Analysis of Underground Water Contamination Caused by a Refilling Station: A Case Study

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Abstract

Awareness on underground water contamination caused by leakage in gas stations has experienced recent increases both in lay people as well as in environmental regulation agencies. The most aggressive pollutants, both to the environment and to living beings, are present in gasoline, namely: benzene, toluene, etilbenzene and xylene, commonly called by the acronym BTEX. The present case-study aims to assess the contamination of underground water by a gas station located in the urban area of Recife, Pernambuco, Brazil. The study was carried out through environmental investigation and step definitions of the preliminary investigation and confirmatory investigation, offering technical orientations throughout the process. Analyzing the highest values from the VOC table, three water samples were collected and submitted to chemical analysis. Based on the results obtained, it was concluded that two samples had BTEX results above the upper limited defined by the regulation IN005. Therefore, a RCBA tier 2 risk analysis was recommended. The mentioned investigation determines the intensity of the contamination, the approximate area of extension and the risk it brings to human health and environment. Based on this result, it was determined whether there is need of intervention in the studied area

Keywords: BTEX, Contamination, Underground Waters, VOC, Analysis

1. *Introduction*

The contamination of hydric resources can be pointed out as one of the major problems faced by both developed and developing countries face. The population increase lead sub sequentially to an increase in industrial activities that has contributed to aggravate already existing environmental problems, especially those regarding conservation of soil and water, both superficial and underground waters. Knowing such, law and law enforcement regarding this area have become progressively sterner. Regardless of that, reports of tons of wastes being dumped in water beds, rivers and sea still remain frequent across the globe (Tiburtius *et al*., 2014). On a less perceptible scale, the amount of water adequate to human consumption has become scarcer. In such context, there is increasing concern over the quantity and quality of hydric resources. As reported by Custodio & Silva Junior (2008), underground waters play an essential role in the hydrologic cycle, being an important agent of biodiversity maintenance as well as sources of water storage for river and other superficial waters such as lakes and streams during periods of draught. The contamination of underground waters can be attributed to a great number of polluting sources, because most of human activities generate substances, waste, and/or effluents that are potential contaminants to different compartments of the environment, which in turn can affect the food chain and extend deleterious effects to human health in the long run (Cabukdhara & Nema, 2012).

Pollution caused by crude oil and its refined products has posed as one of the greatest threats to the environment because contamination of areas by hydrocarbons can cause severe damage to sanitation because of the possibility of contamination of water used for human supply (Cetesb, 2012).

The concern over contamination of soils and underground waters by volatile compounds (VOC) has been more frequently reported due to the awareness raised by recent events of major crude oil leakages and also by the risks offered to society and the environment. Even though these accidents had major repercussions, the most burdening source of this kind of contamination is considered to be the system of fuel storage tanks in gas stations (Brito *et al*., 2005). Contamination of soils and underground water by volatile compounds (VOC) has been on the spotlight in the last decades, mainly because of the frequency with which major contamination episodes have been reported with severe burdens to the environment. Although major oil leakages represent concerning events and draw media coverage, Tiburtius *et al*. (2005) state that the main source of contamination attributable to these compounds are caused by small, yet continuous, fuel leakage in gas stations secondary to the aging of fuel tanks. The complexity of this circumstances are even larger because such products play a major role in the composition of a wide variety of products with different properties and most of which have low relative solubility and small persistence in the soil.

These contaminants are the simple aromatic hydrocarbons, which constitute gasoline, known as BTEX (Brito *et al*., 2005). Such compounds present high water solubility and thus have the greatest potential of contamination of groundwater. Among the BTEX, benzene is considered the most toxic compound (Cetesb, 2012). The activity of gas stations is potentially polluting, given that inadequate structure to store products derived from petroleum, non-compliance to legal regimentation and even operational flaws all add to the already existing risk on this kind of business. According to Neves *et al*. (2012), this subject has drawn special attention from the scientific community due to its impact in both soil and water. According to the National Petroleum, Natural Gas and Biofuel Agency (Anp, 2016), in the State of Pernambuco – Brazil, alone, there are around 2818 gas stations, 516 of which are located in Recife, where average gas consumption in July was 26.471.758 kg of gasoline, and during the period of February to July 2016, the total consumption was of 154.257.574 kg. In this context, the present study aims to obtain the concentration of volatile organic compounds (VOC) in the monitored area of a gas station, detecting possible sources of contamination in order to compare the results with the limits established by the current legislation.

2. *Materials and Methods*

Environmental liability was assessed by a local environmental consulting company who started investigating a filling station located in the Metropolitan Area of Recife, Pernambuco, Brazil, with concerns regarding a possible contamination of an aquifer located in the station's surroundings. Soil contamination was not measured in this study. Three samples of groundwater were collected to assess the BTEX (benzene, toluene, ethylbenzene and xylene). Surveying was performed at strategic sites according to the identification of the highest concentrations of volatile organic compounds (VOC) obtained during VOC scanning, previously performed. Samples were identified as AS-01, AS-02 and AS-03 and sent to be characterized in laboratory.

2.1. Sample collection sites

The samples were collected in the Metropolitan Area of Recife, in the State of Pernambuco, Brazil. This State has an area of 98.076,001 km^2, with an estimate population of 9.410.336 inhabitants and population density of 89,62 inhabitants/km^2 (Ibge, 2016). The hydrology of the state relies heavily on the São Francisco river, which cuts through the southwest region receiving many effluents in its course, with its oriental part bathed by the Capibaribe, Ipojuca and Una rivers. The Metropolitan Area of Recife - RMR comprehends an area of 218,435 km^2, representing 2,82% of Pernambuco's area. Even though it comprises only a small percentage of the state, it contains 42,85% of the state's population with 1.625.583 inhabitants according to the last survey performed by IBGE (2016). The Metropolitan Area is divided in two sub-regions which are geologically distinct and, therefore, possess different natural aptitudes and responses to physical management, namely: Northern Metropolitan Area and Southern Metropolitan area. These two parts comprehend 14 cities, and amongt hem Araçoiaba, Igarassu, Itapissuma, Itamaracá, Paulista, Olinda, Abreu e Lima, Camaragibe, São Lourenço da Mata, Recife, Moreno, Jaboatão dos Guararapes, Ipojuca e Cabo de Santo Agostinho. In RMR there are 703 gas stations, which turns this region susceptible to aquifer contamination issues with petroleum derivatives, particularly gasoline contaminants, the BTEX.

2.2. Studied Area

All facilities of the fuel and oils market follow the standards established by Brazil National Standards Organization - ABNT (2005), which sets the parameters and measurements for the installations in order to prevent them from causing water and soil pollution as well as to secure consumer rights.

The installations found at the filling station were compose by

1. A pump with two nozzles for detergent gasoline and ethanol
2. A pump with two nozzles for gasoline and ethanol
3. A pump with two nozzles for gasoline and diesel
4. An underground gasoline tank with fifteen cubic meters with double walling
5. An underground tank with thirty cubic meters with detergent gasoline, ethanol and diesel, with double walling;
6. Forecourt in concrete;
7. A diesel filter;
8. An oil-water separator (SAO);
9. The pipeline that distributed fuel, made of non-metallic material (PEAD);
10. The tanks possess channel drains, petrol interception and vapor recovery valves
11. Product control is performed by electronic monitoring and LMC

The installations follow the model describe in Figure 1, where all equipment and building locations are represented

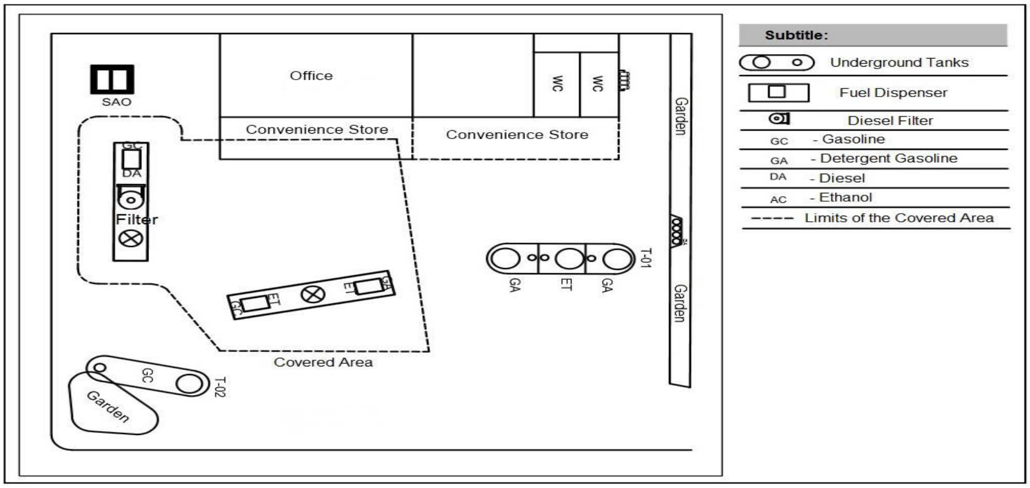

Figure 1: Installation blueprint

2.3. Characterization of the surroundings

In the process of characterization of the surroundings, the kind of territorial occupation in a 100-meter radius was one of the main goals. According to the regulation by ABNT NR 13.786/2005, the studied gas station is classified as Class 2, because it is located in an area of mixed occupation, constituted by local residences and stores as well as a religious temple, inside that 100-meter radius, as show in Figure 2.

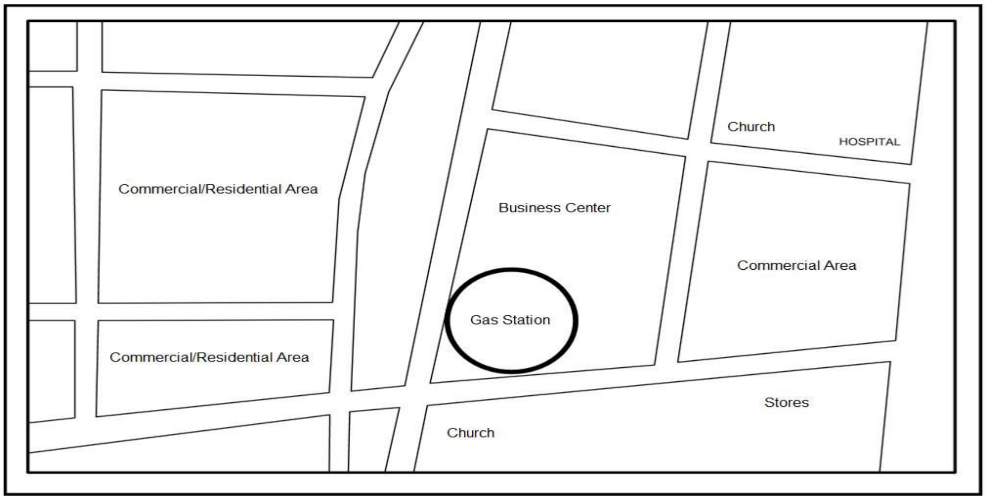

Figure 2: Characterization of the surroundings

2.4. Essay methodology

Measurements of volatile organic compounds (VOC) were performed aiming to identify the hot spots in order to guide the possible existence of contaminated areas through local measurement. The employed method consists in doing perforations of 1" in diameter and 0,5 m; 1,0 m and 1,5 m and inserting a socketed tube in order to screen for gases trapped in the soil, whose concentrations were measured by a vapor monitor attached, with a total of 13 perforations being done in the total area. VOC measurements were performed with the employment of an appropriate electronic device which detects and quantifies the gases, correlating the inherent explosibility of volatile low molecular weight hydrocarbons which are typical of low-weight derivatives (fuels, solvents, naphtha etc.). A portable organic value analyzer PID Ion-Science, Phocheck Tiger was employed. The portable gas monitors PID (Photo Ionization Detector) employ ultraviolet light to ionize the gas molecules. The PID are generally used to the detection of Volatile Organic Compounds (VOC's) in small concentrations. Regarding aromatic compounds, the readings can reach as low as a part per billion scale (ppb).

The calibration of such equipment is performed taking a hydrocarbon as standard. In the mentioned equipment hexane is employed and by its explosibility characteristics the concentration in parts per million (ppm) of the other light weight organic compounds is determined. The range of employment of such devices to Volatile Organic Compounds varies between zero and 10.000 ppm. It is worth pointing out that such device possesses special calibration, which allows excluding methane from the total quantification of volatile hydrocarbons. This avoids the inclusion of natural gas present in some organic soils with high microbiological activity, in order to avoid interfering with the readings. In order to achieve the necessary layer and industrial drilling machine with a 3/4" drill was employed. After drilling was complete, a metal bar with slots, to allow the passage of gas in its interior and make the suction job easier, was inserted. In the superior part of the bar a connection with the measurement device. At the end of each gas measurement, the hole was filled with a layer of cement, avoiding that products that eventually spilled could reach the soil through them. Thirteen perforations to perform the readings of Volatile Organic Compounds – VOC. The position of the perforations is represented in Figure 3.

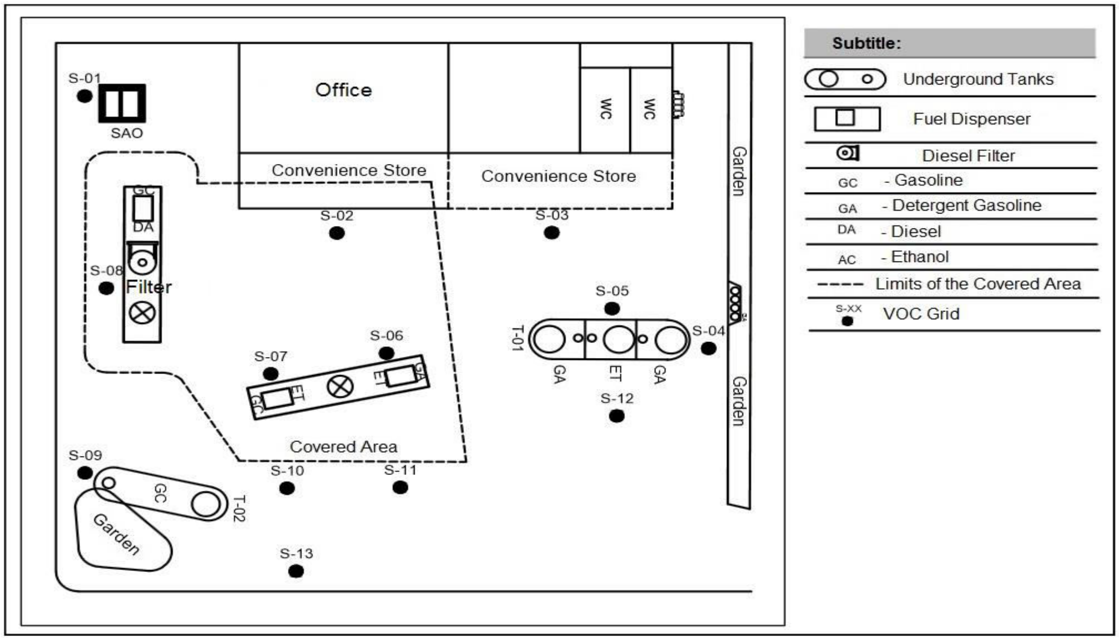

Figure 3: Volatile Organic Compound – VOC grid and perforation sites

2.5. Surveys

Three perforations by manual auger with a diameter of 4", inside the station area, aiming to intercept the aquifer and obtain water samples. The three surveys performed (AS-01, AS-02 and AS-03) were performed with the baseline results of the highest values of the VOC grid. The wells performed to the sampling were drained out, avoiding the collection of stagnant water. Samples were collected using a disposable bailer (specific container composed of a transparent PVC tube equipped with a retention valve made of Teflon, all labeled, and cooled to a target temperature of 15ºC using ice or ice bags, because BTEX contaminants were volatile in the environmental conditions of the collection. Therefore, conditioning is of fundamental importance to maintain integrity of the results to the following analysis at the laboratory.

2.6. Spreading mechanics of the contaminants

The spreading mechanics of the contaminants that are considered to be pollutants found in the samples are: air, for volatile organic compounds and groundwater to BTEX compounds. Such mechanisms allow transportation of pollutants to other regions affecting the surround community.

It has not been considered the soil as a transport mechanism, for its movement depends on human action or other natural causes, as erosion, to move and thus carry the pollutants.

3. *Results and Discussion*

3.1. Preliminary assessment of the contamination

Thirteen perforations (S-01 to S-13) accompanied by VOC readings as a quick response method were performed. The results were obtained from the VOC concentration in ppm for each site at the depths of 0,5 m; 1 m and 1,5 m and are presented in Table 1. The VOC measures ranged from zero ppm to 1098,1 ppm.

Table 1: Concentration of Volatile Organic Compounds - VOC in ppm

Survey	VOC (ppm) Depth 0,5 m	VOC (ppm) Depth 1,0 m	VOC (ppm) Depth1,5 m
S - 01	**901,2**	**922,8**	**954,3**
S - 02	1,2	3,8	5,9
S - 03	1,0	1,0	1,9
S – 04	**221,2**	**283,7**	**298,8**
S – 05	34,5	80,2	88,3
S - 06	107,1	119,0	143,1
S - 07	22,3	30,3	38,4
S – 08	12,90	16,30	19,1
S – 09	**1001,9**	**1066,0**	**1098,1**
S – 10	109,6	120,7	108,3
S – 11	111,2	119,3	123,1
S – 12	10,1	12,8	16,7
S – 13	212,4	240,7	249,9

After assessing possible human interferences in the study site which might have resulted in possible environmental damage, it was noted that points S-01, S04 and S-09 were the ones with the highest concentration of VOC in the soil at a depth of 1,5m. This is probably due to its location in a risk area, close to the water oil separator, underground tanks and supply line, a place where there is more manipulation of the fuels, thus increasing contamination risks. This step served as an orientation to locate the surveys performed in the confirmatory environmental assessment.

3.2. Confirmatory environmental assessment

Three surveys were performed (AS-01, AS-02 and AS-03) with a 2,5 m; 3,0 m and 3,5m depth respectively. AS-01 was performed close to the tank that stores detergent gasoline and ethanol. AS-02 was performed close to the gasoline tank. AS-03 was performed close to the water-oil separator. The location of the perforations is represented in Figure 4.

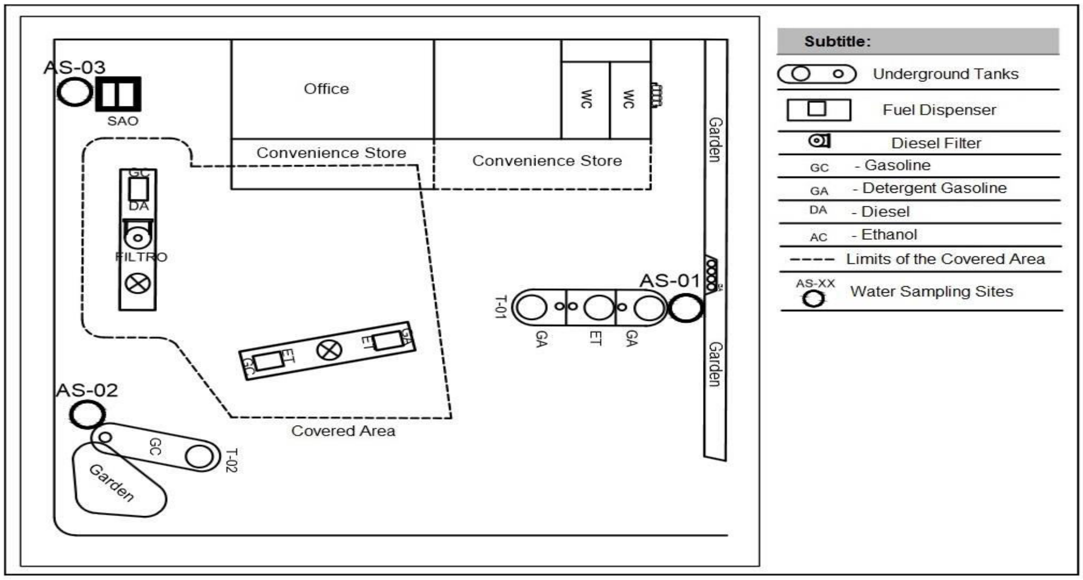

Figure 4: Perforation sites to water sampling

The surveys executed presented concentrations of VOC ranging from 298,8 to 1098,1 ppm, with the highest concentration detected in probe S – 09 at 1,5 m depth. The water sample of the perforations (AS-01, AS-02 and AS-03) were handed to the responsible lab to perform the chemical determination of BTEX. To assess the results found in the samples the regimentation IN nº 005/2006 (Cprh, 2006) was employed. Table 2 presents the comparison between the concentrations of BTEX found in water from the different samples and reference levels established by current legislation.

Table 2: Water analysis results and reference levels - RL

BTEX	UNITY.	AS 1	AS 2	AS 3		RL
Benzene	µg/L	151	8	ND		5,0
Toluene	µg/L	ND	ND	ND		170
Ethylbenzene	µg/L	16	ND	ND		150
Xylene	µg/L	9	ND	ND		70

Where ND = non-detected

According to the analytic results of the sample AS-01, a concentration above the reference levels dictated by IN nº 005/2005 which dictates the process of environmental licensing by Retail Fuel Stations located in the State of Pernambuco, Brazil as well as the procedures should any fuel leakage happen or environmental liability be detected in the stations. The values of benzene are approximately 30 times above the allowed value, which is 5,0 µg/L, indicating a serious risk for the population that consumes this water, who could develop central nervous system diseases or leukemia. The immediate effects of benzene exposure are upper airway irritation, non-productive coughing, dyspnea, nocturne wheezing as well as severe bronchospasm all proportional to the degree of exposure (Gordian *et al.*, 2010). Regarding xylene and ethylbenzene, they both presented abnormal levels yet all within the established limits. No irregularity was found regarding toluene. In the sample AS-02 it was evidenced the presence of the product dissolved in groundwater; however, only benzene was found with abnormal values above the stipulated by the IN 005 of CPRH. In the sample AS-03 no abnormality regarding BTEX compounds were found. In comparison with similar studies, Maranhão (2007) observed that groundwater collected from monitoring well presented the compound in a free phase supernatant with significate thickness, differently from what was found in the present study. However, a trend was noted in investigatory papers directed to collection of a level 2 risk analysis because most of the area is already contaminated by values that surpass the limits of a level 1 risk analysis.

4. Conclusions

The contamination of aquifers by hydrocarbons could end in future inutility of these natural resources. The elevated number of gas stations in the Metropolitan Area of Recife (around 700) justifies a concern over the negative impact that underground waters may suffer in cases of fuel contamination. After thorough laboratorial analysis of the samples collected, it was evidenced the presence of products dissolved in water in samples AS-01 and AS-02 in values that exceed the limits recommended by current legislation. In sample AS-03 even though a significant value (954,3 ppm) was found, no contamination was detected. This fact could be due to the differences in the depths of the survey and sampling, respectively 1,5 m and 3,0 m; double the depth, because the contamination zone could have been left behind because of the depth. The altered data found in samples AS-01 and AS-02 could be attributable to leakages in suction lines which conduct the fuel from the tanks to stations, in the underground fuel storage tanks, errors attributable to the professionals who work in the filling station, small cracks in the floor or even due to the existence of deactivated fuel tanks that remain buried in the perimeter. Generally, this kind of information regarding deactivated underground tanks is deliberately hidden by retail owners because charges and fines would be applicable because new laws regarding regulation, should overseeing institutions become aware of this facts. Such pitiful fact makes a more precise detection of contamination sources more difficult. Based on the analysis results and other assessments performed in the area, which identified the presence of compounds in the water samples in concentrations above the ones determined by IN 005 of the State's Environmental Regulation Agency, a Tier 2 RBCA risk analysis will be necessary. Such investigation aims to determine the intensity of the contamination, its approximate extension, and the risk it offers to human health and to the environment. If the results obtained by environmental investigation and risk analysis present above what is allowed, the remediation of underground waters is recommended until the compound's concentrations falls to within the limits determined by the current legislation. It is also important to point out that the presented recommendation allows for a technical solution that is adequate to the control and monitoring of possible environmental liabilities in the area, to be delivered. The results were obtained during the period of the investigation, any change in the current scenario can result in changes in the present results.

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