

## Bitumen Seepage and Surface Water Contamination: Impact on Physicochemical and Biological Characteristics of Water

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### Abstract

*Seepages and subsequent mining of bitumen could impact negatively on water, by causing pollution and reducing the quality of water needed. The study was conducted in Ode-Irele bitumen belt of Ondo State where there are bitumen seepages, and Ebute-Irele without any record of bitumen seepages served as control. Composite samples of surface water to a depth of 30 cm midstream on the sites were collected. Physico-chemical parameters of water - carbonate, bicarbonate, chloride, sulphur, sulphate, ammonia, nitrate, alkalinity, Total Dissolved Solids (TDS), Total Suspended Solids (TSS), turbidity, temperature, conductivity, Dissolved Oxygen (DO), Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD) and pH were determined using standard analytical methods. Data were analyzed using descriptive statistics, correlation and t-test at  $p = 0.05$ . Values obtained were compared with recommended Federal Environmental Protection Agency (FEPA) and World Health Organization (WHO) Guidelines. Results of the study showed that seepage sites had significantly highest mean values of sulphur,  $17.65 \pm 2.82 \text{ mg/l}$  and sulphate,  $5.99 \pm 0.78 \text{ mg/l}$  in surface water than  $11.42 \pm 2.82 \text{ mg/l}$  and  $3.77 \pm 0.78 \text{ mg/l}$  respectively in control. It was found that positive associations hold between COD and each of BOD and pH with the association between COD and BOD being significant ( $p < 0.05$ ). Sulphate, ammonia, nitrate, and alkalinity, as well as TDS, TSS, turbidity, temperature, electrical conductivity, COD and BOD have positive associations with sulphur. Among these, the levels of ammonia, COD, BOD and electrical conductivity were found to be higher than WHO and FEPA guidelines. Physico-chemical parameters of water such as sulphur, sulphate, COD, turbidity and electrical conductivity which were found to be higher than guideline values in the bitumen belt of Ondo State could have negative impacts on the environment, and this should be closely monitored during bitumen development.*

**Keywords:** Bitumen, Pollution, Physico-chemical, Water, Seepage

### Introduction

Human activity is transforming most of the natural systems of the Earth (Myers *et al.*, 2013). Human development activities may alter the capacity of ecosystems to provide their resources in terms of freshwater and services such as purification of water by the ecosystem, and sequestration of pollutants in water bodies. These ecosystem services are very important for the wellbeing and survival of people (Díaz *et al.*, 2006). Water source that is safe is essential for

good health (Hunter, *et al.*, 2010). The safety of river waters is being compromised by pollution from indiscriminate disposal of sewage, industrial waste and many human activities, which affects the physico-chemical characteristics of the water (Mohammed, 2009; Kolawole *et al.*, 2011). Pollution of water can impact on health in a variety of ways and through complex pathways. The kind of health effects experienced is largely determined by the degree to which local populations depend on ecosystem services and on poverty (WHO, 2010). Pollution of surface water can come from migration of contaminants that are released into it or leaking from an underground structure through gravity. Some pollutants are adsorbed onto soil particles and retained in soil pores. On encountering ground water, the liquid pollutant will typically spread out on the surface of the water and migrate laterally, preferentially in the direction of ground water flow (Department of Environment, 2009).

Water pollution arises from various activities, among which are: sewage leakages, oil spillage, industrial waste dumped into waters, pollution of ground water through drilling activities, heavy metal, toxic waste disposal, mineral processing plant, eroded sediments (Ritter *et al.*, 2002; Khatri and Tyagi 2014). Contamination from bitumen seepage can cause the pollution of water resources, when there is surface runoff into the water. This source of contamination has the potential to increase the levels of some physical, chemical and biological parameters of surface water beyond critical limits, such that this will present health hazard to biodiversity that depend on this resource.

Nitrogen-containing compounds act as nutrients and are the most noxious pollutants of water (Bellos *et al.*, 2004). Alkalinity is defined as a measure of the capacity of water to neutralize a strong acid (Boyd *et al.*, 2011). Alkalinity usually is a product of the dissolution of bicarbonate ( $\text{HCO}_3^-$ ) and carbonate ( $\text{CO}_3^{2-}$ ) from limestone, and feldspars (Ittekkot 2003). The pH of natural water determines the solubility and chemical forms of most substances in water. pH is defined as the intensity of the acidic or basic character of a solution at a given temperature (Qureshimatva *et al.*, 2015). Dissolved Oxygen (DO) is defined as the amount of oxygen gas that is dissolved into water from any source, and it is used in measuring the degree of pollution by organic matter, the destruction of organic substances as well as the self-purification capacity of the water body (Prajapati and Dwivedi, 2016). Chemical Oxygen Demand (COD) is a measure of the oxygen depletion capacity of a water sample contaminated with organic waste matter (Ajayi *et al.*, 2016). Biochemical Oxygen Demand (BOD) measures the oxygen required by aerobic biological organisms in a body of water to break down organic material present in a given water sample (Solanki and Pandit, 2006; Manyuchi and Ketiwa, 2013). COD and BOD are similar in function because they both measure the amount of organic compounds in water and they are the most commonly used parameters for the characterization of wastewaters (Abdalla and Hamman, 2014). Total Dissolved Solids (TDS) are the inorganic matters and small amounts of organic matter, which are present as solution in water. Mining activities and effluents from industries are some of the sources of TDS in water Weber-Scannell and Duffy (2007). The extraction of fossil fuel generates wastewaters that are often high in TDS that can affect drinking water, if these wastewaters enter surface waters (Wilson *et al.*, 2014). Suspended solids (SS) in water bodies refer to the quantity of inorganic and organic matters, which are held by turbulence (Bilotta and Brazier, 2008). Turbidity relates to the expression of optical property as reflected in the intensity of light scattered by the particles present in the water (Umerfarug and Solanki, 2015). Temperature is a measure of the intensity (not amount) of heat stored in a volume of water. Electrical conductivity is the ability of any water medium to transmit an electric current and

serves as a tool to assess the purity of water, while Turbidity is the cloudiness of water brought about by a variety of particles (Qureshimatva *et al.*, 2015; Rahmanian *et al.*, 2015). High or low pH in a river affects aquatic life and alters toxicity of other pollutants in one form or the other (Ogunfowokan *et al.*, 2005). Extreme pH is known to damage biological processes (Gray, 2002). The amount of oxygen required by bacteria for breaking down organic matter in a body of water to simpler substances is measured by Biochemical Oxygen Demand [BOD] (Manyuchi and Ketiwa, 2013). BOD can be used as a robust surrogate of the degree of organic pollution of water (Virendra *et al.*, 2013), as well as gauge the effectiveness of wastewater treatment plants (Penn *et al.*, 2009). Dissolved oxygen concentrations above 5 mg/l is adequate to support aquatic life (Tepe *et al.*, 2005), but, despite the abilities of water bodies to carry out self-cleaning, the number of people affected by BOD pollution is projected to increase (Wen *et al.*, 2017). Increase in BOD can cause water quality problems such as severe dissolved oxygen depletion as well as inhibit aquatic flora and faunal growth, while it also kills these organisms in the receiving water bodies (Penn *et al.*, 2003). High concentrations of TDS have been noted to lower water quality and cause water balance problems for individual organisms and aquatic life (Waziri and Ogugbuaja, 2012), while ecotoxic effects on aquatic organisms have been reported by increase of TSS in water during rain events (Rossi *et al.*, 2006). Electrical conductivity of water is a useful and easy indicator of its salinity or total salt content. Wastewater effluents often contain high amounts of dissolved salts from domestic sewage. Nielsen *et al.* (2003) updated knowledge on how freshwater ecosystems undergo little ecological stress when subjected to salinities beyond critical limits. A number of disease conditions apart from methaemoglobinemia have been reported in humans as a result of drinking water with high concentration of nitrate (Ward *et al.*, 2018). Temperature plays an important role for controlling the physico-chemical and biological parameters of water and considered as one among the most important factors in the aquatic environment particularly for freshwater (Qureshimatva *et al.*, 2014).

Several studies on the bituminous deposit of Ondo state have been carried out (Lameed and Ogunsusi, 2002a; Lameed and Ogunsusi, 2002b; Adebiyi and Asubiojo, 2008; Olajire *et al.*, 2007, 2008; Olabemiwo *et al.*, 2011; Fagbote and Olanipekun, 2013; Victor-Oji *et al.*, 2017). However, most of the studies have focused on the characteristic constituents, hydrocarbon content and metal toxicity of the mineral. Nonetheless, there is dearth of information on the quality of surface water bodies in the bitumen belt of Ondo State, Nigeria, particularly with regards to toxicity of physico-chemical parameters as it affects biodiversity. The presence of high concentrations of these physico-chemical parameters above the critical values stipulated by regulatory bodies is considered unacceptable in receiving water bodies. This is because of their various health impacts in humans and biodiversity. This study, therefore, evaluated the physico-chemical parameters of surface water between seepage and control sites in the Ondo State bitumen belt. The values obtained for the parameters were thereafter compared with guideline values to determine their levels of toxicity. Impact assessment was limited to comparison of values of the physico-chemical parameters with permissible limits to determine whether water is suitable for consumption or safe for the environment (Khatri and Tyagi, 2014).

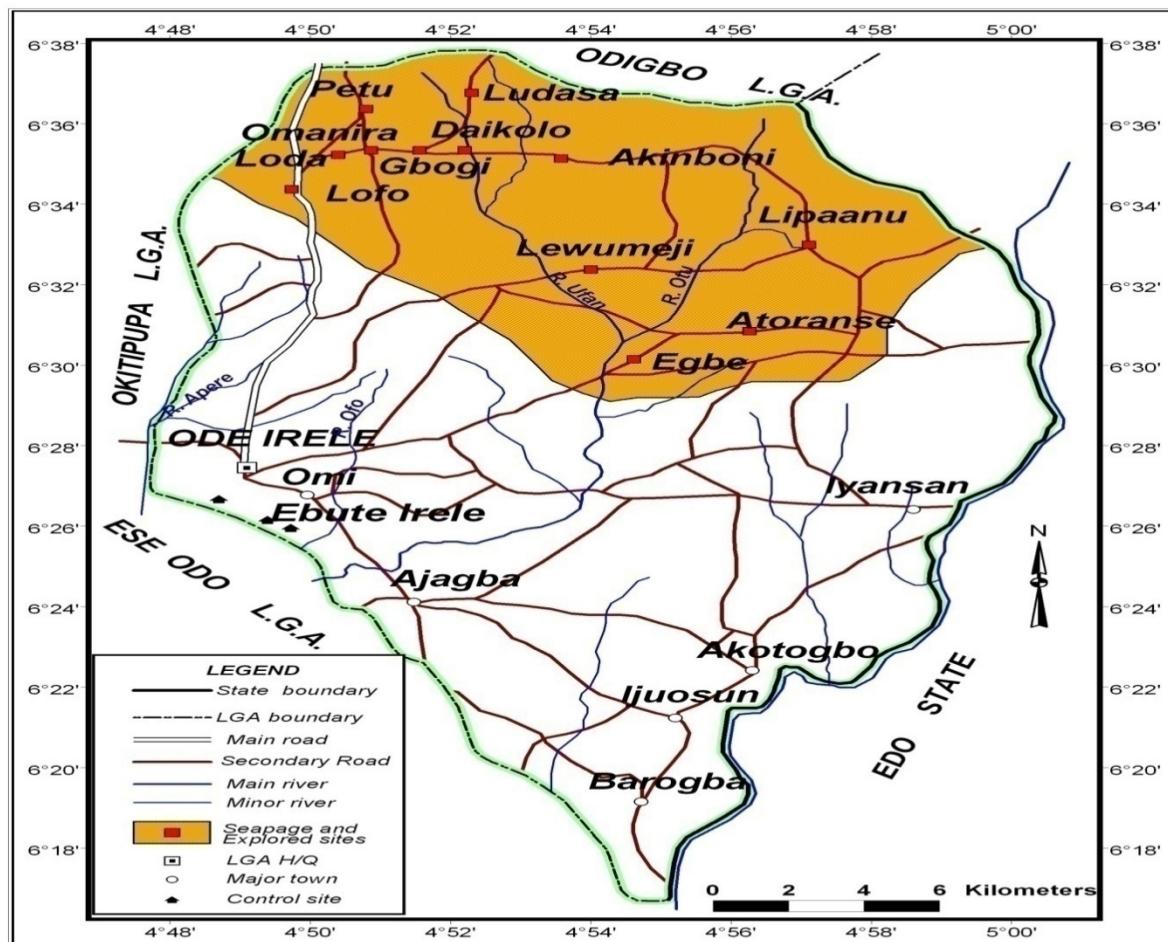
Although, exploitation of the bitumen is yet to commence, seepage of the deposit which flows into surface water and even underground aquifer has been reported (Adegoke, 2000). Adebiyi (2018) showed that the levels of physico-chemical parameters such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and total alkalinity were high in the river very close to capped bitumen well and big rivers but low in small streams. This was corroborated by their pollution index values of moderate, strong and

weak inter-element correlations respectively between the sets of waters and the Nigerian bitumen deposit, and also established relationships between the deposit and the surface waters. Ogbeibu and Eghaghe (2014) also reported DO and TSS levels which indicate degradation of bitumen polluted water. From the foregoing, the seepage of bitumen may pose a serious threat to the quality of surface water in the Ondo State bitumen belt. This study is therefore, aimed at assessing the risk of surface water pollution occasioned by seepage of bitumen, through the determination of the physico-chemical parameters of the surface waters in the bitumen belt of Ondo State.

## Materials and Methods

### Study site

The study was carried out at Ode-Irele in Ondo State, southwest of Nigeria (Fig 1). Ode-Irele is located in the Southern fringe of the state between Latitudes  $06^{\circ} 16' N$  to  $06^{\circ} 40' N$  and Longitudes  $004^{\circ} 47' E$  to  $005^{\circ} 10' E$ .



**Fig 1:** Bitumen exploration belt of Irele local Government Area, Ondo State, Nigeria. **Source.** Ogunsusi and Adeleke (2017)

### *Sampling Techniques*

Composite water samples were collected to a depth of 30 cm midstream at seepage sites in Loda (S1), Ludasa (S2), Petu (S3), and Omanira (S4). Composite samples of water were also collected at four locations in Ebute-Irele which served as the control site, about 12 km away from the seepage sites. The water samples were collected in plastic bottles and were taken to the Department of Agronomy, University of Ibadan, Nigeria within 12 hours where the samples were then subjected to analysis of physico-chemical and biological characteristics. The sample containers (plastic bottles) were pre-rinsed at least three times with the sample water. Carbonate and bicarbonate (alkalinity) were determined by titrating the water sample with  $\text{H}_2\text{SO}_4$  using phenolphthalein and methyl orange indicators (APHA, 2005). Chloride was determined by titrating the water sample with  $\text{AgNO}_3$  using the potassium mercury thiocyanate method as described by APHA (2005). Sulphur and sulphate were determined using turbidimetric method in APHA (2012) standard methods. Nitrate and ammonia in water extracts were determined using Brucine colorimetric method (Greweling and Peech, 1968). Temperatures were measured in the field using thermometer placed about 15 cm below the water surface. Total solids (TS) in water were determined using APHA (2012) standard methods. Oxygen Balance, Biochemical Oxygen Demand and Chemical Oxygen Demand in Water were determined using the methods described in water analysis using atomic absorption and flame emission spectroscopy by American Chemical Society 1968. Conductivity Test for Salt Concentration in Water to determine total dissolved solids was carried out using the method described by the United States Department of Agriculture, USDA, 1969. The pH of water samples was determined using pH meter immediately after sample collection.

### *Data analysis*

Physico-chemical data from the seepage and control sites were analyzed using descriptive statistics and t-test at  $p < 0.05$ . The associations that exist among physical, chemical and biochemical parameters of surface water were analysed using regressive correlation. Values of parameters obtained were compared between seepage and control sites, and with recommended Federal Environmental Protection Agency (FEPA, 1995) and World Health Organization (WHO, 2011) guidelines. The standard guidelines are useful in assessing the risk of surface water pollution as indicated by Song *et al.* (2013). The risk assessment is also useful for proper management of water (Adhikary *et al.*, 2010).

## **Results**

### *Physico-chemical and biological parameters of water in seepage and control sites*

Physico-chemical and biological parameters of the study sites are as presented in Table 1. The results showed that seepage sites had significantly highest mean values of Sulphur,  $17.65 \pm 2.82 \text{ mg/l}$ ; Sulphate ( $\text{SO}_4^{2-}$ ),  $5.99 \pm 0.78 \text{ mg/l}$ ; Chemical Oxygen Demand (COD)  $553.58 \pm 343.68 \text{ mg/l}$ , Turbidity,  $19.27 \pm 11.97 \text{ NTU}$  and Electrical Conductivity (EC),  $473.25 \pm 189.85 \mu\text{S cm}^{-1}$  in surface water than  $11.42 \pm 2.82 \text{ mg/l}$ ,  $3.77 \pm 0.78 \text{ mg/l}$ ,  $116.70 \pm 8.59 \text{ mg/l}$ ,  $2.34 \pm 0.43 \text{ mg/l}$  and  $203.00 \pm 17.47 \mu\text{S cm}^{-1}$  respectively in control ( $p > 0.05$ ) (Table 1).

**Table 1: Physico-Chemical Parameters of Surface Water in Bitumen Seepage and Control Sites**

Parameter	Mean		t-value	df	P	SD			
	Seepage Site	Control Site				Seepage Site	Control Site	WHO (2011)	FEPA (1995)
HCO <sub>3</sub> <sup>-</sup> (mg/L)	26.45	18.30	1.09	6	0.32	14.93	1.36	50	
Cl (mg/L)	21.00	21.60	0.33	6	0.76	3.60	0.82	250	250
S <sup>-</sup> (mg/L)	17.65*	11.42*	3.48*	6*	0.01*	2.82	2.20	500	
SO <sub>4</sub> <sup>2-</sup> (mg/L)	5.99*	3.77*	3.96*	6*	0.01*	0.78	0.79	250	50
NH <sub>3</sub> (mg/L)	16.23	6.10	1.00	6	0.35	20.14	0.76	1.5	
NO <sub>3</sub> <sup>-</sup> (mg/L)	29.45	11.20	1.62	6	0.16	22.40	2.01	50	
Alkalinity (mg/L)	6.73	2.80	1.68	6	0.14	4.59	0.89	150	
pH (mg/L)	5.69	6.20	1.19	6	0.28	0.83	0.19	6.9	6.9
DO (mg/L)	5.13	6.70	1.25	6	0.26	2.32	0.96	6.0	20
COD (mg/L)	553.58*	116.70*	2.54*	6*	0.04*	343.68	8.59	4	40
BOD (mg/L)	307.98	66.20	1.77	6	0.13	272.90	11.99	10	
TDS (mg/L)	0.10	0.08	0.57	6	0.59	0.01	0.03	500	2000
TSS (mg/L)	0.12	0.10	0.88	6	0.41	0.03	0.02	<1500	30
Turbidity(NTU)	20.05*	2.34*	2.88*	6*	0.03*	12.56	0.43	5(100-150)	
Temperature (°C)	27.25	26.80	1.65	6	0.15	0.40	0.37		30
Conductivity ( $\mu\text{S cm}^{-1}$ )	473.25*	203.00*	2.84*	6*	0.03*	189.85	17.47		25

*Physico-chemical parameters of water and their permissible limits*

The range of values of the physico-chemical parameters of water and their comparison with WHO and FEPA guidelines across the bitumen belt are as presented in Table 2. The range of Bicarbonate (HCO<sub>3</sub><sup>-</sup>) as indicated in Table 2 falls below WHO (2011) guidelines for surface water which is 50 mg/l, while the Chloride (Cl<sup>-</sup>) concentration in surface water falls below FEPA (1995) and WHO (2011) guidelines of 250 mg/l. Sulphur range in water across the bitumen belt was found to be lower than WHO (2011) limit of 500 mg/l for discharge into surface water. The amount of sulphate (SO<sub>4</sub><sup>2-</sup>) across all locations was lower than FEPA (1995) and WHO (2011) guidelines of 50 mg/l and 250 mg/l respectively for discharge into surface water. While the level of Ammonia (NH<sub>3</sub>) across the bitumen was higher than the WHO (2011) permissible limit of 1.5 mg/l, the concentration of Nitrate (NO<sub>3</sub><sup>-</sup>) in surface water of the bitumen belt falls below WHO (2011) guidelines of 50 mg/l.

The range of alkalinity across the bitumen belt is far below the WHO (2011) guidelines of < 150. The range of pH across the Bitumen Belt falls below WHO (2011) and FEPA (1995) guidelines of 6.9, while the Dissolved Oxygen (DO) across all locations was low when compared with FEPA (1995) guideline of 20 mg/l. However, the upper limit of DO was higher than WHO (2011) guideline of 6.0 mg/l. Values for COD across the bitumen belt was higher than FEPA (1995) (40.00 mg/l) and WHO (2011) permissible limit of 4.00 mg/l, while Biological Oxygen Demand (BOD) were higher than WHO (2011) permissible limit of 10 mg/l.

The level of Total Dissolved Solids (TDS) in all locations all fall far below WHO (2011) and FEPA (1995) guidelines of 500 mg/l and 2000 mg/l respectively. The Total Suspended Solids (TSS) was below FEPA (1995) and WHO (2011) guidelines of 30 mg/l and < 1500 mg/l respectively. The lower range of Turbidity was below WHO (2011) guideline of 5 NTU, with the upper range higher than that of the guideline. The Temperature across all locations all fall below

FEPA (1995) recommended standard of 30 °C. The Electrical Conductivity (EC) of water across all locations was higher than WHO (2011) guideline of 25  $\mu\text{S cm}^{-1}$ .

**Table 2.** Physical, Chemical and Biological Parameters of Water

Parameter	S1	S2	S3	S4	Mean	C1	C2	C3	C4	Mean	WHO (2011)	FEPA (1995)
HCO <sub>3</sub> <sup>-</sup> (mg/L)	18.30	18.30	48.80	20.40	26.45	17.40	19.20	16.90	19.70	18.30	50	
Cl <sup>-</sup> (mg/L)	25.20	18.00	18.00	22.80	21.00	22.40	20.80	21.00	22.20	21.60	250	250
S <sup>-</sup> (mg/L)	16.08	17.77	21.56	15.19	17.65	9.13	13.71	10.00	12.84	11.42	500	
SO <sub>4</sub> <sup>-2</sup> (mg/L)	5.31	5.86	7.11	5.66	5.99	3.09	4.45	3.07	4.47	3.77	250	50
NH <sub>3</sub> (mg/L)	5.60	46.30	4.20	8.80	16.23	5.18	7.02	6.21	5.99	6.10	1.5	
NO <sub>3</sub> <sup>-</sup> (mg/L)	9.60	51.26	46.20	10.60	29.45	9.01	13.39	10.08	12.32	11.20	50	
Alkalinity (mg/L)	2.40	7.00	13.00	4.50	6.73	2.01	3.59	3.55	2.05	2.80	150	
pH (mg/L)	4.95	6.45	5.00	6.37	5.69	6.41	5.99	6.10	6.30	6.20	6.9	6.9
DO (mg/L)	7.30	3.60	2.70	6.90	5.13	6.40	7.00	5.56	7.84	6.70	6.0	20
COD (mg/L)	112.40	765.60	878.50	457.80	553.58	122.90	108.20	125.20	110.50	116.70	4	40
BOD (mg/L)	61.30	498.20	586.00	86.40	307.98	72.20	52.80	79.60	60.20	66.20	10	
TDS (mg/L)	0.09	0.08	0.09	0.09	0.09	0.09	0.07	0.05	0.11	0.08	500	2000
TSS (mg/L)	0.09	0.09	0.14	0.14	0.12	0.11	0.09	0.08	0.12	0.10	<1500	30
Turbidity/NTU	1.86	28.62	24.86	24.86	20.05	2.04	2.64	2.77	1.91	2.34	5(100-150)	
Temperature (°C)	27.60	27.60	26.90	26.90	27.25	26.40	27.20	26.60	27.00	26.80		30
EC ( $\mu\text{S cm}^{-1}$ )	196.00	627.00	535.00	535.00	473.25	190.00	216.00	186.00	220.00	203.00	25	

#### *Associations among Physico-chemical and Biochemical Parameters of Water in Ondo State Bitumen Belt*

The various associations that exist among physico-chemical and biochemical parameters of surface water are as shown in Table 3. The result shows the following positive associations: Bicarbonate in water positively correlated with each of Sulphur, Sulphate, Nitrate, Alkalinity, Total Dissolved Solutes, Total Suspended Solute, Turbidity, Conductivity, Chemical Oxygen Demand, and Biological Oxygen Demand. As the levels of these parameters rise in water, so did that of Bicarbonate. The rise was, however, statistically significant between Bicarbonate and Alkalinity ( $p < 0.05$ ).

The association between Chloride and Dissolved Oxygen was found to be significant ( $p < 0.05$ ). The levels of the two parameters in water were found to rise and fall at the same time. The following parameters in water – SO<sub>4</sub><sup>-2</sup>, NH<sub>3</sub>, NO<sub>3</sub><sup>-</sup> and alkalinity; TDS, TSS, Turbidity, Temperature, Conductivity, COD and BOD have positive association with S<sup>-</sup>. The level of S<sup>-</sup> in water along with each of the parameters rises and falls together. The rise and fall in the levels of S<sup>-</sup> and SO<sub>4</sub><sup>-2</sup> in water is, however, more significant than those of others ( $p < 0.05$ ).

SO<sub>4</sub><sup>-2</sup> level in water across the bitumen belt is positively correlated with the levels of NH<sub>3</sub>, NO<sub>3</sub><sup>-</sup>, and alkalinity, TDS, TSS, Turbidity, Temperature, Conductivity, COD and BOD. The levels of each of the parameters in water positively influenced SO<sub>4</sub><sup>-2</sup> presence. NH<sub>3</sub> increases or decreases steadily with increasing or decreasing levels of NO<sub>3</sub><sup>-</sup>, alkalinity, turbidity and temperature. Nitrate was found to be positively associated with levels of alkalinity, TDS, turbidity,

temperature, Conductivity, COD and BOD.  $\text{NO}_3^-$  level present in water of the bitumen belt rises and falls with increasing and decreasing levels of these parameters alkalinity, TDS, turbidity, temperature, Conductivity, COD and BOD. The association between  $\text{NO}_3^-$  and COD is significant, ( $p < 0.05$ ).

Alkalinity in water positively correlates with TDS, TSS, turbidity, conductivity, COD and BOD. The relationship between alkalinity and each of COD and BOD is significant, ( $p < 0.05$ ). The levels of TDS fall far below WHO (2011) guideline of 500 mg/L and FEPA (1995) guideline of 2000 mg/L. Levels of TSS, turbidity, conductivity, COD and BOD positively influenced an increase or decrease of TDS in water across the Bitumen belt.

Turbidity, Conductivity, DO, COD and pH of water are positively correlated with the amount of TSS in water. Increase and or decrease in temperature, conductivity, COD, BOD and pH also affect rise and fall of turbidity. The positive association between turbidity and conductivity was, however, found to be significant ( $p < 0.05$ ).

Temperature of water also positively correlates with the conductivity, COD and BOD. The COD, BOD and pH were positively associated with the conductivity, with correlation between conductivity and COD being significant ( $p < 0.05$ ).

DO also positively correlates with pH. The DO and pH in water were seen to rise and fall together. COD also decreases and increases with falls and rises in BOD and pH. However, the association between COD and BOD was significant ( $p < 0.05$ ).

The results showed the following negative associations:  $\text{HCO}_3^-$  in water across the Bitumen Belt is negatively correlated with each of the following parameters –  $\text{Cl}^-$ ,  $\text{S}^-$ ,  $\text{NH}_3$ , Temperature, DO and pH. As  $\text{HCO}_3^-$  rises,  $\text{S}$ ,  $\text{NH}_3$ , Temperature, DO and pH decreases. However,  $\text{HCO}_3^-$  dropped with increasing  $\text{Cl}^-$ .

Chloride in water of the bitumen belt was negatively correlated with each of  $\text{S}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_3$ ,  $\text{NO}_3^-$ , alkalinity, TDS, TSS, Turbidity, Temperature, Conductivity, COD, BOD, DO and pH. The association between  $\text{Cl}^-$  and each of  $\text{NO}_3^-$ , BOD and DO are significant. Chloride increased with decreasing  $\text{S}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_3$ ,  $\text{NO}_3^-$ , alkalinity, TDS, and TSS, while  $\text{Cl}^-$  also decreased with increasing Temperature and Conductivity.

Sulphur was negatively correlated with each of DO and pH. As  $\text{S}^-$  increases, DO and pH in water decreases. In addition  $\text{SO}_4^{2-}$  was negatively correlated with each of DO and pH. As  $\text{SO}_4^{2-}$  level increases in water, pH decreases. As  $\text{SO}_4^{2-}$  decreases, DO increased and vice versa.

Nitrate was correlated with each of DO, TDS and pH. The relationship between  $\text{NO}_3^-$  and DO was, however, significant. As  $\text{NO}_3^-$  increased in water, DO, TDS and pH decreased. The association between alkalinity and each of DO and pH was negative, but the association with DO is significant ( $p < 0.05$ ). As DO and pH rises in water, alkalinity level decreased. Total Dissolved Solute (TDS) in water is negatively correlated with each of Temperature, DO and pH. The association between TDS and DO was significant ( $p < 0.05$ ). As the temperature, DO and pH rises in water, TDS decreased. Total Suspended Solute, TSS, was negatively correlated with each of  $\text{NH}_3$ ,  $\text{NO}_3^-$ , Temperature and BOD. TSS was found to fall with increasing quantities of  $\text{NH}_3$ ,  $\text{NO}_3^-$ , Temperature and BOD.

Dissolved oxygen, DO, shows negative correlation with each of NH<sub>3</sub>, Turbidity, Temperature, Conductivity and COD. The association between DO and COD is significant ( $p < 0.05$ ). DO rises with decreasing NH<sub>3</sub>, and turbidity, while the pH of water samples has negative correlation with each of Temperature and BOD. As Temperature and BOD rise, pH decreases. The lower range of pH (4.95) and the upper range (6.37) across the Bitumen Belt fall below WHO (2011) and FEPA (1995) recommended standard of 6.90.

**Table 3.** Associations among Physical, Chemical and Biochemical Parameters of Water in Ondo State Bitumen Belt

Variable	Physical, Chemical and Biochemical Characteristics															
	HC O <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	S <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	NH <sub>3</sub>	NO <sub>3</sub> <sup>-</sup>	DO	COD	BOD	pH	Alkal.	TDS	TSS	Turbidity	Temp	conductivity
HCO <sub>3</sub> <sup>-</sup>	1.00	-0.54	0.78	0.75	-0.33	0.52	-0.70	0.66	0.68	-0.57	0.91*	0.99*	0.38	0.29	-0.07	0.57
Cl <sup>-</sup>	-	1.00	-0.56	-0.50	-0.52	-0.92*	0.94*	-0.86	-0.91*	-0.20	-0.80	-0.41	-0.02	-0.66	-0.07	-0.80
S <sup>-</sup>	0.78	-0.56	1.00	0.97*	0.16	0.76	-0.80	0.83	0.84	-0.51	0.88	0.79	0.14	0.57	0.50	0.77
SO <sub>4</sub> <sup>-2</sup>	0.75	-0.50	0.97*	1.00	0.12	0.67	-0.72	0.84	0.77	-0.41	0.84	0.77	0.34	0.67	0.39	0.82
NH <sub>3</sub>	-	-0.52	0.16	0.12	1.00	0.63	-0.43	0.44	0.46	0.54	0.09	-0.41	-0.43	0.57	0.53	0.46
NO <sub>3</sub> <sup>-</sup>	0.52	-0.92*	0.76	0.67	0.63	1.00	-0.97*	0.90*	0.98*	-0.01	0.81	0.43	-0.16	0.68	0.44	0.83
Alkal.	0.91	-0.80	0.88	0.84	0.09	0.81	-0.92*	0.90*	0.91*	-0.31	1.00	0.86	0.29	0.60	0.11	0.83
TDS	0.99	-0.41	0.79	0.77	-0.41	0.43	-0.61	0.59	0.61	-0.67	0.86	1.00	0.40	0.23	-0.02	0.51
TSS	0.38	-0.02	0.14	0.34	-0.43	-0.16	0.02	0.27	-0.04	0.14	0.29	0.40	1.00	0.44	-0.64	0.39
Turbidity	0.29	-0.66	0.57	0.67	0.57	0.68	-0.64	0.87	0.66	0.39	0.60	0.23	0.44	1.00	0.11	0.94*
Temp.	-	-0.07	0.50	0.39	0.53	0.44	-0.29	0.22	0.37	-0.36	0.11	-0.02	-0.64	0.11	1.00	0.16
Conductivity	0.57	-0.80	0.77	0.82	0.46	0.83	-0.84	0.98*	0.85	0.14	0.83	0.51	0.39	0.94*	0.16	1.00
DO	-	0.94*	-0.80	-0.72	-0.43	-0.97*	1.00	-0.92*	-1.0*	0.12	-0.92*	-0.61	0.02	-0.64	-0.29	-0.84
COD	0.66	-0.86	0.83	0.84	0.44	0.90*	-0.92*	1.00	0.93*	0.02	0.90*	0.59	0.27	0.87	0.22	0.98*
BOD	0.68	0.91*	0.84	0.77	0.46	0.98	-1.00*	0.93*	1.00	-0.15	0.91*	0.61	-0.04	0.66	0.37	0.85
pH	-	-0.20	-0.51	-0.41	0.54	-0.01	0.12	0.02	-0.15	1.00	-0.31	-0.67	0.14	0.39	-0.36	0.14

\*Correlations that are significant at  $p < 0.05$

## Discussion

The mean values of Sulphur, Sulphate, Chemical Oxygen Demand, Turbidity and Electrical Conductivity in surface water of bitumen seepage site which are significantly higher than the control shows that these parameters in the water samples could have been generated from bitumen seepages. The range of HCO<sub>3</sub><sup>-</sup> level which was found to be lower than the WHO (2011) guideline, cannot cause any environmental hazard. The bicarbonates of magnesium and calcium that are standard alkaline constituents found in almost all surface and ground water bodies, affect alkalinity and hardness of water, which makes the water unsuitable for drinking purpose (Mohsin *et al.* 2013). The Chloride levels which fall below the recommended standards of FEPA (1995) and WHO (2011) cannot pose any potential environmental hazard. Finding of Larson and Belovsky (2013) showed that richness of aquatic species was most negatively affected by salinity. Also the finding of Nielsen *et al.* (2003) revealed that freshwater ecosystems undergo little ecological stress when subjected to salinities beyond critical limits. Sulphur level in surface water across the bitumen belt was lower than WHO (2011) limit for discharge into surface water. Therefore, this low level of sulphur in the form of sulphide may not pose any potential

environmental hazards, despite the higher level of sulphur in the seepage site over the control. Barrett *et al.* (1999) revealed that water containing sulphur tastes bitter and in severe cases, because of its characteristic laxative property, results in dehydration. This foul taste and associated medical conditions serve as an identification of potential sulphur-contaminated groundwater and needs immediate isolation and treatment. Sulphate levels fall below FEPA (1995) and WHO (2011) recommended standards. Even with the attendant significant increase of sulphur levels in the study area over the control, the amount of  $\text{SO}_4^{2-}$  that is leached into aquatic environment may not be enough to cause any potential environmental hazard. Sulphate pollution can lead to higher availability of nutrients and potentially toxic compounds in wetlands (Geurts *et al.* 2009). The range of values for  $\text{NO}_3^-$  across the bitumen belt falls below WHO (2011) recommended standard of 50 mg/L. Notwithstanding, Ward *et al.* (2018) reported potential health risk from nitrate in drinking water above threshold, which may give rise to a condition known as methaemoglobinemia and other disease conditions.

The toxic level of  $\text{NH}_3$  is possibly a reflection of the high rate of organic decomposition in the study area, since its level is not significantly different from that of the control. This can pose a potential environmental hazard. This finding, however, is not in tandem with that of Fadiran and Dube (2009) in which ammonia in surface water and effluents were below permissible limits. The level of alkalinity across the bitumen belt far below the permissible limit set up by CPCB (Kumar and Puri, 2012). It was emphasized that alkalinity is primarily due to carbonate, bicarbonate and hydroxide contents. Alkalinity is used in the interpretation and control of water and waste water processes. The low level of alkalinity is in agreement with Ayandiran *et al.* (2018) in his finding on water quality assessment of bitumen polluted water in Ondo State. The levels of TDS in all locations across the bitumen belt fall far below the WHO (2011) guideline of 500 mg/L and FEPA (1995) recommended standard of 2000 mg/L. The low level of TDS indicates that TDS in the aquatic environment across the bitumen belt at present may not pose any potential threat to environment. This low level is in contrast with Israel *et al.*, (2008) that petrochemical effluents contained very high concentration of TDS. Akan (2008), however, also affirmed that TDS of soils irrigated with wastewater was higher than the maximum permissible limits set by Federal Environmental Protection Agency (FEPA, 1995), Nigeria. Low level of TSS in aquatic medium implies that it does not at present pose any potential environmental hazard. This low level contrasts with Israel *et al.* (2008), that petrochemical effluents contained significant concentrations of TSS, as well as Makwe and Chup (2013) in which TSS in groundwater exceeded WHO (2011) guideline of >1,500mg/L and FEPA (1995) guideline of 30mg/L. High turbidity level in water as indicated in the upper range in the study area is in tandem with Waziri and Ogugbuaja (2012) that rainfall and river flow are related to turbidity. The level of turbidity is significantly higher in seepage site than the control. This could be ascribed to runoff from bitumen seepages and exploratory activities, as could be brought about by the high rainfall characteristic of the tropics. The low temperature range recorded for this study is in line with Ayandiran *et al.*, (2018). A lower temperature level in the aquatic medium is a reflection of its inability to enhance the growth of micro-organisms. But, the lower temperature may have reduced taste, odour, and colour. The surface water in the bitumen belt was discovered to be very clean and is mostly used for domestic purposes by the local population. Since the electrical conductivity of surface water is higher than that of control and WHO (2011) guide level, it does mean that the water contains high amounts of ions (APHA, 2005; Jain *et al.*, 2005; Asare-Donkor *et al.*, 2016). This condition will pose health hazard (Fatoki and Awofulu 2003). High electrical conductivity of surface water in the bitumen belt could, therefore, be of potential

environmental threat. Electrical conductivity of water (Kumar and Sinha, 2010) is a useful and easy indicator of its salinity or total salt content. The result of high amounts of dissolved salts in bitumen seepage site over that of the control is in conformity with Ololade and Ajayi (2009). High salt concentrations in waste effluents (Akan, 2008) can increase the salinity of the receiving water, which may result in adverse ecological effects on aquatic biota. The level of DO which is a measure of the degree of pollution by organic matter, the destruction of organic substances as well as the self purification capacity of water body this parameter which falls below FEPA (1995) guideline and was lower than that of control site is corroborated by Mkawe and Chup (2013) and Ayandiran *et al.* (2018). It is also in tandem with the finding of Sasikala *et al.* (2015) that the DO level of 5.0 – 8.0 mg/L in a surface water body is an important indicator of its health. The presence of DO in water is necessary for maintaining favorable conditions for growth and reproduction of a normal population of fish and other aquatic life. COD is a measure of biochemical activities taking place in aquatic medium and oxygen depletion capacity of a water sample contaminated with organic waste matter. The COD in the study area was high. The findings of Makwe and Chup (2013), Tawati *et al.* (2018), and Israel *et al.* (2008) revealed that petrochemical effluent contained significant concentration of COD. Akan (2008) also confirmed that COD of soils irrigated with wastewater was higher than the guideline set by FEPA (1995). BOD is the dissolved oxygen used by micro-organisms in the biological oxidation of organic matter. The BOD level of surface water across the bitumen belt prior to development is higher than FEPA (1995) guideline, it could then be deduced that BOD in this area may, therefore, be a potential environmental hazard. The level of BOD which is insignificantly higher in seepage site over that of control shows that the toxic level could only have come from organic compounds in water as they are the most commonly used parameters for characterizing wastewaters (Abdalla and Hamman, 2014). The pH across the Bitumen Belt fall below WHO (2011) and FEPA (1995) guidelines which are still within the buffer zone, an indication that the surface waters contains a weak acid and its conjugate base. This low level agreed with the finding of Ayandiran *et al.* (2018) in his finding on water quality assessment of bitumen polluted water in Ondo State. The low pH may not have negative effects on aquatic life and biological processes or alter toxicity of other pollutants (Gray, 2002; Ogunfowokan *et al.*, 2005).

The significant association between DO and BOD ( $p < 0.05$ ) in this study is a further confirmation of DWAF(1996), that BOD is also taken as a measure of the concentration of organic matter present in any water. The greater the decomposable matter present, the greater the oxygen demand and the greater the BOD values.

The positive association between Sulphur and each of  $\text{SO}_4$ ,  $\text{NH}_3$ ,  $\text{NO}_3$ , and alkalinity, as well as TDS, TSS, turbidity, temperature, conductivity, COD and BOD is a reflection that each one of these parameters rises and falls with the level of Sulphur. But, this association was significant with  $\text{SO}_4$ . This positive association of Sulphur with each of the parameters can, therefore, be used as a yardstick in estimating the presence of these parameters in surface water.

The positive correlation of  $\text{SO}_4^{-2}$  with each of  $\text{NH}_3$ ,  $\text{NO}_3$ , and alkalinity, TDS, TSS, turbidity, temperature, conductivity, COD and BOD shows that each of the parameters rises and falls with the level of  $\text{SO}_4$ . Consequently,  $\text{SO}_4$  can be used to estimate the amount of the parameters in polluted water.

The level of COD also decreases and increases with falls and rises in the levels of BOD and pH, but the association between COD and BOD were significant. Abdalla and Hamman (2014)

reported that COD is similar in function to BOD because they both measure the amount of organic compounds in water and they are the most commonly used parameters for the characterization of wastewaters. COD is also used to estimate BOD because a strong correlation exists between both parameters (Ajayi *et al.*, 2016).

Furthermore, the level of turbidity increases and or decreases with rise or fall in temperature, conductivity, COD, BOD and pH, and was particularly significant with conductivity. Because of this correlation, turbidity can be used to estimate the amount of the parameters in polluted water.

## Conclusion

The statistics obtained from the physico-chemical analysis of the surface water samples in the bitumen belt of Ondo State, Nigeria clearly indicates that the difference in values of sulphur, sulphate, Chemical Oxygen Demand and turbidity in surface water of bitumen seepage sites and those of the control were statistically significant, with those of the seepage sites being higher. Therefore, the parameters should be closely monitored. This is to ensure that these parameters do not accumulate in the surface waters beyond the permissible limits.

The surface water has its lower limit of DO and turbidity falling below WHO (2011) guideline, while the upper range is higher. The levels of NH<sub>3</sub>, COD, BOD and electrical conductivity in surface water across the bitumen belt determined in this study were found to be higher than FEPA, 1995 and WHO, 2011's guidelines. The levels of these substances should be closely monitored particularly during the exploitation of the bitumen deposits.

The parameters with which each of sulphur, sulphate, COD, and turbidity has positive correlations especially that are statistically significant should be closely monitored.

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