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CASE STUDY OPEN ACCESS

BTEX CONTAMINATED AREA DIAGNOSIS AND MAPPING: CASE STUDY

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ABSTRACT

With the increase of the vehicle fleet in the country, the demand for fuel grows, thus increasing the number of gas stations in the national territory. However, from the unbridled growth, coupled with the lack of maintenance and wear and tear of the storage and pipelines of the stations can cause very serious problems for the environment and humans. This work aimed to determine and quantify BTEX compounds in soil and groundwater collected from a gas station area at various depths to map contamination surfaces. The primary environmental liability investigation had as its main function to evaluate the soil and groundwater quality. For this study, we found the presence of VOC in most points investigated at a depth of 0.5m. At most of these points, when reaching 1.0m of drilling, the measured concentrations were zero. Based on the environmental research study presented, it was possible to identify the contamination in the gas station area through the samples collected in the drilled wells, and found the presence of dissolved product in groundwater at values above the established by the Dutch List for the BTEX and PAH compounds.

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INTRODUCTION

Environmental pollution today is one of the major problems facing man and is due to several factors such as misuse of natural resources, lack of environmental awareness and inefficiency of legislation. With nearly three decades of environmental policies, degradation of environmental quality continues its course in most parts of the globe. Preventive policies are no longer enough, because to reverse the processes that lead to environmental degradation, concrete initiatives are needed to repair the damage caused in the past, the so-called environmental liability. Soil contamination by industrial activities or waste disposal is one of the most significant evidences of environmental liabilities (Lins *et al*., 2019). Over the years and with the growing economic development, the consumption of petroleum products has increased significantly, and consequently, the increase in the number of gas stations. In Brazil, there are approximately 42,000 gas stations (ANP, 2018), many of them operating under conditions that do not meet the minimum environmental control requirements, causing many problems, such as: storage tank fuel leakage, incorrect disposal of waste generated and contamination of soil and groundwater.

Monoaromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylene, called BTEX compounds, are one of the main soil and water contaminants, as they are found widely in gasoline and other petroleum derivatives (Fogaça, 2015). The main exposure of these pollutants to the environment is a consequence of spills and leaks at gas stations (Martins *et al*, 2015). Environmental accidents at stations are mainly related to fuel leaks and spills generated by construction failures, such as the absence of paving in the station area, and operational failures such as leaks during unloading of product from the tanker. These products are considered toxic and cause the development of health problems, besides being considered carcinogenic (Lins *et al*., 2019). This work aimed to determine and quantify BTEX compounds in soil and groundwater collected from a gas station area at various depths to map contamination surfaces.

MATERIALS AND METHODS

The primary environmental liability investigation had as its main function to evaluate the soil and groundwater quality in the study area. A preliminary assessment of the existence of contamination was carried out by means of a gas survey campaign near the underground tanks and on the runway to assess the presence of volatile organic compounds (VOC) and to indicate where the boreholes should be located. Following the VOC campaign, five locations were selected for the survey location (S-01 to S-05) near the tank and fill areas. During the surveys, new VOC measurements were conducted to guide the collection of soil samples that showed evidence of contamination to perform BTEX and PAH analyzes.

Sample Collection Site

The analyzed gas station is located in a flat topography region in an urban area of mixed occupation (residential and commercial), where the region's water supply is provided by the local public supply network, however some establishments choose to use water from wells and / or tubular wells. Homes located east of the post use water from wells (PC 01 and PC 02) for domestic consumption. According to Technical Standard ABNT / NBR 13.786: 2014, which classifies service stations according to the surrounding environment, within a radius of 100 m from its perimeter, the station is classified as Class 2, due to the use of water from wells. The map with the characterization of the surroundings is shown in Figure.

areas, the facilities of the retail fuel and lubricant trades follow the standards prepared by the Brazilian Association of Technical Standards - ABNT / NBR 13.786: 2014, which establishes parameters and measures for these facilities.

Test Methodology

Mesh of Volatile Organic Compounds (VOC): A preliminary assessment of the existence of contamination was carried out through a gas survey campaign in the gas station area. These measurements were taken at 0.5m and 1.0m depth in order to evaluate the presence of volatile organic compounds (VOC) and indicate the location of soundings for soil sample collection. To determine these VOC concentrations in the soil, a portable photoionizer (PID) was used. The concentration range of the apparatus used for Volatile Organic Compounds ranges from 0 ppm to 10,000 ppm. It is noteworthy that this device has a special calibration device, which allows the exclusion of methane from the total quantification of volatile hydrocarbons.

Surveys and Soil Samples: In the study, 05 drillings (S-01 to S-05) were performed by hand auger, with 04 inches in diameter and depths up to 4.1m, totaling 19.40m drilled.

Source: The Authors (2019).

Figure 1. Gas Station Area

Resort Facilities

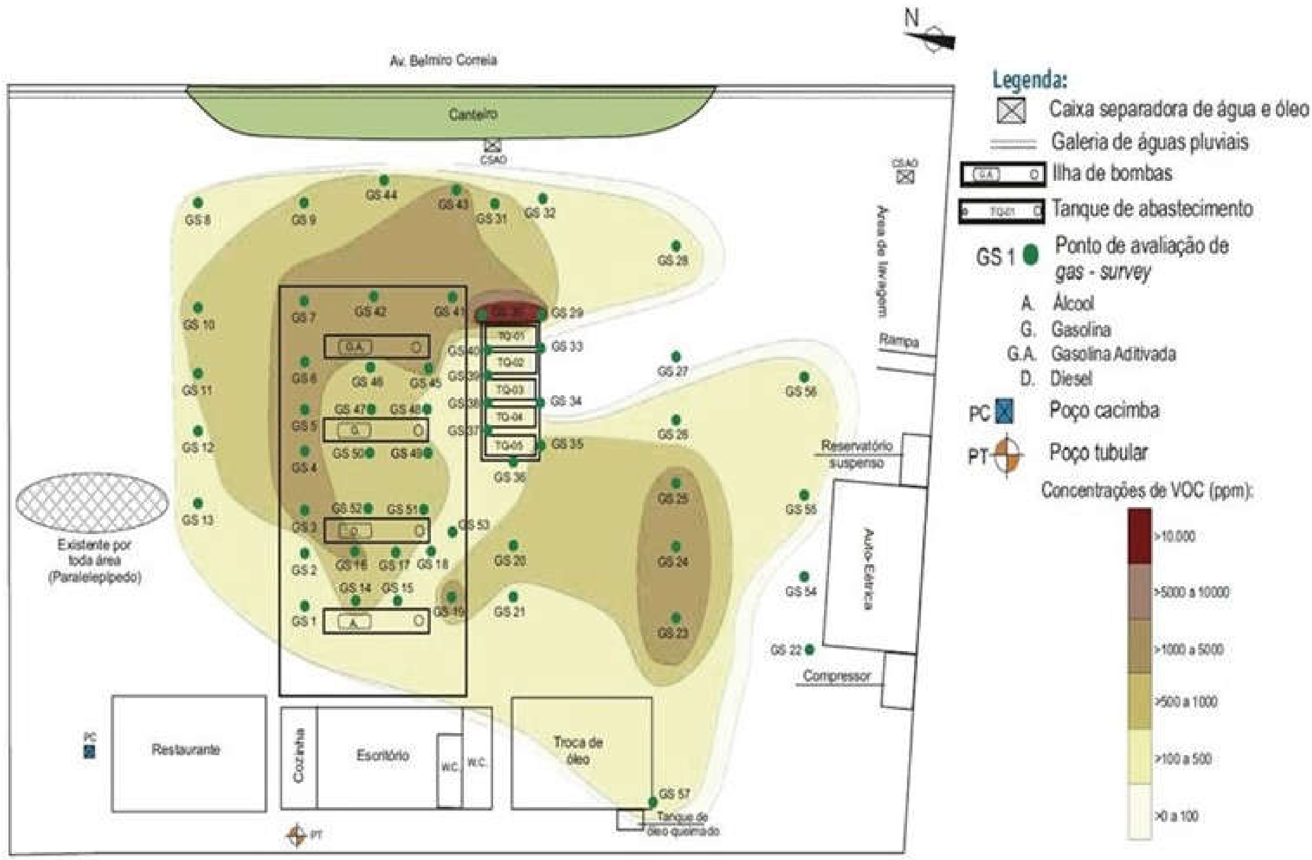
Considering that all installations and storage systems for petroleum products and other fuels are potentially or partially polluting enterprises and generators of environmental accidents, which may cause contamination of underground and surface water bodies, soil and air, In addition to the risk of fire and explosion resulting from leaks, mainly due to the fact that part of these establishments are located in densely populated

The surveys were carried out based on ABNT NBR 9603: 2015 - Trado Survey and ABNT NBR 15492: 2007 - Recognition Survey for Environmental Quality - Procedure, in order to characterize the local geology and collect soil samples for evaluation. of the compounds of interest (BTEX and PAH). Soil samples were collected and stored in 100ml flasks for determination and quantification of BTEX and PAH compounds. All vials were labeled and packaged in thermal containers at an average temperature of 4 ° C with a maximum oscillation of ± 2 ° C until arrival at the laboratory.

Monitoring Wells Installation: In order to monitor local groundwater conditions and to assess the presence of BTEX and PAH compounds, five monitoring wells were installed (S-01 / PM-01, S-02 / PM-02, S-03 / PM-03, S-04 / PM-04, S-05 / PM-05) in the analyzed gas station area. For the construction of monitoring wells, geomechanical-type PVC pipes with a diameter of 2 inches and depth ranging from 3.6m to 4.1m were used. All wells were installed in compliance with the monitoring well construction standard of ABNT NBR 13.895 / 1997.

Groundwater Sampling: Groundwater samples were collected from all monitoring wells (PM-01 to PM-05), tubular well (PT) and well (PC). For groundwater collection, a cylindrical stainless steel sampler was used, previously cleaned and decontaminated after each collection. The groundwater samples were stored in 40ml vials for BTEX determination and 1000ml amber glass vials for PAH determination. Laboratory analyzes were performed by a specialized chemistry laboratory in Brazil. BTEX compounds were analyzed according to US Environmental Protection Agency (US EPA) methods 5021A, US EPA 8015D and US EPA 8021B where the detection limit of the equipment was 0.0001 mg / l. PAH compounds were determined according to the US EPA 8270D method and the detection limit was 0.000008 mg / l.

The concentrations obtained during the VOC campaign are shown in Table 3. For this study, it was found the presence of VOC in most points investigated at a depth of 0.5m. At most of these points, when reaching 1.0m of drilling, the measured concentrations were zero. This configuration of vertical distribution of VOC in the ground is associated with small leaks / spills that occur during routine station services coupled with the type of pavement (parallelepiped) that allows contaminants to percolate during rainfall / vehicle wash events in the station area. However, at points GS 29, GS 30, GS 41 and GS 43, located immediately downstream of the tanks and supply runway, maximum concentrations (> 10,000 ppm) were identified at the two depths evaluated as shown in Figures 3 and 4 showing the distribution of contamination in the study area at depths 0.5m and 1.0m respectively. The results of all chemical analyzes of soil samples from a gas station in Igarassu were performed by Lins *et al*. (2019) for the parameters BTEX and PAH, and did not indicate concentrations above the reference values adopted on the soil surface, however, traces of compounds detected in the samples of a survey were observed. According to Skowronski *et al*. (2016), the highest concentrations of volatile organic compounds were found at a depth of 0.5 m in the area in the basins of two tanks. The main areas impacted by these compounds were 1.0 m deep near the six-tank basins. Lins *et al*. (2016) performed thirteen perforations (S-01 to S-13)



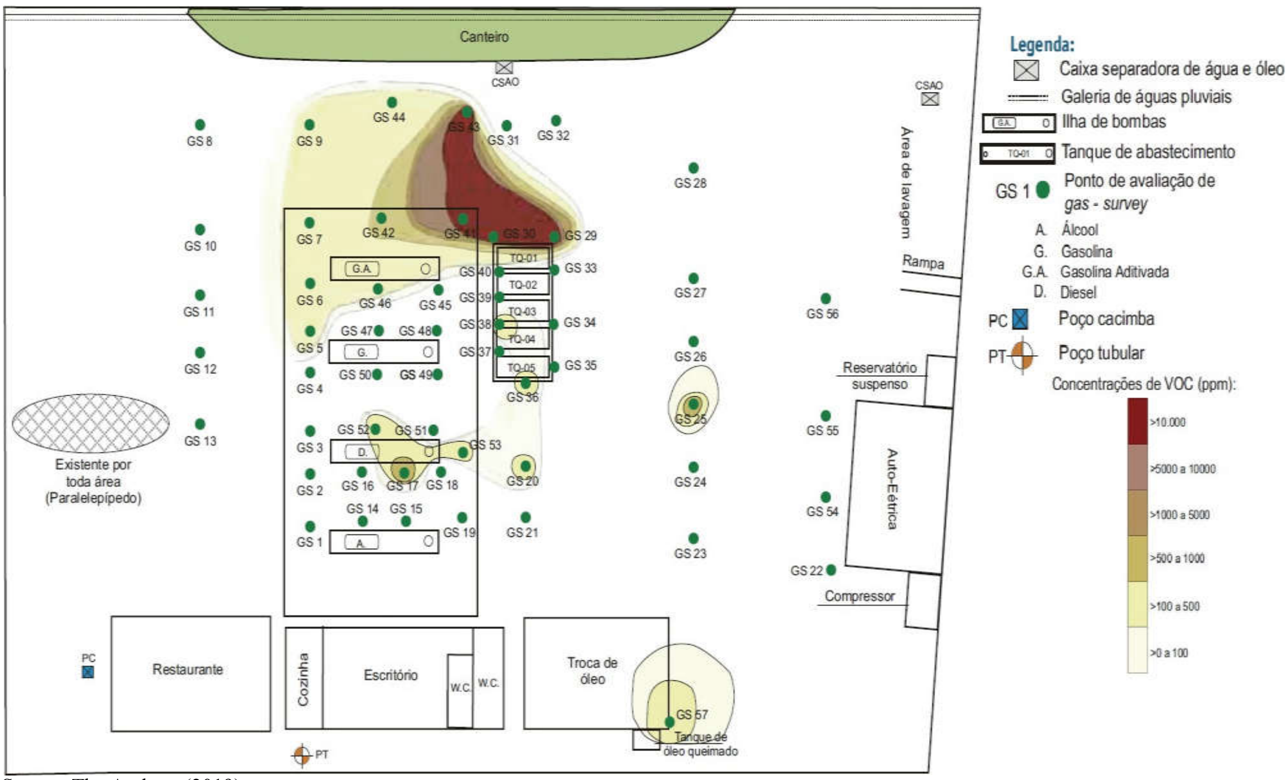
Source: The Authors (2019).

Figure 3. Station area with VOC concentrations at 0.5m depth

RESULTS AND DISCUSSION

VOC Campaign Evaluation: Fifty-seven perforations (GS 1 to GS 57) were performed, accompanied by VOC readings as a rapid response method, throughout the analyzed gas station area, as shown in Figures 3 and 4, for depths of 0.5 m and 1.0 m.

followed by VOC readings and results for each site at depths of 0.5 m; 1 m; 1.5 m ranged from zero ppm to 1098.1 ppm. After evaluating possible human interference at the study site that could have resulted in possible environmental damage, it was observed that the points S-01, S-04 and S-09 presented the highest concentration of VOC in the soil at a depth of 1.5m.



Source: The Authors (2019).

Figure 4. Station area with VOC concentrations at 1.0m depth

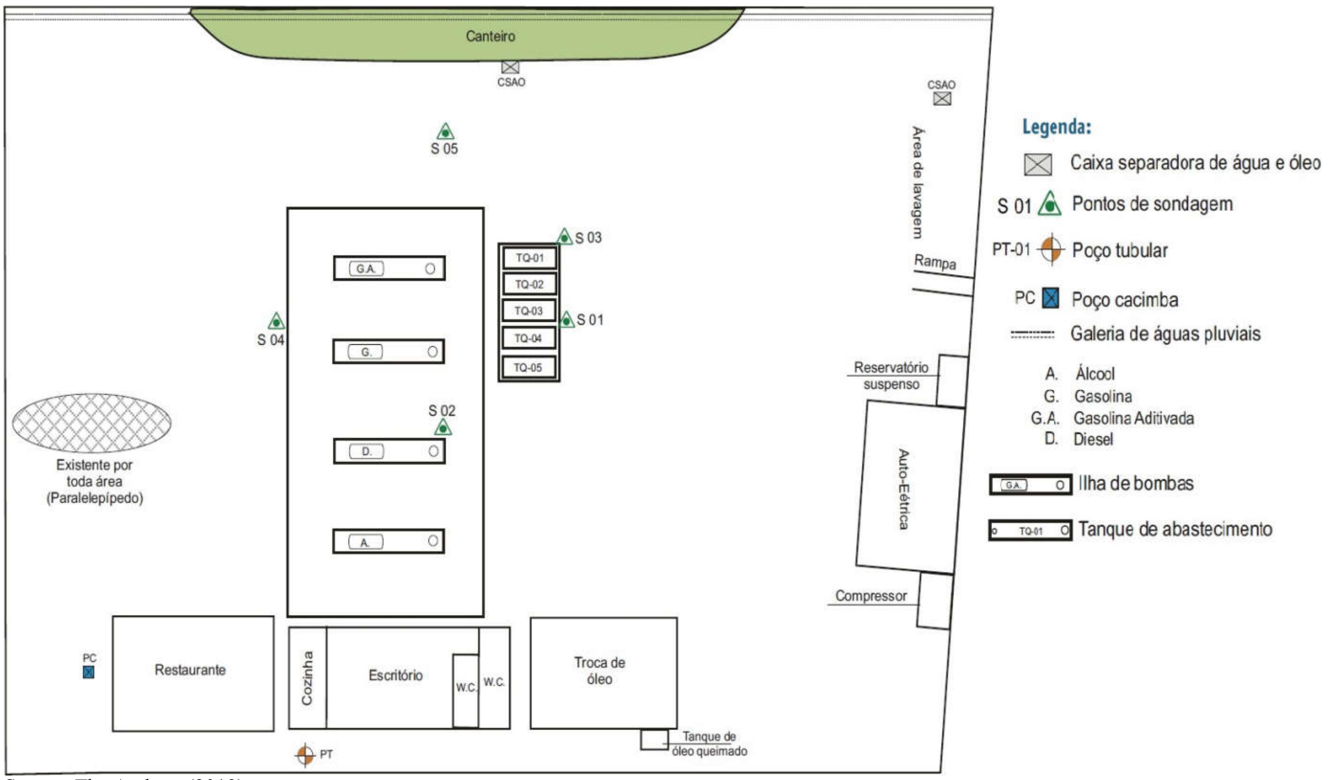
Table 3. VOC concentrations in ppm at 0.5m and 1.0m depth

Measurement point	VOC readings (ppm)		Measurement point	VOC readings (ppm)	
	0,5m	1,0m		0,5m	1,0m
GS 1	180	0	GS 30	> 10.000	> 10.000
GS 2	360	0	GS 31	540	0
GS 3	1260	0	GS 32	360	0
GS 4	1080	0	GS 33	0	0
GS 5	2160	360	GS 34	0	0
GS 6	1260	180	GS 35	900	0
GS 7	1440	180	GS 36	180	360
GS 8	360	0	GS 37	180	0
GS 9	720	180	GS 38	360	360
GS 10	720	0	GS 39	360	0
GS 11	900	0	GS 40	360	0
GS 12	360	0	GS 41	2160	> 10.000
GS 13	360	0	GS 42	1800	540
GS 14	540	0	GS 43	1800	> 10.000
GS 15	360	0	GS 44	720	180
GS 16	3960	0	GS 45	1620	0
GS 17	900	720	GS 46	540	180
GS 18	180	0	GS 47	720	0
GS 19	1260	0	GS 48	180	0
GS 20	540	180	GS 49	900	0
GS 21	360	0	GS 50	540	0
GS 22	0	0	GS 51	720	0
GS 23	4140	0	GS 52	900	180
GS 24	3600	0	GS 53	180	180
GS 25	1800	540	GS 54	0	0
GS 26	360	0	GS 55	180	0
GS 27	0	0	GS 56	180	0
GS 28	360	0	GS 57	360	180
GS 29	> 10.000	> 10.000	-	-	-

Source: The Authors (2019).

Lima *et al*. (2017) studying four gas stations in Cuiabá detected gaseous fumes from volatile organic compounds (VOC) in the soil, ranging from 999 to 4,620 ppm.

Survey Evaluation: Five drillings (S 01 to S 05) were carried out with a maximum depth of 4.1m, totaling 19.4m drilled. Surveys S 01 and S 03 were conducted near the tank area, surveys S 02 and S 04 were conducted near the fueling track and survey S 05 was conducted near the water and oil separator box. The location of the surveys is illustrated in Figure 5. The surveys carried out showed concentrations ranging from 0 to> 10,000 ppm, the highest concentrations found in the S 01 to 1.2 meter survey, the S 03 to 05 survey, 1.0 and 1.5 meters and the S 05 survey. at 1.0 meter depth according to Table 4.



Source: The Authors (2019).

Figure 5. Drilling points from drill holes S 01 to S 05

Table 4. Result of the in-depth VOC campaign during polls

Polling	VOC in-Depth			
	0,5m	1,0m	1,5m	2,0m
S 1/PM 1	0	0	> 10.000	*
S 2/PM 2	0	0	1.260	*
S 3/PM 3	> 10.000	> 10.000	> 10.000	900
S 4/PM 4	360	720	900	*
S 5/PM 5	180	> 10.000	*	*

Table 5. Analytical results of soil samples and Dutch List intervention values

Parameters	Analytical Results					Dutch List
	S 1 (1,2m)	S 2 (1,5m)	S 3 (1,6m)	S 4 (1,5m)	S 5 (1,0m)	
Benzene	0,123	0,006	0,06	0,001	0,217	1,0
Toluene	0,313	0,035	0,049	0,033	2,858	130
Ethylbenzene	0,0065	0,008	0,021	0,006	1,957	50
Xylenes	0,001	0,043	0,057	0,037	2,308	25
∑ PAH	1,911	1,0985	0,0212	0,216	0,6923	40

(concentration in mg/l).
Source: The Authors (2019).

Lima *et al*. (2017), when performing these same studies for the soils affected by gas oline, in the city of Cuiaba, found BTEX values up to 13,836 µg / kg, for depths higher.

Soil Analysis: According to the analytical results, BTEX and PAH concentrations were identified in all samples analyzed. The analytical results obtained were compared with the intervention values established in the Dutch List. None of the identified concentrations was found to exceed these intervention values as shown in Table 5.

Groundwater Analysis: Analytical results from ground water samples identified BTEX concentrations in all monitoring wells and catchment wells. As for PAH group compounds, concentrations of these compounds were identified only in them monitoring wells.

The identified concentrations were compared with the intervention values established in the Dutch List. As regards BTEX, it was found that Benzene concentration was exceeded in wells PM 01, PM 03 and PM 05; Ethylbenzene in wells PM 03 and PM 05 and, Xylenes and Toluenes in well PM 05. Regarding PAH concentrations, it was found that Naphthalene was exceeded in wells PM 03 and PM 05, Phenanthrene in wells PM 01, PM 02 and PM 04 and Chrysene in wells PM 01, PM 02, PM 04 and PM 05 according to Table 6. The results of the analysis of the COVs and PAH parameters (Table 4) for the ground water sample collected from the deep tubular well identified as Well 1, were lower than laboratory detection limits for all compounds considered. Teramoto (2015), during his doctoral studies on ground water contamination by BTEX compounds, also found, in several monitoring wells, benzene concentration values below the detection limit.

Table 6. Analytical results of ground water samples and Dutch List intervention values (concentration in mg / l)

Parameters	Analytical Results							Dutch List
	PM 1	PM 2	PM 3	PM 4	PM 5	PC	PT	
Benzene	0,4267	0,0114	1,2551	0,0085	10,7613	0,0142	0,0076	0,03
Toluene	0,0105	0,1124	0,0185	0,0627	17,6568	0,0212	0,0109	1,0
Ethylbenzene	0,0307	0,0004	0,2683	0,0012	3,7256	0,005	0,0025	0,15
Xylenes	0,0196	0,0115	0,0328	0,0057	15,4927	0,0227	0,011	0,07
∑ PAH	0,8096	0,0384	0,1049	0,0675	0,2708	n.d.	n.d.	n.e.

The problem is only its highest solubility value (1780 mg / L) and its partitioning to water is expected to be more effective. According to Ministério da Saúde No. 2,914 / 2011 (Brasil, 2011), benzeneis considered the most toxic compound among BTEX with potability standard of 5 µg / L and the most important absorption route of this compound is breathing because the area of there spiratory system capable of absorbing benzene is very large. According to Skowronski *et al.* (2016), the highest concentrations of volatile organic compounds at 0.5 m depth occurred: in the area of the two-tankbasins; near the loading platform; and next to the ward. The main areas impacted by these compounds at 1.0 m depth are located near the basins of six tanks.

Final Considerations

Hydrocarbon contamination of aquifers may make future use of these natural resources impossible. The high number offuel distribution stations in the Recife Metropolitan Region (around 700) justifies the concern about the negative impact that ground water may suffer in cases offuel contamination. Based on the environmental research study presented, it was possible to identify the existence of contamination in the gasstation area through the samples collected in the drilled wells, and found the presence of dissolved product in ground water at values above the established by the Dutch List (list of contaminated area management intervention guiding values used in the study year) for BTEX and PAH compounds. It is noticed that the contamination of ground water does not happen directly and with a large amount offuel, but with small quantities that are daily dispersed in the environment and that go unnoticed by the administrators of the posts, who only take action when there is a significant loss offuel.

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