

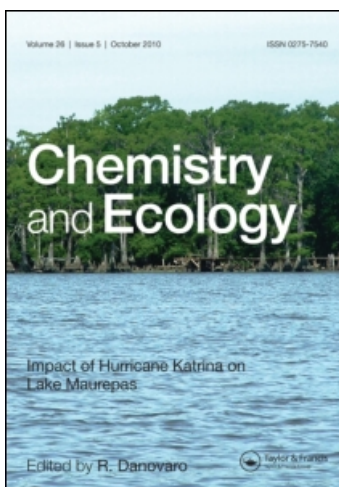
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## Fuzzy comprehensive assessment of metal contamination of water and sediments in Ondo Estuary, Nigeria

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A more reliable methodology for evaluating metal contamination of coastal water and sediments using fuzzy comprehensive assessment (FCA) is presented by this study. Ten metals (As, Cd, Cu, Cr, Fe, Mn, Ni, Pb, V and Zn) were investigated in water and sediments from ten sampling sites and formulated into fuzzy matrix based on three contamination classifications of pristine, moderately enriched and extremely impacted categories using regulatory limits as criteria. The products of the matrices from membership function of the observed data and the weight matrices generate indices that classify the degree of metal impact on the sites. The results of the FCA show that the estuary is negatively impacted by metals in a range of 45.5–75.1% membership in the extremely impacted category with potential adverse effects on the ecosystem of the neighbouring Atlantic Ocean. The crude oil exploration activity at site 1 is the major source input of the metals beside Fe and Mn which are natural to the geological structure of the area while domestic waste discharges contribute notably to metal contamination in some sites.

**Keywords:** fuzzy comprehensive assessment; metals; Ondo estuary; sediments; crude oil exploration

### 1. Introduction

Fuzzy logic is increasingly becoming a powerful and useful tool in assessing and classifying the quality of the environment by reducing inconsistency and vagueness in quality of data to facilitate decision making and management of the ecosystem [1–6]. It is useful in justifying the fuzziness in sharp boundaries where small changes in the contaminants data measuring pollution near regulatory boundaries change the pollution class of the environment considered. Thus, fuzzy-based tools like fuzzy synthetic evaluation and related approaches have been reported and used to model environmental and real situations [7–9]. Fuzzy evaluation methods, based on fuzzy set theory introduced by Zadeh in 1965, are being used to comprehensively evaluate the contributions of various pollutants to environmental pollution according to pre-established weights using membership function to decrease fuzziness [5,10–12]. Thus, its sensitivity is higher than other indices used in the evaluation of contamination or pollution.

Fuzzy comprehensive assessment (FCA) method, a subdivision of fuzzy synthetic evaluation, has been used to effectively solve problems of fuzzy boundaries and control monitoring error

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effects on results of pollution assessment [7,8,13–15]. Shen et al. [14] used FCA in investigating the combined effects of heavy metals and organochlorine pesticides in soil. Metals and persistent organic compounds are priority pollutants. Arsenic and chromium are classified as priority pollutants by the United States Environmental Protection Agency (USEPA) with a carcinogenicity classification A (human carcinogen), while cadmium and lead are classified in the same list as carcinogenicity classification B (probable human carcinogen) [16,17]. The biological activities and ecotoxicity of these metals and metalloid have been widely reported [18–22]. Some of the metals however are essential (Cu, Fe, Mn, and Zn) but at low concentrations. Excess concentrations of these metals have adverse bioactivities. These metals are discharged into the environment from various human activities in the process of development and need to be continually monitored because of their adverse bioactivities, persistence, resistance to degradation and accumulation in the ecosystem. The monitoring of metals in the environment of developed economies have been consistently carried out [23–28] while that of developing economies is becoming increasingly necessary because of the increasing trend of domestic, commercial and industrial activities and the potential effects of such on the fast growing population in the region. Hence, the evaluation of the status of an estuarine environment like the Ondo coastal region is important because of its proximity to the Atlantic Ocean and the crude oil exploration activity in the area. The Ondo coast is contaminated by discharge of untreated domestic wastes, effluents from crude oil exploration, fuelling stations and contributions from transport of people and goods especially crude oil products. The effects of the crude oil exploration, domestic, agricultural and commercial activities on the water and sediments from such areas need evaluation beyond the traditional approach of reporting the concentration of contaminants in ppm to the formulation of reliable indices that can serve as a basis for appreciating the systemic trend of the data, the combinatory effects of multiple contaminants' exposures and for appropriate policy formulation. This will indicate the potential threats the activities in the region have on the neighbouring ecosystem and its vast resources.

Thus, this study presents a methodology of assessing metal contamination in water and sediments using fuzzy comprehensive assessment as against the conventional or traditional approaches that have always been rather technical for the general public and policy makers. This formulation of reliable index from various individual metal concentration values is necessary for effective decision making and policy formulation.

## 2. Methodology

### 2.1. Background and sampling approach

This study was conducted in the south eastern part of Mahin, Ilaje area of Ondo State (Lat.  $5^{\circ}50'N$ – $6^{\circ}09'N$  and Long.  $4^{\circ}45'E$ – $5^{\circ}05'E$ ). It is an estuary adjacent to the Atlantic Ocean. The total area covered by the study was about  $500\text{ km}^2$  with emerging communities dispersed within the coast. The population of the entire state is about 3 million with a population growth rate of 2.2% annually. There are over 50 settlements scattered around the river tributaries that empty into the coastal ocean through this estuary. The area also falls within the oil prospecting states in Nigeria called the Niger Delta region. It consists of rivers and streams which traverse different settlements and discharge into the coastal ocean (Bright of Benin, Atlantic Ocean). Ten sampling points were selected (Figure 1) along the estuarine part of the coast for the evaluation. Samples of water and sediments were collected in April 2006 during the wet season in these sampling points. The choice of sampling points was made considering the anthropogenic activities in the area that are potential sources of contaminants impacting negatively on the zone. Site 1 (Ukua) is an oil prospecting site hosting the crude oil exploration platform of one of the operators of

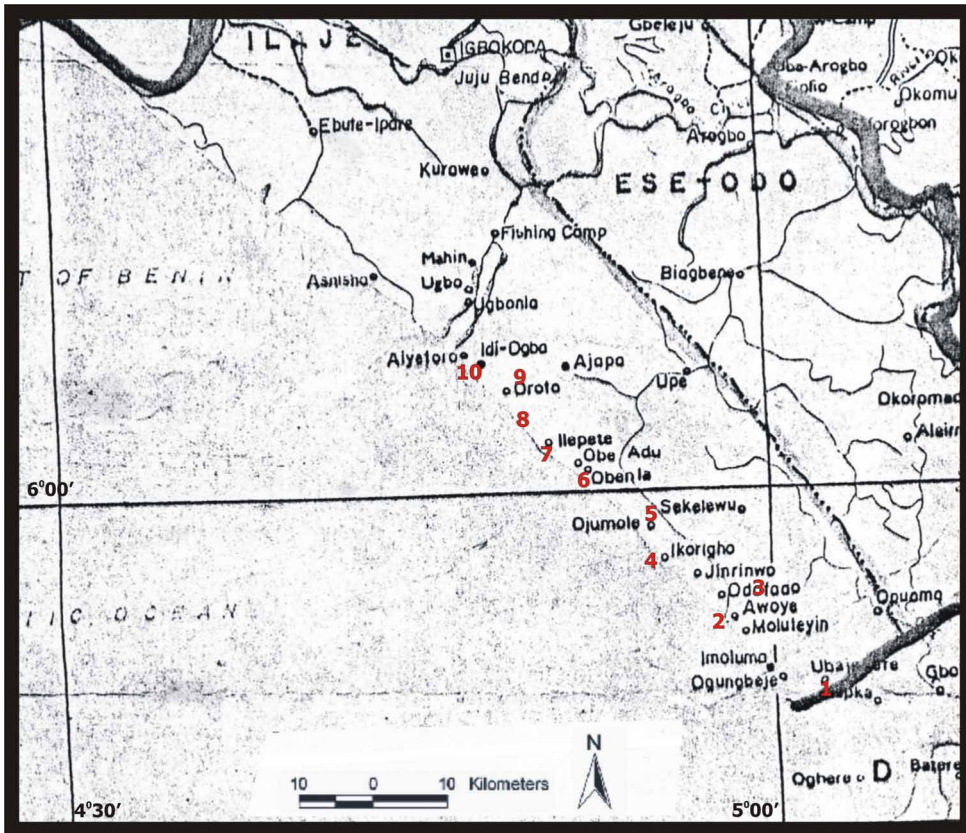


Figure 1. Map of the coastal area of Ondo State and the sampling points.

Nigerian National Petroleum Corporation (NNPC) joint venture while Site 2 (Awoye) is the estuary discharge points. The other eight sites are close to settlements with increasing distance from sites 1 and 2. The occupations of majority of the populace are trading, fishing, and farming. All municipal and domestic wastes are directly discharged via the rivers into the coast. There is no waste treatment plant in the area. Heavy transportation of goods and people in the area and fishing activities are by motorboat. The oil exploration and fuelling stations for motorboats in the area are notable sources of contamination. All these cumulatively informed the sampling strategy.

Water samples were collected into high density polyethylene (HDPE) vessels pre-treated with  $\text{HNO}_3$  for 24 h before finally rinsing in demineralised water. Sampling was done by discrete grab method in a speedboat with engine switched off. A litre each of water sample was collected at each sampling point for determination of metals. Quality assurance/Quality control (QA/QC) steps taken in sampling to ensure the integrity of the samples included rinsing the sampling bottle twice with the water being collected; preservation of these samples with 2 ml of conc.  $\text{HNO}_3$  per litre and at  $4^\circ\text{C}$  to arrest precipitation reaction and microbial activities. Likewise, bottle blank analysis was done by randomly selecting one of the sampling vessels; filling it with demineralised water; taking it along with other vessels to the field and analysing it for all the metals to evaluate external contribution. The external contributions were less than 1% of the metals investigated. Further, replicate samples were taken in few sites analysed for some metals to measure sampling precision and the relative standard deviation (RSD) obtained were less than 10%. The periods between sampling and analysis was kept between the recommended times by Standard Method [29].

Samples of bottom sediments were collected after water sampling to prevent sampling re-suspending particulate matter into water samples which could negatively affect the integrity of the metal content of the water samples. Van Veen grab sampler was used to sample sediments and kept in aluminium foil, air dried and analysed for metals. Replicate sediment samples were also collected in some sites and analysed with other samples and the RSD falls between 10–16%.

## 2.2. Chemical analysis

The acid preserved water samples were agitated and the acid extractable metals were obtained from 100 ml of the sample with 5 ml of the acid HCl (1 + 1) on a steam bath for 15 min [29]. The resulting solutions were filtered with acid washed filters and the filtrates transferred into a 100 ml volumetric flask and the volume adjusted to the mark with deionised water before analysis.

Sediment samples were air-dried at room temperature, ground and sieved to particle size <200  $\mu\text{m}$  diameter with standard sieves. Sediment samples were digested to obtain the acid extractable metals. The choice of acid labile fraction for the assessment is because of the view that the ecotoxic metals are the bioavailable fractions than the total metals which are non-degradable nor available for biological activities. Thus, the digestion was carried out as reported by Hall [30]. The dry weight (0.5 g) of the sediment was treated with 30 ml of 0.5 M HCl at room temperature for 12 h and filtered with acid washed filters (0.45  $\mu\text{m}$  pore size) by suction. The resulting filtrates were made-up in 100 ml volumetric flasks with deionised water.

The analyses of As, Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn in the digested water and sediment samples were done using Flame Atomic Absorption Spectrometer (AAS) Buck Scientific 205 Model with direct air-acetylene flame method while analysis of V was done with the same instrument, but by direct nitrous oxide-acetylene flame method.

All vessels used were acid washed and blank analysis was done for all the processes. The blank concentrations were used for the correction of the contributions of metals from reagents or vessels used in the analyses. Also, reference sediment material from USA National Institute of Standards and Technology (NIST) Standards was subjected to the same digestion and analytical procedures to measure accuracy, precision, and ensure good quality control of the methods. Recoveries of water samples were done by spiking standard solutions of the metals into some chosen samples and were found to be between 92–104%. Blank analyses were all below 3% of the metals investigated while the analysis of reference sediment material gave a recovery between 71–96%. All analyses were done in triplicates to measure reproducibility of methods. Mean values are presented with their respective standard deviations.

## 2.3. Fuzzy Comprehensive Assessment (FCA)

This concept is a subdivision of Fuzzy Synthetic Evaluation method [8,14,15]. It involves the use of simple fuzzy classification where the matrices obtained from fuzzy membership functions are subjected to weighted average method of fuzzy reasoning [9]. Mathematically, it can be expressed as:

$$k_j = \sum_{i=1}^m W_i \lambda_{ij} \quad (1)$$

$$\sum_{i=1}^m W_i = 1 \quad (2)$$

$$k_p = \max\{k_j\} \quad (3)$$

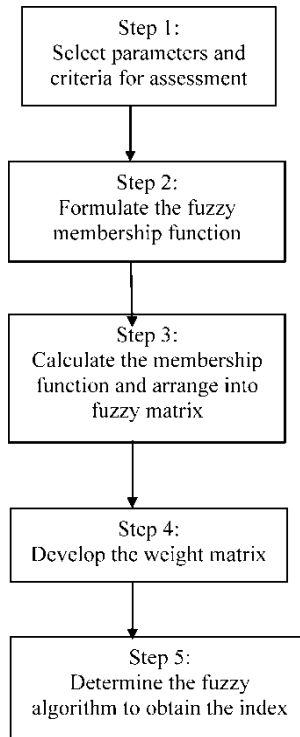


Figure 2. Flowchart of FCA Procedure.

where  $\lambda_{ij}$  are membership function and  $W_i$  is the weight associated with each parameter. The procedure used for FCA is outlined in Figure 2.

#### *Step 1: Parameter selection and establishment of criteria for assessment*

Selection of important parameters that could reliably and accurately assess the pollution status and represent effectively the local environment is fundamental. The parameters could be assigned a set of function:

$$\lambda = \{\lambda_1, \lambda_2, \lambda_3, \dots, \lambda_n\} \quad (4)$$

where  $\lambda_1, \lambda_2, \lambda_3, \dots, \lambda_n$  are the parameters (e.g. metals) assessed for the study and  $n$  is the total number of these parameters investigated ( $n = 10$  for this study). Also, criteria or limits for each parameter are established based on regulatory standards [31,32] or by a consideration of background concentration of such pollutant natural to that environment. The criteria could be defined using the set function:

$$B = \{b_1, b_2, \dots, b_n\} \quad (5)$$

where  $b_1, b_2, \dots, b_n$  are the classifications of the parameters and  $n$  is the total number of classification ( $n = 3$  for this study).

Table 1. Membership function limits for metals.

Metals	The parameter limits for the membership function classes*					
	$b_1$		$b_2$		$b_3$	
	Water (mg/l)	Sediments (mg/kg)	Water (mg/l)	Sediments (mg/kg)	Water (mg/l)	Sediments (mg/kg)
As	0.05	0.50	0.10	1.00	0.20	2.00
Cd	0.01	0.50	0.05	1.00	0.10	5.00
Cu	1.00	20.0	2.00	40.0	5.00	100
Cr	0.05	1.00	0.10	5.00	0.20	10.0
Fe**	2.00	50.0	10.0	200	20.0	500
Mn**	0.50	50.0	1.00	100	2.0	500
Ni	0.05	1.00	0.10	2.0	0.50	10.0
Pb	0.05	1.00	0.10	5.0	0.50	20.0
V	0.10	1.00	0.50	10.0	1.00	10.0
Zn	2.00	20.0	5.00	40.0	10.0	100

\*The classifications  $b_1, b_2, b_3$  correspond to I, II, and III classes which are defined as pristine, moderately enriched and extremely impacted, respectively.

\*\*The criteria limits for Fe and Mn were based on the background concentration because the site is enriched with the two metals.

*Step 2: Formulation of membership function*

The water and sediment quality may be classified into three levels. These classifications are: classification I – pristine condition; II – moderately enriched condition and III – extremely impacted condition.

The criteria limits for each metal under the three classifications used for this study are presented in Table 1. Classification I, II and III correspond to limits  $b_1, b_2, b_3$ , respectively. The limits of each classification were established based on regulatory standards for each metal. The observed concentration of each metal was then used in relation to these limits to formulate fuzzy membership function based on expressions (6) to (8):

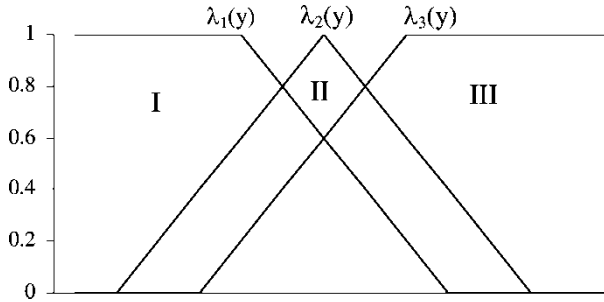
$$\lambda_1(y) = \left\{ \begin{array}{ll} 1 & \text{if } y \leq b_1 \\ \frac{(b_2 - y)}{(b_2 - b_1)} & \text{if } b_1 < y < b_2 \end{array} \right\} \tag{6}$$

$$\lambda_2(y) = \left\{ \begin{array}{ll} 0 & \text{if } y \leq b_1 \\ 1 - \lambda_1(y) & \text{if } b_1 < y \leq b_2 \\ \frac{(b_3 - y)}{(b_3 - b_2)} & \text{if } b_2 < y < b_3 \\ 0 & \text{if } b_2 < y < b_3 \\ 0 & \text{if } y \geq b_3 \end{array} \right\} \tag{7}$$

$$\lambda_3(y) = \left\{ \begin{array}{ll} 0 & \text{if } y \leq b_2 \\ 1 - \lambda_2(y) & \text{if } b_2 < y < b_3 \\ 1 & \text{if } y \geq b_3 \end{array} \right\} \tag{8}$$

where  $y$  is the observed data from chemical analysis of the metals used in the assessment,  $\lambda_1(y), \lambda_2(y), \lambda_3(y)$  are the fuzzy membership functions corresponding to I, II, III, respectively.

This expression will give fuzzy membership results that could be illustrated with this diagram:



### Step 3: Calculation of membership function and matrix formation

The membership functions of the observed monitoring data were formulated with the expressions in step 2 at each site by the substitution of the observed data at each monitoring point and the limits into the expressions (6)–(8) above. They were arranged into a fuzzy matrix  $X_k$  which is:

$$X_k = \begin{bmatrix} \lambda_{11} & \lambda_{12} & \dots & \lambda_{1m} \\ \lambda_{21} & \lambda_{22} & \dots & \lambda_{2m} \\ \vdots & \vdots & \vdots & \vdots \\ \lambda_{n1} & \lambda_{n2} & \dots & \lambda_{nm} \end{bmatrix} \quad (9)$$

where  $\lambda_{ij}$  is the degree of membership of a classification obtained for  $j$ th number of metals and  $i$ th number of limit classification. Thus  $i = 1, 2, \dots, n$  and  $j = 1, 2, \dots, m$  where  $m$  is the number of metals investigated (10) and  $n$  is the number of criteria classifications (3) and  $X_k$  is the fuzzy matrix at  $k$ th site.

### Step 4: Developing weight matrix

Crucial to FCA is a reliable allocation of weight to each parameter ( $j$ ) at each investigated site ( $k$ ). The choice of appropriate and reliable weight influence the outcome of the assessment and several methods have been used. For this study, allocation of weight will be based on the ratio of the contribution of the observed data for each metal to the overall weight which is mathematically expressed as:

$$W_{j(k)} = \frac{a_{j(k)}}{\sum_{i=1}^n a_{j(k)}} \quad (10)$$

$$a_{j(k)} = \frac{C_{j(k)}}{S_j} \quad (11)$$

where  $C_{j(k)}$  is the concentration of metal number  $j$ th in monitoring site  $k$  and  $S_j$  is the average limit in formulating the membership function (Table 1) for each metal. The values obtained from Equation (11) were substituted in Equation (10) to obtain the weight ( $W_{j(k)}$ ) of the assessment



parameters (metals) for each site. The weights obtained can then be expressed as weight matrix  $P_k$ :

$$P_k = \begin{bmatrix} W_{1(k)} \\ W_{2(k)} \\ \vdots \\ W_{m(k)} \end{bmatrix} \quad (12)$$

where  $m$  is the number of investigated metals (10). This approach to weight allocation is logical because it put into consideration the effects of observed concentration of parameter ( $y$ ) that is much above or below the regulatory criteria in the calculation of the weight for each parameter.

#### Step 5: Determination of fuzzy algorithm

Finally, the fuzzy algorithm is computed from the product of the fuzzy matrix (Equation 9) and the weight matrix (Equation 12). The product moment of the fuzzy matrix  $X_k = (\lambda_{ij})_{n \times m}$  and the weight matrix  $P_k = (W_{j(k)})_{1 \times m}$  gives the matrix index which classifies the degree of contamination of the sites into any of the three classes earlier presented. The product of the matrix gives:

$$X_k P_k = \begin{bmatrix} k_1 \\ k_2 \\ \vdots \\ k_j \end{bmatrix} \quad (13)$$

where  $k_j$  is defined in equation (1). The fuzzy algorithm matrix analysis for this study was done using the fuzzy logic toolbox of MATLAB 7.0 package [33].

### 3. Results and discussion

The mean concentrations observed for the metals in the coastal water of Ondo estuary and the sediment samples are presented in Table 2. The concentrations of the metals are higher than regulatory standards, which is a strong indication that the environment is negatively stressed by uncontrolled discharge of untreated domestic and industrial wastes. Fe and Mn are extremely high in both water and sediment samples but are contributed naturally from the geological structure of the area. Fuzzy comprehensive assessment of the results demonstrates a potential helpful tool that could be used to appreciate the systemic trend of the data obtained and serve as basis for decision making and policy formulation.

#### 3.1. Fuzzy comprehensive assessment of metals in water

The fuzzy membership function ( $\lambda_i$ ) obtained for the metals in the order of As, Cd, Cu, Cr, Fe, Mn, Ni, Pb, V and Zn at the ten sampling sites are presented as fuzzy matrix ( $X_k$ ) in Figure 3 along with their corresponding weight matrix ( $P_k$ ) for each site. From the fuzzy matrices, it is obvious that Fe (in sites 1–5), Cd, Ni, Cr and Pb are the major contaminants in the estuary. These metals have high percentage membership classification in extremely impacted range with some significant percentage classification in the moderately enriched class (especially Ni). The contribution of Cr to the environment ranked closely between the moderately enriched and extremely impacted classifications. Fe is natural to the site and is an essential metal at trace level. However, Cd, Ni, Cr and Pb are closely linked with crude oil exploration. Arsenic is moderately contributed. Further,

Table 2. Outcome of acid extractable metal analysis of water and sediment samples from Ondo estuary.

Sites	Sample Types	Metals*									
		As	Cd	Cu	Cr	Fe	Mn	Ni	Pb	V	Zn
Ukua	Water	0.009 ± 0.002	0.121 ± 0.015	2.28 ± 0.208	0.19 ± 0.009	45.3 ± 1.7	1.21 ± 0.03	0.28 ± 0.010	0.59 ± 0.015	0.23 ± 0.008	6.73 ± 0.12
	Sediment	0.330 ± 0.012	3.830 ± 0.120	27.7 ± 1.05	5.33 ± 0.12	473 ± 8.5	654 ± 10.5	7.53 ± 0.18	17.8 ± 0.21	6.58 ± 0.15	58.6 ± 1.23
Awoye	Water	0.011 ± 0.003	0.114 ± 0.010	1.51 ± 0.010	0.15 ± 0.012	29.4 ± 1.2	0.61 ± 0.02	0.26 ± 0.011	0.49 ± 0.012	0.20 ± 0.005	4.19 ± 0.15
	Sediment	0.300 ± 0.017	3.680 ± 0.250	24.5 ± 0.81	5.85 ± 0.11	540 ± 10.7	558 ± 8.8	8.15 ± 0.20	20.0 ± 0.31	6.23 ± 0.080	61.3 ± 2.15
Odonla	Water	0.007 ± 0.001	0.093 ± 0.008	1.36 ± 0.011	0.16 ± 0.011	28.7 ± 0.7	0.57 ± 0.04	0.29 ± 0.012	0.59 ± 0.018	0.20 ± 0.010	4.03 ± 0.18
	Sediment	0.250 ± 0.008	3.080 ± 0.205	26.9 ± 0.85	4.95 ± 0.09	520 ± 8.0	851 ± 15.5	7.78 ± 0.19	15.6 ± 0.11	6.48 ± 0.120	74.5 ± 2.05
Ikoriqho	Water	0.009 ± 0.002	0.110 ± 0.011	1.16 ± 0.013	0.14 ± 0.006	47.9 ± 1.5	1.45 ± 0.05	0.28 ± 0.012	0.49 ± 0.010	0.18 ± 0.009	3.71 ± 0.09
	Sediment	0.330 ± 0.021	3.780 ± 0.258	27.8 ± 1.10	5.65 ± 0.12	428 ± 7.7	742 ± 14.4	7.35 ± 0.12	17.9 ± 0.21	5.20 ± 0.15	49.7 ± 1.15
Ojumole	Water	0.010 ± 0.002	0.091 ± 0.007	1.10 ± 0.012	0.13 ± 0.012	9.30 ± 0.57	0.16 ± 0.01	0.26 ± 0.013	0.49 ± 0.013	0.19 ± 0.011	3.39 ± 0.10
	Sediment	0.230 ± 0.011	3.580 ± 0.302	26.6 ± 1.05	5.10 ± 0.14	552 ± 9.8	797 ± 10.5	7.60 ± 0.15	15.6 ± 0.32	5.28 ± 0.12	53.4 ± 1.65
Obenla	Water	0.012 ± 0.003	0.102 ± 0.012	0.90 ± 0.007	0.17 ± 0.006	2.0 ± 0.07	0.11 ± 0.01	0.20 ± 0.009	0.40 ± 0.009	0.20 ± 0.015	3.23 ± 0.05
	Sediment	0.280 ± 0.016	3.850 ± 0.332	31.3 ± 1.09	5.90 ± 0.21	534 ± 12.8	973 ± 18.4	7.80 ± 0.18	18.1 ± 0.22	5.70 ± 0.21	51.9 ± 1.45
Ilepete	Water	0.011 ± 0.003	0.113 ± 0.018	0.92 ± 0.008	0.16 ± 0.008	2.10 ± 0.09	0.12 ± 0.01	0.22 ± 0.01	0.39 ± 0.008	0.19 ± 0.021	3.07 ± 0.08
	Sediment	0.300 ± 0.021	3.580 ± 0.256	22.4 ± 1.03	4.95 ± 0.18	402 ± 6.8	914 ± 14.0	7.43 ± 0.10	15.0 ± 0.31	5.38 ± 0.23	37.2 ± 1.55
Ilowo	Water	0.008 ± 0.002	0.124 ± 0.012	0.90 ± 0.011	0.12 ± 0.009	1.58 ± 0.08	0.09 ± 0.008	0.18 ± 0.012	0.49 ± 0.012	0.18 ± 0.009	3.87 ± 0.05
	Sediment	0.250 ± 0.010	3.480 ± 0.245	24.4 ± 0.86	5.08 ± 0.30	496 ± 8.8	946 ± 13.4	7.50 ± 0.22	15.0 ± 0.25	5.23 ± 0.33	51.0 ± 1.05
Ibijnmi	Water	0.010 ± 0.002	0.094 ± 0.007	0.85 ± 0.007	0.13 ± 0.010	1.99 ± 0.12	0.12 ± 0.006	0.22 ± 0.011	0.39 ± 0.010	0.20 ± 0.01	3.39 ± 0.09
	Sediment	0.350 ± 0.022	3.850 ± 0.265	25.8 ± 0.98	5.78 ± 0.24	590 ± 12.8	727 ± 5.3	8.05 ± 0.19	23.3 ± 0.32	6.20 ± 0.12	53.4 ± 2.05
Idi Ogba	Water	0.011 ± 0.002	0.101 ± 0.005	0.99 ± 0.006	0.14 ± 0.008	1.59 ± 0.08	0.12 ± 0.009	0.28 ± 0.015	0.49 ± 0.012	0.17 ± 0.007	3.23 ± 0.15
	Sediment	0.330 ± 0.030	4.48 ± 0.350	25.4 ± 0.96	5.48 ± 0.156	527 ± 8.7	778 ± 16.5	7.88 ± 0.31	17.8 ± 0.21	5.78 ± 0.28	66.3 ± 3.05

\*Mean ± sd value of metals in water and sediment samples. The unit of all metals in water samples is mg/l while that of sediment samples is mg/kg dry weight.

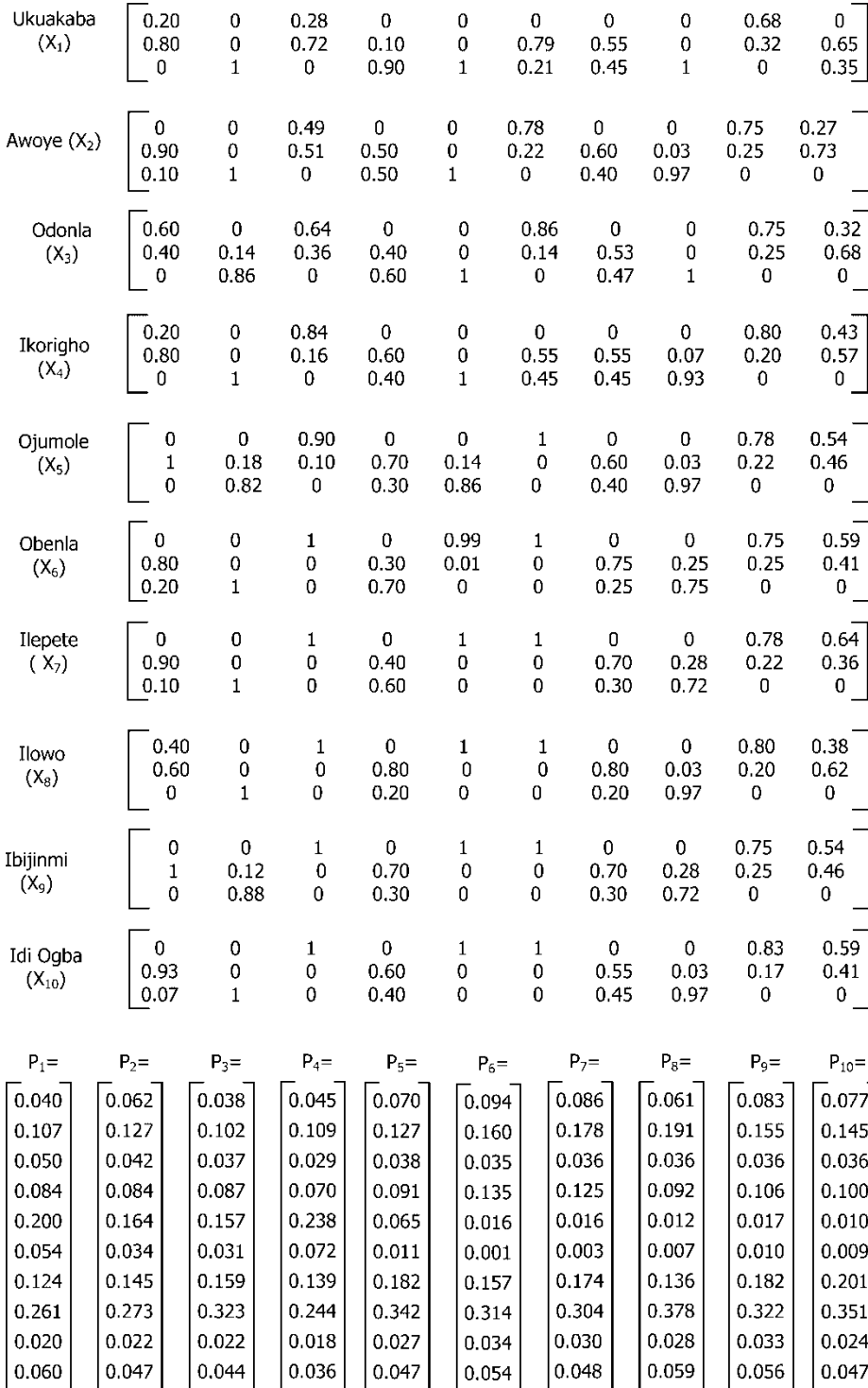


Figure 3. Fuzzy membership matrix  $X_k$  and corresponding weight matrix  $P_k$  for the ten sampling sites and ten metals in water samples. Each column of the  $X_k$  and row of  $P_k$  represents As, Cd, Cu, Cr, Fe, Mn, Ni, Pb, V and Zn, respectively.

Cd, Fe, Ni and Pb contribute weights ( $P_k$ , Figure 3) above 10% in most of the sites with Pb having the highest weight contribution of between 24.4–37.8% of the entire metal load. The contribution of Pb is from additional input sources. The commercial activities involve the use of speedboats for transportation of goods and people. This introduces Pb from the antiknock agent used in fuel.

The weight contribution of Cr is also notable within the range 7–13.5%. Cd, Ni, Pb, Cr and As have been reported as ecotoxic and to disrupt enzyme activities in human and other living organisms [22,34–36]. Thus, the monitoring and control of these metals along this coast is recommended being a coast neighbouring the Atlantic Ocean.

Further, results of fuzzy algorithm of each of the site performed by the product moment of the fuzzy and weight matrices ( $X_k \Theta P_k$ ) are presented as follows:

$$\begin{array}{cccccc} \text{Site 1} & \begin{bmatrix} 0.036 \\ 0.232 \\ 0.732 \end{bmatrix} & \text{Site 2} & \begin{bmatrix} 0.076 \\ 0.262 \\ 0.662 \end{bmatrix} & \text{Site 3} & \begin{bmatrix} 0.104 \\ 0.202 \\ 0.694 \end{bmatrix} & \text{Site 4} & \begin{bmatrix} 0.063 \\ 0.230 \\ 0.707 \end{bmatrix} & \text{Site 5} & \begin{bmatrix} 0.094 \\ 0.315 \\ 0.591 \end{bmatrix} \\ X_1 P_1 & & X_2 P_2 & & X_3 P_3 & & X_4 P_4 & & X_5 P_5 & \\ \\ \text{Site 6} & \begin{bmatrix} 0.109 \\ 0.345 \\ 0.546 \end{bmatrix} & \text{Site 7} & \begin{bmatrix} 0.109 \\ 0.358 \\ 0.532 \end{bmatrix} & \text{Site 8} & \begin{bmatrix} 0.124 \\ 0.273 \\ 0.603 \end{bmatrix} & \text{Site 9} & \begin{bmatrix} 0.118 \\ 0.427 \\ 0.455 \end{bmatrix} & \text{Site 10} & \begin{bmatrix} 0.103 \\ 0.276 \\ 0.621 \end{bmatrix} \\ X_6 P_6 & & X_7 P_7 & & X_8 P_8 & & X_9 P_9 & & X_{10} P_{10} & \end{array}$$

It is very obvious from the results that the coastal water is extremely impacted with metals from both anthropogenic and natural sources. While Fe and Mn are contributed from erosion, runoff from the soil and other geological materials in the area, the other metals are contributed from diverse human activities in the coast. These fuzzy indices obtained from the product moments classified the degree of contamination of the estuarine water within the range of 45.5–73.2% as extremely impacted, 20.2–42.7% as moderately enriched and 3.6–12.4% pristine. The coastal environment is not pristine but requires remediation and strict environmental management policies because of its potential adverse effects on the vast aquatic resources in the neighbouring Ocean and the growing population in the area.

Moreover, site 1 (Ukua) had the highest degree of impact (73.2%: extremely impacted) with a gradual decrease away from this site. There is therefore a strong indication from the results that oil exploration activity in site 1 is a major source input of contamination and dispersion of metals into the estuary. Sites 3, 4, 8 and 10 show notable deviation in the decrease trend observed away from site 1. This deviation observed is an evidence of contributions of metal contamination from discharge of untreated domestic wastes from settlements along the coast. It thus implies that crude oil exploration at site 1 is a major contaminant source negatively affecting the environmental status of the area while domestic wastes discharges also contribute. The contributions from domestic waste however, are not relatively strong compared to industrial crude oil exploration impact. Thus, an effective management of the oil exploration site, a cleaner production approach could significantly improve the quality of the environment.

### 3.2. Fuzzy comprehensive assessment of heavy metals in sediments

The observed concentrations of metals in sediments are expectedly several magnitudes higher than that of the corresponding water samples (Table 2) because sediments are sinks for precipitated metals obtained by either hydrolysis, adsorption to particulate, coagulation into larger particles or bioaccumulation into biological organisms associated with the bottom sediments. Also, the long-term effects of metal contamination could be better appreciated by the evaluation of sediments being major means of demobilizing the metals from the transporting water medium. If there is no perturbation by storm action, which resuspend sediments from the bottom layer nor a change in the biogeochemical reactions like change in pH or organic carbon content to favour partitioning

of metals into the water column, the metals in the bottom sediment remain relatively unchanged with less spatial variation and could serve as a better indicator of long-term contamination effects and metal accumulation in a site.

The FCA of sediment quality was used to evaluate the quality trend of the estuarine environment. The membership function and the resulting fuzzy matrix  $X_k$  obtained based on the order of metal arrangement reported in water samples are presented in Figure 4 along with their corresponding weight matrix  $P_k$ . The criteria limits used for development of fuzzy membership functions in sediments were similar to local and international regulatory standards for soil samples [37,38] which are of higher magnitudes than the limits in water (Table 1).

From the sediments fuzzy matrix (Figure 4), it could be deduced that Cd, Fe, Mn, Ni and Pb are the major metal contaminants in the coastal sediments. These metals ranked highest in extremely impacted category for all the sites. This result correlates with the observed trend in water samples. Cr, V, Zn have their highest membership function in the moderately enriched class while Cu and As exhibit pristine situations in all the sites. The weight matrices  $P_k$  of the metals in sediment samples indicate a close degree of contribution from Cd, Fe, Mn, Ni and Pb to metal contamination of the estuary. Each of these metals contributes over 10% to the entire metal load (Figure 4) which is similar to the trend witnessed in water samples. The membership function and weight of Fe and Mn in the bottom sediments confirm that they are contributed from a natural source by erosion of soil particles enriched with these metals. However, the input sources of Cd, Ni, and Pb are unfit human activities degrading the environment which need to be controlled to safeguard human life and the ecosystem of the Atlantic Ocean. Arsenic is the least contributed metal to the coastal sediment as observed also in water samples. The sources of Cr, V and Zn need to be identified and managed as control measure against further increase in concentration.

Finally, the fuzzy algorithm results ( $X_k \ominus P_k$ ) for the bottom sediments are:

$$\begin{array}{ccccc}
 \text{Site 1} & \begin{bmatrix} 0.035 \\ 0.286 \\ 0.679 \end{bmatrix} & \text{Site 2} & \begin{bmatrix} 0.036 \\ 0.234 \\ 0.730 \end{bmatrix} & \text{Site 3} & \begin{bmatrix} 0.031 \\ 0.291 \\ 0.678 \end{bmatrix} & \text{Site 4} & \begin{bmatrix} 0.035 \\ 0.311 \\ 0.654 \end{bmatrix} & \text{Site 5} & \begin{bmatrix} 0.032 \\ 0.305 \\ 0.663 \end{bmatrix} \\
 X_1 P_1 & & X_2 P_2 & & X_3 P_3 & & X_4 P_4 & & X_5 P_5 & \\
 \\
 \text{Site 6} & \begin{bmatrix} 0.028 \\ 0.259 \\ 0.713 \end{bmatrix} & \text{Site 7} & \begin{bmatrix} 0.045 \\ 0.337 \\ 0.618 \end{bmatrix} & \text{Site 8} & \begin{bmatrix} 0.034 \\ 0.309 \\ 0.657 \end{bmatrix} & \text{Site 9} & \begin{bmatrix} 0.034 \\ 0.215 \\ 0.751 \end{bmatrix} & \text{Site 10} & \begin{bmatrix} 0.034 \\ 0.224 \\ 0.742 \end{bmatrix} \\
 X_6 P_6 & & X_7 P_7 & & X_8 P_8 & & X_9 P_9 & & X_{10} P_{10} & 
 \end{array}$$

The results generally indicate that the degree of contamination of the sediments fall within the range of 61.8–75.1% membership in the extremely impacted classification, 21.5–33.7% moderately enriched and less than 5% in pristine category. It thus implies that the long term contributions of metals from anthropogenic activities have extremely impacted the sediment from the estuary and should be controlled.

The close range of the FCA index of the bottom sediments across the sites is an indication that sediment contamination degree does not vary sharply over time and space. The high values noticed at sites 2, 6, 9 and 10 indicate the possibility of biogeochemical reactions that favours the partitioning of the metals into the bottom sediment phase and the combined effects of contaminants from oil exploration and domestic wastes discharge on the sites. Site 10 surely has significant metal contribution from domestic activities. The index value at site 2 – Awoye (73%) compared with the two adjacent sites 1 and 3 (67.9 and 67.8%, respectively) depicts the effects of coastal water intrusion. Site 2, the discharge point of the estuary, witnesses the highest level of intrusion of saline water which aids the partitioning of the metals into the sediment phase due to competition between cations (Na with other metals). Sodium being abundant in saline water will partition the other metals into the sediment phase. Likewise, the index obtained for site 9 (75.1%) compared with that of water sample from corresponding site which was the lowest among water samples

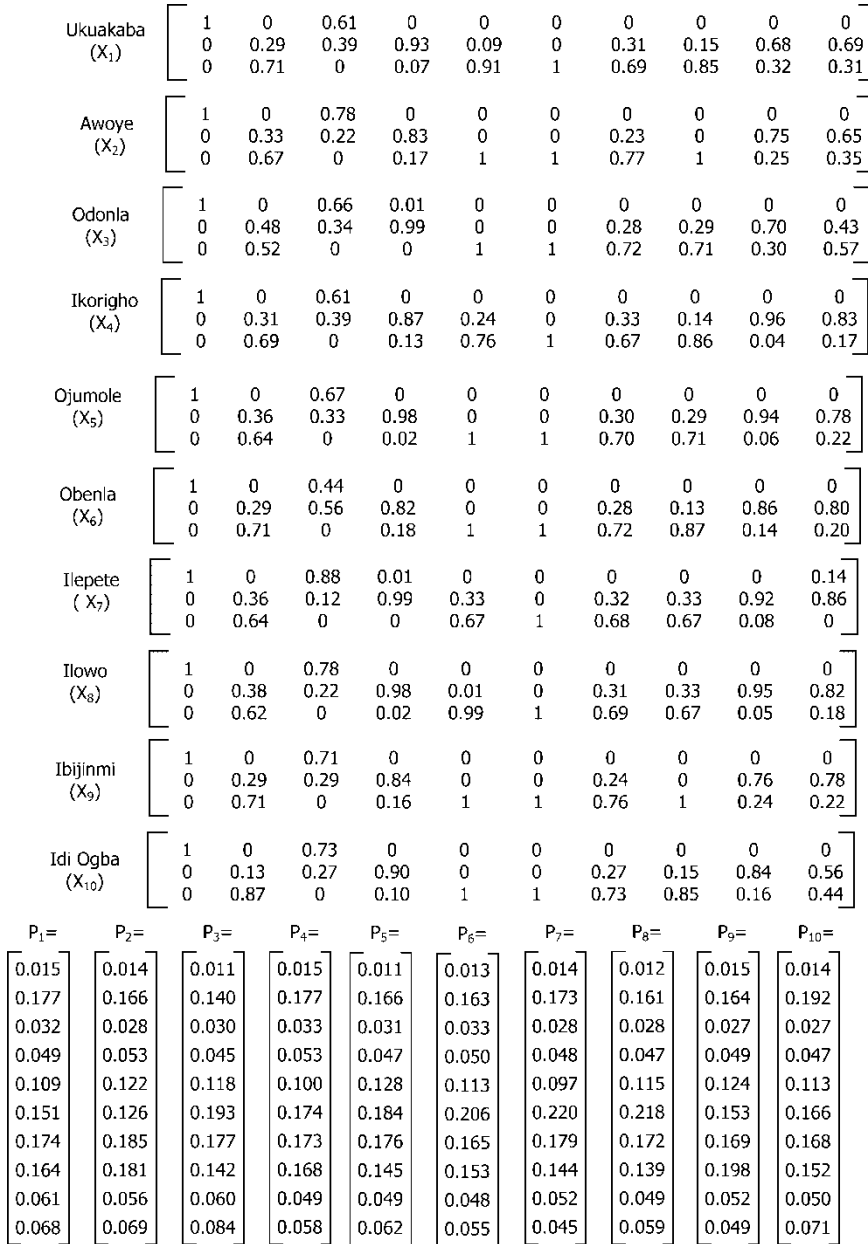


Figure 4. Fuzzy membership matrix  $X_k$  and corresponding weight matrix  $P_k$  for the ten sampling sites and ten metals in sediment samples. Each column of the  $X_k$  and row of  $P_k$  represents As, Cd, Cu, Cr, Fe, Mn, Ni, Pb, V and Zn, respectively.

(45.5%) indicates that the metals that could be observed in water samples have been demobilised by some biogeochemical reactions that favour their partitioning into the sediment phase while similar occurrence is likely in site 6.

The none observance of the decrease trend witnessed in water samples by the assessment of sediments indicates that the metal contamination sourced in site 1 is not localised into the sediment phase of site 1 but transported by the water column into the other sites which are then partitioned into the sediments of other sites by favourable reactions and conditions or kept in the

water column. Hence, crude oil exploration at site 1 is a major contamination source and of metals dispersion in the area with some contributions from domestic and commercial activities.

Thus, an introduction of cleaner technology for the oil exploration activities and treatment or control of domestic wastes discharge will help manage the metal contamination of this estuary and its resultant effects on the Atlantic Ocean.

#### 4. Conclusion

The coastal environment of Ondo State is found to be negatively stressed by metal generated mainly from crude oil exploration with some contributions from domestic wastes which are potential sources of hazard to the ecosystem of the neighbouring Ocean. The FCA has shown that Cd, Pb and Ni are priority metals that must be controlled in the coastal region. However, natural contributions of Fe and Mn from geological structures which may not be easily managed are notable. The effects of intrusion of saline water from the Atlantic Ocean and other reactions are also notable factors affecting the integrity of the coastal environment. Hence, proper management of the crude oil prospecting site is recommended as a means of remarkably improving the quality of the environment. Thus, there is a need to set as a priority the continuous monitoring and control of metal contamination in this estuary to safeguard the neighbouring ecosystem.

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