Jurnal Sains dan Teknologi Lingkungan Volume 10, Nomor 1, Januari 2018 Hal. 67-76
p-ISSN:2085-1227 dan e-ISSN:2502-6119

Investigation of Groundwater Pollution by Petroleum Hydrocarbon from Gas Station in Yogyakarta, Indonesia

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Abstract

Gas stations are common source of groundwater contamination by petroleum hydrocarbons. For example, these pollutants are health concern when people come in contact with the contaminated water when pumping from polluted wells. However, in Indonesia this problem remains largely ignored, despite some prominent leakage incidents at gas stations. The purpose of this study is to investigate the groundwater contamination by petroleum hydrocarbon from gas station in the greater Yogyakarta area in Indonesia. A gas station with a history of leakage incident and located in close proximity with dug wells in which its water had been used for human daily consumption was selected to be the source of groundwater pollution to be investigated. Groundwater samples were then collected from dug wells located in the vicinity to this selected gas station and then analyzed for benzene, toluene, ethylbenzene, xylene (BTEX) by gas chromatography/mass spectrometry. Out of six sampling points, BTEX were detected with concentrations ranging from 0,008 to 25,631 ppb. Concentration of benzene at sampling point 3 exceed the standards of Indonesian drinking water quality and WHO. These findings indicated that BTEX groundwater pollution may be a health hazard of currently unknown proportion in the greater Yogyakarta area. It is recommended to assess health risk associated with human daily consumption of BTEX polluted groundwater and also to test groundwater at all gas stations in this area and remediate those affected by BTEX.

Keywords: *BTEX, gas station, groundwater contamination, petroleum hydrocarbon contamination, risk analysis*

1. INTRODUCTION

Groundwater contamination is one of the prominent water problems in Indonesia. Many studies have shown facts of groundwater contamination by domestic wastewater or heavy metals from industries or landfills. However, sufficient concerns have not been put in place for petroleum hydrocarbon contaminants. Its widespread use of supporting human daily activities may contribute significantly to its high possibility of contamination to environment.

One potential source of groundwater contamination by petroleum hydrocarbon is gas station. There are around 5400 gas stations all over Indonesia mostly belong to Pertamina as state owned oil company and several others which are private-owned (Pertamina, 2016). Groundwater contamination might occur from oil spills or leakage from the underground storage tank (UST) system and pipelines. The failure to meet construction standards, lack of corrosion protection system, environmental contamination detection system and facility maintenance increase the possibility of the occurrence of groundwater contamination from this source. Muryani (2012) reported one prominent leakage incident occurred in gas station in Yogyakarta City area in 1999.

Dikirim/submitted: 16 November 2017
Diterima/accepted: 28 Desember 2017

Groundwater contamination by petroleum hydrocarbon from gas station would become serious health problem in Indonesia. As mostly located in populated area, tank or pipe leakage may reach the groundwater used by the people for their daily water consumption. Petroleum hydrocarbon contains various compounds considered as toxic and carcinogenic such as benzene, toluene, ethylbenzene, and xylene or widely known as BTEX (Turner and Renegar, 2017). While the leakage may occur in small magnitude to get notice, it will contaminate the groundwater continuously. Hence, regular and long term consumption of the particular groundwater for daily consumption would in the future be the cause of noticeable hydrocarbon associated health problems.

The purpose of our study was to investigate petroleum hydrocarbon contamination in groundwater from gas station in one area in Indonesia. The study area was in Greater Yogyakarta which represents the common situation of where gas stations are located in cities in Indonesia. Samples of groundwater from dug wells located in the vicinity to gas station with a history of leakage were taken and analyzed in the laboratory for the presence of BTEX to confirm the presumption of groundwater contamination. The outcome of this study will give input for the precaution measures should be taken to prevent groundwater contamination from gas station, while on the other hand this also gives information to what extent the remediation measure should be taken for the already contaminated sites.

2. MATERIAL AND METHODS

2.1 Selection of gas station

There are 32 gas stations in Greater Yogyakarta Area. Distribution of their location within this area is presented in Figure 1. Gas Station X has a history of prominent leakage in 1999, which was reported in a study by Muryani (2012). It was also located in close proximity to dug wells in which its water was used for people daily consumption.

2.2 Water sampling

The study by Muryani (2012) became the basis for selection of dug wells to be sampling points. Muryani (2012) developed a zonation map to show the level of groundwater contamination potential. According to Muryani (2012), potency of groundwater contamination by petroleum hydrocarbon is higher at wells located within the radius of less than 45 m. Then, based on this study, 6 (six) dug wells which are located 10-70 meters from gas station X were selected to be sampling points. Table 1 and 2 show the properties and coordinate of the sampling points.

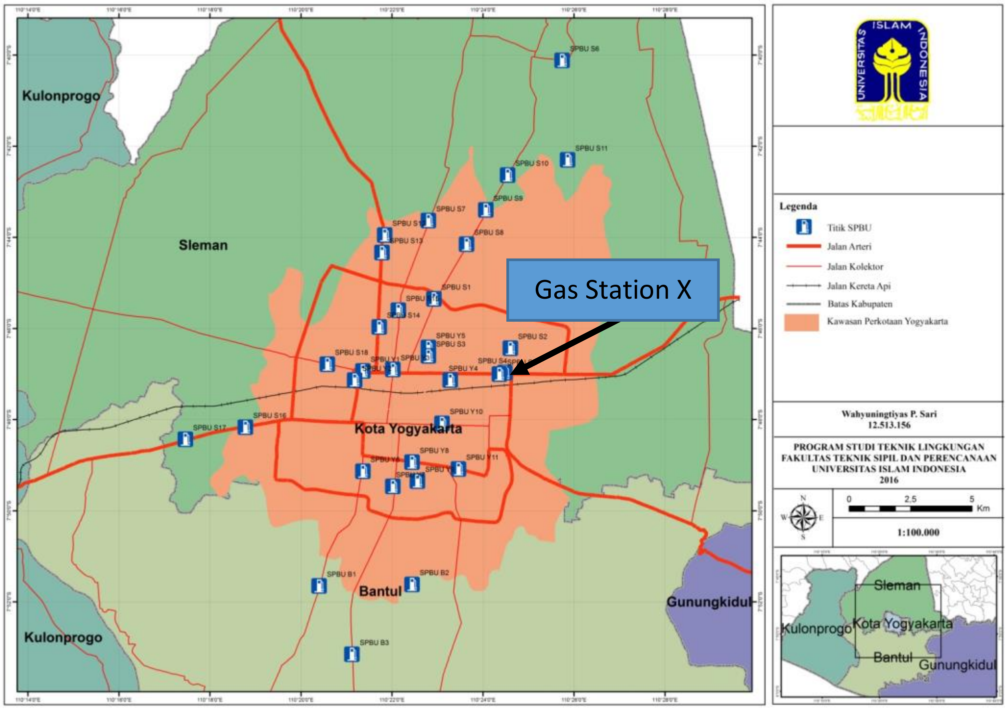

Figure 1. Gas station X among 32 gas stations in study area (Greater Yogyakarta Area)

Table 1. Properties of sampling points

Parameter	Sampling Points					
	1	2	3	4	5	6
pH	7,3	7,1	7,1	7,4	7,1	6,9
Temperature of water	27	27	27	27	27	27
Depth of dug well (m)	10	10	10	n/a*	8	n/a*
Water table (m)	6	6	6	n/a*	6	n/a*
Distance from gas station	±	± 30	± 48,7	±	± 70	± 46
Elevation of soil surface	128	128	128	128	127	128

*) Dug wells 4 and 6 were permanently covered by concrete

Table 2. Coordinate of sampling points

Sampling point	Coordinate
1	110°24'23.90"E
2	110°24'23.99"E
3	110°24'22.52"E
4	110°24'23.17"E
5	110°24'22.02"E
6	110°24'22.36"E

Sampling procedure was following SNI 6989.58:2008 for aromatic hydrocarbon. Samples were put in dark glass bottle to prevent sunlight, contamination and volatilization. During transfer from sampling site to laboratory, all samples were kept in cooler box with ice within to keep the temperature of samples. At the lab, samples were kept in refrigerator 4°C to prevent volatilization.

2.3 Laboratory analysis of BTEX in water samples

Petroleum hydrocarbon contamination was observed through the measurement of BTEX concentration in water samples. Head Space Gas Chromatography Mass Spectrometry (HS-GCMS) type HS Agilent 7697 A, GC Agilent 7820, and MS Agilent 5977B MSD were used to analyzed BTEX concentration in samples. Column HP 5-MS which specialized in BTEX and other semi volatile compound detection was used for analysis. Headspace unit in the instrument reduce the requirement for sample preparation for GCMS analysis. Headspace will volatilize target compound in water samples which will be transferred to GCMS for analysis.

2.4 Method optimization

Optimum condition of GCMS for analysis of BTEX was determined by selection of best optimum peak reading of 500 μg/L BTEX (mixed) standard in methanol solution. Methanol used to solute BTEX standard was HPLC grade from LiChrosolv. During optimization, GCMS was set in scan mode to detect all compounds in sample within certain period of time until all BTEX compounds were detected. SIM mode was then set to measure mass (m/Z) of each BTEX compound.

2.5 Linearity test, LOD and LOQ determination

Linearity test was conducted by GCMS analysis of a set of BTEX standard solution with concentration 0,05; 0,1; 0,2; 0,5; 1,0; and 2,0 ppm. The GCMS method used was that which has been determined during optimization. Correlation between analyte concentration and response of instrument was examined by using linear correlation equation $y = bx + a$ (b is slope, a is intercept, x is analyte concentration, and y is response of instrument). Linear correlation is indicated with $r^2=1$ (positive) or $r^2=-1$ (negative). LOD and LOQ was determined by calibration curve method. From the curve, the value of constant k is determined by dividing standard deviation by slope (b). LOD is 3 times k, while LOQ is 10 times k.

2.6 BTEX analysis of water samples

BTEX concentration in water samples were analyzed by using SIM mode HS-GCMS. Response of instrument which is represented in area of chromatogram was then plotted to calibration curve of linearity test to acquire concentration of BTEX in samples.

3. RESULT AND DISCUSSION

Table 3 presents data on properties of BTEX compound during GCMS preparation including retention time, m/Z value, linear equation and linearity value. Minimum concentration within linear range for benzene is higher compare to other BTEX compound. It means that this method is better for detection of Toluene Ethylbenzene and Xylene than for detection of Benzene. It might be also due to the use of mixed BTEX standard. Each compound may have different most reliable method for detection. So, it is better to use pure standard and develop method for each compounds of BTEX. On the other hand, Benzene has the highest volatile property among BTEX compound, so it is more difficult to detect at low concentration than other BTEX compound. However, the similar results presented by Serrano and Gallego (2004) which stated that the range of benzene and toluene are higher than 0,1 ppb which is in the range of 0,6 – 750. Other compound ranges between 0,5-750 ppb. Study conducted by Pijuan et al. (2012) presented similar result with minimum concentration of 0,2 ppb while for other BTEX compound are lower than 0,2 ppb (0,1 ppb for toluena, 0,07 ppb for ethylbenzene and 0,06 ppb for all xylene compound). Laboratory analysis of water samples from each sampling points is presented in Table 4.

Table 3. Properties of BTEX compound during GCMS preparation

Compound	m/z (mass)	Retention time	Linear regression equation	Linear range	Linearity(r^2)
Benzena	78	2,601	y = 267,62x +	100-1000	0,9987
Toluena	91	4,423	y = 421,09x - 12939	50-1000	0,9975
Etilbenzena	106,1	6,598	y = 514,88x - 16569	50-1000	0,9981
p-Xilena	106,1	6,790	y = 288,8x - 9315,1	50-1000	0,9982
o-Xilena	106,1	7,333	y = 176,55x - 4036,1	50-1000	0,9991
m-Xilena	106,1	7,499	y = 12,302x –	50-500	0,9967

Table 4. BTEX concentration in samples

Sampling Points	Concentration(ppb)						
	Benzene	Toluene	Ethylbenzene	p-xylene	o-xylene	m-xylene	Total xylene
1	9,368	0,340	1,014	2,507	25,631	3,008	31,15
2	ND	ND	0,064	1,125	23,365	7,397	31,89
3	11,509	0,347	0,688	0,724	24,033	7,478	32,24
4	ND	0,375	0,688	0,679	23,541	4,471	28,69
5	ND	0,686	0,008	0,249	ND	2,845	3,09
6	ND	0,686	0,008	0,249	ND	2,845	3,09
LOD	4,530	2,800	2,290	4,083	6,679	49,152	13,59
LOQ	15,100	9,330	7,630	13,610	22,260	163,840	45,30
WHO[b]	10	700	300	-	-	-	500
IND[c]	10	700	500	-	-	-	300

ND : Not detected
[b]Drinking Water Guidelines WHO 2008
[c]Peraturan Menteri Kesehatan No 492/2010 (Indonesian Drinking Water Standard)

Of six sampling points, benzene was only detected in sampling point 1 and 3. However, along with total xylene, concentration of benzene was detected above LOD value. Highest concentration of benzene was detected at sampling point 3 followed by sampling point 1. Study by Muryani (2012) presents zonation of contamination potential of hydrocarbon due to leakage incident of Gas Station X in 1999 based on LeGrand method as presented in Figure 2. This study suggests that the highest potency of contamination might occur in ring 1 which covers an area within the radius of 40 m from Gas Station X. Then, medium contamination potential occurs in ring 2 or area with less than 200 m distance from Gas Station X. Muryani stated than contamination would occur in south-southwesterly direction following groundwater flow. Sampling point 1 is located in ring 1, meanwhile sampling point 3 is located in ring 2. According to study by Muryani, sampling point 1 should have higher BTEX concentration than sampling point 3. At sampling point 2 and 4 which were also located in ring 1, benzene was not even detected. This is probably due to the fact that the leaking incident itself occurred in 1999. During those long years after incident, BTEX in the fuel material has undergone physical, chemical or biological processes. Most important of these processes are adsorption, desorption, and volatilization which influence BTEX migration (Zhang et al., 2015 in Yang et al., 2017). This may be the cause of the difference in the contamination pattern.

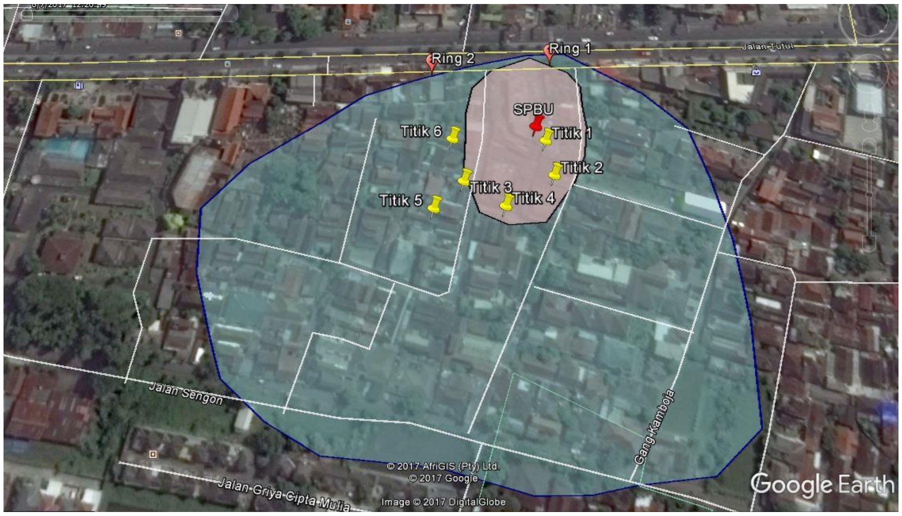

Figure 2. Sampling points (red point is gas station X)

Benzene was not detected at most sampling points except for 1 and 3. According to Weiner (2012), the order of BTEX compound removal in environment is benzene followed by toluene, ethylbenzene and xylene. Hence, benzene is the first to release due to its highest solubility and volatility. On the other hand, percentage of benzene in fuel composition is the lowest among BTEX compound which is around 1-5%. Mitra and Roy (2011) reported a higher composition of benzene in gasoline which is 11 % of benzene, 26 % toluene, 11 % ethylbenzene and the rest is for xylene's isomers. However, the concentration of benzene at sampling point 1 and 3 were higher than toluene and ethylbenzene. The possibility of other source of benzene should be considered. On the other hand, BTEX composition in gasoline products distributed in study area should be also investigated to ensure the source of BTEX contamination in environment.

Comparing to available standard on water quality as presented in Table 4, the benzene concentration in groundwater from dug well of sampling point 3 exceeded Indonesian and WHO drinking water standard. This finding indicates the potential of BTEX compound to be a common problem related to groundwater contamination in urban area in Indonesia as also reported by some studies. Wang et al. (2002) in Fayemiwo et al. (2017) reported the concentration of BTEX at near-surface groundwater (0-5 m) to be 155 µg/l. This study also presented the evidence that BTEX can be transported to great depths in groundwater with the detection of BTEX concentration of 2.6 µg/kg at its deeper level of groundwater (15-60 m).

In Indonesia, groundwater is still the major source of water for daily needs. Hence, the presence of BTEX in groundwater will pose threat to human health. Human can be exposed to BTEX in water through oral (consumption) and dermal route. Among BTEX compound, benzene is the most hazardous that it is considered carcinogenic (Deghani et.al, 2018; Rosales et.al, 2014). Data on BTEX concentration detected in groundwater and drinking water from various sources was reported by Leusch and Bartkow (2010) as presented in Table 5.

Table 5. Reported concentrations of BTEX in water (Leusch and Bartkow, 2010)

Media	Concentration(ppb)			
	Benzene	Toluene	Ethylbenzene	Xylenes
Groundwater	<0,1 – 1,8	<1 - 100	<0,1 – 1,1	<0,1 – 0,5
Contaminated groundwater	Up to 330	Up to 3.500	Up to 2.000	Up to 1.340
Drinking water	<0,1 - 5	<1 - 27	<1 - 10	<0,1 - 12

Leusch and Bartkow (2010) reported the estimation of daily intake of BTEX from drinking water is up to 10 µg for benzene, up to 43 µg for toluene, up to 20 µg for ethylbenzene, and up to 24 µg for xylenes based on 2 liters per day water consumption. As there was also report on bioaccumulation of benzene derivatives in marine organisms (Fayemiwo et al, 2017), then those low concentrations may be accumulated in human body and causing health problem in the future. So, although BTEX at study area were detected at relatively low concentration to cause direct health effect, long term consumption of BTEX contaminated groundwater can cause several health problems such as cancer (especially from benzene), problems on brain, nervous system, liver and kidney. Health risk analysis is necessary to conduct to determine the magnitude of the risk may cause by present state of BTEX contamination in study area.

4. CONCLUSION AND SUGGESTION

BTEX was detected in significant concentration in dug wells used as daily source of water for people surrounding a high-risk gas station in Greater Yogyakarta Area. As the water was used for daily water consumption, further study should be conducted to assess its associated health risk. On the other hand, similar test should be also conducted to all gas stations in this area.

5. ACKNOWLEDGEMENT

This work was supported by research grant funded by Directorate of Research and Public Service of Universitas Islam Indonesia.

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