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Evaluation of the Status of Heavy Metal Pollution of Water (Surface and Ground) and Aquatic Macrophyte (*Ceratophyllum demersum*) of Agbabu Bitumen Deposit Area, Nigeria

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Authors' contributions

This work was carried out in collaboration between the two authors. Author EOO designed the study, and read and approved the final manuscript. Author OEF managed the literature searches, collected the samples, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript.

Research Article

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ABSTRACT

Aims: This research is aimed at determination of heavy metals concentrations in water (surface and ground) and aquatic macrophyte and to compare the values with the standard recommendations.
Study Design: Water (surface and ground) and aquatic macrophyte (*Ceratophyllum demersum*) were analyzed for heavy metals (Fe, Cu, Mn, Cr, Zn, Hg, Pb, Cd, N_i, and V) content. Surface water was collected from six sampling sites in the dry and rainy seasons of years 2008 and 2009. Ground water was also collected from six sampling sites in the dry and rainy seasons of years 2008 and 2009. Aquatic macrophyte was collected from two sampling sites in the dry and rainy seasons of years 2008 and 2009.
Place and Duration of Study: Samples were collected from Agbabu bitumen deposit area, Western Nigeria, in the dry and rainy seasons of years 2008 and 2009
Methodology: Analysis was carried out using atomic absorption spectrometry.
Results: In dry season of 2008, surface and ground water in all sampling stations, except one, had concentrations of Cr and Mn that were higher than WHO recommendations for

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potable water, which is 0.05ppm and 0.01ppm respectively. The mean concentrations of Fe and Ni were also higher than WHO recommendations in most of the water samples examined. Fe had the highest mean concentration in aquatic plant (*Ceratophyllum demersum*) in the dry and rainy season of years 2008 and 2009. Bio-concentration Factor (BCF) of metals in *Ceratophyllum demersum* were as high as 3620.00 (Zn-dry season 2009), showing that it can be used in phytoremediation of surface water polluted with heavy metals. Analysis of variance and multiple comparison of concentration of Cr and Mn in surface and ground water with SPSS 17 (α = .05) showed no statistically significant differences between the sampling points which shows that Cr and Mn in the study must have originated from similar sources.

Conclusions: The study area presently has been impacted by the presence of bitumen. Data available in this study can be used as baseline for monitoring of metal contamination at Agbabu bitumen deposit area.

Keywords: Aquatic macrophyte; Bioconcentration Factor (BCF); bitumen; heavy metal; phytoremediation; water.

1. INTRODUCTION

Bitumen has similar composition as the light crude, that is, hydrogen, carbon, and minor amount of sulphur, oxygen, Zn, Ni, V and Fe [1]. They are believed to have formed from biodegradation and water washing of light crude. The Nigerian bitumen is believed to have formed in a similar process [2]. The probable reserve of bitumen and heavy oil in the entire Nigerian belt is about 120 X 4.3km [3,4], spreading along the bitumen belt stretching from Lagos, Ogun through to Ondo and Edo State. Nigeria has a reserve of 30 – 40 billion barrels of bitumen [5]. Agbabu is one of the farm settlements in Ondo State hosting a vast deposit of bitumen (Fig. 1). This is where bitumen was first spotted in Nigeria in 1910 and the first bitumen well NBC-7 was drilled there. Agbabu bitumen belt consist of the main Agbabu village inhabited by about 5,000 people and other smaller farm settlements such as Temidire village inhabited by about 3,000 people. Farmers in this area deal mainly in cash crops such as cocoa and colanut and food crops such as yam and plantain and fishing along River Oluwa which flows through whole land. These villages depend on River Oluwa for their farming activities and other domestic use while hand dug shallow wells and bore hole serve as their only source of potable water. The two distinct seasons in the year are rainy and dry. The rainy season is at its peak from July to the middle or September while the dry season is from January to March. The annual precipitation of River Oluwa ranges between 2000mm to 2500mm [6]. Discharge records for Rivers Niger (5,589 m^3s^{-1}) and Ikpoba (39m^3s^{-1}) have been reported [7], but there are no discharge records for River Oluwa, like many rivers in Nigeria. The average depth of hand dug well at Oluwa bitumen deposit area was 7.5m.

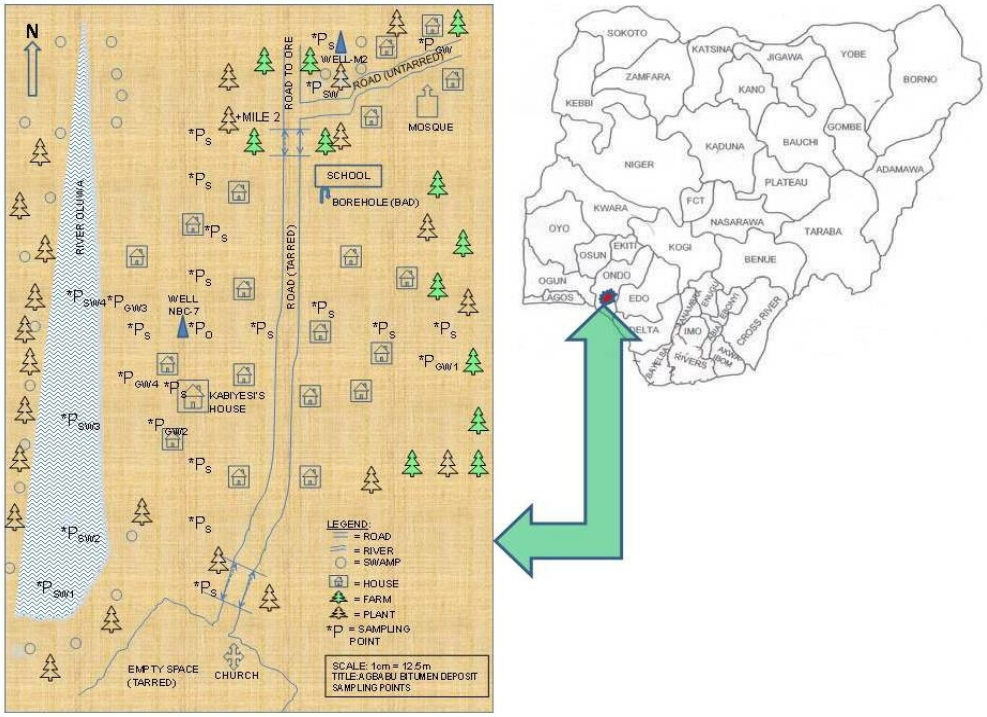

Fig. 1. Map of Nigeria showing sampling points [8]

Natural sources of heavy metals include volcanic emission, whereas anthropogenic sources include combustion of solid wastes, fossil fuels in coal, and oil fired power plants, releases from metal smelters and automobile emissions. Chemical and metallurgical industries are the most important sources of heavy metals in the environment controlled by biological and physicochemical processes. Since there are no industrial activities yet in this bitumen deposit area, the likely sources of heavy metal contamination in the environment are farming, fishing, domestic activities and the presence of bitumen.

Heavy metal pollution is a serious and widespread environmental problem due to the toxic, persistent, non-biodegradable and bioaccumulation properties of these contaminants. Changes in physical and chemical features of the aquatic system may influence the solubility and mobility of heavy metals in that system [9]. Macrophytes are considered as important component of the aquatic ecosystem not only as source of food for aquatic animals, they also act as an efficient accumulator of heavy metals and act as efficient biological filters. Macrophytes concentrate great amount of various substances, such as metals, and are considered as indicators of local pollution [10]. The inputs of pollutants into water bodies are discontinuous and such pollutants are quickly diluted.

This capability is useful in removing toxic heavy metals and trace elements from contaminated soils in a process called phytoremediation [11]. The capability of a plant to be used for phytoremediation can be known by calculating the Bioconcentration factor (BCF). Enugu, called the coal city of Nigeria, is a city in the eastern region of Nigeria with a very large deposit of coal (mainly of sub-bituminous grade), estimated at 1.5 million tons. Local geochemical background in the sediments of River Ekulu, Enugu, showed that the coal city

of Nigeria was affected by coal mining. Moreover, organic chemical and elemental analysis in bituminous sands of Nigeria was carried out, and the sediments of River Ekulu were analyzed for heavy metal content [12]. This research established the presence of toxic metals in the area and called for a follow up study to determine how the human and aquatic lives have been affected.

Most of the works on pollution in the vicinity of Agbabu bitumen field concentrate on Polycyclic Aromatic hydrocarbons (PAH) in surface soil and water [13], n-alkanes in soil and water [14], heavy metals in soil and terrestrial plant [15]. Nevertheless, studies of water and sediment contamination with heavy metals in the bitumen belt are lacking [16] and the present work is aimed to evaluate this.

2. MATERIALS AND METHODS

2.1 Sampling Area and Sample Collection

Samples were collected in the four seasons as follows: Surface water sampling points (6), Ground water sampling points (6), aquatic macrophyte (*Ceratophyllum demersum*) sampling points (2) i.e. PLANT-OLSW1 and PLANT-OLSW4. Sampling points were geo-located using geographical positioning system (GPS) to ensure consistency. More sampling points were taken from Aba Temidire (Mile – 2 bitumen well). Control samples were taken at Okitipupa town which is about 20km to the research site. Water samples were collected to 0.5 l bottles and acidified with conc. HNO_3 (5ml/l) and kept under ice chest while aquatic plant were collected to polythene bags. The aquatic macrophyte (*Ceratophyllum demersum*) samples were later air dried and kept for digestion.

2.2 Sample Analysis

Samples for analysis were prepared according to standard analytical procedures [17, 18]. 50ml distilled water, 0.5ml concentrated HNO_3 and 5.0ml concentrated HCl were added to each sample and the blank. Each beaker was covered with watch glass and digestion carried out on a hot plate in a fume chamber avoiding splattering all through. Digestion was continued until the entire volume was reduced to about 15ml. The beakers were allowed to cool to room temperature. The digests were then filtered into 50ml volumetric flasks and made up to volume with distilled water. Detection limits were 0.008ppm for Fe, 0.001ppm for Cu, 0.005ppm for Mn, 0.007ppm for Cr, 0.001ppm for Zn, 0.006ppm for Pb, 0.002ppm for Cd, 0.002 for Ni and 0.004ppm for V. Accuracy of the method was evaluated by determining the concentration of heavy metals in a standard reference solution.

Aquatic macrophyte (*Ceratophyllum demersum*) samples were washed with water to remove adhered particles. Samples were cut into pieces and air dried. A representative sample (2.5g) of the plant was accurately weighed and subjected to $HClO_4$ (10ml), HNO_3 (4ml) and H_2SO_4 (1ml) wet oxidation digestion at a rate of 5 mL/0.5 g of sample. Digestion was carried out on a hot plate at a temperature of 100^oC. Digestion was continued until the liquid became clear. The entire digest was then made up to 25mls for analysis.

Bio-concentration Factor (BCF) was calculated as the ratio of the heavy metal concentration in the plant tissues at harvest to the concentration of the element in surface water [11].

$$BCF = (P/E)_i$$

Where i = heavy metal.
P = Heavy metal concentration in plant tissues (mg/kg dry wt).
E = Heavy metal concentration in water (mg/l).

Analysis was carried out with AAS using GBC Avanta PM. Ver. 2.02.

2.3 Validation Procedure

To validate the procedure, GBC Avanta PM. Ver. 2.02 atomic absorption spectrophotometer was programmed to carry out metal detection by displaying three absorbance readings and what was reported was the average. Accuracy of the method was evaluated by determining the concentration of heavy metals in a standard reference solution (Table 1). Blanks were also used for correction of background and other sources of error. Apart from calibration before use, quality checks were also performed on GBC Avanta PM. Ver. 2.02 atomic absorption spectrophotometer after every ten sample runs. This was done by checking the absorbance of the blanks again and correction of background.

Table 1. Analytical precision and accuracy

Metal	Certified value (ppm)	Average measured value (ppm)	% Error	% Accuracy
Fe	1.29	1.24	3.876	96.124
Cu	0.541	0.51	5.730	94.270
Mn	2.82	2.79	1.064	98.936
Cr	0.024	0.023	4.167	95.833
Zn	1.27	1.23	3.150	96.850
Pb	0.015	0.013	13.333	86.667
Cd	0.033	0.031	6.061	93.939
Ni	0.411	0.397	3.406	96.594
V	0.08	0.065	18.750	81.250

2.4 Data Analysis

Analysis of variance (ANOVA) of concentration of metals in surface and ground water was carried out with SPSS 17 at $\alpha = .05$ to determine significant statistical differences between the metals, sampling stations and seasons.

3. RESULTS AND DISCUSSION

3.1 Heavy Metal in Surface Water

Table 1 shows the concentration of heavy metals in surface water in year 2008 and Table 3 shows the concentration of heavy metals in surface water in year 2009. Mercury was not detectable in all surface water samples in the study area. In 2008, Fe was not detectable at sampling station AGSWM2 and values of Fe recorded at the remaining sampling points ranged from 0.301ppm to 15.990ppm. These values were higher than 0.3ppm recommended assessment level [19]. Elemental characterization of the Nigerian bitumen by total reflection x-ray fluorescence showed Fe, Cr and Mn to be part of its components [20]. High values of Fe recorded were probably due to the presence of bitumen deposit. Fe was not detectable in surface water in the study area in 2009 probably due to run-off.

Cu was not detectable at all surface water sampling stations in the study area in the dry season of 2008 and 2009. In the rainy season, Cu was not detectable at sampling points AGSWMile2 in 2008 and OLSW2 in 2009. Cu ranged from 0.001ppm to 0.011ppm at the remaining sampling points. These values were below 2.0ppm recommended assessment level [19]. Concentrations of Cu were higher in the rainy season than in the dry season probably due to evaporation of the compound in which it occurred in the dry season.

In 2008, Mn in surface water in the study area ranged from 0.001ppm to 1.373ppm. Values of Mn in all surface water sampling stations, except AGSWMile2, were higher than 0.010ppm recommended by WHO [21]. High values of Mn recorded were probably due to the presence of bitumen. Mn was not detectable in the study area in 2009 probably due to run-off and evaporation.

Cr was not detectable at all surface water sampling stations in the study area in the dry season of 2008 and both seasons of 2009. In the rainy season of 2008, Mn ranged from 0.075ppm to 0.091ppm. Values Cr in surface water sampling stations were higher than 0.05ppm recommended by WHO [21]. High values of Cr recorded were probably due to the presence of bitumen deposit. Concentrations of Cr were higher in the rainy season than in the dry season probably due to evaporation of the compounds in which they occur in the dry season.

In 2009, Zn was not detectable at sampling stations OLSW2 in the dry season and OLSW4 in the rainy season. Zn ranged from 0.002ppm to 0.311ppm at the remaining sampling points in 2008 and 2009. Values were below 3.0ppm recommended assessment level [19]. In 2009, Pb was not detectable at all sampling stations in the study area in the dry and rainy seasons. In 2008, Pb ranged from 0.004ppm to 0.031ppm. Values were below 0.05ppm recommended by WHO.

In 2009, Cd was not detectable at all surface water sampling stations in the study area in both seasons. In 2009, Cd was not detectable at sampling points OLSW3 and AGSWMile2 in dry season. Cd ranged from 0.001ppm to 0.010ppm at the remaining sampling points. These values were below 0.05ppm recommended by WHO.

Ni was not detectable at all surface water sampling stations in the study area in the dry season of 2008. In the rainy season of 2009, Cu was not detectable at sampling points OLSW2 and OLSW3. Ni ranged from 0.007ppm to 0.111ppm at the remaining sampling points. Values of Ni in surface water sampling stations, except OLSW4 and AGSWMile2 in the rainy season of 2009, were higher than 0.010ppm recommended by WHO [21]. The Nigerian bitumen components (asphatene, oil and resins) were subjected to trace metal analysis and were found to contain high concentrations of Zn, Ni, V and Fe [1]. Therefore, high values of Ni recorded were probably due to the presence of bitumen.

Table 1a. Heavy metal analysis of surface water (dry and rainy season, 2008)

S/N	Sampling points	Fe (ppm)		Cu (ppm)		Mn (ppm)		Cr (ppm)		Zn (ppm)	
		Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy
1	OLSW – 1	1.663	1.612	ND	0.008	1.373	0.058	0.091	ND	0.138	0.041
2	OLSW – 2	1.321	0.973	ND	0.003	0.331	0.024	0.083	ND	0.184	0.024
3	OLSW – 3	1.416	2.183	ND	0.005	0.720	0.064	0.083	ND	0.092	0.080
4	OLSW – 4	15.990	3.089	ND	0.001	1.112	0.073	0.091	ND	0.311	0.054
5	AGSW – MILE2	ND	0.301	ND	ND	0.001	0.025	0.075	ND	0.101	0.054
6	CONTR-SW	0.258	0.361	ND	0.003	0.044	0.011	0.070	ND	0.210	0.047

ND = Not Detectable

Table 1b. Heavy metal analysis of surface water (dry and rainy season, 2008)

S/N	Sampling points	Pb (ppm)		Cd (ppm)		Ni (ppm)		V (ppm)	
		Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy
1	OLSW – 1	0.029	0.011	0.003	0.010	ND	0.049	ND	ND
2	OLSW – 2	0.024	0.006	0.012	0.004	ND	0.055	ND	ND
3	OLSW – 3	0.031	0.007	ND	0.005	ND	0.062	ND	ND
4	OLSW – 4	0.026	0.005	0.001	0.005	ND	0.053	ND	ND
5	AGSW – MILE2	0.022	0.004	ND	0.003	ND	0.059	ND	ND
6	CONTR-SW	0.024	0.016	0.003	0.008	ND	0.053	ND	ND

ND = Not Detectable

Table 2a. Heavy metal analysis of aquatic macrophyte (dry and rainy season, 2008)

S/N	Sampling points	Fe (ppm)		Cu (ppm)		Mn (ppm)		Cr (ppm)		Zn (ppm)	
		Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy
1	PLANT OLSW1	712.10	296.40	2.70	1.65	29.35	21.38	1.55	1.10	19.03	14.86
2	PLANT OLSW4	370.84	210.70	4.23	2.37	16.70	11.96	1.44	1.29	6.31	8.27
3	MEAN AQ.PL.	541.47	253.33	3.47	2.01	23.03	16.67	1.50	1.20	12.67	11.57

Table 2b. Heavy metal analysis of aquatic macrophyte (dry and rainy season, 2008)

S/N	Sampling points	Pb (ppm)		Cd (ppm)		Ni (ppm)		V (ppm)	
		Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy
1	PLANT OLSW1	1.46	0.88	1.50	1.01	2.93	1.96	0.21	0.14
2	PLANT OLSW4	1.59	1.22	1.46	0.99	3.17	2.06	0.37	0.19
3	MEAN AQ.PL.	1.53	1.05	1.48	1.00	3.05	2.01	0.29	0.17

Table 3a. Heavy metal analysis of surface water (dry and rainy season, 2009)

S/N	Sampling points	Fe (ppm)		Cu (ppm)		Mn (ppm)		Cr (ppm)		Zn (ppm)	
		Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy
1	OLSW – 1	ND	ND	ND	ND	ND	ND	ND	ND	0.012	0.014
2	OLSW – 2	ND	ND	ND	0.004	ND	ND	ND	ND	ND	0.008
3	OLSW – 3	ND	ND	ND	0.007	ND	ND	ND	ND	0.008	0.002
4	OLSW – 4	ND	ND	ND	0.011	ND	ND	ND	ND	0.023	ND
5	AGSW – MILE2	ND	ND	ND	0.005	ND	ND	ND	ND	0.021	0.001
6	CONTR-SW	ND	ND	ND	0.005	ND	ND	ND	ND	0.112	ND

**ND = Not Detectable*

Table 3b. Heavy metal analysis of surface water (dry and rainy season, 2009)

S/N	Sampling points	Pb (ppm)		Cd (ppm)		Ni (ppm)		V (ppm)	
		Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy
1	OLSW – 1	ND	ND	ND	ND	0.082	0.007	ND	ND
2	OLSW – 2	ND	ND	ND	ND	0.084	ND	ND	ND
3	OLSW – 3	ND	ND	ND	ND	0.052	ND	ND	ND
4	OLSW – 4	ND	ND	ND	ND	0.08	0.008	ND	ND
5	AGSW – MILE2	ND	ND	ND	ND	0.111	0.016	0.054	ND
6	CONTR-SW	0.020	ND	ND	ND	0.368	0.004	0.000	ND

**ND = Not Detectable*

Table 4a. Heavy metal analysis of aquatic macrophyte (dry and rainy season, 2009)

S/N	Sampling points	Fe (ppm)		Cu (ppm)		Mn (ppm)		Cr (ppm)		Zn (ppm)	
		Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy
1	PLANT OLSW1	43.11	22.10	5.60	1.94	30.80	5.98	9.30	0.43	36.20	8.39
2	PLANT OLSW4	NA	27.57	NA	1.34	NA	3.79	NA	0.67	NA	8.43
3	MEAN AQ.PL.	43.11	24.84	5.60	1.64	30.80	4.89	9.30	0.55	36.20	8.41

**NA = Not Applicable*

Table 4b. Heavy metal analysis of aquatic macrophyte (dry and rainy season, 2009)

S/N	Sampling points	Pb (ppm)		Cd (ppm)		Ni (ppm)		V (ppm)	
		Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy
1	PLANT OLSW1	0.77	2.78	0.24	1.87	4.48	6.36	0.36	0.61
2	PLANT OLSW4	NA	2.73	NA	1.22	NA	3.54	NA	0.34
3	MEAN AQ.PL.	O.77	2.76	0.24	1.55	4.48	0.18	0.36	0.48

**NA = Not Applicable*

V was not detectable at all surface water sampling stations in the study area, except AGSWMile2 in the dry season of 2009. Surface water samples were also collected from Okitipupa to serve as control sampling point. Okitipupa is about 20km away from Agbabu bitumen deposit area. Concentrations of heavy metals in the surface water of Agbabu bitumen deposit area were higher when compared with the values recorded at the control station (CONTR-SW).

The concentrations Fe, Mn, Cr, Zn and Pb were higher in surface water in the dry season than in rainy season probably due to dilution by rainwater which influences concentration and heavy metal dynamics. Domestic activities in the dry season, which include washing and bathing at the surface water sampling stations, could also increase the concentration of contaminants. This agreed with the report of Onwerenmadu et al. [22]. Mobility of heavy metals depends not only on the total concentration but also on the metal properties and environmental factors. Concentrations of Cu, Cd and Ni were higher in the rainy season than in the dry season probably due to evaporation of the compounds in which they occur in the dry season. Higher concentration of Cu, Cd and Ni in the rainy season can also be due to evaporation of the compounds in which they occur in the dry season. This agrees with the findings of Lokeshwary and Chandrappa [23].

3.2 Heavy Metal in Aquatic Macrophyte (*Ceratophyllum demersum*)

Table 2 shows the concentration of heavy metals in aquatic macrophyte (*Ceratophyllum demersum*) in year 2008 and Table 4 shows the concentration of heavy metals in aquatic macrophyte (*Ceratophyllum demersum*) in year 2009.

Mercury was not detectable in all aquatic macrophyte samples in the study area. At sampling points PLANT-OLSW1 and PLANT-OLSW4 in years 2008 and 2009, Fe ranged from 22.10ppm to 712.10ppm, Cu from 1.65ppm to 5.60ppm, Mn from 5.98ppm to 30.80ppm, Cr from 0.43ppm to 9.30ppm, Zn from 6.31ppm to 36.20ppm, Pb from 0.77ppm to 8.39ppm, Cd from 0.24ppm to 1.87ppm, Ni from 1.96 ppm to 4.48ppm, V from 0.14ppm to 0.37ppm.

Samples of aquatic macrophyte (*Ceratophyllum demersum*) were collected from River Oluwa. River Oluwa was considered as surface water at Agbabu bitumen deposit area. Sampling point PLANT-OLSW1 was located at the southern part of the River Oluwa while sampling point OLSW4 was located at the northern part (Fig. 1).

The concentrations of heavy metals in aquatic macrophyte were low when compared with the acceptable normal and critical ranges in plants [9], as shown in Table 5. The critical range of the concentration of a heavy metal in plant is the concentration of the heavy metal in the plant above which it is not safe to eat the plant.

3.4 Bioconcentration Factor

Bioconcentration Factor (BCF) was calculated as the ratio of the heavy metal concentration in the plant to the concentration of the same heavy metal in the external environment [11]. BCF's calculated for metals in aquatic plants (*Ceratophyllum demersum*) are shown in Table 6.

The minimum BCF of the metals in aquatic plant (*Ceratophyllum demersum*) calculated in the dry season was 4.40 (Ni – Dry season, 2009) and the maximum was 3620.00 (Zn – Dry

season, 2009). In the rainy season, the minimum BCF calculated was 36.15 (Ni – Rainy season, 2008) and the maximum was 1682 (Zn – Rainy season, 2009). High values of BCF show that aquatic plant (*Ceratophyllum demersum*) can be used for phytoremediation of surface water polluted with Fe, Cu, Zn, Pb and Cd.

3.2 Heavy Metal in Ground Water

Table 7 shows the concentration of heavy metals in surface water in year 2008 and Table 8 shows the concentration of heavy metals in surface water in year 2009.

Hand dug wells and bore hole were the two major sources of drinking water for the rural dwellers at Agbabu bitumen deposit area. Hand dug wells at sampling stations AGGW1, AGGW2, AGGW3, AGGW4, AGWMile2 and the bore hole at sampling station AGBH, were sampled for water analysis of heavy metals in ground water (Fig. 1).

Mercury was not detectable in all ground water samples in the study area.

Fe was not detectable at all the sampling stations in both seasons in 2009 and sampling station AGGW4 in the rainy season of 2008.Values of Fe recorded at the remaining sampling points ranged from 0.500ppm to 3.81ppm. These values were higher than 0.3ppm recommended assessment level [19]. High values of Fe recorded were probably due to the presence of bitumen deposit because total reflection x-ray fluorescence of the Nigerian bitumen showed that Fe is part of the components. Ingesting too much of iron through drinking water is not associated with adverse health effects. However, consuming large amounts of iron can lead to iron overload; this can lead to hemochromatosis, a severe disease that can damage the body's organs [24]. Fe was not detectable in ground water in the study area in 2009 probably due to evaporation. Cu was not detectable at all ground water sampling stations in the study area, except AGGW3 in the rainy season of 2008.

In 2008, Mn was not detectable at sampling point AGWMile2 in the dry season. Mn in ground water in the remaining stations in the study area ranged from 0.021ppm to 1.280ppm. Values of Mn in all ground water sampling stations were higher than 0.010ppm recommended by WHO [21]. High values of Mn recorded were probably due to the presence of bitumen deposit because total reflection x-ray fluorescence of the Nigerian bitumen showed that Mn is part of the components. Mn effects occur mainly in the respiratory tract and in the brains. Symptoms of Mn poisoning are hallucinations, forgetfulness and nerve damage. Mn can also cause Parkinson, lung embolism and bronchitis. In 2009, Mn was not detectable at all ground water sampling points in the dry season and sampling point AGWMile2 in the rainy season, probably due to evaporation.

Table 5. Heavy metal concentration in aquatic plant (*Ceratophyllum demersum*) in this study compared with the critical and normal ranges in plant [9]

Heavy metal	Normal range (µg/g)	Critical range (µg/g)	*Ceratophyllum demersum* Conc. (ppm)			
			Dry 2008	Rainy 2008	Dry 2009	Rainy 200i
Zn	1 – 400	100 – 400	12.67	11.57	36.20	8.41
Cu	7.53 – 8.44	25 – 90	3.47	2.01	5.60	1.64
Ni	0.89 - 2.04	10 – 50	3.05	2.01	4.48	4.95
Pb	0.2 – 2.0	30 – 300	1.53	1.05	0.77	2.76
Cd	0.2 – 2.0	10 – 30	1.48	1	0.24	1.55

Table 6a. Bio-concentration factor of aquatic macrophyte in surface water (dry and rainy season, 2008)

S/N	Year	Fe (ppm)		Cu (ppm)		Mn (ppm)		Cr (ppm)		Zn (ppm)	
		Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy
1	2008	106.22	155.26	-	472.00	32.65	341.6	17.73	-	76.69	228.66
2	2009	-	-	-	32.80	-	-	-	-	3620.00	1682.00

Table 6b. Bio-concentration factor of aquatic macrophyte in surface water (dry and rainy season, 2008)

S/N	YEAR	Pb (ppm)		Cd (ppm)		Ni (ppm)		V (ppm)	
		Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy
1	2008	57.93	159.09	296.00	185.19	-	36.15	-	-
2	2009	-	-	-	-	56.00	30.00	36.00	-

Table 7a. Heavy metal analysis of ground water (dry and rainy season, 2008)

S/N	Sampling points	Fe (ppm)		Cu (ppm)		Mn (ppm)		Cr (ppm)		Zn (ppm)	
		Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy
1	AGGW – 1	3.810	0.508	ND	ND	0.997	0.028	0.108	ND	0.111	0.051
2	AGGW – 2	0.720	0.340	ND	ND	1.222	0.029	0.091	ND	0.179	0.076
3	AGGW – 3	0.640	0.394	ND	0.004	1.280	0.023	0.083	ND	0.181	0.092
4	AGGW – 4	0.500	ND	ND	ND	0.416	ND	0.099	ND	0.164	ND
5	AGW – MILE2	1.220	1.433	ND	ND	0.898	0.021	0.075	ND	0.170	0.005
6	CONTR-GW	0.470	0.178	ND	0.004	0.400	0.016	0.061	ND	0.120	0.074

**ND = Not Detectable*

Table 7b. Heavy metal analysis of ground water (Dry and Rainy season, 2008)

S/N	Sampling points	Pb (ppm)		Cd (ppm)		Ni (ppm)		V (ppm)	
		DRY	RAINY	DRY	RAINY	DRY	RAINY	DRY	RAINY
1	AGGW – 1	0.007	0.019	0.007	0.009	ND	0.057	ND	ND
2	AGGW – 2	0.016	0.012	0.003	0.020	ND	0.065	ND	ND
3	AGGW – 3	0.029	0.010	0.013	0.009	ND	0.067	ND	ND
4	AGGW – 4	0.016	ND	0.014	ND	ND	ND	ND	ND
5	AGW – MILE2	0.008	0.008	0.021	0.003	ND	0.072	ND	ND
6	CONTR-GW	0.010	0.011	0.015	0.014	ND	0.082	ND	ND

**ND = Not Detectable*

Table 8a. Heavy metal analysis of ground water (dry and rainy season, 2009)

S/N	Sampling points	Fe (ppm)		Cu (ppm)		Mn (ppm)		Cr (ppm)		Zn (ppm)	
		Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy
1	AGGW – 1	ND	ND	ND	ND	ND	0.021	ND	ND	ND	0.014
2	AGGW – 2	ND	ND	ND	ND	ND	0.027	ND	ND	0.032	0.008
3	AGGW – 3	ND	ND	ND	ND	ND	0.024	ND	ND	0.012	0.002
4	AGGW – 4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
5	AGW – MILE2	ND	ND	ND	ND	ND	ND	ND	ND	0.046	0.001
6	AGBH	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA
7	CONTR-GW	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND

**ND = Not Detectable*
**NA = Not Applicable*

Table 8b. Heavy metal analysis of ground water (dry and rainy season, 2009)

S/N	Sampling points	Pb (ppm)		Cd (ppm)		Ni (ppm)		V (ppm)	
		Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy
1	AGGW – 1	ND	ND	ND	ND	0.048	ND	ND	ND
2	AGGW – 2	ND	ND	ND	ND	0.072	0.005	ND	ND
3	AGGW – 3	0.059	ND	ND	ND	0.059	0.007	ND	ND
4	AGGW – 4	ND	ND	ND	ND	0.035	ND	ND	ND
5	AGW – MILE2	ND	ND	ND	ND	0.107	ND	ND	ND
6	AGBH	ND	NA	ND	NA	0.047	NA	ND	NA
7	CONTR-GW	NA	ND	NA	ND	NA	0.005	NA	ND

**ND = Not Detectable*
**NA = Not Applicable*

Cr was not detectable at all ground water sampling stations in the study area in the rainy season of 2008 and both seasons of 2009. In the dry season of 2008, Cr ranged from 0.075ppm to 0.108ppm. Values of Cr recorded at ground water sampling stations were higher than 0.05ppm recommended by WHO [21]. High values of Cr recorded were probably due to the presence of bitumen deposit because total reflection x-ray fluorescence of the Nigerian bitumen showed that Cr is part of the components. High concentration of Cr in the ground water is dangerous for these rural dwellers because Cr and its compounds can cause cancers of lungs, nasal cavity and para nasal sinus and suspected cause cancer of the stomach and larynx [25]. Considering the concentrations of Fe, Cr and Mn in hand dug wells at Agbabu bitumen deposit area, this source of water is not fit for human consumption based on WHO's recommendations.

In 2009, Zn was not detectable at sampling stations AGGW2 and AGGW4 in the dry season. Zn was also not detectable at sampling point AGGW4 in the rainy seasons of 2008 and 2009. Zn ranged from 0.002ppm to 0.181ppm at the remaining sampling points in 2008 and 2009. Values were below 3.0ppm recommended assessment level.

In 2009, Pb was not detectable at all sampling stations in ground water in the study area in the dry and rainy seasons, except sampling point AGGW3 in dry season. Pb was also not detectable in the rainy season of 2008. Pb ranged from 0.007ppm to 0.059ppm at the remaining sampling points. Values were below 0.05ppm recommended by WHO. In 2009, Cd was not detectable at all ground water sampling stations in the study area in both seasons. In 2008, Cd was also not detectable at sampling point AGGW4 in the rainy season. Cd ranged from 0.003ppm to 0.021ppm at the remaining sampling points. These values were below 0.05ppm recommended by WHO.

Ni was not detectable at all ground water sampling stations in the study area in the dry season of 2008. In the rainy season of 2009, Ni was not detectable at sampling points AGGW1, AGGW4, AGWMile2. Ni ranged from 0.035ppm to 0.107ppm at the remaining sampling points. Values of Ni recorded in ground water sampling stations, including AGBH (bore hole), were higher than 0.010ppm recommended by WHO [21]. High values of Ni recorded were probably due to the presence of bitumen deposit because trace metal analysis of the Nigerian bitumen showed that it contained high concentration of Ni [1]. Workers who accidentally drank water containing very high levels of nickel had stomach aches, and blood and kidney disorders [26].

V was not detectable at all ground water sampling stations in the study area. In the study area, ground water sampling station

AGGW1 had the highest concentration of Fe and Cr. Ground water sampling station AGGW3 had the highest concentration of Cu, Mn, Zn and Pb. Ground water sampling station AGWMile2 had the highest concentration of Cd and Ni.

The concentrations of Fe, Mn, Cr, Zn and Cd were higher in ground water in the dry season than in the rainy season probably due to dilution and run off. Concentrations of Cu, Pb and Ni were higher in the rainy season probably due to evaporation of the compounds in which they occurred. The concentrations of Fe, Cr and Mn were very high at Agbabu bitumen deposit area compared with the values obtained in control sampling points. High concentrations of Fe, Cr and Mn in most of the surface water and ground water samples considered in this study may likely be due to the deposit of bitumen. Trace elements such as transition metals get into bitumen in form of porphyrin complexes at its early stages of

formation. Adebiyi et al. [21] in an elemental characterization of the Nigerian bitumen by total reflection x-ray fluorescence showed Fe, Cr and Mn to be part of its components. The Nigerian bitumen components (asphatene, oil and resins) were subjected to trace metal analysis and were found to contain high concentrations of Zn, Ni, V and Fe [1].

3.5 Data Analysis

Analysis of variance and multiple comparisons of concentrations of Cr and Mn in surface water in the sampling points showed no statistically significant differences. This shows that Cr and Mn in the study area must have originated from similar sources in a particular season.

Analysis of variance of the concentrations of Cr and Mn in surface water in the four seasons showed statistically significant differences indicating that sources of Cr and Mn varied from one season to another. This implies that Cr and Mn in the study will probably originate from bitumen and anthropogenic sources which include farming and laundry. Sources of Cr and Mn varied, depending on the season.

Analysis of variance of Cr and Mn in ground water in the sampling points also showed no statistically significant differences. This indicates that Cr and Mn probably came from the same source at all the sampling points in a particular season. ANOVA of Cr and Mn in the four seasons also showed statistically significant differences. This means when dry season 2008, rainy season 2008, dry season 2009 and rainy season 2009 were compared, Cr and Mn probably came from different sources. Multiple comparisons of concentrations of Cr and Mn between the seasons showed no statistically significant differences between rainy season in 2008 and dry season in 2009, and rainy season in 2008 and rainy season in 2009. This shows that Cr and Mn in the study must have originated from the similar sources when these specific seasons were compared. Apart from the deposit of bitumen in the study area, which may be a natural source of heavy metals, other sources of heavy metals in the study area are anthropogenic sources which included farming, fishing and domestic activities.

4. CONCLUSION

Data available in this study can be used as base line data at Agbabu bitumen deposit area. The mean concentrations of Fe, Cr, Mn and Ni were higher than WHO recommendations in most of the water samples examined. The concentrations of Fe, Cr, Mn and Ni in ground water samples examined rendered the hand dug wells considered as ground water unfit for human consumption. High values of BCF showed that aquatic macrophyte (*Ceratophyllum demersum*) can be used for phytoremediation of surface water polluted with Fe, Cu, Zn, Pb and Cd. Analysis of variance and multiple comparisons of concentration of Cr and Mn in surface water and ground water considering the sampling points at a particular season showed that they probably originated from the similar sources. When the four seasons were considered, analysis of variance and multiple comparisons showed that Cr and Mn probably came from several sources which included bitumen deposit, domestic activities, laundry, fishing and farming.

Further research can be carried out to determine the concentration of heavy metals in various parts of the aquatic macrophyte in the environment. It is also recommended that further research be carried out on speciation of the heavy metals in aquatic macrophyte to determine the forms in which they occur.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Adebiyi FM, Omode AA. Chemical and elemental characterization of components of Nigerian bitumen sands. Energy Sources. 2007;29(8):669-676.
2. Akinmosin A, Osinowo OO, Oladunjoye MA. Radiogenic components of the Nigeria Tarsand Deposits. Earth Sci Res J. 2009;13(1):64-73.
3. Adegoke OS, Ibe EC. The tar sand and heavy crude resources of Nigeria. 2nd International Conference on heavy crude and tarsands, Caracas, Venezuela. 1982;32:280–285
4. Oboh OB, Ilori MO, Akinyemi JO, Adebusoye SA. Hydrocarbon Degrading potentials of bacteria isolated from a Nigerian bitumen (Tarsand) deposit. Nature and Sci. 2006;4(3):51-57
5. Oguntimehin II, Ipinmorroti KO. Solvent extraction of vanadium from Nigerian bitumen using Tri-butylphosphate. J of Applied Sci. 2007;7(24):4028-4031.
6. Olaleye VF, Adedeji AA. Water and Planktonic Quality of a Palm Oil Effluent Impacted River in Ondo State, Nigeria. Int J of Zoological Res. 2005;1(1):15–20.
7. Ikhile CI. The Impacts of Climate Change on the Discharge of Osse-Ossiomo River Basin, South Western Nigeria under Different Climatic Scenarios. Afr Res Review in Sci and Technol. (AFFREV STECH). 2012;1(1):208-220
8. Fagbote EO, Olanipekun EO. Seasonal and depth effects on the physico-chemical parameters of the soils of farm settlements with bitumen deposit. Int Res J of Biotech. 2011;2(9):198-212
9. Rios-Arana JV, Walsh EJ, Gardea-Torresdey JL. Assessment of arsenic and heavy metal concentrations in water and sediments of the Rio Grande at El Paso-Jaurez metroplex region. Environ Int. 2003;29:957-971
10. Amaal MA, Yasser AG. Evaluation of Heavy metal status in ecosystem of Lake Manzalah, Egypt. Global J of Environ Res. 2009;3(3):194-204.
11. Shao-wei L, Wen-Lian C. Heavy metal phytoremediation by water Hyacinth at constructed wetlands in Taiwan. J of Aquatic Plant Mgt. 200;442:60-68
12. Adaikpor EO, Nwajei GE, Olada JE. Heavy metals concentration in coal and sediments from River Ekulu in Enugu, coal city of Nigeria. J of Applied Sci and Environ Mgt. 2005;9(3):5-8.
13. Abass AA, Abass OA, Adejare AA, Ojeyemi MD. Distribution of Polycyclic Aromatic Hydrocarbons in surface soils and water from the vicinity of Agbabu bitumen field of south-western Nigeria. J of Environ Sci and Health, Part A. 2007;42(8):1043–1049.
14. Olajire AA, Olojubade M, Olabemiwo O. n-Alkanes distributions in soil and water samples collected near Agbabu bitumen field of Southwestern Nigeria. Int J of Environ Studies. 2008;65(6):769-779
15. Fagbote EO, Olanipekun EO. Evaluation of the Status of Heavy Metal Pollution of Soil and Plant (*Chromolaena odorata*) of Agbabu Bitumen Deposit Area, Nigeria.American-Eurasian J of Sci Res. 2010;5(4):241-248.
16. Balarabe ML, Abubakar MM. 2005, Contribution to some elemental accumulation in Nguru Lake, North Eastern Nigeria. Int J of Pure and Applied Sci. 2005;1(1):26-29
17. International Institute For Tropical Agriculture (IITA). Selected methods for Soil and Plant Analysis, Oyo road, Ibadan, Nigeria. Analysis. 1979;102.

18. ASTM D 3974. Standard Practices for Extraction of Trace Elements from Sediments. ASTM International, 100 Barr Harber Drive, West Conshohocken, United States. 1981;393–395.
19. Department of Environment Protection (DEP), (2003), Assessment levels for soil, sediment and water. Contaminated Sites Management series. Accessed 12 January 2010. Available: http://portal.environment.wa.gov.au/pls/portal/docs/page/doe_admin/guideline_repository/assessment%20levels%20for%20soil,%20sediment%20and%20water.pdf.
20. Adebiyi FM, Asubiojo OI, Ajayi FR. Multi-elemental analysis of Nigerian bitumen by TXRF spectrometry and the physical constants characterization of its hydro-carbon component. Fuel. 2006;85:396-400.
21. World Health Organization (WHO), 1982, Guidelines for drinking water quality. WHO General. Accessed 17 October 2012. Available: http://www.who.int/water_sanitation_health/dwq/gdwq0506.pdf.
22. Onwerenmadu EU, Eshett ET, Onyi GE. Temporal variability of selected heavy metals in automobile soils. Int J of Environ Sci and Technol. 2007;4(1):35-41.
23. Lokeshwary H, Chandrappa GT. Impact of heavy metal Contamination of Bellandur Lake on Soil and cultivated vegetation. Current Sci. 2006;91(5):622-627.
24. Sinclair V. Health effects of iron in drinking water. Livestrong. Accessed 26 December 2012; 2011. Available: http://www.livestrong.com/article/155098-health-effects-of-iron-in-drinking- water/.
25. Agency for toxic substances and diseases registry (ATSDR), 2008. Toxicological profile for chromium 46. 1600 Cliffon road NE, Atlanta Georgia 30333. Accessed 17 October 2012. Available: http://www.atsdr.cdc.gov/toxprofiles/tp7.pdf.
26. Australian Drinking Water Guidelines, 1996, Nickel & compounds: Health effects. Accessed 26/12/12. Available: http://www.npi.gov.au/substances/nickel/health.html.

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