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A comparative study of chemical trends and models of deck- drain samples from some oil wells in the Niger delta basin, southeastern Nigeria

C. A. Ahiarakwem

Department of Geosciences, Federal University of Technology, Owerri, Nigeria.

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ABSTRACT

Deck- drain samples obtained from five oil wells in the Niger Delta Basin of Nigeria were analyzed using Atomic Absorption Spectrophotometer (AAS), digital meters , American Standard and Testing Materials. The results shows that the pH of the deck-drain samples varies from 5, 10 to 5.4 while the total dissolved solids(TDS) varies from 4,585 to 27,170 mg/l. The electrical conductivity varies from 7,054 to 21,277µS/cm while the chloride content varies from 4 ,000 to 4,400mg/l. The H_2S concentration ranges from 0.80 to 1.10 mg/l. These values do not conform with the Nigerian Department of Petroleum Resources (DPR) effluent water standard and thus constitute a threat to the environment. The result also show that the deck-drain samples are hard and contains high concentrations of calcium and sodium. The concentrations of the major cations in decreasing order is: $Na^+ > Ca^{2+} > Mg^{2+} >. K^+$ while that of the anions is: $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^-$ implying that the fluid type is NaCl. The pollution index (PI) of the samples varies from 17.81 to 42.47; this is in excess of the PI critical value of 1 and thus confirms high rate of degradation of the deck-drain samples.. The Sodium Adsorption Ratio (SAR) values of the samples ranges from 28.04 to 28.97 indicating that the deck-drains are poor for irrigation purposes. Piper and Stiff diagrams shows that the deck-drain samples exhibits the same chemical trend and model. Although, the deck-drain samples contains high concentrations of pH, TDS, electrical conductivity, H_2S, Cl^-, Ca^{2+} and Na^+; these parameters can be treated and reduced to tolerable levels using soda ash, reverse osmosis , electro dialysis and aeration methods thus preventing soil and water pollution which can arise from the discharge of untreated deck-drains into these environments.

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Introduction

Exploration, development and production are three vital aspects of oil industry activities which have a lot of impact on the environment. Oil activity produces a variety of wastes which can be classified into three broad categories (solid, liquid and gaseous). The solid wastes include drill cuttings and mud and they are usually characterized by high concentrations of barium, manganese and iron. They also contains significant concentrations of copper, chemical oxygen demand (COD), sulphate, oil and grease (Ahiarakwem and Okonkwo, 2004).Liquid effluent associated with oil activities include rig effluents, work over fluids and deck-drains (which are usually collected at deck-drain holding tanks).The pollutants commonly found in liquid effluents include pH, total dissolved solids (TDS), H_2S, salinity and electrical conductivity (Ahiarakwem and Onyeike, 2008). The discharge of untreated liquid effluent into the environment can result in sol and water pollution. The gaseous effluent include,CH_4, SO_2, NO_2,and H_2 S. Apart from direct health impacts such as asthma and respiratory illness, these gases contributes to global warming and also causes formation of photochemical smog and acid rain deposition. There is therefore need for regular monitoring of the bio-chemical character of these wastes so as to to put in in place appropriate pollution mitigation measure. A comparative study in this regard is quite essential, Although some studies (Olowokere and Ojo, 2008;Obi, et al., 2008; Eneogwe and Ekundayo, 2004; Inyang and Enang, 2002) have been carried out on different aspects of the Niger Delta Basin, there is paucity of information on wastes (such as deck- drains and drill cuttings) which are associated with oil drilling activities.The few Studies (Ahiarakwem and Onyeike, 2008; Ahiarakwem and Okonkwo, 2004) examined some chemical parameters of deck-drain samples and geochemical properties of drill cuttings obtained from some oil wells in the Niger Delta Basin of Nigeria. However, the chemical trends and models (PI,SAR, Piper and Stiff diagrams) of wastes such as deck-drain sampls are yet to be investigated. It is important to note that most information on wastes associated with oil activities such as deck-drain samples are restricted to Oil companies and regulatory bodies such as Department of Petroleum Resources (DPR) and Federal Environmental Protection Agency (FEPA).This study examines the chemical trends and models of deck-drain samples obtained from some oil wells in the Niger Delta Basin (Fig.1). The results of this investigation provides relevant information that are useful in putting in place appropriate pollution mitigation measures which would ameliorate the threat of deck-drain samples on the soil and water resources.

Climatic Conditions

The study area is located within the equatorial rain forest belt with a mean annual rainfall of about 2,500mm; most of which falls between the months of May and October. This period is

Tele: +234-080-33738340

E-mail addresses: cosahia@yahoo.com

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characterized by moderate temperatures and high relative commodities. The months of November to April have Scanty rains, higher temperatures and low relative humidities` (National Root Crop Research Institute ,2012) . The vegetation cover of the area, is characterized by shrubs, short trees, raffia palms and palm trees. Most of the vegetation have been removed due to human activities (oil and natural gas exploration and exploitation, construction of civil structures such as buildings and roads).

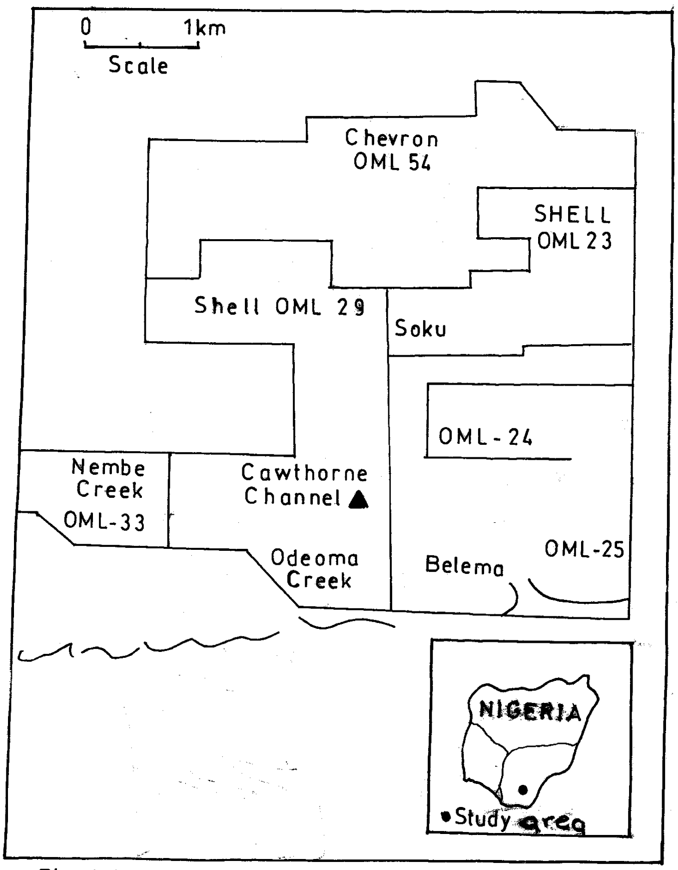

Fig. 1 Map showing Cawthorne Channel-45 Oil Well

Geology

The study area is within the Niger Delta Basin of Nigeria(Fig.1). The basin is characterized by three litho-stratigraphic units, namely from top to bottom: Benin, Agbada and Akata Formations. These Formations cut across time intervals (Fig.2). The Benin formation consists of continental sands, very coarse sandstone, conglomerates and clay intercalations. The clay inter-beds includes Qua Iboe, Agbada and Soku clays. The formation also contains isolated gravel units in some places (Ananaba et al., 1993). The Benin Formation is underlain by the Agbada Formation which consists essentially of sands and clay units and serves as the reservoir rock of the Niger Delta Basin. The Formation is highly porous and permeable and contains an avalanche of both structural and stratigraphic traps (growth faults, roll-over anticlines. Salt domes and unconformities).The Agbada Formation overlies the Akata formation which consists of pro-delta marine shale and acts as the main oil source rock in the Niger Delta Basin (Short and Stauble, 1967; Murat,1970, Whiteman, 1982; Odigi, 1986). All the five oil wells investigated penetrated both the Benin and Agbada formations

Methodology

A total of five (5) deck- drain samples were obtained from five different oil wells (designated A, B, C, D, and E) were collected at the deck-drain holding tank (DHT) with the aid of sterilized plastic containers and glass bottles. Twenty six chemical parameters (Table 1) were analyzed using various methods. Total dissolved solids (TDSI, Total Alkalinity, electrical conductivity, dissolved oxygen (DO) and pH were measured in-situ using digital meters. Salinity (Chloride) was measured in accordance with American Standard and Testing Materials (ASTM) d D512. Oil and grease were determined using the photometric method while ASTM D3579 method was employed in the determination of total organic carbon (TOC).ASTM D516 and APHA 425D methods were employed for sulphates and phosphates analysis respectively. Surfactant and hydrogen sulphide were analyzed using the methylene blue method.. Metal analysis (Ba^{2+}, Cu^{2+}, Cd^{2+}, $Cr^{2+}$and Zn^{2+}) were carried out using Atomic Absorption Spectrophotometer (AAS). Bio-chemical oxygen demand (BOD) was measured by incubating the samplesinthe dark at $25^oC$for five days and measuring the dissolved xygen consumed.

The concentrations of the major cations and anions in milligram/liter (mg/l)were converted to milliequivalent/liter (meq/l) using the equation 1 beloe (Clark et. al.,1977):

$$\text{Milliequivalent/liter (meq/l)} = \frac{\text{Milligram /liter}}{\text{Equivalent mass}} \qquad \text{..equ. 1}$$

The concentrations in meq/l were used to prepare Piper trilinear and Stiff diagrams as well as calculation of Sodium Adsorption Ratio (SAR). The SAR was determined using the equation developed by Wilcox (1955).

$$SAR= \frac{Na+}{\sqrt{\frac{(Ca^{2+} + Mg^{2+})}{2}}} \qquad \text{.equ. 2}$$

The parameters considered for the determination of the pollution index (PI) of the deck-drain samples were pH, Total Alkalinity, Total Hardness, ,Total dissolved solids (TDS), sulphate and chloride. The PI was calculated using the equation developed by Horton (1965).

$$PI= \sqrt{\frac{(maxC_i/L_j)^2 + (meanC_i/L_j)^2}{2}} \qquad \text{.equ.3}$$

Where

C_i = concentration of chemical parameters

L_j = World Health Organization (2006) permissible limit.

Results and discussion

The results of the chemical analysis of the deck-drain samples is summarized in Table 1 while the concentrations of the major cations and anions in milliequivalent/liter, Sodium Adsorption Ratio (SAR) and Pollution Index (PI) values are shown in Table 2 and 3 respectively.

Physical parameters

The pH of the deck-drain samples varies from 5.00 (well E) to 5.40 (well C). The pH of the deck-drain samples indicates that they are acidic and constitute a threat to both soil and water resources if disposed to these environments in untreated form. The deck-drains are capable of destroying soil fertility and aquatic life such as fish. At a pH of about 4.50, all fish in surface water resources would die and at a pH of about 6.00, freshwater shrimps cannot survive (Bourodemos, 1974). Certain crops such as legumes, vegetable and some aritiesof fruits cannot thrive under highly acidic soils. However, acidic surface water resources is not favourable for the growth of aquatic plants such as Water Hyacinth as they grow best between pH of 7.00 and

9.20 (Bouurodemos, 1974). The pH of the deck-drain samples can be corrected using sodium bicarbonate (soda ash).

The total dissolved solids (TDS) varies from 4,585 (well D) to 27, 170mg/l (well C). Except for wells D and E with TDS values of 4,585mg/l and 5,000 mg/l respectively, other wells have TDS concentrations in excess of the DPR recommended maximum limit of 5,000mg/l. Generally, the deck-drain samples are characterized by high concentrations of TDS. Water sample with a TDS range of 0 to 1,000 mg/l is classified as fresh while that with a TDS range of 1,000 to 10,000 mg/l is classified as brackish. Water sample with a TDS range of 10,000 to 100,000 mg/l is saline while tha with TDS in excess of 100,000 mg/l is classified as brine (Carrol, 1962).It is evident from the TDS concentrations that the deck-drains falls between brackish and saline water and this implies that their disposal to the recipient environment (soil and water resources) can cause destruction of crops, vegetation and aquatic life.

Electrical conductivity varies from 7,054 (well B) to 21,277µS/cm (well C) and this is in excess of DPR maximum limit of 40µs/cm. This is also inimical to soil fertility and survival of aquatic life; it can also cause pollution of coastal aquifers.

Total Alkalinity varies from 185 (well C) to 200mg/l (well B) while total hardness varies from 1,170 (well D) to 1,225mg/l (well B). The deck-drain samples are very hard (Wilcork, 1993)and this because of high concentrations of Ca^{2+} and Mg^{2+} .The disposal of deck-drains can increase the alkalinity and hardness of coastal aquifers, streams and rivers. Excessive Alkalinity concentrations is inimical to survival of aquatic life such as fish (B0yd and Lightropper, 1979).

Major cations and anions

The concentration of calcium varies from 316 (well D) to 324mg/l (well E) while that of sodium varies from 2,275 (well B) to 2,310mg/l (well C). This is not in conformity with DPR limits for these parameters. However, the concentrations of the major cations in decreasing order is: $Na^+ > Ca^{2+} > Mg^{2+} > K^+$. The chloride content varies from 4,000 (well B) to 4,400mg/l (well C) and this is also not in conformity with DPR limit of 2,000mg/l for deck-drain effluent water. Except for chloride, all other measured anions conformed with DPR standard. The concentrations of the major anions in decreasing order is: $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^-$. High concentrations of chloride can pollute the soil thus destroying its fertility; it can result in mass destruction of certain species of fish. When discharged into small streams, it can cause laxative effects in humans and animals and can also cause large scale pollution of coastal aquifers.

Ba^{2+}

The concentrations of barium varies from 4.50 mg/l (well C) to 7.00 mg/l (well D). Except for wells A and C with Ba^{2+} concentrations of 5.00 and 4.50 mg/l respectively, other wells have Ba^{2+} concentrations in excess of DPR maximum limit of 5.00 mg/l. The Ba^{2+} owe their source from barite that is usually used in oil drilling operation as a weighting material (fluid). Generally, the deck-drain samples contains high concentrations of Ba^{2+} . Excessive concentrations of Ba^{2+} in water resources causes hypertension that may eventually lead to stroke.

H_2S

The concentration of H_2S varies from 0.80 to 1.10mg/l and this does not fall within the DPR recommended maximum limit of 0.20mg/l. H_2S contributes to the acidic nature of deck- drain samples because the sulphur can be oxidized to form SO_2 which reacts with the effluent water forming both sulphurous (H_2SO_3)and sulphuric (H_2SO_4) acids. Bubbles of H_2S gas is inimical to survival of crabs and fish.

Other parameters

The deck- drain samples contains significant concentrations of BOD, COD, Mn^{2+}, surfactants, oil and grease and total organic carbon although all of them conformed with DPR standard. However, these parameters can increase the levels of similar ones that are already contained in soil and water resources.

Except for Cd^{2+} and Cr^{6+}, other determined heavy metals (Zn^{2+} and Cu^{2+}) in the deck- drain samples were within the DPR limit (Table1). It should be noted that excessive concentrations of Cd^{2+} in water resources is toxic to the kidney while high levels of Cr^{6+} causes cancer.

Treatment

The high concentrations of certain chemical parameters in the deck-drain samples can be reduced to tolerable levels using various methods (Ahiarakwem and Onyeike, 2008). For instance the pH can be corrected using soda ash (Na_2CO_3) while H_2S can be reduced using aeration method. TDS and electrical conductivity can be reduced using aeration, sedimentation, coagulation and filtration method while chloride can be reduced to a tolerable level using reverse osmosis. The high concentrations of barium, calcium and sodium can be reduced using ion exchange method while oil and grease in the samples can be reduced through coagulation and filtration. Surfacants and total organic carbon can be reduced using aeration and reverse osmosis. Heavy metals can be reduced using aconic acids.BOD and COD in the samples can be reduced using a process equipment which utilizes compounds low in sulpide contents (Daniel and Walter, 1987).

Chemical Trends and Models

It is evident from the result of the chemical analysis (Table 1) that the deck-drain samples exhibits close chemical character. For instance, all the samples from the five different oil wells, generally contains high concentrations of pH, TDS, electrical conductivity, chloride, Ba^{2+} and H_2S . The chemical trends of the measured parameters in the five different locations are also similar. The similarity in the chemical character and model of the deck- drain samples can be appreciated by considering the Piper and Stiff diagrams (Figures 3 and 4), SAR and PI values.

Piper trilinear plot

The Piper trilinear plot (Fig.3) shows a close chemical relationship of the deck-drain samples. From the plot, the dominant cations and anions are sodium and chloride respectively implying that the deck-drain samples are dominantly NaCl effluent water. Consequently, the samples plotted in the saline portion of the diamond portion of the Piper trilinear diagram (Fig.3). The plot of the samples also coincides with the zone of permanent hardness. The diagram, therefore, confirms the high pollution level of the deck –drain samples irrespective of their different locations in the Niger Delta Basin.

Stiff diagram

The Stiff diagram (Fig.4) of the deck-drain samples indicates that they have similar shape and close size of concentrations of parameters at each well. The same shape of the deck-drain samples indicates a common source; this source is the drilling fluids including additives used during the construction of the oil wells.

SAR

The SAR values of the deck-drain samples varies from 28.04 to 28.97 (Table 2) thus implying a close relationship in chemical character and model. According to Wilcox (1955), water sample with SAR range of 0- 10 is excellent for irrigation purposes while that with an SAR value greater than 26 is considered poor for irrigation purposes. The SAR values of the deck –drain samples shows that the cannot be used for irrigation purposes. The deck-drain effluent water are therefore poor for irrigation purposes as such must be adequately treated if they must be used.

Pollution index

The pollution index (PI) of the deck-drain samples is another evidence of the similar chemical trend of the effluent water. The PI varies from 17.81 to 42,47 (Table 3). Horton ,(1965) observed that the critical PI value is about 1; this implies that any water with PI value of more than 1 is considered polluted and thus requires treatment. Based n this findings, the deck-drains are thus highly polluted and requires adequate treatment before disposal.

Major Cations and Anions

The relative abundance of the major cations and anions in the deck-drain samples follows the same pattern signifying a similar chemical trend. The relative abundance of the major cations of the deck-drain samples in decreasing order is: $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ while that of the anions is: $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^-$.

Conclusion

The deck-drain effluent water from five different oil wells in the Niger Delta Basin generally contains high concentrations of PH, TDS, H_2S, Ba^{2+} ,electrical conductivity and chloride (Table 1). The samples also contains significant concentrations of Mn^{2+}, BOD, COD oil and grease. However, the high levels of certain parameters in the samples can be reduced to a tolerable levels using appropriate treatment methods.

Piper diagram indicates that the deck-drain samples fall within the saline portion which also coincides with the permanent hardness portion of the diamond section of the diagram. The diagram shows that the effluent water consists dominantly of NaCl. The SAR values of the samples indicates that the deck-drains are poor for irrigation purposes while the PI values confirms the high level of pollution of the samples.

The Piper and Stiff diagram, SAR and PI values shows that the samples have similar chemical trend and model because of their common source.

The concentrations of the major cations in decreasing order is: $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ while that of the anions is: $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^-$. This model is consistent for all the five oil wells studied.

Generally, the deck-drain samples are acidic, saline, highly conductive and contains high concentrations of TDS and H_2S and thus requires treatment before they are disposed to the recipient environment. Oil producing companies should ensure that deck-drain samples obtained at the deck-drain holding tank (DHT) are adequately treated before being disposed; the treatment procedures should be properly monitored by regulatory bodies such as Department of Petroleum Resources (DPR), Nigeria and Federal Environmental Protection Agency (FEPA) of Nigeria. Government should impose stiff penalty for defaulting oil companies.

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Figure 2. Stratigraphic sequence of the tertiary Niger Delta (modified after Amajor, 1986)

AGE	SURFACE FORMATION		SUBSURFACE EQUIVALENTS	MEGA DEPOSITIONAL
PLIOCENE-RECENT	COASTAL PLAIN SANDS		BENIN FORMATION AFAM AND QUA IBOE CLAY MEMBERS	CONTINENTAL
MIOCENE-RECENT	OGWASHI ASABA FM	IJEBU FM	AGBADA FM	PARALIC
EOCENE-RECENT	AMEKI FM ILARO FM OSHOSUN FM		AGBADA FM	PARALIC
PALEOCENE	IMO FM		AKATA FM	MARINE

Table 1. Chemical Analysis of Deck-Drain samples from some Oil Wells in the Niger Delta Basin SAMPLE LOCATIONS

PARAMETERS	A	B	C	D	E	DPR
PH	5.10	5.30	5.40	5.36	5.00	6.5-8.5
TDS (mg/l)	11,092	13,830	27,170	4,585	5,000	5000
H_2S (mg/l)	1.00	0.80	0.90	1.10	1.00	0.20
Mn^{+-} (mg/l)	0.80	0.60	0.45	0.98	0.55	5.00
E.Conductivity (µS/Cm)	15,210	7,054	21, 277	9,010	17,064	40
COD (mg/l)	32	30	34	40	28	40
BOD (mg/l)	6.20	6.50	5.50	5.10	6.20	10
Oil and grease (mg/l)	10	6	12	9	8	20
Surfactant (mg/l)	0.50	0.45	0.30	20.40	0.55	1.5
Total organic carbon (mg/l)	7.5	10	12	8.60	6.80	-
Total. iron (mg/l)	0.20	0.10	0.15	0,24	0.32	1.00
Total Alkalinity (mg/l)	190.17	200	185	194.50	189	-
Total Hardness (mg/l)	1,200	1,225	1,193	1,170	1,220	150
Ca^{2+} (mg/l)	320	322.6	318.50	316	324	200
Mg^{2+} .(mg/l)	100	105.4	98.70	95	103	150
Na^{+} (mg/l)	2,300	2,275	2,310	2,288	2,309	500
K^{+}(mg/l)	21.30	23.20	20.40	19.80	20.02	50
HCO_3^- (mg/l)	360.50	374.20	356.24	350.10	351.80	500
Cl^- (mg/l)	4,150	4,000	4,400	4,080	4,250	2000
NO_3^- (mg//l)	30.20	25.80	35.30	27.90	24.87	70
SO_4^{2-}(mg/l)	96.30	100	93.40	110.40	98.90	500
Zn^{2+} (mg/l)	0.10	0.21	0.16	0.24	0.13	10
Cd^{2+} (mg/l)	0.26	0.34	0.43	0.22	0.37	0.05
Cr^{6+} (mg/l)	0.03	0.04	0.06	0.02	0.01	0.05
Cu^{2+} (mg/l)	0.40	0.15	0.48	0.30	0.23	1.00
Ba^{2+} (mg/l)	5.00	6.20	4.50	7.00	5.70	5.00

Table2. Concentrations of major cations and anions of deck- drain samples in meq/l and SAR values Con. Of Deck-Drains of oil wells %, epm

PARAMETER	EQUIVALNT MASS	A	B	C	D	E	A	B	C	D	E
Ca^{2+} (meq/l)	20.00	16.00	16.13	15.93	15.80	16.20	12.83	12.98	12.75	12.79	12,90
Mg^{2+} (meq/l)	12.20	8.20	8.60	8.09	7.79	8.44	6.57	6.92	6.47	6.30	6.72
Na^{+} (meq/l)	23.00	100.00	98.91	100.43	99.48	100.39	80.17	79.62	80.36	80.50	79.97
K^{+} (meq/l)	39.10	0.54	0.59	0.52	0.51	0.51	0.43	0.48	0.42	0.41	0.41
TOTAL		124.74	124.23	124.97	123.58	125.54	100	100	100	100	100
HCO_3^- (meq/l)	61.00	5.91	6.14	5.89	5.78	4.93	4.72	5.06	4.45	4.68	3.88
Cl^- (meq/l)	35.50	116.90	112.68	123,94	114.93	119.72	93.30	92.88	93.65	93.11	94.18
NO_3^- (meq/l)	62.00	0.49	0.42	0.57	0.42	0.40	0.39	0.35	0.43	0.35	0.32
SO_4^{2-} (meq/l)	48.00	2.00	2.08	1.95	2.30	2.06	1.59	1.71	1.47	1.86	1,62
TOTAL		125.30	121.32	132.35	123.43	127.11	100	100	100	100	100
SAR		28.74	28.04	28.97	28.92	28.60					

Table 3. Pollution Index of the Deck- DrainSamples Con.ofDeck-Drains of oil wells (C_i) (C_i/L_j)

PARAMETER	A	B	C	D	E	L_j	A	B	C	D	E5	
Ph	5.10	5.30	5.40	5.36	5.50	6.5	0.79	0.82	0.83	0.83	0.85	
TDS (mg/l)	11,092	13,830	27,170	4,585	5,857	500	22.18	27.66	59.34	9.17	11.71	
Total Alkalinity (mg/l)	190.17	212.56	206.00	185.00	168.78	100	1.90	2.13	2.06	1.85	1.69	
Total Hardness (mg/l)	1,200	1,225	1,192	1,170	1,220	50	24.00	24.50	23.84	23.40	24.40	
SO_4^{2-} 9mg/l0	96.30	100	89.55	110	120	400	0.24	0.25	0.22	0.28	0.30	
Cl^- (mg/l)	4,150	4,000	4,400	4,080	4,250	250	16.60	16.00	17.60	16.32	17.00	
Total							65.71	71.36	103.89	51.85	55.95	
Pollution Index (PI)							18.21	20.08	42.47	17.81	18.21	

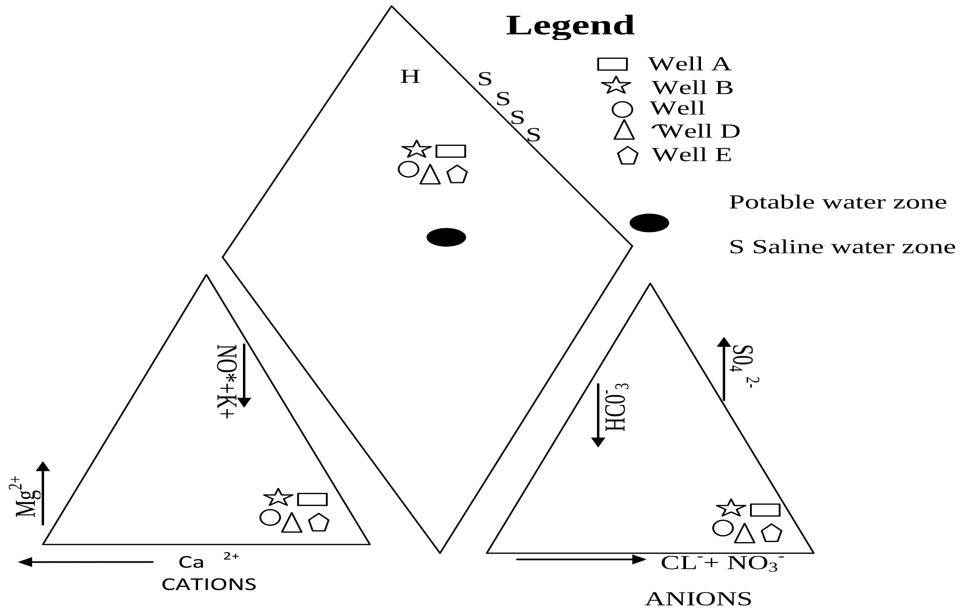

Figure 3: Piper Trilinear Plot of the Deck Drain samples

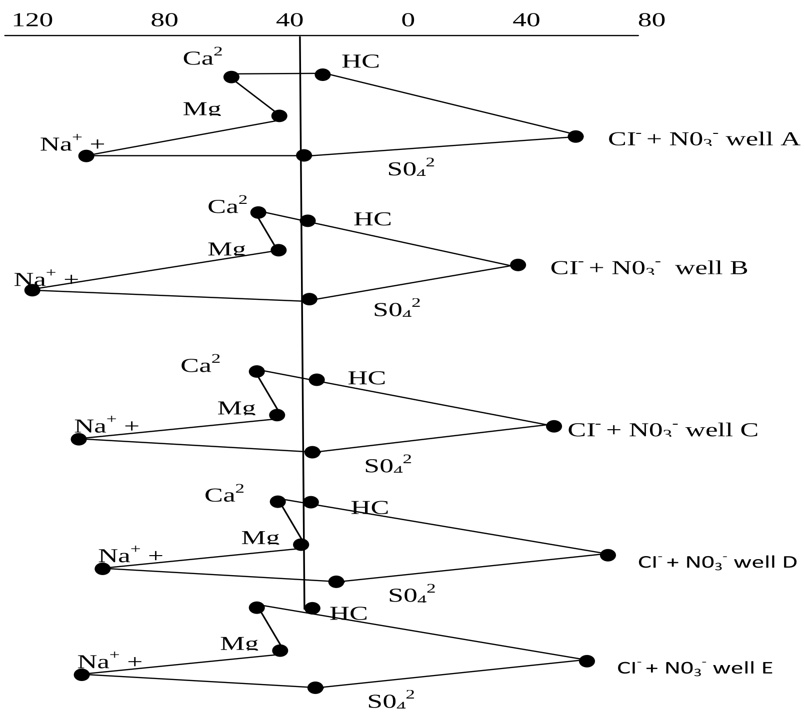

Figure 4: Still diagram of the deck drain sample