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Research Article

Environmental Impact of Untreated Produced Water: Hydrocarbon Analysis from Sadqal Oil & Gas Field, Pakistan

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Abstract

Produce water without treatment from oil and gas fields causes contamination of the environment. This study was conducted to analyze the hydrocarbons present in produce water and soil of Sadqal Oil & Gas Field, Fateh Jhung, Pakistan. Sample points for produced water collection were identified and collected from outside the oil and gas field, from various locations including two ponds and their outgoing stream. While composite samples of soil were collected from adjacent pond area to analyze potential impacts of produce water on surrounding soils. Hydrocarbon analysis was conducted through GC-MS, area normalization method. Detailed analysis through GC-MS indicate that hydrocarbons i.e. saturated, unsaturated, cyclic and aromatic hydrocarbons were found in significant percentage in produce water and soil samples taken from outside oil and gas field. Saturated hydrocarbons and aromatic hydrocarbons found in a relatively higher percentage than unsaturated and cyclic hydrocarbons. Produce water samples without treatment contain average 46.86% saturated hydrocarbons and 38% aromatic hydrocarbons. While in soil samples unsaturated hydrocarbons present in the average percentage of 54.47% and aromatic hydrocarbons present in the average percentage concentration of 45.19%. In addition to these, unsaturated hydrocarbons were present in average percentage of 3.8% and 3.27% in water and soil, respectively while cyclic hydrocarbons were present in average percentage concentration of 1.54% and 7.21% in water and soil, respectively. Results reflect that continuous accumulation of hydrocarbons increased the concentration of hydrocarbons in soil lead to higher percentage concentration. Moreover, results suggest that care should be exercised in the disposal and release of produced water containing these organic substances into the environment because of the potential toxicity of many of these substances. To reduce environmental impact there is a need to provide proper treatment for the removal of hydrocarbons from produce water so that their impacts on soil can be reduced.

Keywords: Produced water, hydrocarbon contamination, oil and gas field, soil pollution, saturated hydrocarbons, aromatic hydrocarbons

1. Introduction

In contemporary world oil and gas industry is under severe criticism owing to its significant environmental impacts. Extraction of crude oil results generation of various byproducts and the biggest challenge to the industry is large amount of subsurface formation that comes to the surface during extraction of oil and gas, formerly known as produce water [1]. Across the globe, production of produced water has increased from 95,000 million barrels per day (MBD) in 2010 to 158,900 MBD in 2020 and continuous activity may cause to reach this count near to 240,000 MBD by 2030 [2]. The fluid raised from the hydrocarbon-bearing strata during oil and gas extraction, as well as any chemicals added downhole or during the oil/water separation process, is known as produced water. When it is present, it is also referred to as formation water or injection water (US-EPA). During the oil and gas exploration, produce water is the result of two types of processes i.e., water injection and extraction [3]. Produced water composition varies based on factors like the geographical positioning of oil extraction, gas production site location, specific geological formation, extraction methodology, lifespan of the reservoir and the concurrent operation of multiple wells extracting water [4]. Produce water may come from an unconventional source, such as water trapped in a reservoir, or from a traditional source, such as water that can be immediately drawn from the reservoir. [5]. Usually, unconventional sources of oil and gas production require specialized techniques and equipment for extraction of product. Water extracted from these sources contains a wide range of various organic and inorganic compounds like aliphatic and aromatic hydrocarbons i.e. toluene, ethylbenzene, xylenes (BTEX), naphthalene, phenanthrene, dibenzothiophene (NPD) and polyaromatic hydrocarbons (PAHs). In addition to these, phenols, corymbose substances, soluble salts and different heavy metals are also present in produce water [6]. According to study petrogenic sources are the primary source of n-alkanes with a maximum carbon number of C20 and predominant alkyl substituted naphthalene and phenanthrenes in water [7].

The exploration and production industry have severe environmental impacts particularly during drilling and production phase. These activities require large amount of water and other chemicals and eventually cause severe environmental pollution [8]. Accumulation of polycyclic aromatic hydrocarbons in the human body cause health issues like persistent cough, tachycardia, headache, inflammation and nasal congestion [9]. Infants, unborn children, pregnant women, children, adults with major health issues already present, and those surviving in such a situation that is already health stressed out make up most victims of hydrocarbon impacts [10]. Mutagenicity and Carcinogenicity caused by PAHs on their presence in ambient air result to make them of higher concern [11]. Pakistan is also affected by the increased level of PAHs accumulation in the atmosphere as it causes oxidative stress on the proper functioning of enzymes and hormones. In this manner, 1-hydroxypyrene considered significant in impacting rickshaw drivers and traffic police officers in Lahore [12]. Likewise, a study conducted in Rawalpindi, Pakistan, revealed that along with 1-hydroxypyrene, α and β naphthol also have serious health effects including inflammation/infection and oxidative DNA damage [13]. Hydrocarbons exposure to human severely affects those living particularly near to oil fields. It may cause irritation to eyes, skin, mucous membrane, liver and kidney and reproductive disorder such as infertility and early abortion, childhood leukemia and DNA damage [14].

This study focuses on the analysis of hydrocarbons in produced water and nearby soil through gas chromatography-mass spectrometry (GC-MS). Samples were taken from external ponds and nearby soil of Sadqal Oil and Gas field Fatehjang, Punjab Pakistan. The Oil and Gas Development Company Limited (OGDCL) has started exploration and production activities in Sadqal area in 1992. This oil field expanded in an area of approximately 100 kanals. In this field, 70 barrels of oil are produced daily, and 300 barrels of produce water are produced daily. Wastewater is released one kilometer away from the plant into the ponds located near a residential area. Moreover, excess water overflows from the pond and make its way into a stream. The excessive wastewater seepages from the ponds thereby contaminating the nearby soil to a distance of < 1.5 km [15].

2. Materials and methods

Water samples were collected in 1.5-liter glass bottles from various points. Points of water sample include inlet, outlet, and ponds areas. Six points were selected for collection of produce water samples discharged directly into stream outside the boundary of oil and gas field. It includes the inlet, pond A, pond B, inlet of pond B, outlet of pond B and external stream. These water sample prevented from sunlight to avoid any change in physicochemical properties of water sample [16]. Five composite soil samples (≈ 1 kg) in zip lock polythene bags from selected points were collected by digging 0-15 cm deep. Soil samples were obtained from points near inlet, pond A, pond B, between pond A&B and external stream. These points were at a zero-meter distance from produce water pond area and located in various directions i.e., East, West, and South. At North of pond areas, it was hard rock land.

2.1 Preparation of sample

100 ml of produce water sample was taken in separating funnel and mixed with 20 ml of n-hexane, after shaking well samples were allowed to settle in separating funnel. The lower layer was separated and further 20 ml n-hexane was added. This step repeated three times. In the end, 60 ml of n-hexane containing hydrocarbons was separated. This solution was placed in a water bath for evaporation of n-hexane at 30-40°C until 1 to 2 ml of solution left behind in a beaker. The sample was taken using dropper in an Eppendorf tube and transferred to a laboratory for analysis [17]. Oil and grease concentration was determined in samples by extraction of hydrocarbons using n-hexane as stated above and after evaporation weight was measured and results calculated in mg/L.

2.2 Analysis

Prepared samples were analyzed from GC-MS and interpreted from chromatogram for their detailed results. Following are the GC-MS conditions used to determine hydrocarbons in produce water and soil samples. GC-MS, SHIMADZU, made in Japan, QP-2010, model and area normalization method used for the analysis of hydrocarbons. In GC, the column oven temperature was 35.0°C and 300°C is the temperature of injection oven. Split injection mode was used with the pressure of 70.1kPa. While in case of MS, ACQ mode was scan with speed of 1666. DD-Pipe of MS has the total length of 30 m while its internal diameter (ID) is 2.5mm. The film used in MS is 0.025 µm thin. NIST mass spectral library used to find out hydrocarbons present in the sample considering their mass to charge (m/z) ratio. Helium gas used as a carrier gas owing to its environmentally friendly attributes and had fewer chances of outburst because of its use.

3. Results and discussion

3.1 Results of produced water samples

After sample preparation and their analysis through GC-MS, it was found that hydrocarbons present in samples include saturated, unsaturated, cyclic and aromatic hydrocarbons as discussed by [15]. Overall percentage range of saturated hydrocarbons present in the sample was ranged from 0.11 to 10.11% in inlet, 0.01 to 11.41% in pond A, 0.003 to 12.46% in pond B, 0.003 to 12.45% in inlet of pond B, 0.01 to 11.38% in outlet of pond B and 0.01 to 8.1% in external stream as shown in Figure 1. Among saturated hydrocarbons, Heptane octane was found with significantly highest average percentage concentration of 10.42 and 9.64, respectively. The higher percentage of accumulation of hydrocarbons pose toxic effects and toxicity of aliphatic hydrocarbons depends on exposure route and their concentration. In rat and fish, bioconcentration accumulation indicates the same mode of action for aliphatic hydrocarbons cause severe toxicity [18]. Nonane was present in samples with an average percentage concentration of 3.9 and its derivatives found with average concentration of 0.36, 0.36 and 1.28%, respectively, as shown in Table 1. Other saturated hydrocarbons in samples were decane, undecane, dodecane, tridecane, tetradecane, and pentadecane with average percentage concentration of 1.28, 0.43, 0.2, 0.04, 0.06 and 0.13%, respectively. In addition to these, hexadecane, heptadecane, octadecane, nonadecane, eicosane, heneicosane, docosane, tetracosane, pentacosane and hexacosane with average percentage concentration of 0.13, 0.17, 0.24, 0.27, 0.3, 0.32, 0.27, 0.39, 0.15 and 0.11, respectively. Petroleum contamination is the main source of distribution of alkanes in water bodies thus, accumulation of n-alkanes effect quality of the river and stream water [19]

Unsaturated hydrocarbons present in water samples had concentration percentage range between 0.01 to 1.3% in inlet, 0.02 to 1.62% in pond A, 0.01 to 1.28% in pond B, 0.01 to 1.68% in inlet of pond B, 0.01 to 1.71% in outlet of pond B and 0.002 to 1.31% in external stream as shown in Table 2.

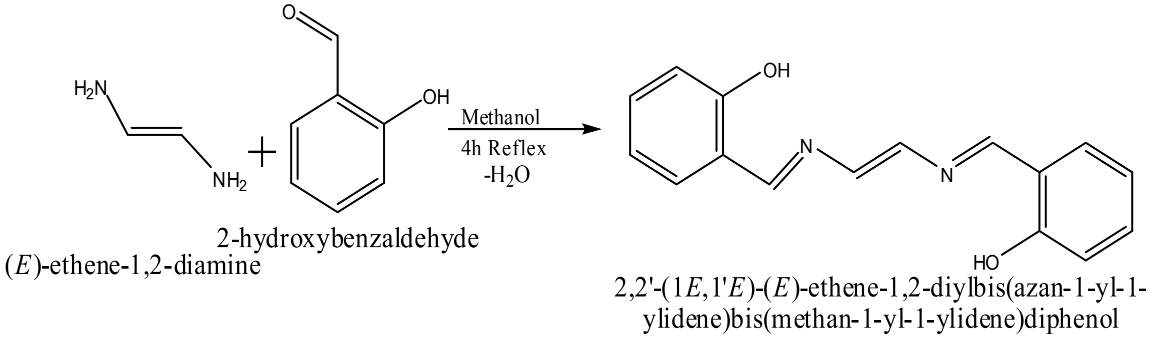

Figure 1. Chemical reaction for the synthesis of 2,2'(1E, 1E')-(ethane-1,2-diylbis (azan-1-yl-1-yidene)bis(methan-1-yl-1ylidene)-diphenolpreparation.

Table 1. Saturated hydrocarbons in produce water at point 1 to 6.

Open chain hydrocarbons (Acyclic hydrocarbons)							
Saturated hydrocarbons	Inlet	Pond A	Pond B	Inlet of Pond B	Outlet of Pond B	External Stream	Average
	Percentage concentration						
Pentane, 3-ethyl-2,4-dimethyl	0.06	0.05	0.04	0.03	0.03	0.05	0.04
Heptane	10.09	10.81	11.46	11.36	10.82	8	10.42
Heptane,3-methyl	3.72	4.05	4.75	4.62	4.3	4.39	4.31
Heptane. 2,5,5-trimethyl	0.04	0.06	0.06	0.06	0.15	0.08	0.08
Octane	10.11	11.41	12.46	12.45	11.38	0	9.64
Octane, 2,5-dimethyl-	7.02	7.75	8.96	8.67	8.16	8.1	8.11
Octane, 2,6-dimethyl-	0.66	0.63	0.63	0.58	0.54	0.79	0.64
Octane, 4-methyl	1.6	2.09	2.28	2.26	1.99	2.52	2.12
Octane, 3-ethyl-2,7-dimethyl	1.6	2.08	2.12	2.2	1.98	2.41	2.07
Octane, 2,3,6-trimethyl	0.12	0.17	0.17	0.17	0	0	0.11
Nonane	3.19	3.6	4.23	4.12	3.81	4.45	3.90
Nonane, 3-methyl-	0.26	0.33	0.36	0.36	0.38	0.46	0.36
Nonane, 2-methyl-	0.28	0.33	0.36	0.36	0.37	0.47	0.36
Nonane 3,7-dimethyl	0.05	0.08	0.07	0.07	0.19	0.1	0.09
Decane	0.92	1.15	1.23	1.24	1.64	1.52	1.28
Undecane	0.21	0.34	0.29	0.3	1.07	0.39	0.43
Undecane, 5-methyl-	0.01	0.02	0.02	0.02	0.1	0	0.03
Undecane, 3-methyl-	0.01	0.02	0.01	0.01	0	0.01	0.01
Undecane, 2,6-dimethyl-	0.02	0.04	0.033	0.03	0.17	0.04	0.06
Undecane, 3,9-dimethyl-	0.01	0.01	0.01	0.01	0.08	0.01	0.02
Dodecane	0.08	0.15	0.09	0.09	0.64	0.13	0.20
Tridecane	0.03	0.07	0.05	0.04	0.33	0.05	0.10
Tridecane, 6-methyl	0	0.01	0.003	0.003	0.03	0	0.01

Continued table 1.

Socarbons	Inlet	Pond A	Pond B	Inlet of Pond B	Outlet of Pond B	External Stream	Average
	Percentage concentration						
Tridecane, 3-methyl	0	0.01	0.004	0.004	0.03	0.01	0.01
Tetradecane	0.04	0.07	0.01	0.04	0.2	0.03	0.07
Tetradecane, 3-methyl	0	0.01	0.01	0.01	0.2	0	0.04
Pentadecane	0.05	0.08	0.06	0.04	0.22	0.33	0.13
Hexadecane	0.09	0.16	0.1	0.06	0.3	0.04	0.13
Heptadecane	0.1	0.19	0.1	0.06	0.54	0.01	0.17
Octadecane	0.14	0	0.05	0.08	0.85	0.07	0.20
Nonadecane	0.13	0.16	0.14	0.07	1.05	0.07	0.27
Eicosane	0.14	0.16	0.15	0.08	1.21	0.09	0.31
Henicosane	0.11	0.15	0.13	0.06	1.16	0	0.27
Docosane	0.11	0.14	0.12	0.06	1.13	0.07	0.27
Tetracosane	0.07	0.1	0.08	0.04	2	0.04	0.39
Pentacosane	0.04	0.08	0.07	0.03	0.64	0.03	0.15
Hexacosane	0.04	0.06	0.05	0.02	0.47	0.01	0.11

These unsaturated hydrocarbons had a significant average percentage concentration of 1.19, 1.48 and 1.12 for 2-Pentene, 2,3,4-trimethyl, 1-heptene and 1-octene, 3,7-dimethyl. Other than these, 1-hexane, 2,3-dimethyl was found with the highest concentration of 1.16% in pond A than other points. Unsaturated hydrocarbons present in the produce water have toxic effects even if they are present in small concentration. Accumulation of hydrocarbons in the surrounding can cause acute toxicity which exerts long-term health impacts. It may include both malignant and non-malignant respiratory diseases [20].

The other group of hydrocarbons present in produce water sample was close chain hydrocarbons which further categorized into cyclic hydrocarbons and aromatic hydrocarbons. Cyclic hydrocarbons can be aliphatic hydrocarbons in a cyclic structure while aromatic hydrocarbons are those hydrocarbons having at least one benzene ring in their structure. Produce water samples contain various cyclic hydrocarbons including cyclobutane, cyclopentane, cyclohexane and cycloheptane (Table 2). Their derivatives have varied concentration in produce water samples. Among these, Cyclohexane, 1,1,3-trimethyl- has highest average percentage concentration of 1.41.

Cyclic hydrocarbons found in less percentage among all samples as compare to other group of hydrocarbons (Table 3). This may be due to hydrogen solubility of cyclic hydrocarbons more than aromatic hydrocarbons [21]. Monocyclic aromatic hydrocarbons, heterocyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbons considered as the toxicants present in produce water [22]. Table 4 shows aromatic hydrocarbons present in samples with a percentage concentration range between 0.01 to 36.37, 0.01 to 21.58, 0.01 to 23.7, 0.01 to 22.84, 0.03 to 23.1 and 0.01 to 17.35 in inlet, point A, point B, inlet of point B, outlet of point B and an external stream, respectively.

Other saturated hydrocarbons present in soil sample were undecane, dodecane, tridecane, tetradecane, pentadecane, hexandecane, heptadecane, octadecane, nonadecane, eicosane, henicosane, docosane, tetracosane, pentacosane and hexacosane with average concentration percentage of 0.25, 0.25, 0.08, 0.1, 0.13, 0.28, 0.53, 0.68, 0.64, 0.66, 0.54, 0.5, 0.3, 0.23 and 0.15, respectively.

Table 2. Cyclic hydrocarbons in produce water at point 1 to 6.

Cyclic hydrocarbons	Close chain hydrocarbons (Cyclic hydrocarbons)						
	Inlet	Pond A	Pond B	Inlet of Pond B	Outlet of Pond B	External Stream	Average
	Percentage Concentration						
Cyclobutane, (1-methylethylidene)	*	0.02	0.03	0.03	0.02	*	0.02
Cyclopentane, 1-butyl-2-ethyl	0.33	*	*	*	*	*	0.33
Cyclohexane, 1,1,3-Trimethyl-	1.11	1.36	1.51	1.49	1.34	1.67	1.41
Cyclohexane, propyl-	0.17	0.19	0.22	0.22	0.20	*	0.2
Cyclohexane, 1-methyl-3-propyl-	0.10	0.13	0.15	0.05	0.16	0.07	0.11
Cyclohexane, butyl-	0.04	0.06	0.06	0.06	0.01	0.08	0.05
Cyclohexane, 1,2,3-trimethyl	*	*	0.01	*	*	0.06	0.04
Cyclopentene, 1- (2-Methylpropyl)	0.01	0.02	*	0.02	*	0.02	0.01
Cyclopentene, 1-propyl	*	0.01	0.01	0.01	0.01	0.01	0.01
Cyclohexene, 1-methyl	0.10	0.01	0.01	*	0.01	*	0.01

*Not Detected

Table 3. Aromatic hydrocarbons in produce water at point 1 to 6.

Aromatic hydrocarbons	Close chain hydrocarbons (Cyclic hydrocarbons)						
	Inlet	Pond A	Pond B	Inlet of Pond B	Outlet of Pond B	External Stream	Average
	Percentage concentration						
Naphthalene,1,8-dimethyl-	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Phenanthrene	*	*	*	*	0.03	*	0.03
Toluene	36.4	21.58	23.7	22.84	23.10	17.35	24.15
Ethyl benzene	7.19	7.78	8.82	8.64	8.42	8.88	8.28
Benzene, 1,3-dimethyl	5.18	13.02	5.91	5.37	5.20	15.80	8.41
Benzene, 1-ethyl-3-methyl-	0.68	0.87	0.96	0.98	0.95	1.15	0.93
Benzene, 1,3,5-trimethyl-	2.91	3.42	4.04	3.90	*	4.23	3.7
Benzene, 1,2,4- trimethyl	0.58	0.75	0.82	0.80	0.99	0.99	0.82
Benzene, 1-methyl-3-(1-methylethyl)	0.13	0.18	0.18	0.18	0.39	0.23	0.22
Benzene, (1,1-dimethylpropyl)-	0.01	0.03	0.02	0.02	0.11	0.03	0.03

*Not Detected

These compounds were also present at various points in produce water sample but in soil sample most of these compounds found near pond A and B. This clearly showed that produce water contain hydrocarbon and have its significant impact on surrounding soil. Hydrocarbon like n-alkane seeps down into the ground water source which cannot be used for drinking purpose [30]. Not only this, it also affects microbial activity of soil. Some of microbes consume n-alkanes as source of energy but at higher amount, it effects microbial activity. Without proper salinity and particle size of soil, hydrocarbons can be biotoxic to plant growth [31].

Unsaturated hydrocarbons were present in an unusual manner in soil samples. 2,3,4-trimethyl-2-pentene was only hydrocarbon found in all points of soil sample with average percentage concentration of 0.81%. Moreover, 1-hexene, 2-methyl found at point 2 with the concentration percentage of 3.07%. The 1-hexene, 2,3-dimethyl was found in produce water sample as well as in soil sample with concentration of 0.50% as shown in Table 4 and 5.

Table 4. Unsaturated hydrocarbons in produce water at point 1 to 6.

	Open Chain hydrocarbon (Acyclic hydrocarbons)					
Saturated hydrocarbons	Inlet	Pond A	Pond B	Between Pond A&B	External Stream	Average
	Percentage concentration					
Pentane, 3-ethyl-2,4-dimethyl	*	0.41	0.06	*	*	0.094
2,3-Dimethylhexane	1.79	0	0	2.61	0.44	0.968
Heptane	13	15.58	11.75	20.17	20.16	16.132
Heptane,3-methyl	5.26	3.78	4.24	7.04	4.07	4.878
2,4-Dimethylheptane	0.77	*	*	1	*	0.354
Octane	10.5	10.78	11.36	14.15	11.75	11.7
Octane, 2,5-dimethyl-	*	6.99	8.01	*	7.47	4.494
Octane, 4-methyl	*	1.62	1.77	*	1.93	1.064
Octane, 3-ethyl-2,7-dimethyl-	*	1.58	1.77	*	*	0.67
3-Methyloctane	2.63	*	*	2.89	*	1.104
4-Methyloctane	2.21	*	*	2.51	*	0.944
2-Methyloctane	2.21	*	*	2.51	*	0.944
Nonane	3.51	2.83	3.49	4.04	3.34	3.442
3-Methylnonane	6.16	*	*	8.32	*	2.896
Nonane, 2-methyl-	*	0.21	0.31	*	0.3	0.164
Isononane	2.24	*	*	2.63	*	0.974
Decane	2.58	0.8	0.97	0.87	1.01	1.246
5,6-Dimethyldecane	1.53	*	*	0.56	*	0.418
Undecane	*	0.24	0.21	0.18	0.38	0.202
Dodecane	*	0.19	0.07	*	0.478	0.1476
Hexandecane	*	0.23	0.34	*	*	0.114
Heptadecane	*	0.33	0.72	*	*	0.21
Octadecane	*	0.53	0.83	*	*	0.272
Nonadecane	*	0.53	0.74	*	*	0.254
Eicosane	*	0.53	0.78	*	*	0.262
Henicosane	*	0.41	0.67	0	0	0.216
Docosane	*	0.39	0.6	0	0	0.198
Tetracosane	*	0.23	0.36	0	0	0.118

*Not detected

Other than these, heptene was found in soil at three points i.e. near pond A, pond B and near the external stream with concentration percentage of 1.85, 1.67 and 4.66, respectively. Another group of hydrocarbons found in soil sample was cyclic hydrocarbons. Cyclopentane, 1,2-dimethyl was found at two points i.e. near inlet and between pond A&B with percentage concentration of 3.11 and 4.87, respectively. Cyclopentane, -butyl-2-ethyl was present with average percentage concentration of 0.37 (Table 6). Cyclopentane, 1-Methyl-2-(2- Propenyl)-Trans was another cyclic hydrocarbon found near pond A with percentage of 1.86. Cyclohexane, 1,1,3-trimethyl was found in soil with average percentage concentration of 1.15 while in produce water this average percentage concentration was slightly higher i.e. 1.41. Methylcyclohexane was present at two-point, highest percentage was found in soil between pond A&B i.e. 7.21. Other derivatives of cyclohexane present in sample were found in average percentage range of 0.04 to 0.95. Other than these 1,3,5-cycloheptatriene, 7-ethyl and ethylcyclooctane was present in sample with average percentage concentration of 3.6 and 0.29.

Aromatic hydrocarbons present in soil sample include naphthalene, 1,8-dimethyl- and sec-butylbenzene with average percentage concentration of 0.02 and 2.65. 1-methyl-2-propylbenzene was found in soil near inlet and between pond A&B with percentage concentration of 2.58 and 2.71.

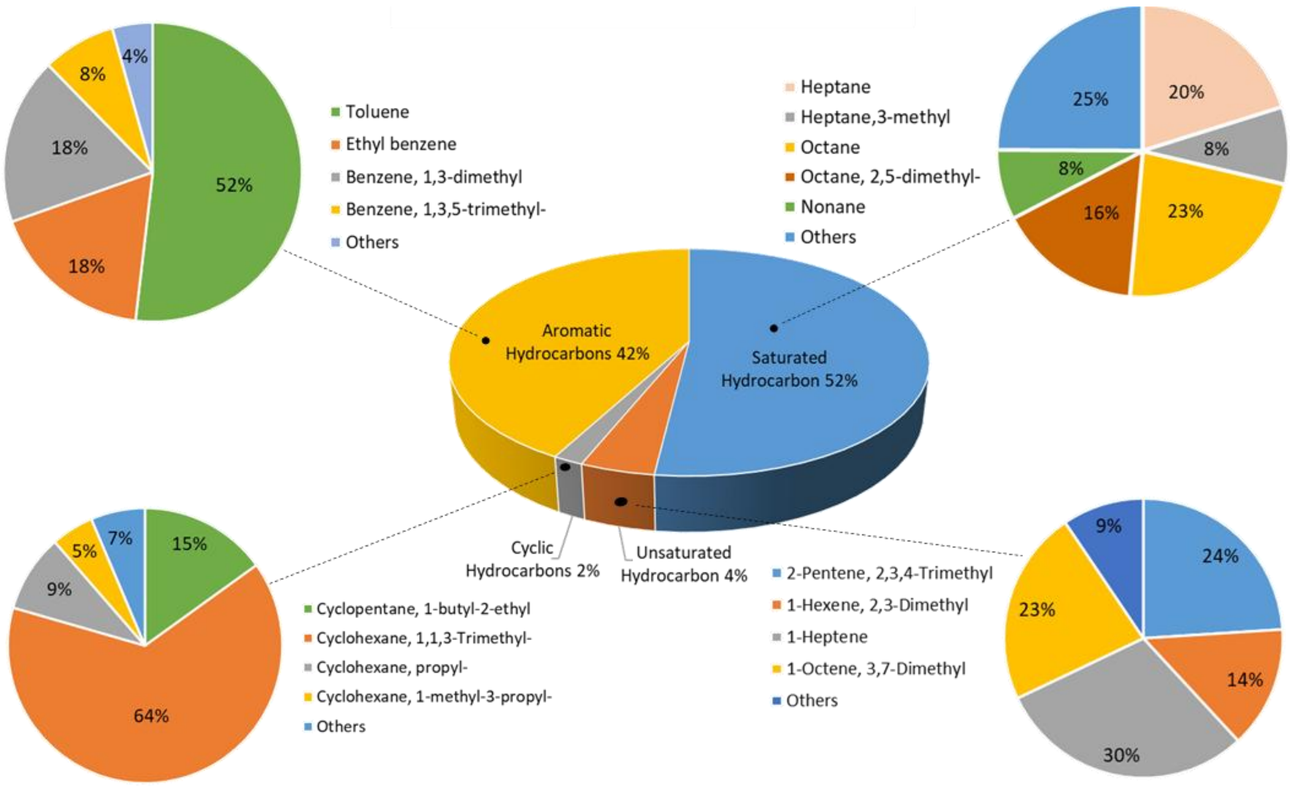

Figure 2. Total hydrocarbon in produced water.

Table 5. Unsaturated hydrocarbons in soil at point 1 to 5.

	Open Chain Hydrocarbons (Acyclic Hydrocarbons)					
Unsaturated Hydrocarbons	Inlet	Pond A	Pond B	Between Pond A&B	External Stream	Average
	Percentage concentration					
2,3,4-Trimethyl-2-pentene	0.48	0.9	1.08	0.6	0.98	0.808
1-Hexene, 2-methyl	*	3.07	*	*	*	0.614
1-Heptene	*	1.85	1.67	*	4.66	1.636
2-Heptene, 2-Methyl-	*	0.03	0.06	*	*	0.018
1-Heptene, 2,6-dimethyl	*	*	0.06	*	*	0.012
1-Octene, 3,7-dimethyl	*	*	0.43	*	*	0.086
2-Octene, (E)-	*	*	0.04	*	*	0.008
4-Nonene	*	0.1	0.18	*	*	0.056
1-Decene	*	0.16	*	*	*	0.032

Toluene was found with almost same average percentage in soil as it was present in produce water, presented in Table 3. In soil near external stream, toluene was present in the least percentage concentration of 22.75 while maximum percentage was detected in soil samples near pond A i.e. 25.51%. Other aromatic compounds in soil sample were ethyl benzene, benzene, 1,3-dimethyl, benzene, 1-ethyl-3-methyl, benzene, 1,3,5-trimethyl and benzene, 1,2,4- trimethyl with average percentage concentration of 7.2, 5.53, 0.72, 3.14, and 0.6, respectively shown in Table 7. Concentration percentage of hydrocarbons in soil more than 0.1% also inhibit seed germination. It also produces ecotoxic effects by affecting plant growth and living of earthworm and disturbs bacterial activity at 0.5% [32, 33]. Results of the study illustrate that as compared to produce water results, in soil samples, there was no proper hydrocarbons' distribution pattern. It may be due to accumulation of hydrocarbon at some points in the soil like in the bottom of slopes more than plain areas. Other factors may include evaporation and rainfall which is responsible for dilution.

Table 6. Cyclic hydrocarbons in soil at point 1 to 5.

Close chain hydrocarbons (Cyclic hydrocarbons)						
Cyclic hydrocarbons	Inlet	Pond A	Pond B	Between Pond A&B	External Stream	Average
	Percentage concentration					
Cyclopentane,1,2-dimethyl-	3.11	0	0	4.87	0	1.596
Cyclopentane, 1butyl-2-ethyl	0	0.33	0	0	0.41	0.148
1,2,3-Trimethylcyclopentane	0.4	0	0	0.56	0	0.192
Cyclohexane, 1,1,3-Trimethyl-	0	0.98	1.22	0	1.26	0.692
Methylcyclohexane	4.69	0	0	7.21	0	2.38
1,3-Dimethylcyclohexane	0.57	0	0	0.79	0	0.272
p-Dimethylcyclohexane	0.59	0	0	0.81	0	0.28
1,2-Dimethylcyclohexane	0.48	0	0	0.6	0	0.216
1,3,5-Cycloheptatriene, 7-ethyl	3.45	0	0	3.75	0	1.44

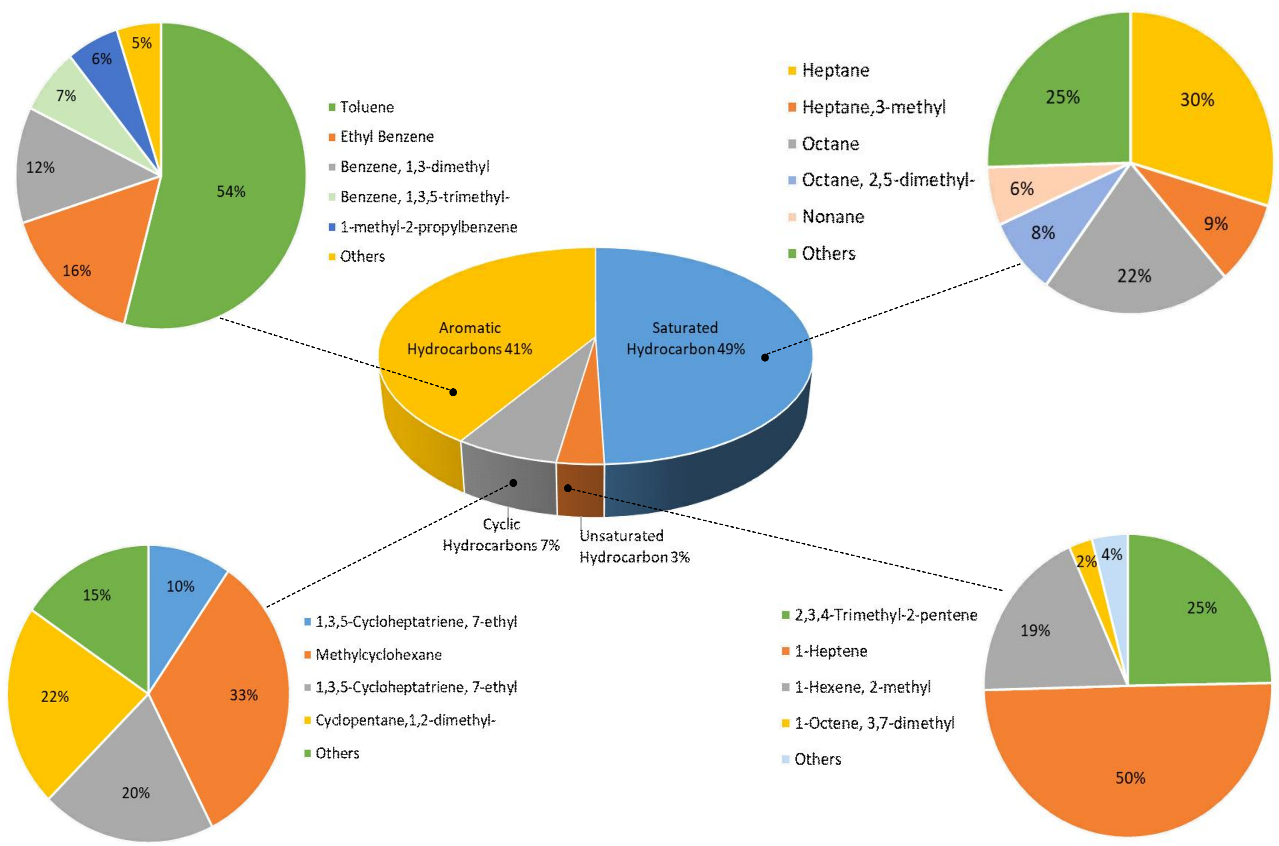

Figure 3. Total hydrocarbons in soil.

Table 7. Aromatic hydrocarbons in soil at point 1 to 5.

Aromatic hydrocarbons	Close chain hydrocarbons (Cyclic hydrocarbons)					
	Inlet	Pond A	Pond B	Between Pond A&B	External Stream	Average
	Percentage concentration					
Sec-Butylbenzene	0.92	0	0	0.91	0	0.91
1-methyl-2-propylbenzene	2.58	0	0	2.71	0	2.64
Toluene	0	25.51	25.11	0	22.75	24.45
Ethyl Benzene	0	6.61	8	0	7	7.2
Benzene, 1,3-dimethyl	0	5.5	5.46	0	5.65	5.53
Benzene, 1-ethyl-3-methyl-	0	0.59	0.76	0	0.83	0.72
Benzene, 1,3,5-trimethyl-	0	2.58	3.23	0	3.61	3.14
Benzene, 1,2,4- Trimethyl	0	0.49	0.63	0	0.68	0.6

Table 8. Comparison of distribution of hydrocarbons concentration in produce water and soil.

Hydrocarbons		Produce Water	Soil
		Average Percentage concentration	
Saturated	Heptane	10.23	16.13
	Heptane,3-methyl	4.31	4.88
	Octane	11.56	11.7
	Octane, 2,5-dimethyl	38.11	7.49
	Nonane	3.9	3.44
Unsaturated	2-Pentene, 2,3,4-trimethyl	1.19	0.81
	1-heptene	1.48	2.73
	1-Octene, 3,7-dimethyl	1.12	0.43
Cyclic	Cyclohexane, 1,1,3-Trimethyl-	1.41	1.153
Aromatic	Naphthalene, 1,8-dimethyl-	0.01	0.02
	Phenanthrene	0.03	-
	Toluene	24.15	24.45
	Ethyl benzene	8.28	7.2
	Benzene, 1,3-dimethyl	8.41	5.53
	Benzene, 1,3,5-trimethyl-	3.7	3.14

Figure 2 is the graphical illustration of total hydrocarbons distribution in soil.

3.3. Comparison of significant hydrocarbons concentration in produce water and soil

Following were the hydrocarbons concentration found in produce water and had their distribution in nearby soil as well (Table 8). These compounds have toxic nature and find in significantly higher concentration percentage of total hydrocarbons (Figure 3). Thus, they continue to persist in environment for longer period and have their toxic impacts.

Most of hydrocarbons present found in all the sample of produce water continue to accumulate in nearby soil as well. Thus, it can be summarized as same compounds of hydrocarbons also found in soil sample with varied percentage. Percentage of hydrocarbons reduces in the soil sample, while in some cases few hydrocarbons vanishes while some of them continue to accumulate even with reduced or somehow greater percentages due to accumulation.

4. Conclusion

Produce water discharge from oil and gas production field is a huge problem for oil and gas production companies. Large volume of water discharge during extraction process raises concerns for environmental regulators as well. This study was conducted to analyse the hydrocarbons distribution in produce water and surrounding soil of Sadqal Oil and Gas Field, Fateh Jang, Pakistan. Produced water and soil samples were collected from outside oil and gas field. Overall concentration of oil and grease found in produce water and soil was above permissible limits. However, average percentage concentration of hydrocarbons in produce water was 46.86%, 3.8%, 1.54% and 38%, for saturated, unsaturated, cyclic and aromatic hydrocarbons, respectively. Impacts of produce water on surrounding soil were also studied and it was found that saturated, unsaturated, cyclic and aromatic hydrocarbons, present in the soil with average percentage concentration of 54.47, 3.27, 7.21 and 45.19%, respectively. This study clearly showed that produce water contain significant amount of saturated and aromatic hydrocarbon. Persistent accumulation of hydrocarbons causes contamination of surrounding soil and increase in concentration of hydrocarbons in soil.

Authors Contribution

Conceptualization, Said Akbar Khan (S.A.K). and Ayesha Hafeez (A.H).; Methodology, S.A.K and A.H..; Formal analysis, A.H.; Writing original draft preparation, A.H.; Editing, review and writing, S.H.Z., and A.H.; Supervision, S.A.K. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

There are no conflicts of interest reported by the writers.

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Data Availability statement

The data presented in this study are available on request from the corresponding author.

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