the subsurface for the presence of organic substances and they have been proposed several models to interpret the tomographic profiles: an insulating layer model that assumes that the presence of hydrocarbons, usually with a hydrophobic character, in the subsurface can be inferred because of a lower electrical conductivity than the surrounding zone (King and Olhoeft, 1989; Daniels et al., 1992; Endres y Greenhouse, 1996; Campbell et al., 1996). This model attributes a low resistivity to mineral weathering resulting from microbial redox processes in the subsoil. A newly proposed geoelectrical model for hydrocarbon contaminated sites predicts high conductivities coincident with the contaminated zone as opposed to the traditionally accepted low conductivity (Werkema et al., 2003).

Environmental contamination by diesel and gasoline can be quantified by DROs (Diesel Range Organics) and GROs (Gasoline Range Organics) analysis. The main problem to determine volatile and semivolatile organic compounds in the environmental soil samples is the losses by volatilization of target analytes during the sampling stage and storage. Most determination methods are designed with dry soil samples previously.

In order to minimize losses of analytes and optimize the sampling design, a combined geophysical and geochemical methodology has been designed in this study for former petrol stations.

Materials and Method

ERT 2D at petrol stations

An environmental monitoring was carried out by applying the non destructive geophysical technique: Electrical Resistivity Tomography 2D (ERT) in a petrol station located in the semiarid Murcia Region (SE Spain) (Fig. 1.). The application of electrical tomography technique involves performing variable-length profiles as a function of electrode gap (Bernard, 2003, Martínez-Pagán, 2006). Thus, the survey design requires covering the zone where fuel storage tanks are and optimizing the resolution of the shallow layers by the application of different measurement configurations. In order to minimize the error and to obtain good results, the dipole-dipole and Wenner-Schulmberger configurations were tested in the study areas. After tuning, it was performed a dipole-dipole configuration for measurements due to good results in all petrol stations with a electrode gap of 2 meters, getting a depth of investigation of 12 meters. Dipole-Dipole device is very sensitive to horizontal resistivity changes, but relatively insensitive to vertical changes, so it is useful in vertical structures such as buried walls, pits, and contaminant plumes, but relatively poor in horizontal structures such as sedimentary layers (Lopez et al. 2009).

Figure 1. "Petronor" Petrol Station location

Placement of three tomography profiles at petrol station was performed according to the location of the filling mouths in the underground storage tanks (USTs) and to cover the largest possible area (Fig.2). A

SYSCAL R1 geophysical resistivimeter by IRIS Instruments (France) has been used at petrol station. After performing field tomographic profiles we proceeded to download the experimental data on a laptop through the PC connection with ProSYS II software. It was made a filtered process and elimination of outliers to obtain a lower error than the permissible for obtaining the best quality results.

Similarly, we proceeded to perform the topographic corrections in those profiles where it was necessary. For the correct interpretation of the results, it was performed a investment process with RES2DINV software, a process based on several iterations comparing the measured results with those calculated by the software configurations taking into account the device used: dipole-dipole. A new implementation of the least squares technique based on quasi-Newton optimization (Loke and Barker 1996) is used for the inversion process in RES2DINV software. As a result of the geoelectric data treatment process, it is obtained a pseudosection representing soil resistivity contours as a function of the depth and length of the profile drawn. The isovalue outlines are defined by a colour scale.

The main purpose of the ERT surveys is a design optimization of the soil sampling at different depths for the physico-chemical characterization and the identification of organic pollutants due to the anthropogenic activity in located areas. The sampling was carried out by mechanical drillings.

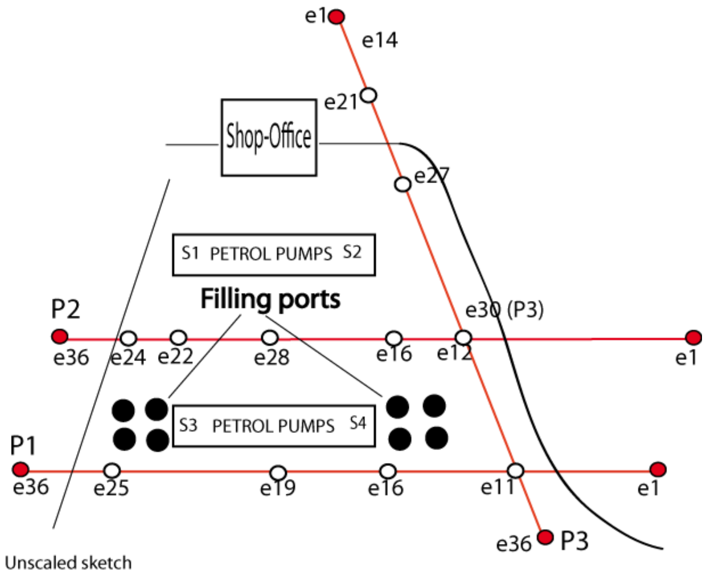

Figure 2. Layout of ERT profiles in the selected petrol station for electrical measurements

Handling and Storage: soil samples for VOCs and semi-volatile determinations

In this paper, it's proposed a general method for the sampling and preparation of VOCs and semi-volatile in soil and sediment for further determinations by gas chromatography (GC). Soil samples were taken each meter by mechanical drillings in the selected zones by ERT results and stored into two kind of glass vials at the same time of sampling. For VOCs analysis (GROs), a soil sampler has been designed for this purpose in order not to handling the contaminated soil (Fig. 3).

Figure 3. Soil sampler designed for collection of environmental samples without handling

This soil sampler provides different quantities of soil to put in a headspace glass vial containing 10 mL of modified matrix solution (MMS) (Fig. 4.) in order to minimize volatilization losses, until the introduction in a Headspace device previous GC/MS determination (HS-GC/MS) for VOCs. Three samples into headspace vials have been taken from each meter depth. The MMS for soil samples was KCl 250 g/L (Serrano and Gallego, 2006). Headspace vials containing soil samples must be stored at 4ºC in the field. This methodology is applicable to a wide range of organic compounds which have a high volatility sufficiently to be effectively removed from soil samples using an equilibrium headspace procedure.

For semi-volatile analysis (DROs), a composed soil sample from each meter is stored into a 40 mL amber glass vial without headspace, keeping the vial completely full (Fig. 4.). Amber vials containing soil samples must be stored at 4ºC in the field for analytes determination by gas chromatography-flame ionization detector (GC/FID) without previous drying samples.

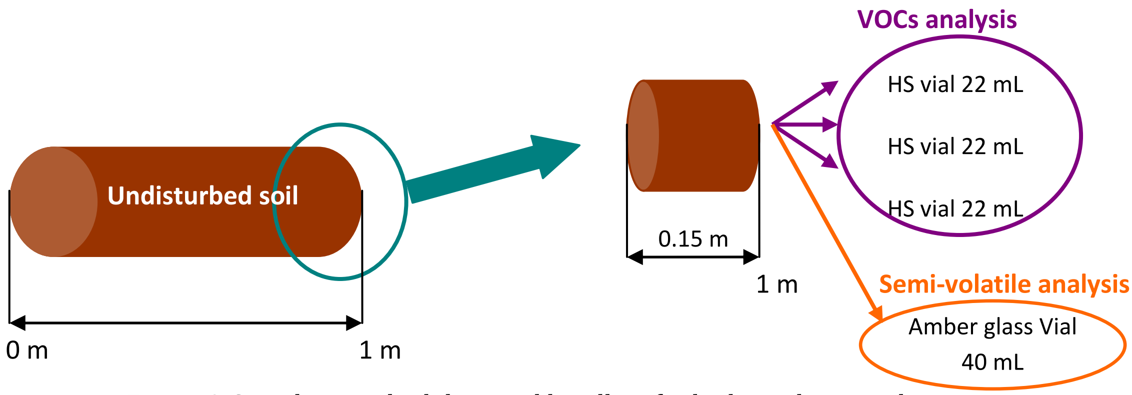

Figure 4. Sampling methodology and handling for hydrocarbons analysis

We have followed the US Environmental Protection Agency recommendations (US EPA 5000) for the cleaning of sampling glass containers and glass material. For semi-volatile analysis, the glass material is rinsed with distilled water-MilliQ} water-acetone twice while for VOCs it is rinsed with distilled water-MilliQ} water-dichloromethane before using them to store samples.

Results and Discussion

Results from the ERT 2D application at the petrol station are shown in Fig. 5. The geoelectrical pseudosection for ERT profile 1 in wet season shows several resistive regions called A, B, C, D, E and F. The A and C regions have moderate electrical resistivity values between 80 Ω·m to 600 Ω·m due to the compressed natural soil influence out of the asphalted zone. On the other hand, D and E regions show resistivity values above 500 Ω·m, getting even 2000 Ω·m. These regions are located between 4 to 5 m depth matching up with the UST filling mouths positions in the surface. These resistivity anomalies could be caused by the UST positions. The F region is a non natural anomaly produced during the data processing step and it can't be related to the presence of any hydrocarbons leak in the subsoil.

In the electrical pseudosection from ERT profile number 2, it must be highlighted the F anomaly with values above 2000 Ω·m because of its size and large expanse. This anomaly is situated between electrodes 14 to 24 where filling mouths and auxiliary services, like piping, are located. A moderate resistivity layer (H) with values between 10 Ω·m to 80 Ω·m is located above F anomaly. The insulating layer model (Sauck, 1998; Atekwana, 2000) assumes that the presence of hydrocarbons, usually hydrophobic, in the subsoil can be inferred due to contaminated groundwater and lower electric permittivity than its surroundings, so, F region could be related to the presence of petroleum organic pollutants in the subsoil.

WET SEASON **DRY SEASON**

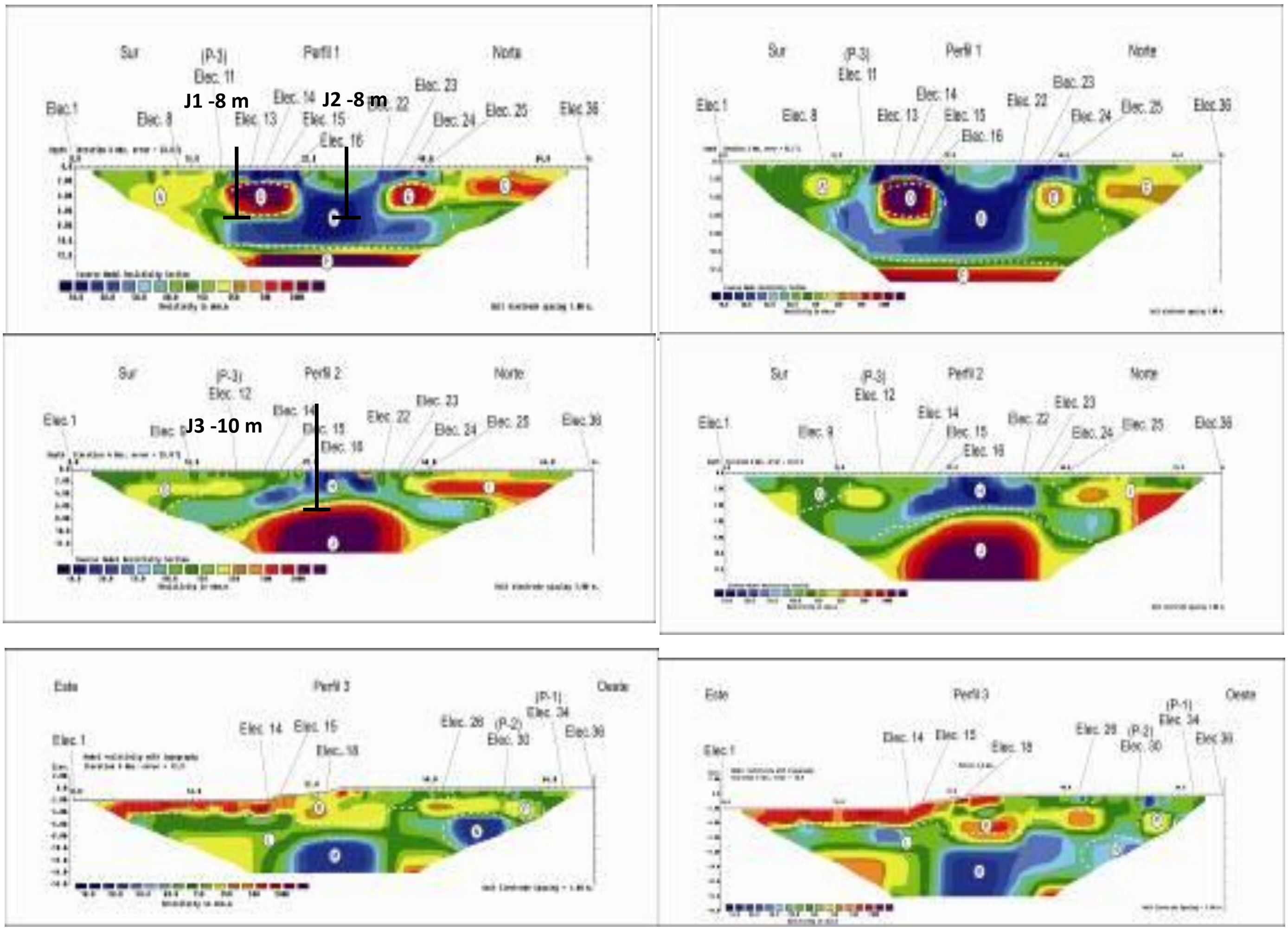

Figure 5. ERT processed pseudosections from "Petronor" petrol station in wet and dry seasons and selected areas for sampling.

Data measurements from ERT profile number 3 have given a pseudosection with two main moderately resistivity anomalies, M and N whose resistivity values are below 50 Ω·m that could be related to old fuel spills. K and L layers, with values between 80 Ω·m and 500 Ω·m, could be produced by different geologic materials and slightly porous but not by the presence of hydrocarbons in this zone.

Following the geophysical interpretation, the sampling design stage should be consistent with these results. Thus, the anomalies B, H and J from ERT profiles 1 and 2 were selected as potential hydrocarbons contaminated areas for sampling, reaching 8 m depth. In this way, if the results of hydrocarbons determinations are negative in the selected soil samples for both drillings, it could rule out the existence of important fuel contamination plumes in the subsoil of the petrol station.

For each mechanical drillhole (J1, J2 and J3), soil samples were taken as it is defined in Fig. 6, using the appropriate containers and the soil sampler designed for that purpose. Subsequently, the GROs and DROs analysis in the environmental samples were carried out by HS-GC/MS and GC / FID analytical techniques, respectively, confirming the existence of some petroleum hydrocarbons in the subsoil below 50 mg/kg.

In short, combining the geophysical technique Electrical Resistivity Tomography with a specific sampling design methodology is presented as an useful tool for the location of USTs and the detection of areas with anomalous values which could indicate the existence of hydrocarbons in the subsoil due to leakage at petrol stations.

Acknowledgment

First author thanks Seneca Foundation: Agency of Science and Technology in the Murcia Region (Spain) for the Research Grant to carry out this study.

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