Effect of Associated Produced Water with Crude Oil On Groundwater

Saleh A. Emhanna[1 (*)], Dr. Ghaith H. Abdalrahman[2], Widad A. Mukhtar[3], Aida A.Mohmmed[4]

[1,2, 3] Dept. Of Petroleum Engineering, Faculty Of Engineering, University of Ajdabiya, Libya

[4] Data Palm Research Center, Jalu, Libya

Abstract

The oil production operations create large quantities of contaminated water which is known as "Produced Water". All the produced water in the Nafoora oil field dispelled to water pit without treatment and /or re-used in injection. Due to concerns over the effects of oil production activities on groundwater quality, heavy metals, physical and chemical properties were analyzed in 7 samples collected from Gas

(*) Email: salehemhanna@uob.edu.ly

Oil Separation Plant ***GOSP*** *and Shallow Water Well from the field. A combination of newly collected and historical data was used to determine whether produced water have mixed with groundwater. Then, comparing the results with standards of World Health Organization WHO and Food and Agriculture FAO.*

The analysis results of physical and chemical properties shows that the pH values in all GOSPs stations ranging between 4.4 -7.2 and high concentrations of Total Dissolved Salts TDS (28000 to 101000 ppm) and Chloride CL concentrations ranging between 111600 ppm to 136700 ppm and have as well high EC values (122200 to 568200 µS/cm). The Nafoora oil field contains heavy metals such as Hg, Cr, Zn, Cu, Cd, Ag and Pb. Three minerals with concentration above WHO and FAO standards; Cr, Cu and Cd. While Hg, Zn, Ag and Pb have concentration in acceptable range. The results indicated the produced water mixed with the ground water.

According to WHO and FAO standards the associated production water from all GOSPs stations unsuitable for drinking or agriculture. Without proper treatment the produced water is harmful as source of drinking water and other daily activity. Consequently, the produced water requirements to be handled and fulfill the quality standards before being discharged to the environment or reused in the EOR process.

Keywords*: oil, produced water, groundwater, heavy metals, pollution*

1. Introduction

Increased oil and gas production in many areas has led to concerns over the effects these activities may be having on groundwater quality. Produced water is water trapped in subsurface formations that is brought to the surface during oil and gas explorations. This water has been in contact with the hydrocarbon-bearing formation for centuries, and as a result, it contains some of the chemical characteristics of the formation and the hydrocarbon itself (Fig, 1). Produced water may include water from the reservoir, water injected into the formation, and any chemicals or surfactant added during the production and treatment processes. Produced water is sometimes referred to as brine or formation water **[1].**

The physical and chemical properties of produced water are not consistent. Variation depends on factors such as reservoir geology, hydrocarbon composition, geographical location, and water injection history. Produced water contains contaminants that require removal before proper disposal or reuse. Some of the impurities or substances likely to be found in produced water include: oil, naturally occurring radioactive materials, waxes, sand, scales, dissolved salts, CO_2 (carbon dioxide) and H_2S (hydrogen sulfide) gases, hydrocarbons, production chemicals, and various metals **[2].**

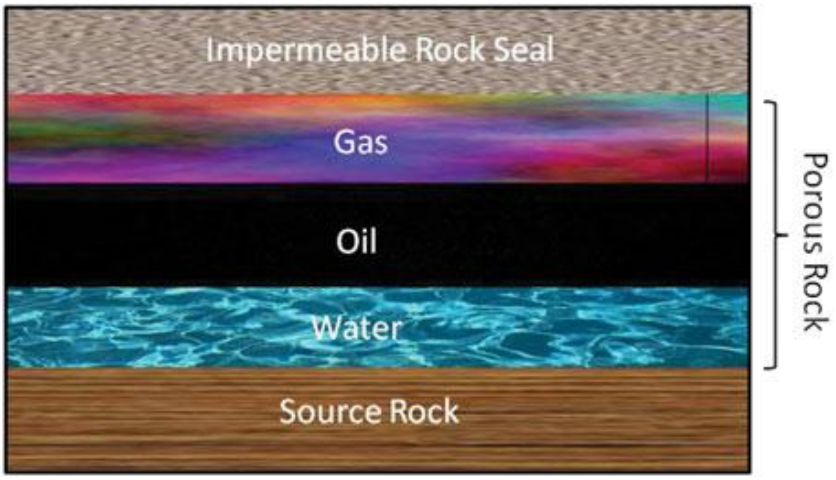

Figure 1: Sketch of a typical reservoir.

The treatment of produced water will differ according to the intended disposal method or reuse purpose. Filtration, flotation, and evaporation are among the commonly used treatment techniques. Posttreatment, there are a number of options available for disposal or reuse. Due to increasing environmental awareness and regulations, disposal to surface waters and evaporation ponds is becoming less prevalent. Produced water is considered an industrial waste, subject to standards defined and issued by the U.S. Environmental Protection Agency **[3].**

2. Environmental Impacts Caused by Produced Water

Environmental impacts caused by the disposal of produced water have been reported since the mid-1800s when the first oil and gas wells were drilled and operated. The most commonly reported environmental concerns are as follows: degradation of soils, ground water, surface water, and ecosystems they support. Because many produced waters contain elevated levels of dissolved ions (salts), hydrocarbons, and trace elements, untreated produced water discharges may be harmful to the surrounding environment **[4].**

Large water volumes also can cause environmental impacts through erosion, large land area disposal basins, and pipeline and road infrastructure. Water hauling spills and unplanned discharges are all risks when managing produced water. Physical water properties of concern include temperature, effervescence, low dissolved oxygen concentrations, as well as high and low pH depending on the well type. Infiltration of Associated Produced Water with Oil into shallow ground water sources is concern when water is applied for irrigation use. Mineral accumulation due to subsurface ion exchange can change the water quality of shallow, underlying aquifers.

In general most of produced water will be contaminated by some subset or mixture of Water:

- Dissolved oil
- Dissolved solids
- Dissolved gases (particularly hydrogen sulfide and carbon dioxide)
- Dispersed oil droplets,
- Dispersed solid particles.
- Bacteriological matter
- Added materials (treatment chemicals, destroy fluids, acids, such as corrosion inhibitors, biocides, disinfectants, scale inhibitors, neutralizing agents (alkalinity control) **[5].**

3. Materials and Methods

The objectives of this study are to determine the physical properties, chemical properties and heavy metals concentrations in the produced water associated with crude oil production in the Nafoora oil field and comparing the results with WHO and FAO standards.

The Nafoora oil field is study area which the central Sirte Basin in the east of Libya. Nearby cities: Ajkhera, Jalu and Awjila (Fig, 2).The field has an estimated 7.5 billion barrels of oil in place, making it one of Libya's major oil fields. It is operated by the Arabian Gulf Oil Company (AGOCO), which is a partnership of NOC.

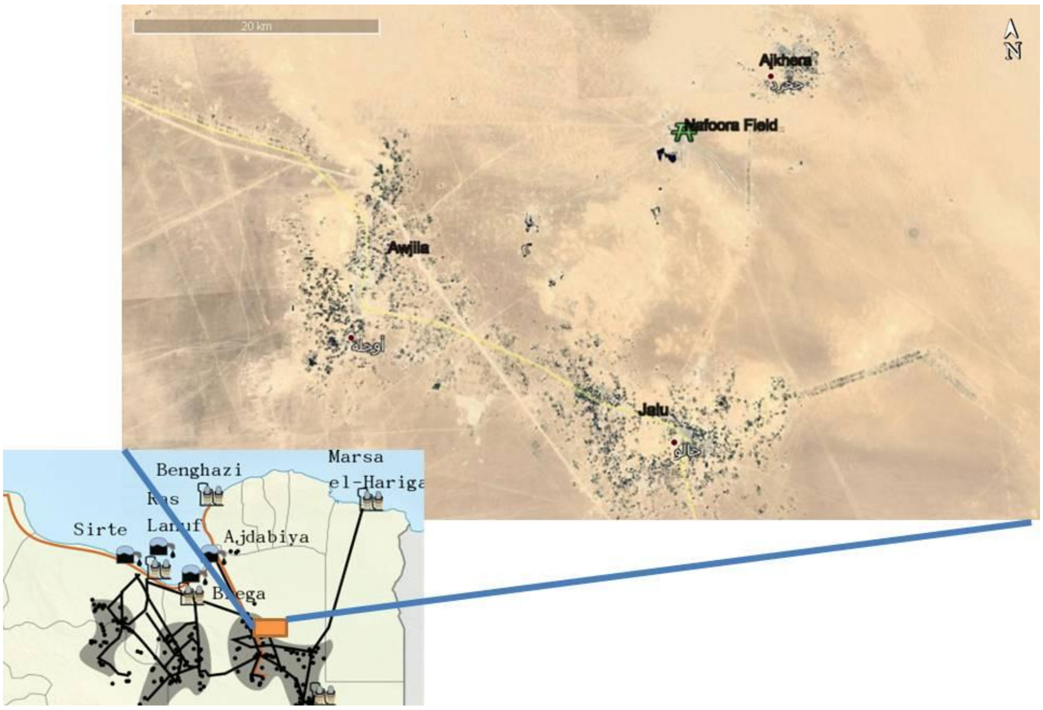

Figure 2: Location of the Nafoora oil Field and nearby cities

Figure 3: Shows discharge produced water PW pit and water well (WSW216) in study area.

3.1 Produced Water Rate

The amount of produced water, and the contaminants and their concentrations present in produced water usually vary significantly over the lifetime of a field. Early on, the water production rate can be a very small fraction of the oil production rate, but it can increase with time to tens of times the rate of oil produced. In terms of composition, the changes are complex and site-specific because they are a function of the geological formation, the oil and water (both in-situ and injected) chemistry, rock/fluid interactions, the type of production, and required additives for oil-production-related activities **[6].**

In the Nafoora oil field the daily produced water about 37393 barrels about 1159276 barrels monthly measured during January 2017 associated with production 70000 barrels daily about 2170000 barrels of oil monthly(Fig, 4). All the produced water dispelled to disposal water pit without treatment and /or re-used in injection (Fig, 5).

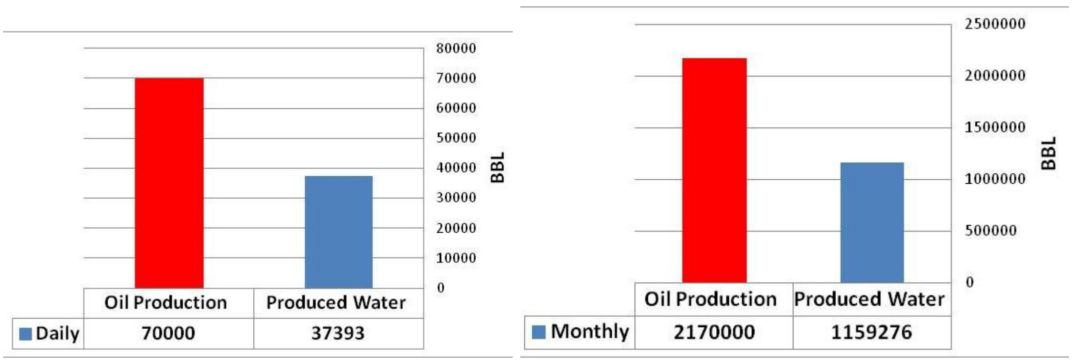

Figure4: Shown the estimated daily and monthly of production rates of crude oil and Associated water in the Nafoora Oil Field January 2017.

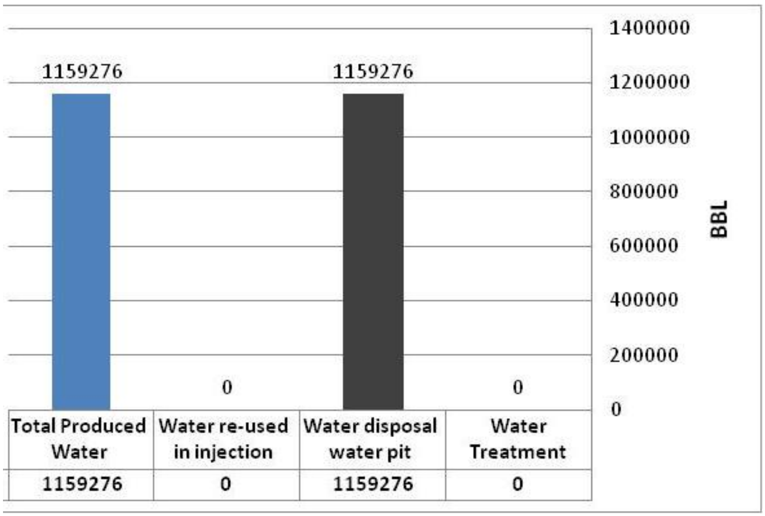

Figure 5: Shown the volume of produced water Nafoora Field during January 2017

3.2 Collect the samples

Produced water samples were taken from six Gas Oil Separation Plant **GOSP** from 6 production areas in the Nafoora oil field GOSPs; (GOSP2, GOSP3, GOSP4, GOSP5,GOSP6 and GOSP8) on 29 march 2017 and one sample was taken from shallow groundwater well (WSW216), which located away from Nafoora field about 4km, depth of well: 240 ft (73m) (Fig, 3). Table 1; shows more information about the GOSPs.

Table 1.Shown numbers of well that link of each GOSP& range of depth

THE GOSPS	Number of wells	Range of depth
GOSP 2	8	8000-8500
GOSP 3	21	9500-10000
GOSP 4	53	8000-9500
GOSP 5	27	8000-9500
GOSP 6	27	8000-9000
GOSP 8	16	10000-10200

3.3 Techniques used for Analysis of produced water

There are a wide variety of analytical techniques used to determine the concentration of contaminants in produced water. In this study three methods have been used;

- pH conductivity meter and Chloride measurement methods in the Sirte Oil Company lab for physical properties analysis such as; pH, Total Dissolved Solids TDS, Electrical Conductivity EC and Chloride Cl.
- Atomic Absorption method in Ras Lanuf Company lab to calculate approximately heavy chemical metal concentrations such as;. Mercury (Hg), Chromium (Cr), Zinc (Zn), Copper (Cu), *Cadmium* (Cd), Silver (Ag) and Lead (Pb).

4.Produced Water Managing

The general objectives for operators treating produced water are: de-oiling (removal of dispersed oil and grease), desalination, removal of suspended particles and sand, removal of soluble organics, removal of dissolved gases, removal of naturally occurring radioactive materials (NORM), disinfection and softening (to remove excess water hardness). To meet up with these objectives, operators have applied many standalone and combined physical, biological and chemical treatment processes for produced water management. Some of these technologies are reviewed in this section.

1. Membrane filtration technology
2. Thermal technologies
3. Biological aerated filters
4. Hydrocyclones
5. Gas flotation

6. Evaporation pond
7. Adsorption
8. Media filtration
9. Ion exchange technology
10. Chemical oxidation
11. Electrodialysis/electrodialysis reversal
12. Freeze thaw evaporation
13. Dewvaporation: Aletta Rain^{SM} process
14. Macro-porous polymer extraction technology **[7].**

5. Results

The physical -chemical properties of produced water from Al Nafoora oilfield were measured to characterize the pollutants contained within it.

5.1Physical properties Analysis

The physical properties are summarized in Tables (2 and 3);showing the pH, Electrical Conductivity EC (µS), Total Dissolved Solids TDS (ppm), and salinity calculated as Chloride (ppm).Table2: included results produced water samples from six GOSPs and Table3: included results from the shallow water well (WSW216).

Table2. Shownthe physical properties of produced water in the Nafoora Oil Field.

Location	pH	EC (µS/cm)	TDS ppm	CL ppm
GOSP2	5.5	185,400	92,000	111,600
GOSP3	4.5	203,100	101,000	127,200
GOSP4	6.2	132,400	66,000	136,700
GOSP5	6.6	122,200	61,000	-
GOSP6	7.2	568,200	28,000	131,300
GOSP8	4.7	200,500	100,000	-

Table 3. Shown the physical properties of the shallow water well (WSW216).

Shallow Water Well (WSW216)	
pH	7.7
EC (µS/cm)	8318
TDS (ppm)	4000
CL (ppm)	80,500

5.2 Result Test Analysis of Heavy Metals

The results analysis of heavy chemical elements recoded from the produced water and shallow water well (WSW216) in the Nafoora oil field, (Tables. 5 and 6).

Table 5. Shows the values of heavy chemical elements concentration in the produced water

SAMPLE CODE	ELEMENT	Hg ppm	Cr ppm	Zn ppm	Cu ppm	Cd ppm	Ag ppm	Pb ppm
GOSP 2		<1.00	0.50<	0.43	0.22	0.516	<0.20	<1.00
GOSP 3		1.00<	0.54	***	0.30	0.464	<0.20	<1.00
GOSP 4		1.00<	0.50<	1.60	0.20<	0.32	<0.20	<1.00
GOSP 5		1.00<	0.50<	0.30	0.20<	0.327	<0.20	<1.00
GOSP 6		1.00<	0.50<	0.20<	0.20<	<0.20	<0.20	<1.00
GOSP 8		1.00<	0.51	***	0.30	0.296	<0.20	<1.00

Table 6. Shows The Values of Heavy Chemical Elements concentration in the shallow water well

SAMPLE CODE	Hg ppb	Cr ppm	Zn Ppm	Cu ppm	Cd ppm	Ag ppm	Pb ppm
WSW 216	1.00<	0.50<	0.20<	0.20<	<0.20	<0.20	<1.00

6. Discussion

Produced water is considered to be an important source of environmental pollution due to the foreign matter carried by it, since this is toxic and negatively impacts on the environmental ecosystem. A series of physical and chemical tests were carried out in order to identify and assess the impact of produced water from the Nafoora oilfield on the environment and to propose the proper measures to deal with it.

6.1 pH

The pH is a numeric scale from 0-14 to determine the acidity and basicity of the water solution. The pH of pure water is neutral, pH=7. Solutions with pH less than 7 are acidic and solutions with pH more than 7 are basic**.**

The pH results presented in tables (2 and 3) show that pH values of all GOSPs samples ranging between 4.7 and 7.2. All samples are acidic except one sample (GOSP 6) is basic with pH values more than 7. The shallow water well (WSW216) also is has pH value more than 7 (7.7).

By comparing the current results with Ghaith Abdulrahman and et al study in the 2015 **[8]**. We notice that all values of the pH in all GOSPs stations decreased except value in the GOSP3 and GOSP 6 stations, where the value of pH rising from 6 to 7.2 in the GOSP 6 station. Therefore changed the medium from acidic to basic (Fig, 6).

The results analysis of the pH values in all GOSPs stations ranging between 4.4 and 7.2. According to WHO and FAO standard for the pH values (Table, 6) **[9]**, the associated production water from all GOSPs stations are Not suitable for drinking or agriculture uses.

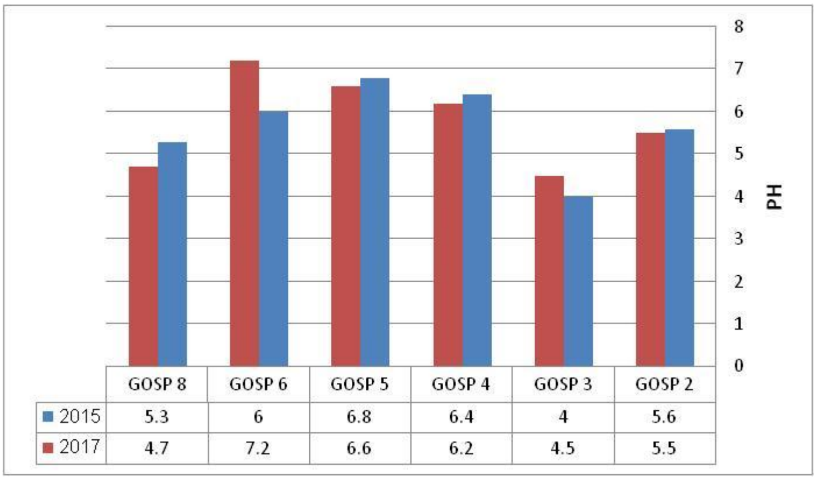

Figure 6: Shown the difference in pH between 2015 and 2017 studies.

Table 6: Shown pH WHO-FAO standards of groundwater sample**[9].**

	PH 7.5-8.5
ground water	7.7
irrigation water	7.5
drinking water	7.5

6.2 Salinity

Salinity is major concern in onshore operations. Salinity refers to the amount of total dissolved salts (TDS) in the water. This is in reality primarily due to dissolved sodium and chloride ions along with lower levels of Ca^{2+}, Mg^{2+} and K^{+} **[10]**. Due to the high cost of the TDS analysis; it is frequently measured by electrical conductivity EC, because ions dissolved in water conduct electricity **[6]**.

6.2.1 Total Dissolved Solids (TDS)

Total dissolved salts are the major constituents in produced water and the majority of these salts consist of sodium chloride. The ionic composition of these waters varies. Sodium, calcium, magnesium and potassium listed in generally decreasing concentrations are the major cations in it. However, some basins tend to have much lower median values of TDS, which is measured in parts per million or (mg/l), and the concentrations range from less than 100 ppm to over 300,000 ppm **[11].** Waters with higher TDS concentrations will be relatively conductive. Irrigation waters that are high in TDS can reduce the availability of water for plant use and also reduce the ability of plant roots to incorporate water, and reduce crop yield **[6].**

The amount of the TDS values in all GOSPs stations between 28000 to 101000 ppm. The highest TDS concentrations were about 100000 ppm in stations GOSP 3 and GOSP 8. While, the lowest concentration was in the GOSP 6 with concentration about 28000 ppm. Comparison the current results with the 2015 results shows decreasing in the TDS concentration in same stations (Fig, 7).

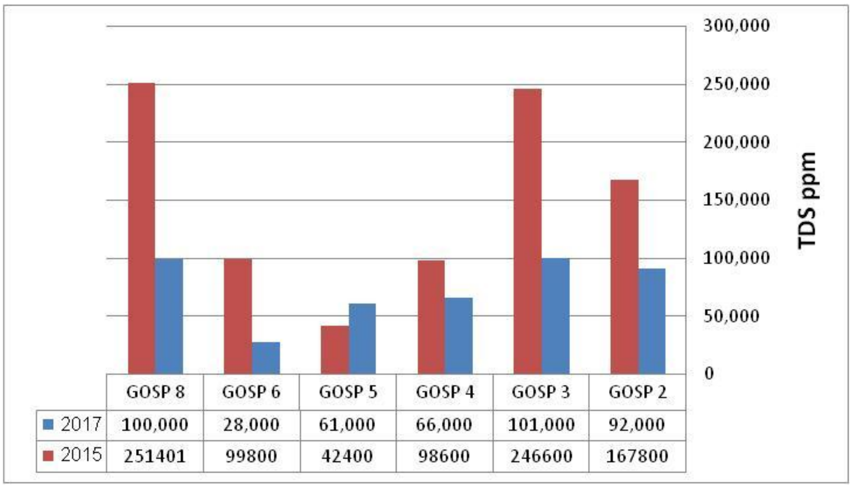

Figure 7: Shown the difference of TDS between 2015 and 2017 for same the stations.

According to WHO and FAO standard for the TDS values (Table, 7), the water production from all GOSPs stations have very high concentration of the TDS. So, it not suitable for drinking or agriculture. The concentration of the TDS in the shallow water well (WSW216) in the field was 4000 ppm and this percentage is reasonable according to the WHO concentration of the TDS for the groundwater. TDS in fresh water ranges from 500 ppm to 1,000 ppm. And in irrigation water 3000 ppm. When TDS levels exceed 1,000 ppm (parts per million) it is deemed unfit for human consumption.

Table 7: Shown TDS WHO-FAO standards of groundwater sample [9].

	TDS ppm
ground water	4000
Irrigation water	3000
drink water	1000

6.2.2 Electrical conductivity (EC)

Conductivity, in particular specific conductance, is one of the most useful and commonly measured water quality parameters. In addition to being the basis of most salinity and total dissolved solids calculations, conductivity is an early indicator of change in a water system. However, significant increases in conductivity may be an indicator that polluting discharges have entered the water. The conductivity value is the measure of the level of soluble salts. EC is measured in micro-Siemens per centimeter (μS /cm)[6]. EC levels of more than 3,000 micros/cm are considered saline. The conductivity that exceeds 3,500 micros\cm in produced water could be toxic **[12].**

All analyzed produced water samples (Table, 2) shows that the high EC level ranging from 122200 (μS/cm) to 568200 (μS/cm), the highest level of the EC presented in the GOSP 6 station with EC level about 568200 (µS/cm), while the lowest level of the EC presented in the GOSP 5 station with EC level about 122200 (µS/cm). The water sample also has EC level about 8313 (µS/cm).

According to the world level of the EC standard all the analyzed samples from the produced water or from the shallow water well have EC level higher than the standard level, so they are considered saline and toxic.

6.2.3 Chloride

Chlorides are widely distributed in nature as salts of sodium (NaCl), potassium (KCl), and calcium (CaCl2). Chloride CL concentrations in excess of about 250 mg/litre = 250 ppm can give rise to detectable taste in water, but the threshold depends upon the associated cations. Consumers can, however, become accustomed to concentrations in excess of 250 mg/litre. No health-based guideline value is proposed for chloride in drinking-water **[13].**

In the Nafoora oil field the produced water associated with oil contain high ratios of salts since Cl^- in all samples were over range and this is indicator of water salinity. The CL concentrations ranging between 111600 ppm in the GOPS 2 to 136700 ppm in the GOPS 4. Also in the shallow water well (WSW 216) was high with percentage about 80500 ppm. The chloride concentrations exceeds the WHO standard, so the water in the field is saline.

6.3 Heavy Metals Analysis

The heavy metals can have severe impact on human health and the environment. Heavy metals when entered into the body of water directly can cause special effects on living things, such as the damage to the nervous system, influence on fetal development, carcinogenicity and impaired immune function, so that it can be said that all heavy metals can become toxic when accumulated in the body for a long time **[7].** Discarding without proper treatment of the produced water can result in severe environmental damage and even kill the surrounding environment, kill water and plant life, and damage the soil that will affect humans.

Table (5) shows the values of heavy chemical elements in the produced water in the Nafoora oil field. Seven Heavy metals; Mercury (Hg), Chromium (Cr), Zinc (Zn), Copper (Cu), *Cadmium* (Cd), Silver (Ag) and Lead (Pb) have been analyzed by using Atomic Absorption method.

The concentrations of heavy elements in the produced water samples recoded significant increasing especially in Cr, Cu and Cd elements with concentration above WHO and FAO standards.

- Copper concentrations are accepted range (about **<**0.20 ppm) except two samples GOSP 3 and GOSP 8 recorded concentration 0.3 ppm,
- *Cadmium* present in all samples with high concentrations between 0.20 - 0.516 ppm, GOSP 2 and GOSP 3 recorded highest concentrations; 0.516 ppm and 0.46 ppm respectively.
- Chromium present in all samples over range (about 0.50 ppm), where the highest concentration in the GOSP 3 sample with 0.54 ppm

While the rest of heavy elements have concentrations in the acceptable ranges.

- Lead concentration was high in most of samples (<1.00 ppm).
- Silver is also have low values in all samples with concentration < 0.20 ppm.

- Mercury have low values too in all samples with concentration < 1 ppm.
- Zinc have values less than WHO and FAO standards with values between <0.20 to 1.60 ppm.

The shallow water well (WSW216) also has same concentrations in the heavy metals, this indicates the groundwater affected and their characteristics have been changed as a result of its mixing with the production water associated with crude oil in the field (Table. 6).

Comparison of heavy metal analysis results from the selected stations and water well in this study with the standards of the WHO and FAO standards (Table, 8) shows the produced water and shallow water well in the field have high concentrations in three minerals; Cr, Cu and Cd. While Hg, Zn, Ag and Pb have concentration in acceptable range less than the world standard concentration**.**

Table 8: Shows Standards of heavy metals in WHO& FAO [9].

Standard	Pb ppm	Ag ppm	Cd ppm	Hg ppm	Cu ppm	Zn ppm	Cr ppm
Drink water	0.05	0.01	0.005	1	0.2	5	0.05
Irrigation water	0.2	0.05	0.005	1	0.2	5	0.05

7. Conclusion

- Nafoora oil field the produced water about 1159276 barrels monthly measured during January 2017 associated with production 2170000 barrels of oil monthly. The produced water is discharged directly into disposal pit without treatment or reused.
- The pH values in all GOSPs stations ranging between 4.4 -7.2. According to WHO and FAO standard for the pH values, the

associated production water from all GOSPs stations are not suitable for drinking or agriculture.

- The TDS values in all GOSPs stations ranging between 28000 to over 101000 ppm. The highest TDS concentrations were about 100000 ppm in stations GOSP 3 and GOSP 8. While, the lowest concentration was in the GOSP 6 with concentration about 28000 ppm. All samples have TDS concentration higher than WHO and FAO standard. The concentration of the TDS in the WSW216 well is 4000 ppm and this percentage is reasonable for the groundwater according to the WHO. But not suitable for irrigation and drinking.
- Electrical conductivity values are very high (122200 to 568200 μS/cm). Hence, from the EC values, the groundwater of this study area can be said to have high salt concentration. According to the world level of the EC standard all the analyzed samples from the GOSPs or from the shallow water well have EC level higher than the standard level, so they are considered saline and toxic.
- The CL concentrations ranging between 111600 ppm in the GOPS 2 to 136700 ppm in the GOPS 4. Also in the shallow water well (WSW 216) the Cl was high with percentage about 80500 ppm. The concentrations exceeds the WHO standard, so the water in the field is saline.
- This study ensured that produced water in Nafoora oil field contains heavy metals such as Hg, Cr, Zn, Cu, Cd, Ag and Pb. Three minerals such as; Cr, Cu and Cd have concentration above WHO and FAO standards. While, Hg, Zn, Ag and Pb metals concentrations in acceptable concentration. So, without proper treatment to eliminate heavy metals content, produced water is harmful source of the drinking water and other daily activity.

8. Recommendation

The most crucial recommendations that have to be taken seriously for the produced water are:

- It should not be consumed by humans and animals or for irrigation of crops or plants.
- Future investigation studies should be carried on the groundwater in the field to check whether it is polluted with the oilfield chemicals before consumption.
- Use Produced water in injection to enhance oil recovery (EOR) in Nafoora oil field

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