Acta Scientiarum

http://periodicos.uem.br/ojs
ISSN on-line: 1807-8664
Doi: 10.4025/actascitechnol.v46i1.64564

CIVIL ENGINEERING

Critical review of the environmental management of a DNAPL contaminated site in Resende, Rio de Janeiro, Brazil

Marcelo Reitor de Castro Faria* **and Ana Cristina Malheiros Gonçalves Carvalho**

Departamento de Engenharia Civil e Ambiental, Pontifícia Universidade Católica do Rio de Janeiro, Rua Marquês de São Vicente, 225, Rio de Janeiro, Rio de Janeiro, Brazil. *Author for correspondence. E-mail: marcelo_rcfaria@hotmail.com

ABSTRACT. The current nonconformity of most Brazilian states regarding the environmental guidelines established by the Conama 420 resolution makes clear that there are still many challenges to be faced on the management field of contaminated sites. The analysis of a factual remediation operation in an industrial site in the city of Resende, Rio de Janeiro state, show that traditional site investigation techniques are still being applied as main tools of characterization, data collection and decision-making in the management of the area. The site has had its investigation start in the late 90's through multiple soil sampling and monitoring wells installation, pointing DNAPLs (dense non-aqueous phase liquids) among the chemicals of interest. The industrial site has undergone remediation for over 10 years now and has not been closed yet. More recently, the efficiency reduction of the primary remediation system, a dual-phase extraction system with over 50 installed wells, led to the implementation of *in-situ* stimulated bioremediation. Performance reports show lower efficiency than expected, hinting that a lackluster CSM (conceptual site model) might be leading to poor decision making. Despite being adequate remediation techniques, previous efforts and literature indicate that the site must undergo new investigation steps employing high-resolution site characterization (HRSC) techniques such as the MIP (membrane interface probe), allowing the refinement of the current CSM and the optimization of current remediation efforts.

Keywords: contaminated areas; DNAPL; environmental investigation; conceptual site model; high-resolution site characterization techniques.

Received on July 31, 2022.
Accepted on January 26, 2023.

Introduction

Analyzing a potentially contaminated area usually requires three main investigation steps: preliminary, confirmatory and detailed (*Conselho Nacional do Meio Ambiente* [Conama], 2009). Each step aims to gather information in different detail levels, which will then be used to build a conceptual site model (CSM), a theoretical model that must represent the areas conditions, as well as regard potential damage or risk factors associated with it, whether environmental or human. For that, different types of environmental investigation techniques can be employed, but the most usual are the collection of soil and groundwater samples, and also the installation of groundwater monitoring wells. Although these had been, for decades, the basis of contaminated sites characterization, it is long acknowledged that, when used alone, they are insufficient, being unable to gather the necessary data volume at reasonable costs (Suthersan, Quinnan, & Welty, 2015; Milani & Carvalho, 2017).

New technologies had brought innovation to the investigation field, allowing the collection, processing and interpretation of much higher data volumes in shorter time frames. Some techniques developed under this concept are called 'high-resolution' and are able, for instance, to provide precise and continuous information about contaminant concentrations, groundwater levels or chemistry and the investigated media's physical properties, all in real-time. Despite being spread and almost standardized in many countries, such technologies still find barriers for its application in Brazil (Milani & Carvalho, 2017).

A predominantly descriptive analysis of the environmental management of a real site, including its investigation and remediation steps, will be discussed in this article. The management's main goal was to lower contaminant levels to legally accepted concentrations, but over a decade later it has been unable to reach its goal and close the site. The analysis indicate that the overuse of traditional investigation techniques might have led to a poorly detailed CSM, that lacks enough information to support the decisions taken, and that the employment of high-resolution techniques would have likely benefited the process given the detected contaminants and the area's complexity.

Material and methods

Site description

Located in the city of Resende, Rio de Janeiro state, alongside the Presidente Dutra Road, the site (Figure 1) can be described as an industrial plant with roughly 600,000 square meters of constructed area, split into two main sectors named 'South Plant' and 'North Plant'. This research will focus on the South Plant for it is the most impacted area.

From 1997 to 2000, a series of environmental investigations took place in the site in order to evaluate the extension of potentially present contaminants in both soil and groundwater (Gradient Corporation, 2000). The main tools employed for these studies were the sampling of both soil and groundwater paired with monitoring wells installation, which had also been used in further studies (Gradient Corporation, 2018a), following the records shown on Table 1.

The site's stratigraphy had been defined through multiple borehole drillings in which soil samples were extracted and analyzed to detect VOC (volatile organic compound). The campaign had been done in two steps, with a total of 93 drillings in South Plant. The local hydrogeology defined by the studies is characterized by the alternation of thicker sand layers and thinner ones composed of silt and clay. Four main aquifer units had been characterized according to their scale and depth, in order to support the conceptual site model. A hydrostratigraphic profile had been made to illustrate the sites characteristics (Figure 2).

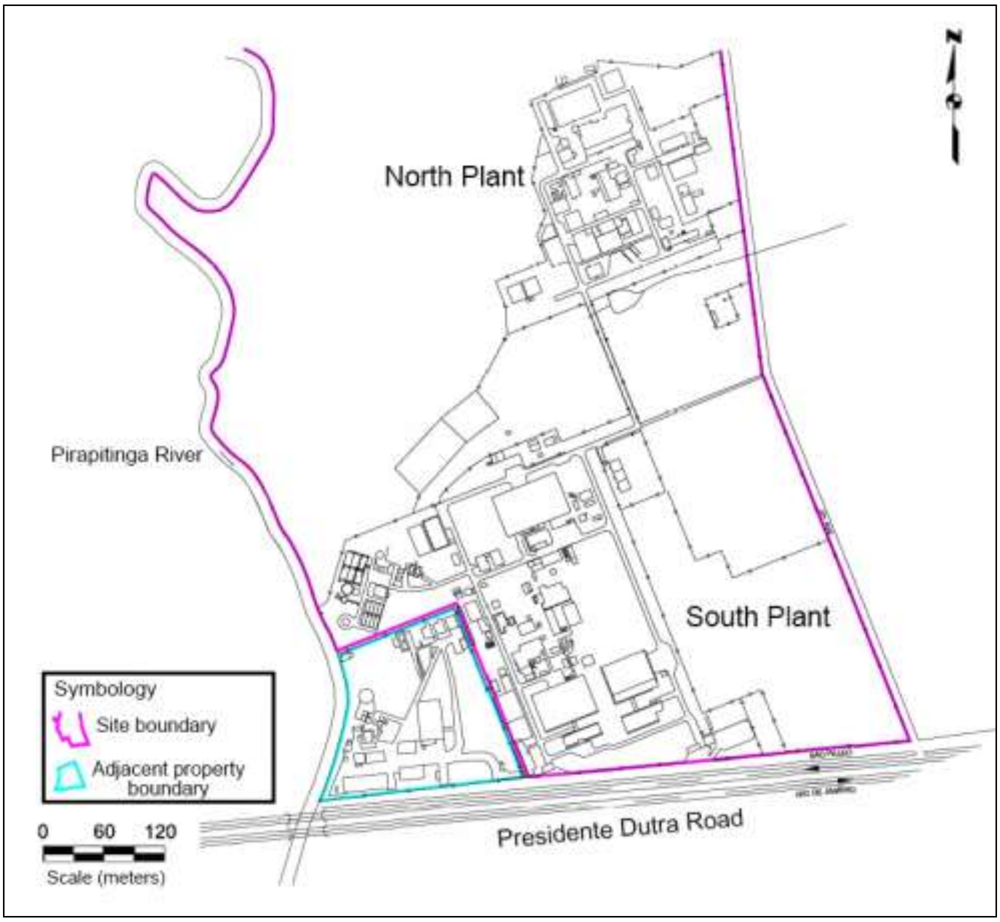

Figure 1. Plan view of the site's area. The purple line limits the site itself, while the blue one marks an adjacent smaller industrial plant. Source: Adapted from Gradient Corporation (2000).

Table 1. Chronological distribution of the multiple investigation campaigns that took place at the South Plant section of the site.

	South Plant investigation campaigns							
	1997	1998	1999	2000	2001	2002	2018	Total
Soil samples collected	19	-	14	396	-	-	-	429
Monitoring wells installed	14	-	18	9	-	-	16	57

Source: Adapted from Gradient Corporation (2000; 2018a).

Detected contaminants at the South Plant

The investigation campaign held in 2002 pointed both chlorinated and non-chlorinated VOCs as the main classes of contaminants detected at the South Plant. A risk assessment study had then been conducted and highlighted the following contaminants as the most relevant: toluene, trichloroethene (TCE), 1,2-dichloroethane (1,2-DCA) and cis-1,2-dichloroethene (cis-1,2-DCE). Analyzing their densities, out of the four highlighted contaminants, only toluene is a LNAPL (light non-aqueous phase fluid), while the other three fit into the DNAPL contaminant category (National Library of Medicine [NLM], 2019).

The VOC plume mapped based upon the investigation campaigns had been vertically split according to the site's stratigraphy. For total VOC levels on the Local A aquifer (the uppermost aquifer unit), concentrations of up to 1.743 mg L^{-1} had been detected on the South Plant (Figure 3).

Remediation strategies

Based upon the environmental investigations and risk assessment held at the site, a remediation plan had then been formulated including actions to prevent both contaminant migration to outer areas as well as reducing the overall contaminant mass and concentrations on the site. The first action held was the installation of a groundwater extraction wells system (which began its operation in 2003) designed to function as an emergency hydraulic barrier (EHB), preventing contaminated water migration to adjacent areas (Gradient Corporation, 2000; 2018a). A total of 8 wells were installed in both Local A and Local B aquifers, connected to a locally installed treatment system for the water. Then, for the South Plant, a dual-phase extraction (DPE) system was then designed and installed in order to remove contaminants from both saturated (Local A and B aquifers) and unsaturated zones of the area (Figure 4).

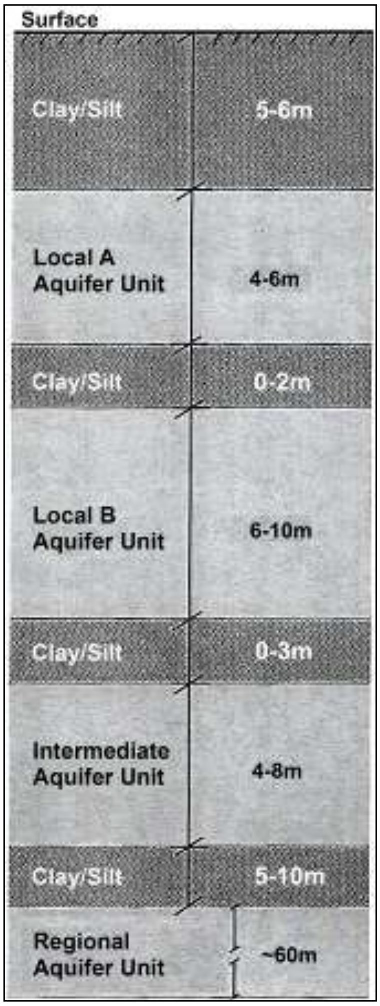

Figure 2. Simplified stratigraphic profile exhibiting the general arrangement and thickness of the aquifer layers and the silt and clay ones between them. Source: Modified from Gradient Corporation (2000).

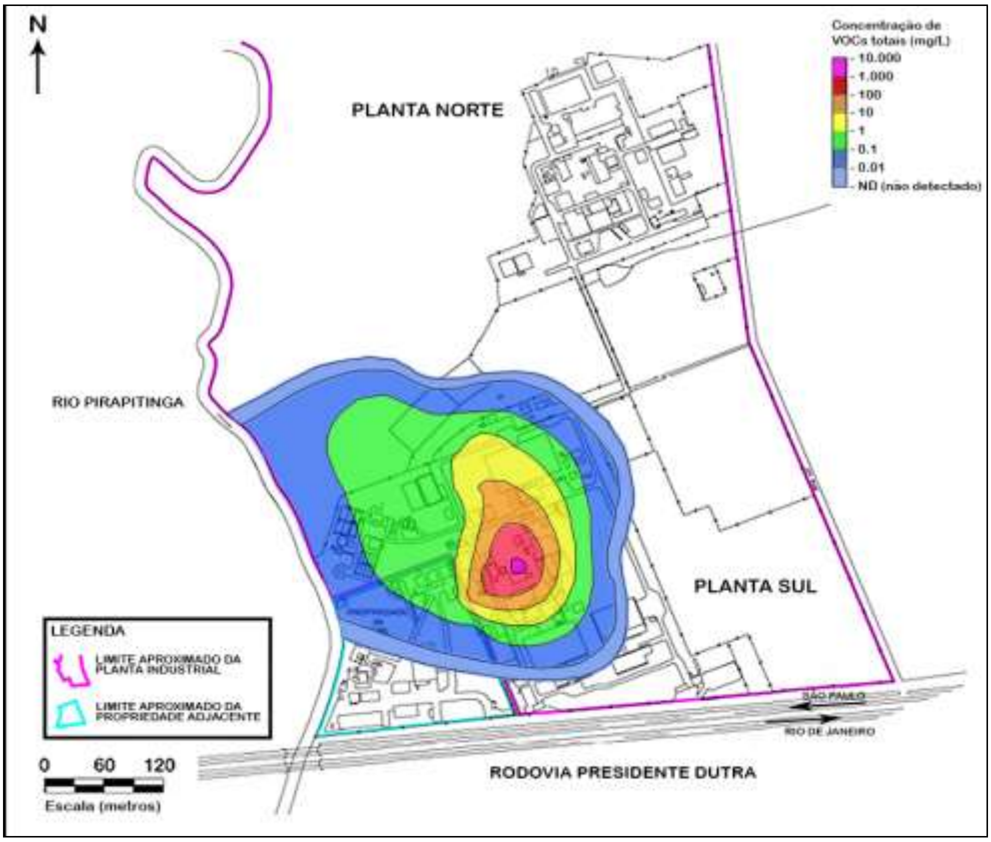

Figure 3. Plan view of the VOC plume detected at the Local A aquifer unit. Source: Modified from Gradient Corporation (2000).

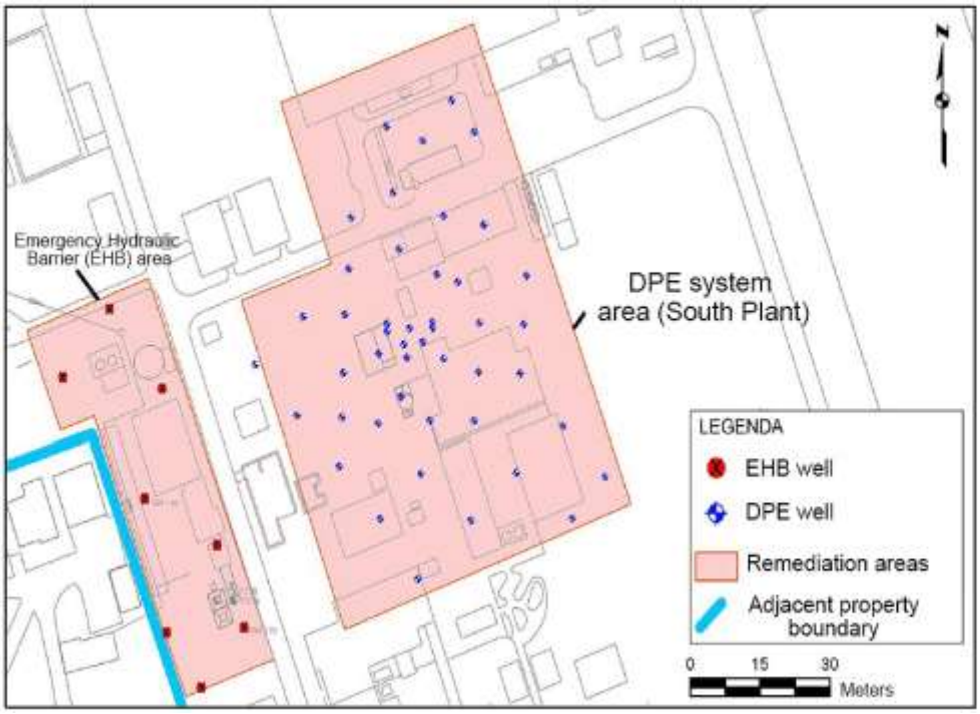

Figure 4. Site plan view of the initial DPE and the wells systems of emergency hydraulic barrier. Source: Adapted from Gradient Corporation (2000).

After almost a decade in operation, the DPE system has approximately 62 wells and has shown a clear decrease in its capability of consistently lowering the main contaminants concentration. In order to accelerate the decontamination, alternative remediation strategies had been evaluated and, in agreement with the local environmental authorities, tests with *in-situ* bioremediation strategies had been authorized. In 2016, a pilot test took place on the most contaminated areas in the South Plant, holding injections of a biostimulant compound containing both lecithin and zero-valent iron at 28 specific points, covering and area of approximately 90 square meters, and intercepting both Local A (21 injections) and B (7 injections) aquifer units (Gradient Corporation, 2018a).

The subsequent performance reports had shown a slower than anticipated decontamination process, attributing it to the presence of harder lens and layers of clay, which would hinder the dispersion of the biostimulant compound (Gradient Corporation, 2018b). The most recent accessed biannual report (Q2 2019) indicates that also the groundwater pH is lower than the desired levels required to favor the biodegradation processes. Sodium bicarbonate injections had already been made by then in order to regulate the pH levels, though to no avail until then.

Discussion

The studied site has been investigated by traditional techniques, including the setup of over 90 groundwater monitoring wells and over 600 soil samplings for off-site laboratory analysis through multiple campaigns. The use of these tools as main sources of data goes against what modern approaches suggest: high precision and low detection limit analyses paired with monitoring well installation on strategic spots, planned upon a CSM built with high volumes of data gathered by high-resolution techniques.

The traditional techniques repeatedly applied during site investigation are not considered adequate for the detailing of the architecture distribution of DNAPL contaminants in porous media, one of the most crucial factors for the correct addressing of the issue (Stroo et al., 2012; Interstate Technology & Regulatory Council [ITRC], 2015). As a response to the efficiency decline of the dual phase pump, site managers had opted for more recent investigation campaigns. Still, the same traditional techniques had been employed again.

In 2000, a study published by the ITRC (Interstate Technology and Regulatory Council) already pointed out issues regarding the use of conventional investigation techniques for DNAPL-contaminated sites, taking into consideration the great heterogeneity the distribution of these compounds can present in porous media (ITRC, 2000). Newer investigation technologies previously used, like geophysics or cone penetration tests, were already pointed as valid, more adequate alternatives for the characterization of physical media, contaminated plume delineation or contaminant mass quantification on those sites. Therefore, two decades ago these technologies were already present in the environmental investigation field, at least internationally.

Aiming to point valid high-resolution techniques capable of collecting data in adequate detail scale for the Resende site, a tool published by the ITRC was used to find viable options for DNAPL-contaminated sites (ITRC, 2015). The software works based on setting four main parameters related to the site itself, as well as the investigation goals, which will then be considered when selecting the most compatible technologies.

The parameters include: type of substrate (consolidated or unconsolidated), nature of the analysis (chemical, geological or hydrogeological), saturation of the media (saturated or unsaturated), nature of the collected data (qualitative, semi-quantitative or quantitative) and, lastly, the parameters to be analyzed (porosity, hydraulic conductivity, contaminant concentration, among others). For the Resende site, two parameters were fixed: the unconsolidated substrate and the semi-quantitative nature of the data. Those were then tested with the given combinations of the remaining ones:

- Chemical analysis to determine contaminant concentrations on both unsaturated and saturated zones;
- Physical media analysis for geological mapping in both unsaturated and saturated zones;
- Physical media analysis to determine hydrogeological features such as hydraulic conductivity of the media in saturated zones.

For the combinations above, the membrane interface probe (MIP) was pointed as an applicable technology for both the saturated and unsaturated zones of the site (ITRC, 2015). The MIP is a tool capable of detecting VOCs in the porous media, allowing the continuous collection of data (vertically). This tool is employed with the support of direct push rigs and can also bear other kinds of sensors, allowing parameters such as the electrical resistivity or hydraulic permeability to be determined at the same time. The MIP can be efficient in high-resolution characterization of contaminant plumes, helping identify source-zones, plume delineation, preferential contaminant flux zones and improving the CSM in general. Moreover, when paired with electrical resistivity sensors and hydraulic profiling tools (HPT), it is also a viable alternative to outline stratigraphic and aquifer units (McAndrews, Heinze, & DiGuiseppi, 2003; Adamson et al., 2014;

Milani & Carvalho, 2017). In this way, the MIP presents itself as a tool capable of analyzing multiple parameters, physical or chemical, being of great use to the refinement of the conceptual model of the Resende site, at least on the most impacted and still under remediation areas.

As for the site remediation, the applied techniques such as dual-phase pump and treat, and the injection of biostimulants for bioremediation, are considered efficient in treating plumes with high rates of advective transport in flow zones. However, even under remediation by those techniques, contaminant concentrations can remain high in storage zones even after an initial successful remediation of the more hydraulic conductive zones, since silt or clay layers, through diffusion mechanisms, are able to store significant amounts of contaminants. Therefore, back-diffusion mechanisms can sustain these plumes over long periods of time, potentially hindering remediation goals unachievable (Chapman & Parker, 2005).

The analyzed biannual site reports indicate that, in fact, the DPE (dual-phase extraction) system on the South Plant had removed significant amounts of contaminants: about 30 tons in the 30 initial months of operation. It is noticeable, though, that after this period there is a clear reduction and stabilization of the contaminant removal rates (Figure 5). This pattern shows that most of the hydraulically recoverable segments of the plume had been quickly reached and removed, while harder to reach sections, probably adsorbed or stored in clay bodies, remain untouched. This way, the DPE system had become subject to slower back-diffusion, dissolution or desorption rates, potentially active for extensive time frames.

Introduced as a response to the efficiency loss of the DPE system, the stimulated bioremediation method recently employed is also an efficient treatment alternative for chlorinated solvent contaminated sites, able to induce or accelerate contaminant dissolution or degradation by reductive chlorination mechanisms (The Parsons Corporation, 2004; Interstate Technology & Regulatory Council [ITRC], 2007; Peale, Mueller, & Molin, 2010; Stroo et al., 2012). The degradation occurs mainly on the contaminant dissolved fractions, which also accelerates its dissolution when in contact with water by increasing concentration gradients, since the water-dissolved portion is primarily addressed. Furthermore, TCE degradation generates more soluble byproducts, such as DCE, which commonly generates a spike in its detection in dissolved phase portions of the plume. In this way, the bioremediation also works in supplementary way to the DPE system, since the dissolved contaminants can be extracted by it. The monitoring reports indicate difficulties to maintain optimal chemical conditions to the biodegradation process and also mention the 'heterogeneous stratigraphy' of the soils targeted by the biostimulant injections as a hindering factor (Gradient Corporation, 2018b), which further highlights the importance of adequate scale mapping of the area's stratigraphy. The low-resolution characterization of the physical media makes it harder to map preferential migration pathways and overall reach both contaminants and the biostimulant compounds injected, significantly affecting the technique's odds of success. (Moretti, 2005). Based on this scenario, the planning phase of this technique is also questionable, since it could have also included steps for the CSM refinement of the targeted area.

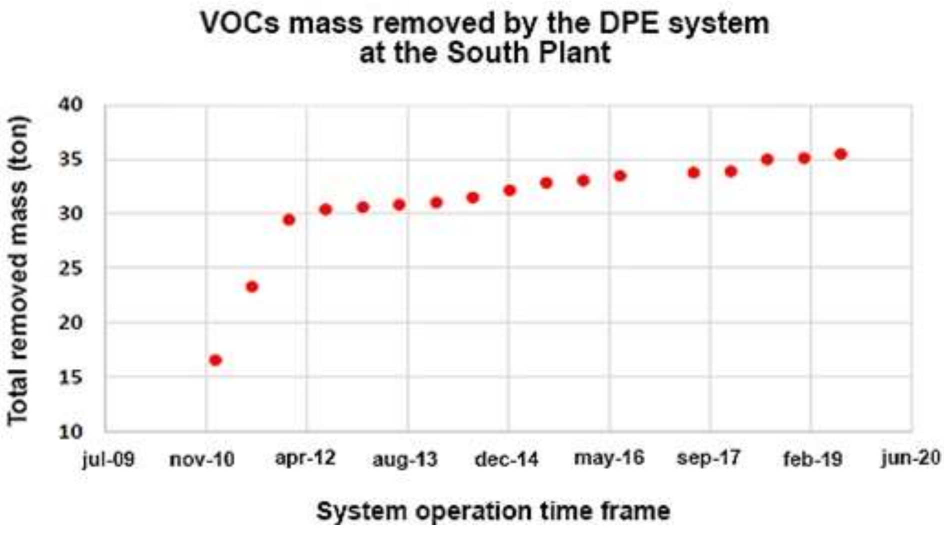

Figure 5. Total VOC mass removed in the South Plant by the DPE system across time. The pattern indicates great initial results followed by a noticeable decrease in the amounts removed after 2012. About 80% of the total VOC mass removed (30.5 tons) had been carried out in the first 30 months of operation time of the system depicted above.

Conclusion

The continuous usage of investigation techniques considered insufficient by themselves to address the complexity of the issues on the Resende site is the main critique to the management of the area. Using a CSM purely built upon data gathered by these techniques to carry risk assessment analysis, remediation goals and the multiple steps of the remediation process has proved inadequate, considering the many difficulties faced to finish the remediation of the South Plant. If during the initial stages of the management one can argue that more advanced and/or efficient techniques were not yet available, the same does not hold true when considering the more recent efforts. The bioremediation that started in 2016 was still planned and implemented without further refinement of the conceptual site model. The cited literature makes it possible to estimate that the targeted goals could have been achieved in a much smaller time frame and possibly in a less costly manner if high-resolution characterization techniques, such as the MIP, had been employed. These techniques are provenly efficient in adequate scale data gathering for reducing the conceptual model uncertainties.

The effort of stimulating more detailed studies in areas such as the Resende site is partly governmental. For that, the previous experiences of organizations such as the Environmental Protection Agency (EPA, 2011; 2019) or the ITRC show that private and public agents need to be aligned when it comes to technical and legal guidelines, assuring that there is a favorable framework for the adoption of more advanced techniques and methodologies.

The low conformity state of many local authorities regarding the Conama 420/2009 resolution makes it impossible to define the actual dimension of contamination issues in their territory, therefore undermining their capability of adequately managing the issue. Legal aspects also need attention and discussion in order to contemplate the necessary adjustments to include managing and technological advancements for contaminated sites. High complexity areas, specially DNAPL contaminated ones, are not usually addressed by the necessary techniques due to low legal requirements, scarce technical material and clear legal guidelines.

References

Adamson, D. T., Chapman, S., Mahler, N., Newell, C., Parker, B., Pitkin, S., ... Singletary, M. (2014). Membrane interface probe protocol for contaminants in low-permeability zones. *Ground Water, 52*(4), 550-665. DOI: https://doi.org/10.1111/gwat.12085

Chapman, S. W., & Parker, B. L. (2005). Plume persistence due to aquitard back diffusion following dense nonaqueous phase liquid source removal or isolation. *Water Resources Research, 41*(12), W12411. DOI: https://doi.org/10.1029/2005WR004224

Conselho Nacional do Meio Ambiente [Conama]. (2009). *Resolução nº 420, de 28 de Dezembro de 2009*. Brasília, DF: Diário Oficial da União.

Environmental Protection Agency [EPA]. (2011). *Using high resolution site characterization to improve remedy design and implementation*. EPA Office of Superfund Remediation and Technology Innovation. Retrieved from https://frtr.gov/pdf/meetings/may11/presentations/dyment-presentation.pdf

Environmental Protection Agency [EPA]. (2019). *Dense Nonaqueous Phase Liquids (DNAPLs)*. Retrieved from https://bitlybr.com/ipsvt

Gradient Corporation. (2000). *Investigação do local em apoio ao projeto corretivo*. Resende, RJ: Ministério Público Federal, Procuradoria da República.

Gradient Corporation. (2018a). *Plano de trabalho - ações de remediação e cronograma atualizado – planta sul da unidade da servatis*. Resende, RJ: Ministério Público Federal, Procuradoria da República.

Gradient Corporation. (2018b). *Relatório semestral referente ao período de 01 de julho a 31 de dezembro de 2018*. Resende, RJ: Ministério Público Federal, Procuradoria da República.

Interstate Technology & Regulatory Council [ITRC]. (2000). *Dense Non-Aqueous Phase Liquids (DNAPLs): review of emerging characterization and remediation technologies*. Retrieved from https://encurtador.com.br/beoK5

Interstate Technology & Regulatory Council [ITRC]. (2007). *In situ bioremediation of chlorinated ethene DNAPL source zones: case studies*. Retrieved from https://encurtador.com.br/vABTZ

Interstate Technology & Regulatory Council [ITRC]. (2015). *Integrated dnapl site characterization and tools selection*. ITRC.

McAndrews, B., Heinze, K., & DiGuiseppi, W. (2003). Defining TCE plume source areas using the Membrane Interface Probe (MIP). *Soil and Sediment Contamination: An International Journal, 12*(6), 799-813. DOI: https://doi.org/10.1080/10588330390254838

Milani, M. G., & Carvalho, A. C. M. G. (2017). Estudo de tecnologias de investigação ambiental em alta resolução para refinamento do modelo conceitual — estudo de caso: Duque de Caxias (RJ), Brasil. *Engenharia Sanitaria e Ambiental, 26*(2), 327-337. DOI: https://doi.org/10.1590/S1413-415220190043

Moretti, L. (2005). *In situ Bioremediation of DNAPL source zones*. Retrieved from https://clu-in.org/download/studentpapers/moretti_dnaplbioremediation.pdf

National Library of Medicine [NLM]. (2019). *PubChem*. Retrieved from https://pubchem.ncbi.nlm.nih.gov

Peale, J. G. D., Mueller, J., & Molin, J. (2010). Successful ISCR-Enhanced Bioremediation of a TCE DNAPL source utilizing EHC® and KB-1®. *Remediation, 20*(3), 63-81. DOI: https://doi.org/10.1002/rem.20251

Stroo, H. F., Leeson, A., Marqusee, J. A., Johnson, P. C., Ward, C. H., Kavanaugh, M. C., ... Unger, M. (2012). Chlorinated ethene source remediation: lessons learned. *Environmental Science and Technology, 46*(12), 6438-6447. DOI: https://doi.org/10.1021/es204714w

Suthersan, S., Quinnan, J., & Welty, N. (2015). The new ROI: return on investigations by utilizing smart characterization methods. *Groundwater Monitoring & Remediation, 35*(3), 25-33. DOI: https://doi.org/10.1111/gwmr.12118

The Parsons Corporation. (2004). *Principles and practices of enhanced anaerobic bioremediation of chlorinated solvents*. Arlington, VA: Parsons.