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## EVALUATION OF AROMATIC HYDROCARBONS IN SOIL AND GROUNDWATER AT A GAS STATION IN THE CITY OF NATAL/RN- BRAZIL

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***Djalma Ribeiro da Silva***

*In Memoriam*

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**Abstract:** Fuel retailing stations are economically important activities, but they are classified as potential sources of pollution and environmental accidents, presenting significant risks of contamination of ground and surface water resources, soil and the atmosphere. This study develops a case analysis of contamination at a gas station located in the city of Natal, RN, Brazil, using BTEX compounds (benzene, toluene, ethylbenzene and xylenes) and polyaromatic hydrocarbons (PAHs) as markers of environmental contamination. Gas chromatography techniques with different detectors were used to identify and quantify the hydrocarbons: gas chromatography with a flame ionization detector coupled to a photoionization detector for BTEX and gas chromatography coupled to mass spectrometry for PAHs. It was found that benzene concentrations in soil ranged from 1.164 to 4.503 mg.Kg<sup>-1</sup>, while in groundwater samples the values ranged from 12.097 to 27.638.6 µg.L<sup>-1</sup>. Among the PAHs, naphthalene and anthracene stand out, with soil concentrations ranging from 0.420 mg.Kg<sup>-1</sup> to 15.46 mg.Kg<sup>-1</sup> and 0.110 mg.Kg<sup>-1</sup> to 0.970 mg.Kg<sup>-1</sup>, respectively. In the groundwater samples, naphthalene showed values between 0.759 and 614.7 µg.L<sup>-1</sup>. The results obtained were compared with the limits established by CONAMA Resolution 420, showing that the concentrations of benzene substantially exceed the maximum value allowed by Brazilian legislation. This is particularly relevant given that approximately 70% of Natal's water supply comes from underground sources.

**Keywords:** Aromatic hydrocarbons, Benzene, Groundwater, Environmental contamination, Fuel stations.

## INTRODUCTION

In recent decades, with the growing contamination of surface water in urban areas and water scarcity due to climate change, groundwater has come to play an important role, especially in metropolitan areas. In Brazil, the use of this resource is essential, with 52% of municipalities using groundwater for supply, 36% of which is supplied exclusively by this source, and the use of this resource is divided into domestic supply (30%), the agricultural sector (24%), urban public supply (18%) and multiple supply (14%) and for other purposes (12%) (Joaquim Nabuco Foundation, 2021; International Association of Hydrogeologists, 2020). In Natal/RN, for example, approximately 73% of the water supply comes from the Dunas/Barreiras aquifer.

However, the intensification of anthropogenic activities, especially in urban areas, has introduced various sources of contamination into this vital resource, such as septic tanks, unintentional spills, saltwater intrusion, waste disposal in dumps, the application of agrochemicals, pesticides and fertilizers, and leaks from underground fuel storage tanks (TASC) into the ground, significantly impacting groundwater quality. Fuel retailing is a potential source of pollution and environmental risks not only to groundwater quality, but also to surface water, soil and air (ANJOS, 2012; LICO et al. 2019; DE FRANÇA et al, 2024; FEI-BAFFOE et al. 2024).

In 2009, in the city of Natal, there were 110 fuel resale stations, according to a study carried out by the 45th Public Prosecutor's Office for the Defense of the Environment (MPRN) in partnership with UFRN and the Secretariat for the Environment and Urbanism (SEMURB), only one station was in compliance with environmental standards and resolutions, the others did not have the environmental adjustments (RAMALHO et al., 2014; RAMALHO, 2013). The risks of fuel

retailing have been described by DE FRANÇA et al (2024), ANJOS (2015), RAMALHO et al (2014), RAMALHO (2013), ANJOS (2012), AQUINO SOBRINHO (2011), reporting the contamination of the Dunas/Barreiras aquifer by leaks from gas stations in the city of Natal/RN.

In a subsurface petroleum hydrocarbon leak and/or spill, several phases can form, where the contaminants can move from one phase to another, and their permanence in each is determined by their physicochemical properties and environmental conditions (COLOMBANO et al., 2020). Hydrocarbons are distributed in four phases of subsurface contamination (COLOMBANO et al., 2020; ABDANUR, 2005): 1) Vapor phase - consists of volatile organic compounds present in fuels that occupy soil pores. These vapors can condense and adsorb into the soil or dissolve in soil water; 2) Residual or sorbed phase - consists of hydrocarbons adsorbed to organic colloids (organic matter) and soil minerals and/or retained by capillary forces in soil pores; 3) Free phase - constitutes the portion of hydrocarbons that are not miscible in water, supernatant or floating in the water; and 4) Dissolved phase - constitutes when the free phase in contact with water eventually or partially dissolves the hydrocarbons present in the LNAPL (e.g. BTEX), forming the so-called dissolved phase plume which is distributed by diffusion and flow.

The hydrocarbons that make up the majority of petroleum-based fuels are low-density compounds and most of their components consist of a phase that is not soluble in water, called *Non-Aqueous Phase Liquid* - NAPL. Petroleum-derived hydrocarbons are classified as a *Light Non-Aqueous Phase Liquid* (LNAPL) (DE FRANÇA et al, 2024), and among the compounds that indicate environmental contamination by petroleum fuels are monoaromatic hydrocarbons and polycyclic aromatics,

which are usually quantified by chromatographic techniques. In order to quantify these contaminants, samples must be properly collected to maintain their chemical and physical characteristics. In addition, the sample preparation method and quantification method must be chosen correctly to ensure the best analytical quality of the results (ANJOS 2012).

In order to fulfill the objective of this work, to evaluate aromatic hydrocarbons (BTEX and HPA) in soil and groundwater contaminated by fuels and/or lubricants, a real case of contamination at a gas station in the metropolitan area of Nata/IRN was used. The information collected about the gas station in this study is part of the investigation into environmental liabilities (preliminary assessment and confirmatory investigation) resulting from leaks or spills of fuels and/or lubricants, carried out by the 45th Public Prosecutor's Office of Rio Grande do Norte.

## WORKING METHODOLOGY

### STUDY AREA

The fuel retail station chosen for this study is located in the eastern part of the municipality of Natal-RN, delimited by the points P1, P2, P3 and P4, as shown in Figure 1. The enterprise carries out fuel retailing and convenience store activities, occupying a built-up area of 174.60 m<sup>2</sup>, comprising the roof over the fueling lane, the underground fuel storage system, and the building area that includes the administrative office and sanitary facilities, with six fueling pumps, fed by five fuel storage tanks, two of which are for regular gasoline, one for diesel, one for ethanol and one for additive gasoline. All the tanks have a capacity of 15,000 liters, and one tank has been deactivated. According to CONAMA resolution 273, the station is classified as Class 3, as the groundwater is used for the city's public water supply.

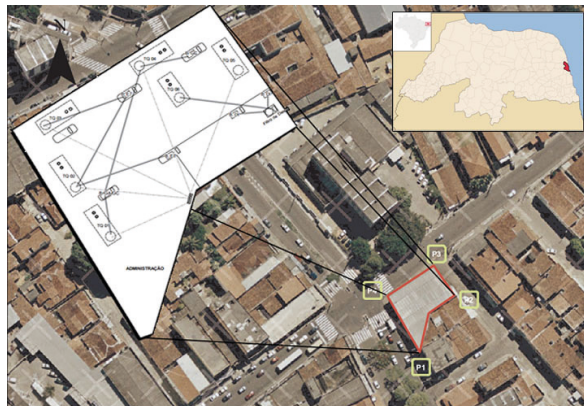


Figure 1: Location of the study area

### SAMPLE COLLECTION

The samples were collected by a technician from a qualified company, accompanied by a NUPPRAR technician. The soil samples were collected by drilling using a hand auger. After probing, the soil samples were packed in plastic bags and then transferred to wide-mouthed glass jars with Teflon-coated lids. The samples were collected in such a way that there were no empty spaces inside the bottles, thus avoiding the loss of the most volatile compounds.

For groundwater sampling, a purge was first carried out to remove stagnant water in the wells, and then the water samples were collected using a *bailer* and transferred to different types of vials: one for volatile organic compound (VOC) analysis, a 40 mL glass vial with a Teflon cap, and the other for semi-volatile organic compound (SVOC) analysis, a 1 liter amber glass vial. All the samples were collected in duplicate, and the bottles were duly labeled and identified with the location data, sampling depth (soil samples), time of collection, sampler and sample matrix (water or soil). The samples were packed and kept refrigerated with ice in a cool box during transportation to the Laboratory of Environmental Analysis Primary Processing and Biofuels/NUPPRAR for analysis.

## SAMPLE PREPARATION

### *Headspace extraction*

The extraction method for BTEX analysis in groundwater and soil was based on EPA 8021b for aromatic and halogenated volatiles by gas chromatography using photoionization and/or electrolytic conductivity detectors. *Headspace* extraction was carried out using the *Thermo Scientific TriPlus - TP100* autosampler. After the incubation/extraction period (15 minutes), 1.00 mL of the *headspace* confined in the flask was collected using a *gastight* syringe, previously heated to 85 °C, and then injected into the chromatograph.

### **Solid phase extraction - SPE**

The extraction method for HPA samples in groundwater was based on EPA 3535a - Solid Phase Extraction. The adsorbent used for extraction was 1000 mg C18-octadecylsilane in a 6 mL cartridge. The extraction was carried out in the *Dionex AutoTrace*® 280.

### **MICROWAVE-ASSISTED EXTRACTION - MAE**

The extraction method used for the HPA samples in soil was based on EPA method 3546 - Microwave Extraction. The extraction was carried out in *Anton Paar's Multiwave 3000*. The equipment has a capacity of up to 48 simultaneous extractions, with pressure and temperature monitoring in a control vessel. The power used for the extraction was 1200 W and the pressure was 0.5 bar/s.

## QUANTIFICATION OF HYDROCARBONS

### **BTEX**

For the quantitative analysis of BTEX in water and soil samples, the components were separated using a capillary column (OV-624, 30m x 0.53mm, 3.0 µm film) with temperature programming by gas chromatography (GC). Detection was carried out using a *photoionization detector* (PID) in series with a flame ionization detector (DIC), *Trace GC Ultra* from *Thermo Scientific*. Quantification was carried out by external standardization, based on the response of the PID, determined by the retention time using a calibration curve with previously prepared BTEX standards.

### **HPA**

For the quantitative analysis of PAHs in water and soil samples, the components were separated using a capillary column (DB-5/MS, 30m x 0.25mm, 0.25 µm film) with temperature programming. Detection was carried out using a mass spectrometry (MS) detector. *Trace GC* model coupled to a *Thermo Scientific PolarisQ* mass spectrometer. The PAHs were quantified by internal standardization, using a mixture of deuterated PAHs as an internal standard, determined by retention time, and their identification was confirmed by the mass spectra obtained on the spectrometer by means of a more intense ion and some other confirmatory ions. The mass spectrometer operated in positive mode, *electronic impact* (EI) with an energy of 70 eV and the analysis was carried out in *full scan* mode (40-350 m/z) with acquisition starting at 2 minutes.



## RESULTS AND DISCUSSIONS

### PRELIMINARY ASSESSMENT (AP)

To assess the concentrations of aromatic hydrocarbons, CONAMA Resolution 420 of 2009 was used as a reference. The preliminary assessment consisted of carrying out an initial diagnosis of the potentially contaminated areas, through a survey of available information about the area and reconnaissance of the area through field inspections, in order to gather evidence and facts that lead to suspicion or confirmation of contamination in the assessed area. For this reason, two boreholes were carried out to collect soil samples (S-01 and S-02), collected strategically in order to confirm and characterize possible hydrocarbon contamination in the soil. The soil samples were collected during the surveys, at strategic points according to the identification of the highest VOC concentrations obtained during the *screening*, carried out with *Gastech Innova* equipment (Figure 2) and the samples that showed the highest VOC in the soil layers were analyzed in the laboratory.

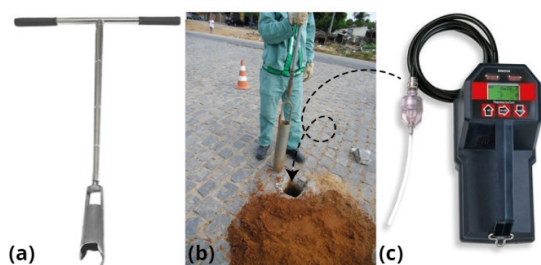


Figure 2: (a) Hand auger, (b) hand auger survey and (c) VOC meter - *Gastech Innova*.

The results obtained from the analysis of the samples showed indications of contamination in borehole S-01, with BTEX concentrations ranging from 10.68 mg.Kg<sup>-1</sup> to 1368.00 mg.Kg<sup>-1</sup> and concentrations for the PAHs: anthracene, phenanthrene and naphthalene, ranging from 4.17 mg.Kg<sup>-1</sup> to 12.03 mg.Kg<sup>-1</sup>. Borehole S-02 did not show results within the quantification method for the parameters analyzed.

Based on the results of the chemical analysis and the *on-site* VOC results of sample S-01, the soil is classified as class 4, according to CONAMA resolution no. 420, in which soil has a concentration of at least one chemical substance greater than the Residential Intervention Value. Once the contamination by petroleum hydrocarbons in the soil in the area of the gas station was confirmed, we moved on to the Detailed Confirmatory Investigation phase.

### DETAILED ANALYSIS OF CONTAMINATION

At this stage, the aim was to dimension and three-dimensionally delimit the contamination plumes in the physical environment based on the concentrations of the chemical substances of interest. Initially, five boreholes named S-03, S-04, S-05, S-06 and S-07 were drilled to a depth of 15 meters to collect soil and install groundwater monitoring wells named PM01, PM02, PM03, PM04, PM05 and PM06. The well (PM01) was installed at the site of borehole S-01, carried out in the preliminary assessment as shown in Figure 3. In order to better characterize the contamination plume in the soil, two additional boreholes S-08 and S-09 were requested by the MPRN.

### SOIL

Prior to the analysis of BTEX and HPAs, the analytical method was optimized. The method for analyzing BTEX was based on EPA method 8021b, while the method for analyzing HPAs was based on EPA method 8270. The analytical curve showed a correlation coefficient ( $R^2$ ) in the range of 0.999 to 0.99 for all the compounds analyzed, with the limit of quantification (LQ) for BTEX being 1  $\mu\text{g.L}^{-1}$  and 10  $\mu\text{g.L}^{-1}$  for the HPAs analyzed. The acceptance criterion for checking the calibration curve was based on verifying the response of all the analytes before analysis, with a variation of less than 20%.

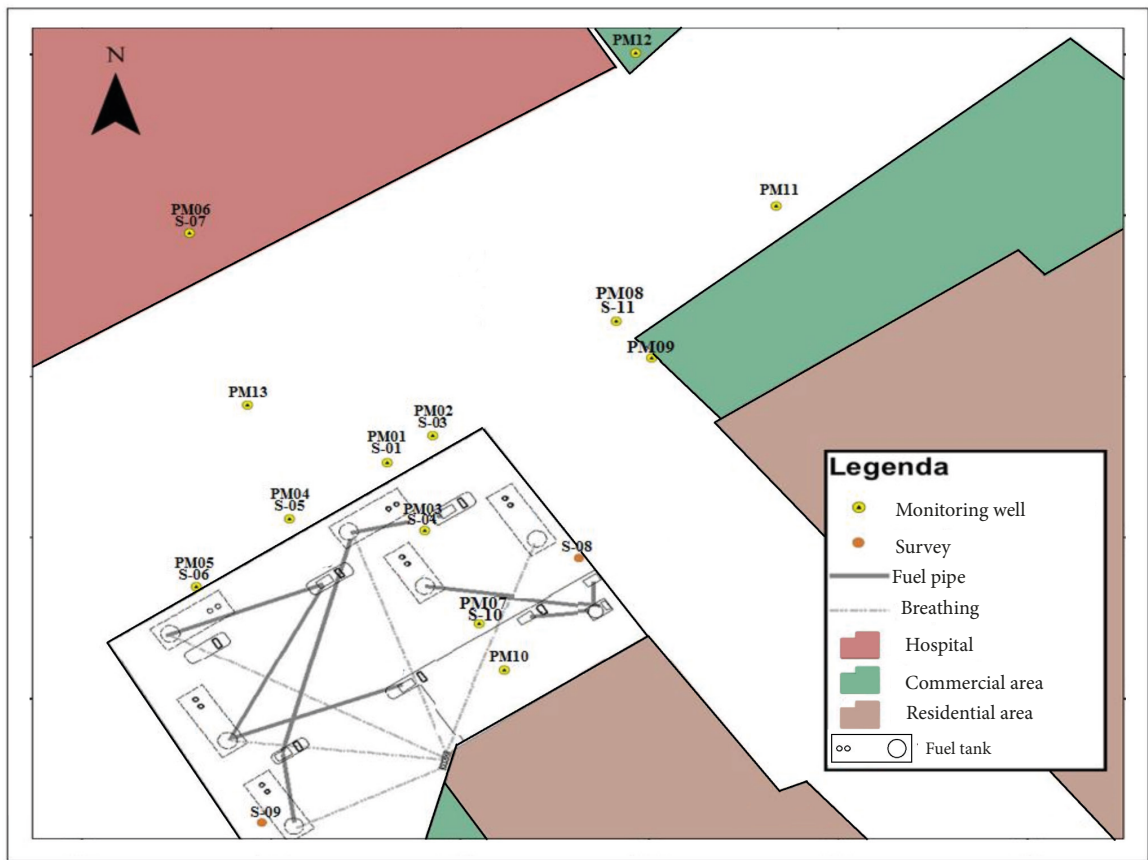


Figure 3: Location of the boreholes and installation of the monitoring wells.

COMPOSITES	S-03 9m	S-03 4m	S-04 2m	S-04 3m	S-05 2m	S-05 3m	S-06 2m	S-06 3m	S-07 8m	S-07 2m	S-08 7m	S-09 8m
<b>BTEX</b>	<b>mg.Kg<sup>-1</sup></b>											
Benzene	4,50	1,98	0,04	0,03	2,60	1,16	2,62	2,59	< LQ	< LQ	< LQ	< LQ
Toluene	5,35	8,49	0,24	< LQ	0,99	0,67	0,77	2,33	< LQ	0,47	< LQ	< LQ
Ethylbenzene	6,44	3,13	< LQ	0,06	0,97	0,81	0,75	0,53	< LQ	< LQ	< LQ	< LQ
Xylenes	2,91	10,08	0,63	< LQ	0,49	0,34	0,26	0,45	< LQ	< LQ	< LQ	< LQ
<b>HPA</b>	<b>mg.Kg<sup>-1</sup></b>											
Anthracene	0,19	< LQ	0,13	0,11	0,14	0,14	0,14	0,13	0,12	0,97	< LQ	< LQ
Benzo(a)ant.	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
Benzo(k)flo.	< LQ	< LQ	0,06	0,05	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
Benzo(g,h,i)pyr.	< LQ	0,02	0,02	0,02	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
Benzo(a)pyr.	0,09	< LQ	< LQ	0,09	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
Chrysene	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
Dibenzo(a,h)ant.	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	0,14	< LQ	< LQ	< LQ	< LQ	< LQ
Phenanthrene	0,21	0,08	0,10	0,09	0,15	0,13	0,14	0,11	0,09	0,92	< LQ	< LQ
Fluoranthene	79,27	< LQ	0,15	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	0,89	< LQ	< LQ
Indeno(1,2,3)	< LQ	< LQ	< LQ	0,15	< LQ	< LQ	< LQ	< LQ	0,16	< LQ	< LQ	< LQ
Naphthalene	< LQ	0,05	0,42	0,11	15,46	13,7	6,52	7,35	0,02	< LQ	< LQ	< LQ

Table 1 - Results of chemical analysis of BTEX and HPA in soil samples

**Highlighted values (red) indicate concentrations above the guideline value of CONAMA resolution no. 420;**  
 < LQ - Values below the detection limit of the quantification methods adopted / equipment used for analysis.

All the results from the soil samples had their masses corrected for humidity and converted to units of mass, given that it was a solid sample. To do this, the weight of the dry mass was used to convert the concentration into  $\text{mg.Kg}^{-1}$  according to Equation 1. Samples that exceeded the concentrations of the last point on the analytical curves (BTEX and HPA) were diluted and quantified within the working ranges.

$$\text{mg / Kg} = \frac{\text{Volume (mL)}}{\text{Massa seca (g)}} * \text{Concentration } (\mu\text{g.L}^{-1})$$

### Equation 1

Thus, the LQs for BTEX and HPAs respectively were  $0.0010 \text{ mg.Kg}^{-1}$  and  $0.010 \text{ mg.Kg}^{-1}$ , considering the approximate sample mass used of 2 g and 20 g and a final extract volume for analysis of 10 mL and 25 mL, respectively.

The concentrations of BTEX and HPA in the soil samples are shown in Table 1. The results of the chemical analysis of boreholes S-03 (9 and 14 m), S-05 (12 and 13 m) and S-06 (12 and 13 m) showed concentrations of benzene ranging from  $1.16 \text{ mg.Kg}^{-1}$  to  $4.50 \text{ mg.Kg}^{-1}$ , 50 times higher than the residential investigation value of CONAMA resolution no. 420. Among the PAHs, naphthalene and anthracene were quantified in most of the samples, with concentrations ranging from  $0.42 \text{ mg.Kg}^{-1}$  to  $15.46 \text{ mg.Kg}^{-1}$  and  $0.11 \text{ mg.Kg}^{-1}$  to  $0.97 \text{ mg.Kg}^{-1}$ , respectively. Of the 12 surveys carried out, 67% showed concentrations above the CONAMA residential prevention values.

Almost all of the contaminants analyzed in the samples were detected, albeit in concentrations below the CONAMA Residential Prevention limits. It should also be noted that most of these compounds are present in the composition of gasoline and diesel oil, which corroborates the hypothesis that the primary source of contamination at the site was caused by leaks from fuel tanks or pipelines.

## GROUNDWATER

The analysis methodologies followed the same methods mentioned in section 3.2.1. The water samples from monitoring wells PM04, PM05 and PM06 did not show concentrations above the CONAMA residential investigation values, while wells PM07, PM08 and PM09 showed extremely high levels of benzene, toluene, ethylbenzene and xylenes, ranging from  $2788 \mu\text{g.L}^{-1}$  to  $27,639 \mu\text{g.L}^{-1}$ . Due to the high concentration levels detected in PM07, PM08 and PM11, it was necessary to re-collect groundwater samples from these wells. The samples collected were named PM07\_B, PM08\_B and PM11\_B.

The results of the 6 water samples from the monitoring wells and the 12 soil samplings were not enough to completely delineate the plume of contamination in the soil and groundwater, so it was necessary to install more monitoring wells to collect soil and groundwater in order to be able to delineate these plumes. Based on the results obtained from the new boreholes S-10 and S-11, it was possible to delineate the benzene and naphthalene plumes in the soil. The benzene and naphthalene plumes in the soil can be seen in Figure 4.

The analysis of the PM07 and PM08 results was not enough to determine the dissolved phase in the groundwater, and it was necessary to install five new wells, named PM9 to PM13. Of the 13 monitoring wells, 54% showed contamination by aromatic hydrocarbons, with concentrations above the investigation values of CONAMA resolution 420, as shown in Table 2.

Based on Table 2, BTEX was found to be the most abundant contaminant, and consequently had the greatest potential to reach critical exposure points and pose a risk to human health in the surrounding area, due to the high mobility of BTEX in groundwater and the compounds' high carcinogenic and mutagenic potential. The highest concentrations of



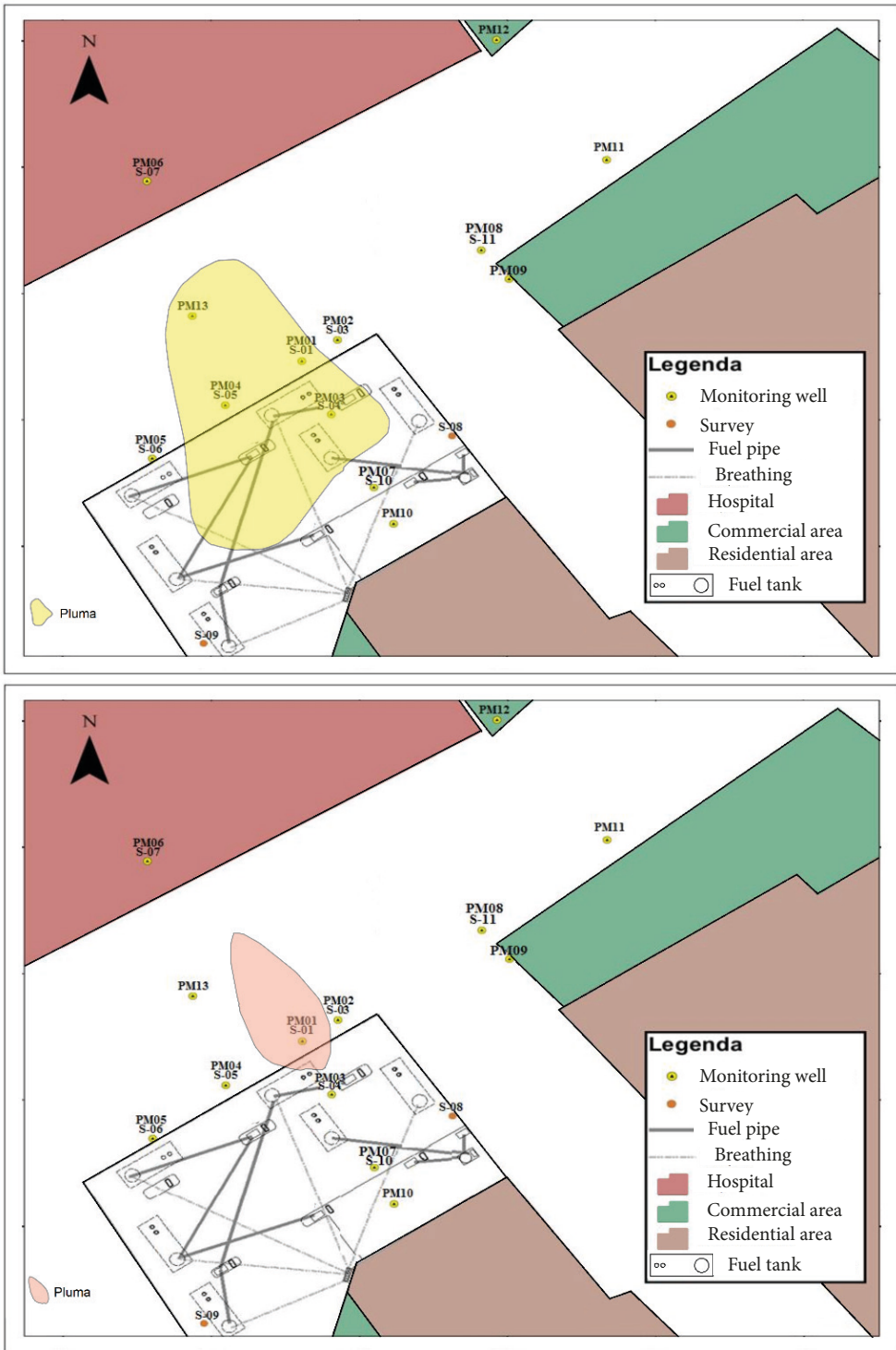


Figure 4: Delimitation of benzene and naphthalene contamination plumes in the soil.

COMPOSTITES	PM01	PM02	PM03	PM04	PM05	PM06	PM07	PM08	PM09	PM10	PM11	PM12	PM13	PM07_B	PM08_B	PM11_B	
<b>BTEX</b>																	
Benzene	<b>493,0</b>	0,400	<b>14,60</b>	< LQ	< LQ	1,050	< LQ	<b>27639</b>	<b>3893</b>	<b>8941</b>	<b>12,10</b>	<b>832,3</b>	< LQ	< LQ	<b>2856</b>	<b>2,293</b>	<b>544,6</b>
Toluene	<b>793,5</b>	6,400	20,90	< LQ	0,860	0,912	<b>25071</b>	<b>5535</b>	<b>6976</b>	10,11	<b>1000</b>	< LQ	< LQ	<b>2601</b>	<b>2,093</b>	293,1	
Ethylbenzene	66,67	< LQ	< LQ	< LQ	< LQ	< LQ	<b>2788</b>	372,3	519,5	< LQ	< LQ	< LQ	< LQ	<b>1070</b>	347,5	< LQ	
Xylenes	304,5	3,100	4,90	< LQ	0,520	< LQ	<b>13,09</b>	<b>1781</b>	<b>1917</b>	< LQ	<b>839,3</b>	< LQ	< LQ	<b>2439</b>	<b>1,525</b>	375,4	
<b>HPA</b>																	
$\mu\text{g}\cdot\text{L}^{-1}$																	
Anthracene	0,15	< LQ	< LQ	0,23	0,08	< LQ	2,09	1,38	< LQ	< LQ	< LQ	< LQ	< LQ	-	-	-	
Benzo(a)ant.	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	0,119	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	-	-	-	
Benzo(k)flo.	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	-	-	-	
Benzo(g,h,i)pyr.	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	-	-	-	
Benzo(a)pyr.	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	-	-	-	
Chrysene	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	0,10	0,06	< LQ	< LQ	< LQ	< LQ	< LQ	-	-	-	
Dibenzo(a,h)ant	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	-	-	-	
Phenanthrene	0,19	< LQ	< LQ	0,23	0,10	< LQ	0,81	0,55	< LQ	< LQ	< LQ	< LQ	< LQ	-	-	-	
Fluoranthene	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	-	-	-	
Indeno(1,2,3)	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	-	-	-	
Naphthalene	<b>614,70</b>	<b>459,40</b>	< LQ	56,87	4,78	< LQ	1,134	0,76	38,12	< LQ	9,56	< LQ	< LQ	-	-	-	

Table 2 - Results of the BTEX and HPA analyses in the monitoring wells  
 Highlighted values (red) indicate concentrations above the guideline value of CONAMA resolution no. 420; < LQ - Values below the detection limit of the quantification methods adopted / equipment used for analysis.

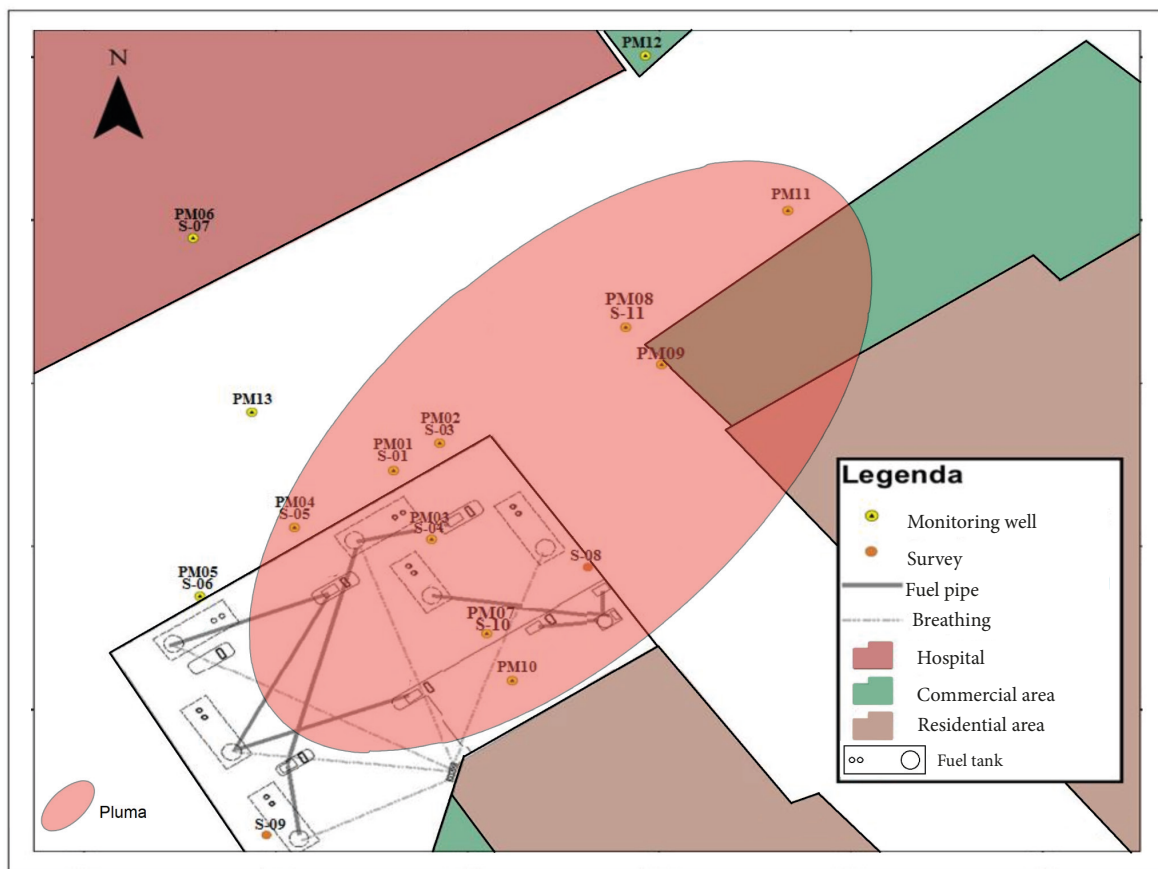


Figure 5: Delimitation of the benzene plume in groundwater.

BTEX in the subsurface are located mainly in wells PM09, PM08 and PM11. These wells are located outside the gas station yard and close to commercial areas (Figure 5). The delimitation of the benzene plume dissolved in the groundwater can be seen in Figure 5.

## CONCLUSIONS

The gas station under study is contaminating both the soil and the local groundwater, creating a risk of human exposure in the surrounding areas. The groundwater showed benzene contamination around 400 times higher than the investigation value in CONAMA Resolution 420 and 54% of the groundwater samples showed aromatic hydrocarbon contamination, above the investigation values in the Resolution. In addition, the soil was also contaminated, with 67% of the quantified samples showing concentrations

above the CONAMA resolution's residential prevention values. Therefore, a potential risk of contamination of the local water table by hydrocarbons, mainly benzene, was proven, making its waters unsuitable for consumption by the population surrounding the gas station, requiring actions to remediate and recover the area.

## ACKNOWLEDGMENTS

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