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2 **A study of heavy metals pollution in the coastal marine**
3 **sediment of Ondo State, Nigeria**

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11 This work was carried out in collaboration between all authors. All authors
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20 **Abstract**
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: The present study was carried out to assess the pollution status of heavy metals (As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn) in the marine sediment in Ondo coastal area. A total of 36 sediment samples were collected from the three locations (Awoye, Abereke and Ayetoro) once in a month in 2015 covering both dry and wet season. The sediment samples were subjected to digestion and Atomic Absorption Spectrophotometer (AAS) was used to measure the concentrations of As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn. The measured concentrations data were used for evaluating the contamination level and accumulation status of heavy metals in sediment by employing several pollution indices: contamination factor (CF), degree of contamination (C_{deg}), pollution load index (PLI), enrichment factor (EF) and index of geoaccumulation (I_{geo}). The results showed that Fe had the highest average concentration values of 248.00 ± 20.00 and 324.33 ± 5.80 mg/kg at Awoye sampling site for wet and dry season, respectively while the highest mean concentration of Mn were 271.77 ± 9.50 and 295 ± 10.06 mg/kg at Abereke and Ayetoro, respectively. The contamination factor (CF) values for As, Cd and Mn were $1 < CF < 3$, indicating a moderate contamination. The results of C_{deg} were ranged from 8.6 to 12.5 for both dry and wet season except in Ayetoro site that had 7.8 in the wet season. The PLI values were 0.47, 0.50 and 0.54 (< 1) for Abereke, Awoye and Ayetoro sites, respectively, denoting unpolluted conditions. The EF values for Pb and Ni obtained from all the sites ranged from 20.8 to 38.9, showing their significantly enriched in sediment. The I_{geo} values of As, Cr, Fe, V, Zn and Cu were less than one ($I_{geo} < 1$) for the three sampling locations in both seasons, implying that the sediments in the study area are practically uncontaminated by these metals. Pb had the I_{geo} values of 2.80 and 2.85 during dry and wet season at Awoye sampling site while Ni had 2.57 at Abereke only in the dry season. The heavy metals in sediment might be derived from the upstream rivers from the top soil, mechanically weathered rock materials and anthropogenic activities.

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Keywords: Sediment, Heavy metals, Pollution, Indices.

24 1 INTRODUCTION

25 Sediment is a mixture of weathered materials and mineral species from the
26 parent rocks. It contains organic debris that are transported by detrital process
27 from the upstream and deposited at the river bed [1]. Sediment, because of
28 their variable physical and chemical properties acts as repository for heavy
29 metals in the aquatic environment [2]. Naturally, sediment pollution due to
30 heavy metals are caused by geologic weathering of the bedrock and direct
31 atmospheric deposition. The interactions between water and crustal materials
32 with which water is in contact is a major process by which heavy metals
33 content in the sediment can be increased [3]. The anthropogenic activities
34 such as sea transportation, energy generation and utilisation, dredging, fishing,
35 oil exploration, farming, infrastructural development and mining are crucial for
36 several socio-economic reasons [4], however, they are probable sources of

37 sediment pollution when their wastes are discharged into the river body by
38 urban surface water runoff [5]. The increased concentration and accumulation
39 of heavy metals alter sediment quality as well as the food stuff available for the
40 aquatic organism, leading to loss of aquatic biodiversity [6].

41 In recent years, heavy metals pollution of the aquatic environment has become
42 a worldwide problem due to their persistence in nature and their capacity to
43 accumulate in living organism [7]. Ahmadipour et al. [8] reported that heavy
44 metals have negative health implications due to their toxicity potential and
45 tendency to accumulate in environmental media such as water, soil, sediment
46 and other biological media. Several heavy metals persist in the sediment
47 with varied concentrations most especially in fine grain [9]. The increased
48 concentration of the heavy metals in the sediment has adverse health implication
49 due to possibility of entering the food chain through aquatic organism uptake
50 and direct consumption of aquatic organism by man [10]. Polluted sediment
51 can act as a metal pool, thereby release metals to the overlying water column
52 via natural or anthropogenic processes, causing potential adverse health effects
53 to the ecosystem and degrade the sediment quality [11]. Heavy metals are not
54 destructible and non-biodegradable, thus they may exist in an environmental
55 medium for a long period of time [12]. Moreover, heavy metals in the sediment
56 can undergo sorption and complexation, ion exchange, dissolution and precipitation
57 reactions which influence their behaviour and bioavailability during transportation
58 [13].

59 The capacity of the sediment to accumulate heavy metals make them relevant
60 indicators for monitoring purposes as well as the evaluation of their pollution
61 levels and patterns of the aquatic system [14]. Based on these, several studies
62 had been conducted on degradation of sediment quality due heavy metals
63 using several pollution indices [15, 16, 17, 18] while few studies were based
64 on heavy metals speciation and potential bioavailability in the sediment. In
65 the study area, quite a few studies had been undertaken on the distribution of
66 heavy metals in the sediment [19]. In this study, the sediment samples and
67 the concentrations of heavy metals were determined using Atomic Absorption
68 Spectrophotometer (AAS) technique. This was with a view to assessing the
69 pollution status due to heavy metals in the sediment. The main objective of this
70 work was to assess the level of heavy heavy metal pollution in the sediment
71 samples by employing the combination of pollution indices: contamination
72 factor (CF), degree of contamination (D_{deg}), pollution load index (PLI), index
73 of geo-accumulation (I_{geo}) and enrichment factor (EF) analysis.

74 2 MATERIALS AND METHODS

75 2.1 Description of the study area

76 Ondo State coast is strategically located along the gulf of guinea as the Transgressive
77 Mud Beach (TMB) lying in the east of the West African lagoon system and on
78 the west of the Benin Flank of the Niger Delta Basin. Most of the creeks and
79 rivers (Omila and Edo)in the inland area are drained into the Atlantic ocean
80 through Awoye and Abereke estuaries. Also, the sandy beach materials of
81 the Nigeria coastal plain are replaced by mud and lacustrine deposits in Ondo
82 state coast. Another unique features of this coast are overlying mud of about
83 60 m and massive incursion of the sea into the inland swamps. It is one of
84 the longest coastlines in Nigeria (more than 10 % of the country coastline)
85 which favour fishing activities in the riverine areas. The major anthropogenic
86 activities around the study area are transportation services, seismic investigations,
87 crude oil exploration, commercial and agricultural activities. The study area
88 lies within the tropical rain forest zone and bounded by the latitude 5.56 -
89 6.30°N and longitude 4.40 - 5.43 °E with 21.38 m above the sea level. The
90 study area is characterized with two distinct seasons namely: dry and wet
91 season. The dry season spans through the month of November to March
92 while wet season occurs between April to October with the annual rainfall of
93 about 3000 mm [20].

94 2.2 Sample collection and preparation

95 Sediment samples were collected at approximately 2.0 nautical mile from the
96 Ondo state coastline at 10 m depth using a VanVeen grab sampler. A representative
97 samples were taken with plastic spatula from the middle of the grab bulk
98 sediment. Samples were collected once in a month from January to December,
99 2015. Three sampling locations were chosen based on their proximity to
100 various anthropogenic activities such as oil exploration, ship breaking yard,
101 market activities and fishing and the areas of incursion of the estuaries into the
102 Atlantic ocean. Figure 1 shows the map of the Ondo section of the southwest
103 coast of Nigeria with the study locations (Abereke, Ayetoro and Awoye) and
104 other settlements along the coast. After sampling, each sample was transported
105 to the laboratory and air dried at room temperature for two weeks, then grounded
106 in a pre-washed agate mortar and pestle. In order to remove coarse debris,
107 the samples were screened through a 160 μm stainless steel sieve. The
108 samples of the fine-grained sediment were retained for chemical analysis. All
109 the sampling materials were washed with water and clean with acetone after

110 each sampling to avoid possible contamination.

111 2.3 Elemental analysis

112 The samples were subjected to wet digestion in Foss Tecator digestion vessel.
113 One (1) gram of sediment sample was added in a 15 mL mixture of nitric
114 (HNO_3) and perchloric acid (HClO_4) in ratio 1:3. The whole content was placed
115 on a heating electric plate at about 334 - 350⁰C for 2 hours. The mixed solution
116 was boiled until the evaporation of the acid solution and a clear solution was
117 obtained. Upon cooling, the solution was filtered to a 100 mL volumetric flask
118 and then diluted to 50 mL with distilled de-ionized water and kept in the sample
119 bottle at 4⁰C before analysis. The concentrations of As, Cd, Cr, Cu, Fe, Mn, Ni,
120 Pb, V and Zn were determined using Atomic Absorption Spectrophotometer
121 (Buck Scientific VGP 210 Model) at the Central Science Laboratory (CSL),
122 Obafemi Awolowo University, Ile-Ife, Nigeria. All reagent were of analytical
123 grade. The operating conditions consisting of maximum wavelength λ_{max} ,
124 energy, current and slit width of the ASS instrumental analytical set up are
125 presented in table 1. The detection limits of As, Cd, Cr, Cu, Fe, Mn, Ni, Pb
126 and Ni were 0.05,0.001, 0.005, 0.001, 0.005, 0.001, 0.003, 0.003 and 0.002
127 mg/kg, respectively. The heavy metal concentrations data were subjected to
128 descriptive statistic using the statistical package for social science software
129 (SPSS 16.0).

130 2.3.1 Contamination factor and Degree of contamination (C_{deg})

The contamination factor (CF) is a single pollution index which indicates the contamination level of a particular toxic substance or elements in a given environmental medium [21]. In this study, the sediment contamination due to As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn were assessed using the contamination factor (CF). The CF of i^{th} heavy metal was calculated as:

$$C_f^i = C_s^i / C_m^i \quad (2.1)$$

131 where C_s^i is the mean concentration of the element i^{th} . C_m^i is the background
132 concentration which is the maximum level of that metal in a given, beyond
133 which the medium is said to be contaminated [22]. In this study, Taylor and
134 McLennan [23] continental crustal average data was used as the background
135 concentration. The CF is classified into four main groups: $CF < 1$ means low
136 contamination; $1 \leq CF < 3$ means moderate contamination; $3 \leq CF \leq 6$ implies
137 considerate contamination and $CF > 6$ indicates very high contamination [10].
138 The degree of contamination (C_{deg}) is an indicator that shows the extent to

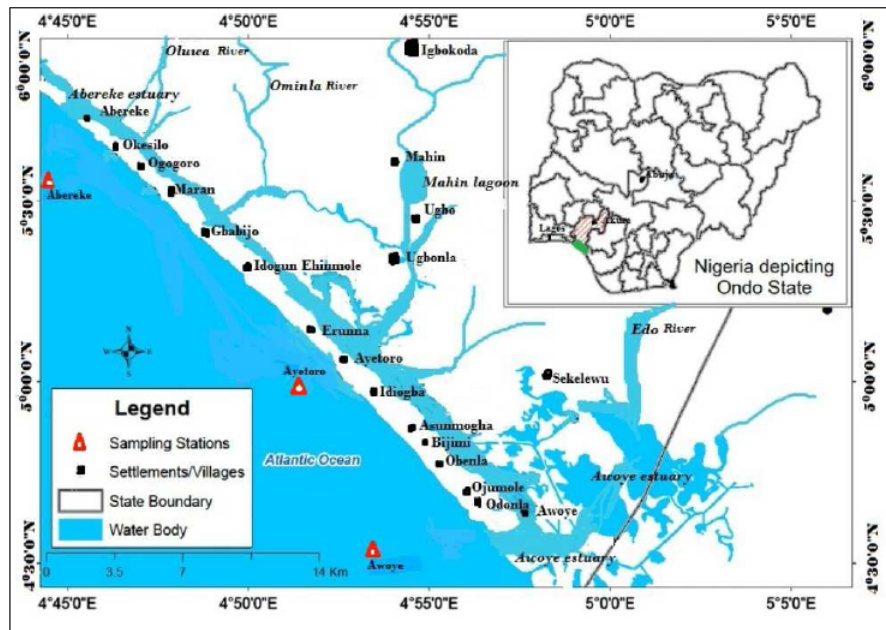


Figure 1: Map of the study area showing the sampling sites

139 which the environmental media is polluted. The C_{deg} is estimated as the sum
 140 of the contamination factors ($C_{deg} = CF_1 + CF_2 + CF_3 + \dots CF_n$) of all the
 141 heavy metals in the sediment for a site. Four major category of the degree of
 142 contamination have been identified: < 8, 8-16, 16-32 and > 32 indicate low,
 143 moderate, considerable and very high degree of contamination, respectively
 [22].

Table 1: The operating conditions of the AAS instrumental set up

Elements	λ_{max}	Current	Energy	Slit width
As	193.00	10	75	0.7
Cd	228.80	4	69	2.7/0.80
Cr	357.87	25	97	2.7/0.80
Cu	324.75	15	80	2.7/0.80
Fe	248.33	30	66	1.8/1.35
Mn	279.48	20	62	1.8/1.35
Ni	232.00	25	67	1.8/1.35
Pb	283.31	10	75	2.7/1.05

144

145 2.3.2 Pollution load index

The pollution load index (PLI), as proposed by Tomlinson et al. [24], is a simple mathematical model use to determine the pollution status of a particular site taking into consideration the metal concentrations of that site as a single value. In this study, the PLI was evaluated as:

$$PLI = \sqrt[n]{(CF_1 * CF_2 * CF_3 * \dots CF_n)} \quad (2.2)$$

146 CF is the contamination factor of each of the heavy metals obtained from
 147 equation 1 while n is the number of heavy metals under consideration. The
 148 PLI values could be < 0, > 0 and 1 implying unpolluted condition, progressive
 149 degradation in the sediment quality and the occurrence of baseline pollution
 150 level, respectively [24].

151 2.3.3 Enrichment factor (EF) analysis

The Enrichment Factor (EF) is used to evaluate the magnitude of the elements in air, water, soil and sediment samples. It provides information on the relative abundance of species in a given medium to the background values. It is also employed to assess the degree of pollution and to differentiate the elements of anthropogenic and natural sources [25]. Its approach is based on the

standardization of the measured element against a reference element. The EF_x was estimated using the equation:

$$EF_x = \frac{\left[\frac{X_s}{E_{s(ref)}} \right]}{\left[\frac{X_c}{E_{c(ref)}} \right]} \quad (2.3)$$

152 where EF_x is the enrichment values for the element x. X_s and X_c are concentrations
153 of the element of interest in the sample and in the crust while $E_{s(ref)}$ and $E_{c(ref)}$
154 are the concentrations of the reference element used for normalization in the
155 sample and in the crust. A reference element is often characterized by low
156 occurrence variability and stable chemical properties. The common reference
157 elements for EF analysis are Sc, Mn, Ti, Al, Si and Fe. In this study, Fe was
158 selected as the reference element due to its lithogenic origin and abundance.
159 Taylor and McLennan [23] continental crustal average data was adopted as
160 the background concentration. The EF values were categorized as < 2, 2-
161 5, 5-20, 20-40 and ≥ 40 and considered as deficiency to minimal, moderate,
162 significant, very high and extremely high enrichment, respectively [26].

163 2.3.4 Index of geoaccumulation

The index of geoaccumulation (I_{geo}) was originally proposed by Muller [28]. It is a quantitative index which indicate the metal contamination in soil, water and sediment [1]. The (I_{geo}) compares the measured concentration C_m of the elements in a given sample with the geochemical background concentrations B_m for the element m in the sample [27]. The I_{geo} was calculated using the logarithmic function:

$$I_{geo} = \log_2(C_m/1.5B_m) \quad (2.4)$$

164 Taylor and McLennan [23] continental crustal average data was used as the
165 background elemental concentrations. The factor 1.5 was introduced to minimize
166 the effect of possible variations in the background values, B_m , which may
167 be attributed to the lithogenic variations in the sediment [1, 27, 22]. In this
168 study, I_{geo} was estimated using the seasonal average values of the measured
169 elemental concentrations. The categories of I_{geo} values are <0, 0-1, 1-2, 2-3,
170 2-4, 4-5 and >5 and their respective interpretations are practically unpolluted,
171 unpolluted to moderately polluted, moderately polluted, moderately to strongly
172 polluted, strongly polluted, strongly to extremely polluted and extremely polluted
173 [28].

174 3 RESULTS AND DISCUSSION

175 3.1 Average elemental concentrations of heavy metal results

176 Table 2 shows the results of the seasonal average concentrations of As, Cd,
177 Cr, Cu, Fe, Mn, Ni, Pb, V and Zn. Fe had the highest average concentration
178 values of 248.00 ± 20.00 and 324.33 ± 5.80 mg/kg at Awoye sampling site for
179 wet and dry season, respectively. The highest mean concentration of Mn are
180 271.77 ± 9.50 and 295 ± 10.06 mg/kg at Abereke and Ayetoro, respectively.
181 The high concentrations of Fe and Mn are most likely related to the local
182 mineralogy and lithogenic origin, rather than the anthropogenic activities [35].
183 Fe had been reported as being an elements whose origin is fundamentally
184 natural and one of the most common elements in the earth's crust [29]. The
185 mean concentrations of Fe and Mn were similar to high values of 463.0 and
186 321.4 mg/kg for both wet and dry season reported by Iqbal and Shah [30] in
187 the sediment samples obtained from Khanpur Lake, Pakistan. A few differences
188 in seasonal concentrations of Cd, Cr, Ni, V and Zn could be related to their
189 regional deposition and the heavy metal accumulation rate in the sediment.
190 The erosion activities, runoff by the action of water and land based sources
191 might introduce heavy metal into the water body. Atmospheric deposition of
192 anthropogenic metals have been reported to be the probable sources for the
193 variation in metal concentrations in the sediment in study area [19]. Most
194 industries such as oil exploration which are located around the sites discharged
195 industrial waste directly into the water without treatment. This might contain
196 heavy metals such Pb, Ni, V, Cr and Cd. The commercial ship and industrial
197 flying boat for the transportation of the workers during oil exploration and
198 seismic investigation could also released significant amount of Pb, Cd, V and
199 Ni-containing contaminants into the sediment. In each site, the average values
200 of Cd, Cu and Cd were lower than the World Health Organisation [31] sediment
201 quality guidelines values of 6, 25 and 123 mg/kg, respectively. These shows
202 the unpolluted conditions of the sediment by Cu, Cr and Cd. The Ni and Cr
203 mean concentration values in each site exceeded the [31] values of 20 and 25
204 mg/kg, suggesting that a minute pollution due to Ni and Cr.

205 3.2 Contamination factor, degree of contamination and pollution load 206 index results

207 Table 3 shows the results of contamination factor, degree of contamination
208 and pollution load index for the wet and dry season of the three studied areas.
209 In the dry season, Cr, Cu, Fe, Ni, Pb, V and Zn had a CF values to be
210 < 1 , signifying the low contamination status of the sediment. The CF values

Table 2: Average elemental concentrations of the heavy metals results (mg/kg)

	Dry			Wet		
	Abereke	Awoye	Ayetoro	Abereke	Awoye	Ayetoro
As	2.67±0.12	4.33±0.23	2.47±0.06	5.27±0.15	6.97±0.32	3.3±0.20
Cd	0.57±0.06	1.02±0.03	0.31±0.03	0.53±0.03	0.67±0.03	0.32±0.03
Cr	0.32±0.02	0.33±0.06	0.02±0.01	0.71±0.02	1.15±0.01	0.45±0.01
Cu	2.10±0.10	1.26±0.29	1.17±0.06	2.73±0.06	1.30±0.18	2.4±0.10
Fe	185.67±5.80	324.33±5.80	126.67±5.80	153.00±10.00	248.0±20.00	108.33±11.50
Mn	271.77±9.80	265.77±14.00	215.53±10.0	273.57±9.50	288.2±9.20	295±10.60
Ni	7.09±0.02	7.42±0.03	3.07±0.06	7.63±0.04	8.44±0.13	4.39±0.12
Pb	0.71±0.02	2.05±0.01	0.05±0.01	0.63±0.02	2.08±0.08	0.10±0.02
V	3.02±0.02	4.73±0.06	2.33±0.06	4.13±0.02	5.03±0.02	3.07±0.03
Zn	11.23±0.23	28.30±0.20	1.27±0.06	17.43±0.06	22.0±0.10	3.60±0.09

211 for As Cd and Mn were $1 < CF < 3$, indicating a moderate contamination.
 212 The results of the CF showed similar trend in the three sites both seasons
 213 indicating that CF values were less influenced by the seasons. The results of
 214 C_{deg} ranged from 8.6 to 12.5 for both dry and wet season except in Ayetoro
 215 site that had 7.8. This classified the sediment from the three sites as a
 216 moderate degree of contamination. The PLI values were 0.47, 0.50 and 0.54
 217 (<1) for Abereke, Awoye and Ayetoro sites, respectively, denoting unpolluted
 218 (perfection) conditions [24]. The little seasonal variations in PLI values might
 219 be associated with upstream discharged into the water and the alteration in
 220 various phases of elements in solution. In the wet season, a similar pattern of
 221 CF, C_{deg} and PLI values were observed in the three sites. This shows that the
 222 pollution of sediment is most likely less affected by the season. Although, there
 223 might be progressive accumulation of the heavy metals in the sediment which
 224 depends on the increased man-made activities such as oil exploration and
 225 waste discharge into the river from the upstream location. The wet season in
 226 2015 was a period of heavy rainfall, leading to high fluvial inputs. The mobility
 227 of the industrial waste alongside with the soil materials into the ocean should
 228 increase the pollution of the sediment by the heavy metals in the wet season.
 229 However, in this study, the results of CF, C_{deg} and PLI showed that the sediment
 230 quality were less affected by wet season.

231 3.3 Enrichment factor and index of geoaccumulation results

232 The results of the enrichment factor (EF) analysis for the three locations are
 233 presented in the Table 4. The EF values of As and Cr were <2 for the three
 234 sites, signifying deficiency to minimal enrichment. Zn and V had EF between
 235 $2 < EF < 5$ and $5 < EF < 10$ for dry and wet season, respectively, indicating

Table 3: Contamination Factor, Degree of Contamination and Pollution Load Index

Elements	Dry			Wet		
	Abereke	Awoye	Ayetoro	Abereke	Awoye	Ayetoro
As	1.3	2.2	1.2	2.6	3.5	1.7
Cd	3.2	5.7	1.7	2.9	3.7	1.8
Cr	0.3	0.1	0.1	0.1	0.2	0.5
Cu	0.1	0.2	0.2	0.4	0.3	0.4
Fe	0.3	0.6	0.6	0.3	0.4	0.2
Mn	2.7	2.7	2.2	2.7	2.8	2.9
Ni	0.1	0.1	0.4	0.2	0.2	0.6
Pb	0.2	0.2	0.5	0.1	0.2	0.1
V	0.8	0.4	0.4	0.2	0.3	0.2
Zn	0.3	0.3	0.5	0.2	0.3	0.4
C_{deg}	9.3	12.5	7.8	9.7	11.9	8.6
PLI	0.47	0.50	0.54	0.43	0.56	0.52

236 moderate and significant enrichment while Cd and Mn had the EF values of
 237 $5 < EF < 20$ in the three sites, classifying them as significant enrichment in
 238 both seasons. The moderate and significant enrichment of Zn and V could
 239 also be related to the anthropogenic sources such as boat exhaust systems,
 240 antifouling paints and fossil fuel from mechanized boat used in fishing and
 241 transportation which were common in the studied area. The EF values for Pb
 242 and Ni were > 20 in all the sampling sites at dry and wet season, indicating
 243 that the sites were highly enriched with Pb and Ni. The high enrichment of
 244 Pb and Ni might be linked to the fact that Pb and Ni are mostly anthropogenic
 245 elements associated with oil pollution which is prevalent in the study area. The
 246 enrichment of Pb might also be attributed stable isotopic nature of Pb in crustal
 247 materials and it takes a considerable period of time before an appreciable
 248 depletion can occur. The difference in the EF values of heavy metals in the
 249 coastal sediment might be related to the difference in the magnitude of input
 250 for each metal in the sediment as well as difference in the removal rate of
 251 each metal from the sediment [32, 33]. Largely, the low EF values of As and
 252 Cr indicating that they are mostly derived from soil. The high EF values of Zn,
 253 V, Pb and Ni might be attributed to contribution from anthropogenic activities
 254 such as oil exploration in the study area.

255 Table 5 shows the results index of geoaccumulation (I_{geo}) of As, Cd, Cr,
 256 Cu, Fe, Mn, Ni, Pb, V and Zn. The I_{geo} values of As, Cr, Fe, V, Zn and Cu
 257 were negative for the three sampling sites in the both seasons. These indicate
 258 that the sediment in the study area are practically uncontaminated by As, Cr,
 259 Fe, V, Zn and Cu. This is in agreement with the study of Salah et al. [1]

Table 4: Elemental enrichment factor (EF) analysis results

Elements	Dry			Wet		
	Abereke	Awoye	Ayetoro	Abereke	Awoye	Ayetoro
As	1.6	1.5	1.4	2.4	1.50	2.2
Cd	12.1	12.4	9.6	13.6	8.3	11.6
Cr	1.2	0.7	1.9	3.2	2.9	2.7
Cu	10.0	5.7	0.9	6.8	2.1	4.0
Mn	7.4	5.2	8.6	9.0	5.5	13.8
Ni	25.7	21.4	26.3	33.6	20.7	27.3
Pb	33.8	38.9	35.0	36.4	22.5	28.2
V	5.0	4.2	4.8	8.3	5.1	8.7
Zn	5.3	3.7	4.9	10.1	6.2	9.2

260 that obtained negative I_{geo} values for most metals in the sediment samples of
 261 Euphrates River in Iraq. Also, the negative I_{geo} values signify that the average
 262 heavy metal concentrations in sediment are lower than the average crustal
 263 concentration [1]. The I_{geo} values for Cd, Mn, Ni and V were $0 < I_{geo} < 1$
 264 implying uncontaminated to moderately contaminated [27]. Pb has the I_{geo}
 265 values of 2.8 and 2.85 during dry and wet season at Awoye sampling site
 266 while Ni has 2.57 at Abereke only in the dry season. The accumulation of
 267 heavy metal in sediment might be derived from the discharge of Omila and
 268 Edo rivers into the ocean and the mechanically weathered surface materials.

Table 5: Index of geoaccumulation (I_{geo}) results

Elements	Dry			Wet		
	Abereke	Awoye	Ayetoro	Abereke	Awoye	Ayetoro
As	-1.73	1.4	0.79	-1.05	0.50	0.50
Cd	0.75	1.33	0.17	0.67	0.14	0.14
Cr	-1.56	-1.53	-1.22	-0.76	-4.34	-4.34
Cu	0.62	0.12	-1.54	0.88	-2.26	-2.26
Fe	-1.74	-0.18	-2.28	-1.93	-2.12	-2.12
Mn	0.26	0.26	0.34	0.26	0.03	0.03
Ni	2.57	1.55	1.03	1.57	1.67	1.67
Pb	1.78	2.84	1.08	1.65	2.85	1.88
V	-0.13	0.32	-1.12	0.18	0.37	-0.39
Zn	-0.07	0.86	-1.20	0.37	0.61	-2.25

269 Generally, the results of all the pollution indices employed in this study agreed
 270 well. However, few differences exist among the pollution indices which could
 271 be attributed to their various approach of computation since the same background

272 concentrations data were used . The CF, C_{deg} and PLI results all confirmed
273 the uncontaminated status of most heavy metal in all the sites. The results
274 of EF revealed that sediment were enriched by Pb, Cd and Ni but the I_{geo}
275 values showed that the the sediments were uncontaminated to moderately
276 contaminated with respect to Pb and moderately contaminated with Cd. Also,
277 the EF values of Cd and Mn were $5 < EF < 20$, classifying the sites as
278 significant enriched by Cd and Mn in both seasons. Meanwhile, Cd and Mn
279 had the I_{geo} values in between 0 and 1 ($0 < I_{geo} < 1$) indicating uncontaminated
280 to moderately contaminated. This implies that the calculations of I_{geo} had more
281 reliability than those of EF. The differences in the results of the I_{geo} and EF in
282 this study might be associated with the methods of their computations. The
283 nature of the I_{geo} computation, which involved the logarithmic function and
284 matrix correction factor of 1.5 was quite different from enrichment factor which
285 normalised heavy metal concentration as the ratio to another constituents in
286 the sediment. The difference in classification and interpretation of the each
287 classes might also contribute to little differences in the results.

288 4 CONCLUSION

289 In this study, the bottom sediment samples were obtained in Abereke, Awoye
290 and Ayetoro sites in Ondo state coastal marine area, Southwestern Nigeria
291 in order to study the pollution status of heavy metals contents. The of heavy
292 metals analysis of the sediment samples was performed using Atomic Absorption
293 Spectrophotometer (AAS). The heavy metals concentrations data were processed
294 using statistical analysis and pollution indices: contamination factor (CF), degree
295 of contamination (D_{deg}), pollution load index (PLI), enrichment factor (EF) and
296 index of geoaccumulation (I_{geo}). Fe had the highest average concentration
297 values of 248.00 ± 20.00 and 324.33 ± 5.80 mg/kg at Awoye sampling site for
298 wet and dry season, respectively. Cr, Cu, Fe, Ni, Pb, V and Zn had a CF values
299 to be < 1 , signifying the low contamination status of the sediment. The PLI
300 values were 0.47, 0.50 and 0.54 (< 1) for Abereke, Awoye and Ayetoro sites,
301 respectively. The EF values of As and Cr were < 2 for the three sites. The I_{geo}
302 values of As, Cr, Fe, V, Zn and Cu were negative for the three sampling sites in
303 the both season, implying practically uncontaminated condition. Generally, the
304 results of pollution indices due to heavy metals showed low pollution status.
305 Transportation, fishing boat and ship breaking yard, direct discharge of industrial
306 waste from the upstream and oil exploration activities in the coastal area
307 contributed insignificantly to the pollution of the sediment. Despite the low
308 pollution level, continuous monitoring of the heavy metals is necessary to
309 provide information on the alteration in the sediment quality from gradually

310 increase in heavy metals loading in the sediment.

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322 **Competing Interests**

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327 **References**

328 **References**

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