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Article

Distribution and Seasonal Variation of Arsenic and Iron in Different Grain Sizes of Sediments and Water from Hunki Ox-bow Lake, Awe LGA of Nasarawa State-Nigeria

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Abstract: This research aimed at determination of the levels and speciation of arsenic (As) and iron (Fe) in water and sediments from Hunki Ox-bow Lake in Awe L.G.A of Nasarawa State, using Atomic Absorption Spectrophotometer (AAS), during the dry and wet seasons. The mean concentration of As in water and whole (raw) sediment samples of both dry and wet seasons was lower than that of Fe. For both seasons, the baseline levels of As and Fe in water samples were 1.674 mg/L and 4.551 mg/L, respectively, which revealed that As content in water was higher than the WHO Guidelines for Drinking Water Quality. The baseline levels of As and Fe in sediment samples (mg/kg) were as follows: As (93.935) and Fe (264.429) which showed that As was higher than both Interim Sediment Quality Guidelines – Low of 20 mg/kg and Interim Sediment Quality Guidelines – High of 70 mg/kg. This study revealed that: concentration of As and Fe from sediments and water were generally higher in wet season than dry season, levels of As and Fe from sediments were higher than that of water, concentrations of As and Fe were more of natural than anthropogenic sources and the ecological risk indices evaluated evidenced As to be of greater ecological risk than Fe.

Keywords: Distribution; seasonal variation; arsenic; iron; sediments; grain sizes

1. Introduction

The growth in human population density and anthropogenic activities has led to increase in contamination of air, water and land/soil through misuse of environmental resources and improper disposal of wastes. The circulation and migration of metals and other pollutants in the natural environment are mainly linked to processes such as rock decay, volcanic eruptions, evaporation of oceans, forest fires and soil formation processes. The sources of anthropogenic contamination or pollution of the environment by heavy metals and other pollutants include different branches of industry, transport, municipal and domestic wastes, waste dumping sites, agrochemical residues and wastes used to fertilize soil. The pollutants from these sources are dispersed in the environment and they contaminate soil, water and air. They also (directly or indirectly through plants) get into human and animal bodies [1, 2].

The heavy metals pollution of aquatic ecosystems is often most obviously reflected in high metal levels in sediments than in water. Heavy metals are always present in aquatic ecosystems and redistribute among different components. Arsenic is an extremely toxic metalloid element. It is a key additive in rat poison, and with constant exposure, it is thought that arsenic may affect the chromosomes of humans and their health. For most people, the greatest source of exposure is from food with an average intake of about 50 μg per day. Exposure from air, water and soil are usually much smaller, but exposure from these media may become significant in areas of arsenic contamination [3]. Impairment of cellular respiration by the inhibition of several mitochondrial enzymes, and the uncoupling of oxidative phosphorylation is one of mechanisms by which arsenic exerts its toxic effect [3]. Toxicity of arsenic mostly results from its ability to interact with sulfhydryl groups of proteins and enzymes, and to substitute phosphorous in a variety of biochemical reactions [3]. Iron is an essential nutrient that is vital to the processes by which cells generate energy. Most of the body's iron is found in two proteins: hemoglobin in the red blood cells and myoglobin in the muscle cells. In both, iron helps accept, carry and then release oxygen. Enzymes involved in the making of amino acids, hormones and neurotransmitters require iron [3]. Iron also can be damaging when it accumulates in the body. In fact, iron is a problem nutrient for millions of people. Some people simply do not eat enough iron-containing foods to support their health optimally while others have so much iron that it threatens their well-being. Consuming dietary iron supplements may acutely poison young children [4]. Ingestion accounts for most of the toxic effects of iron because iron is absorbed rapidly in the gastrointestinal tract. The corrosive nature of iron seems to further increase the absorption [4]. Other sources of iron are drinking water, iron pipes, and cook wares. Target organs are the liver, cardiovascular system, and kidneys [4, 5]. There are four stages of acute iron toxicity, which is usually the result of an iron overdose. The first stage happens when iron is still present in the stomach and circulating in the blood. Symptoms include

abdominal pain, nausea, vomiting and diarrhea. The lining of the intestine can become damaged, leading to blood in the vomit or stool. Irritability and lethargy may also occur. If the toxicity is severe, rapid heartbeat, low blood pressure and rapid breathing may develop. As the body loses fluid and blood, a person may go into shock, in which the heart is unable to pump a sufficient amount of blood throughout the body. People who survive the first stage of acute iron toxicity may appear to improve for a while. This latent period is the second stage and can happen within 6 to 48 hours of an iron overdose. However, if the iron overdose was moderate or severe, symptoms will reappear as iron causes direct damage to the body's cells. Symptoms of the third stage of iron toxicity include low blood pressure and fever. Liver failure may occur, causing low blood sugar, excessive or prolonged bleeding and jaundice - yellowish eyes and skin. It is rare for people with such severe iron toxicity to survive, but those who do enter the fourth stage do not survive. During this stage, the intestines may become blocked due to scarring, which prevents fluids and food from moving through the digestive tract. Chronic iron toxicity, also known as iron overload, has a variety of causes. Hereditary hemochromatosis is an inherited condition that leads to abnormally increased absorption of iron from food. Iron overload may also be caused by repeated blood transfusions to treat anemia, excessive iron therapy or liver disease due to chronic hepatitis C or alcoholism. As excessive iron accumulates in the body, it may result in liver or heart failure, as well as severe diabetes. Heart failure can cause swelling of the legs, shortness of breath, trouble exercising, fatigue, fast or irregular heartbeat and nausea. Diabetes symptoms include frequent urination, increased thirst and hunger, fatigue, blurry vision, numbness or tingling in the arms or legs and slow wound healing [4, 5].

Speciation analysis is the process leading to the identification and determination of the different chemical and physical forms of an element existing in a sample [6]. It has been well reported that sediments serve as the largest pool of metals in aquatic environments [7, 8, 9]. Most analytical measurements deal with the total content of specific element in an analyzed sample. The accumulation of heavy metals in sediments from both natural and anthropogenic sources occurs in the same way, thus making it hard to identify and determine the origin of heavy metals present in the sediments [10]. Furthermore, the total concentration of metals often does not accurately represent their characteristics and toxicity. In order to overcome the above mentioned obstacles it is helpful to evaluate the individual fractions of the metals to fully understand their origin and potential environmental effects [11]. Therefore to get information on the origin and toxicity of As and Fe, it is necessary to determine not only the total content of the elements but also their individual fractions in Hunki Ox-bow Lake sediments. This will serve as a guide to help in various remediation processes and also to create awareness about their exposure to humans. As to the best of my Knowledge, there is no available data from the literature on speciation of heavy metals in Hunki Ox-bow Lake.

1.1. A Brief Description of the Study Area

The Hunki Ox-bow Lake (Longitude 8º 20' E and Latitude 9º 38' N) is located 30 km from Awe town, Headquarter of Awe Local Government Area and 130 km from Lafia, the Capital of Nasarawa State. The lake is like an Ox-bow, shaped in two arms with each of them measuring 6-7 km long and 70 km wide as shown in Figure 1 [12].

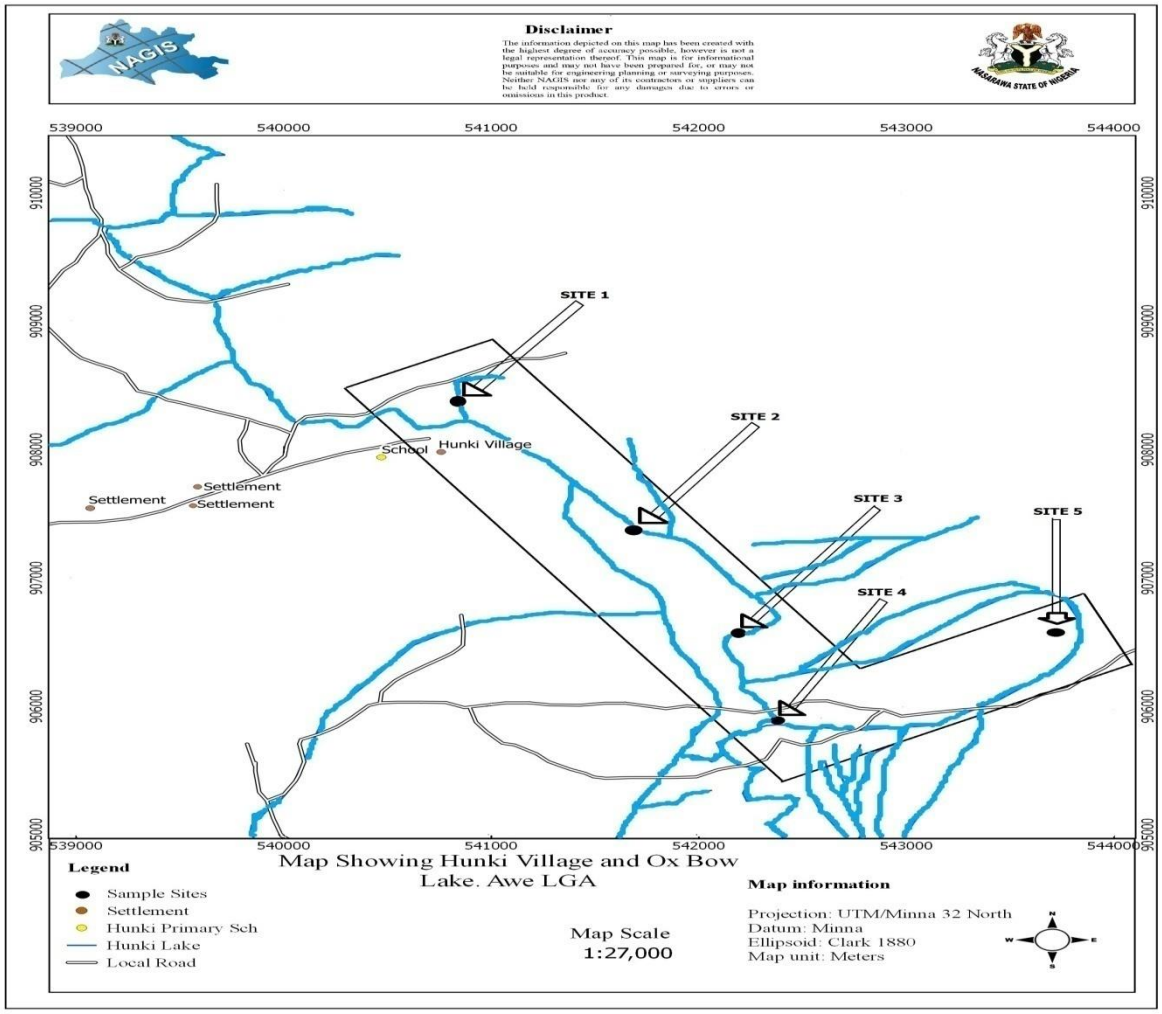

Figure 1: Map of Hunki Ox-bow Lake Showing the Sample Sites

2. Materials and Methods

2.1. Chemicals and Apparatus

The reagents used were of analytical grades obtained from Sigma-Aldrich, Germany and M & B LTD, England. The apparatus used for this research include: Oyster pH/Electrical Conductivity meter (Model: 34135A), a Handheld Pometer pH meter (Model: PH-009 (III), Noki lab centrifuge (TG-16) Bioevopeak hot plate and stirrer (Model: MGS-M8), Decent mechanical sieve shaker (Model: DSS200),

MRC digital orbital laboratory shaker (Model: TOS-4030RD), an atomic absorption spectrometer (ELICO PVT LTD, Model:SL168), Volumetric flasks (100 mL, 1000 mL), Decent laboratory oven (Model: DVM150), beakers (100 mL, 500 mL), 200 mL measuring cylinders, filter funnels, an agate mortar and pestle, sample bottles, petri-dishes, Whatman No. 42 Filter paper and electronic analytical balance (Gallenkamp 80).

2.2. Sampling Design, Sample Collection and Pretreatment

Five sampling sites at approximately 1 km intervals were mapped out along the Hunki Ox-bow Lake (Figure 1). Sediment sampling was carried out in dry season (3rd March, 2018) and wet season (15th September, 2018) from the five (5) sites using a stainless Eckman grab and placed in a pre-cleaned polythene bag. At each site, five samples of surface sediment (5 – 10 cm depth) were taken along transect across the lake. Composite samples were prepared on the spot by mixing equal amounts of five replicates from the same site. Samples from each of the five sites were placed in each polythene bag. The wet sediments (60.0 g each) was continuously stirred for 12 hours in order to homogenize the samples, and transferred into a mechanical shaker with set of standard sieves arranged from the largest to the lowest mesh size [13]. Based on the particle size, sediment samples were generally classified into five groups as follows: clay (<2 μm); silt (4–74 μm); fine sand (74–500 μm); medium sand (500–2,000 μm) and coarse sand (>2,000 μm) [14]. These were air-dried, ground with clean laboratory mortar and pestle, and stored in separate polythene bags until analysis. Some of the sediments samples from each sample site were not sieved but air-dried, ground and unwanted materials were removed. This represented the whole or raw sediments.

Water samples were also collected from the five sampling sites of approximately 1 km intervals at the depth of 30 cm below the surface using 2 litre High Density Polyethylene (HDPE) bottles with screw caps which were acid washed and rinsed with deionized water prior to the sampling. Water sampling was also carried out in dry season (3rd March, 2018) and wet season (15th September, 2018) at the same sampling points of the sediments. The samples were preserved at pH < 2 in situ with concentrated nitric acid [15].

2.3. Physicochemical Characterization of the Sediments

2.3.1. pH and electrical conductivity

The pH and electrical conductivity were measured by a glass electrode pH meter and electrical conductivity meter, respectively [16, 17].

2.3.2. Moisture content

A 10 g of wet sediment sample was weighed using a weighing balance and dried separately in an oven at 105 °C for 24 hours. The sample was removed, cooled in a desiccator and reweighed and percentage moisture content calculated according to the standard method [18, 19] as follows:

$$\text{Moisture (\%)} = \frac{weight\ loss\ (g)}{weight\ of\ sample\ (g)} \times 100 \qquad (1)$$

2.3.3. Organic matter and organic carbon contents

The organic matter content of the sediments was determined by Walkley and Black method [20] as modified by Nelson and Sommers [21].

2.3.4. Carbonate

The carbonate content of the sediments was determined by Rowell method [22] as used by Elfaki *et al*. [19].

2.3.5. Sediments grain size analysis

The sediment grain sizes were analyzed by a method used by Adiyiah and Kelderman [23].

2.4. Determination of Total As and Fe Levels in Sediments and Water

A 1.0 g sample of each ground whole (raw) sediment and the five particle sizes of sediment samples: clay (<2 μm); silt (4–74 μm); fine sand (74–500 μm); medium sand (500–2,000 μm) and coarse sand (>2,000 μm) were digested and the concentration of As and Fe, determined by a method used by Fabunmi *et al.* [24].

A 100 mL sample of water was placed was digested and the concentration of As and Fe determined by APHA method [15].

2.5. Sequential Extraction Procedure

A five-step Sequential Extraction Procedure (SEP) proposed by Tessier *et al*. [11] was used to extract As and Fe contained in the sediment particle fractions as shown in Figure 2.

After each extraction, the residue was washed by adding 20 mL of deionized water, shaken for 15 min and then centrifuged for 5 min. The supernatant liquid was discarded without any loss of the residue.

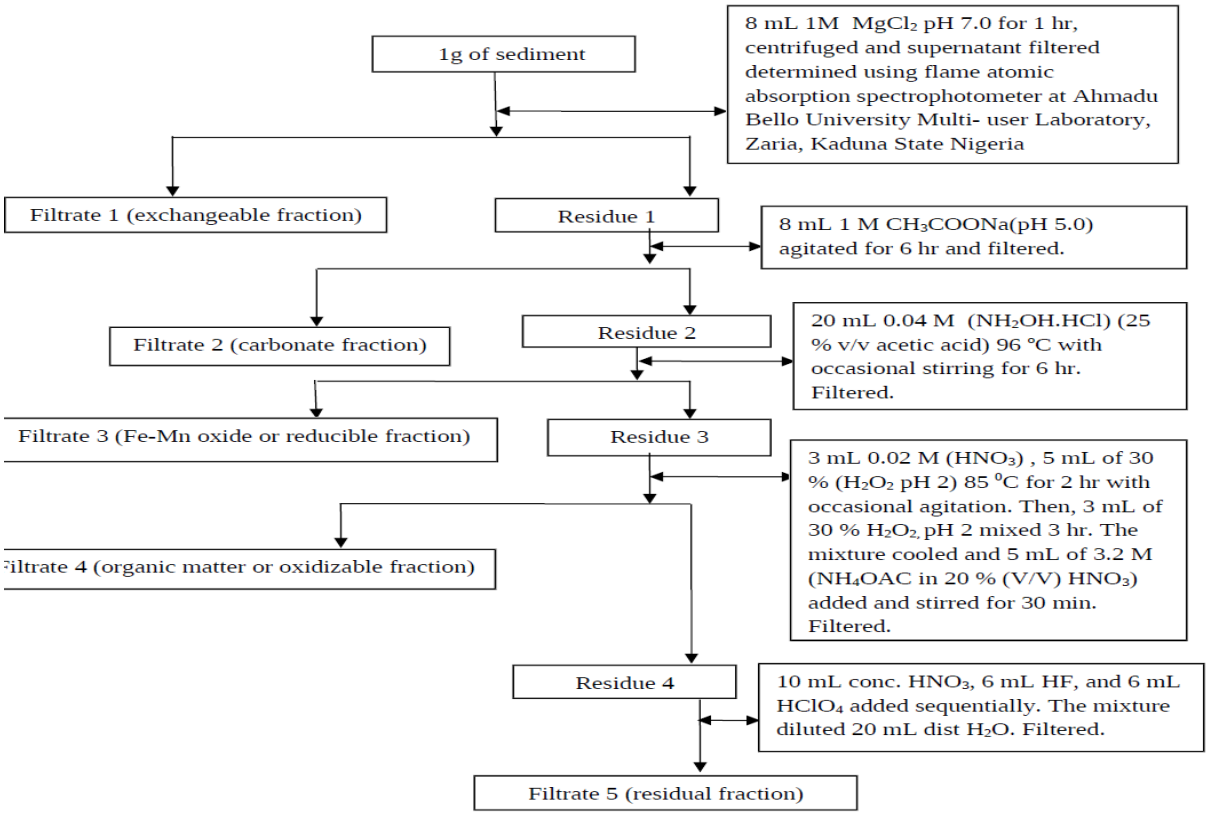

Figure 2: Sequential Extraction Procedure

2.6. Quality Assurance/Quality Control and Statistical Treatment of Data

The reliability of experimental results was obtained by replicate analysis of water and sediment samples. For metal analysis, standard solutions (1000 mg mL^{-1}) were used for calibration and standardization of instrument. Intermediate solutions were prepared by carefully dilution of stock standard solution (1000 mg mL^{-1}) with freshly prepared doubly distilled deionized water using micropipette.

Each analytical process/batch consisting of method blank and standard solutions were analyzed after every 10 samples to check instrument performance. An internal check on the sequential extraction method was performed by comparing the total amount of metal extracted by different reagents using sequential extraction procedure with the results of the pseudo total metal (total levels) concentration of different particle sizes of sediments [25]. The recovery of the sequential extraction procedure was evaluated as follows:

$$\% \, Recovery = \frac{C_{EF} + C_{MC} + C_{IM} + C_{OM} + C_{RF}}{C_{Pseudototal}} \times 100 \qquad (2)$$

where:

C_{EF} = Concentration of heavy metals bound to exchangeable fraction of sediments,

$C_{MC} =$ Concentration of heavy metals bound to carbonate fraction of sediments

$C_{IM} =$ Concentration of heavy metals bound to Fe – Mn oxides fraction of sediments

C_{OM} = Concentration of heavy metals bound to organic matter fraction of sediments

C_{RF} = Concentration of heavy metals bound to residual fraction of sediments

$C_{Pseudototal}$ = Concentration of total levels of heavy metals in different particle sizes of the sediments (clay, silt, fine sand, medium sand and coarse sand).

All statistical analyses were conducted using Statistical Package for Social Science, SPSS 26.0 for Windows as used by Tao *et al.* [17]. A two-way Analysis of Variance (ANOVA) was employed to test differences among various data sets. The Pearson correlation matrix was conducted according to the data distribution. Descriptive statistics which include range, mean and standard deviation were also performed.

3. Results and Discussion

3.1. Distribution of Grain Sizes of the Sediment Samples for Dry and Wet Seasons

The percentage mean of the distribution of grain sizes of the sediment samples for dry and wet seasons are given in Figure 3. The sediment samples of sample sites one (1) to five (5) had higher contents of the finer sizes than the larger ones. This evidenced the higher concentration of As and Fe in finer sediment grains with larger surface area than the larger ones with smaller surface area. The results were in line with works done by Lin et *al*. [14] and Xuming *et al.* [31].

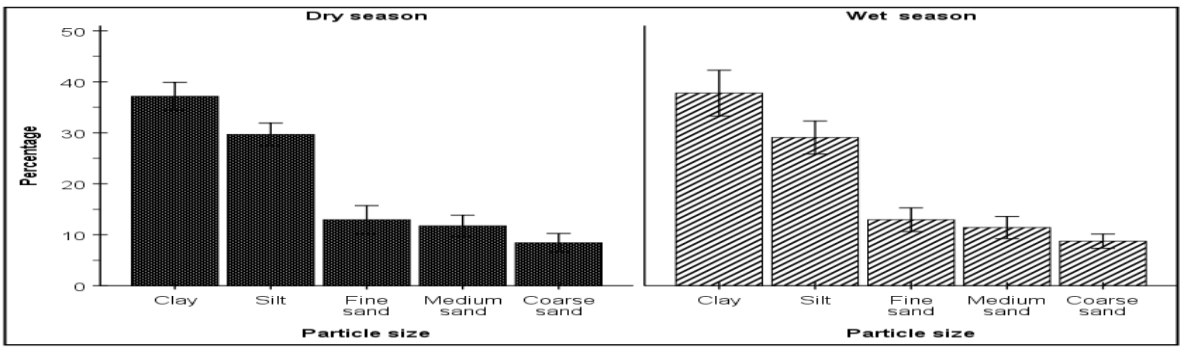

Figure 3: Distribution of particle Sizes of the Sediment Samples for Dry and Wet Seasons (%)

3.2. Physicochemical Properties of the Whole Sediment Samples for Dry and Wet Seasons

The physicochemical properties of the whole (raw) sediment samples for dry and wet seasons are as presented in Table 1. The pH of the whole sediment samples for both dry and wet seasons did not vary greatly from site to site and season to season ($P < 0.05$). The pH of the two seasons ranged from acidic to slightly acidic (4.69 – 5.63). In general, the pH values of the wet season whole sediment samples

were lower than that of dry season. There was no also much variation on the electrical conductivity of whole sediment samples for both dry and wet seasons but the wet season generally had higher values than the dry seasons ($P< 0.05$). Again, moisture content, organic carbon and organic matter of whole sediment samples for both dry and wet seasons did not vary much from site to site, and season to season ($P< 0.05$). Organic matter and pH are considered as two essential factors that influence metal species and distribution in sediments [17]. The wet season had higher percentages of electrical conductivity, moisture content, organic carbon and organic matter than the dry season sediments. The lower values of pH, and the higher electrical conductivity, moisture content, organic carbon and organic matter in wet season might be an indication that the wet season whole sediment samples should have higher mobility of the heavy metals than that of the dry season. The carbonate contents did not have much variation from site to site, but there was a greater variation between dry and wet seasons (11.60 – 15.00 % and 7.80 – 11.10 % for dry and wet seasons, respectively) ($P< 0.05$). Lower values of carbonate contents from sediments of wet season was also an indication that the wet season whole sediment samples might have higher mobility of the heavy metals than that of the dry season.

3.3. Physicochemical Properties of Different Grain Sizes of Sediment Samples for Dry and Wet Seasons

The mean values of the physicochemical properties of different grain sizes of sediment samples for dry and wet seasons are as presented in Table 2. The pH of different particle sizes of sediment samples followed the order of increase from finest to the largest sediment particle sizes for both dry and wet seasons, and this showed that the finer sediment particles sizes with larger surface area had lower pH values than the bigger particle sizes with smaller surface area. The electrical conductivity values of wet season sediment particle sizes had higher values than the dry season. An indication of more ions on wet season sediment particle sizes. The organic carbon and organic matter both followed the decrease order from finest to the largest sediment grain sizes for both dry and wet seasons. The carbonate content of the sediment samples followed an increase order from finest to the largest sediment particle sizes for both dry and wet seasons. This was an indication that the finer sediment particles sizes with larger surface area generally had higher values of organic carbon and organic matter than the bigger particle sizes with smaller surface area, but of the opposite for the carbonate contents for both dry and wet seasons. In general, electrical conductivity, organic carbon, organic matter of dry season sediments were lower than those of wet seasons, but the carbonate and the pH values were lower in wet season. These might have attributed to higher concentration of the heavy metals from sediments in wet seasons than the dry season.

Table 1: Physicochemical Properties of the Whole Sediment Samples for Dry and Wet Seasons (mean$\pm SD$ values, n = 3)

Sample Code	pH	Electrical Conductivity (µS/cm)	Moisture Content (%)	Organic Carbon (%)	Organic Matter (%)	Carbonate (%)
SA_1	5.65±1.31	90.00±3.55	63.90±4.98	4.99±0.58	8.60±1.99	15.00±1.98
SA_2	5.40±0.45	100.00±4.34	58.70±3.37	4.87±0.99	8.39±0.58	13.80±2.45
SA_3	5.47±2.42	90.00±5.24	54.50±5.12	4.71±1.05	8.12±0.45	14.60±2.99
SA_4	5.44±1.13	110.00±4.12	50.00±7.33	3.47±0.87	5.98±0.25	12.80±1.33
SA_5	5.40±2.33	100.00±3.87	66.70±4.88	4.15±0.69	7.15±0.58	11.60±1.34
SB_1	5.63±0.98	130.00±5.12	69.50±2.99	5.07±1.23	8.74±0.87	11.10±2.92
SB_2	5.10±1.62	110.00±5.89	78.50±3.98	4.95±0.59	8.53±0.94	9.90±1.55
SB_3	4.69±0.65	140.00±5.55	85.20±5.65	4.91±0.93	8.46±0.88	9.30±2.00
SB_4	5.52±1.39	110.00±5.87	85.20±4.15	4.83±0.77	8.33±0.75	8.10±1.55
SB_5	4.89±0.89	150.00±4.87	81.80±6.77	4.55±0.91	7.84±0.97	7.80±2.15

Key: S = Sediment Samples, A = Dry season, B = Wet season, 1-5 = Sample Sites 1 to 5.

Table 2: Physicochemical Properties of Different Grain Sizes of Sediment Samples for Dry and Wet Seasons

Particle sizes	pH	Electrical Conductivity (µS/cm)	Organic Carbon (%)	Organic Matter (%)	Carbonate (%)
Clay A	5.40±0.55	88.00±2.51	4.83±0.71	8.33±0.89	11.30±4.11
Silt A	5.55±0.67	90.00±3.29	4.67±0.59	8.05±2.44	11.90±3.22
Fine sand A	5.88±0.88	110.00±6.92	3.99±0.32	6.88±1.34	14.60±1.29
Medium sand A	6.20±0.97	90.00±6.85	2.95±0.12	5.07±0.75	15.80±2.59
Coarse sand A	6.79±0.78	84.00±7.22	2.47±0.22	4.26±0.86	16.20±3.26
Clay B	4.89±0.15	130.00±8.25	4.95±0.35	8.53±2.45	7.40±3.33
Silt B	5.20±1.05	131.00±5.28	4.87±0.19	8.39±3.21	7.65±1.58
Fine sand B	5.64±0.99	115.00±6.34	4.27±0.45	7.36±1.89	9.40±2.95
Medium sand B	5.93±0.28	120.00±4.24	3.11±0.15	5.36±0.47	10.30±2.48
Coarse sand B	6.11±0.53	124.00±5.11	2.91±0.27	5.02±0.65	11.60±3.19

Key: A = Dry season, B = Wet season. Values are mean$\pm SD$ of the five sites (n = 5)

3.4. Total As and Fe Levels in Water and Whole Sediments for Dry and Wet Seasons

The results of the mean of total As and Fe levels in the whole sediments and water for dry season are as presented in Table 3. It can be depicted from Table 3 that levels of all the As and Fe in sediments were higher than those of the water samples from Hunki Ox-bow Lake irrespective of season. This was in agreement with the fact that sediments may act as large sinks or reservoirs of contamination [32, 8, 9, 33]. In general, Fe had the higher concentration of 2.799 mg/L and 296.584 mg/kg in both water and sediment samples, respectively. In water samples, As was detected in all sample sites. Arsenic levels in water samples were all above the World Health Organization Guidelines for Drinking Water Quality (WHO GDWQ) of 0.01 mg/L [34]. The levels of arsenic above 0.01 mg/L may be carcinogenic and teratogenic to humans. It may also have other effects in man which include peripheral arteriosclerosis (black foot disease), peripheral neuritis resulting in motor and sensory paralysis of the nerves extremities and so on [35, 36]. Iron has no specified WHO GDWQ but at levels above 0.3 mg/L, it stains laundry and plumbing fixtures, develop turbidity and colour [34]. The levels of Fe in water samples of this study were all above 0.3 mg/L which can lead to such effects.

The results of total As and Fe in whole sediments and water samples for wet season are as presented in Table 3. Arsenic and iron were detected in all the water samples of WB_1 to WB_5. Arsenic levels in water samples were all above the World Health Organization, WHO, Guidelines for Drinking Water Quality, GDWQ value of 0.01 mg/L [34], and this may result to earlier mentioned effects. As mentioned earlier, Fe has no specified WHO GDWQ but at concentrations above 0.3 mg/L, it stains laundry and plumbing fixtures, develop turbidity and colour [34]. The levels of Fe in all the water samples were all above 0.3 mg/L which can cause the above effects.

Agency for Toxic Substance and Disease Registry (ATSDR) had set regulatory guidelines for heavy metals in sediments. Interim sediment quality guidelines – low (trigger value) have the following concentrations: 20 and not applicable to Fe, respectively. Interim sediment quality guidelines – high have the following concentrations: 70 mg/kg for As and not applicable to iron, respectively [37, 4]. In this present research, the mean levels of arsenic from whole sediments for dry and wet seasons were higher than the interim sediment quality guidelines – low (trigger value) of 20 mg/kg. Sites one to four mean levels of arsenic for dry season were lower than interim sediment quality guidelines – high, but site five of dry season and all sites of wet season were all higher than interim sediment quality guidelines – high of 70 mg/kg. Interim sediment quality guidelines – low refers to probable effects concentrations below which biological effects would rarely occur. Interim sediment quality guidelines – high means probable effects concentrations below which biological effects would possibly occur. Concentrations above these values for the affected sediments in this study represent a probable-effects range within which biological effects would be expected to occur frequently [37].

Based on the mean concentrations of As and Fe in water and whole (raw) sediments of all sample sites for dry and wet seasons, their baseline levels were calculated. The baseline levels of As and Fe in water samples (mg/L) were as follows: As (1.674) and Fe (4.551). This revealed that baseline levels of As in water samples was higher than the WHO GDWQ [34] of 0.010 mg/L. Iron was not specified in WHO GDWQ [34]. The baseline levels of As and Fe in sediment samples (mg/kg) were as follows: As (93.935) and Fe (264.429). The baseline levels of heavy metals in sediment samples (mg/kg) showed that As was higher than both Interim Sediment Quality Guidelines – Low (trigger value, 20 mg/kg), ISQG-L and Interim Sediment Quality Guidelines – High, ISQG-H (70 mg/kg), and this can lead to biological effects on organisms [37]. The ISQG-L and ISQG-H was not specified for Fe. The mean concentration of As and Fe from both water and whole (raw) sediment samples for all sample sites of both dry and wet seasons was of the decrease order: Fe > As.

3.5. Total As and Fe Levels in the Five Sediment Grain Sizes of Dry and Wet Seasons

The mean total As and Fe levels from the five sediment grain sizes of the five sites for dry and wet seasons (mg/kg) are as presented in Table 3. The mean total As and Fe levels from the five sediment

grain sizes had the following decrease order for both dry and wet seasons: clay > silt > fine sand > medium sand >coarse sand. The higher concentration of heavy metals on finer sediment grain sizes than the bigger particle sizes was probably due to the fact that finer sediment particles have larger surface areas than the bigger particle sizes with smaller surface areas. This was in agreement with works done by Lin *et al.* [14] who researched on assessment of sediment toxicity by metal speciation in different grain fractions of river sediment and Xuming *et al.* [31] who investigated the speciation of heavy metals in different grain sizes of Jiaozhou Bay sediments, and contrary to the work done by Tao *et al*. [17] who researched on the distribution and bioavailability of heavy metals in different particle-size fractions of sediments in Taihu Lake, China, which did not follow a particular pattern of distribution of heavy metals on the particle sizes of sediments.

3.6. As and Fe Concentration in Different Sediment Grain Sizes of the Sum of Extraction Steps

The mean of sum of extraction steps (exchangeable fraction, bound to carbonates, Fe-Mn oxides bound, organic matter fraction and residual fraction) of two- way ANOVA and its post-hoc Tukey's test ($P < 0.05$) for both dry and wet seasons of all sample sites are given in Table 4. The Tukey HSD (Honestly Significant Difference" or Honest Significant Difference") test is a statistical tool used to determine if the relationship between two sets of data is statistically significant – that is, whether there is a strong possibility that an observed numerical change in one value is causally related to an observed change in another value. The mean concentrations of As and Fe based on sum of speciation extraction steps were all significantly higher in the wet season than the dry season ($P < 0.05$). There was also a significant difference ($P < 0.05$) on the mean concentration of As and Fe among the five sediment grain sizes, and was of the following decrease order: clay > silt > fine sand > medium sand > coarse sand. Post-hoc Tukey's test revealed that for both dry and wet seasons, there was a significant difference between the mean concentration of As on clay and coarse sand grain sizes. There was also a bit significant difference between coarse sand and silt, fine sand and medium sand on the mean concentration of As. The mean concentration of Fe from post-hoc Tukey's test revealed that there was a significant difference between clay and coarse sand grain sizes of the sediments, but there was no significant difference amongst silt, fine sand, and medium sand for both dry and wet seasons.

3.7. Sum of Extraction Steps, Pseudo-total and Percentage Recovery of Heavy Metal Concentration in Different Sediment Grain Sizes

The sum of extraction steps (mg/kg), pseudo-total (mg/kg) and percentage recovery of heavy metal concentration in different sediment grain sizes (mean of all sites) are as presented in Table 5. The results of the sum of five-step sequential extraction procedure used in this research as shown in Table 5 were generally in good agreement with the pseudo total digestion results of all sites, with acceptable

recoveries ranging from 92.86 – 99.85, 92.31– 99.87, 91.67 – 100.00, 90.00 – 100.00 and 90.48 - 100.00 % for clay, silt, fine sand, medium sand and coarse sand sediment grain sizes, respectively for As and Fe of both seasons. This therefore indicated that the five-step Sequential Extraction Procedure (SEP) proposed by Tessier *et al*. [11] used in this research was found reliable and can be reproduced.

Table 3: Total As and Fe Levels in Water (mg/L), Whole Sediments and Different Grain Sizes of Sediments (mg/kg) for Dry and Wet Seasons (mean values)

Sample Code	As	Fe	Sample Code	As	Fe	Grain sizes	As	Fe
WA_1	0.747	2.799	WB_1	2.617	7.423	Clay A	26.100±3.76	95.336±6.11
WA_2	0.773	BDL	WB_2	2.490	7.791	Silt A	21.103±2.91	58.684±6.05
WA_3	0.667	0.988	WB_3	2.681	8.098	Fine sand A	17.934±1.33	39.617±3.12
WA_4	0.640	BDL	WB_4	2.553	8.712	Medium sand A	16.132±1.45	21.421±0.95
WA_5	0.640	0.738	WB_5	2.936	8.957	Coarse sand A	11.414±3.13	8.330±0.58
TMA_1	44.783	243.044	TMB_1	94.400	453.927	Clay B	49.961±4.98	217.220±0.72
TMA_2	65.348	240.020	TMB_2	117.800	360.578	Silt B	41.102±1.98	195.113±7.29
TMA_3	23.913	242.499	TMB_3	104.133	92.552	Fine sand B	36.854±3.45	170.121±5.29
TMA_4	42.391	296.584	TMB_4	159.600	65.546	Medium sand B	33.152±2.54	151.982±6.93
TMA_5	130.850	243.736	TMB_5	156.133	405.807	Coarse sand B	27.448±3.11	111.043±10.12
*WHO (2017)	0.010	NS	*WHO (2017)	0.010	NS			
ISQG-LOW	20.000	NS	ISQG-LOW	20.000	NS			
ISQG-HIGH	70.00	NS	ISQG-HIGH	70.000	NS			

Key: W = Water Samples, TM = Total Metal Levels of whole sediments, A = Dry season, B = wet season, 1-5 = Sample Sites 1 to 5. BDL = Below Detection Limits. NS = Not Specified, *WHO (GDWQ) = WHO Guidelines for Drinking Water Quality (2017), ISQG = Interim Sediment Quality Guidelines (ANZECC AND ARMCANZ, 2000; ATSDR, 2004).

Table 4: Heavy Metal Concentration in Different Sediment Particle Sizes of the Sum of Extraction Steps (mg/kg)

		Particle sizes										
		Clay	Silt	Fine sand	Medium sand	Coarse						
HM	Season	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	F^1	F^2	F^3	P^1	P^2	P^3
As	WS	49.24 ± 11.96^a	40.22 ± 13.84^{ab}	36.43 ± 9.52^{ab}	32.94 ± 8.13^{ab}	26.85 ± 4.37^b	38.93	4.11	0.21	**<0.001**	**0.003**	0.933
	DS	25.50 ± 2.18^a	20.98 ± 2.63^{ab}	17.78 ± 1.08^{ab}	15.90 ± 1.39^{ab}	11.30 ± 1.50^b						
Fe	WS	216.90 ± 22.54^a	194.86 ± 29.59^{ab}	169.79 ± 16.56^{ab}	151.66 ± 18.55^{ab}	110.73 ± 12.01^b	48.35	3.38	0.11	**<0.001**	**<0.01**	0.979
	DS	94.02 ± 8.03^a	58.41 ± 8.48^{ab}	39.58 ± 9.77^{ab}	21.34 ± 4.47^{ab}	8.24 ± 2.87^b						

WS = wet season, DS = dry season, HM = heavy metals. Values with the same superscripts are statistically significant at P <0.05.
F^1 = F-value for season, F^2 = F-value for particle size, F^3 = F-value for interaction between season and particle, P^1, P^2 and P^3 corresponding *P-values* for F1, F2 and F3 respectively. Significant difference is expressed in boldface. The metal concentration results are the sum of extraction steps and mean values of all site

Table 5: Sum of Extraction Steps (mg/kg), Pseudo-total (mg/kg) and Percentage Recovery of Heavy Metal Concentration in Different Sediment Particle Sizes (Mean of all sites)

	Particle sizes/ Seasons	**Clay**			**Silt**			**Fine sand**			**Medium sand**			**Coarse**		
HM		Sum of ES	Pseudo-total	% R	Sum of ES	Pseudo-total	% R	Sum of ES	Pseudo-total	% R	Sum of ES	Pseudo-total	% R	Sum of ES	Pseudo-total	% R
As	Dry	25.50	26.10	97.70	20.98	21.10	99.43	17.78	17.93	99.16	15.90	16.13	98.57	11.30	11.41	99.04
	Wet	49.24	49.86	98.56	40.22	41.10	98.10	36.43	36.85	98.86	32.94	33.15	99.37	26.85	27.45	97.81
Fe	Dry	94.02	95.34	98.62	58.41	58.68	99.54	39.58	39.61	99.92	21.34	21.42	99.62	8.24	8.33	98.92
	Wet	216.90	217.22	99.85	194.86	195.11	99.87	169.79	170.12	99.81	151.66	151.98	99.79	110.73	111.04	99.72

Key: HM = Heavy Metals, ES = Extraction Steps, % R = Percentage Recovery.

3.8. Correlation between Physicochemical Properties and Phase Distribution of As and Fe Metals in the Sediments for Dry and Wet Seasons

The Pearson correlation matrix between sediments physicochemical properties (pH, electrical conductivity, EC, Organic Carbon, OC, Organic Matter, OM and carbonates, CO_3^{2-}) and different speciation phases (exchangeable fraction, metals bound to carbonates, Fe-Mn oxides bound, organic matter fraction and residual fraction) of As and Fe for dry and wet seasons are given in Tables 6 to 10. In exchangeable fraction, there was no correlation between As and the physicochemical properties for both seasons as shown in Table 6. This indicated that the source of As in exchangeable fraction had nothing to do with physicochemical properties from sediments of both seasons. For dry season, there was a positive significant correlation between Fe and OC ($P < 0.01$, 1.00)/OM ($P < 0.01$, r = 1.00).

The correlation matrix between sediments physicochemical properties and metals bound to carbonate fraction of As and Fe for dry and wet seasons are given in Table 7. In carbonate fraction for dry season, there was no statistical correlation between As and physicochemical properties of sediments. There was a positive correlation between Fe and EC and OC /OM ($P < 0.01$, r = 1.00) respectively. Therefore, EC and OC /OM influence the increase Fe on the sediments. Furthermore, in wet season, the carbonate fraction of As ($P < 0.01$, r = -0.97) had a negative correlation with pH ($P < 0.05$, r = -0.01) respectively. There was a positive significant correlation between As and OC(As: $P < 0.01$, r = 0.96) /OM (As: $P < 0.01$, r = 0.97). There was no correlation between Fe and carbonate fraction and physicochemical properties of the sediments in wet season. Iron might have been sourced differently.

The correlation matrix between sediments physicochemical properties and iron-manganese oxide fraction of As and Fe for dry and wet seasons are as presented Table 8. The iron-manganese oxide fraction of As from sediments had a positive significant correlation with OC /OM; As-OC ($P < 0.01$, r = 0.96) /OM ($P < 0.01$, r = 0.97); but a negative significant correlation with the CO_3^{2-} (As: $P < 0.01$, r = 0.999). There was also a positive significant correlation between Fe and pH ($P < 0.05$, r = -0.89), OC($P < 0.01$, r = 0.92) and OM($P < 0.01$, r = 0.97) respectively ($P < 0.01$, r = 1.00), but a negative significant correlation with CO_3^{2-}($P < 0.05$, r = -0.92). For wet season, there was a positive significant correlation between As iron-manganese oxide fraction and OC/OM; As-OC($P < 0.05$, r = 0.93)/OM($P < 0.05$, r = 0.94). but had a negative significant correlation with pH (As: $P < 0.01$, r = -0.97) There was no correlation of iron-manganese oxide fraction of Fe and sediments physicochemical properties in wet season, and therefore were sourced differently.

Correlation matrix between sediments physicochemical properties and organic matter fraction of As and Fe for dry and wet seasons were as shown in Table 9. In dry season, there was a positive correlation between As and Fe organic matter fraction and OC/OM with the following values: As: $P < 0.05$, r = 0.89 and Fe: $P < 0.05$, r = 0.92 respectively. Iron had a positive significant correlation with pH

(Fe: $P < 0.05$, r = 0.89). There was a positive significant correlation between As organic matter fraction and (pH, OC, OM) with the following values pH ($P < 0.05$, r = 0.94), OC/OM($P < 0.05$, r = 0.95), but with a negative correlation with CO_3^{2-}($P < 0.05$, r = -0.92) in wet season. There was a positive significant correlation between Fe organic matter fraction and OC/OM ($P < 0.05$, r = 0.92), but significantly correlated negatively with both pH ($P < 0.01$, r = -0.98) and CO_3^{2-}($P < 0.01$, r = -0.97) in wet season.

Correlation matrix between sediments physicochemical properties and residual fraction of As and Fe for dry and wet seasons are given in Table 10. The residual fraction of Fe had positive significant correlation with OC/OM ($P < 0.05$, r = 0.89), but significantly correlated negatively with CO_3^{2-} ($P < 0.05$, r = -0.95). There was no correlation between As residual fractions and physicochemical properties of the sediments. This showed that As might have been sourced differently. In wet season, there was a negative significant correlation between As residual fraction and pH ($P < 0.05$, r = -0.93), but did not correlate with other physicochemical properties of the sediments. There was a positive significant correlation between Fe residual fraction and OC/OM (Fe: $P < 0.05$, r = 0.93) in wet season but correlated negatively with both pH ($P < 0.01$, r = -0.91) and CO_3^{2-} ($P < 0.05$, r = -0.96).

Table 6: Correlation between Sediments Physicochemical Properties and Exchangeable Fraction of the As and Fe for Dry and Wet Seasons

	Dry Season						Wet Season					
SPP	pH	EC	OC	OM	CO_3^{2-}	As	pH	EC	OC	OM	CO_3^{2-}	As
pH	-	-0.31	-0.90^b	-0.93^b	0.87	-0.94	-	-0.71	-0.97^a	-0.95^a	0.98^a	-0.28
EC		-	0.34	0.35	-0.00	-0.36		-	0.54	0.48	-0.59	-0.45
OC			-	1.00^a	-0.93^b	0.64			-	1.00^a	-1.00^a	0.51
OM				-	-0.94^b	0.74				-	-0.99^a	0.56
CO_3^{2-}					-	0.76					-	-0.45
As						-						-
pH	-	-0.31	-0.90^b	-0.93^b	0.87	-1.00^b	-	-0.71	-0.97^b	-0.95^a	0.98^b	-0.96
EC		-	0.36	0.35	-0.00	-1.00^b		-	0.54	0.48	-0.59	0.87
OC			-	1.00^a	-0.93^b	1.00^b			-	1.00^a	-1.00^a	0.92
OM				-	0.94^b	1.00^b				-	-0.99^a	0.96
CO_3^{2-}					-	-1.00^b					-	-0.96
Fe						-						-

Table 7: Correlation between Sediments Physicochemical Properties and Metals Bound to Carbonate Fraction of the As and Fe for Dry and Wet Seasons

	Dry Season						Wet Season					
SPP	pH	EC	OC	OM	CO_3^{2-}	As	pH	EC	OC	OM	CO_3^{2-}	As
pH	-	-0.18	-0.99[b]	-0.99[b]	0.93[a]	-0.77	-	-0.61	-0.96[a]	-0.95[a]	0.90[a]	-0.96[b]
EC		-	0.14	0.15	0.82	-0.04		-	0.51	0.52	-0.50	0.66
OC			-	0.99[b]	-0.97[b]	0.79			-	1.00[b]	-0.86[a]	0.96[a]
OM				-	-0.97[b]	0.76				-	-0.89[a]	0.97[b]
CO_3^{2-}					-	-0.83					-	-0.94[a]
As						-						-
SPP	pH	EC	OC	OM	CO_3^{2-}	Fe	pH	EC	OC	OM	CO_3^{2-}	Fe
pH	-	-0.18	-0.99[b]	-0.99[b]	0.93[a]	-1.00[b]	-	-0.61	-0.96[a]	-0.95[a]	0.90[a]	0.61
EC		-	0.14	0.15	0.08	1.00[b]		-	0.51	0.52	-0.50	0.14
OC			-	0.99[b]	-0.97[b]	1.00[b]			-	1.00[b]	-0.86[a]	-0.34
OM				-	-0.96[b]	1.00[b]				-	-0.89[a]	-0.34
CO_3^{2-}					-	-1.00[b]					-	-0.32
Fe						-						-

KEY: SPP = Sediment Physicochemical Properties, EC = Electrical Conductivity, OC = Organic Carbon, OM = Organic Matter bound, CO_3^{2-} = Carbonates, [a]Correlation is significant at the 0.05 level (2-tailed), [b]Correlation is significant at the 0.01 level (2-tailed)

Table 8: Correlation between Sediments Physicochemical Properties and Iron-Manganese Oxide Fraction of the As and Fe for Dry and Wet Seasons

	Dry Season						Wet Season					
SPP	pH	EC	OC	OM	CO_3^{2-}	As	pH	EC	OC	OM	CO_3^{2-}	As
pH	-	-0.27	-0.90[b]	-0.96[b]	0.92[a]	-0.92	-	-0.56	-0.93[a]	-0.94[a]	0.98[b]	-0.97[b]
EC		-	0.22	0.19	0.04	-0.03		-	0.45	0.48	-0.57	0.71
OC			-	1.00[b]	-0.96[b]	0.96[b]			-	1.00[b]	-0.97[b]	0.93[a]
OM				-	-0.97[b]	0.97[b]				-	-0.97[b]	0.94[a]
CO_3^{2-}					-	-0.99[b]					-	-0.98[b]
As						-						-
pH	-	-0.27	-0.97[b]	-0.96[b]	0.92[a]	0.89[a]	-	-0.56	-0.93[a]	-0.94[a]	0.98[b]	-0.77
EC		-	0.22	0.19	0.04	0.26		-	0.45	0.48	-0.57	0.39
OC			-	1.00[b]	-0.96[b]	0.92[b]			-	1.00[b]	-0.97[b]	0.54
OM				-	-0.97[b]	0.97[b]				-	-0.97[b]	0.58
CO_3^{2-}					-	-0.92[a]					-	-0.62
Fe						-						-

Table 9: Correlation between Sediments Physicochemical Properties and Organic Matter Fraction of the As and Fe for Dry and Wet Seasons

	Dry Season						Wet Season					
SPP	pH	EC	OC	OM	CO_3^{2-}	As	pH	EC	OC	OM	CO_3^{2-}	As
pH	-	-0.30	-0.91[a]	-0.92[a]	0.92[a]	-0. 81	-	-0.66	-0.97[b]	-0.97[b]	0.99[b]	-0.94[a]
EC		-	0.29	0.32	-0.11	0.28		-	0.50	0.49	-0.59	-0.40
OC			-	1.00[b]	-0.98[b]	0.89[a]			-	1.00[b]	-0.96[b]	0.95[a]
OM				-	-0.97[b]	0.89[a]				-	-0.96[b]	0.95[a]
CO_3^{2-}					-	-0.81					-	-0.92[a]
As						-						-
pH	-	-0.30	-0.91[a]	-0.92[a]	0.92[a]	0. 89[a]	-	-0.66	-0.97[b]	-0.97[b]	0.99[b]	-0.98[b]
EC		-	0.29	0.32	-0.11	0.01		-	0.50	0.49	-0.59	0.66
OC			-	1.00[b]	-0.98[b]	0.92[a]			-	1.00[b]	-0.96[b]	0.92[a]
OM				-	-0.97[b]	0.92[a]				-	-0.96[b]	0.92[a]
CO_3^{2-}					-	-0.97[b]					-	-0.97[b]
Fe						-						-

KEY SPP = Sediment Physicochemical Properties, EC = Electrical Conductivity, OC = Organic Carbon, OM = Organic Matter bound, CO_3^{2-} = Carbonates, [a]Correlation is significant at the 0.05 level (2-tailed), [b]Correlation is significant at the 0.01 level (2-tailed).

Table 10: Correlation between Sediments Physicochemical Properties and Residual Fraction of the As and Fe for Dry and Wet Seasons

	Dry Season						Wet Season					
SPP	pH	EC	OC	OM	CO_3^{2-}	As	pH	EC	OC	OM	CO_3^{2-}	As
pH	-	-0.05	-0.99[b]	-0.99[b]	0.89[a]	-0.63	-	-0.65	-0.92[a]	-0.91[a]	0.93[a]	-0.93[a]
EC		-	0.05	0.03	0.34	-0.41		-	0.49	0.50	-0.57	0.61
OC			-	1.00[a]	-0.90[a]	0.68			-	1.00[a]	-0.96[b]	0.74
OM				-	-0.91[a]	0.68				-	-0.96[b]	0.74
CO_3^{2-}					-	-0.81					-	-0.84
As						-						-
pH	-	-0.05	-0.99[b]	-0.99[b]	0.89[a]	-0.86	-	-0.65	-0.92[a]	-0.91[a]	0.93[a]	-0.80
EC		-	0.05	0.03	0.34	-0.35		-	0.49	0.50	-0.57	0.37
OC			-	1.00[a]	-0.90[a]	0.89[a]			-	1.00[a]	-0.96[b]	0.93[a]
OM				-	-0.91[a]	0.89[a]				-	-0.96[b]	0.93[a]
CO_3^{2-}					-	-0.95[a]					-	-0.96[a]
Fe						-						-

KEY: SPP = Sediment Physicochemical Properties, EC = Electrical Conductivity, OC = Organic Carbon, OM = Organic Matter bound, CO_3^{2-} = Carbonates, [a]Correlation is significant at the 0.05 level (2-tailed), [b]Correlation is significant at the 0.01 level (2-tailed).

3.9. Proportion of As and Fe Bound to Different Sediment Speciation Phases of the Five Sample Sites for both Dry and Wet Seasons

The mean percentage proportions of As and Fe bound to different sediment speciation phases for sample sites one to five of both dry and wet seasons are given in Figure 4. Arsenic and iron were found in the five extracts of the sequential procedure. A large concentration of metals introduced by human activities is usually present in the exchangeable fraction and the carbonates fraction - the first two steps. These steps can be assumed the fractions of metals that are most liable to be released from sediment into water column [38]. Metals bound to the easily reducible phase (Fe-Mn oxides) and to organic matter may be better held by a scavenging effect (i.e., this fraction acts as a sink of metals) [38]. Generally, the first four steps (exchangeable, carbonates, Fe-Mn oxides and organic matter fractions) are regarded as non-residual fractions, while the fifth step is known as residual fraction. Metals in the residual fraction are strongly bound to solid matter, and originate mainly from natural sources [38]. The mean percentage proportions of As and Fe bound to different extraction phases (Sequential Extraction Steps, SEP) of studied sediments for sample sites one to five of both dry and wet seasons were as follows:

4.9.1. Arsenic

The partitioning of various fractions of As from sediments in dry season was similar to that of wet season for all sample sites (Figures 4a and b). The As dominated the residual fraction more than other fractions with the following range: 50.37 – 70.5 % of the total percentage for dry season, and 57.54 – 61.03 % of As total percentage for wet season. This revealed that the As contents from the sediments of this study was more of geochemical (lithogenic) background rather than the anthropogenic sources. Exchangeable fraction accounted for 2.15 – 9.75 % of As total percentage for dry season, and 9.91 – 12.23 % of As total percentage for wet season. Carbonates fraction accounted for 3.08 – 11.89 of As total percentage for dry season, and 4.74

– 10.16 % of As total percentage for wet season. The Fe – Mn oxides fraction of As had 6.69 – 11.11 % for dry season, and 4.91 – 9.32 % for wet season. The organic matter fraction of As from sediments was relatively high in both seasons. The organic matter fraction of As ranged from 8.25 – 21.98 % for dry season, and 13.03 – 16.36 % of As total percentage for wet season. This was similar to work done by Xuming *et al*. [31] on Jiaozhou Bay and that of Bungala *et al*. [39] on coastal marine area of Tanzania which had more dominance of As on the residual fraction than other fractions. However, a research work by Wang *et al*. [40] on a Lake had more As contents on the non-residual fractions than the residual fraction (19.2 % of the total fraction) due to intensive industrial and urban activities around the Lake. Despite the fact that residual fraction was the dominant for As, the sum of extraction steps one and two, usually easily mobilized to the water column accounted for a bit more than 20 % in sample site one of dry season (21.64 %) and sample site three of wet season (22.39 %). The non-residual fraction which consists of the first four sequential extraction steps (exchangeable, carbonates, Fe – Mn oxides and organic matter fractions) amounted to a bit more than 30 % of the percentage total of As except sample site five which was a bit lower. This was probably due the fact that herbicides, pesticides and phosphate fertilizers applied to crops contained arsenic that enhanced a relatively significant amount of it on sediments [31].

3.9.2. Iron

Iron dominated mostly the residual fraction, followed by the organic matter fraction in both dry and wet seasons (Figures 4c and d). Iron had the following ranges for each of the sequential extraction steps: exchangeable fraction (0.57 – 6.95%), carbonates fraction (0.55 – 6.71 %), Fe - Mn oxides fraction (8.08 – 17.29 %), organic matter fraction (20.52 – 31.36 %), residual fraction (48.96 – 63.31 %) for dry season, and exchangeable fraction (1.26 – 3.22 %), carbonates fraction (2.46 – 7.26 %), Fe - Mn oxides fraction (3.13 – 13.49 %), organic matter fraction (21.87 – 29.99 %), residual fraction (46.02 – 69.22 %) for wet season. This was similar to work done by Malsiu *et al*. [41] on Badovci Lake where Fe dominated more of the residual fraction (> 63 %) than other fractions. Even though the residual fraction of Fe was more than the non-residual fraction for both seasons, the later had more than 30 % fraction for both season. This revealed that the fraction of Fe from sediments was dominantly lithogenic and to some extent anthropogenic origin.

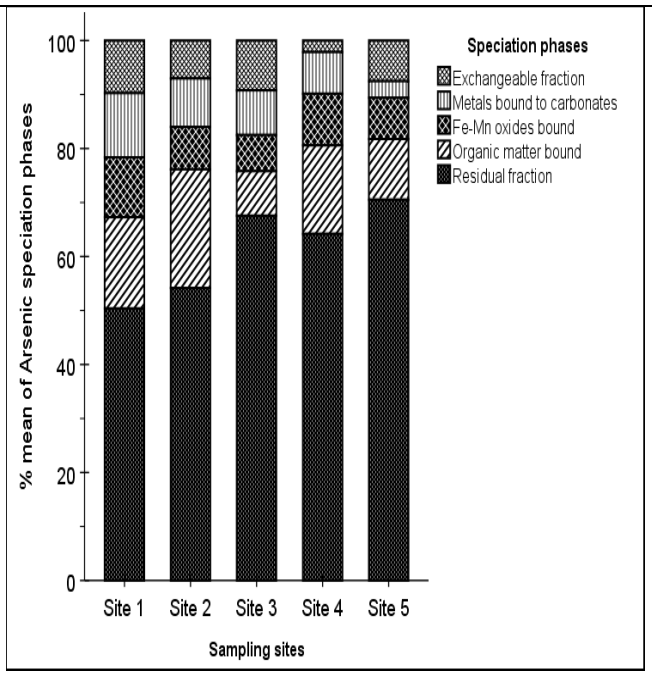

Figure 4A: Proportion of Arsenic Bound to Different Sediment Phases for Dry Season (%)

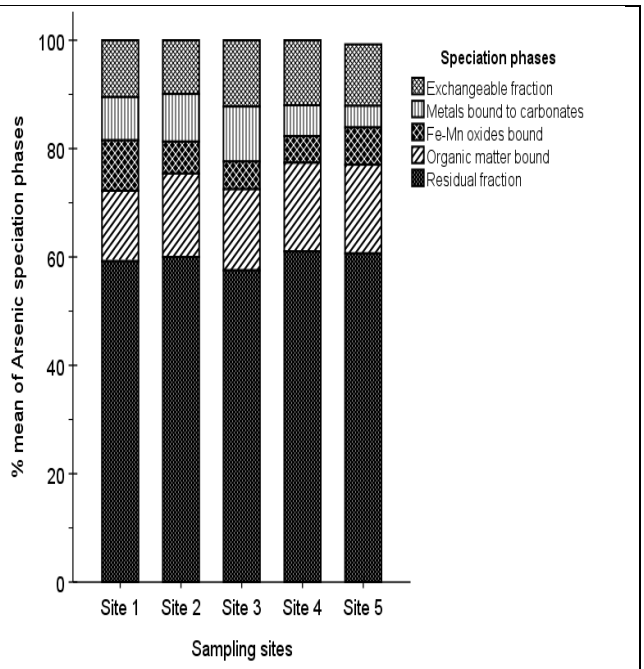

Figure 4B: Proportion of Arsenic Bound to Different Sediment Phases for Wet Season (%)

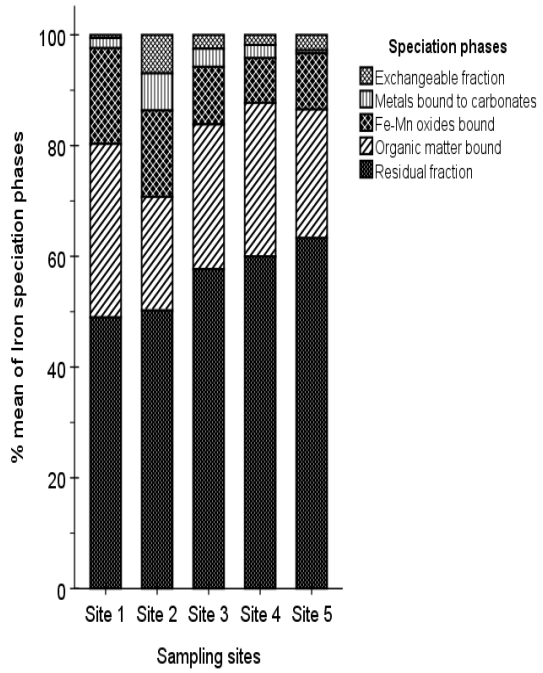

Figure 4C: Proportion of Iron Bound to Different Sediment Phases for Dry Season (%)

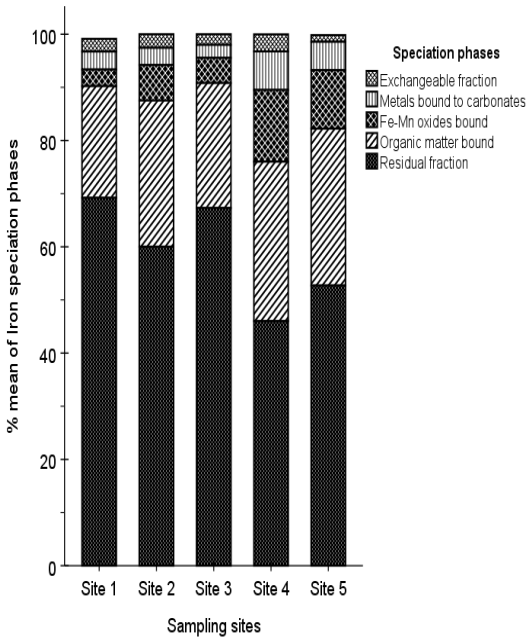

Figure 4D: Proportion of Iron Bound to Different Sediment Phases for Wet Season (%)

Figure 4: Proportion of As and Fe Bound to Different Sediment Speciation Phases for Dry and Wet Seasons

3.10. Seasonal Variation of Heavy Metals Concentration Based on Sediment Phases and Sites of the Sediment Samples

The statistical mean of seasonal variation of heavy metals concentration based on sediment phases and sites of the sediment samples (mg/kg) are given in Figure 5. Generally, sediments of the wet

season had significantly higher concentration of heavy metals than the dry season ($P < 0.05$). This was similar to a research work done by Ntakirutimana *et al.* [42] in a Lake where for winter season, a period of heavy rainfall, with high fluvial inputs flows into the lake carrying heavy metals was responsible for the increased concentration of heavy metals in the same season. It was also in line with a study done by Solomon *et al*. [43] on River Ilaje-Nigeria where there was generally higher concentration of studied heavy metals in wet season than the dry season. This seasonal variation might be due to run-off of agrochemicals used on the farm lands around the Hunki Ox-bow Lake as there is a massive commercial farming at Hunki village during the wet season of which agrochemicals such as fertilizer, insecticides and herbicides/weedicides are usually applied. These agrochemicals might have contained the studied heavy metals that contributed to higher concentration of the heavy metals at wet season. Again, Lakes are known to have inlet or outlet (for draining) from river or stream, and hence most of the toxic substances such as the agrochemicals that entered the Hunki Ox-bow Lake remained more on the sediments [44]. All Lakes are temporary over geologic time scales, as they will slowly fill in with sediments or the water spill out of the basin containing them [44]. There were variations in sites and seasons on different extraction phases for all the sample sites. This was probably due to the fact that in wet season water flows along with the sediments and its contents (containing heavy metals) than in dry season, thereby having different concentration of heavy metals on different sample sites and seasons. This might also be due to transport, redistribution and remobilization on the heavy metals from sediment samples of the lake. However, there was no significant variation based on different extraction phases of the sediments ($P < 0.05$).

The As concentration dominated the residual fraction for both seasons (Figure 5a). The highest concentration of As in dry season was at sample site two of residual fraction (58.74±4.74 mg/kg) ($P<0.05$) followed by sample site one (39.05±2.74 mg/kg) ($P < 0.05$) with the least concentration at sample site two of exchangeable fraction (9.61±1.54 mg/kg) ($P<0.05$). The highest concentration of As in wet season was at sample site five of residual fraction (136.09±24.34 mg/kg) ($P < 0.05$) followed by sample site four (110.31±26.28 mg/kg) ($P < 0.05$) with the least concentration at sample site two of carbonate fraction (10.32±2.46 mg/kg) ($P < 0.05$).

Iron concentration from the sediment samples was more on the residual fraction for both seasons (Figure 5b). Iron had the highest concentration at sample site four (164.48±95.19 mg/kg) ($P < 0.05$) followed by sample site five (105.64±83.79 mg/kg) ($P <0.05$) of residual fraction with the least concentration at sample site three (BDL) ($P < 0.05$) of carbonate fraction in dry season. Iron had the highest concentration at sample site five (784.29±190.03 mg/kg) ($P < 0.05$) followed by sample site four (232.64±81.25 mg/kg) ($P < 0.05$) of residual fraction with the least concentration at sample site five (5.81±0.99 mg/kg) ($P < 0.05$) of exchangeable fraction in wet season.

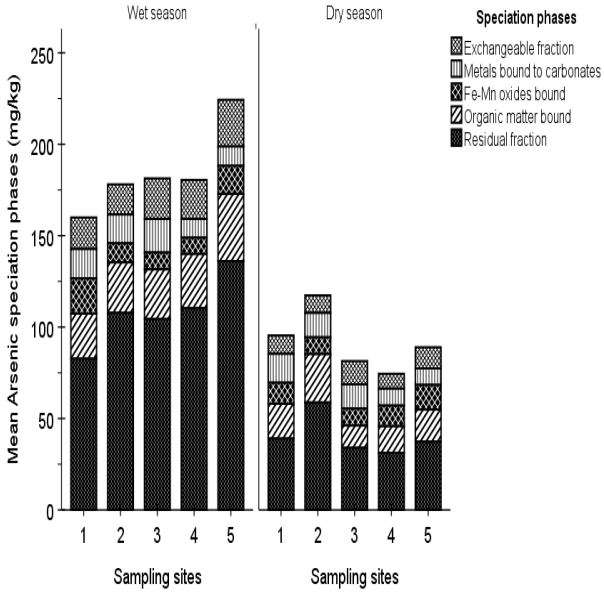

Figure 5A: Mean Concentration of Arsenic from Sediments Speciation Phases for Wet and Dry seasons (mg/kg)

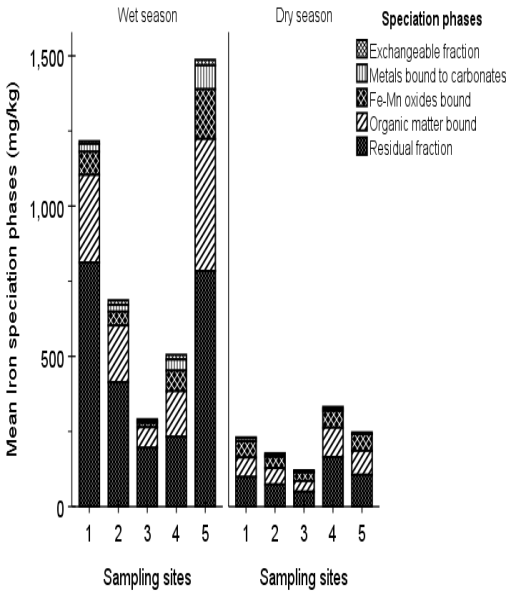

Figure 5B: Mean Concentration of Iron from Sediments Speciation Phases for Wet and Dry seasons (mg/kg)

Figure 5: Seasonal Variation of Arsenic and Iron from Sediments Speciation Phases for Wet and Dry seasons

3.11. Risk Assessments by Bioavailability Index (BI), Mobility Factor (MF), Geo-accumulation Index (I-geo) and Contamination potential (Cp) for Dry and Wet Seasons

The risk assessments by Bioavailability Index (BI), Mobility Factor (MF) and Geo-accumulation Index (I-geo) for dry and wet seasons are as presented in Tables 11. The calculation of BI was based on the fractions of heavy metals in Tessier *et al.* [11] and the equation is as follows:

$$BI = \frac{[\text{Exchangeable (F1)} + \text{Bound to Carbonates (F2)} + \text{Bound to Fe– Mn Oxides (F3)}]}{[\text{Bound to Organic Matter (F4)} + \text{Residual (F5)}]} \quad (3)$$

The average BI values for both dry and wet seasons were in the decrease order: As > Fe. The decrease order of MF average for both dry and wet seasons were of the following: As > Fe. The results of risk assessment by Bioavailability Index (BI) for dry and wet seasons are given in Table 11. Bioavailability index (BI) has been widely used to calculate the accumulation extent in living organism and evaluate the potential harm of heavy metals [45]. The Bioavailability Index (BI) of this study for dry and wet seasons was calculated based on the concentration of five sequential extraction steps of the sediments from Hunki Ox-bow Lake. The mean of BI for all sites of As in sediment samples as shown in Table 11 were generally high for both dry and wet seasons, but the values of BI for Fe was low, which

were below 1.00 for both seasons. These values of BI less than 1.00 may not be of any threat to the ecosystem. The average BI for wet season was relatively higher than that of dry season. The high BI values of As in this study suggested that it may pose potential risk to the aquatic ecosystem and could easily enter the food chain and pose serious threat to man due to its higher toxicity and availability.

Table 11: Risk Assessment by Bioavailability Index (BI), Mobility Factor, MF and Geo-accumulation Index (I-geo) of Heavy Metals in the Sediments for Dry and Wet Season

	Bioavailability Index (BI)		**Mobility Factor, MF (%)**		**Geo-accumulation Index (I-geo)**	
Sample Code/HM	**As**	**Fe**	**As**	**Fe**	**As**	**Fe**
SA_1	0.84	0.71	33.20	5.60	1.78	-7.36
SA_2	0.65	0.43	31.60	7.40	2.34	-7.38
SA_3	1.55	0.10	51.10	6.20	0.89	-7.37
SA_4	2.35	0.35	50.70	4.00	1.72	-7.08
SA_5	1.76	0.41	41.30	2.30	3.34	-7.36
$\bar{x}$ SA	1.43	0.40	41.58	5.10	2.01	-7.31
SB_1	0.67	0.56	26.96	1.80	2.87	-6.46
SB_2	0.95	0.67	38.67	9.23	1.08	-6.80
SB_3	0.79	2.30	33.10	7.13	3.01	-8.76
SB_4	6.60	1.02	28.02	9.96	3.63	-9.26
SB_5	0.71	0.63	25.50	7.25	3.60	-6.62
$\bar{x}$ SB	1.94	0.86	30.45	7.04	2.84	-7.58

Key: HM = Heavy metals, S = Sediment Samples, A = Dry season, B = Wet season, 1-5 = Sample Sites 1 to 5, $\bar{x}$ = mean of all sites per heavy metal

In a five-stage sequential extraction scheme, Salbu and co-workers [26], employed fraction 1 (F1) and fraction 2 (F2) of Tessier *et al.* [11] to represent the easily remobilizable fractions. Based on their proposal, the mobility factor of metals may be obtained using the following equation:

$$MF = \frac{F1+F2}{F1+F2+F3+F4+F5} \times 100 \quad (4)$$

Where, F1 = adsorptive and exchangeable fraction; F2 =carbonate fraction; F3 = Fe-Mn oxide fraction; F4 = organic fraction and F5 = residual fraction.

The results of risk assessment by Mobility Factor, MF (%) of As and Fe from sediments for dry and wet seasons are as presented in Table 11. The fate of metal ions in sediment of the overlying water column is dependent on its MF. Salbu and co-workers [26] revealed that MF of metals provides an indication of the bioavailability or non-bioavailability of the metal. This was also adopted and used by Ma *et al.* [46]. The average values of MF (%) as presented on Table 11 revealed that As had higher values than Fe irrespective of season. This indicated based on MF risk assessment values that As will be more mobilizable and bioavailable compared to Fe to the aquatic ecosystem irrespective of seasons.

The I-geo values of all studied heavy metals for dry season ranged from -9.08 - 3.34 for all sample sites, and those of wet season ranged from -9.26 – 7.68. Geo-accumulation index (I-geo) is a quantitative indicator proposed by Muller [27] that estimates the heavy metal pollution status of sediment in water. This method directly reflects the degree of enrichment of heavy metals in sediment and the equation is given below.

$$I_{geo} = log_2 \left[\frac{C_n}{1.5\, B_n}\right] \quad (5)$$

Where C_n is the measured concentration of the sediment from a water body, B_n is the geochemical background value of a particular heavy metal, and 1.5 is the coefficient of variation that may be caused by earth movement and rock formation or other lithogenic effects.

The results of the calculation of risk assessment by Geo-accumulation Index (I-geo) of heavy metals from sediments for dry and wet seasons are given in Table 11. Taylor and McLennan [47] distinguished seven classes of geo-accumulation index as used by Tytla and Kostecki [48]. The classes include: I-geo < 0 (Class 0 for practically unpolluted, PU, samples); 0 < I-geo < 1(Class 1 for practically unpolluted to moderately polluted, MP, samples); 1 < I-geo < 2 (Class 2 for moderately polluted, MP, samples); 2 < I-geo < 3 (Class 3 for moderately polluted, MP, to heavily Polluted, HP, samples); 3 < I-geo < 4 (Class 4 for heavily polluted, HP, samples); 4 < I-geo < 5 (Class 5 for heavily polluted to very heavily (extremely) polluted, VHP, samples); I-geo > 5 (Class 6 for very heavily (extremely)polluted, VHP, samples). In this present study, I-geo values of As in dry season ranged from 0.89 to 3.34, indicating practically unpolluted to heavily polluted. The I-geo values of Fe for both dry and wet seasons ranged from -9.26 to -7.08 for all sample sites, indicating practically unpolluted. In wet season, the I-geo values of As ranged from 1.08 to 3.63 which showed moderately polluted to heavily polluted.

Potential contamination index (Cp) was calculated by a method adopted by Hakanson [28] and used by Davanesan *et al*. [29] as follows:

$$C_P = \frac{(Metal)_{Sample\ maximum}}{(Metal)_{Background}} \quad (6)$$

where $(Metal)_{Sample\ maxmium}$ is the maximum concentration of a metal in sediment, and $(Metal)_{Background}$ is the average value of the same metal in a background level. Potential contamination index (Cp) values were interpreted as suggested by Davaulter and Rognerud [30], where Cp < 1 indicates low contamination; 1 < Cp < 3 is moderate contamination; and Cp > 3 is severe or very severe contamination.

The Potential Contamination Index (Cp) of As and Fe for dry season were 15.220 and 0.010, respectively, while that of wet seasons were 18.560 and 0.020, respectively. In this research (both seasons), the Cp values of As were all greater than 3 which revealed a severe or very severe contamination of the sediments by As. The Cp values of Fe irrespective of seasons were all less than one, indicating low contamination of the sediments.

4. Conclusion

This research work aimed at assessment of the levels and speciation of As and Fe in water and sediments from Hunki Ox-bow Lake. Physicochemical properties of the sediments which include: pH, electrical conductivity, moisture content, organic carbon, organic matter, carbonates and grain sizes of the sediments were also characterized.

The results generally revealed that the pH and carbonate content values of the wet season whole (raw) and different grain sizes of the sediment samples were lower than that of dry season. The wet season had higher percentages of electrical conductivity, moisture content, organic carbon and organic matter than the dry season.

The mean concentration of As and Fe from water and whole (raw) sediment samples for all sample sites of both dry and wet seasons was of the decrease order: Fe > As. The baseline levels of As and Fe in water samples were as follows, irrespective of seasons: As (1.674) and Fe (4.551) mg/L, which revealed that As in water samples was higher than the WHO Guidelines for Drinking Water Quality, GDWQ [34], but that of Fe was not specified. The baseline levels of As and Fe on the sediments were: As (93.935) and Fe (264.429) mg/kg. This baseline levels showed that As was higher than both Interim Sediment Quality Guidelines – Low (ISQG-L) of 20 mg/kg and Interim Sediment Quality Guidelines – High, ISQG-H (70 mg/kg), while that of Fe was not specified [37,4].

The mean concentrations of As and Fe based on sum of speciation extraction steps were all significantly higher in the wet season than the dry season ($P < 0.05$).

The results of the sum of five-step sequential extraction procedure were generally in good agreement with the pseudo total digestion results of all sites, with acceptable recoveries, an indication that the five-step Sequential Extraction Procedure (SEP) proposed by Tessier *et al*. [11] used in this study was found reliable and can be reproduced.

Arsenic and Iron dominated the residual fraction of the sediments more than other sequential extraction fractions, irrespective of seasons, and hence were more of natural sources.

The ecological risk indices evaluated evidenced As to be of greater ecological risk than iron.

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