ASSESSMENT OF OIL AND GREASE, TOTAL PETROLEUM HYDROCARBONS AND SOME HEAVY METALS IN SURFACE AND GROUNDWATER WITHIN THE VICINITY OF NNPC OIL DEPOT IN APATA, IBADAN METROPOLIS, NIGERIA

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ABSTRACT

The present study discusses an assessment of oil, grease, total petroleum hydrocarbons (TPH) and some heavy metals in surface and ground water within and around the Nigeria National Petroleum Corporation (NNPC) depot, in Apata, Ibadan metropolis in other to assess the pollution status of the water. Samples were collected randomly within and around the depot. Control samples were taken from Awba dam and Obafemi Awolowo hall of residence, within the University of Ibadan. TPH, oil and grease were analyzed gravimetrically while the levels of heavy metals were determined by atomic absorption spectrophotometry (AAS) The results revealed the presence of oil and grease in both surface and ground water with a value ranging from 59.74±4.92 to 67.35±2.21, and 10.48±1.21 to 34.94±5.04 mg/l compared to control sample with a value of, 37.21±4.77 and 12.17±0.78 mg/l respectively. Conversely, high values of TPH were recorded for both surface and groundwater in the studied area ranging from, 20.34±1.79 to 27.40±5.32 and 2.67±0.80 to 13.03±2.21mg/l respectively as against the control of 13.18±2.41 and 1.58±0.22 mg/l. The level of heavy metals concentration recorded in both surface and groundwater samples of studied sites were ranged from 0.162±0.015 to 0.195±0.011mg/l Pb, 0.279±0.088 to 0.315±0.085mg/l Cd, 5.063±0.377 to 5.096±0.373mg/l Zn, 0.103±0.0207 to 0.133±0.036mg/l Ni, 8.744±0.112 to 10.307±0.387mg/l Cu and 0.052±0.006 to 0.059±0.013mg/l Cr for surface water respectively while groundwater contained as much as 0.046±0.016 to 0.156±0.023mg/l Pb, 0.016±0.004 to 0.045±0.003mg/l Cd, 1.560±0.061mg/l to 2.972±0.136mg/l Zn, 0.015±0.006 to 0.315±0.037mg/l Ni, 2.256±0.121 to 4.820±0.288mg/l Cu and 0.0033±0.013 to 0.073±0.009mg/l Cr. A statistically significant difference at $p<0.05$ was found to exist between the concentrations of oil and grease, TPH and the analyzed metals collected from the sites and the control sites. Based on this study, the human and environmental risk to TPH, oil and grease, Pb, Cr, Ni, Cu, Cd and Zn in surface and ground water are high for now, as the concentrations were higher than those of the control sites and the recommended permissible limit of the World Health Organization (WHO), European and Union (EU). It is therefore recommended among others that primary treatment plant be install in all NNPC depot for the uptake of these toxicants which may pose treat to human health on bioaccumulation.

Keywords: *Surface and ground water; petroleum products depot; total petroleum hydro carbons, oil and grease; heavy metals.*

1. INTRODUCTION

Nigeria has been exploring and exploiting crude oil for decades and the consequences on the oil producing and processing areas have become highly problematic in the onshore and offshore installations. The unpleasant and environmentally undesirable pollution effects of the waste from these explorations calls for best practicable technology in conversion process involved in obtaining petroleum and petrochemical products from crude oil which generate various types wastes [1-3]. The wastes can be generally classified into oily materials, spent catalyst, spent chemicals and other residuals which found there ways into the environment due to incessant release. The increased oil activities have resulted in extensive environmental pollution by oil spills involving blowouts, leakages from tanks or tanker trucks and dumping of waste petroleum products into the environment. The aftermaths of these activities have been documented [4-5]. Crude oil, when refined contains a wide range of components such as hydrocarbons, heavy metals, dye additives, antioxidants, corrosion inhibitors, etc [6-7].. The refined products show higher toxicity compared to crude oil since metal speciation is altered and new metals added to the matrix during the refining processes [1,8] The waste generated from such processes may contain spent catalysts which are not recovered in most cases but discharged into soil and receiving water bodies where they accumulate in surface waters, sediments of rivers, and ultimately groundwater.

Water support all forms of biological resources (plant and animal life) and are normally obtained from two major natural sources which are surface water (water bodies) such as rivers, streams, fresh water lakes and ground water (geological water) such as borehole and well water [9-10]. Water is capable of dissolving, absorbing, and adsorbing or suspending many different compounds [11] as well as contaminants from its surrounding and those arising from humans and animals as well as other biological activities due to its distinctive chemical properties [9]. Ground water contamination is one of the most essential environmental issues confronting mankind today [12] and between the wide diversity of contaminants affecting water resources in recent time heavy metals receive particular concern as a result of their strong toxicity even at low concentrations[13-15). Groundwater contamination, with its subsequent degradation is more threatening, more so when it is realized that dynamic equilibrium maintained by gravity and capillary exists between surface and groundwater [16-17]. Also contaminated soil causes subsequent pollution of groundwater, though infiltration; hence, groundwater is a receiver of contaminants from both soils and surface water and from other direct sources like leakages from buried chemical tanks [1, 15].

The world demand for energy has increased tremendously since World War II, [18]. This is as a result of rapid increase in urbanization and industrialization and since Nigeria is one of the world's major producers and exporters of crude oil and importer of petroleum, the economy is very much dependent on the revenue earnings from oil which has amounted to billions of dollars annually. The Nigeria National Petroleum Cooperation (NNPC) has evolved different strategies for effective distribution of refined products to different parts of the country [19]. There are about 5,00km worth of pipelines and about 20 oil depots (An industrial facility for the storage of oil and or petrochemical products and from which, they are transported to end users or further storage facilities) altogether in Nigeria [19-20]. Leakages and spills associated with loading and offloading of petroleum products in these depots as well as washing of oil storage tanks has adversely impact the environment [21]. These impacts depend primarily on the petroleum products, its concentration after release and the biotic community that is exposed. A huge bulk of waste generated from depot activities are oil discharges and since oil contains mostly hydrocarbons (petroleum hydrocarbons) and heavy metals, these discharges has significantly impact on the pollution levels of underground and surface water near depots [4,19-22].

The NNPC depot that supplies refined petroleum products to consumers in Oyo state and some other southwestern states in Nigeria, is located in Apata, Ido Local government area of Oyo state. This used to be a remote area well suited for an oil depot, however, due to rapid increase in population and urbanization, sparse of land around the depot are now being used for residential estates and the inhabitants depend mostly on ground water for domestic purposes. A shallow stream also runs across the depot through the residential area. These waters might constitute a huge health and environmental hazards to humans, aquatic resources and other forms of life in Apata environs, when contaminated by the oil products in the depot. The thematic foci of this present study, is to examine the levels of oil and grease, total petroleum hydrocarbon (TPH) and consequents heavy metals; leads (Pb), cadmium (Cd), chromium (Cr), copper (Cu) , zinc (Zn) and nickel (Ni) in ground and surface waters within the vicinity of the NNPC oil depot in Apata, Ibadan, Oyo State. This study is expected to provide baseline data as an aspects of environmental impact assessments that will assist in determining the level of remediation that these water sources may require overtime if contaminated as well as to alert the appropriate environmental regulatory agencies on the need to formulate and enforce a comprehensive environmental action plan towards protecting the environment.

2. MATERIALS AND METHODS

2.1 Sampling and samples description

Nigeria National Petroleum cooperation depot is located between latitude (07^0 23^0 26.9)N and longitude (03^0 49, 02.3)E in Ibadan Metropolis, Oyo state Nigeria. Four ground water sources were randomly selected within the vicinity of the depot, but at different distances from each other for the purpose of this study. Also, two sites within and outside the vicinity of the depot were selected for surface water samples. The control site is situated at the Awba dam and Obafemi Awolowo Hall of residence of the University of Ibadan. The distance descriptions of the sampling points from the depot are illustrated in table 1.

Table 1: Sample Description

Sample code	Site	Distance from depot
SW1	Surface water inside depot	Within the depot
SW2	Surface water outsides depot	Approximately 160m
UW1	Groundwater outside depot	Within the depot
UW2	Ground water outside depot	Approximately 20m
UW3	Groundwater outside depot	Approximately 60m
UW4	Groundwater outside depot	Approximately 100m
CSW	Control site for surface water	Approximately 6km
CUW	Control site for underground water	Approximately 6km

Two sets of samples were collected at each sampling point for heavy metals and total petroleum hydrocarbon analysis respectively.

The collection of the sample was done with the aid of plastic sampler that as been previously prewashed with an acid for heavy metals analysis and a small acid prewashed aluminums bucket suspended on a rope was used for collection of samples for total petroleum hydrocarbon analysis. Sample containers were tightly sealed immediately after sample collection. Sampling was carried out twice between December, 2008 and January, 2009.

2.2 CHEMICALS

Analytical grade reagents and metal stock standard solution (1 mg/L) were purchased from Aldrich chemical company and fluka AG.

2.3 EXTRACTION OF SAMPLES FOR TPH DETERMINATION

Liquid-liquid extraction procedure as reported by [21, 24-25] was used in this study. One litre of sample was extracted in a two litre (2 L) glass separatory funnel fitted with a glass stopper using 30 ml hexane as extractant.

The separatory funnel was shaken vigorously for at least 3 minutes and the organic layer was allowed to separate clearly from the aqueous phase for a minimum of 5 minutes, after which, the organic layer was collected into a separate glass bottle. The extraction was repeated thrice for each sample. Water residues were expelled from the organic layer by passing extracts through funnels containing anhydrous sodium sulphate. Extracts were concentrated using rotary evaporators with water bath preset at 85^0C. Concentrated extracts was transferred to a pre-weighed sample bottle and evaporated to dryness. The difference in weight is equivalent to oil and grease in the sample.

$$mg/L\,(oil\ and\ grease) = \frac{A-B\,(mg)\,x\,1000}{Sample\ volume}$$

Where A= Total gain in weight for experimental sample (mg)
B = Gain in weight for blank (mg)

2.4 INSTRUMENTATION

2.5 DETERMINATION OF TOTAL PETROLEUM HYDROCARBON (TPH)

Silica gel for column chromatography was activated at 200 ^{0}C for 4 hrs. The silica gel was then deactivated by adding 5% of its weight of distilled water to it in a bottle. The bottle was tightly capped and the content mixed and allowed to equilibrate overnight to prevent the formation of artifacts. 4 g of the silica gel was weighed into a bottle and capped tightly. The oil and grease obtained was re-dissolved in dichloromethane (DCM) and the solution of extract was transferred to the bottle in which 100 ml of hexane had been added.

The mixture was stirred for 5 minutes with a magnetic stirrer with the bottle properly and tightly capped. The solution was filtered into a pre-weighed flask through a filter paper moistened with hexane. The silica gel and filter paper was washed down with 10 ml hexane. The solvent was then concentrated and evaporated to dryness in a rotary evaporator and water bath preset at 85 ^{0}C. The flask was reweighed to constant weight. Oil and grease derived from the blank determination was subject to the same procedure to obtain the blank for total petroleum hydrocarbons.

$$Total\ petroleum\ hydrocarbon\,(TPH)\,mg/L\ ) = \frac{A-B\ \ x\,1000}{Sample\ volume\,(ml)}$$

A = Gain in weights of flask from experimental sample
B = Gain in weight of flask from blank determination.

2.6 HEAVY METALS ANALYSIS

The determination of heavy metals was performed with a bulk scientific 205 atomic absorption spectrophometer. The instrument's setting and operational conditions were done in accordance with manufacturer's specifications. The instrument was calibrated with analytical-grade metal standard stock solutions (1 mg/L) in replicate. 150 ml of sample was transferred to a beaker, 5 ml concentrated HNO_3 was added and the mixture evaporated almost to dryness on a hot plate. 1-2 ml of concentrated HNO_3 was added to dissolve the residues on the walls of the beaker. The distilled, digested samples were filtered and made up to 50 ml and analyzed using AAS. Blank was prepared by carrying distilled deionized water through the whole procedure above. Sample were prepared for analysis, following the methods described earlier [23]. 150 ml of water sample in 5 ml concentrated HNO_3 was used. Samples pH was determined insitu using portable pH meter after calibration with buffer solutions of pH 4.00 and 7.00 respectively.

3. RESULTS AND DISCUSSION

The results of the determination are presented in tables 2, 3,4,5,6 respectively. The mean pH values for surface water ranged between 6.35±0.06 and 6.37±0.06 while that of control sample for surface water was 6.97±0.06 (table 4) which was found to be high.

The mean pH values for ground water samples ranged between 6.40±0.04 and 7.46±0.01 compared to values 7.64±0.003 obtained for the control sample of the ground water, It can be deduced from this result that variety of contaminations may be attributed to the spilling of petroleum products in the vicinity of the depot, these may include acidic gases which in solution slightly increased the acidity of both surface and ground water. The obtained pH values for both surface and ground water were generally lower than the pH values obtained for their respective control samples which revealed a likely alteration in the natural chemistry of the environment within the depot as a result of the oil activities. The result of the heavy metals analysis of both surfaces and groundwater are presented in table 4 and 5, respectively. The metals analysis result indicates contaminations of the surface water by metals. Concentrations of metals in the various sites were generally higher than those of the control site. Metal concentration of surface water analyzed increased in the order of (Cu>Zn>Pb>Cd>Ni>Cr). The mean concentration of the various metals ranged between 8.744 and 10.307 mg/l, 5.063 and 5.096 mg/l, 0.162 and 0.195 mg/l, 0.279-0.319 mg/l, 0.103-0.133 mg/l and 0.052-0.020 mg/l for Cu, Zn, Pb, Cd, Ni, and Cr, respectively. The mean metals concentrations in the surface water control site were 3.264, 0.2112, 0.022, 0.026, 0.008 and 0.020 mg/L for Cu, Zn, Pb, Cd, Ni and Cr

Table 2: Mean oil and grease and TPH concentration in surface water Samples

Sample	Oil and grease (mg/l)	TPH (mg/l)
SW_1	59.74±4.92	27.40±5.32
SW_2	67.35±2.21	20.34±1.79
CSW	37.21±4.77	13.18±2.41

Table 3: Mean oil and grease and TPH concentration in ground water samples

Sample	Oil and grease (mg/l)	TPH (mg/l)
UW_1	34.94±5.04	13.03±2.21
UW_2	12.52±2.01	2.67±0.80
UW_3	13.93±2.20	3.19±1.45
UW_4	10.48±1.21	2.72±0.60
CUW	12.17±0.78	1.58±0.22

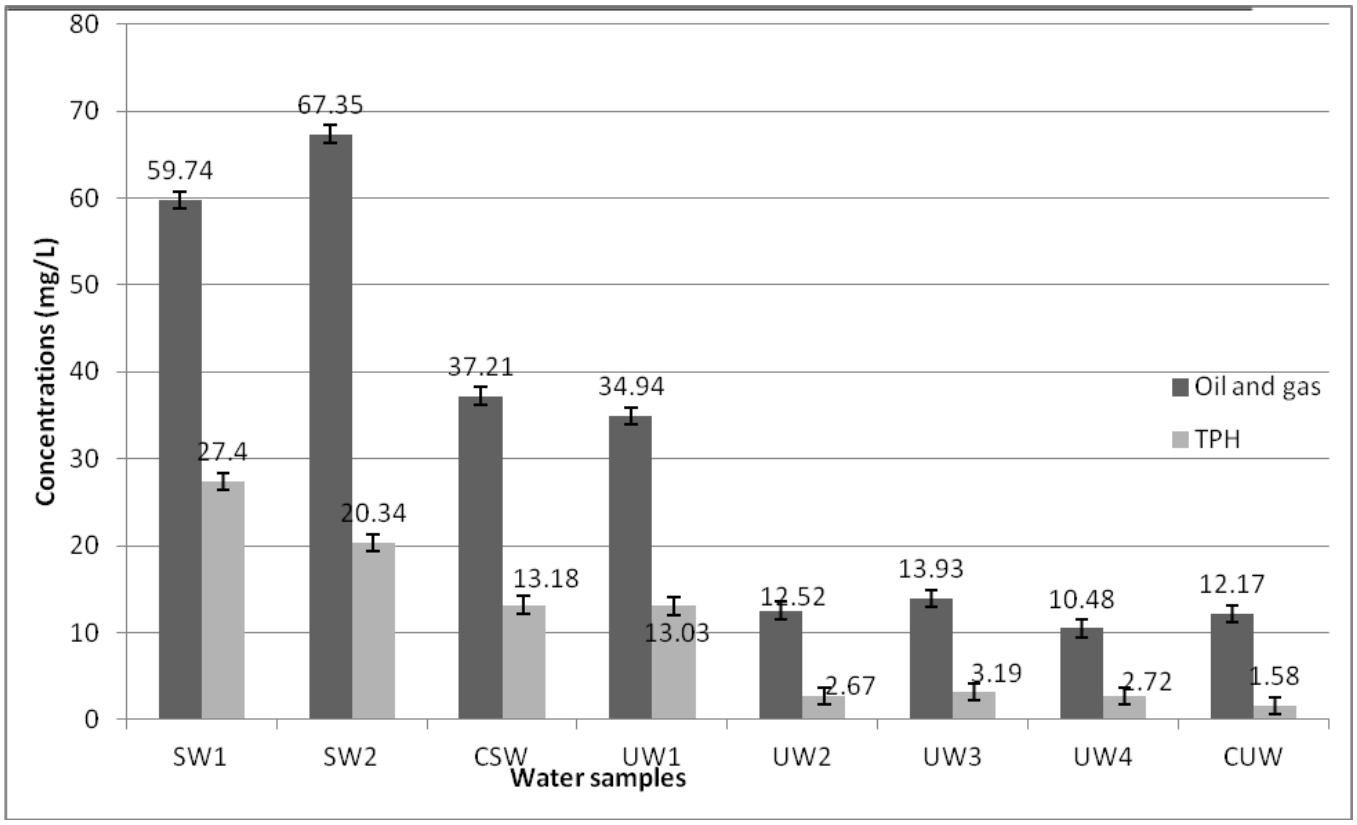

Figure 1 Descriptive bar chart of the sampling sites for Oil and grease and the total petroleum hydrocarbons

Table 4: pH values and mean heavy metal concentration (mg/l) in the surface water samples

Sample	pH	Pb(mg/l)	Cd (mg/l)	Zn (mg/l)	Ni (mg/l)	Cu (mg/l)	Cr (mg/l)
SW_1	6.37±0.60	0.195±0.011	0.315±0.085	5.096±0.373	0.135±0.036	8.744±0.112	0.052±0.006
SW_2	6.35±0.06	0.162±0.015	0.279±0.088	5.063±0.377	0.103±0.027	10.307±0.387	0.059±0.013
Control	6.97±0.06	0.022±0.009	0.026±0.005	2.112±1.428	0.008±0.004	3.264±0.209	0.020±0.002

Table 5: Result of pH and mean metal concentration (mg/l) in groundwater samples

Sample	pH	Pb(mg/l)	Cd (mg/l)	Zn (mg/l)	Ni (mg/l)	Cu (mg/l)	Cr (mg/l)
UW_1	6.40±0.04	0.156±0.023	0.045±0.003	2.972±0.136	0.315±0.037	4.820±0.288	0.073±0.009
UW_2	7.23±0.04	0.046±0.016	0.020±0.002	1.560±0.061	0.089±0.060	2.576±0.306	0.033±0.013
UW_3	7.34±0.04	0.059±0.024	0.016±0.004	1.631±0.031	0.015±0.006	2.256±0.121	0.059±0.032
UW_4	7.46±0.01	0.086±0.035	0.019±0.011	1.713±0.188	0.019±0.012	2.788±0.456	0.043±0.011
Control	7.64±0.003	0.019±0.006	0.010±0.005	1.310±0.128	0.002±0.001	1.142±1.266	2.021±0.008

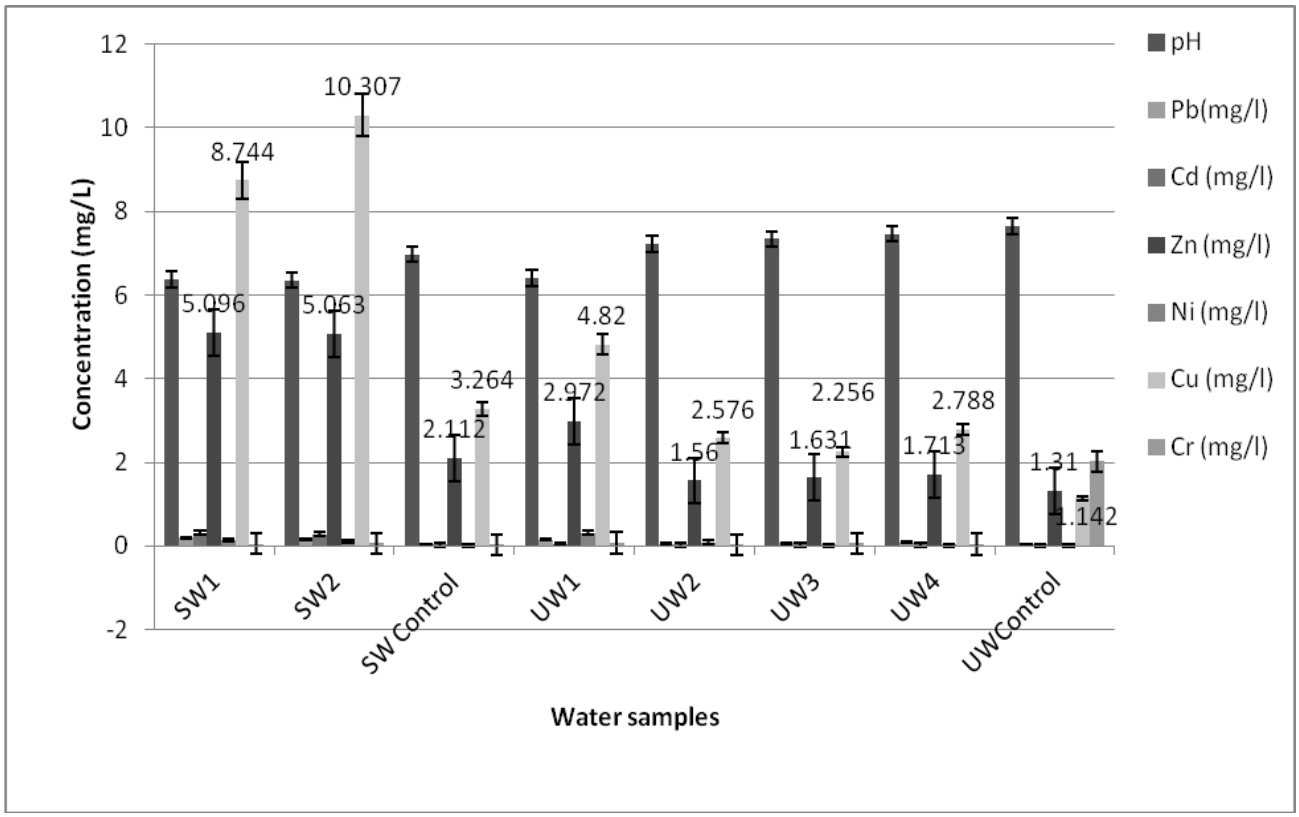

Figure 2 Descriptive bar chart of the pH and heavy metals concentrations in water samples

Table 6: t-test (95% confidence level) of oil and grease and TPH concentration in surface and groundwater samples

Sample	Oil and grease	TPH
SW_1	4.65	3.44
SW_2	8.11	3.77
UW_1	6.30	7.29
UW_2	0.18	1.86
UW_3	1.07	1.55
UW_4	1.66	2.52

T tab = 2.920 (01-2 degree of freedom) at 95% confidence level.

Table 7: t-test (95% confidence level) of heavy metals in surface and groundwater samples

Sample	Pb	Cd	Zn	Ni	Cu	Cr
SW_1	17.214	4.800	6.358	4.975	32.684	7.155
SW_2	11.318	4.059	6.234	4.922	22.646	4.193
UW_1	8.151	8.489	12.585	11.959	4.006	6.107
UW_2	2.234	2.626	2.493	2.050	1.557	1.112
UW_3	2.287	1.325	3.447	3.022	1.239	1.629
UW_4	2.668	1.053	2.506	1.997	1.729	2.289

Ttab = 2.920 (95% confidence level) (N-2degree of freedom)

Table 8: Comparison of pH values and mean metal concentration with standard recommended values

Sample	SW	CSW	UW	CUW	WHO	EU
pH (mg/l)	6.35-6.37	6.97	6.40-7.46	7.64	6.5-8.5	6.5-9.5
Pb (mg/l)	0.694-0.710	0.022	0.046-0156	0.019	0.01	0.01
Cd (mg/l)	0.279-0.315	0.026	0.016-0.045	0.010	0.003	0.005
Zn (mg/l)	5.063-5.096	2.112	1.560-2.972	1.310	5.0	5.0
Ni (mg/l)	0.103-0.133	0.008	0.015-0.315	0.002	0.02	0.02
Cu (mg/l)	8.744-10.307	3.264	2.256-4.820	1.142	2.0	2.0
Cr (mg/l)	0.052-0.059	0.020	0.033-0.073	0.021	0.05	0.05

respectively. The result of the metal analysis indicates a generally high level of metals contamination in surface water within the vicinity of the petroleum products depot. The results obtained for the different metals were generally higher than those of the control sites and standard recommended values by the World Health Organization and European Union guidelines for surface water (Table 8). The result also shows a high contamination load by Cu and Zn (figure 2) which as found to be above earlier report of was reported for surface and underground water in Ubeji settlement [20,26]. Table 7, shows that a statistically significant difference (0.05α level) existed between values among Pb, Cd, Zn, Ni, Cu and Cr levels in the surface water samples in the vicinity of the NNPC petroleum products depot when compared with control samples. This observation is not far-fetched since lead (Pb) are employed an anti knocking agent in petroleum products and other heavy metals are constituents of crude oil.

Heavy metals analysis in groundwater around and within the vicinity of the depot indicates a generally high metals contamination with Zn and Cu having the highest metal burden which exceed the Nigeria Industrial Standards for drinking water quality [27] and those reported earlier from similar environmental media [20,26]. The high concentration level of this surface and underground water may be attributed to spillage from the petroleum product due to intense activities that takes place within the vicinity of the petroleum deport which is in agreement with earlier report [20,26-28] .

The pH of the ground water samples was found to be slightly acidic and below that of the control sites. The levels of heavy metals in all ground water sites were higher than those of the control with Pb, Cd, Ni, Cu and Cr being higher than recommended values by WHOs and EU [.11,29]. The high value of Cd and Pb in this area underground and surface water calls for serious attention because elevated value of Cd result in kidney damage, impair skeletal and reproductive system [12-13,15] as well as other health related problems while Pb at elevated level is known to affect intellectual performance in children, increase in blood pressure as well as impairment of cognitive development in adults problems [15,30-32]. Among all ground water sites the site within the depot (UW_1) has the highest heavy metals concentration, furthermore, a statistically significant (t-calculated at 0.05α level) difference existed for all metals analyzed in UW_1, while UW_3 showed statistically significant difference for Zn and Ni (Table 7).

It is note-worthy to conclude that the levels of Pb, Cd, Zn, Ni, Cu and Cr (Table 8) are particularly high enough to cause public concerns. Literature had revealed that the ability to Pb_2 to undergo metathesis reactions with Zn^{2+} and Ca^{2+} metalloprotein result in loss of metabolic function, and this continues to be a primary hypothesis underlying the detrimental effects of Pb exposure [30, 32].

The results of the oil and grease and TPH (mg/l) for both surface and ground water samples are as presented in table 1 and 2. The results indicated an unusually high oil and grease and TPH contents (figure 1) in the surface water which ranged between 59.74±4.92 and 67.35±2.21 27.40±5.32mg/l for TPH is lower than earlier report of 380 mg/l and 250 mg/l. obtained by Etchi (2011) and his coworkers in the same environmental media [26] The control sites for the surface water showed a relatively content of oil and greases and TPH, with values of 37.21±4.77mg/l 4.77mg/l and 13.18±2.41mg/l for oil and grease and TPH respectively. The results indicates a high contamination of surface water by petroleum products within the vicinity of the depot. A statistically significant difference (0.05α level) existed for the concentrations of oil and grease and TPH in the surface water samples in comparison with those of the control sites. This is an indication of contamination of the surface water by petroleum products. These contaminations may not be far from the fact that all effluents from the depot are as a result of petroleum product tank washings, petroleum products spills and other cleaning activities that take place in the depot are channeled to outlet along the course of this stream.

The observed high oil and grease content in the surface water may also be associated with industrial and commercial cleaning solutions.

The oil and grease and TPH content of the groundwater samples were generally higher than those of control sites with exception of UW_4. The values ranges in the order 34.94±5.04, 12.52±2.61, 13.93±2.20, and 10.48±1.21, for UW_1, UW_2, UW_3 and UW_4 respectively for oil and grease 13.03±2.21, 2.67±0.80, 3.19±1.45 and 2.72±0.60 mg/l for UW_1, UW_2, UW_3 and UW_4 respectively for TPH. The control sites was 12.17±0.78mg/l and 1.58±0.22mg/l, for oil

and grease and total petroleum hydrocarbon (TPH), respectively. These values also shows contamination by petroleum products as they are also higher than 1 mg/l reported earlier for an uncontaminated site [17, 29]. There was a statistically significant difference (0.05α level) in comparison with control sites.

In comparison with control sites, a statistically significant difference (0.05α level) existed for UW, for both oil and grease and TPH. This is an indication of groundwater contamination. The results of these study were generally lower than those obtained by other researcher earlier [17,20,26]. Oil and grease represent the total petroleum hydrocarbon and non petroleum hydrocarbon components present in the sample. The results of the a TPH in this study were in line with an earlier studies on TPH in a local streams of Sam Carlos in North Eastern Ecuardor, where the TPH values in samples of groundwater and soil were found to be 10 to 288times higher than EU guideline limit [29]

4. CONCLUSIONS

The activities in NNPC petroleum product depot, should be of environmental concern, as adverse effects arising from TPH, oil and grease and heavy metals cannot be over-emphasized. Hence, it is pertinent, that standard environmental management and appropriate environmental regulations should be established and enforced within the vicinity of the depot and if possible primary treatment plant be install in all NNPC deport for the uptake of these toxicants which may pose treat to human health on bioaccumulation. Adequate remediation and cleanup measures should be carried out on the sites to save the environment of these chemical time bomb arising from TPH, oil and grease as well as heavy metals, in order to ensure best environmental management practices (BEMP).

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