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Heavy metal contamination in stream water and sediments of gold mining areas of South Western Nigeria

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This study assessed the seasonal variation in heavy metal contamination of stream water and sediments in the gold mining area of Atakunmosa West local Government, Osun State, Nigeria. Twelve villages of prominence in illegal gold mining were selected for the study covering dry and wet seasons of 2012. Stream water and sediment samples were randomly sampled for both seasons. Samples were analyzed with atomic absorption spectrometric method (AAS) and X-ray fluorescence spectroscopy (XRF) for Cd, Zn, Pb, Fe, Zn, Mn, Cu and As. The trend observed for the metals analyzed in the stream water for both seasons are Cu > Zn > Fe > Cd > Pb > As. In stream sediments, higher mean concentration values were generally recorded in the dry season than in wet season. Four metals (Cd, Pb, Cu and Fe) in stream waters and sediments were found to be higher than allowed limits both by the World Health Organisation (WHO, 2004) and the Nigerian standard for drinking water quality (NSDWQ, 2007) in some villages for both seasons, attesting to pollution of the environment resulting from the mining operations and this call for concern.

Key words: Heavy metal, surface water, sediments, atomic absorption spectrometry (AAS), x-ray fluorescence spectroscopy (XRF), gold mining.

INTRODUCTION

Introduction of harmful substances into the environment has many adverse effects on human health, biological systems, agricultural productivity and natural ecosystem (Alloway and Ayres, 1993). Environmental pollution by heavy metals has become a question of public concern considering their hard consequences. It produces substances whose existence poses major threats to quality living and existence of man and animals when

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above allowable limits (Fatoki et al., 2002).The ecosystem has been constantly disturbed by mining operations (Howard and Beck, 1986). Its adverse effects on both surface and groundwater in such mining areas where adequate measures are not in place to safeguard them are always immeasurable, rendering the water unsafe for human usage and inhabitable for aquatic and benthic organisms. Tailings from small scale and even abandoned gold mining operations have been shown to contaminate streams and sediment as well as agricultural products with high concentrations of toxic metals (Grosser et al., 1994). This could result in metal poisoning in areas where water from such stream is used for some domestic applications.

Official mining of gold began in Nigeria in 1913 and gradually rose to a peak between 1933 and 1943, with 1.4 tonnes of the metal produced. Production however became halted due to world war outbreak. The discovery of oil in economic value finally shifted attention from mining. Gold occurs in alluvial and eluvia placers and primary veins in the schist belts, in some North West and South West communities in the country.

The area selected for the study is known for unofficial, small-scale artisanal gold mining operations for decades with less detailed and updated information on the environmental impact of the mining operation in relation to heavy metal pollution. This is evident in the uncountable number of pits dug close to streams which serve as water supply for both agricultural and domestic purposes (Figure 1). Thus, this work aimed at carrying out a heavy metal analysis of stream water and sediment samples from the mining areas, with a view to assessing the impact of mining operations on the aquatic environment.

MATERIALS AND METHODS

Study area

Twelve villages in the mining area of Osun state, with high rate of artisanal mining of gold were selected for the study. The villages are Sabo, Oke-ora, Okutu-Omo, Oko Ogboni, Alaba, Itagunmodi, Ariyelepe, Alaba-Oke, Iyere, Igun, Aba-Isobo and Mokuro. Figure 2a and b shows the map of the state and the sampling points obtained using a hand-held global positioning system (GPS). The control site is Tonkere village in Ife Central Local Government area of Osun State, there is no evidence of mining or ‘digging’ for gold or any precious metal. Streams were located inside farm lands similar to those obtained in the study area with cash crops like Cocoa or Cassava grown on the farms.

Sampling and sample preparation

One liter each of water samples were collected in washed plastic bottles and was digested using standard procedure and used for atomic absorption (AAS) analysis for metal concentration determination. Stream sediment samples, on the other hand, were collected randomly around each mining site with stainless steel trowel to the depth of 0 to 15 cm. In all, 52 stream water and 35 sediment samples were collected covering both dry and wet seasons. Sediment samples were air dried for 2 to 3 days and kept in labeled polythene bags. They were sieved using a 2 mm mesh to remove large grains, then properly grinded with an agate mortar and made into pellets of 13 mm diameter and 1 mm thickness with an hydraulic pelletizing machine for X-ray fluorescence (XRF) analysis.

Analysis of samples

Stream water samples were digested with aqua-regia (HNO_3:HCl 1:3) and analyzed with atomic absorption spectrophotometer (AAS) using PG990 atomic absorption spectrophotometer. Analysis of sediment samples for metal concentration was carried out with an ECLIPSE III, X-ray fluorescence spectrometer (XRF). To ensure quality for the procedure, estuarine standard reference material (SRM 1646a) was irradiated for 1000 s, with the X-ray tube operating at 25 Kv and 50 µA, respectively. Table 1 shows the results obtained for the triplicate analysis of the standard reference materials for estuarine sediments (SRM 1646a purchased from NIST) for data validation. Seven elements (Cd, Pb, Cu, Fe, Mn, Cr and Zn) were detected. Comparison was made between experimental and certified value for the standard reference material used as a measure of quality for the analytical procedures used for stream sediment analysis. Reasonable agreement was observed for the elements with available certified values and this gives a measure of validation for the data generated.

RESULTS

Results obtained from the AAS analysis of the stream water samples collected from April to August and October to December, covering both seasons of 2012 are presented in Table 2. The table showed generally higher mean concentration of heavy metals in the dry season compared to wet season (Figure 3). The mean concentration obtained for Cd in stream water samples ranged from 0.007 ± 0.002 mg/L to 0.027 ± 0.005 mg/L recorded in the dry season and 0.004 ± 0.001 to 0.011 ± 0.004 mg/L obtained in the wet season (Figure 3A). Concentration of lead ranged from 0.002 ± 0.001 to 0.012 ± 0.004 mg/L in the dry season and 0.001 ± 0.001 to 0.007 ± 0.003 mg/L in the wet season. In control samples, mean values obtained for Pb was also higher in dry than wet season (Figure 3B) with (0.003 ± 0.002 to 0.002 ± 0.001) mg/L recorded in both dry and wet seasons, respectively. Arsenic was more pronounced in Itagunmodi and Alaba-Oke water samples with mean concentration in dry season well above those of wet season (Figure 3C), concentration ranges between (0.005 ± 0.001 to 0.011 ± 0.004) mg/L and (0.003 ± 0.001 to 0.008 ± 0.002) mg/L in dry and wet seasons, respectively. The control site recorded lower concentrations of As in both seasons (0.005 ± 0.002 mg/L in dry season and 0.003 ± 0.001mg/L in the wet season) compared to mining sites. Copper was high in all the sites compared with other heavy metals, with the

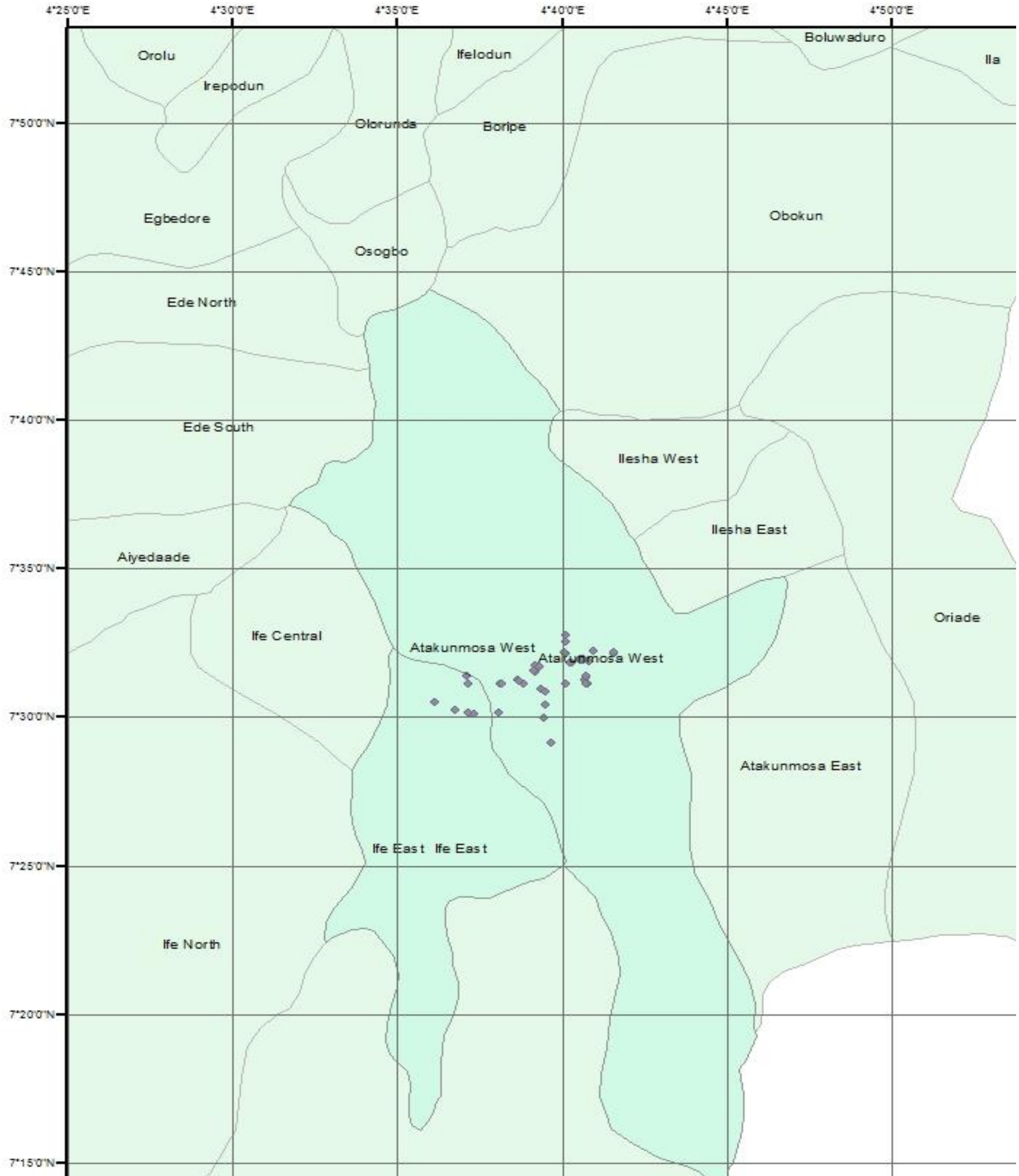
Figure 1. Different uses of stream water in the area: (A) Drinking, (B) Laundry, (C and D) Sieving to concentrate dug pit, (E) Production of palm oil from palm fruit.

highest mean concentration recorded in dry season from stream water sample at Oko-Ogboni while Sabo village water sample had the least concentration of Cu (Figure 3D) with 0.457 ± 0.061 and 0.364 ± 0.056 mg/L in dry and wet seasons. The mean range concentration of copper in both seasons (dry and wet) was (0.294 ± 0.021 to 0.890 ± 0.006) mg/L and (0.280 ± 0.024 to 0.801 ± 0.028) mg/lL. Zn concentration ranges from (0.041 ± 0.009 to 0.776 ± 0.027) mg/L in the dry season and (0.030 ± 0.011 to 0.701 ± 0.022) mg/L in the wet season. Occurrence of zinc in the stream water samples from the study and control sites followed the same trend for both seasons

Figure 2a. Map of Osun State, Nigeria showing the studied area (B) and the sampling points.

(Figure 3E).

Occurrence of iron in the stream water samples in this study did not follow a regular pattern for both seasons (Figure 3F). Mean concentration of the Fe was lower at Oke-Ora, Ariyelepe, Igun and Itagunmodi in dry season. Samples with the lowest and highest concentration were found in Alaba village. However, the mean concentrations values of Fe were generally higher than 0.100 ± 0.013 mg/L obtained in control samples for the dry season but lower in some villages than the 0.192 ± 0.024 mg/L recorded in the wet season for control sample and the mean concentration was much lower in control samples for both seasons Results of the stream sediment analysis for both seasons are presented in Table 3. Generally, the mean concentrations of metals in sediments samples in all the twelve villages were higher in dry season than wet season. The mean concentration values for Fe ranged from 24.886 ± 2.039 to 42.077 ± 3.043 mg/kg in dry season and 17.755 ± 2.911 to 36.800 ± 3.901 mg/kg in wet season, having the highest mean value of 42.077 ± 3.043 mg/kg in the dry and 36.800 ± 3.901 mg/kg in wet season. The highest values of 26.113 ± 2.711 mg/kg for Fe were found at Itagunmodu in both seasons, while the lowest value 24.886 ± 2.039 mg/kg for both seasons were recorded in sediment samples from Alaba-Oke. Concentrations of non-essential elements Pb and Cd in the stream sediment ranged from 2.114 ± 0.410 to 4.991 ± 0.518 mg/kg of Pb and 2.911 ± 0.560 to 4.341 ± 1.111



B

Figure 2b. Map of Osun State, Nigeria showing the sampling points.

mg/kg of Cd in wet season and a higher concentration of 3.951 ± 1.001 to 5.447 ± 1.326 mg/kg and 4.007 ± 0.792 to 6.809 ± 1.315 mg/kg of the metals in the dry season, respectively. The highest values of Cd and Pb (6.809 ± 1.315 mg/kg and 5.447 ± 1.328) obtained in this study were from sediment samples of Itagunmodi village while

Table 1. XRF results of NIST standard reference material (SRM 1646a).

Metals	Certified value	Observed value	% Deviation
Fe	2.008±0.039%	1.672±0.008%	16.7
Pb	11.7±1.2 ppm	10.81±0.9 ppm	7.61
Cu	10.01±0.34 ppm	8±1 ppm	20.0
Zn	48.9±1.6 ppm	43±2 ppm	12.1
Mn	234.5±2.8 ppm	192±7 ppm	18.1
Cr	40.9±1.9 ppm	36.86±1.2 ppm	9.88
Cd	0.148 ppm	0.136 ppm	8.10

* (Values are expressed as a mean of triplicate analysis).

sediment from Oko-Ogboni had lowest concentrations of Cd and Pb (4.007 ± 0.792 and 3.951 ± 1.001) mg/kg in dry season (Table 3). In the wet season however, the highest value of Cd and Pb were found in sediment samples from Oke-Ora and Itagunmodu villages and the lowest values for these metals were found at Alaba-Oke (2.911 ± 0.560 mg/kg) and Mokuro (2.114 ± 1.400 mg/kg). In dry season, except samples from Igun and Itagunmodi with concentrations of 6.418 ± 1.297 and 6.809 ± 1.315 mg/kg, all other sediment samples had concentrations of Cd below 6 mg/kg recommended limit for sediment.

Zinc ranged from 1.305 ± 0.099 to 2.813 ± 0.300 mg/kg in the dry season and 0.506 ± 0.028 to 2.100 ± 0.104 mg/kg of the metal in the wet season (Table 3). The concentration of Mn also ranged from 2.200 ± 0.100 mg/kg to 4.531 ± 0.261 mg/kg in the dry season and1.088 ± 0.151 mg/kg to 3.820 ± 0.222 mg/kg in the wet season, while that of Cr was between 0.889 ± 0.034 mg/kg to 4.002 ± 0.301 mg/kg in the dry season and 0.321 ± 0.107 mg/kg to 2.711 ± 0.201 mg/kg in the wet season. Generally, the metals in the sediment followed these order in both dry and wet seasons:

Cr<Zn<Mn<Pb<Cu<Cd<Fe (dry season)
Cr<Zn<Mn<Pb<Cd<Cu<Fe (wet season)

Sediment samples from the control site had lower mean concentration values for all elements except Cu and Cr in the dry season and Cu and Cr in wet season.

DISCUSSION

The higher concentration of metals observed in the dry season might be due to effect of evaporation which reduces the volume of the water in the stream thus concentrating the mineral component of the stream. Erosion and runoff into the streams are minimal which reduces the volume of water and therefore increased the concentration of the toxic heavy metals. Higher mining (digging) activity observed during the dry season which turns up more contaminants into the stream during washing (separation) to concentrate the precious metal will also be another reason. Cd is known to cause damage to all types of body cells by increasing their permeability and allowing other heavy metals enter into it. A safe limit of 0.003 mg/l has been recommended for Cd by the Nigerian standard for drinking water quality (NSDWQ, 2007). However, this limit was exceeded in all stream water samples in both the dry and wet season in the study area, which makes the water unsafe with respect to Cd contamination. Mean concentration values (0.005 ± 0.001 mg/L in dry season and 0.004 ± 0.001 mg/L in wet season) recorded for this metal in samples from control site were also higher than the recommended safe limit clearly indicating that Cd contamination of the stream water might be coming from other sources other than mining. The control site selected for the study was a farm land where chemicals like fertilizers are constantly used.

Lead is another non-essential heavy metal that is found in association with gold and a major pollutant in mining environments. It has been reported to be a probable human carcinogen (USEPA, 2007). It causes serious damage to brain and nerve cells. Lead is bioaccumulated in humans and can be transferred from mother to child during pregnancy. Apart from the use of herbicides and other farming chemicals which might have lead as impurity, one other major source of lead contaminant in the study area is the formation of acid mine drainage. The Nigerian regulating body has stipulated a safe limit of 0.01 mg/L for water meant for domestic applications to which most of the stream waters in the study area are been used. Other possible anthropogenic sources of the metal in stream water are burning of fossil fuel and contribution from road side dust (Oluyemi et al., 2009) etc., however, all these other sources were absent in the study area limiting the possible contamination to contribution from the active digging for gold metal as well as contamination from using of agriculture related chemicals.

Table 2. Mean variation of As, Cd, Pb, Cu, Fe and Zn (mg/l) in stream waters in the mining area.

Location	As		Cd		Pb		Cu		Fe		Zn	
	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
Mokuro	0.005±0.002	0.008±0.001	0.008±0.002	0.014±0.003	0.005±0.002	0.008±0.002	0.588±0.028	0.624±0.031	0.110±0.020	0.100±0.032	0.118±0.020	0.124±0.018
Oke-Ora	0.006±0.002	0.008±0.002	0.009±0.003	0.012±0.002	0.006±0.002	0.010±0.003	0.322±0.018	0.376±0.022	0.547±0.036	0.563±0.055	0.162±0.019	0.198±0.012
Okutu-Omo	0.004±0.001	0.006±0.001	0.007±0.002	0.015±0.004	0.005±0.002	0.009±0.004	0.399±0.023	0.579±0.019	0.226±0.021	0.233±0.025	0.154±0.017	0.188±0.014
Oke-Ogboni	0.003±0.001	0.008±0.003	0.007±0.002	0.011±0.003	0.007±0.003	0.012±0.004	0.734±0.015	0.890±0.006	0.028±0.009	0.035±0.011	0.297±0.021	0.400±0.019
Alaba	0.006±0.002	0.011±0.003	0.008±0.003	0.010±0.003	0.002±0.001	0.004±0.002	0.251±0.031	0.400±0.005	0.016±0.003	0.020±0.002	0.701±0.022	0.776±0.027
Ariyelepe	0.006±0.003	0.009±0.002	0.004±0.001	0.007±0.002	0.002±0.001	0.005±0.002	0.382±0.023	0.403±0.004	0.045±0.003	0.051±0.003	0.587±0.028	0.502±0.022
Iyere	0.004±0.001	0.007±0.003	0.005±0.002	0.011±0.003	0.001±0.001	0.003±0.001	0.525±0.033	0.599±0.026	0.051±0.002	0.057±0.004	0.208±0.020	0.214±0.014
Aba-Isobo	0.005±0.001	0.007±0.002	0.007±0.002	0.013±0.003	0.003±0.001	0.006±0.002	0.801±0.028	0.886±0.020	0.013±0.002	0.022±0.003	0.102±0.016	0.122±0.008
Sabo	0.003±0.001	0.005±0.001	0.009±0.004	0.016±0.003	0.002±0.001	0.003±0.001	0.280±0.024	0.294±0.021	0.016±0.002	0.020±0.004	0.065±0.022	0.081±0.011
Igun	0.007±0.002	0.010±0.003	0.007±0.002	0.018±0.005	0.006±0.002	0.010±0.003	0.501±0.039	0.455±0.031	0.051±0.011	0.038±0.005	0.423±0.025	0.400±0.019
Itagunmodi	0.008±0.002	0.011±0.004	0.011±0.004	0.027±0.005	0.007±0.003	0.011±0.002	0.654±0.043	0.623±0.055	0.059±0.020	0.041±0.005	0.589±0.021	0.581±0.025
Alaba-Oke	0.004±0.001	0.006±0.002	0.010±0.003	0.017±0.004	0.001±0.001	0.002±0.001	0.486±0.039	0.504±0.048	0.014±0.005	0.013±0.003	0.030±0.011	0.041±0.009
Mean ± SD	0.005±0.001	0.007±0.002	0.008±0.002	0.018±0.003	0.003±0.001	0.007±0.002	0.494±0.026	0.578±0.029	0.090±0.017	0.092±0.007	0.286±0.021	0.279±0.015
Control site	0.003±0.001	0.005±0.002	0.004±0.001	0.005±0.001	0.002±0.001	0.003±0.002	0.364±0.056	0.454±0.061	0.007±0.003	0.015±0.001	0.192±0.024	0.100±0.013
WHO Limit (2004)	0.05	0.05	0.005	0.005	0.01	0.01	1	1	0.3	0.3	5	5
NSDWQ (2007)	0.05	0.05	0.003	0.003	0.01	0.01	1	1	0.3	0.3	3	3

Arsenic is often found as a by-product of both acid mine drainage and of neutral pH leaching of mining wastes from many precious and base metal ore deposits. Arsenic minerals associated with gold mining include arsenopyrite (FeS_2, FeAs, FeAsS) and tennatite [(Cu, Fe, Zn,) As_4S] (Smedley, 1996). Oxidation of these minerals has been known to impact on the environment; they act as sources of sulphate acidity and heavy metals contamination of streams and groundwater (Appelo and Postma, 1993). Exposure to As has been linked to still births and defects; it can move to the fetus from the placenta and is transferable from mother to child during breastfeeding. Other important sources of arsenic exposure include coal burning, use of arsenic in pesticides, consumption of contaminated foodstuffs and exposure to wood preserving arsenicals. Water for domestic applications has permissible limit of 0.01 mg/L as recommended by environmental regulatory bodies in Nigeria (NSDWQ, 2007) as well as the World Health Organization (WHO, 2004). The stream water of the study area was not contaminated with As, water from ten villages in the area had mean concentration of As below the safe limit of 0.01 mg/L recommended by the Nigerian drinking water quality standards (NSDWQ, 2007). The value recorded in the control samples indicates contamination from use of agrochemicals. Copper had the highest mean concentration in all the sites both during dry and wet seasons, this might be due to its association with gold ore satellite materials such as bournonite ($PbCuSbS_3$), tennantite [(Cu, Fe, Zn,) As_4S] and the more common ore formed with iron and sulphur, chalcopyrite ($CuFeS_2$). This element is also a major constituent of some important farm chemicals such as $CuSO_4$ commonly used as herbicides in cocoa plantations of these agrarian communities. All the stream water samples obviously had lower concentration value compared to the 1 mg/l safe limit recommended for Cu in water meant for domestic purposes (USEPA, 2007). The stream water in all the areas will also be suitable if considered for use in small scale livestock watering as the 5 mg/L target water quality range (TWQR) for Cu was not exceeded (DWAF, 1996), however, using the water for irrigation purpose might be a problem as the TWQR of0 to 0.2 mg/L for the metal was clearly exceeded in all stream water samples from all the

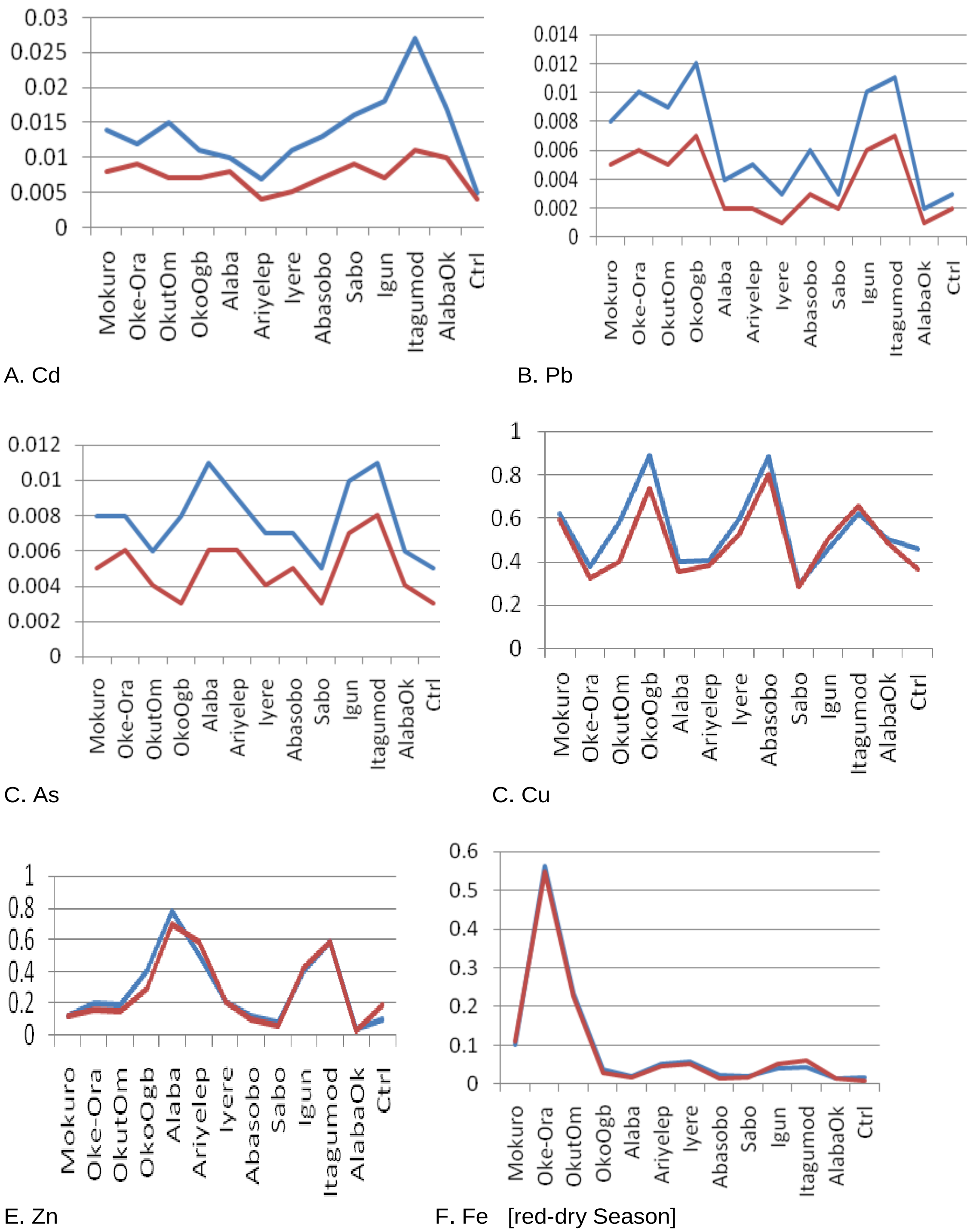


Figure 3. Seasonal Variations of Cd, Pb, As, Cu, Zn and Fe in Stream Waters in the mining area.

villages regardless of the season. Long-term exposure to copper can cause irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhea. Intentionally high uptakes of copper may cause liver and kidney damage and even death, though, the carcinogenic effect of the essential element has not yet been determined but all the above symptoms call for remediating these sites.

In a similar trend, the concentration of iron recorded in all the stream water samples and controls for both types

Table 3. Mean variation of Cd, Pb, Cu, Fe, Mn, Cr, and Zn (mg/Kg) of stream sediments in the study area during dry and wet seasons.

Location	Cd		Pb		Cu		Fe		Mn		Cr		Zn	
	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
Mokuro	4.312±0.991	5.711±1.033	2.114±1.400	4.389±1.312	4.611±0.300	4.532±0.330	26.113±2.711	39.588±1.020	2.001±0.441	2.901±0.602	1.000±0.300	1.118±0.521	1.023±0.031	1.832±0.023
Oke Ora	4.510±0.779	5.932±1.301	3.116±0.811	4.500±0.991	4.188±0.291	4.822±0.381	17.755±2.911	36.112±2.116	1.822±0.103	2.996±0.184	1.211±0.143	1.277±0.305	1.609±0.064	2.312±0.103
Okutu Omo	4.005±0.710	4.542±0.877	4.011±0.511	4.005±0.800	2.813±0.311	3.778±0.300	17.855±1.643	32.008±0.023	1.711±0.122	2.321±0.164	0.665±0.100	1.002±0.071	1.166±0.100	1.523±0.410
Oko -Ogboni	3.811±0.601	4.007±0.792	3.310±0.788	3.951±1.001	3.442±0.201	3.602±0.274	22.543±0.911	30.072±0.015	1.441±0.099	2.533±0.188	0.321±0.107	0.889±0.034	0.908±0.112	1.342±0.331
Alaba	4.341±1.111	5.644±1.002	3.712±1.200	4.473±0.789	2.833±0.291	4.941±0.198	29.877±0.198	39.311±0.031	2.065±0.221	3.361±0.205	0.442±0.100	1.102±0.085	1.305±0.201	2.100±0.446
Ariyepele	3.897±1.099	5.640±1.216	2.187±0.510	4.473±0.789	4.099±0.110	4.938±0.132	29.651±2.712	39.289±0.023	1.889±0.122	3.701±0.089	0.410±0.055	1.100±0.088	1.187±0.099	1.995±0.144
Iyere	3.755±0.591	4.498±0.997	2.87±0.811	3.991±0.900	2.892±0.133	3.407±0.115	20.599±1.900	31.700±0.033	1.440±0.141	2.200±0.1002	0.500±0.081	0.992±0.076	0.873±0.101	1.402±0.300
Aba Isobo	3.908±0.600	5.054±0.908	2.891±0.55	4.008±0.803	3.033±0.238	3.769±0.200	25.810±2.099	28.990±0.028	1.088±0.151	2.297±0.110	2.041±0.198	3.111±0.481	0.531±0.079	1.800±0.097
sabo	4.001±0.501	4.111±0.653	2.342±0.771	4.218±0.823	2.441±0.201	3.998±0.188	25.771±1.800	28.979±0.024	1.110±0.095	2.431±0.104	0.519±0.108	1.001±0.089	0.506±0.028	1.305±0.099
Igun	3.907±0.991	6.418±1.297	4.089±1.100	5.005±1.322	5.911±0.355	6.117±0.391	33.851±1.077	41.098±0.039	3.044±0.190	4.044±0.255	2.012±0.111	3.455±0.501	1.032±0.211	2.604±0.322
Itagunmodi	4.200±0.711	6.809±1.315	4.991±1.218	5.447±1.326	6.448±0.441	6.623±0.400	36.800±3.901	42.077±0.043	3.820±0.222	4.531±0.261	2.711±0.201	4.002±0.301	2.100±0.104	2.813±0.300
Alaba Oke	2.911±0.560	4.503±1.009	3.003±0.499	3.961±0.552	2.848±0.161	3.570±0.121	15.008±2.009	24.886±0.039	1.900±0.201	2.754±0.114	0.884±0.194	2.511±0.211	1.021±0.066	1.786±0.095
Mean	3.963±0.763	5.241±1.033	3.220±0.806	4.038±0.904	3.794±0.253	4.508±0.252	25.119±1.989	34.509±0.286	1.944±0.175	3.005±0.198	1.273±0.141	1.796±0.230	1.105±0.010	1.901±0.222
Control	1.880±0.332	3.235±0.338	1.4370.229	3.039±0.507	3.616±0.527	4.147±0.228	3.424±0.558	9.644±0.883	0.863±0.098	1.889±0.421	0.342±0.067	1.606±0.288	0.196±0.039	0.980±0.119
Permissible limit	6	40	40	40	25	25	30	30	30	30	25	25	123	123

of seasons were all below the recommended limit by the Nigerian and world regulatory bodies except those from Oke-Ora village. The lower mean concentration values of Fe observed during the dry season in some of the areas might be due to reduction in the influx of oxide and clay minerals associated with runoff during wet season. Clay minerals have a large specific surface area that favors the adsorption of ions (Espeby and Gustaffson, 2001) while the stream waters in the areas will be safe as well as Fe contamination is concerned because of the lower mean concentration than the 0.1 mg/L limit, the waters will however not be suitable for use in livestock watering as it is above the 0 to 10 mg/L TWQR (DWAF, 1996) for iron in water for that purpose. Water contaminated with excess Fe may have taste and develop aesthetic problems thus preventing their usage for domestic purpose. Fe occurs in minerals such as arsenopyrite FeS_2, FeAs, FeAsS, chalcopyrite $CuFeS_2$, Pyrite FeS_2 and tennantite [(Cu, Fe, Zn,) As_4S] which are all associated with mining of gold. Zn is known to be less toxic to humans (Ayenimo et al., 2006). It is widely available in the environment and is an essential element for human health. People with too little zinc in the body system can experience loss of appetite, deceased sense of taste and small, slow wound healing and skin sores. Zinc shortages can even cause both defects.

Pollution of stream sediments with heavy metals has been an important issue of environmental concern. Many toxic metals are released from both anthropogenic and natural origin where they get attached to suspended materials and finally get settled on to the sediment harming important microorganisms and indirectly affecting humans. Though, some metals are essential to living organisms, above certain levels, they become toxic to the biota (Wendy, 2005).

The results of heavy metal analysis of the sediments showed a generally higher mean values in the dry season. Cd content in the stream sediment was elevated in two villages from the studied area in the dry season, while Pb content was lower in all sediment samples for both seasons. Mean concentration of Fe in the sediment was clearly above recommended values in 75% of sampling population in the dry season and only in two villages in the wet season. Fe is a major element closely associated with gold mining. Higher values of this metal in the dry season are an indication of the effect of the mining activity on the contamination of stream

Table 4. Enrichment factor of metals for both seasons.

Location	Cd		Pb		Cu		Mn		Cr		Zn	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Mokuro	0.43	0.3	0.35	0.19	0.29	0.16	0.37	0.3	0.16	0.38	0.45	0.68
Oke Ora	0.49	0.46	0.39	0.41	0.33	0.22	0.42	0.4	0.21	0.68	0.6	1.58
OkutOm	0.42	0.41	0.39	0.53	0.33	0.14	0.37	0.38	0.18	0.37	0.46	1.14
Okogbon	0.4	0.31	0.41	0.34	0.35	0.14	0.43	0.25	0.17	0.14	0.43	0.7
Alaba	0.43	0.26	0.36	0.29	0.3	0.08	0.43	0.27	0.16	0.14	0.52	0.76
Ariyelepe	0.43	0.24	0.36	0.17	0.3	0.13	0.48	0.25	0.16	0.13	0.49	0.69
Iyere	0.42	0.33	0.39	0.33	0.34	0.13	0.35	0.27	0.18	0.24	0.43	0.74
Abasobo	0.52	0.28	0.43	0.26	0.37	0.11	0.4	0.16	0.64	0.79	0.61	0.35
Sabo	0.42	0.28	0.46	0.21	0.39	0.08	0.42	0.17	0.2	0.2	0.44	0.34
Igun	0.47	0.21	0.38	0.28	0.32	0.16	0.5	0.35	0.5	0.59	0.62	0.53
Itagmodi	0.48	0.21	0.41	0.32	0.34	0.16	0.54	0.41	0.57	0.73	0.65	0.99
AlabOke	0.53	0.35	0.5	0.47	0.42	0.17	0.56	0.5	0.6	0.58	0.7	1.18

sediments in the area.

Lead, apart from being a major constituent of galena, an important associated mineral of gold mines, is also leached together with Cd by the weathering of heaps of rock materials dug during the mining operations by acids. It is also contained in some farm chemicals as impurity where it finds its way eventually into stream sediment as the sink for this and other metals. The higher concentration of these metals in the dry season might be as a result of the more active digging obtained during the dry season due to improved accessibility thereby turning out into the water and stream bed more of the toxic heavy metals. The United State Environmental Protection Agency (USEPA) has recommended a safe limit of 40 µg/g (US-EPA, 1999) Pb for the toxic metal in stream sediment above which such sediment body becomes dangerous for benthic organisms. Observably, all sediment samples collected for both seasons were below this recommended limit. Of the essential elements analyzed in the stream sediment samples in this study, only Fe has mean concentration values clearly above the US EPA (USEPA, 1999), recommended safety limit of 30 µg/g which is 75% of the total population (9 of the villages understudied).

The WHO safe limit for Zn in sediment is 123 µg/g (WHO, 2004). All stream sediments analyzed in this study has mean concentration of Zn lower than this limit and thus the sediment could be regarded as safe of Zn contamination. Similarly, the same inference could be made for Cr and Mn contamination as they have mean values that are both much lower than the limit recommended by USEPA as sediments containing more than 25 and 30 µg/g of Cr and Mn metals are unsafe for benthic organism in stream sediments (US EPA, 1999). The low concentration of Zn and Mn recorded in this study is surprising, considering the crustal abundance of the two metals and might be due to bio-accumulation by benthic microinvertebrate (Maret et al., 2003; Ellen and Jerry, 1982).

Grain size has been noted as one of the determining factors of metals retention by sediments (Krauskopf, 1956; Goldberg and Arhenius, 1958); increasing grain size reduces trace metal concentration. Sediments with smaller grain sizes adsorb and retain metals more commonly than large grain size ones as a result of the large surface areas (Jenne, 1968; Jones and Lee, 1978). The effect of run off during the wet season is such that debris with large grain size are moved along and deposited onto the surface of sediments disturbing the surface chemical reactions by affecting the adsorption of the metals due to smaller surface area, hence, the lower concentration of these metals in the sediments observed in the wet season.

Other anthropogenic sources that might be responsible for the presence of high values of these metals in the study samples such as presence of waste dump sites, leaching from incineration points, discharge from industries and many more, but these are obviously absent in the sampling areas limiting the sources to contribution from the mining activities, atmospheric deposition as well as use of agro-chemicals. The fact that the mean concentration of metals like Cu and Cr are higher even in the control samples than in some villages buttressed the fact that agrochemicals plays an important role in adding the metals to the stream and sediments. Cu and Cr are important metals in some farm chemicals such as $CuSO_4$ with Cr as major impurity, on the other hand, higher mean values of metals like Pb, As, Fe and Zn in the samples than in the control in the study area attested to the fact that mining activity contributes largely to the contamination of the environment with regard to the metals that are closely associated with gold ores.

While Pb and Cu are found in galena (PbS) and bournonite ($PbCuSbS_3$); Fe, As and Zn occurs in pyrites (FeS_2), arsenopyrites (FeAsS) and tennantite (Cu, Fe, Zn) As_4S), Zn metal is associated with sphalerite (ZnS).

Table 4 shows the enrichment factors for the metals in the sediment samples for both dry and wet seasons. The table revealed the metals Cd, Cu and Mn to be more enriched in the sediment samples in the dry season while for Pb, two of the villages have higher EF in the wet season. For Cr, seven villages have their EF values higher in the dry season. However, almost all the villages, except Abasobo, Sabo and Igun, have their EF values higher in the wet season. Enrichment factor is used to estimate anthropogenic effect on sediment by measuring pollution as a ratio of the metal enrichment in the sample above the concentration of the metal in the reference sample. The determined heavy metal is normalized with respect to reference sample such as Fe, Zn Al, Zr, Sc or Ti (Mediolla et al., 2008; Blaser et al., 2000; Schiff and Weishberg, 1999; Schropp et al., 1990) and is calculated as (Loska et al., 2008):

$$EF = [C_m \text{ in sediment} \div C_m \text{ in control sample}] / [C_{Fe} \text{ in sediment} \div C_{Fe} \text{ in control sample}]$$

Where C_m and C_{Fe} is the concentrations of metal and Fe in both the sediment and control samples, respectively, using Fe as the normalizing reference metal. Generally, except for Zn, all the metals have their factors lower than 1, a value accepted to indicate no enrichment while an EF value of 2 indicates minimum enrichment (Sutherland, 2000); this may be an indication of leaching and depletion of those elements higher than their accumulation (Uduma and Jimoh, 2014). The EF values of Zn are however higher than 1 in Oke-Ora, Alaba oke and Okutu-Omo in the wet season, indicating minor enrichment.

Conclusion

The higher concentrations of heavy metals found in the stream water and sediments samples in the study area had been associated with gold ore and the use of agrochemicals in the farming activities. There is a need for proper and continuous monitoring of the study area to safeguard the lives of the villagers. Authorities should set up a small scale mining industry in this area with proper environmental monitoring and evaluation as well as a standard environmental impact assessment program to be put in place in order to prevent outbreak of diseases and control the activities of the illegal mining.

Conflict of Interest

The authors have not declared any conflict of interests.

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