Extended Abstract

Milani, Mariana Gava; Carvalho, Ana Cristina Malheiros Gonçalves (Advisor); Study of high resolution site characterization technologies for the improvement of the conceptual site model - Case study: Duque de Caxias - RJ. Rio de Janeiro, 2017. 152p. Dissertação de Mestrado – Departamento de Engenharia Civil e Ambiental, Pontifícia Universidade Católica do Rio de Janeiro.

The sources of contaminated sites are related to several factors such as the lack of knowledge of safe procedures for handling hazardous and / or toxic substances, disrespect to these safe procedures and the occurrence of accidents or leaks during industrial processes, transportation or storage of unprocessed materials and products. In addition, contamination is usually associated with the exploration of natural resources and with the expansion of the industry and/or agrarian activities, which have happened, and are still happening, at the cost of high environmental and social risks. A contaminated site is considered a risk, since its existence can generate several problems such as damages to health, impairment of the quality of water resources, restrictions on land use and damage to public and private property, and damage to the environment. These situations, in general, involve complex risks with regard to the effects of exposure to contaminants on human health (CETESB, 2013), and may have short-, medium- or long-term effects.

The increasing use of petroleum derivatives in industrial processes provides the generation of a diversity of products increasingly used by the current society. One of the negative consequences of the use and manipulation of hydrocarbons is the generation of highly polluting waste and effluents (Moreira & Dourado, 2005), such as the contaminants classified as light non-aqueous phase liquid (LNAPL), which are lighter than water, such as benzene, toluene, ethylbenzene and xylenes (BTEX). LNAPLs are present in the subsurface in free-phase form in thousands of areas under investigation around the world and are often the focus of investigation and remediation efforts. In general, LNAPLs represent potential long-term sources for continuous groundwater contamination and may function as a potentially long source of secondary impacts to soil, soil gas and groundwater. LNAPLs cause concern because of their persistence in the subsurface and their ability to contaminate large volumes of soil and groundwater (Kim & Corapciogly, 2003). Thus, the presence of LNAPLs has been and
continues to be one of our most difficult challenges in cleaning up contaminated sites (Sutherson et al., 2015).

Among the chemical compounds typically found in LNAFL, BTEX are of great environmental importance, especially benzene, since it is the most toxic. Benzene is a confirmed human carcinogen with evidence of carcinogenicity from all routes of exposure in both animals and humans. Non-carcinogenic effects include skin irritation after dermal contact, characterized by erythema, vesiculation, and dry and scaly dermatitis (Clayton & Clayton, 1994). The main manifestation of long-term effects is aplastic anemia, though central nervous system and gastrointestinal effects are also apparent (Hardman et al. 1996).

LNAFL contaminated sites may remain under investigation and / or undergoing remediation for years without achieving an acceptable risk, mainly due to poor characterization of the area. Additionally, in some cases traditional investigations may not identify the LNAFL, which will remain a secondary source of contamination for a long period of time.

The management of contaminated sites in the State of Rio de Janeiro is under the environmental licensing board, currently through the State Decree No. 44,820 of 2014, which reviewed the concepts and procedures of the environmental licensing system (Sistema de Licenciamento Ambiental - SLAM). The Operation and Recovery License (LOR) and the Environmental Recovery License (LAR) introduce the investigation of soil and groundwater quality in the licensing process. The specific legislation for contaminated sites management in the State of Rio de Janeiro is the Resolution of the Environmental State Council (Conselho Estadual do Meio Ambiente - CONEMA) No. 44 of 2012, which is based on the concepts of Resolution the Environmental National Council (Conselho Nacional do Meio Ambiente - CONAMA) No. 420/09. In addition, the environmental standards for soil and groundwater established by CONEMA Resolution No. 44/12 are the ones listed in Appendix II of CONAMA Resolution No. 420/09. CONEMA Resolution No.44/12 established the steps that must be followed in the contaminated sites management: identification, diagnostic and intervention.

The activities developed in the identification and diagnostic steps give support to the contaminated site model (CSM), which is as a primary planning and decision making tool used to identify and manage site uncertainty that can inhibit
effective project decision making (USEPA, 2010). Therefore, those steps are extremely important in order to adequately comply with current legislation. However, in the State of Rio de Janeiro, site characterization is usually carried out by established and mandatory environmental investigation methods (traditional investigation methods), which most of the times cannot provide an understanding of the physical and geochemical aspects of the area required for the success of the investigation phases and, consequently, the intervention phases. Therefore, in more complex cases, or cases involving greater environmental risk the investigations should be carried out based on non-traditional characterization methods, in order to increase the efficiency of investigation, reduce uncertainties regarding sources of contamination, and thus, adequately comply with current environmental management legislation.

High Resolution Site Characterization (HRSC) techniques are an example of more efficient investigation techniques. HRSC techniques are recommended for more complex sites, since they use scale-appropriate measurement and sample density to define contaminant distributions, and the physical context in which they reside, with greater certainty, supporting faster and more effective site cleanup, thus reducing the uncertainties of the CSM. HRSC techniques are still poorly applied in Brazil due to the low level of requests from the environmental agencies and lack of knowledge regarding the available investigations techniques. In addition, there are not many publications on these techniques in Brazil.

The Environmental Agency of the State of São Paulo (Companhia Ambiental do Estado de São Paulo - CETESB) was the first environmental agency to recommend the use of HRSC methods in its Board Decision (DD) No. 38 of February 7, 2017. However, there are no guidelines in Brazil related to these methods of investigation. In this context, the main objective this study was to use different investigations techniques to obtain a more representative CSM of an area of concern, when compared to what it is obtained through investigation techniques usually adopted in the state of Rio de Janeiro. To achieve the main objective of this study, two HRSC techniques were applied: (1) passive soil gas (PSG) survey; and, (2) investigation using Membrane Interface Probe (MIP).

It is worth mentioning that HRSC techniques are not intended to completely replace traditional investigations, but to ensure a greater accuracy in determining the location of the monitoring wells, and to allow the installation of a
reduced number of wells. The main objective of the HRSC techniques is to identify quickly and efficiently the impacted areas, allowing more efficient future actions and decisions (Coutinho, 2002).

Methodology

(1) Passive Soil Gas Survey

PSG surveys are routinely performed to identify source areas and release locations of volatile organic compounds (VOCs) and/or semi-volatile organic compounds (SVOCs), focus soil and groundwater sampling locations, focus remediation plans, track groundwater plumes, among others. The contamination detected by this technology include VOC, SVOCs, total petroleum hydrocarbons (TPH), solvents, organochlorine compounds, nitroaromatics, alcohols, explosives, pesticides, mercury, among others.

The PSG survey was conducted using the PSG sampler which is composed of several granular adsorbent materials, encapsulated in a hydrophobic and chemically inert microporous membrane. The membrane allows the diffusion of only the vapors present in the media. Volatile contaminants diffuse through the membrane and are adsorbed to the material.

The PSG samplers are analyzed by thermal desorption-gas chromatography / mass spectrometry (TD-GC / MS) instrumentation, and provide mass values of the adsorbed compounds, which qualitatively represent the presence of contamination in the subsurface.

(2) Investigation using Membrane Interface Probe (MIP)

MIP is a direct push tool with real-time direct measurement. The probe used in this study contemplates three different systems: MIP, Hydraulic Profiling Tool (HPT), and Electrical Conductivity (EC) device.

The MIP probe is equipped with a porous polytetrafluoroethylene membrane impregnated into a stainless steel screen for support, which is heated electrically to the optimum temperature range (i.e., 100 to 120 degrees Celsius) to stimulate the partition of the VOCs present in the soil and/or groundwater near the tip of the probe, causing these compounds to volatilize. VOCs up to a certain
molecular size (i.e., naphthalene-size or smaller) diffuse through the membrane under the effect of a concentration gradient. Once the compound has passed through the membrane, it is transported by a carrier gas (i.e., nitrogen) through a tubing loop (i.e., trunkline). Sweep gas from the MIP membrane is directed to detectors that are part of the MIP instrument system at ground surface: (1) Photoionization detector (PID); (2) Halogen specific detector (XSD); and (3) Flame ionization detector (FID).

PID consists of a 10.2 electron volt (eV) ultraviolet (UV) lamp, mounted in a thermostatically controlled, low volume, continuous flow electrolytic cell. The UV lamp ionizes compounds with ionization potential less than 10.2 eV. The FID detector uses a hydrogen flame to promote combustion of the compounds within the carrier gas. It responds to any molecule with a carbon-hydrogen bond (e.g., methane) and rarely to compounds such as hydrogen sulfide (H2S), carbon tetrachloride or ammonia. The XSD detector consists of a ceramic probe, a platinum wire (anode) and a platinum pellet (cathode) mounted inside a high temperature reactor. XSD is sensitive to halogen atoms, including bromine, chlorine and fluorine. The detectors responses are reported in microvolts (μV), representing the total relative concentrations of VOCs.

For the measurement of electrical conductivity (EC) of soil and eventual fluids the probe has a set of dipoles at its tip. EC is measured in millisiemens per meter (mS / m). EC values can be used as indications of stratigraphic changes. Higher detections of EC are commonly related to more clayey soils due to the higher presence of ions. Similarly, low EC detections commonly indicate the presence of more sandy soils.

The HPT system creates profiles of soil hydraulic properties that can be used to measure the permeability and hydraulic conductivity of the site.

Case Study

The case study focused on an area of concern (the site) located in the Municipality of Duque de Caxias, State of Rio de Janeiro, contaminated by petroleum hydrocarbons, mainly benzene. The site is a sub-area of an industrial plant (confidential), and includes the following plant operational units: utilities
area, water treatment plant, effluent treatment plant and part of the cooling tower area.

The site environmental management process began in 2012 and included the identification and diagnostic steps, which are required by the current legislation of the state, and included preliminary investigation, confirmatory investigation and detailed investigation.

The confirmatory and detailed investigations were conducted using traditional methods, contemplating the conduction of 14 boreholes and the installation of 14 monitoring wells. No soil impacts were detected. In groundwater, impacts were detected mainly by benzene.

After the investigations it was not possible to delineate the contamination plumes and to identify all sources of contamination. To achieve the delineation of the plumes continuing with the traditional investigation approach, the installation of other monitoring wells would be necessary. However, considering that the site has an area of approximately 73,000 m², the level of uncertainty regarding the locations of the new monitoring wells was considered high. So, HRSC techniques were selected to reduce the level of uncertainty and improve the conceptual model to obtain adequate compliance with current legislation.

The PSG survey was carried out by distributing the PSG samplers in a triangular grid pattern with 15 meters (m) spacing in the areas where a higher impact was expected, and 20 m spacing in the areas where moderate impact was expected. At the eastern site limit, PSG samplers were installed with 15 m spacing.

The PSG samplers were allocated in 1.0 m in depth (unsaturated zone) boreholes with 1.0 inch diameters. The samplers were allocated at a depth of approximately 30 cm. The residence time of the PSG samplers in the subsurface was 14 days, following the laboratory instructions (i.e., Beacon Environmental Services Inc.), to ensure the adsorption of the contaminants present in the media. After that period, 189 PSG samplers were recovered and sent to laboratory for analysis of the adsorbed VOCs, SVOCs and TPH mass.

From the results it was possible to identify the approximate location of the main hot spots and a potential contamination off-site migration. It was possible to obtain a horizontal delineation of the contamination. However, the results obtained do not necessarily reflect the exact position of the contamination, since
the dynamics of migration of the volatiles in the unsaturated zone is different from the migration dynamics of contaminants present in the saturated zone. Thus, the investigation using MIP was carried out with the aim of complementing the results obtained in the PSG survey.

The MIP probe was advanced by direct push technology and the following information was continuously collected and displayed by the probe (in real time): electrical conductivity; HPT response parameters; chemical and MIP operational parameters; the speed of the advance; and, the temperature.

The interpretation of HPT and EC profiles indicated the presence of three distinct layers (landfill, sand and organic clay), corroborating with the layers previously identified in the confirmatory and detailed investigations.

The MIP probe was advanced at a rate of approximately thirty centimeters per minute (equivalent to 1 feet per minute) until it reached the organic clay layer and / or until the contamination was successfully delineated. The depth varied according to the location and field information. In general, the probe was advanced to a depth between 5 and 7 meters.

Elevated EC values were observed when the probe reached the interface of the sand layer with the organic clay, which was associated with the high concentrations of salts present in the organic clay layer. The probe was advanced until the next layer (marine clay), depending on the responses obtained in the organic clay. At the interface of organic clay with marine clay, a decrease in EC values was observed.

32 HPT dissipation tests were conducted. The resulting inferred water levels varied between 0.50 m to 1.50 m, with an average value of 1.26 m.

Simultaneous detections in the PID and FID sensor were related to the presence of BTEX (main compounds of concern). Responses of less than 0.3 V were considered "trace" or background, based on the results obtained during field work. FID detection only was associated with the presence of methane, since it indicates the absence of aromatic organic compounds. Methane is a natural gas, derived from the anaerobic decomposition of organic matter and its occurrence is expected in the area, due to the existence of the organic clay layer. No response from the XSD sensor exceeded 0.035 V, indicating the absence of this type of compound in the area.
The average water level (1.26 m) was used to estimate the vadose zone and the saturated zone. In the vadose zone, 10 MIP locations presented significant results in PID and FID (> 0.3 V). Four MIP locations presented high PID and FID readings (> 1.0 V) which indicate the possible presence of residual free phase at those locations.

Of the 51 MIP locations, 25 presented significant results in the saturated zone in the PID and FID (> 0.3 V) sensors, and 10 presented high results (> 1.0 V), which indicate the presence of very high concentrations of dissolved phase, or even the presence of free phase (> 10 V).

**Integration of Results and Conclusions**

Integrating the results of benzene detections obtained in the PSG survey and the PID detections in the vadose zone through the investigation using MIP, it was possible to observe that the main hot spots identified by both techniques were the same, confirming the accuracy of the obtained results.

Based on the interpretation of the results, a complementary investigation plan was developed with the objective of quantifying/confirming the impacts observed with the HRSC techniques, and it included the installation of only nine monitoring/extraction wells, including soil and groundwater sampling for VOCs analysis. The analytical results of the soil samples collected during the monitoring well installation activities confirmed the impact identified in the vadose zone. The analytical results of the groundwater samples collected in the monitoring wells confirmed the results obtained by the investigation using MIP and indicated the presence of impact in the saturated zone. LNAPL was identified in one of the investigation location (MIP-24/PE-27). And off-site migration of the contamination plume was detected at the eastern site limit.

After the HRSC, and a complementary investigation that contemplated the installation of only nine wells, it was possible to identify five different hot spots and their respective sources, as well as their correlations with the groundwater sampling results.

The results obtained were determinant for a conclusive improvement of the CSM. The integrated results show that the distribution of VOCs in groundwater
occurs discontinuously throughout the area of study, indicating different sources of contamination.

To illustrate the new CSM, four geological sections were elaborated to present the MIP and the vertical distribution of VOCs. The sections were prepared by combining MIP results and the analytical results of the groundwater samples in the September 2016 sampling.

The section AA' presents hot spot 5 area (eastern site limit). According to MIP profiles, the depth of the clay layer varies from 2.7 m to 3.0 m below ground level, and the depth of the MIP drilling ranged from 5.67 m to 7.38 m. All significant PID readings from this section were detected in the sand layer, vertically delimiting VOC impacts.

The section BB' presents hot spot 4 area. In this section, the depth of the clay layer varies from 2.74 m to 3.72 m and the depth of drilling varied from 5.65 m to 7.38 m. VOC impacts were also vertically delimited.

The section CC' presents hot-spot 2 area (CP-04). According to the MIP profiles, the depth of the clay layer starts at 2.59 m, where the values of the electrical conductivity (EC) of the soil increased and the drilling depth varies from 5.52 to 8.24 m. All PID peaks were detected in the sand layer, with the exception of MIP-32 and MIP-23, where PID sensor responses were detected in the clay layer. Both locations were deepened for vertical delimitation.

The section DD' is parallel to section AA' and the drilling depths ranged from 5.64 m to 7.16 m. The presence of the organic clay was identified at approximately 3.00 m, where EC values increased. All PID peaks were detected in the sand layer, except for MIP-12, where the PID peak (0.9 V) was found at 5.43 m. The probe was deepened to 7.09 m. The impacts by VOCs were also vertically delimited in this section.

Based on the results, it is possible to affirm that the HRSC techniques allowed a significant advance in the understanding of the CSM reducing the need for possible future conventional investigations, allowing the visibility of a scenario with less uncertainty regarding the next steps. It would be unlikely to achieve the same results from a traditional investigation, in the way it is usually applied (by installing a minimum number of monitoring wells). And to achieve a similar result, the installation of a large number of monitoring wells would be necessary, which would probably be done during years of investigation work.
The recommended immediate next steps, based on current legislation, are:
(1) Conduct a Human Health and Ecological Risk Assessment to verify the risks
due to exposure to contamination present in the dissolved phase by on-site
receivers, and off-site receptors due to the migration of contamination identified
at the eastern site limit; (2) If unacceptable risks are identified for the current
scenario, conduct a feasibility study of remediation techniques and implement
intervention measures in order to achieve acceptable levels of risk; (3) Carry out
the delimitation and removal of the detected LNAPL (as it is known that it
presents high concentrations of BTEX, in addition to other VOCs); and, (4) Carry
out a feasibility study of remediation techniques for the site limit and implement
the intervention measures in order to restrain the off-site migration of the
contamination plume.

Keywords
High Resolution Site Characterization; Contaminated Areas; Petroleum
Hydrocarbons; Conceptual Site Model.