

**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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25 Running head: **Heavy Metals in Water and Aquatic Macrophyte**

26 **ABSTRACT**

27 **Aims:** This research is aimed at determining the levels of some heavy metals in
28 water (surface and ground) and aquatic macrophyte and to compare the values
29 with the standard recommendations.

30 **Study design:** Ten heavy metals (Fe, Cu, Mn, Cr, Zn, Hg, Pb, Cd, Ni, and V) were
31 analyzed in water (surface and ground) and aquatic macrophyte (*Ceratophyllum*
32 *demersum*).

33 **Place and duration of study:** Samples were collected from Agbabu bitumen
34 deposit area, Western Nigeria, in the dry and rainy seasons of years 2008 and
35 2009

36 **Methodology:** Analysis was carried out using atomic absorption spectrometry.

37 **Results:** In dry season of 2008, surface and ground water in all sampling stations,
38 apart from AGSW5-M2, had concentrations of Cr and Mn that were higher than
39 WHO recommendations for potable water, which is 0.05ppm and 0.01ppm
40 respectively. The lowest mean concentration of heavy metals in aquatic plant
41 (*Ceratophyllum demersum*) in the dry season of years 2008 and 2009 was
42 0.29 ± 0.07 ppm (Vanadium) while the highest was 541 ± 104.50 ppm (Fe). In the
43 rainy season of years 2008 and 2009, the lowest concentration is 0.17 ± 0.007 ppm
44 (Vanadium) and the highest was 253.55 ± 74.49 ppm (Fe). Bio-concentration Factor
45 (BCF) of metals in *Ceratophyllum demersum* were as high as 2828.13 (Zn- dry
46 season 2009), showing that it can be used in phytoremediation of surface water
47 polluted with Fe, Cu, Mn, Cr, Zn, Pb, Cd, Ni and V. Analysis of variance and
48 multiple comparison of concentration of Cr and Mn in surface and ground water
49 with SPSS 17 ($\alpha = .05$) showed no statistically significant differences between the
50 sampling points which shows that Cr and Mn in the study must have originated
51 from similar sources.

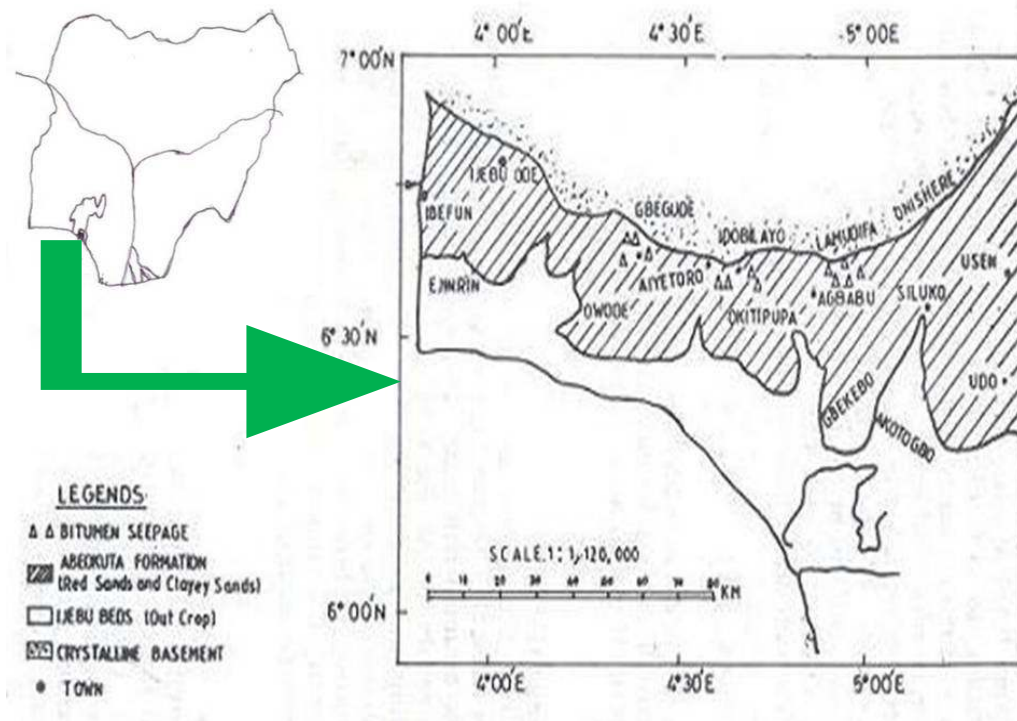
52 **Conclusions:** The environment presently has been impacted by the presence of
53 bitumen. Data available in this study can be used as base line data at Agbabu
54 bitumen deposit area.
55 **Keywords:** Aquatic macrophyte, Bioconcentration Factor (BCF), bitumen, heavy
56 metal, phytoremediation, water.

57

58 **1. INTRODUCTION**

59 Bitumen has similar composition as the light crude, that is, hydrogen, carbon, and minor
60 amount of sulphur and oxygen. They are believed to have formed from biodegradable and
61 water washing of light crude. The Nigerian bitumen is believed to have formed in a
62 similar process [1]. The probable reserve of bitumen and heavy oil in the entire Nigerian
63 belt is about 120 X 4.3km [2], [3], spreading along the bitumen belt stretching from
64 Lagos, Ogun through to Ondo and Edo State. Nigeria has a reserve of 30 – 40 billion
65 barrels of bitumen [4]. Agbabu is one of the farm settlements in Ondo State hosting a vast
66 deposit of bitumen (Fig. 1). This is where bitumen was first spotted in Nigeria in 1910
67 and the first bitumen well NBC-7 was drilled there. Agbabu bitumen belt is made of the
68 main Agbabu village inhabited by about 5,000 people and other smaller farm settlements
69 such as Temidire village made up of about 3,000 people. Farmers in this area deal mainly
70 in cash crops such as cocoa and colanut and food crops such as yam and plantain and
71 fishing along River Oluwa which flows through whole land. These villages depend on
72 River Oluwa for their farming activities and other domestic use while hand dug shallow
73 wells and bore hole serve as their only source of potable water. The two distinct seasons
74 in the year are rainy and dry. The rainy season is at its peak from July to the middle or
75 September while the dry season is from January to March.

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77

78 Figure 1: Map of Nigeria showing bitumen deposit area [5]

79

80 Heavy metals find their ways into terrestrial and aquatic environments through point and
 81 non-point sources. Natural sources include volcanic emission and anthropogenic sources
 82 such as combustion of solid waste, fossil fuels in coal, and oil fired power plants, releases
 83 from metal smelters and automobile emissions. Chemical and metallurgical industries are
 84 the most important sources of heavy metals in the environment. Biological and
 85 microbiological factors also contribute. Since there are no industrial activities yet in this
 86 bitumen deposit area, the likely sources of heavy metal contamination in the environment
 87 are the basic natural processes, farming, fishing, domestic activities and the presence of
 88 bitumen.

89 Metals are classified as 'heavy metals' if in their standard state they have a specific
 90 gravity of more than 5g/cm^3 . There are known sixty heavy metals. They get accumulated

91 in time in soils and plants and would have a negative influence on physiological activities
92 of plants (e.g. photosynthesis, gaseous exchange and nutrient absorption). In small
93 concentrations, the traces of the heavy metals in plants or animals are not toxic [6], [7].
94 Lead, Cadmium and Mercury are exceptions; they are toxic even in low concentrations
95 [8]. Heavy metal pollution is a serious and widespread environmental problem due to the
96 toxic, persistent, non-biodegradable and bioaccumulation properties of these
97 contaminants. Changes in physical and chemical features of the aquatic system may
98 influence the solubility and mobility of heavy metals in that system [9]. The pollution of
99 aquatic ecosystems could be more obvious in macrophytes and aquatic animals than in
100 water [10]. Macrophytes are considered as important component of the aquatic ecosystem
101 not only as source of food for aquatic animals [11], they also act as an efficient
102 accumulator of heavy metals and act as efficient biological filters. Macrophytes
103 concentrate great amount of various substances, such as metals, and are consequently
104 indicators of local pollution [10]. The inputs of pollutants into water bodies are
105 discontinuous and such pollutants are quickly diluted. Analysis of plant tissues provide
106 time integrated information on the quality of aquatic system [12].
107 Metal-accumulation plants can be used for remediation of polluted soils. This capability
108 is useful in removing toxic heavy metals and trace elements from contaminated soils in a
109 process called phytoremediation [13]. The capability of a plant to be used for
110 phytoremediation can be known by calculating the Bioconcentration factor (BCF).
111 Adaikpoh *et al.* [14], studied heavy metals concentration in coal and sediments
112 from River Ekulu in Enugu, coal city of Nigeria. This research established the
113 presence of toxic metals in the area and called for a follow up study to determine
114 how the human and aquatic lives have been affected.

115 Adebisi and Omode [15], studied the organic, chemical and elemental
116 characterization of components of Nigerian bituminous sands bitumen. The results
117 showed high concentration of Zn, Ni, V and Fe in the bituminous components.
118 Abass *et al.* [16], investigated the distribution of Polycyclic Aromatic
119 hydrocarbons (PAH) in surface soils and water from the vicinity of Agbabu
120 bitumen field. The research showed that the total PAH levels in water samples
121 from all the sampling stations, except one, were sufficiently high to cause acute
122 toxicity to the exposed organisms.

123 n-Alkanes distributions in soil and water samples collected near Agbabu field of
124 South Western Nigeria has been studied [17]. They suggested that both natural
125 and anthropogenic sources contribute to the n-alkanes load in soil and water
126 samples of the area. Ololade *et al.* [18], examined the distribution of heavy metals
127 in stream bed sediment from an oil-producing region in Nigeria in the two seasons
128 (dry and wet) of the year. Comparison of sediment with guidelines values
129 indicated anthropogenic enrichment and it was considered that only Cu, and
130 possibly Pb posed potential threats to the ecology of the area.

131 Uses of biotic parameters to assess the level of pollution of many water bodies in the
132 developing countries are few. Where such data exist, they are not properly utilized in
133 most cases. Extensive investigations have been carried out in limnology of temperate
134 waters while there is much to be done in tropical waters [19]. The aim of this study was
135 to evaluate the status of heavy metal pollution in ground water, surface water and aquatic
136 plant of Agbabu bitumen deposit area.

137

138

139 2. MATERIALS AND METHODS

140 2.1 Sampling Area and Sample Collection

141 Samples were collected every season as follows: 6 surface water samples 6 ground water
142 sample and 2 aquatic macrophyte (*Ceratophyllum demersum*) samples. Sampling points
143 were geo-located using geographical positioning system (GPS) to ensure consistency.
144 More sampling points were taken from Aba Temidire (Mile – 2 bitumen well). Control
145 samples were taken at Okitipupa town which is about 20km to the research site. Water
146 samples were collected inside 500ml clean plastic bottles and acidified with conc. HNO_3
147 (5ml/l) and kept under ice chest while aquatic plant were collected inside polythene bags.
148 The aquatic macrophyte (*Ceratophyllum demersum*) samples were later air dried and kept
149 for digestion.

150 2.2 Sample Analysis

151 Samples for analysis were prepared as follows [20], [21]:
152 50ml distilled water, 0.5ml concentrated HNO_3 and 5.0ml concentrated HCl were
153 added to each sample and the blank. Each beaker was covered with watch glass
154 and digestion carried out on a hot plate in a fume chamber avoiding splattering all
155 through. Digestion was continued until the entire volume was reduced to about
156 15ml. The beakers were allowed to cool to room temperature. The digests were
157 then filtered into a 50ml volumetric flask and made up to volume with distilled
158 water.

159 Plant samples were digested by thoroughly washing with water to remove all
160 adhered particles. Samples were cut into pieces and air dried. A representation
161 sample (2.5g) of the plant was accurately weighed and subjected to HClO_4 , HNO_3

162 and H₂SO₄ digestion (wet oxidation). The entire digest was then made up to 25mls
163 for analysis.

164 Bio-concentration Factor (BCF) can be calculated as the ratio of the heavy metal
165 concentration in the plant tissues at harvest to the concentration of the element in
166 the external environment [13].

167 $BCF = (P/E)_i$

168 Where i = heavy metal

169 P = Heavy metal concentration in plant tissues (mg/kg dry wt)

170 E = Heavy metal concentration in water (mg/l)

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

172 **2.3 Procedure Validation**

173 To validate the procedure, the instrument was programmed and it carried out
174 metal detection by displaying three absorbance readings and what was reported
175 was the average. Blanks were also used for correction of background and other
176 sources of error. Apart from calibration before use, quality checks were also
177 performed on the instrument by checking the absorbance after every ten sample
178 runs.

179 **2.4 Data Analysis**

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

183

184

3. RESULTS AND DISCUSSION

3.1 Heavy Metal in Surface Water

Concentrations of heavy metals in surface water and aquatic plant in dry and rainy seasons of year 2008 are shown in Tables 1 and 2 respectively. Concentrations of heavy metals in surface water and aquatic plant in dry and rainy seasons of year 2009 are shown in Tables 3 and 4 respectively. Bar charts of the concentration of heavy metals in surface water in dry and rainy seasons of years 2008 and 2009 are shown in Fig. 2.

Table 1: Heavy metal analysis of surface water and aquatic plant (Dry season, 2008)

S/ N	SAMLE ID	Fe (ppm)	Cu (pp m)	Mn (ppm)	Cr (ppm)	Zn (ppm)	Pb (ppm)	Cd (ppm)	Ni (pp m)	V (pp m)						
1	OLSW – 1	1.66	±0.06	ND	1.37	±0.02	0.09	±0.03	0.14	±0.04	0.03	±0.02	0.00	±0.01	ND	ND
2	OLSW – 2	1.32	±0.04	ND	0.33	±0.07	0.08	±0.01	0.18	±0.06	0.02	±0.01	0.01	±0.05	ND	ND
3	OLSW – 3	1.42	±0.03	ND	0.72	±0.065	0.08	±0.02	0.09	±0.02	0.03	±0.02	0.00	±0.02	ND	ND
4	OLSW – 4	15.99	±1.24	ND	1.11	±0.05	0.09	±0.25	0.31	±0.06	0.03	±0.01	0.00	±0	ND	ND
5	AGSW – MILE2	ND	ND	0.00	±0	0.08	±0.15	0.10	±0.04	0.02	±0.01	ND	ND	ND	ND	ND
	MEAN	5.10	±0.274	-	0.71	±0.041	0.08	±0.20	0.17	±0.044	0.03	±0.14	0.01	±0.02	-	-
	AQ.PL.(p pm)	541.47	3.47	23.03	1.50	12.67	1.53	1.48	3.05	0.29						
	BCF	106.22	-	32.56	17.73	76.69	57.95	296.00	-	-						
6	CONTR- SW	0.26	±0.06	ND	0.04	±0.01	0.07	±0.03	0.21	±0.07	0.02	±0.01	0.00	±0.01	ND	ND

ND = Not Detectable

Table 2 Heavy metal analysis of surface water and aquatic plant (Rainy season, 2008)

S/ N	SAM LE ID	Fe (ppm)	Cu (ppm)	Mn (ppm)	Cr (pp m)	Zn (ppm)	Pb (ppm)	Cd (ppm)	Ni (ppm)	V (pp m)
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1	OLS W-1	1.61	±0.6 5	0.01	±0.0 01	0.06	±0.0 04	ND	0.04	±0.0 02	0.01	±0.0 02	0.01	±0.0 01	0.0 5	±0.0 03	ND
2	OLS W-2	0.97	±0.0 85	0.00	±0	0.02	±0.0 03	ND	0.02	±0.0 06	0.01	±0.0 01	0.00	±0	0.0 6	±0.0 02	ND
3	OLS W-3	2.18	±0.0 36	0.01	±0.0 01	0.06	±0.0 02	ND	0.08	±0.0 03	0.01	±0.0 01	0.01	±0.0 01	0.0 6	±0.0 05	ND
4	OLS W-4	3.09	±0.2 83	0.00	±0	0.07	±0.0 06	ND	0.05	±0.0 02	0.01	±0.0 01	0.01	±0.0 01	0.0 5	±0.0 02	ND
5	AGS W-MILE 2 MEA N	0.30	±0.0 06	ND	ND	0.03	±0.0 03	ND	0.05	±0.0 04	0.00	±0.0 01	0.00	±0	0.0 6	±0.0 03	ND
	AQ.P L (ppm)	1.63	±0.2 12	0.00 4	±0.0 00	0.05	±0.0 04	-	0.05	±0.0 03	0.01	±0.0 01	0.01	±0.0 01	0.0 6	±0.0 03	-
		253. 33		2.01		16.6 7		1.20	11.5 7		1.05		1.00		2.0 1		0.17
		155. 26		472. 94		341. 60		-	228. 66		159. 09		185. 19		36. 15		-
6	BCF CON TR- SW	0.36	±0.0 45	0.00	±0	0.01	±0.0 02	ND	0.05	±0.0 01	0.02	±0.0 03	0.01	±0.0 01	0.0 5	±0.0 03	ND

ND = Not Detectable

Table 3: Heavy metal analysis of surface water and aquatic plant (Dry season, 2009)

S/N	SAMLE ID	Fe (ppm)	Cu (ppm)	Mn (ppm)	Cr (ppm)	Zn (ppm)	Pb (ppm)	Cd (ppm)	Ni (ppm)	V (ppm)
1	OLSW-1	ND	ND	ND	ND	0.012 ±0.01	ND	ND	0.082 ±0.01	ND
2	OLSW-2	ND	ND	ND	ND	ND ND	ND	ND	0.084 ±0.03	ND
3	OLSW-3	ND	ND	ND	ND	0.008 ±0.001	ND	ND	0.052 ±0.02	ND
4	OLSW-4	ND	ND	ND	ND	0.023 ±0.01	ND	ND	0.08 ±0.02	ND
5	AGSW-MILE2	ND	ND	ND	ND	0.021 ±0.01	ND	ND	0.111 ±0.05	0.054 ±0.02
	MEAN	-	-	-	-	0.01 ±0.007	-	-	0.08 ±0.26	0.01 ±0.004
	AQ.PL.(ppm)	43.11	5.60	30.80	9.30	36.20	0.24	4.48	0.36	0.29
	BCF	-	-	-	-	2828.13	-	-	4.40	-
6	CONTR-SW	ND	ND	ND	ND	0.112 0.06	0.02	0.00	ND	ND

ND = Not Detectable

Table 4: Heavy metal analysis of surface water and aquatic plant (Rainy season, 2009)

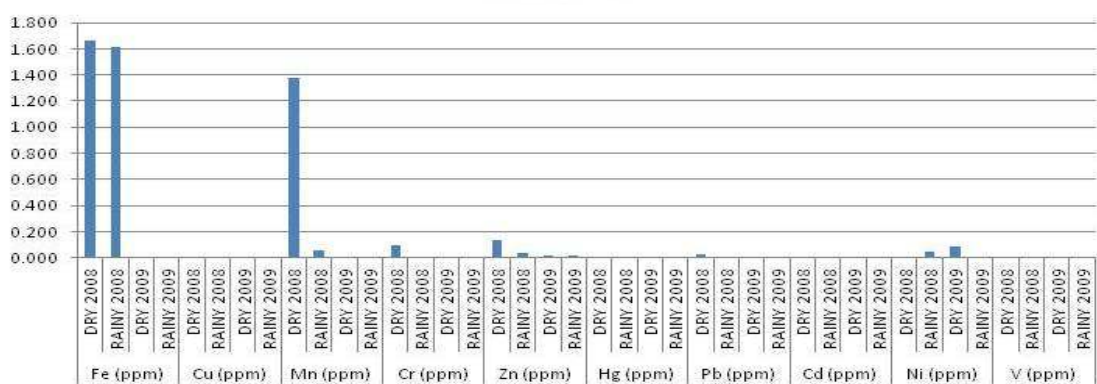
S/ N	SAMLE ID	Fe (ppm)	Cu (ppm)	Mn (ppm)	Cr (ppm)	Zn (ppm)	Pb (ppm)	Cd (ppm)	Ni (ppm)	V (ppm)
1	OLSW-1	ND	ND	ND	ND	0.014 ±0.01	ND	ND	0.007 ±0.02	ND
2	OLSW-2	ND	0.004 ±0.001	ND	ND	0.008 ±0.001	ND	ND	ND	ND
3	OLSW-3	ND	0.007 ±0.002	ND	ND	0.002 ±0.001	ND	ND	ND	ND

4	OLSW – 4	ND	0.01 1	±0.0 1	ND	ND	ND	ND	ND	ND	0.0 08	±0.0 02	ND					
5	AGSW – MILE2	ND	0.00 5	±0.0 01	ND	ND	0.00 1	±0.0 01	ND	ND	0.0 16	±0.0 05	ND					
	MEAN	-	0.05	±0.0 03	-	-	0.00 5	±0.0 03	-	-	0.0 06	±0.0 02	-					
	AQ.PL.(ppm)	24. 84	±4. 49	1.64	±0.6 3	4.8 9	±2. 75	0.5 5	±0. 04	8.41	±3.0 2	2.7 6	±0. 56	1.5 5	±0. 04	0.1 8	±0.0 09	ND
	BCF	-	303. 70	-	-	-	1682 .00	-	-	-	-	-	-	-	-	-	-	-
	CONTR -SW	ND	0.00 5	ND	ND	ND	ND	ND	ND	ND	0.0 04	ND	ND					

ND = Not Detectable

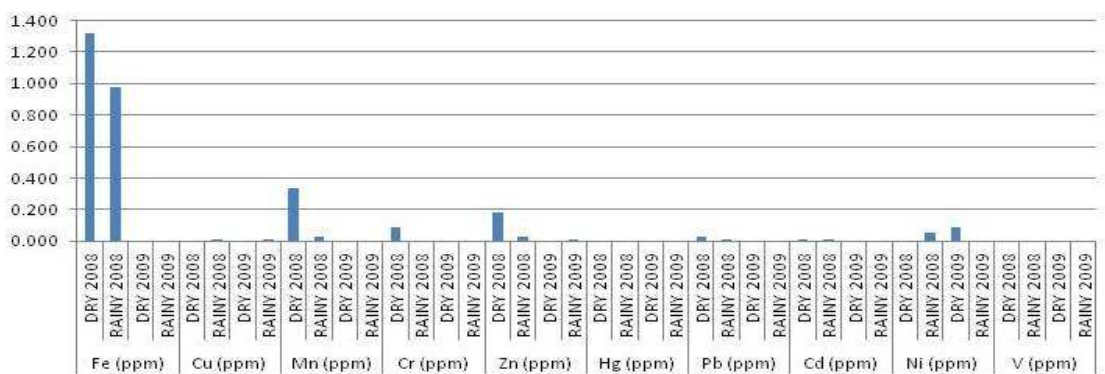
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OLSW – 1



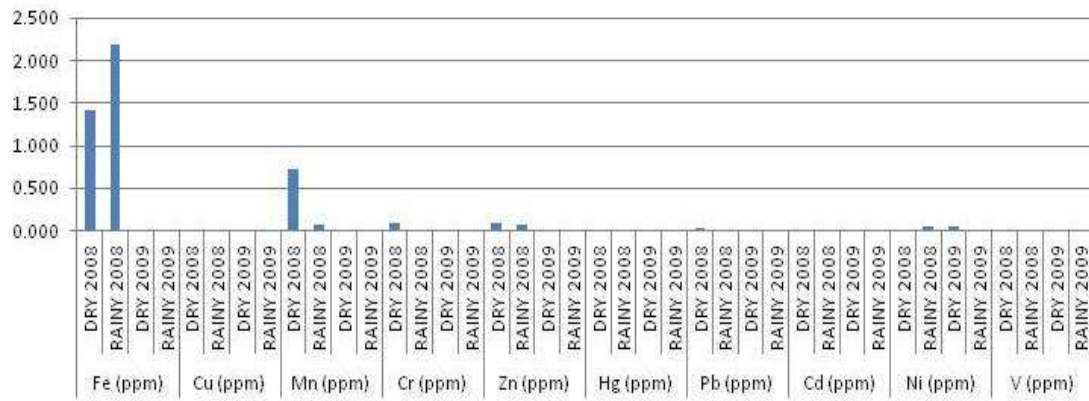
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OLSW – 2

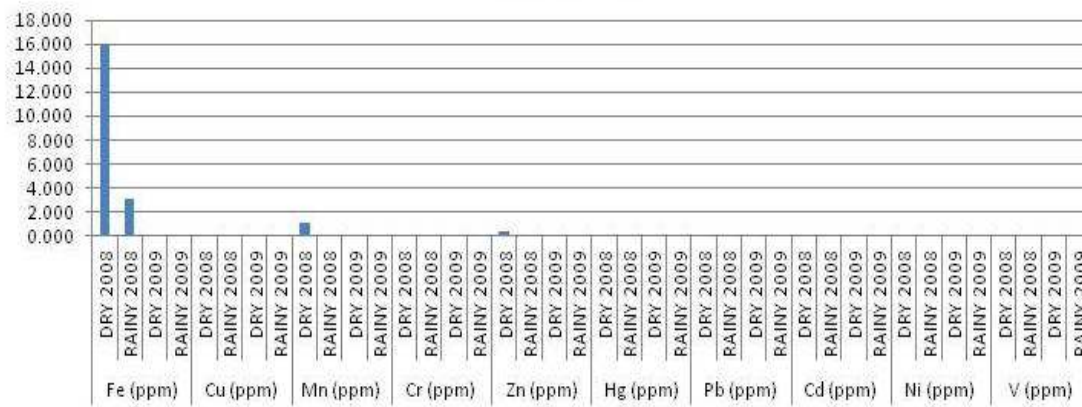


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OLSW – 3



OLSW – 4



AGSW – MILE2

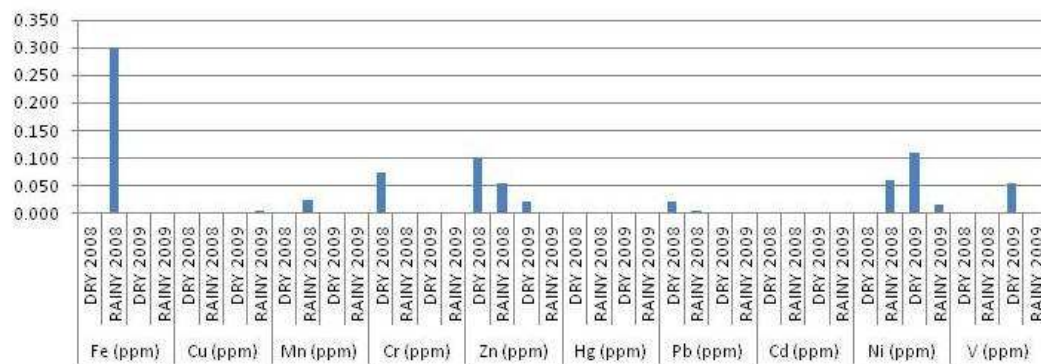


Fig. 2: Bar Charts of concentration of metals in surface water (Dry and Rainy Seasons 2008 and 2009)

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222 Mercury was not detected in the samples. The lowest mean concentration in the
223 dry season in surface water was 0.01 ± 0.007 ppm (Zn – dry season 2009) and the
224 highest mean concentration was 5.10 ± 0.274 ppm (Fe – dry season 2008). The
225 lowest mean concentration in the rainy season in surface water was
226 0.004 ± 0.001 ppm (Cu) and the highest mean concentration was 1.632 ± 0.212 ppm
227 (Fe). All the metals were below detectable level in at least one out of the four
228 seasons considered.

229 The most polluted surface water station with heavy metals in the four seasons was
230 OLSW4 probably due to its proximity to NBC-7 bitumen well. Compared with
231 the control station the concentrations of heavy metals in the surface water of
232 Agbabu settlement were higher. The concentrations Fe, Mn, Cr, Zn and Pb were
233 higher in surface water in the dry season than in the rainy season probably due to
234 dilution by rainwater which influences concentration and heavy metal dynamics.
235 This agreed with the report of Onwerenmadu et al. [22]. However, it has been
236 reported that mobility of heavy metals depends not only on the total concentration
237 but also on the metal properties and environmental factors. The concentrations of
238 Cu, Cd and Ni were higher in the rainy season than in the dry season probably due
239 to rainfall and run off. This agrees with the findings of Lokeshwary and
240 Chandrappa [23].

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3.2 Heavy Metal in Ground Water

Concentrations of heavy metals in ground water in dry and rainy seasons of year 2008 are shown in Tables 5 and 6 respectively. Concentrations of heavy metals in ground water in dry and rainy seasons of year 2009 are shown in Tables 7 and 8 respectively. Bar charts of the concentration of heavy metals in ground water in dry and rainy seasons of years 2008 and 2009 are shown in Fig. 3.

Table 5: Heavy metal analysis of ground water (Dry season, 2008)

S/N	SA MLE ID	Fe (ppm)		Cu (ppm)	Mn (ppm)		Cr (ppm)		Zn (ppm)		Pb (ppm)		Cd (ppm)		Ni (ppm)	V (ppm)
1	AG GW -1	3.8 10	±1.1	ND	0.9 97	±0.0 3	0.1 08	±0.0 6	0.1 11	±0.0 8	0.0 07	±0.0 01	0.0 07	±0.0 01	ND	ND
2	AG GW -2	0.7 20	±0.1 2	ND	1.2 22	±0.0 4	0.0 91	±0.0 2	0.1 79	±0.0 5	0.0 16	±0.0 02	0.0 03	±0.0 01	ND	ND
3	AG GW -3	0.6 40	±0.2	ND	1.2 80	±0.0 2	0.0 83	±0.0 3	0.1 81	±0.0 4	0.0 29	±0.0 1	0.0 13	±0.0 04	ND	ND
4	AG GW -4	0.5 00	±0.0 22	ND	0.4 16	±0.1	0.0 99	±0.0 4	0.1 64	±0.0 3	0.0 16	±0.0 1	0.0 14	±0.0 02	ND	ND
5	AG GW - MIL E2	1.2 20	±0.5	ND	0.8 98	±0.2	0.0 75	±0.0 3	0.1 70	±0.0 25	0.0 08	±0.0 01	0.0 21	±0.0 05	ND	ND
	ME AN	1.3 78	±0.3 0	-	0.9 63	±0.0 78	0.0 91	±0.0 36	0.1 61	±0.0 45	0.0 15	±0.0 05	0.0 12	±0.0 03	-	-
6	CON TR- GW	0.4 70	±0.1	ND	0.4 00	±0.1 2	0.0 61	±0.0 2	0.1 20	±0.0 5	0.0 10	±0.0 04	0.0 15	±0.0 03	ND	ND

ND = Not Detectable

Table 6: Heavy metal analysis of ground water (Rainy season, 2008)

S / N	SA ML E ID	Fe (ppm)		Cu (ppm)		Mn (ppm)		Cr (ppm)	Zn (ppm)		Pb (ppm)		Cd (ppm)		Ni (ppm)		V (ppm)
1	AG GW -1	0.50 8	±0.0 35	ND		0.02 8	±0.0 03	ND	0.05 1	±0.0 03	0.01 9	±0.0 01	0.00 9	±0.0 01	0.05 7	±0.0 02	ND
2	AG GW -2	0.34 0	±0.0 24	ND		0.02 9	±0.0 03	ND	0.07 6	±0.0 02	0.01 2	±0.0 02	0.02 0	±0.0 02	0.06 5	±0.0 03	ND
3	AG GW -3	0.39 4	±0.0 28	0.00 4	±0.0 01	0.02 3	±0.0 03	ND	0.09 2	±0.0 02	0.01 0	±0.0 03	0.00 9	±0.0 01	0.06 7	±0.0 03	ND
4	AG GW -4	NA		NA		NA		NA	NA		NA		NA		NA		NA

AG GW -																	
5	MIL	1.43	±0.0			0.02	±0.0		0.00	±0.0	0.00	±0.0	0.00		0.07	±0.0	N
	E2	3	82	ND		1	02	ND	5	01	8	01	3	±0	2	02	D
	ME	0.66	±0.0	0.00	±0.0	0.02	±0.0		0.05	±0.0	0.01	±0.0	0.01	±0.0	0.06	±0.0	
	AN	9	42	1	01	5	03	-	6	02	2	02	0	01	5	03	-
CO																	
6	NTR	0.17	±0.0	0.00	±0.0	0.01	±0.0		0.07	±0.0	0.01	±0.0	0.01	±0.0	0.08	±0.0	N
	-GW	8	06	4	01	6	02	ND	4	02	1	01	4	02	2	04	D

ND = Not Detectable NA = Not Applicable

Table 7: Heavy metal analysis of ground water (Dry season, 2009)

S/N	SAMLE ID	Fe (ppm)	Cu (ppm)	Mn (ppm)	Cr (ppm)	Zn (ppm)		Pb (ppm)		Cd (ppm)		Ni (ppm)	V (ppm)	
1	AGGW – 1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.048	±0.01	ND
2	AGGW – 2	ND	ND	ND	ND	0.032	±0.01	ND	ND	ND	ND	0.072	±0.02	ND
3	AGGW – 3	ND	ND	ND	ND	0.012	±0.01	0.059	±0.02	ND	ND	0.059	±0.02	ND
4	AGGW – 4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.035	±0.01	ND
5	AGGW – MILE2	ND	ND	ND	ND	0.046	±0.02	ND	ND	ND	ND	0.107	±0.04	ND
6	AGBH	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.047	±0.01	ND
	MEAN	-	-	-	-	0.02	±0.007	0.01	±0.003	-	-	0.061	±0.02	-

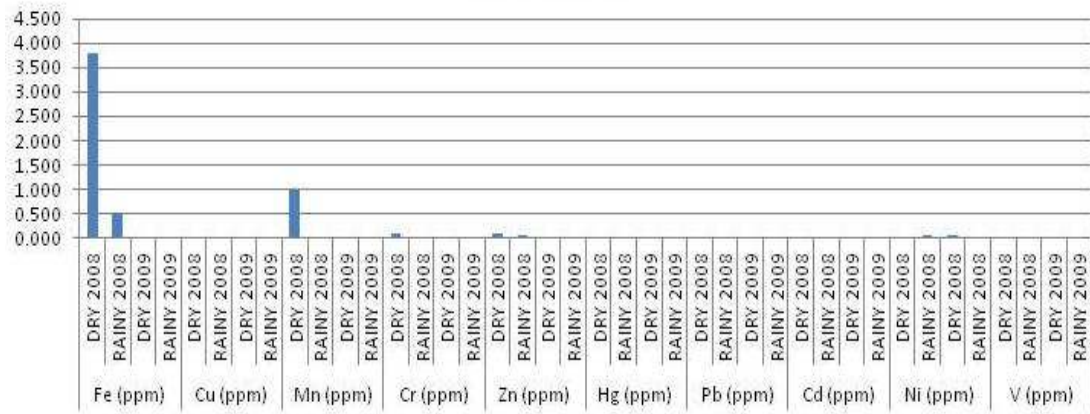
ND = Not Detectable

Table 8: Heavy metal analysis of ground water (Rainy season, 2009)

S/N	SAMLE ID	Fe (ppm)	Cu (ppm)	Mn (ppm)	Cr (ppm)	Zn (ppm)	Pb (ppm)	Cd (ppm)	Ni (ppm)	V (ppm)
1	AGGW - 1	ND	ND	0.021	±0.01	ND	0.014	±0.01	ND	ND
2	AGGW - 2	ND	ND	0.027	±0.01	ND	0.008	±0.002	ND	ND
3	AGGW - 3	ND	ND	0.024	±0.01	ND	0.002	±0.001	ND	ND
4	AGGW - 4	ND	ND	ND	ND	ND	ND	ND	ND	ND
5	AGGW - MILE2	ND	ND	ND	ND	0.001	±0.001	ND	ND	ND
MEAN		-	-	0.014	±0.06	-	0.005	±0.003	-	-
OWGW-CNTR		ND	ND	ND	ND	ND	ND	0.005	±0.002	ND

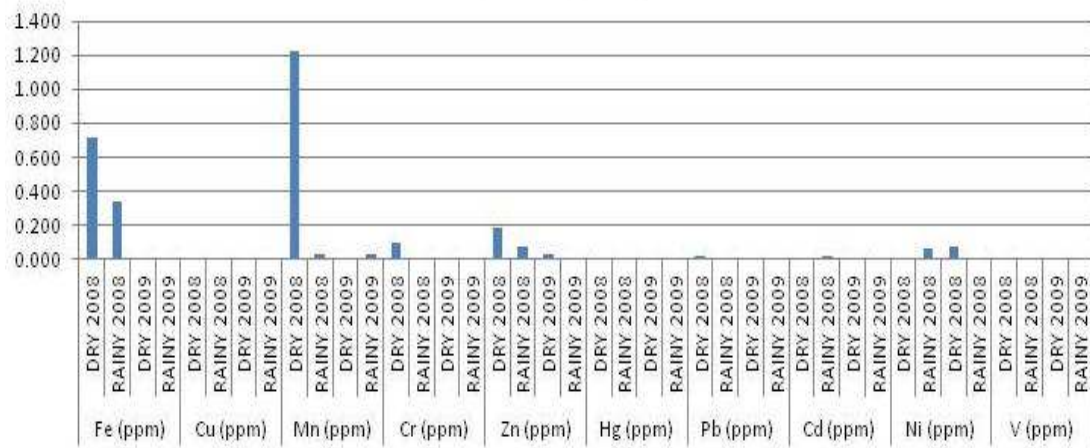
ND = Not Detectable

AGGW – 1



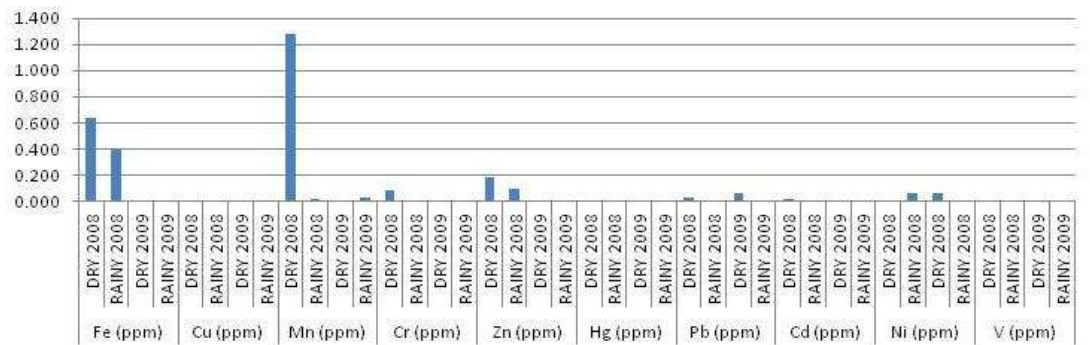
259
260

AGGW – 2



261
262

AGGW – 3



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264

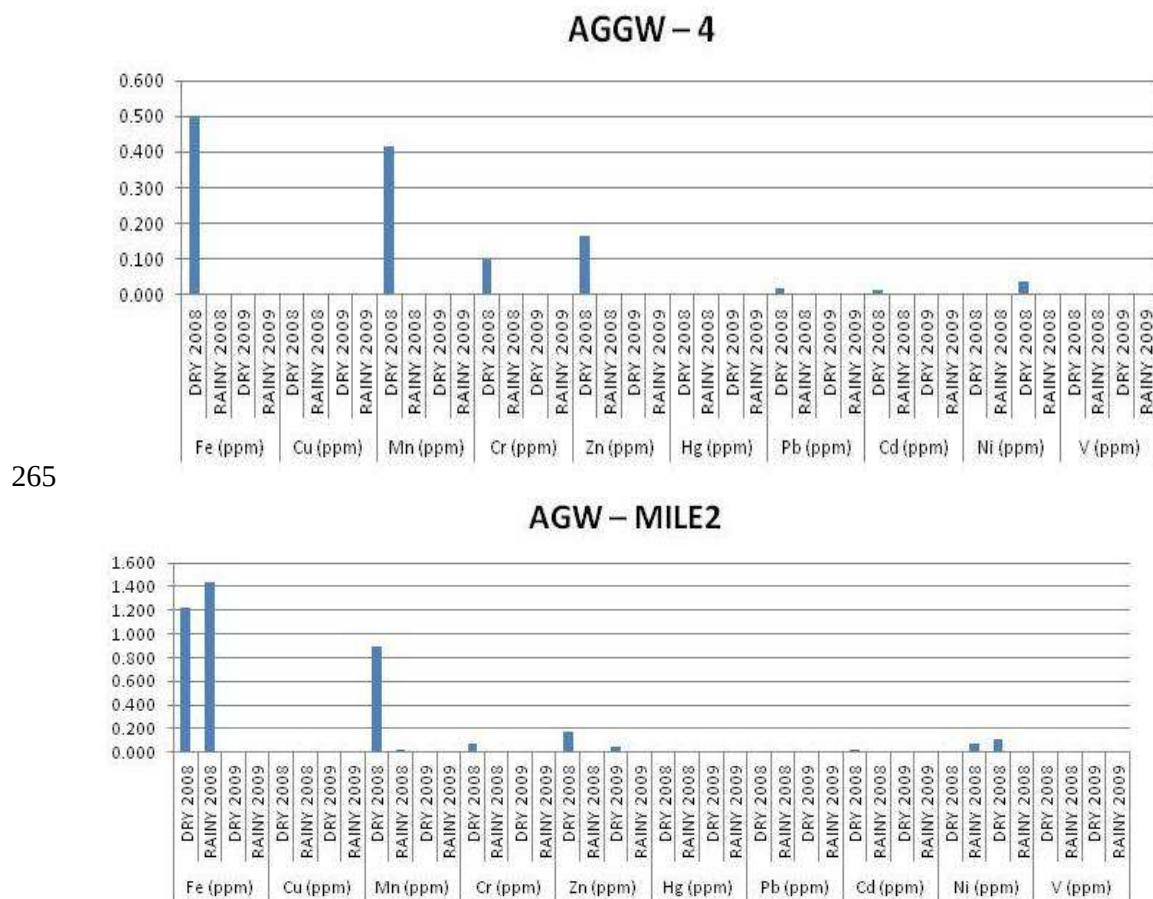


Fig. 3: Bar Charts of concentration of metals in ground water (Dry and Rainy Seasons 2008 and 2009)

At Agbabu bitumen deposit area, hand dug wells and bore hole were considered as ground water for the analysis of heavy metals. The hand dug wells and bore hole serve as the major source of potable water for the rural dwellers. Mercury was not detected in the samples. The lowest mean concentration in the dry season in ground water was 0.01 ± 0.003 ppm (Pb – dry season 2009) and the highest mean concentration was 1.378 ± 0.300 ppm (Fe – dry season 2008). The lowest mean

276 concentration in the rainy season in ground water was 0.001 ± 0.001 ppm (Cu –
277 rainy 2008) and the highest mean concentration was 0.669 ± 0.042 ppm (Fe – rainy
278 2008). All the metals were below detectable level in a least one out of the four
279 seasons considered. Sampling stations AGGW1 and AGGW-Mile2 had the
280 highest concentrations of heavy metals in the four seasons. The concentrations of
281 Fe, Mn, Cr, Zn and Cd were higher in ground water in the dry season than in the
282 rainy season while the concentrations of Cu, Pb and Ni were higher in the rainy
283 season. The mean concentrations of Cr of 0.085 ± 0.020 ppm in surface water in dry
284 season, 2008 and 0.091 ± 0.036 ppm in ground water in the dry season in dry
285 season, 2008 were higher than 0.05 ppm recommended by WHO [26]. However,
286 the concentrations of Cr in the rainy season were less than 0.003 ppm probably due
287 to dilution effects. Ground water sampling points considered in form of hand dug
288 wells were the major source of potable water for the rural dwellers at Agbabu and
289 Temidire communities. High concentration of Cr in the ground water is dangerous
290 for these rural dwellers because Cr and its compounds are known to cause cancers
291 of lungs, nasal cavity and para nasal sinus and suspected cause cancer of the
292 stomach and larynx [25]. In year 2008, apart from AGSW5-Mile2 in the rainy
293 season, all surface water sampling points had Mn concentrations between
294 0.024 ppm and 1.373 ppm in both dry and rainy seasons. Also, the ground water
295 sampling points in both dry and rainy seasons had Mn concentration values
296 between 0.21 ppm and 1.28 ppm. These values were all higher than 0.010 ppm
297 recommended by WHO [24], for drinkable water. In year 2009, Mn was not
298 detected in surface water in year 2009, probably due to dilution effects. Most of

299 the ground water sampling points also had values that were higher than WHO's
300 recommendation of a maximum of 0.01ppm in the rainy season of 2009. Mn
301 effects occur mainly in the respiratory tract and in the brains. Symptoms of Mn
302 poisoning are hallucinations, forgetfulness and nerve damage. Mn can also cause
303 Parkinson, lung embolism and bronchitis. Considering the concentrations of Cr
304 and Mn in the surface water and hand dug wells at Agbabu bitumen deposit area,
305 these sources of water are not fit for human consumption based on WHO's
306 recommendations. The concentrations of Fe, Cr and Mn were very high at Agbabu
307 bitumen deposit area compared with the values obtained in control sampling
308 points. High concentrations of Fe, Cr and Mn in most of the surface water and
309 ground water samples considered in this study may likely be due to the deposit of
310 bitumen in the environment. Adebisi F.M. *et al.* [26] in an elemental
311 characterization of the Nigerian bitumen by total reflection x-ray fluorescence
312 showed Fe, Cr and Mn to be part of its components. Trace elements such as
313 transition metals get into bitumen in form of porphyrin complexes at its early
314 stages of formation. The Nigerian bitumen components (asphaltene, oil and resins)
315 were subjected to trace metal analysis and were found to contain high
316 concentrations of Zn, Ni, V and Fe [15].

317

318 **3.3 Heavy Metal in Aquatic Plant**

319 Concentrations of heavy metals in aquatic plants in dry and rainy seasons of year
320 2008 are shown in Tables 9 and 10 respectively. Concentrations of heavy metals

in aquatic plants in dry and rainy seasons of year 2009 are shown in Tables 11 and 12 respectively.

323

324 Table 9: Heavy metal analysis of aquatic plant- *Ceratophyllum demersum* (Dry
325 season 2008)

S/ N	SA ML E ID	Fe (ppm)		Cu (ppm)		Mn (ppm)		Cr (ppm)		Zn (ppm)		Pb (ppm)		Cd (ppm)		Ni (ppm)		V (ppm)	
1	PL. OLS W1	712 .10	±12 2	2. 70	±0. 56	29. 35	±5. 97	1. 55	±0. 58	19. 03	±4. 77	1. 46	±0. 36	1. 50	±0. 54	2. 93	±0. 86	0. 21	±0. 06
2	PL. OLS W4	370 .84	±87 23	4. 23	±1. 23	16. 70	±5. 38	1. 44	±0. 46	6.3 1	±2. 37	1. 59	±0. 48	1. 46	±0. 44	3. 17	±1. 10	0. 37	±0. 08
	ME AN	541 .47	±10 4.5	3. 47	±0. 90	23. 03	±5. 68	1. 50	±0. 52	12. 67	±3. 57	1. 53	±0. 42	1. 48	±0. 49	3. 05	±0. 98	0. 29	±0. 07

326

327 Table 10: Heavy metal analysis of aquatic plant- *Ceratophyllum demersum* (Rainy
328 season 2008)

S/ N	SA ML E ID	Fe (ppm)		Cu (ppm)		Mn (ppm)		Cr (ppm)		Zn (ppm)		Pb (ppm)		Cd (ppm)		Ni (ppm)		V (ppm)	
1	PL. OLS W1	296 .40	±80 .50	1. 65	±0. 58	21. 38	±8. 00	1. 10	±0. 04	14. 86	±3. 68	0. 88	±0. 35	1. 01	±0. 05	1. 96	±0. 65	0. 14	±0. 05
2	PL. OLS W4	210 .70	±68 .48	2. 37	±0. 68	11. 96	±3. 5	1. 29	±0. 05	8.2 7	±2. 35	1. 22	±0. 76	0. 99	±0. 03	2. 06	±0. 88	0. 19	±0. 08
	ME AN	253 .55	±74 .49	2. 01	±0. 63	16. 67	±5. 75	1. 20	±0. 04	11. 57	±3. 02	1. 05	±0. 56	1. 00	±0. 04	2. 01	±0. 77	0. 17	±0. 07

329

330 Table 11: Heavy metal analysis of aquatic plant- *Ceratophyllum demersum* (Dry
331 season, 2009)

S/ N	SA ML E ID	Fe (ppm)		Cu (ppm)		Mn (ppm)		Cr (ppm)		Zn (ppm)		Pb (ppm)		Cd (ppm)		Ni (ppm)		V (ppm)	
1	PL. OLS W1	431 1.00	±60 .25	5. 60	±1. 36	30. 80	±5. 38	9. 30	±1. 20	36. 20	±5. 00	0. 77	±0. 18	0. 24	±0. 10	4. 48	±1. 22	0. 36	±0. 12
2	PL. OLS W4	NA		N A		N A		N A		N A		N A		N A		N A		N A	

332

Table 12: Heavy metal analysis of aquatic plant- *Ceratophyllum demersum* (Rainy season, 2009)

S/ N	SA ML E ID	Fe (ppm)		Cu (ppm)		Mn (ppm)		Cr (ppm)		Zn (ppm)		Pb (ppm)		Cd (ppm)		Ni (ppm)		V (ppm)	
1	PL. OLS W1	22.10	±3.02	1.94	±0.20	5.98	±1.42	0.43	±0.01	8.39	±2.00	2.78	±0.23	1.87	±0.01	6.36	±0.42	0.61	±0.05
2	PL. OLS W4	27.57	±2.10	1.34	±0.31	3.79	±1.33	0.67	±0.3	8.43	±1.02	2.73	±0.22	1.22	±0.3	3.54	±0.35	0.34	±0.02
	ME AN	24.84	±5.12	1.64	±0.51	4.89	±2.75	0.55	±0.04	8.41	±3.02	2.76	±0.56	1.55	±0.04	4.95	±0.77	0.48	±0.07

The lowest mean concentration of heavy metals in aquatic plant (*Ceratophyllum demersum*) in the dry season of years 2008 and 2009 was 0.29 ± 0.07 ppm (Vanadium) while the highest was 541 ± 104.50 ppm (Fe). In the rainy season of years 2008 and 2009, the lowest concentration is 0.17 ± 0.007 ppm (Vanadium) and the highest was 253.55 ± 74.49 ppm (Fe). The concentrations of heavy metals in the aquatic plant were low when compared with the acceptable normal and critical ranges in plants [9], as shown in Table 13.

Table 13: 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 ($\mu\text{g/g}$)	Critical Range ($\mu\text{g/g}$)	<i>Ceratophyllum demersum</i> 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

344

345 **3.4 Bioconcentration Factor**

346 Bioconcentration Factor (BCF) was calculated as the ratio of the heavy metal
347 concentration in the plant to the concentration of the same heavy metal in the
348 external environment [13]. BCF's calculated for metals in aquatic plants
349 (*Ceratophyllum demersum*) are shown in Tables 1 to 4. The minimum BCF of the
350 metals in aquatic plant (*Ceratophyllum demersum*) calculated in the dry season
351 was 4.40 (Ni – Dry season, 2009) and the maximum was 2828.13 (Zn – Dry
352 season, 2009). In the rainy season, the minimum BCF calculated was 36.15 (Ni –
353 Rainy season, 2008) and the maximum was 1682 (Zn – Rainy season, 2009). High
354 values of BCF show that aquatic plant (*Ceratophyllum demersum*) can be used for
355 phytoremediation of surface water polluted with Fe, Cu, Mn, Cr, Zn, Pb, Cd, Ni
356 and V.

357 **3.5 Data Analysis**

358 Analysis of variance (ANOVA) of concentration of metals in surface and ground
359 water was carried out with SPSS 17 at $\alpha = .05$ to determine significant statistical
360 differences between the concentration of metals, sampling stations and seasons.
361 Analysis of variance and multiple comparisons of concentrations of Cr and Mn in
362 surface water in the sampling points showed no statistically significant
363 differences. This shows that Cr and Mn in the study area must have originated
364 from similar sources in a particular season. Analysis of variance of concentration
365 of Cr and Mn in surface water in the four seasons showed statistically significant
366 differences indicating that sources of Cr and Mn varied from one season to
367 another. Analysis of variance of Cr and Mn in ground water in the sampling
368 points also showed no statistically significant differences. Anova of Cr and Mn in
369 the seasons also showed statistically significant difference but multiple
370 comparisons of concentrations of Cr and Mn between the seasons showed no
371 statistically significant differences between rainy season in 2008 and dry season in
372 2009, and rainy season in 2008 and rainy season in 2009. This shows that Cr and
373 Mn in the study must have originated from the similar sources. Apart from the
374 deposit of bitumen in this environment, which may be a natural source of heavy
375 metals in the environment, other sources of heavy metals in the environment are
376 anthropogenic sources such as faming, fishing and domestic activities.

377 **4. CONCLUSION**

378 Data available in this study can be used as base line data at Agbabu bitumen
379 deposit area. The environment presently has been impacted by the presence of
380 bitumen. The mean concentrations Cr and Mn were found to be higher than the

381 WHO recommendations in most of the water samples examined. The
382 concentrations of Cr and Mn in ground water samples examined rendered the
383 hand dug wells considered as ground water unfit for human consumption. The
384 high values of BCF show that this aquatic plant (*Ceratophyllum demersum*) can
385 be used for phytoremediation of surface water polluted with Fe, Cu, Mn, Cr, Zn,
386 Pb, Cd, Ni and V. Analysis of variance and multiple comparisons of concentration
387 of Cr and Mn in surface water and ground water considering the sampling points
388 and seasons showed that they must have originated from the similar sources.
389 Further research can be carried out to determine the concentration of heavy metals
390 in various parts of the aquatic plants in the environment. It is also recommended
391 that further research should be carried out on the speciation of the heavy metals to
392 determine the forms in which they occur.

393

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