



Characterization of a suspected hydrocarbon contaminated site near Mamanguape (Paraíba, Brazil) using integrated geophysical and geochemical methods

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Abstract

A dark stain was detected by chance on a bank of the B-101 highway from Natal to João de Pessoa near Mamanguape (Paraíba State, Brazil). A detailed visual examination suggested that the stain might be a hydrocarbon pollution plume resulting from an unintentional or furtive spill (Fig. 1).

Some organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) are considered carcinogenic (Warshawsky, 1999) and therefore their occurrence on the soil surface and their migration to underlying aquifers constitutes a serious environmental concern and a risk to public health. Because of the gravity of this environmental problem it is crucial to identify the approximate boundaries of a contaminant plume, examine its constituents, identify its origin and evaluate the environmental hazard it represents in order to plan remedial actions (Menzie et al, 1992).

The goal of this study was to assess the geometry and extension of the contaminated zone, as well as to characterize the composition and concentration levels of the pollutants. To this end, an integrated geophysical and geochemical study was conducted of the site. The toxicity, extension and characteristics of the pollutant must be considered when planning the most suitable remedial action, which may involve excavation and safe disposal in a specific landfill, "in situ" treatments using microbial or electrochemical degradation, or any other specific clean-up program.

Geological setting

The geology of the study area consists of two main lithostratigraphic units: a) the basement rocks, and b) the sedimentary cover. The basement rocks include granites, migmatites, gneisses and biotite schists of the São Caetano Complex cut by thin, intrusive pegmatite dikes, whereas the sedimentary cover includes Tertiary sediments of the Barreiras Formation and Quaternary deposits.

The bank where the dark stain was located presents a cross-section of the Quaternary sediments lying directly over basement. The outcrop has been described following the criteria formulated by Miall (1978). Four individual facies can be recognized: matrix supported gravels (Gm and Gmg) and compacted sands (Sm and Sg).

The Gm facies appears in the upper segment of the outcrop as a poorly stratified conglomerate, with few overlapping pebbles. This body has well defined channel geometry, approximately 13m wide and more than 2m thick, interpreted as longitudinal bars of a braided fluvial channel. The grains are constituted by basement rocks (gneiss, granites, pegmatites) with different degrees of roundness, varying from very round to angular, where diameter of the larger axis varies from 2 to 23 cm. The matrix is built by coarse to intermediate quartz grains.

The Gmg facies is distributed along the outcrop in the form of prolonged, partially eroded conglomerates, with channel geometry from 7.5 to 10m wide and thickness lower than 50 cm. These bodies appear to have their origin in the lateral migration of interlaced fluvial channels. The grains are mainly fragments of gneiss, granites and quartz pebbles. The matrix is sandy, constituted essentially by coarse quartz grains. Imbrications are usually absent; however, tabular pebbles adopt a horizontal orientation.

The Sg facies is composed of sands of grain sizes ranging from thick to very thick with dispersed pebbles, and presents either slight bedding or total absence of sedimentary structures. The matrix is essentially built by the diagenetic alteration resulting from the instability of some minerals, such as feldspars which have been transformed into kaolin. These sands are interpreted as deposits placed in the marginal portion of the fluvial channels.

Finally, the Sm facies occurs in lateral and/or vertical contact with all the other conglomeratic facies, showing coarse to intermediate texture, with total absence of primary sedimentary structures and a thinning upwards trend. Its matrix is also a diagenetic alteration resulting from the conversion of feldspars to kaolin.

Geophysical methods

Two geophysical methods were used, ground probing radar (GPR) and electrical resistivity tomography (ERT), both of which have demonstrated their suitability in shallow environmental subsurface investigations (Mazac et al, 1990; Castro and Branco, 2003). The geophysical dataset was collected along a path parallel to the BR-101 highway, close to a well-exposed 10 m deep by 100 m long outcrop.

Four two-dimensional DC resistivity data were collected over the same profile using a Syscal Pro system with 48 electrodes spaced 1 m and 2 m apart and configured using both a Wenner–Schlumberger and a Dipole-dipole array. The Wenner–Schlumberger configuration was chosen to maximize sensitivity to vertical resistivity variations, while the Dipole-dipole array was selected for resolving horizontal variations (i.e. channels). The aim of these repeated tests was to determine the efficiency of each. The apparent resistivity data were processed with RES2DINV software (Loke 2004), which uses the field data to automatically determine a two-dimensional model of resistivity for the medium. The RES2DINV is an inversion program for resistivity and induced polarization.

The same profile was recorded continuously using a GSSI SIR-3000 GPR instrument attached with an odometer based survey wheel. 200 and 400 MHz shielded monostatic antennas were selected because they offer the best compromise between resolution and investigation depth. The data were processed using ReflexW software, version 4.0 (Sandmeier 2006). GPR data processing consisted of 1) dewow filtering, 2) static correction, 3) manual gain, 4) bandpass filtering and 5) background removal. Gain functions were adapted to each profile in order to obtain the best image but the gain was kept constant for all traces belonging to a given profile in order to map the attenuation.

Geochemical analytical method

Sixteen typical aromatic polycyclic compounds were analyzed: phenanthrene, anthracene, fluoranthene, benzo[a]anthracene, benzo[a]pyrene, chrysene, fluorene, benzo[b]fluoranthene, benzo[k]fluoranthene, indene[1,2,3-cd]pyrene, anthracene-d₁₀, benzo[ghi]perylene, pyrene, dibenz[ah]anthracene, and benzo[b]fluoranthene-d₁₂.

The preparation, extraction, and analytical procedures for the PAH compounds in the original soil sample were adapted from standard EPA protocol. Soil samples were air dried, homogenized and milled in a ring mill before analysis. All analytes were quantified through a Soxhlet extract of each soil sample. In brief, 30 g each of soil sample was mixed with 10 g of anhydrous sodium sulphate, spiked with a 250 µL solution containing two surrogate PAHs (benzo[b]fluoranthene-d₁₂ and anthracene-d₁₀) and placed in pre-extracted Whatman extraction thimbles. The thimbles were placed into a 250 ml Soxhlet unit and extracted after 24 h with a 250 mL solution of hexane: acetone (1:1, v/v). Extracts were then reduced to near dryness in a rotary evaporator (T=35±0.5°C), take to 10 mL and transferred into pre-washed and baked glass vials. The samples were then reduced to dryness under a gentle stream of N₂, after which a 250 µL solution containing three deuterated PAHs (naphthalene, acenaphthylene and acenaphthene) was added. The concentrate was spiked with 5 µl solvent containing the following internal standards: naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂ and perylene-d₁₂. The capillary column was DB-5MS. The sample was analyzed via GC–MS (Trace GC Ultra coupled to a ThermoFisher Scientific ITQ900 mass spectrometer) with He as carrier gas at a constant flow of 1 mL/min. The injection and detector port temperatures were 270°C, and the oven temperature was ramped from 50°C to 550°C. The total procedure was carried out in duplicate, and calibration curves were used as the basis of the quantitative analysis.

A preliminary test of the analytical technique was conducted in order to verify the efficiency of the preparation and extraction procedures. The test was carried out by using samples without polycyclic aromatic compounds. These three “blank” samples were obtained through several extraction steps.

Geophysical results

The ERT profile shows a model coherent with the geological structure but with an evident decrease in resistivity under the polluted area (Fig 2). This conflicts with the argument that electrical conductivity should be lower since pore water is partially replaced by insulating LNAPL, as has been reported elsewhere. However, Atekwana et al. (2000 and 2004) assumed that the higher bulk conductivities at the contaminated location were associated with microbial activity stimulated by the presence of petroleum hydrocarbons.

Figure 3 shows the GPR profile recorded with the 200 MHz antenna. The lateral contact of a channel is quite clear at the position 8 m from the beginning of the profile. The reflectors between the positions 23 and 40 m show an increase in wavelength and amplitude. This is caused by the increase in EM wave propagation velocity because the pore water has been replaced by the fuel. This result is in agreement with Bano et al (2009), who reported that GPR data acquired on a oil polluted sand box did not show clear reflections but main changes were on the velocity anomalies. Underlying this layer, the reflections are weak and unclear (Cassidy, 2007).

Geochemical results

Gas chromatography–mass spectrometry provided an extracted ion chromatogram for a number of discrete m/z channels. Characterization of hydrocarbons from different sources is a decisive feature of any oil spill study. Petroleum oils are distinguished by differences in the patterns (known as ‘hydrocarbon fingerprints’) they exhibit in their chromatogram. From among the thousands of different compounds that exist in oils, those which are “source specific” and “weathering stable” are used to identify the source of oil spills.

The most abundant PAH compound in the polluted soils was benzo[b]fluoranthene with a concentration of 102.8 µg/kg in the most polluted sample. This compound represented about 58 to 83% of the total PAHs. Other compounds detected were phenanthrene and fluoranthene, with main values of 12.6 and 13.8 µg/kg, respectively. Therefore, the concentrations of PAHs in soil samples suggest that the source is of anthropogenic origin.

A number of diagnostic ratios of target PAH species have been successfully used as indicators for oil spill identification. However, weathering and biodegradation alter the chemical composition of spilled oil, rendering an unambiguous identification of the source something of a challenge (Wang et al., 1999). Generally, a petroleum source contains relatively higher concentrations of 2-3 ring PAH compounds, whereas a large proportion of high molecular weight parent PAHs is a typical characteristic of a combustion origin. Ant/(Ant+Phe) ratios lower than 0.10 are usually taken as an indication of unburned petroleum, while a ratio higher than 0.10 indicates a predominantly combustion effect. Ant/(Ant+Phe) ratios in the soil samples from the site ranged from 0.09 to 0.36, indicating a complex origin.

In addition, the ratio of low to high molecular weight PAHs (LPAHs/HPAHs) has generally been used as a tool for discriminating the petroleum/combustion sources of PAHs. For example, 0.4, the ratio of Flu/(Flu+Pyr), has been proposed as the boundary of petroleum and combustion sources, whereas ratios >0.50 are typical of coal combustion. Flu/(Flu+Pyr) ratios in the soil samples from the site ranged from 0.42 to 0.68, confirming the mixed origin of the spill.

Conclusions

The integration of geophysical and geochemical methods used in this research has provided significant information about the origin and extension of the polluted site, reducing the ambiguity of data interpretation.

The geophysical survey provided cost-effective spatial information on the contamination of a near surface vadose zone, and the particular geophysical signature of hydrocarbon contamination has been discussed. ERT proved to be very useful for assessing the geological characteristics of the contaminated area and extension of the plume, which, in this case, was characterized by low resistivity values. The GPR data permitted detection of bright reflections coincident with the most polluted area, while downwards the signal was highly attenuated.

Geochemical analysis detected high concentrations of PAHs present in soils at the site, with a predominance of benzo[b]fluoranthene, whilst an evaluation of different hydrocarbon fingerprints demonstrated that the plume was relatively heterogeneous. This suggests that the spill is probably of a furtive origin, in the form of clandestine dumping directly onto the soil.

Acknowledgments

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Fig 1. – Geological cross-section of a bank of the BR-101 highway near Mamanguape, showing the hydrocarbon plume.

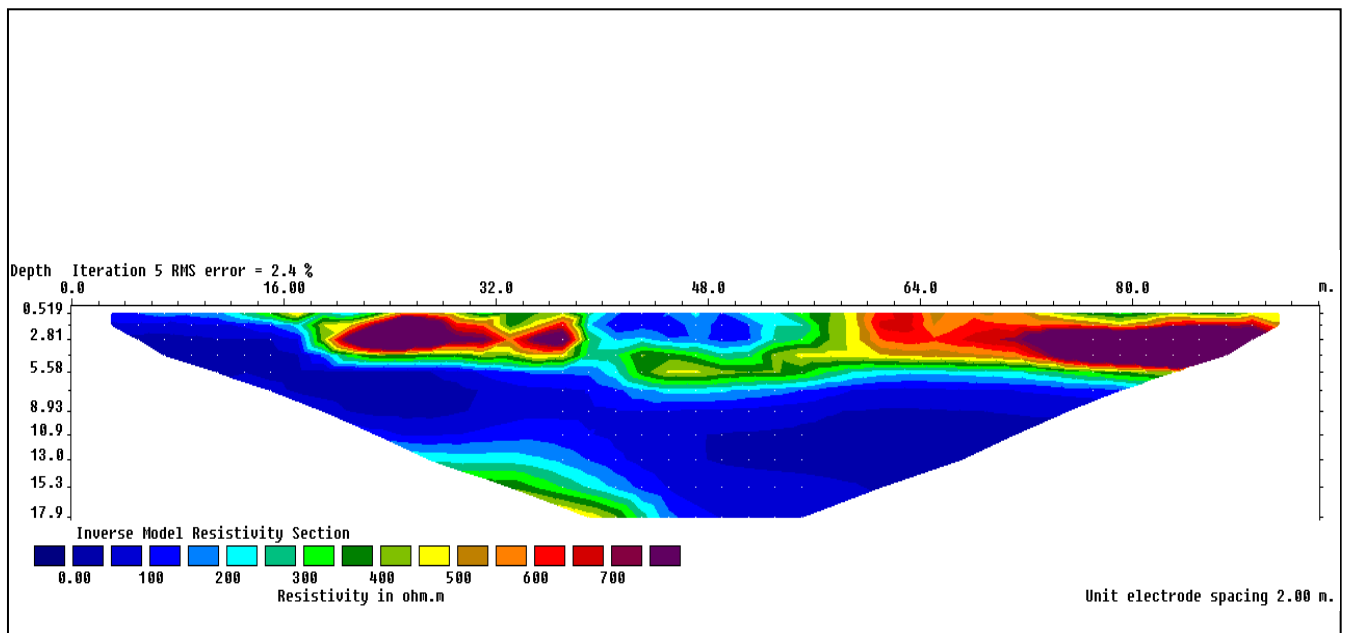


Fig 2. – Inverted resistivity profiles recorded using the Wenner-Schlumberger array with electrodes 1 m (top) and 2 m (bottom) apart. The low resistivity anomaly in the central upper part of both profiles is evident.

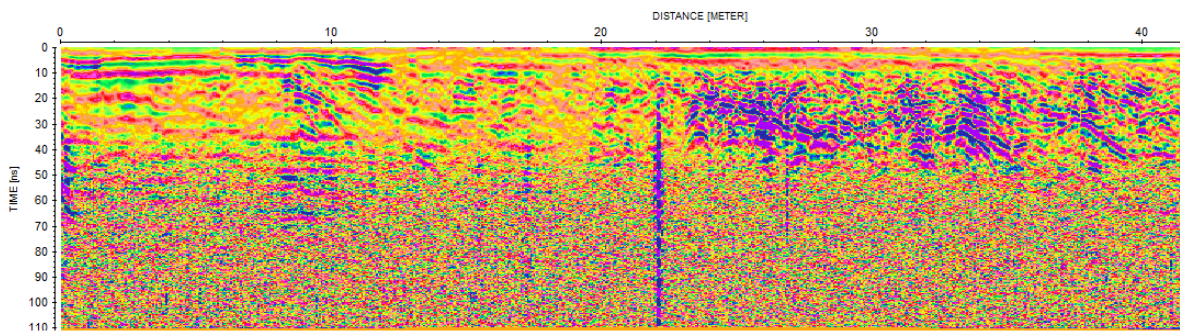


Fig 3. – GPR profile recorded with the 200 MHz antenna