Determination of Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) in Produced Water by Solid Phase Microextraction with Gas Chromatography Flame Ionization Detector (GC-FID)

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Abstract

During the production of crude oil and gas, large amounts of produced water are generated. These waters have to be analyzed with relation to the chemical composition to figure out the environmental impact of its discharge. Therefore, a study was carried out to evaluate concentration of the BTEX (benzene, toluene, ethylbenzene and xylenes), in produced water samples taken from production facilities and the disposal pit at the oilfield, Libya. SPME with Gas Chromatography Flame Ionization Detector (GC-FID) methods was optimized to determine the target compounds. The results showed that concentrations of the target compounds in the produced water samples ranged from 0.13 to 1.86 ppm. In addition, BTEX values are much higher, (1.86 and 1.70 mg/l), at storage tank outlet (TA,) and discharged stream (pump) respectively, where the produced water is in the earlier steps, before discharging to the pits. In the pit samples (Spt1, Spt2, Spt3 and Spt4) the BTEX values range between 0.11 to 0.22 mg/l. In general, produced water sample taking from the disposal pit contained lower BTEX concentrations than those from the production facilities.

1 Introduction

Oilfield produced water is a term used in the oil industry to describe the water that is produced associated with the crude oil and/or nature gas. Basically, produced water is a combination of formation and injection process water that contains oil, salts, solids, trace elements and production chemicals. It is the largest waste product discharged into the surrounding environment during crude oil and gas production. The volume of PW is continuously increasing, as long as the oilfields reach maturity (Stephenson, 1992, Abdol-Hamid, et al., 2008, Yeung, et al., 2011 and Ebrahimi, et al., 2012). These waters contains elevated concentrations of dissolved solids, high salt content, heavy metals, dispersed oil, dissolved organic compounds (including hydrocarbon), organic acid, phenols, production chemicals and gases as well as production chemicals which use to protect the production facilities from corrosion and scale deposition and in oil water separation. Besides these constituents, produced water may also contain low levels of Naturally Occurring Radioactive Material (NORM) (Stephenson, 1992, Gray, et al., 1993, Neff, 2002, Thomas, et al., 2004 and Ebrahimi, et al., 2012). Produced water as discussed above usually contain organic constituents such as dispersed droplets of crude oil, dissolved hydrocarbon (volatile hydrocarbon BTEX and aromatic hydrocarbon PAH). These hydrocarbons in produced water can be found with varying concentrations as free floating, emulsified, dissolved, or adsorbed to suspended solids which are discharged into the environment associated with the produced water (Thomas, et al., 2004 and Lu, et al., 2006). Produced water discharged to the environment contains large amounts of various hazardous organic compounds including benzene, toluene, ethylbenzene, and xylenes (BTEX) (AlSalka, et al., 2010). However, BTEX are toxic and the most harmful contaminants present in the produced water since it is recognized as a carcinogenic and has an adverse effect to human health and the environment. Contamination of water by these compounds is a very serious problem (Neff, 2002, AlSalka, et al., 2010, Deriszadeh, et. al., 2010, AlSalka, et al., 2011, Sundt, 2011 and Costa, et al., 2012). The discharge of produced water containing these pollutants can lead to contamination of soil and aquifers. The chemical composition of produced water is field dependent. Therefore, the detailed chemical characterization of produced water from oilfield is necessary in order to predict the fate and effects of the produced water discharged to the open environment. Taking into account the above considerations and considering that, to date, no data on chemical composition of the oilfield produced water collected from the oilfield have been reported in the literature. So, this paper gives a preliminary evaluation of the levels of BTEX in the produced water from the production facilities and the disposal pit taken from the oilfield, Libya by using solid phase microextraction (SPME) and gas chromatography with flame ionization detector (GC-FID).

2. Materials and Methods

2.1 Sample collection

Produced water samples were collected from one of the Libyan oilfield, i.e. two from production facilities (TA and Pump) and the four from disposal pit (Spt1, Spt2, Spt3 and Spt4).

For the BTEX analysis the sample bottle was filled to capacity with produced water to avoid any headspace, then the bottles were sealed and transported to the laboratory and were preserved at a temperature of 4ºC until analysis.

2.2 Standard preparation

Stock solutions of BTEX (2000 µg/ ml) were prepared at six different concentrations by dissolving a calculated amount of each concentration in methanol to obtain working standards. A series of BTEX standards solutions were prepared in water by injecting known volume of 100 ppm BTEX in methanol to the 25 ml organic free water in the sample vial which gives spiked water solutions to cover the range of interested concentration (CH424 Instrumental Analysis Lab, 1998 and Li, et al., 2010). Six point calibrations (based on peak areas) were obtained over the concentration range of interest. Linear calibration curves were obtained for all sample concentration ranges that were determined. Calibration curve correlation coefficients were higher than 0.9944. The analytical calibration curves were used for quantification of each BTEX in produced water samples.

2.3 BTEX Extraction Method

In order to obtained standard BTEX calibration curves the series of standards BTEX prepared in water were analyzed under the same GC-FID condition as the samples. Beginning from the lower BTEX standard in water, a 25 ml was taken and transferred to sample vial containing magnetic stirrer and start starrier the solution then, a syringe needle containing the 100 µm polydimethylsiloxane fibre (PDMS) penetrated the vial stopper, and the fibre was then lowered into the headspace located above the sample solution by depressing the plunger. The solution was vigorously stirred at 40 °C for 15 min at 1000 rpm. When the adsorption step was completed, the fibre was withdrawn into the needle, and the syringe was removed from the vial. The final step was thermal desorption of the analytes from the solid-phase microextraction fibre in the GC injector at 270 °C for 2.5 min (CH424 Instrumental Analysis Lab, 1998, Gaujac, et al., 2008 and Li, et al., 2010). The other concentrations of BTEX standards prepared were then carried out under the same experimental condition in order to construct the calibration curves by plotting the peak area against the concentration of standards BTEX used.

For produced water, a 25 ml aliquots of non filtrated produced water sample was placed into the 25 ml sample vial containing a magnetic stirring which were then sealed using butyl rubber stoppers wrapped with Teflon sealing tape. A syringe needle containing the 100 µm polydimethylsiloxane fibre (PDMS) penetrated the vial stopper, and the fibre was then lowered into the headspace located above the sample solution by depressing the plunger. The solution was vigorously stirred at 40 °C for 15 min at 1000 rpm. When the adsorption step was completed, the fibre was withdrawn into the needle, and the syringe was removed from the vial. The final step was thermal desorption of the analytes from the solid-phase microextraction fibre into the GC injector at 270 °C for 2.5 min. The SPME was conditioned by desorption for 5 minutes in a GC injector in order to flush out any of the fibre impurities before the next sample analysis (Gaujac, et al., 2008 and Li, et al., 2010).

2.4 GC-FID conditions

A Varian 3800 gas chromatograph equipped with a flame ionisation detector and a splitless injector was used for the quantification of BTEX. A chrompack capillary column [CP. Sil-8] CB with 60 meter length × 0.32 mm internal diameter and 0.40 µm film thickness supplied by J and W Scientific (UK) was employed with helium as carrier gas at flow rate of 1.5 ml/min and 1µl injection volume. The column temperatures programs of the gas chromatography (GC) system were as the follows: initially temperature at 35°C for 1 min, and then the temperature were increased to 300 at a rate of 5°C/min and holding for 4 min to give a total run of 38 min. The injection and detector were operated at 270 and 300°C respectively (Gaujac, et al., 2008 and Li, et al., 2010).

3.0 Results and Discussion

Monoaromatic hydrocarbon compounds are benzene, toluene, ethylbenzene, ortho-, metha-, and para-xylenes (BTEX) which are not strongly adsorbed by soil and are relatively highly soluble in water when compared to the other hydrocarbons, such as aliphatic hydrocarbons and aromatic hydrocarbon (AlSalka, et al., 2010 and AlSalka, et al., 2011).

Benzene, toluene, ethyl benzene, and Xylene isomers (BTEX) were used as target analysts in this investigation using SPME-GC-FID, since they are common produced water pollutants. Table-1 shows some properties of BTEX.

Table-1 Standard BTEX properties

Compound	Molecular Weight (g/mol)	Density (g/cm^3)	Structure
Benzene	78.11	0.8787	C_6H_6
Toluene	92.14	0.8669	C_7H_8
Ethylbenzene	106.16	0.867	C_8H_{10}
p+m-Xylene	106.17	0.861-0.88	C_8H_{10}
o-Xylene	106.17	0.861-0.88	C_8H_{10}

To calibrate the SPME-GC-FID system an external standard was established, that is, serial dilutions of BTEX standard solution were prepared and each standard was measured as described previously. The peak area was, obtained from the chromatography of benzene, toluene, ethylbenzene, o−xylene, and p, m−xylene and the peak area against the concentration of each standard linear correlation was obtained. Calibration curves for BTEX standards over the concentrations range of interest were obtained. The correlation coefficients ranged from 0.9944 to 0.9994.

Analysis of BTEX in produced water samples collected from the area of the oilfield, Libya was achieved by using SPME coupled with GC-FID. For the SPME analysis, first the analytes were sorbed on to a fibre and then desorbed from the fibre to the GC inlet. The proposed method was used to quantify BTEX in produced water. The SPME was operated under the optimum conditions. Triplicates analyses were performed in selected produced water samples. SPME method was applied for the determination of BTEX in produced water samples collected from the study site under the optimum conditions. The results in Table-2 show a summary of the occurrence and the concentrations of target compound in produced water samples and clearly show that BTEX was present in produced water.

Table.2 Concentrations of BTEX in produced water samples collected from the study oilfield

Sample Code	Concentration in mg/l					
	Benzene	Toluene	Ethylbenzene	p+m-Xylene	o-Xylene	Total BTEX
TA	1.38±0.12	0.39±0.012	0.020±0.009	0.04±0.008	0.03±0.008	1.86
Pump	1.31±0.10	0.34±0.028	0.013±0.007	0.02±0.008	0.03±0.008	1.70
Spt1	0.049	0.072	0.0033	0.010	0.0093	0.15
Spt2	0.078	0.107	0.0038	0.016	0.0159	0.22
Spt3	0.035	0.056	0.0019	0.011	0.0102	0.11
Spt4	0.021	0.087	0.0025	0.0095	0.0069	0.13

The values shown in Table-2 vary according to the sampling points. BTEX values are much higher, (1.86 and 1.70 mg/l), at storage tank outlet (TA,) and discharged stream (pump) respectively, where the produced water is in the earlier steps, before discharging to the pits. In the pit samples (Spt1, Spt2, Spt3 and Spt4), the values range between 0.11 to 0.22 mg/l, and are much lower due to volatilization and cracking reactions which are catalyzed by sun light and heat. In general, produced water taken from the pit contained lower BTEX concentrations than those from the areas close to oil installations (i.e. Facilities). It is clear from Figure-1 that the highest amounts of BTEX are found on production facilities where the place of produced water in the early stage of production.

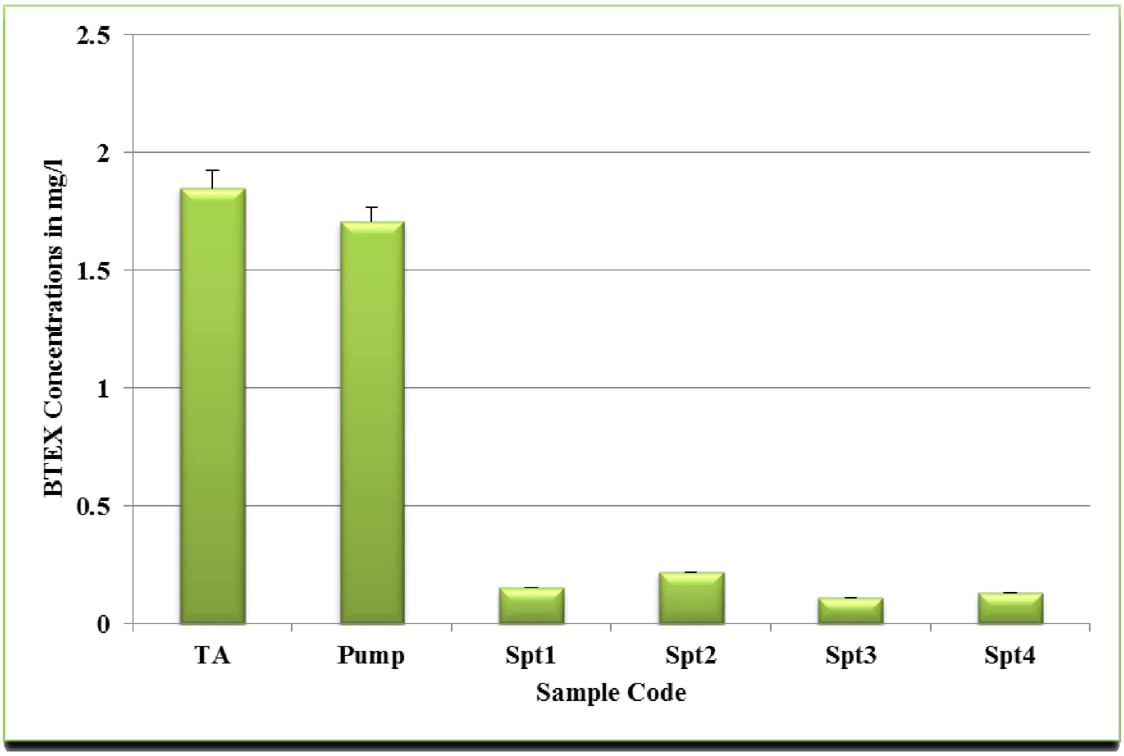

Figure-1 Totals BTEX concentration in produced water from the study oilfield

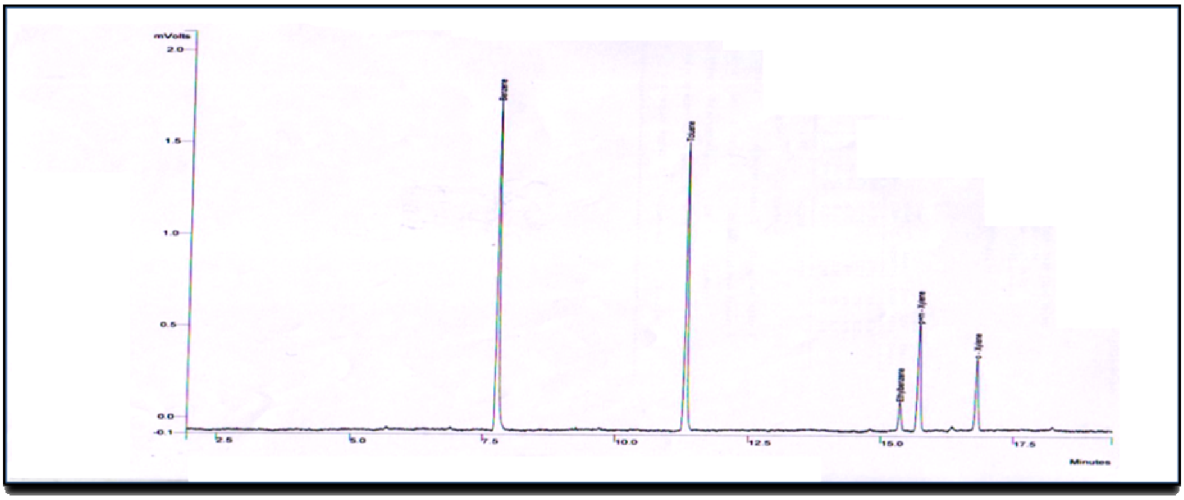

Figure 4-23 GC-FID chromatogram of BTEX compounds extracted from produced water sample at settled tank (TA)

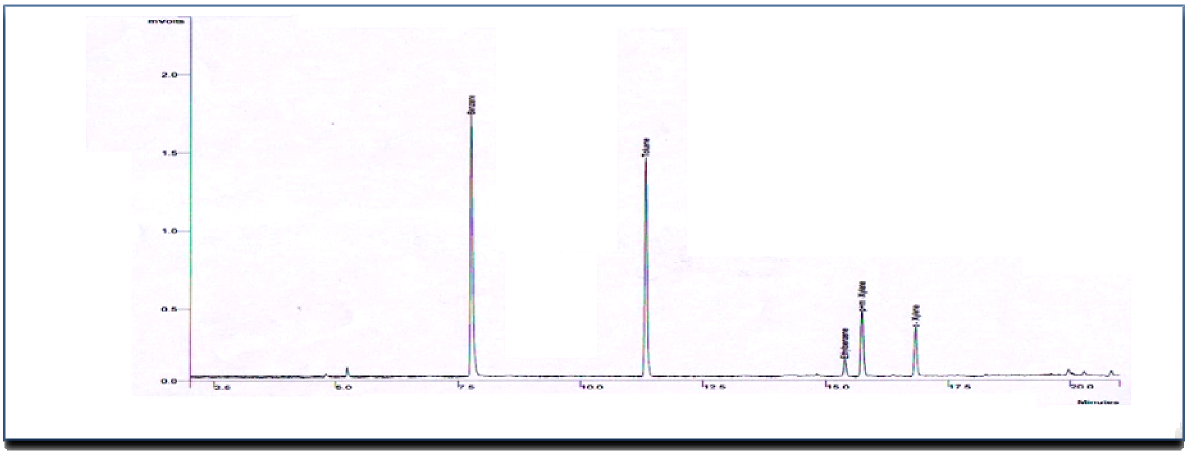

Figure 4-24 GC-FID chromatogram of BTEX compounds extracted from produced water sample at Pump station (Pump)

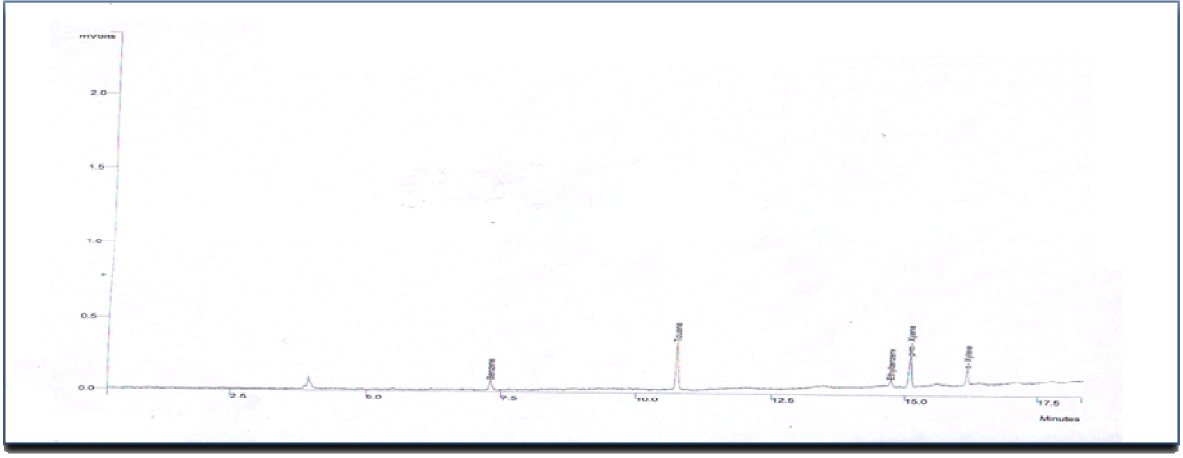

Figure 4-25 GC-FID chromatogram of BTEX compounds extracted from produced water sample at pit location (Spt1)

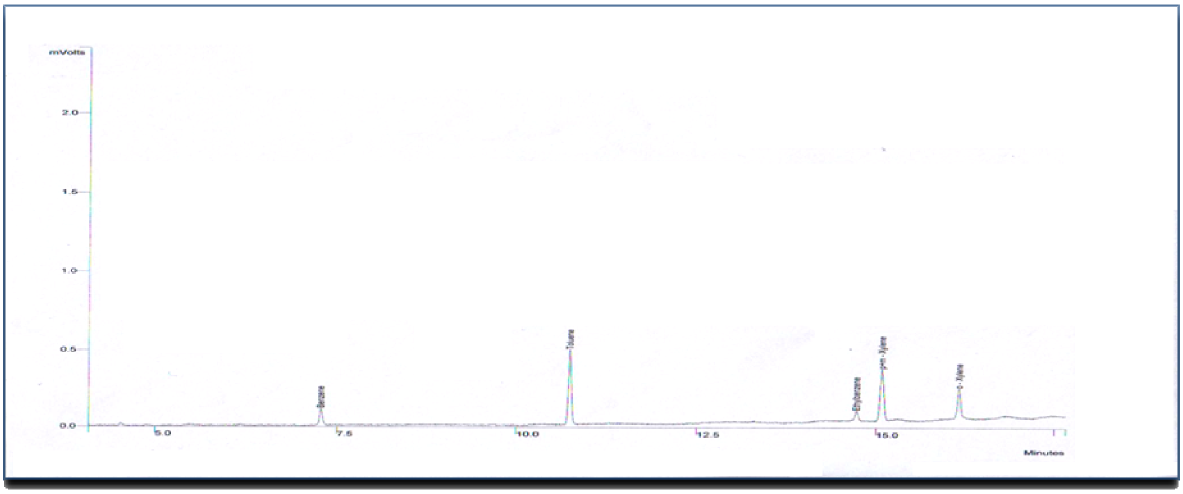

Figure 4-26 GC-FID chromatogram of BTEX compounds extracted from produced water sample at pit location (Spt2)

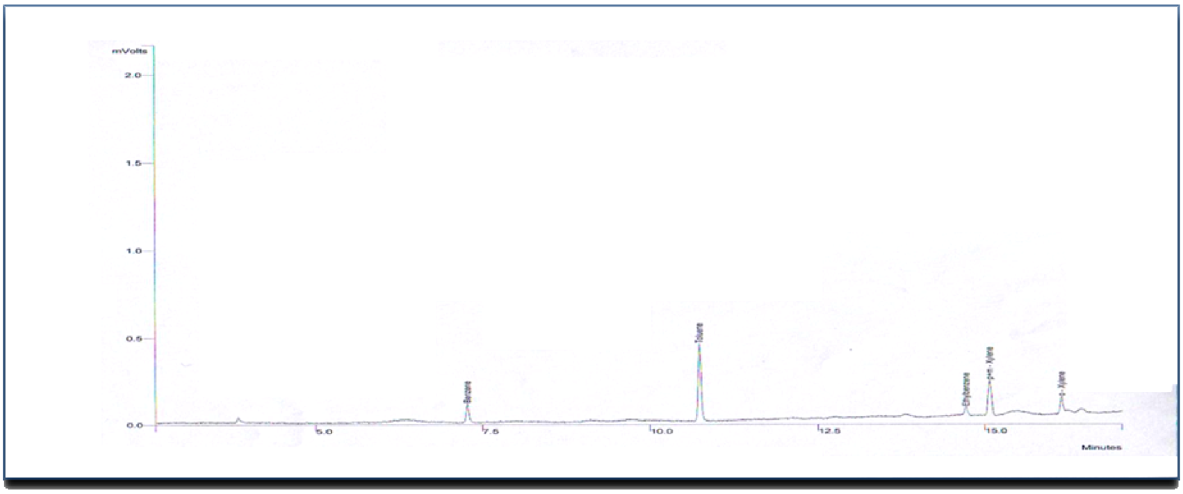

Figure 4-27 GC-FID chromatogram of BTEX compounds extracted from produced water sample at pit location (Spt3)

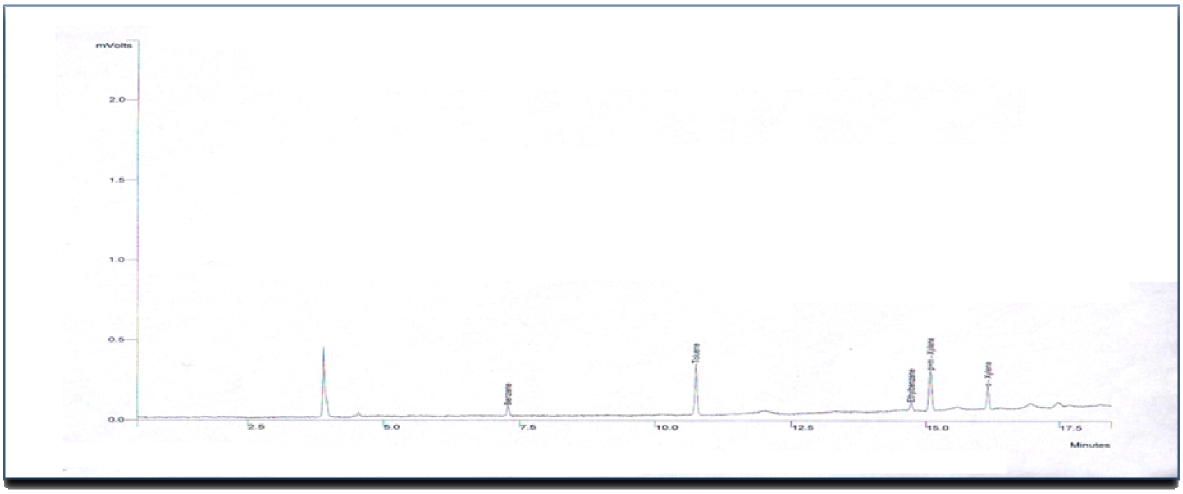

Figure 4-28 GC-FID chromatogram of BTEX compounds extracted from produced water sample at pit location (Spt4

The average concentrations of BTEX in produced water ranged from 0.11 mg/l to 1.86 mg/l as shown in Figure-1. Concentrations of Benzene ranged from 0.021 mg/l to 1.38 mg/l. High concentrations of Benzene were observed in the location of TA, where the produced water is in the earlier steps, before discharging to the pits. Low amount of Benzene was detected at the pit samples Spt4, due to volatilization and cracking reactions which are catalyzed by sun light and heat. Sampling locations TA and Pump shows average concentrations of Toluene of 0.39mg/l ± 0.012 and 0.34 mg/l ± 0.028 respectively (Table-2). There is considerable decrease in concentration of the Toluene in the disposal pit of the study oilfield at sampling locations i.e. Spt1, Spt2 Spt3 and Spt4 (0.056 to 0.107 mg/l), Toluene had the highest concentrations found for BTEX compounds at pit location. Ethylbenzene concentrations at sampling locations TA and Pump were 0.020 mg/l ± 0.009 and 0.013 mg/l ± 0.007 respectively. The concentrations of Ethylbenzene at the sampling locations Spt1, Spt2, Spt3 and Spt4 ranged between 0.0019 and 0.0038 mg/l. Lower concentration of Ethylbenzene was observed at sampling point Spt3. The highest concentrations of p-m xylene and o-xylene 0.04 mg/l ± 0.008 and 0.03 mg/l ± 0.008 respectively were observed at sampling location TA, while the lowest concentration of p-m xylene and o-xylene 0.0095 mg/l and 0.0069 mg/l respectively, were detected at sampling point Spt4 as shows in Table-2 In general the highest concentrations of total BTEX at the study site were observed at the outlet of storage tank (TA), where the produced water is in the earlier steps before discharging to the pits. The lowest total BTEX was detected in the pit due to volatilization and cracking reactions which are catalyzed by sun light and heat. However, the levels recorded in this study for the total BTEX in produced water are infact much lower than those found in some other locations.

The effluent of produced water from the Bonsucesso treatment plant located in the city of Carmopolis which is the most important oil and gas producer in the State of Sergipe, North-east of Brazil has been found to have a total BTEX 3.12 mg/l, Benzene was 1397 µg/l for Toluene was 1263 µg /l, Ethylbenzene 148 µg /l, m+p Xylenes 216 µg /l and for o-Xylenes 96 µg /l (Dorea, et. al., 2007). In the Statoil operated platforms Statfjord B and Gullfaks C which are located in the area of the North Sea the concentration of BTEX were 8900 µg/l and 8350 µg/l respectively (Faksness, et al., 2004).

Utvik, 1999 has been reported that the concentrations of total BTEX in produced water from North Sea Norwegian oil production fields Osberg, Brage and Troll ranged from 5.8 to 9.0 mg/l, for Benzene 3.7 to 4.5 mg/l, Toluene 1.5 to 3.5 mg/l, Ethylbenzene 0.3 to 0.6 mg/l and the combined concentrations of Xylenes 0.2 to 0.7 mg/l (Utvik, 1999). Jones R.J. and Heyward have reported that the concentrations of total BTEX in produced water collected from the platform of Harrlet oilfield on the Australian mainland was 33.86 mg/l. The concentrations of individual compounds were Benzene 2.0 mg/l. Toluene 30 mg/l, Ethylbenzene 0.16 mg/l and the combined concentrations of xylenes 1.7 mg/l (Jones, et al., 2003). All of these values are much higher than the levels measured in this study.

In addition, Al-Salka, et al., 2011 reported significant concentrations of BTEX in produced water samples from the Dier Azzor area, Syria. They found Benzene 1.16 mg /l, Toluene 0.995 mg/l, Ethylbenzene 0.131 mg/l, m+p- xylenes 0.623 mg/l and o-xylene 0.36 mg/l to give a total BTEX concentration of 3.27 mg/l. This is also higher than level measured in this study. Furthermore, Tellez, et al., 2002 who is found the concentrations of BTEX in produced water taken from an oil separation facility located in South Western US within the mineral rich Permian Basin Lea County, New Mexico in the average of 7.7 mg/l ±2.0.

The GC–FID chromatograms for BTEX extracted from the produced water samples are given in Figures 3 to 6, for samples TA, Pump, and Spt1 to Spt4. The peaks in the chromatograms are clearly seen and were identified separately as benzene, toluene, ethylbeneze, p-m xylene and o-xylene according to the retention time of each compound.

4.0 Conclusion

The large volume (315,000 barrels per day) of oily produced water generated from the study oilfield and directly discharged to the soil surface into open environment cause an environmental problem to the ecosystem and could be a possible health risk for local people. The identification of pollutants allows for development of reliable treatment design criteria to help ensure that effective treatment is achieved to meet guideline levels required for disposal, or other beneficial uses. The most important conclusions which could be drawn from this study are summarized in the following:

Analytical method for the determination of BTEX in produced water using SPME and GC–FID indicate that this method is a precise for reproducibly analyzing of BTEX in produced water. The results shows that the produced water samples contaminated by BTEX compounds and when produced water released onto the open environment these contaminated will cause serious damage to the ecosystem. The results also indicated that the produced water from the study oilfield containing varying concentration of BTEX depending on sampling point and it is discharged directly without any sort of treatment into the surface soil onto open environment and this is of environmental concern.

References

Abdol Hamid H. R. , Kassim W. M. S., El Hishir A. & El-Jawashi S. A.,. (2008). Risk assessment and remediation suggestion of impacted soil by produced water associated with oil production. Environ Monit Assess 145:95–102.

AlSalka Y., Karabet F.and Hashem S. (2010). Development and optimisation of quantitative analytical method to determine BTEX in environmental water samples using HPLC-DAD, Analytical Methods, 2, 1026–1035.

AlSalka Y., Karabet F., and Hashem S. (2011). Evaluation of electrochemical processes for the removal of several target aromatic hydrocarbons from petroleum contaminated water, Journal of Environmental Monitoring, 13, 605-613.

Costa A.S., Romao L.P.C., Araujo B.R., Lucas S.C.O., Maciel S.T.A., Jr A. W.., and Alexandre M.R. (2012). Environmental strategies to remove volatile aromatic fractions (BTEX) from petroleum industry wastewater using biomass, Bioresource Technology, 105, 31–39.

CH424 Instrumental Analysis Lab. Determination of BTEX in Water by SPME-*bama.ua.edu/~sstreet/Instrumental/BTEXSPME.PDF. Online.*

Deriszadeh A., Husein M. M., and Harding T. G. (2010). Produced water treatment by micellar-enhanced ultrafiltration, Environmental Science and Technology, 44, 1767–1772.

Dorea H. S., Kennedy J. R.L. B., Aragao A.S., Cunha B.B., Navickiene S. Alves J.P.H., Romao L.P.C., and Garcia C. A.B. (2007). Analysis of BTEX, PAHs and metals in the oilfield produced water in the State of Sergipe, Brazil, Microchemical Journal 85, 234–238.

Ebrahimi M., Kovacs Z., Schneider M., Mund P., Bolduan P., and Czermak P., (2012). Multistage filtration process for efficient treatment of oil-field produced water using ceramic membranes, Desalination and Water Treatment, 42, 17-23.

Faksness L.G., Grini P. G. and Daling P. S. (2004). Partitioning of semi-soluble organic compounds between the water phase and oil droplets in produced water, Marine Pollution Bulletin 48, 731–742.

Gaujac A., Emídio E.S., Navickiene S., Ferreira S.L. and Dorea H.S. (2008). Multivariate optimization of a solid phase microextraction-headspace procedure for the determination of benzene, toluene, ethylbenzene and xylenes in effluent samples from a waste treatment plant, Journal of Chromatography A, 1203, 99–104.

Gray, P. R., and Peter G., (1993). NORM Contamination in the Petroleum Industry. Journal of Petroleum Technology, 12- 16.

Jones R. J., and Heyarad A. J. (2003). The effects of produced formation water (PFW) on coral and isolated symbiotic dinoflagellates of coral, Marine and Freshwater Research, 54, 153-162.

Li Q., Ma X., Yuan D. and Chen J. (2010). Evaluation of the solid-phase microextraction fiber coated with single walled carbon nanotubes for the determination of benzene, toluene, ethylbenzene, xylenes in aqueous samples, Journal of Chromatography A, 1217, 2191–

2196.

Lu J., Wang X., Shan B., Li X., and Wang W. (2006). Analysis of chemical compositions contributable to chemical oxygen demand (COD) of oilfield produced water. Chemosphere, 62, 322-331.

Neff J. M. (2002). Bioaccumulation in marine organisms "Effect of contaminants from oil well produced water" 1st edition Published by Elsevier, Ltd, 1-35.

Stephenson, M.T., 1992 A survey of produced water studies, In: Ray, J.P., Engelhardt, F.R. (Eds.), Produced Water: Technological/Environmental Issues and Solutions. Plenum Press, New York, USA, 1-11.

Sundt R. C., Pampanin D. M., Grung M., Barsiene J., and Ruus A. (2011). PAH body burden and biomarker responses in mussels (Mytilus edulis) exposed to produced water from a North Sea oil field: Laboratory and field assessments, Marine Pollution Bulletin, 62, 1498–1505.

Tellez G.T., Nirmalakhandan N., and Garadea-Torresdey J. L. (2002). Performance evaluation of an activated sludge system for removing petroleum hydrocarbons from oilfield produced water, Advances in Environmental Research, 6, 455-470.

Thomas K. V., Balaam J., Hurst M. R. and Thain J. E. (2004). Bio-analytical and chemical characterisation of offshore produced water effluents for estrogen receptor (ER) agonists, Journal of Environmental Monitoring, 6, 593-598.

Utvik T.I.R., (1999). Chemical characterization of produced water from four offshore oil production platforms in the North Sea, Chemosphere, 39, 2593-2606.

Yeung C.W., Law B. A., Milligan T.G., Lee K., Whyte L.G., and Greer C.W. (2011). Analysis of bacterial diversity and metals in produced water, seawater and sediments from an offshore oil and gas production platform, Marine Pollution Bulletin, 62, 2095–2105.