

Petroleum spills and assessment of heavy metals in water, sediment, soil from Afiesere River, Ughelli, Delta State, Nigeria

Abstract

The study which was to determine the concentrations of heavy metals in water, sediment and soil of Afiesere river because of the anthropogenic activities of petroleum exploration and attendant spills in the area. Surface water, sediment, surface soil and sub-surface soil samples were collected from Afiesere River, Ughelli, Delta State. Some physiochemical parameters of water were analysed using standard methods and Hanna water quality checker. The concentrations of five heavy metals, namely; lead (Pb), cadmium (Cd), zinc (Zn), copper (Cu) and nickel (Ni) were determined in water, sediment, surface soil, and sub-surface soil using Flame Atomic Absorption Spectrophotometer (Flame-AAS). The results obtained show the mean values of pH, temperature, total dissolved solid, conductivity, dissolved oxygen, biological oxygen demand, phosphate, nitrate, and sulphate as follows: 6.87 ± 0.18 , $27.40 \pm 0.28^{\circ}\text{C}$, 4.00 ± 0.00 mg/L, 8.67 ± 0.25 $\mu\text{S}/\text{cm}$, 4.23 ± 0.08 mg/L, 0.65 ± 0.17 mg/L, 0.01 ± 0.00 mg/L, 0.01 ± 0.03 mg/L, and 2.17 ± 0.18 mg/L respectively. The heavy metals; Pb, Cd, Zn, Cu and Ni mean concentrations are as follows: in water, 0.06 ± 0.02 , 0.02 ± 0.01 , 0.46 ± 0.01 , 0.03 ± 0.01 and 3.56 ± 0.07 mg/L; in sediment, 0.52 ± 0.03 , 0.02 ± 0.00 , 0.21 ± 0.02 , 0.07 ± 0.01 and 0.26 ± 0.01 mg/kg; in surface soil, 0.50 ± 0.03 , 0.02 ± 0.00 , 0.07 ± 0.01 , 0.03 ± 0.00 and 2.91 ± 0.03 mg/kg; in sub-surface soil, 0.55 ± 0.02 , 0.02 ± 0.01 , 0.26 ± 0.02 , 0.06 ± 0.01 and 0.36 ± 0.08 mg/kg respectively. The results showed a significant difference at $P < 0.05$. The results obtained in this study were within and above the set standard for water, sediment and soil by World Health Organization (WHO). The metals are toxic, can bio-accumulate and are potential carcinogens; therefore treatment of water is very important. Periodic medical examination of the inhabitants of the area must be a top priority.

Keywords: petroleum, oil spills, crude oil pollution, heavy metals, contamination

Volume 9 Issue 4 - 2024

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Received: August 19, 2024 | **Published:** August 30, 2024

Introduction

Petroleum, also popularly identified as crude oil is a vast composition of hydrocarbons and other numerous elements occurring naturally deep down the earth's crust in the form of gas, liquid or solid.¹ The formation is from the remnants of sea organisms which lived and died millions of years ago, buried in the earth's crust under very high pressure and temperature.¹ The chemical composition of petroleum shows that hydrocarbons which are basically hydrogen and carbon have the highest percentage by weight compared to other components. It is estimated that hydrogen is about (13%), carbon (85%), nitrogen (0.5%), oxygen (1%), sulphur (0.5%) and each various metal (less than 0.1%).^{1,2} Petroleum is the source or the raw material for the production of various automotive and combustible fuels and a wide range of other petrochemical products. Petroleum spills are the discharge of the product during exploration, mining, production, or transportation on the surface of water, soil or mangrove accidentally or otherwise.³ Petroleum spills are a regular occurrence in the Niger Delta region of Nigeria where intense petroleum activities are ongoing.⁴ The quantity of spills of the product in the Niger-delta from the inception of petroleum exploration in the year 1958 in barrels is approximately 13 million from about 7000 occurrences.⁵ It is important to know that as of the year 2006, there are about 5284

oil wells with about 7000 kilometres of petroleum pipeline across the oil-producing areas.^{4,5} Some of these facilities are located within residential communities, farmlands, and across rivers and streams. Petroleum activities have been a major source of environmental pollution with attendant health effects on humans and food quality in the Niger-delta region of Nigeria. Nigeria being a major producer and exporter of crude oil normally suffers oil spills and this is hazardous to the environment with effects on agricultural lands and the quality of plant growth and development.⁶ Cases of oil pollution have been reported in many areas and these pollutants contain a lot of chemical compounds that may be hazardous. One of the notable elements in petroleum that is a potential toxin is the heavy metals. Heavy metals are chemical elements that, when compared with water shows a higher relative density.⁷ The atomic densities of metals are generally higher than $4000 \text{ kg}/\text{m}^3$.⁸ They are widespread in distribution, occurring naturally from the earth's crust and also from various human activities ranging from household, industrial, agricultural and transportation channels.⁷⁻⁹ At a very low concentration, heavy metals are toxic and potential carcinogens, having the ability to bioaccumulate in the human body on exposure causing various illnesses or damage to tissues and organs.^{9,10} One of the important body systems and corresponding organs which some of these metals may affect is the neurological system.^{7,8} The neurological system comprises the brain,

spinal cord and nerves which regulate and coordinate the other parts of the body systems and organs.¹¹ Also, significant toxicity effects on humans may be experienced from exposures to heavy metals, particularly cadmium, lead and nickel which are contained in crude oil.¹² Worldwide, heavy metal contamination affects the bio-sphere in several ways.¹³ Most plants not only accumulate metals in their roots but also move by capillary action from roots to the shoots or leaves.¹⁴ Contamination of soils and water by heavy metals is a major part of environmental challenges and most conventional remediation methods do not provide lasting solutions.¹⁵ Due to the importance of this element, there are previous studies on the assessment of heavy metals in contaminated water, sediment and soil.¹⁶⁻²¹

In this study determination of the concentration of cadmium (Cd), copper (Cu), zinc (Zn), lead (Pb) and nickel (Ni) in water, sediment, surface soil and sub-surface soil were carried out. Also, some basic parameters of water like; temperature, pH, conductivity, dissolved oxygen, total dissolved solids, biological oxygen demand, nitrate, sulphate and phosphate were measured. The study is aimed at the assessment of concentrations of heavy metals in water, sediment and soil of Afiesere River, Ughelli, Delta State. To show that components of crude oil pollutants may be retained in the matrix long after the source of pollution has ceased. Also, it provides data for policymakers and environmental regulators for monitoring and control, with the view of achieving sustainability and improving human and environmental health. It is important to note that this river was affected by petroleum spillage many years ago as a result of a pipeline boost.

Materials and methods

In other to ensure accuracy of the results, precautionary measures and all required quality assurance procedures were adhered to. All sampling materials ranging from polyethylene material, sample containers and glass wares used were soaked with a 1 mol dm⁻³ nitric acid for 48 hours and then rinsed with distilled water many times immediately before use in accordance with the standard methods. This is to avoid any form of contamination.²²

Study area

The study area is Afiesere River in Ughelli, Ughelli North local government area, Delta state. The river is about 32km as the crow flies, from Ujevbe to Oguname-olomu. It has suffered pollution in the past years as a result of an accidental crude oil pipe blow-up at Agbarha due to excavation. The area hosts about 40 oil wells and crude oil pipelines are a common sight. Sampling spots are at Afiesere, Oteri and Oguname-olomu. Water, soil and sediment samples were collected from each sampling spot. The major occupations of the inhabitants of this area are farming, fishing and animal husbandry. Similar samples were also collected from Adada River, Aku, Uzuwani local government area, Enugu State to serve as control. It is a rural area and the river traverses bushes and farmlands (Figure 1).

bottom flask, and 5 ml of hydrofluoric acid was added with slight shaking followed by the addition of 15 ml of concentrated HNO₃ with slight shaking for perfect mixing and heated in a water bath for 15 minutes until the gases disappeared. The residue was left to cool and transferred into a 100 ml volumetric flask then made up to the mark with deionised water, and then filtered into the sample bottle. A portion was taken and analyzed for heavy metals using the VARIAN Spectra AA-400 plus Flame Atomic Absorption Spectrometer (Flame-AAS).

Sub-surface soil sample: The sub-surface sample was air-dried, crushed and sieved. 1.016 g was obtained using an electronic

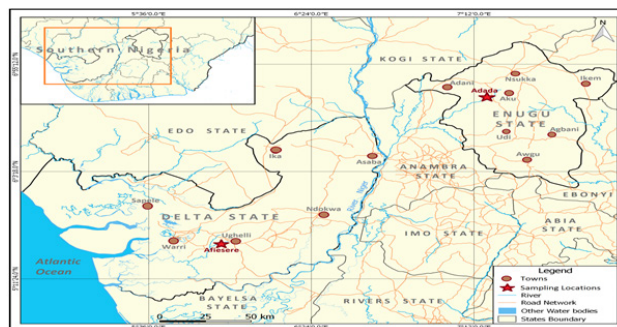


Figure 1 Map of the study area.

Sample collection

Surface water samples were collected with the aid of a 1-litre plastic sampling bottle at each of the spots. A composite sampling method was employed in the collection of surface water samples.²³ The samples were then treated with 2ml of concentrated HNO₃, which stabilizes the original valence state of the metals before they were taken to the laboratory.¹⁶ Samples for Biochemical Oxygen Demand (BOD) and Dissolved Oxygen (DO) were collected with 250 ml amber BOD and DO bottles respectively and were fixed with Winkler's reagent. Surface and sub-surface soil samples were collected using soil auger. The composite samples were wrapped with aluminium foil and then placed in polyethene bags. Sediment samples were collected by the grab method at each of the spots and then mixed to obtain a composite sample. These were then wrapped with aluminium foil to avoid contamination. All the samples were transported in ice chests to the laboratory for analysis.

Analytical methodology

Analytical reagent grade chemicals were used from Sigma-Aldrich, USA.

Analysis of the collected samples

Water sample: Aliquot portions of the water sample for heavy metals were taken and concentrated, then analyzed with VARIAN spectraAA-400 plus Flame Atomic Absorption spectrometer (AAS). Some of the water quality parameters were; pH, total dissolved solid, conductivity and temperature were measured in situ using the Hanna water quality checker. The other parameters, DO, BOD, Phosphate (PO₄³⁻), Nitrate (NO₃⁻) and Sulphate (SO₄²⁻) were analyzed in accordance to standard methods.²⁴

Surface soil sample: The surface soil sample was air-dried, crushed and sieved. 1.019g was obtained using an electronic weighing balance. For the 1.019g dry surface soil sample, mixed acid digestion was carried out with concentrated hydrofluoric acid (HF) and concentrated nitric acid (HNO₃). The sample was transferred into a 500 ml round-bottom weighing balance. For the 1.016 g dry sub-surface soil sample, mixed acid digestion was carried out with concentrated HF and concentrated HNO₃. The sample was transferred into a 500 ml round-bottom flask, 5 ml of concentrated HF was added with slight shaking followed by the addition of 15 ml of concentrated HNO₃ with slight shaking for perfect mixing and heated in a water bath for 15 minutes until the gases disappeared. The residue was left to cool and transferred into a 100 ml volumetric flask and made up to the mark with deionised water, then filtered into the sample bottle. A portion was taken and analyzed for heavy metals using the VARIAN Spectra AA- 400 plus flame Atomic Absorption spectrometer (AAS).

Sediment sample: The sediment sample was air-dried, crushed and sieved. 1.008 g was obtained using an electronic weighing balance. For the 1.008 g dry sediment sample, mixed acid digestion was carried out with concentrated HF and concentrated HNO₃. The sample was transferred into a 500 ml round-bottom flask, 5 ml of concentrated HF was added with slight shaking followed by the addition of 15 ml of concentrated HNO₃ with slight shaking for perfect mixing and heated in a water bath for 15 minutes until the gases disappeared. The residue was left to cool and transferred into a 100 ml volumetric flask then made up to the mark with deionised water, and then filtered into the sample bottle. A portion was taken and analyzed for heavy metals using the VARIAN Spectra AA - 400 plus flame Atomic Absorption Spectrometer (AAS). All the analysis in the various sub-sections is in triplicates.

Statistical analysis

The data analysis is by descriptive and one-way ANOVA and reported in two significant figures using Statistical Package for Social Sciences version 20 (SPSS Inc. USA) at significance level P<0.05.

Results and discussion

Results of the physicochemical parameters and heavy metal concentrations obtained from the samples collected from Afiesere River are presented in Tables 1–4 show that of Adada River (water, sediment, surface soil and sub-surface soil samples).

Table 1 Mean values of concentration of some physicochemical parameters of water (Afiesere River)

Parameters	Upstream	Midstream	Down stream	Mean value/SE
pH	7.2	6.8	6.62	6.87 ± 0.18
Temperature (oC)	26.6	27.6	28	27.40 ± 0.28
Total dissolved solid (mg/L)	4	4	4	4.00±0.00
Conductivity (µs/cm)	9	8	9	8.67± 0.25
Dissolved oxygen (mg/L)	4.2	4.3	4.2	4.23±0.08
BOD(mg/L)	0.5	0.5	0.95	0.65 ± 0.17
PO43-(mg/L)	0.01	0.01	0.01	0.01 ± 0.00
NO3- (mg/L)	0.01	0.01	0.02	0.01 ± 0.03
SO42- (mg/L)	2	2.5	2	2.17± 0.18

Table 2 Mean values of concentration of some heavy metals in the water, sediment, surface soil and sub-surface soil (Afiesere River)

Heavy metals	Water (mg/L)	Sediment (mg/kg)	Surface soil (mg/kg)	Sub-surface soil (mg/kg)
Pb	0.06± 0.02	0.52± 0.03	0.50± 0.03	0.55± 0.02
Cd	0.02± 0.01	0.02± 0.00	0.02± 0.00	0.02± 0.01
Zn	0.46± 0.01	0.21± 0.02	0.07± 0.01	0.26± 0.02
Cu	0.03± 0.01	0.07± 0.01	0.03± 0.00	0.06± 0.01
Ni	3.56± 0.07	0.26± 0.01	2.91± 0.03	0.36± 0.08

Table 3 Mean values of concentration of some physicochemical parameters of water (Adada River)

Parameters	Upstream	Midstream	Down stream	Mean value/SE
pH	8.2	8.4	7.92	8.17 ± 0.23
Temperature (oC)	25.24	26.5	25.32	25.69 ± 0.17
Total dissolved solid (mg/L)	2.63	3.01	2.7	2.78 ± 0.03
Conductivity (µs/cm)	5.41	5.2	4.91	5.17 ± 0.48
Dissolved oxygen (mg/L)	7.1	8.3	7.94	7.78 ± 0.18
BOD (mg/L)	1.4	1.61	2.65	1.89 ± 0.10
PO43-(mg/L)	0.11	0.08	0.08	0.09 ± 0.02
NO3- (mg/L)	0.02	0.03	0.01	0.02 ± 0.01
SO42- (mg/L)	1.71	1.5	1.4	1.54 ± 0.02

Table 4 Mean values of concentration of some heavy metals in the water, sediment, surface soil and sub-surface soil (Adada River)

Heavy metals	Water (mg/L)	Sediment (mg/kg)	Surface soil (mg/kg)	Sub-surface soil (mg/kg)
Pb	0.01± 0.00	0.02± 0.01	0.10± 0.02	0.20± 0.01
Cd	0.00± 0.00	0.00± 0.00	0.00± 0.00	0.00± 0.00
Zn	0.01± 0.00	0.21± 0.02	0.07± 0.01	0.22± 0.01
Cu	0.00± 0.00	0.01± 0.01	0.01± 0.01	0.01± 0.00
Ni	0.00± 0.00	0.00± 0.00	0.00± 0.00	0.00± 0.00

The pH of the water has a mean value of 6.87 ± 0.18 and is near neutral. The pH value is within the range of 6.5 - 8.5 limits of the World Health Organization (WHO) standard for drinking water.²⁵ The pH which is used to ascertain the alkalinity or acidity of water needs to be balanced, that is not acidic and not alkaline. A similar study in the region recorded a mean value of 6.41 ± 0.03 ,²⁶ which is not acceptable for domestic use. Surface water can easily be acidified especially during the rainy season due to wet depositions, leachates from run-off, and spills from petroleum activities. The use of such water by the inhabitants of the area for drinking and other household chores may pose a health challenge like gastro-intestinal diseases.²⁷ It can also impair the development and proper functioning of some of the aquatic life forms.

The temperature has a mean value of $27.40 \pm 0.28^\circ\text{C}$ which depicts the temperature of the surrounding area. The study,²⁶ recorded a mean value of $25.2 \pm 0.15^\circ\text{C}$. Total dissolved solid of $4.00 \pm 0.00 \text{ mg/L}$ is very low which may indicate little or no leachate into the river.²⁸ WHO limit is 500 mg/L and the study²⁶ recorded a mean value of 1432 mg/L which is very high compared with this study. The mean value of conductivity is $8.67 \pm 0.25 \text{ ms/cm}$ and is low compared to the WHO limit of 1000 $\mu\text{s/cm}$. The study²⁶ recorded a mean value of $2701 \pm 319.35 \mu\text{s/cm}$ which is higher than the value of this study and above the standard limit. Conductivity indicates the presence of dissolved solids which may be chemical substances with no specific known chemical configuration.²⁹ Water with very high conductivity is not good for consumption because it can cause illness.

Dissolved oxygen mean value is $4.23 \pm 0.08 \text{ mg/L}$ which is lower than the WHO standard of 5 mg/L required for the survival of aquatic life. Very low DO may result in anaerobic conditions that cause bad odours,²⁹ thereby making the water unfit for domestic use. The odour may affect the aquatic organisms resulting in migration which can create an imbalance in biodiversity.

The BOD mean value is also low, $0.65 \pm 0.17 \text{ mg/L}$. The biochemical oxygen demand was a fair measure of the cleanliness of any body of water.³⁰ WHO limit for drinking water sources is expected to be less than 5 mg/L. The study²⁶ recorded a mean value of $19.64 \pm 3.98 \text{ mg/L}$. When this value is exceeded there may be coagulation resulting in water turbidity.²⁹

The anions PO_4^{3-} , NO_3^- , and SO_4^{2-} with mean values of $0.01 \pm 0.00 \text{ mg/L}$, $0.01 \pm 0.03 \text{ mg/L}$ and $2.17 \pm 0.18 \text{ mg/L}$ respectively are within the WHO recommended value of 5.50 mg/L, 10.00 mg/L and 500 mg/L.²⁵ A previous study in the region recorded the mean values of the anions in River Ethiopie as follows; PO_4^{3-} ($0.16 \pm 0.15 \text{ mg/L}$), NO_3^- ($0.19 \pm 0.13 \text{ mg/L}$) and SO_4^{2-} (4434.29 ± 16) and also in River Ishaka; $2.10 \pm 0.20 \text{ mg/L}$, $0.16 \pm 0.08 \text{ mg/L}$ and $3846.10 \pm 18 \text{ mg/L}$ respectively.³¹ All the values are higher than that of this study but within the limits of WHO except SO_4^{2-} which is very high and above the recommended limit. A high concentration of phosphate in surface water is an indication of pollution, although it has no direct adverse effect on humans, it has the potential to change the water environment which can lead to conditions that pose a health challenge to humans.³² High nitrate content in water is unacceptable because it affects humans, especially children causing a rare blood disorder that hinders the red blood cells from effective distribution of oxygen in the body.³³ Naturally, sulphate occurs in surface water,³² but very high content as a result of contamination can make the water unpalatable and as well have adverse effects like diarrhoea, and stomach pains on humans who depend on it for domestic uses.³⁴

The contamination of water by heavy metals due to one form of anthropogenic activities or another is a very big challenge in recent times because the substances are toxic, do not degrade easily and have the ability to accumulate in organisms.^{27,35}

The mean concentration of lead in water, sediment, surface soil and sub-surface soil is $0.06 \pm 0.02 \text{ mg/L}$, $0.52 \pm 0.03 \text{ mg/kg}$, $0.50 \pm 0.03 \text{ mg/kg}$ and $0.55 \pm 0.02 \text{ mg/kg}$ respectively as clearly shown in Figure 2. This shows a high level of this metal in the matrixes which exceeds the established standard. The WHO limits for surface water, sediment and soil are 0.01 mg/L, 5 ppm and 85mg/kg respectively.^{25,36,37} The studies^{16,19, 26,38,39} recorded mean concentrations of lead in water (mg/L); 0.18 , 0.05 ± 0.01 , < 0.01 and < 0.01 , 0.012 ± 0.000 , 0.22 ± 0.09 respectively. Then for sediment, the values obtained from the studies^{17,19,39} are $0.39 \mu\text{g/g}$, $0.15 \pm 0.03 \text{ mg/kg}$ and $0.25 \pm 0.1 \mu\text{g/g}$ respectively. Also for the soil, the mean values recorded from the studies^{19,40} are $0.25 \pm 0.13 \text{ mg/kg}$, $0.34 \pm 0.13 \text{ mg/kg}$. The high concentration of Pb in surface water could be associated with its presence in trace amounts in crude oil. Lead does not easily break down in the environment and it is known to be very toxic.⁴¹ The amount of lead in sediment, surface soil and sub-surface soil are almost the same and much higher than the amount in water. The levels reveal that the bottom sediments and soils of the study area act as a sink for the metal. Lead has the potential to bio-accumulate in aquatic environments and other organisms including humans causing illnesses.⁴² It is important to note that the concentrations of lead in the soil around the Afiesere River are high and may result in health challenges. Humans can be affected by the contaminants in the soil by inhalation of dust, dermal absorption, and ingestion of soil particles and also from the food chain.⁴³

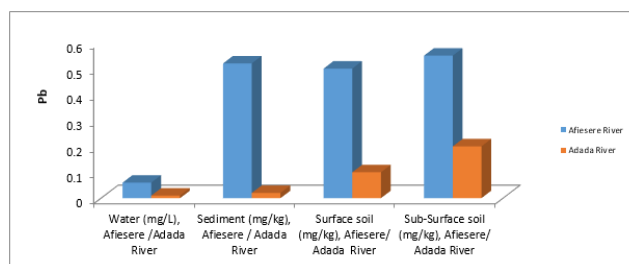


Figure 2 Pb concentrations in water, sediment, surface soil and sub-surface soil (Afiesere and Adada Rivers).

The mean concentration of cadmium in water is $0.02 \pm 0.01 \text{ mg/L}$ while sediment, surface soil and sub-surface are the same at $0.02 \pm 0.00 \text{ mg/kg}$ as shown in Figure 3. This is above the recommended limit for water (0.003 mg/L)²⁵ and the mean concentrations in sediment and soil are below the permissible limits of 0.1 ppm and 0.8 mg/kg.^{36,37} The mean concentration of Cd in water recorded by the studies^{16,19,38,39} is 0.01 , 0.28 ± 0.32 , 0.007 ± 0.001 and $0.03 \pm 0.01 \text{ mg/L}$ respectively. Then the mean concentration in sediment as recorded by the studies^{17,19,39} are $0.02 \mu\text{g/g}$, $1.36 \pm 0.41 \text{ mg/kg}$ and $0.09 \mu\text{g/g}$. Also, the mean concentration of Cd in the soil as recorded in the study¹⁹ is 1.08 ± 0.44 . Cadmium contamination of soil and water is a potential health risk to humans. Exposure to cadmium can impair the proper function of some organs like kidney, liver and reproductive systems.⁴⁴ Cd was identified as one of the trace metals contained in crude oil in varying concentrations. It is known to have the potential to accumulate across the food chain, is toxic, very hazardous and of no known use to biological activity.⁴⁵

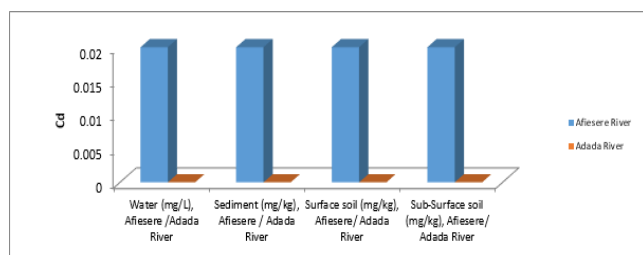


Figure 3 Cd concentrations in water, sediment, surface soil and sub-surface soil (Afiesere and Adada Rivers).

The mean concentrations of zinc in water, sediment, surface soil, and sub-surface soil are as follows 0.46 ± 0.01 mg/L, 0.21 ± 0.02 mg/kg, 0.07 ± 0.01 mg/kg, and 0.26 ± 0.02 mg/kg respectively as shown in Figure 4. It shows that the amount of water is very high. The amount in sediment and sub-surface soil are almost the same, this indicates that zinc moves easily down the soil strata. However, the continuous discharge of oily wastes containing Zn metal should be discouraged. The acceptable WHO limits for Zn in water, sediment and soil are 3.00 mg/L, <1 ppm and 50 mg/kg.^{25,36,37} The mean concentration of Zn water as recorded in the studies^{16,19,26,38,39} are 0.23 , 4.72 ± 0.63 , < 0.01 and < 0.01 , 0.145 ± 0.015 and 0.38 ± 0.16 mg/L respectively. Then the mean concentrations of Zn in sediment as recorded by the studies of^{17,19,39} are 1.61 $\mu\text{g/g}$, 5.01 ± 1.05 mg/kg and 1.70 ± 0.7 $\mu\text{g/g}$. And also the mean concentrations of Zn in the soil samples as recorded by the studies^{19,40} are 7.82 ± 0.89 mg/kg and 9.84 ± 0.93 mg/kg. Human exposure to zinc metals in high concentrations may cause dehydration, vomiting, electrolyte imbalance, abdominal discomfort, nausea, and lethargy, and may also affect the central nervous system.⁴⁶

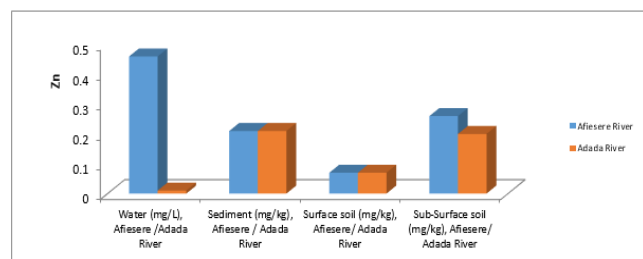


Figure 4 Zn concentrations in water, sediment, surface soil and sub-surface soil (Afiesere and Adada Rivers).

The mean concentrations of copper in the samples of water, sediment, surface soil and sub-surface soil are 0.03 ± 0.01 mg/L, 0.07 ± 0.01 mg/kg, 0.03 ± 0.00 mg/kg and 0.06 ± 0.01 mg/kg respectively as shown in Figure 5. The concentration in water and surface soil is very low; whereas sediment and sub-surface soil have a higher concentration indicating that copper which is in trace amounts in crude oil accumulates downward in the soil and sediment. The WHO acceptable limits in water, sediment and soil are 0.05 mg/L, 20 ppm and 36 mg/kg.^{25,36,37} The previous studies of^{19,26,39} recorded the mean concentration of Cu in water as follows 0.30 ± 0.24 , 0.01 ± 0.00 and 0.08 ± 0.03 mg/L respectively. Then the mean concentrations of Cu in sediment as recorded by the studies^{19,39} are 4.10 ± 1.04 mg/kg and 0.21 ± 0.09 $\mu\text{g/g}$. And also the mean concentrations of Cu in soil samples as recorded by the studies^{19,40} are 3.96 ± 0.71 mg/kg and 0.32 ± 0.11 mg/kg. Copper is essential in human nutrition but it may cause intestinal discomfort at elevated concentrations.⁴³

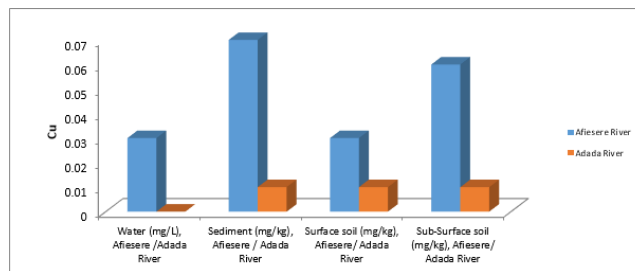


Figure 5 Cu concentrations in water, sediment, surface soil and sub-surface soil (Afiesere and Adada Rivers).

The nickel mean concentration in water, sediment, surface soil and sub-surface soil are as follows: 3.56 ± 0.07 mg/L, 0.26 ± 0.01 mg/kg, 2.91 ± 0.03 mg/kg and 0.36 ± 0.08 mg/kg respectively as shown in Figure 6. The concentration in water and surface soil are much higher than the values in sediment and sub-surface soil, indicating that Ni which is in trace amounts in crude oil are easily retained in surface water and soil. The WHO acceptable limit of Ni in water is 0.07 mg/L, in soil is 35 mg/kg and in sediment as well.^{25,36,37} The mean concentration of Ni in water as recorded by the previous studies^{16,19,38,39} is 0.02, 0.08 ± 0.01 , 0.011 ± 0.003 , and 0.07 ± 0.03 mg/L respectively. Then the mean concentrations of Ni in sediment as recorded by the studies^{17,19,39} are 0.24 $\mu\text{g/g}$, 0.17 ± 0.02 mg/kg and 0.19 ± 0.08 $\mu\text{g/g}$. And also the mean concentrations of Ni in the soil as recorded by the studies^{19,40} are 0.41 ± 0.02 mg/kg and 0.48 ± 0.07 mg/kg. Ni is a known toxicant to marine life and is easily accessible to these organisms.⁴⁷ The continual spills of petroleum or its products into the marine environment would result to the metal bio accumulation.⁴⁸ Nickel is a potential carcinogen to humans as shown in studies.⁴⁹

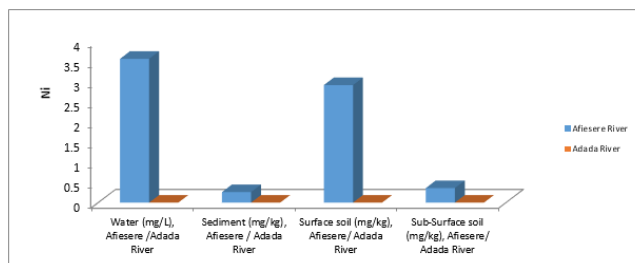


Figure 6 Ni concentrations in water, sediment, surface soil and sub-surface soil (Afiesere and Adada Rivers).

Most of the values of the parameters obtained in this study and some of the values recorded in the previous studies cited above have slight variations. This may be due to the processes or activities that are the major sources of contaminants in the various mediums. The season of the sampling is also a factor to be considered. Also, since the river is the centre of the study, tidal movement, water volume, depth of the water and surface area may be a determinant of the concentrations of parameters studied. In addition, other anthropogenic activities that go on in the study areas apart from petroleum exploration may increase contamination.

The control location is Adada River in Uzo-uwani Local Government Area, Enugu State, and a non-oil producing state. In a rural area, mainly farmlands, Pb, Zn and Cu were identified in water, sediment, surface soil and sub-surface soil as shown in Table 4. This may be due to the original composition of the soil or from run-off of

fertilizer and pesticides in use by the farmers. It may also be from depositions from the atmospheric transport of metals.⁹

Conclusion/Recommendation

This study showed that Afiesere River and the surrounding soil, and sediment are contaminated with heavy metals: Pb, Zn, Cu and Ni in a high degree that is toxic to life forms. The analysis showed also that crude oil pollution can be retained in the environment for years after the source of pollution has ceased. This pollution, which was caused by accidental damage to oil pipelines due to excavation, should be avoided. It was observed that almost all the caution signs placed by the Nigerian National Petroleum Corporation (NNPC) have corroded and defaced. NNPC should as a matter of urgency replace all caution signs in this area. Awareness programmes should be conducted periodically to inform the people not to build or engage in farm activities near the pipeline routes. Government and other stakeholders should form rapid oil spill response groups to tackle accidental spills and pipe blow-ups. Oil operators in these areas should be active in corporate social responsibility as a means of compensation to the people for the damage to their environment. They should provide an alternative source of water supply or an effective water treatment facility in the area. They should provide health care facilities as much as possible and encourage people to go for periodic medical examinations. Continual monitoring of installations by the operators and relevant government agencies must be adhered to. Future studies on the determination of the concentration of heavy metals in the body fluids and tissues of the inhabitants of this region are highly recommended.

Acknowledgments

The authors sincerely acknowledge the support of the Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka towards the completion of this study.

Funding

No funding was received for conducting this study.

Conflicts of interest

The authors declare no competing interests.

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