original article

Determination of BTEX concentration in the groundwater of east region of Isfahan using passive sampling method

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ABSTRACT

Aims: This study was conducted to determine Benzene, Toluene, Ethylbenzene, and Xylene (BTEX) concentration regarding broken petroleum transmission pipeline in the east region of Isfahan, using passive sampling method.

Materials and Methods: Dialysis bags as passive sampling devices with molecular cut-off diameter of 12000 Dalton, 3.2 cm width and around 12 cm lengths were used that contain 2 ml of olive oil as an absorbent. These devices were placed, in 10 sampling wells for 45 days. In order to determine the absorption efficiency of these devices, laboratory calibration operations were performed at the same time. Nitrate as an indicator of contamination of groundwater with chemical fertilizers and also electrical conductivity (EC) as an indicator for cations and anions concentration was measured.

Results: The laboratory absorption efficiencies of BTEX were found to be 90%, 85%, 79%, and 81%, respectively. Concentration of these compounds in field samples were less than 10 μg/l. Nitrate concentration varied between 2.1 to 69.2 mg/l, and EC varied between 1.7 to 15.1 mS/cm.

Conclusion: BTEX compounds were absorbed with high efficiency in the laboratory test, but their concentrations in wells were found to be negligible. Average concentration of nitrate in the wells was less than water quality guidelines, and had no relation with the direction of movement or depth of water. EC tended to increase in the direction of groundwater movement, but there were no correlations among depth of water, nitrate concentration, and mean of EC.

Key words: Isfahan, BTEX, groundwater, passive sampling, semi-permeable membrane

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INTRODUCTION

BTEX compounds belong to oil hydrocarbons group. BTEX stands for the four oil compounds of Benzene, Toluene, Ethyl-benzene, and Xylene.[1] This compound enters the body through consumption of contaminated water, breathing, or absorption into the skin. BTEX is inhaled at gas stations, and is absorbed into the skin while swimming in contaminated

waters. Exposure to BTEX compounds can cause damage to skin, disorder of respiratory system, and damage to central nervous system. Long term exposure could have really undesirable effects on skin, blood circulation system, and kidneys.[2] Chemical characteristics of BTEX compounds are presented in Table 1.[3]

In recent years, some new methods of water quality monitoring have replaced conventional active sampling methods. Among these methods, passive sampling method could be mentioned in which a highly absorptive membrane is used for isolation of a phase from a water medium.[4] This method is based on pollutant transmission across a semi-permeable membrane with concentration gradient between two membranes sides. When the membrane is exposed to a solution, the specified compound is absorbed onto it. Then, the analysts tend to move in the direction of the least concentration until transmission level on both sides reaches a stable condition.[5]

Passive sampling has several benefits, regarding its operation, including effectiveness, low cost, little training required for operating the equipment, and no need to energy source. In addition, this method is often used for collection of data on mean concentration of a compound over a particular period of time, and this is called average time-weighted concentration.[6]

One of the most important difficulties in connection with the quality of groundwater is the level of nitrate concentration in these waters consumed by communities. Usually inside body, nitrate rapidly transforms into nitrite, and in infants this transformation can cause Methemoglobinemia. Also, some forms of cancer related to formation of nitrosamines inside body have been found in older age group.[7,8]

In 2009, Ebrahimi *et al.*, conducted a study on application of passive sampling technique in measuring chlorinated pesticides in groundwater of south Lenjan, Isfahan. The results showed that some small amounts of contaminants that could not be measured by conventional methods previously could now be measured using passive sampling method.[9]

In a study conducted by Faina *et al.*, in occupied Palestine, 2 km from Mediterranean shore on natural reduction of MTBE and BTEX compounds in a shallow coastal aquifer contaminated with petroleum used passive sampling method over a period of 21 days.[10]

Martin *et al.*, in Germany, in their study on field monitoring of groundwater pollution to comparison of time-integrated

ceramic dosimeters and conventional water sampling, succeeded to detect benzene in groundwater.[11]

The results of study was carried out by Kamal *et al.*, indicated that level of BTEX in groundwater could be estimated using gas chromatography-mass spectrometry technique.[12]

This study aimed to use passive sampling method as a new technique in determination of BTEX concentration in the east region of Isfahan. In this study, level of EC in sampling wells as an indicator of concentration of cations and anions, and also, concentration of nitrate as an indicator of contamination of groundwater with chemical fertilizers also were measured.

MATERIALS AND METHODS

In this descriptive-cross sectional study, 10 wells out of a total of 80 agricultural wells were chosen. The nearest well was less than 1 km away from the location of incidence, and the farthest well was more than 3 km away. The location of sampling wells in the study area are depicted in Figure 1.

Selection of sampling wells
Considering the high number of wells in a vast area, and also high cost of BTEX compounds analysis, the first stage of this study was to select sampling wells through field survey. After inspection of the area, 10 private agricultural wells were selected. The criteria for selection were the depth and activity of the wells, coverage of the whole area, and also direction of movement of groundwater in the area of incidence.[13] Details of these sampling wells, which were found through inspection of the area and databanks of Isfahan regional water organization, are shown in Table 2. Groundwater levels in the wells were 18 to 30 m.

PREPARATION OF SAMPLING DEVICES

Preparation of passive sampling devices was as follows:
Dialysis bag provided by Supelco company with molecular cut-off diameter of 12000 Dalton and 3.2 cm width, was placed in distilled water for a few hours, until two layers of the bag opened up. Then around 12 cm of the membrane was cut and one side was completely fastened with a thread so that the effective length of each membrane became 10 cm. Two ml of olive oil was analyzed to make sure it did not contain any BTEX compounds, and poured into the membrane as an absorbent. The other side of the membrane was sealed tightly with the same thread.

Table 1: Chemical characteristics of BTEX compounds[3]						
Properties	Benzene	Toluene	m-Xylene	o-Xylene	p-Xylene	Ethyl benzene
Water solubility (mg/l)	1700	515	160s	175	198	152
Octanol-water partition coeff. (at 20 C)[log kow]	2.13	2.69	3.20	2.77	3.15	3.15
Polarity	Non-polar	Non-polar	Non-polar	Non-polar	Non-polar	Non-polar
Maximum contaminant level (mg/l)	0.005	1	10	10	10	0.7

MCL: Maximum contaminant level, BTEX: Benzene, Toluene, Ethyl-benzene, and Xylene

Laboratory calibration

The purpose of performing laboratory calibration was to find effectiveness of the passive sampling devices in absorbing BTEX compounds. For this purpose, solutions with concentrations of 1000, 1500, 2000 µg/l and also a blank sample prepared in 1 liter dark glass containers with lids were used. Then the prepared passive sampling devices were placed inside three containers and to prevent evaporation of BTEX compounds container lids were secured with parafilm and glue. These containers were then placed on a magnetic stirrer to simulate real conditions of the wells.

Placing sampling devices in the wells

To protect the membranes when placing in water, prepared membranes were put inside plastic containers with lids and some holes were made around the container walls to cause free flow of water. To produce a suitable weight and also to prevent floating, a piece of lead was attached to these containers. These sampling containers were placed inside the sampling wells for 45 days, which was the same duration as in laboratory.

Samples for nitrate and electrical conductivity analysis

Samples volume for analysis of nitrate and EC was 1.5 liter and sampling was carried out using conventional grab sampling method in accordance with standard methods.[14]

Analysis of samples

Analysis of BTEX compounds in olive oil samples were done using an Agilent Technologies gas-chromatography system (model: 7890A GC system), equipped with mass detector and a capillary column of HP5 MS (30 m length, 0.25 mm diameter, and 0.25 µm film thickness) containing the carrier gas of helium with flow rate of 1.5 ml/min and by means of headspace method. Duration and temperature of incubation were 30 min and 90°C, respectively. Magnetic rotational speed, volume of injection, and injection temperature were 700 rpm, 1 ml, and 200°C, respectively. The temperature of the column was first 30°C for 10 min and then reached 60°C with the ramp of 5°C/min. After one minute, temperature reached 200°C with the ramp of 20°C/min and remained at this temperature for 2 min.[15]

Samples taken for nitrate and EC analysis were transferred to the chemical laboratory immediately. Concentration of nitrate was measured using a spectrophotometer, DR-5000 system (HACH LANGE, Germany), and level of EC was determined in the sampling location using HACH EC meter model of Sension 7. ArcGIS 9.3 was used for zoning map production using information obtained from analysis of these compounds.

RESULTS

With regard to contamination caused by the breakage of a 16 inch petrol transmission pipeline, in the 37 km the east region of Isfahan, Iran, due to road construction operations in march 2011, which leaked one million liters of petrol into the ground, this study was conducted to assess groundwater contamination with BTEX, within 3 months in 2011. As, there has never been any concerns regarding oil compounds pollutions in the east region of Isfahan, or have not been detected by conventional analytical methods.

After analyzing laboratory samples, efficiency of passive sampling devices for absorbing compounds of Benzene, Toluene, Ethyl-benzene, and Xylene was 89.7%, 85.3%, 79.2%, and 81.3%, respectively. These results are presented in Table 3.

Table 2: Sampling locations details in the study area						
Location number	Type	Distance from incidence point (m)	Aquifer type	Longitude Utm-x	Latitude Utm-y	Surface of water (m)
1	VDTW[1]	289	Deep	605877	3617847	22.3
2	AW[2]	248	Shallow	605900	3617889	30.3
3	STW[3]	291	Shallow	605917	3617849	27.3
4	AW[2]	3200	Shallow	606339	3614950	18.3
5	AW[2]	3000	Shallow	605887	3615120	23.3
6	AW[2]	2800	Shallow	605853	3615361	24.3
7	AW[2]	1900	Shallow	605437	3616292	24.3
8	AW[2]	2800	Shallow	606026	3616147	27.3
9	AW[2]	2000	Shallow	606578	3615400	25.3
10	AW[2]	3200	Shallow	606602	3615024	26.3

[1]VDTW: Very deep test well, [2]AW: Agricultural well, [3]STW: Shallow test well

Table 3: Determination of BTEX compounds absorption efficiency by oil								
P.C. (ppm)	Benzene		Toluene		Ethyl benzene		Xylene	
	S.C. (ppm)	A.E. (%)	S.C. (ppm)	A.E. (%)	S.C. (ppm)	A.E (%)	S.C. (ppm)	A.E. (%)
1	0.83	83	0.74	74	0.59	59	0.63	63
1.5	1.3	86.7	1.28	85.3	1.2	80	1.29	86
2	1.99	99.5	1.93	96.5	1.97	98.5	1.9	95
MA(%)		89.7	-	85.3	-	79.2	-	81.3

PC: Primary concentration = Prepared concentration in water solution at the beginning of laboratory calibration, SC: Secondary concentration = Read concentration in oil at the end of laboratory calibration operation, AE: Absorption efficiency, MA: Mean absorption (%)

Results of the analysis of oil samples inside field passive sampling membranes showed that concentrations of BTEX in all samples were less than 10 µg/l. Results of nitrate analysis showed that nitrate concentration during the study varied between 2.1-69.2 mg/l, with the average ± standard deviation of 15.8 mg/l ± 21.3 mg/l. Electrical conductivity in the wells also varied between 1.69 to 15.10 mS/cm, with the average ± standard deviation of 5.4 mS/cm ± 4.9 mS/cm. The results obtained from nitrate and EC analysis are presented in Figures 2 and 3, respectively.

DISCUSSION

The results obtained from analysis of BTEX compounds in laboratory sampling devices showed that passive sampling method with a semi-permeable membrane and olive oil as absorbent was highly efficient. Results of this study were consistent with other studies including studies done by Ebrahimi *et al.*,[9] and Esteve *et al.*,[16] in which olive oil was used as absorbent for absorption of organochlorine pesticide compounds and BTEX, respectively.

As mentioned previously, BTEX concentrations in all field samples were less than 10 µg/l. In a study by Faina *et al.*, BTEX concentration in the studied area varied between 5 and 4230 µg/l[10] which has been several times more than BTEX concentration found in this study. Also, Martin *et al.*, in their study found concentration of benzene in groundwater between 150 and 250 µg/l.[11] Method of passive sampling in both studies identified various concentrations of BTEX, which conformed to the results of this study.

In the area of the incidence, BTEX compounds could not be detected and this might be due to volatility of these compounds or their absorption into the earth. The unpublished results of the grab sampling done from some wells near the incidence location by the local authorities, one month after the incidence, also confirmed that concentrations of three compounds of toluene, ethyl-benzene, and xylene in the agricultural wells in the study area were lower than the drinking water quality guidelines, and only the concentration of benzene was higher than standard for drinking water. Based on the mean speed of the groundwater flow, it was expected that the contaminants would reach the first well in the 1 km away from the location of incidence after 166 days and reach the farthest well in the more than 3 km away after 2 years. However, sampling in this study, 8 months after the incidence, in the wells in the direction of water flow detected none of the BTEX compounds even with the use of passive sampling method in which even negligible concentrations are detectable.

Based on the results of statistical analysis, there was a significant difference between the mean concentration of nitrate in the sampling wells and the water quality guideline
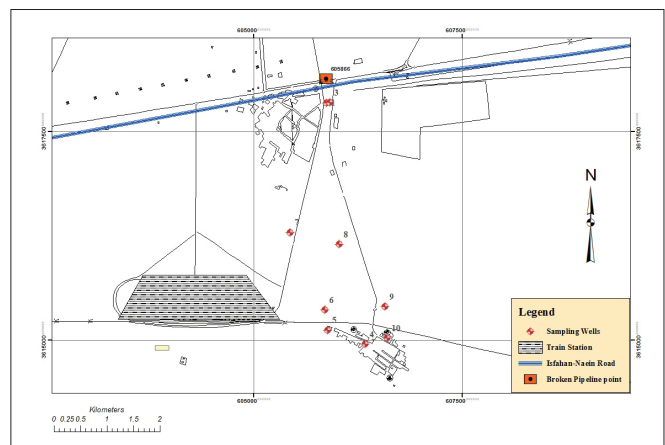

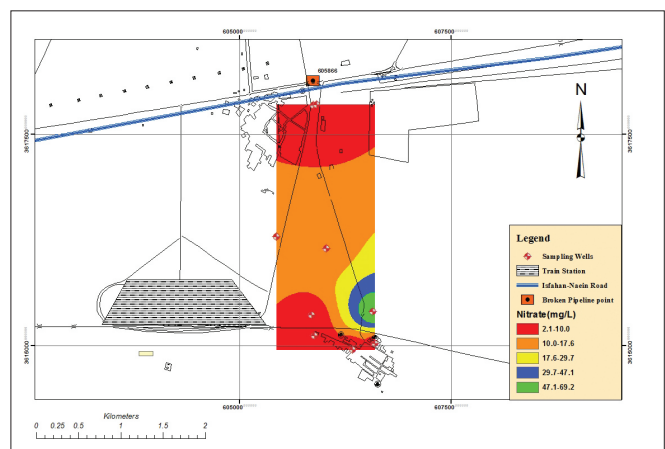**Figure 1:** Location of sampling wells in the area under study

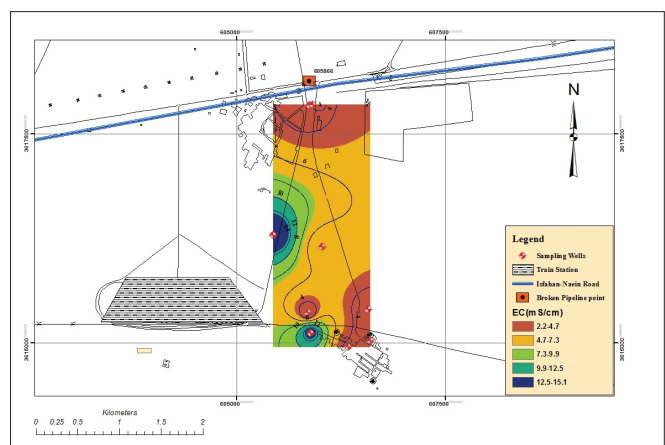**Figure 2:** Zoning the studied area with respect to nitrate concentration

Figure 3: Zoning the studied area with respect to level of electrical conductivity

value (50 mg/l) ($P < 0.001$), i.e., mean nitrate concentration in sampling wells during the study was less than the standard. Results of this study conformed to the results obtained by Amin *et al.*, on the concentration of nitrate in the south Lenjan region, Isfahan, Iran.[13] However, the results do not agree with those obtained by Gheysari *et al.*,'s study

on evaluation of nitrate contamination of groundwater in the east region of Isfahan in which sampling that nitrate concentrations were over 50 mg/l in 80% to 90% of wells.[17]

According to Figure 2, the highest concentration of nitrate (69.2 mg/l) was in the southeastern region of the area, and the lowest one was in the south of the area. As, direction of the groundwater flow is toward the south and southwest of the area, no correlation could be found between increase or decrease of the nitrate concentration and the direction of groundwater flow. In the case of a well containing nitrate concentration higher than water quality guidelines due to proximity to housing estates, sanitation activities and preventing entrance of agricultural and human sewage could solve the problem of contamination of water with nitrate.

Correlation analysis results showed that there was no correlation between mean nitrate concentration and depth of water in the wells ($P = 0.80$, $r^2 = 0.091$). This means there was no relationships between nitrate concentration and variation in depth of water in the wells.

Based on Figure 3, the highest value for EC (15.10 mS/cm) was found in the west of the area and the lowest value was found in the north. Comparison of the increase rate of EC value with the direction of groundwater movement showed a positive correlation. Regarding that EC is a function of dissolved solids in the water, these compounds are dissolved in water when it moves over the earth and bedrocks. That is why value of EC increases with direction of movement of groundwater. Also, as CO_2 is dissolved in rain drops falling to the ground, its amount increases in the water. Due to the effects of evaporation of compounds, ion exchange, and topographic conditions, EC values increases in the direction of groundwater.[18]

Correlation analysis results showed no relationship between mean value of EC and depth of water in the sampling wells ($P = 0.61$, $r^2 = -0.187$), which means there was no relationship between value of EC and depth of water. Results of this part of the study showed no correlation with results of the study by Amin *et al.*, which considered EC value of groundwater in Lenjan region, Isfahan, center of Iran.[11] Correlation analysis results showed no relationship between value of EC and nitrate concentration in the sampling wells ($P = 0.85$, $r^2 = -0.068$), which means there was no relationship between EC values and nitrate concentrations. Results of this part of the study showed a good agreement with those obtained by Amin *et al.*, on EC values in the groundwater of Lenjan region, Isfahan, Center of Iran.[13]

Presenting of high value of EC in a water resource possibly indicates a high concentration of other contaminants such as nitrate and other compounds.[13] In the studied area, as mentioned before, there was no relationship between measured concentration of nitrate and EC values. Therefore, a direct relationship between nitrate concentration and BTEX compounds is understandable.

CONCLUSIONS

Concentration of BTEX compounds in the east region of Isfahan, 8 months after the petroleum transmission pipeline damage, was less than $10\,\mu g/l$. Mean nitrate concentration in the sampling wells during the study was less than the water quality guidelines. Also, no correlation were found between increase or decrease in nitrate concentration and direction of water flow and mean nitrate concentration and depth of water in the sampling wells. Value of EC increased in the direction of water flow, and mean EC value, nitrate concentration, and depth of water had no correlation with each other.

As passive sampling method is a new method of sampling low-level contaminants with high precision, application of this method for assessment of BTEX concentration in earth and groundwater in the regions exposed to oil compounds leakage is highly recommended. Application of this method with other absorbents could also be useful for assessment of concentration of other contaminants.

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