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Heavy Metals Contamination of Soils and Plants in the Vicinity of Barite Mines in Parts of Oban Massif and Cretaceous Sediments of Southeastern Nigeria

GE Ikpi, CI Adamu*, G Eyong and TN Nganje

Department of Geology, University of Calabar, Nigeria

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***Corresponding author:** CI Adamu, Department of Geology, University of Calabar, P.M.B.1115 Calabar, Nigeria

Abstract

This work focused on the influence of barite mining on heavy metals in soils and plants in the vicinity of barite mines in Southeastern Nigeria. Soil (0-30cm and 30-60cm depths) and plant samples were collected from cultivated farmlands in and around three barite mines (Ibogo, Ekukunela and and Iyametet) and analyzed for some heavy metals (As, Ba, Cr, Cu, Fe, V, Mn, Ni, Pb and Zn). Control soil samples collected from nearby forests were also analyzed for the heavy metals using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Some physical properties (pH, LOI and Clay content) of the soil samples were also determined. Results show that soils from cultivated farmlands have acidic pH values for the surface (5.00-5.70) and subsurface (4.70-5.32) layers respectively. Organic matter contents for both the surface and subsurface soils were generally < 2%. Similarly, low clay values were obtained for both the surface soils (0.6-5.1%) and sub surface soils (0.9-4.3%). Levels of heavy metals in cultivated soils were higher than the concentrations obtained from the control site. These heavy metals are most probably sourced from the barite mine spoils in the study area. Metal concentrations measured in plant parts revealed that leaves (Cassava leaves and pineapple leaves) accumulated heavy metals more than tubers (Cocoyam and cassava tubers). But the heavy metals were found in plant parts at average concentrations normally observed in plants grown in uncontaminated soils when compared with results from the control area. A step wise linear regression analysis identified soil metal contents, pH and LOI as some of the factors influencing soil - plant metal uptake.

Keywords: Heavy metals; Contamination; Barite mining; ICP-MS; Regression analysis

Introduction

Barite mining is an important source of metals contamination in soils. This is because of the processes that are involved such as the open cast mining as used in the study area. This inevitably produces major environmental degradation since vegetation, topsoil and underlying materials have to be removed in order to gain access to the mineral deposit. The tonnes of rocks removed during mining are disposed on the earth's surface as mine spoils. At the exhaustion of the barite deposits, the mine spoils and mine pits are abandoned without proper demobilization. The pulverized rocks consisting of fragments of barite, sulphides and host rocks are exposed to weathering in two stage processes that can cause environmental pollution either singly or in association. One is the generation of acidic mine drainage from the oxidation of pyrite from the waste rocks [1-3]. The second is the mobilization of potential toxic metals in the surface environment stimulated by the oxidizing weathering environment under acid conditions from pyrite oxidation [4].

Mine wastes are point sources of potential toxic metals to the ecosystem as elements are released to the biosphere at a faster rate than would have occurred by the natural weathering of underlying parent materials [5]. Once potential toxic metals are mobilized into the (sub) surface, they may have detrimental effects on the environment. Generally, barite as a mineral is not considered as a major source of environmental contamination because it is an insoluble compound [6]. However, [7] has revealed that the problem of mining is a complex function of lithology, climate, hydrology and the local inventory of acid generating sulphides and acid-neutralizing carbonates. Thus, contamination is not only associated with the mineral deposit. Globally, limited studies have been carried out on trace metal contamination around barite mine dump sites [8,9]. In Nigeria, studies on the impact of barite mining on soil, sediment and water is limited to that of [10-12]. There is thus, scarcity of information on the impact of barite mining activities soil and plant in the study area and, indeed the whole of Nigeria. The objective of this study was therefore, to assess the degree and extent of trace metal contamination of soil and plants around the barite mine dump sites in parts of the area of study.

Study Area Description

The study area lies between latitude 05⁰ 37¹ and 05⁰ 58¹N and longitude 08⁰ 06¹ and 08⁰ 38¹E and covers part of Oban Massif and the Cross River Plain. It is located within the sub equatorial climate of Nigeria with a total annual rainfall of between 180 and 200cm. the annual temperature is between 25 and 30⁰C [13]. The area experiences two seasons: the wet season which last from April to October and the dry season which last from November to March. The mean humidity drops from 80% in the rainy season to as low as 60% in the dry season. The elevation of the study area ranges from 100m in the Cross River Plain to more than 500m above sea level in Oban Massif. The relief is characterized by rugged and undulating topography of alternating hills and plains. The relief of the area varies from the low-lying northern fringes in the sedimentary areas to high elevations towards Oban Massif in the south. The principal land forms are upland, plains and valleys.

The study area is located within the thick equatorial rainforest which is inhabited by tall trees and Wildlife. The vegetation hinders easy access to geological features and structures in the area. Mine sites are only accessible by footpaths and stream channels because of the thick vegetation and rugged topography. Geologically, the study area falls within the Mamfe Embayment and the Oban Massif in southeastern Nigeria (Figure 1). The Ekukunela and Iyametet mines which fall within the sedimentary cover of Mamfe Embayment range in age from Cretaceous to Tertiary and consist mainly of conglomerates, sandstone, shale, silt stone, mud stone, limestone, marl, clay and loose sand [14]. The Ibogo mine falls within the Precambrian basement province of Western Oban Massif [15]. Rocks in this area are dominantly Schists and gneisses [16]. The Schists of the area are characterized by well-developed biotite and Muscovite Crystals. Where weathering activity is severe on these rocks, numerous Muscovite flaks can be seen glittering on the surface of the ground. Regional tectonic trend obtained from measured foliation and fracture planes indicate a NE - SW trend of the pan African Orogeny [17,18].

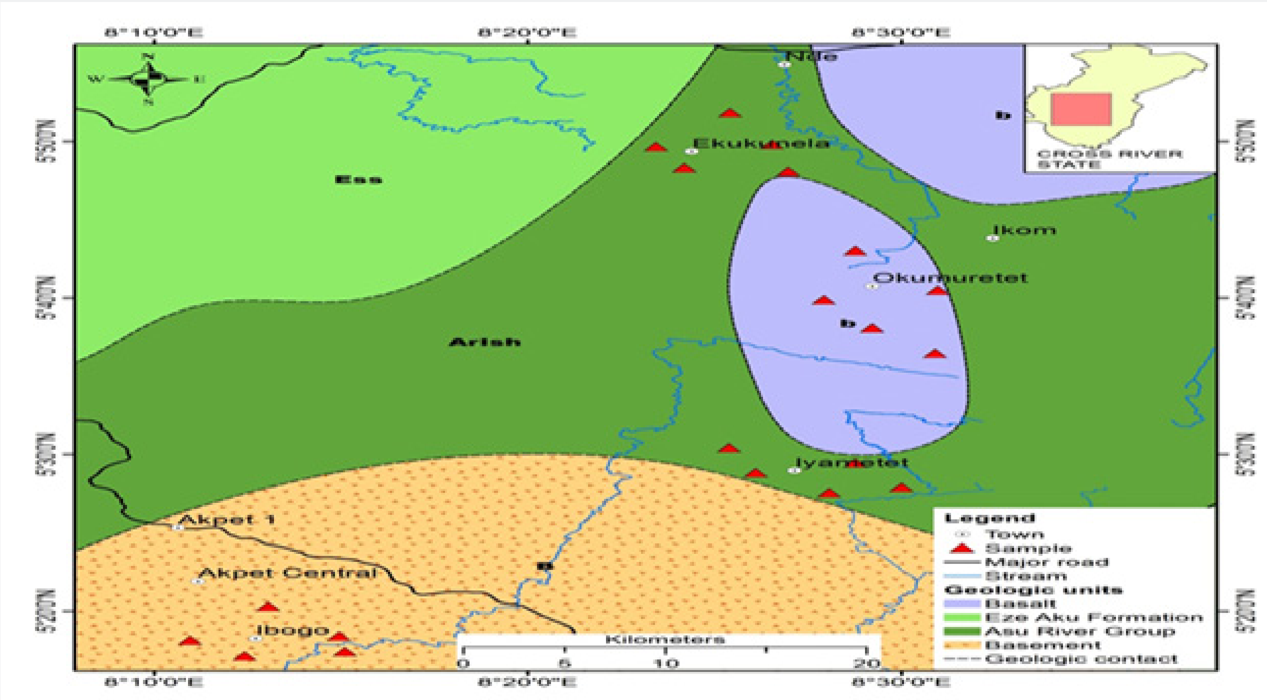

Figure 1: Geological map of the study area showing sample points.

Brief Description of the Mines

Ibogo mine

This mine is located about 100km away from Calabar along Calabar* Ikom highway. The mine is situated about 12km east of the major settlements. Schists, Phyllites and Pegmatites dominate the lithology of western parts of Uwet which covers part of the mine area. The mine is located on a hill with high gradient. Three barite veins occur in this mine which trend E-W and they appear to have been emplaced at the contact of the Schist and sandstone. The soils here are reddish, reddish–brown to brownish red due to hydrated Fe – Oxides and good drainage [4].

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Ekukunela mine

This mine is located about 50km from Ikom along Calabar-Ikom high way. The geology of this mine is dominated by sandstone of the Albian Mamfe Formation. There are also shale and limestone intercalations. Three extensive barite veins (> 2km) occur at Ekukunela. The largest vein cuts across the Calabar- Ikom road and is intensively mined.

Iyametet mine

This mine is located at the hill slope close to cultivated farmland. The geology consists of black backed, fractured slaty shale that is intruded by dolerite sills. The sills contain spherules of magmatic rock and trends N –S. At this mine, only the top part of the shale sequence with siltstone /sandstone intercalations is observable at the top of the mine pit because the pit is now full of water all year round. Detailed description of the mines is contained in [11,12].

Materials and Methods

Composite soils and plant samples were collected randomly within and around the three barite mines (Ibogo, Ekukunela and Iyametet) under study. A total of thirty composite soil samples were collected in cultivated farm lands close to the three mine locations using a hand auger. The soil samples were collected at depths of 0-30cm and 30-60cm to reflect the surface and sub-surface soils respectively. In addition, three soil samples (0-30cm and 30- 60cm) were collected about 1km away from each of the mines to serve as control samples. The control locations were considered to have suffered little anthropogenic inputs. The samples were put into polythene bags and labeled accordingly using paper tape and marker pen.

Random samples of cassava leaves and tubers, pineapple leaves and cocoyam tubers were taken from cultivated fields in the three mine locations and properly labeled to reflect the locations from where they were collected. Soil samples were air dried at room temperature of about 25^0C-30^0C, disaggregated using mortar and pestle and then sieved to < 2mm. After quartering, the samples were ground to 80 mesh (< 180µm) in a stainless steel blender. The resulting powered samples were collected into properly labeled separate envelopes for chemical analysis. Plant samples were thoroughly washed with deionized water and dried in a clean room at 25^0C for 5days, then ground to fine powder and repackaged in sealed plastic bags. The cassava and cocoyam tubers were carefully peeled and rinsed with tap water to remove surface dirt before drying the tubers. After the preparation stage, 0.5g of soil samples was digested in 4:1 ratio of concentrated nitric : perchloric acids and heated to dryness. The residue was leached with 5ml of 2m HCl [19] and the solution made up to 10ml with deionized water in already calibrated and labeled test-tubes. The samples were analyzed for As, Ba, Cr, Cu, Fe, V, Mn, Ni Pb and Zn using a Perkin Elmer Elan 6000/9000 Inductively Couple Plasma Mass Spectrophotometer (ICP- MS) in Acme laboratory, Canada.

0.5g of powered plant samples were digested in fuming $HN0_3$ followed by Mg $(N0_3)_2$, leached with the same procedure as that used for soil and analyzed using the same inductively coupled plasma Mass Spectrometry (ICP – MS) for As, Ba, Cr, Cu Fe, V, Mn, Ni, Pb and Zn. Soil pH was determined by using a pH meter in the field, soil organic matter content was estimated from loss – on – ignition (LOI) and the clay content was measured [20].

A rigorous quality control programme was used to assess the accuracy and precision of the chemical data for the soils and plants. The programmes included regent blanks, replicate and duplicate samples as well as in-house and standard materials.

Results

Physical parameters

The soils from the study area are generally characterized by low pH, low organic matter content (LOI) and low clay content. The results of the physical properties of the soils are presented in Table 1. The soil pH at Ibogo mine ranged from 5.46 to 5.76 with an average of 5.60 for the surface soils. The sub-surface pH ranged from 4.98 to 5.60 with an average of 5.16 at Ekukunela Mine, soil pH ranged from 5.45 to 5.68 with an average of 5.56 for the surface soils whereas the sub-surface pH ranged from 4.70 to 5.32 with an average of 4.50. At Iyametet mine soil pH ranged from 5.00 to 5.42 with an average of 5.24 for the surface soils while sub-surface pH ranged from 4.70 to 5.32 with an average of 4.50. Soil pH from the three mine locations have acidic pH values including soil pH from the control area with values of 6.1 and 5.8 for Ibogo, 5.8 and 5.6 for Ekukunela, 6.0 and 5.8 for Iyametet respectively for surface and sub-surface soils respectively. The organic matter content of cultivated soils was generally very low, less than 2% (loss-on-ignition, LOI). Whereas the soils from the control area had relatively higher organic matter content with the highest values of 5.9% at Ibogo. The clay contents were also low for all the soil samples in all the mine sites (less than 5%).

Concentration of heavy metals in soils

The concentration, minimum, maximum and standard deviation values of all the heavy metals considered in soil samples in this study for the three mine locations are presented in Table 2. At Ibogo mine As for instance had a mean concentrations of 79.20mg/kg and 21.60mg/kg for the surface and sub-surface soils respectively while much lower concentrations 9.30mg/kg and 8.5 mg/kg were found in the soils from the control area underlain by the same geology as the mine site but without mining activities. Same was noticed of all other metals; Ba, Cr, Cu, Fe, V, Mn, Ni Pb and Zn with elevated concentrations when compared with results from the control area. At Ekukunela mine for example. As mean concentration was 29.81mg/kg and 23.78mg/kg for the surface and sub-surface soils respectively whereas the mean concentration of the same As from the control were 9.73mg/kg and 8.17mg/kg respectively for the surface and sub-surface soils. The concentrations of these metals from the

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control areas fall within the recommended range of metals in soils [21]. Metal concentrations in soils from Iyametet mine also show elevated concentrations in surface soils than in sub-surface soils. For instance, As mean concentration for surface soil here was 24.06mg/kg whereas the sub surface mean concentration was 18.24mg/kg. In the control As recorded values of 9.20mg/kg and 8.94mg/kg for the surface and sub-surface respectively. In all the three mine locations in this study, all the metals show elevated concentrations at the surface soils (0-30cm) than the sub-surface soils (30-60cm) respectively.

Table 1: Physical properties of soils in the vicinity of the mines.

Depth (cm)	0 - 30									30 - 60								
Mine	Ibogo			Ekukunela			Iyametet			Ibogo			Ekukunela			Iyametet		
	LOI(%)	Clay(%)	pH	LOI(%)	Clay(%)	pH	LOI(%)	Clay(%)	pH	LOI(%)	Clay(%)	pH	LOI(%)	Clay(%)	pH	LOI(%)	Clay(%)	pH
1	5.50	1.21	1.20	5.45	1.04	1.60	5.30	0.86	4.20	5.00	1.03	1.80	5.20	0.90	1.40	5.20	0.74	3.50
2	5.65	1.08	3.30	5.65	1.14	4.50	5.00	0.45	4.30	5.60	0.92	1.20	4.70	0.61	4.20	4.87	0.68	4.20
3	5.70	1.32	0.70	5.55	1.24	3.70	5.42	0.96	3.50	5.20	0.94	1.50	5.32	0.72	2.00	5.24	0.57	2.00
4	5.68	1.02	0.60	5.48	1.18	2.30	5.28	0.94	5.10	4.98	0.84	2.10	4.82	0.86	1.40	5.06	1.03	1.40
5	5.46	1.01	1.40	5.68	1.18	0.90	5.18	0.88	3.50	5.02	0.88	0.90	4.95	0.69	3.30	4.96	0.92	3.30
Min	5.46	1.01	0.60	5.45	1.04	0.90	5.00	0.45	3.40	4.89	0.84	0.90	4.70	0.61	1.40	4.87	0.57	1.40
Max	5.70	1.32	3.30	5.68	1.24	4.50	5.42	0.96	5.10	5.60	1.03	2.10	5.32	0.90	4.20	5.24	1.03	4.20
Mean	5.60	1.13	1.44	5.56	1.16	2.60	5.24	0.82	4.10	5.16	0.92	1.50	4.50	0.76	2.50	5.07	0.72	3.06
S.D	0.27	0.13	1.09	0.39	0.57	1.80	0.37	0.38	2.30	0.26	0.07	0.47	0.32	0.22	1.24	0.16	0.19	1.02
Control	6.10	5.90	3.00	5.80	4.80	3.20	6.00	2.70	3.70	5.80	3.40	3.50	5.60	3.70	3.00	5.80	2.40	3.40

Table 2: Concentration(mg/kg) of heavy metals ftom soils in the vicinity of the mine area.

Depth		0-30cm										30 - 60cm									
Mine		As	Ba	Cr	Cu	Fe	V	Mn	Ni	Pb	Zn	As	Ba	Cr	Cu	Fe	V	Mn	Ni	Pb	Zn
Ibogo	1	62	165.4	60.21	102.6	1.372	82.84	66.8	64	123.8	103.2	28	104.6	52.39	89.4	1.025	78.63	60.29	43	101.2	98.2
	2	311	459	34	475	1.32	600	2620	41	424	550	16	3460	110	318	1.012	150	69.2	41	482	450
	3	93.2	756.3	72.05	148.5	1.555	84.22	41.66	56.91	138.5	73.3	32.33	485.4	68.45	122.8	1.058	82.56	38.26	48.2	122.4	68.74
	4	33	236	630	514	5.19	1060	37.3	107	225	500	12.7	2010	110	448	3.478	210	1370	53	441	410
	5	131	384	520	419	5.915	770	1210	141	331	410	19	2697	590	357	3.348	890	2620	122	188	570
	Min	33	165.4	60.21	102.6	1.32	82.84	41.66	41	123.8	73.3	12.7	104.6	53.39	89.4	1.012	78.63	38.26	41	101.2	68.74
	Max	131	756.3	630	514	5.915	1060	2620	141	424	550	32.33	2697	590	448	3.478	890	2620	122	482	570
	Mean	79.24	400.1	324.1	331.8	3.07	519.4	795.2	81.98	248.5	327.3	21.61	1751	186.2	267	1.98	282.2	631.6	61.44	267	319.3
	SD	48.51	230.5	257.6	192	2.28	430.6	1137	41.1	133	224.9	53.97	1431	256.1	154.8	1.305	344	1150.4	34.2	181.1	223.5
	Control	9.3	520	84.67	24.33	2.53	66.53	210.7	40.8	59.2	71.33	8.5	480.2	57.4	22	2.42	62.54	205.6	32.6	52.67	69.67
Ekukunela	1	29	344	40	64.7	1.12	68.22	120	11	954	360	24	575	30	22.1	1.09	64.52	190	15	79.3	180
	2	36.9	844.2	12.86	508	0.5	66.5	75.2	22.3	505.4	508.3	14.4	152.2	10.4	331.8	0.382	60.42	27.5	18.2	158.2	169.8
	3	55.9	883.2	48.8	86.9	0.77	67.74	241	16.01	424.3	469.7	53.62	802.4	22.12	80.1	1.438	66.78	229.7	14.76	180.7	189.9
	4	13.23	376	12	35.3	1.86	68.42	670	69	229	290	12.9	180	10.2	17.6	1.361	66.44	26.12	37	284	240
	5	14	376	110	353	1.62	150	670	37	299	290	14	800	120	176	1.22	170	1260	69	284	270
	Min	13.23	344	12	35.3	0.55	66.5	67	11	229	290	12.9	152.2	10.2	17.6	0.382	60.42	26.12	15	79.3	169.8
	Max	55.9	844.2	110	508	1.86	15	670	69	954	508.3	53.62	800	120	176	1.438	170	1260	69	284	270
	Mean	29.81	564.7	44.73	209.6	1.184	84.18	384.2	31.06	482.3	383.6	23.78	501.9	38.54	125.2	1.098	85.63	355.7	30.79	197.2	209.9
	S.D	17.72	273.6	39.96	209.8	0.55	36.8	303.3	23.34	285.1	101.3	17.27	320.3	46.3	131.8	0.42	47.23	256.2	23.26	87.7	43.07
	control	9.73	204	28.62	187.4	1.06	64.4	120	3064	106.4	65.2	8.17	182.4	22.42	106.2	1.02	42.2	102.5	26.82	80.82	42.5

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Iyame-tet	1	15.01	543	35.76	339.1	1.83	97.42	56.78	44	694	339.7	2.4	173.7	26.77	252.9	1.18	94.86	42.18	24	237	102.4
	2	21.5	449	70	297	2.24	99.9	570.2	77.8	458	250	15.2	228	60	222	0.882	95.86	181.7	38.4	186.1	20
	3	19.7	107.3	60.3	329.1	1.28	99.8	82.71	61.2	279.7	147.2	16.4	96.4	42.3	252.3	1.083	97.86	66.4	41.42	127.2	108.4
	4	32.2	430.2	52.83	244.5	1.202	93.05	102.4	66.4	320	186.7	28.47	223.4	29.76	176.5	0.9	92.22	88.6	42.8	152.8	120.3
	5	31.9	320.4	27.4	249.6	1.024	92.56	42.95	28.7	116.5	107.2	28.74	114.8	25.52	202.1	0.89	90.48	39.29	22.88	102.3	101.5
	Min	15.01	107.3	27.4	244.5	1.024	92.56	42.95	77.8	116.5	107.2	2.4	96.4	25.52	176.5	0.882	90.84	39.29	22.88	102.3	20
	Max	32.2	543	70	339.1	2.24	99.9	570.2	55.62	694	339.7	28.74	228	60	252.9	1.18	97.86	181.7	42.8	237	120.3
	Mean	24.06	369.9	49.26	291.9	1.515	96.55	171.01	19.36	373.6	206.2	18.24	167.3	36.87	220.9	0.987	94.26	83.63	33.9	161.1	90.52
	S.D	7.67	166.7	17.5	43.8	0.5	3.57	219.9	19.36	216.6	191.5	10.94	60.33	14.54	32.92	0.14	2.29	58.35	26.15	243.4	135.4
	Control	9.2	102	28.2	104.8	1	60.72	85.2	38.86	89.9	82.3	8.16	86.46	18.66	88.94	0.06	40.88	43.24	20.24	84.8	62.6
	**	6--13		5 - 100	2 -100	0.5 - 4.3	20 - 500	12 - 400	10 - 100	10 - 100	10 - 100										

** Normal range [21]

Although, soils from the control area revealed much lower concentrations of metals for both the surface and sub-surface soils which invariably falls within the recommended range of heavy metals in soils by [21].

Concentration of heavy metals in plants

The mean and range concentration of As, Ba, Cr, Cu, Fe, V, Mn, Ni, Pb and Zn in crop plants (Cassava, Cocoyam and Pineapple) grown on agricultural soils in the different mine location of Ibogo, Ekukunela and Iyametet mines are presented in Table 3 while Table 4 shows the results of the different plant parts from the control area. The concentrations of heavy metals were different in the same plant species in the different mine locations. But in all the three locations, leaves of the crops tend to accumulate higher metals concentrations than the tubers. For mean concentration at

Table 3: Mean concentrations(mg/kg) and ranges of heavy metals in plants from Ibogo, Ekukunella and Iyametet barite mines.

Mine	Plant Species	As	Ba	Cr	Cu	Fe	V	Mn	Ni	Pb	Zn
Ibogo	Cassava leaves	0.4 (0,08-1.15)	202.6 (880-508)	0.83 (0.18-1.20)	9.4 (5.2-12. 6)	539 (5.2-12.6)	0.89 (0.1-2.4)	64.2 (202-90.4)	13(0.6-32)	2.3 (1.1-5.6)	38 (21-90.0)
	Cassava tuber	0.17 (0.30-3.2)	156 (58-251)	0.51 (0.13- 1.8)	12.9 (3.6- 15.0)	607 (127-820)	0.7 (0.3-1.8)	14.3 (2.8-20.2)	1.8 (0.4-2.5)	3.3 (2.4-4.5)	40 (25.0-50)
	Pineapple leaves	0.8 (0.01-4.70)	51.4 (23-68.5)	0.85 (0.16-2.0)	41.35 (3.6-58)	829 (74-1120)	0.12 (0.0- 2.8)	55.2 (9.0-108)	2.42 (1.3 -4.7)	3.12 (2.1-5.6)	81 (13.8-108)
	Cocoyam tuber	0.23 (0.1-050)	41.5 (22.2-508)	0.81 (0.12 -0.60)	9.8 (3.5-13.8)	95.5 (65.2-120)	0.01 (0.0-0.03)	9.05 (1.2-10.5)	0.01 (<0.01–0.03)	1.03 (1.30–1.80)	28.4 (19.8-30.4)
Ekuku-nela	Cassava leaves	0.62 (0.12-1.25)	184.9 (640-204)	14.3 (2.0-26.2)	12.8 (3.6-14.8)	603 (138-1480)	1.6 (0.5 -2.6)	21.4 (5.8-25.2)	4.7 (1.5-8.6)	12.5 (1.8- 14.0)	78.4 (13.8-90.5)
	Cassava tuber	0.18 (0.25 -3.4)	27.5 (18-30.2)	0.62 (0.1- 1.6)	10.5 (2.5 -12.6)	480 (116-720)	0.5 (0.2 -1.4)	15.8 (3.5-18.2)	2.2 (1.5-3.8)	2.8 (1.2-2.6)	36.7 (182-42.3)
	Pineapple Leaves	0.6 (0.2-1.2)	48.8 (21- 52.2)	0.66 (0.1-1.8)	44.5 (3.8-50.1)	720 (82.0 -1106)	0.24 (0.1-1.2)	58.2 (42.0–68.4)	1.9 (0.8-2.4)	2.6 (1.8-2.8)	42.5 (18.6-52.0)
	Cocoyam Tuber	0.16 (20.2-2.2)	60.2 (20.2-72.0)	0.12 (0.00-1.4)	10.4 (2.2-16.0)	78.9 (20.1-108)	0.02 (0.00-060)	10.2 (1.8-12.0)	0.4 (0.01-1.2)	3.2 (2.2-6.2)	23.3 (22-66)
Iyame-tet	Cassava leaves	0.7 (0.1-0.9)	184 (48-240)	16.2 (4.0 18.2)	14.2 (4.0-18.4)	1050 (188-1,120)	2.2 (0.2-5.1)	25.8 (6.2-384)	3.6 (1.2-4.8)	16.4 (1.2-20.1)	72.8 (20.2-98.4)
	Cassava tuber	0.14 (0.01-1.9)	30.2 (208-35.0)	0.45 (0.1-1.2)	10.2 (2.5-18.6)	580 (120-800)	0.8 (0.2-1.1)	20.9 (2.8-30.2)	1.3 (0.5-2.8)	2.4 (1.0 -5.8)	16.9 (3.4-22.2)
	Pineapple Leaves	0.9 (0.1-1.8)	62.2 (10.2-80.4)	1.22 (0.6-1.56)	51.2 (28.2-80.5)	880.2 (56.0–-1220)	1.2 (0.2-1.30)	60.4 (18.2-110)	2.2 (1.2-3.6)	2.8 (1.4-3.2)	72.2 (18.5 -80.4)
	Cocoyam tuber	0.42 (0.1-0.6)	52.8 (10.6-68.2)	0.16 (0.05-0.18)	16.4 (3.8-20.4)	86.5 (45 -115)	0.16 (0.0–0.82)	12.2 (3.2-15.0)	0.02 (0.00-0.60)	1.34 (0.40–1.88)	30.2 (18.2-41.6)

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Table 4: Control results of heavy metals concentrations(mg/kg) in plants from the mines sites.

Mine	Plant Part	As	Ba	Cr	Cu	Fe	V	Mn	Ni	Pb	Zn
Ibogo	Cassava leaves	0.18	82.2	0.12	1.74	120.5	0.22	18.2	0.2	0.24	20.2
	Cassava tuber	0.1	48.4	0.08	1.12	65	0.1	1.64	0.12	0.18	16.4
	Pineapple leaves	0.2	65.4	0.14	1.82	108.6	0.15	8.06	0.4	0.19	22
	Cocoyam tuber	0.14	20.8	0.05	1.64	72.8	0.01	1.02	0.01	0.16	18.2
Ekukunela	Cassava Leaves	0.16	50.5	0.16	1.22	102.5	0.12	16.6	0.82	0.12	12.8
	Cassava Tuber	0.12	20.5	0.1	1.8	112	0.18	1.74	0.65	0.42	16.8
	Pineapple	0.17	28.6	0.12	1.75	101.5	0.12	7.5	0.44	0.16	20
	Cocoyam tuber	0.1	18.8	0.01	1.05	100.2	0.01	1.22	0.01	0.15	18
Iyametet	Cassava tuber	0.16	40.5	0.14	1.55	101.5	0.2	16.4	0.2	0.13	18.8
	Cassava tuber	0.11	22.1	0.12	1.66	102.8	0.02	1.24	0.11	0.16	16.5
	Pineapple leaves	0.14	26.2	0.11	1.68	102.2	0.1	6.24	0.28	0.14	20.3
	Cocoyam Tuber	0.12	18.1	0.02	1.52	101.8	0.02	1.25	0.02	0.16	18.2

Ibogo mine, As was lowest 0.40mg/kg (dry Wt) in cassava leaves and 0.17mg/kg (dry Wt) in cassava tubers, whereas V tend to be the lowest 0.12mg/kg (dry Wt) in pineapple leaves and 0.01mg/ kg in Cocoyam tubers. At Ekukunela mine, As was lowest 0.62mg/ kg(dry Wt) in cassava leaves and 0.18mg/kg (dry Wt). in cassava tubers, whereas V was lowest 0.50mg/kg (dry Wt) in pineapple leaves and 0.02mg/kg (dry Wt) in cocoyam tuber. At Iyametet mine, As was lowest 0.70mg/kg (dry Wt) in cassava leaves but V became lowest 0.80mg/kg (dry Wt) in cassava tubers while As became lowest 0.90mg/kg (dry Wt) in pineapple leaves, Ni was lowest 0.02mg/kg (dry Wt) in cocoyam tubers.

Discussion

The soil in the three mine locations (Ibogo, Ekukunela and Iyametet) are weakly to moderately acidic with mean pH values 5.60 & 5.16, 5.56 & 4.50, and 5.24 & 5.07 for surface and sub- surface soils respectively. This acidic nature of the soils in the three locations could be attributed to the decomposition of organic matter content in the soils, a process which is often rapid in tropical environments such as the area of study. It can also be attributed to sulphides oxidation associated with the mines. The soils also recorded low organic matter contents (LOI) in all the locations with mean values of 1.13 & 0.92 at Ibogo, 1.16 & 0.76 at Ekukunela and 0.82 & 0.97 at Iyametet for the surface and sub-surface soils respectively which are all less than 10%. In addition the soils in the three mine areas show low clay contents with mean values of 1.44 & 1.50 at Ibogo, 2.60 & at Ekukunela and 4. 1 & 3.06 at Iyametet respectively for surface and sub-surface soils and this can have low sorption capacity for metal ions.

At Ibogo mine, agricultural soils are contaminated by As, Cr, Cu, Mu, Pb and Zn at both surface (0-30cm) and sub-surface (30-60cm) soils when compared with the normal range of metals in soils [21], (Table 2) and when compared with the levels of metals from the control area. The contamination could be attributed to mine drainage and contents of heavy metals in the soil. [22] reported that large amount of metals in mine waste and associated soils provided an important source for continuing dispersion downstream and have led to a moderate degree of contamination of soils used for crop production. In the study area, the heavy metals in surface soils (0-30 depth) were higher than those in sub-surface soils (30-60cm depth). This concentration difference could be due to the effects of mining activities and mineralization. The contamination levels of the heavy metals vary among the mines depending on the size of mineralization. Also, the contamination levels of the heavy metals vary among the sample locations depending on the distance from the mine.

At Ekukunela mine, elevated concentrations of As, Cu and Zn were observed in both surface (0-30cm) soils and sub-face soils (30-60cm) when compared with the normal range of metals in soils [21] but when compared with result from the control area, all the metals considered in this study show enhanced concentrations. Also, the heavy metals levels. in surface soils were higher than metal levels in subsurface soils. At Iyametet mine, agricultural soils were contaminated by heavy metals like As, Cu, and Pb for both surface soils and sub-surface soils when compared with the normal range of metals in soils [21]. But when compared with heavy metal contents in soils from the control area, all the metals considered in this study show enhanced concentrations both for surface and sub-surface soils respectively. This is reasoned to be as result of the effect of barite mining activities in the area.

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The comparison of heavy metal levels in soils from the three mine locations revealed that Ibogo barite mine recorded the highest level of metals contaminations(As, Cr, Cu, Mn, Pb and Zn) [21]. This highest level of contamination in soils of this mine location could be attributed to several factors among which includes the geology of the area which is the basement complex of the Oban Massif, the nature of barite which seemed to be stained and coloured by its association with other minerals. Other factors are the jarge size of the mine and the location of the mine. Next in terms of contamination are soils from the Ekukunela barite mine with As, Cu, Pb and Zn being above the normal range of metals in soils and finally soils from the Iyametet barite mine with As, Cu, and Pb concentrations being little above the recommended range [21]. Both the Ekukunela and Iyametet barite mines fall within the Cretaceous sediments of the Mamfe Embayment of the study area and the barite found in these two locations were cleaner when compared with the one from Ibogo barite mine. Ba recorded the highest concentrations in soils from the three mine locations for the surface and sub-surface soils including the control area. This is because barite ($BaS0_4$) in soils has very low mobility due to its insolubility and inability to form soluble complexes with humic Organic matter [23].

Nevertheless, agricultural soils do not seem to have been seriously contaminated because of the properties of the soils such as low clay contents, mild acidic pH, low organic matter contents as well as Fe and Mn which are known to absorb and retain metals [24]. Plants can accumulate heavy metals in their tissues due to their great ability to adapt to variable chemical conditions of the environment. It is well known that heavy metal concentrations vary with plant species [19,22,25] and that leaves tend to accumulate higher concentrations than roots or tubers and grains or fruits [26]. Results from this study show that metal concentrations were higher in cassava and pineapple leaves than in cassava and cocoyam tubers confirming that leaves tend to concentrate more metals than tubers. A comparison of heavy metal levels in plants from the mine sites with those from the control sites revealed higher concentrations in plants from mine sites implying that plants can absorb metals when planted within mining areas. In the Ibogo mining area, metal concentrations in plants varied with plant species. For example, the average concentration of As ranged from 0.40mg/kg (dry Wt) in cassava leaves, 0.80mg/kg (dry Wt) in pineapple leaves, 0.17mg/kg (dry Wt) and 0.20mg/kg (dry Wt) of cassava and cocoyam tubers respectively. Whereas in the control area, As ranged from 0.18mg/kg (dry Wt) and 0.02mg/kg (dry Wt) and 0.14mg/kg (dry Wt) of cassava and cocoyam tubers respectively confirming that mining activities, geology, nature of barite among others had impacted in the metal content of plants in the area. Plant parts also show variation of other metals within the same location indicating differnt abilities of plant species to uptake an accumulate metals.

In Ekukunela mining area, concentration of heavy metals in plant parts also varies. For example, the mean concentration of As in cassava leaves was 0.62mg/kg (dry Wt) and 0.06mg/kg (dry Wt) for pineapple leaves whereas cassava and cocoyam tubers had 0.18mg/kg (dry Wt) and 0.16mg/kg (dry Wt) respectively. In the control area, As concentration in cassava and pineapple leaves was 0.16mg/kg (dry Wt) and 0.17mg/kg (dry Wt) while cassava and cocoyam tubers had 0.12mg/kg (dry Wt) and 0.10mg/kg (dry Wt) respectively. Similar results were found in Iyametet mining area where mean As level in plant parts was 0.70mg/kg (dry Wt) and 0.90mg/kg (dry Wt) for cassava and pineapple leave while cassava and cocoyam tubers had 0.14mg/kg (dry Wt) and 0.42mg/kg (dry Wt) respectively. This was different in the result from the control area. Here As level in cassava and pineapple leaves recorded 0.16mg.kg (dry Wt) and 0.14mg/kg (dry Wt) respectively while cassava and cocoyam tubers recorded 0.11mg/kg (dry Wt) and 0.12mg/kg. A similar metals levels variation in the different plant parts applies to all other metals like Ba, Cr, Cu, Fe V, Mn, Ni, Pb and Zn that are in focus in this study. Generally, most elements were found in plant parts in the study area at concentrations found in crops grown in uncontaminated soils [3].

Relationship Between Soils and Plants Metal Content

Heavy metals concentrations in plant parts are highly comparable with those of soil, although this can differ between plant species and parts. It is well known that total metal content in soils is an important factor influencing the uptake of metals into plants [19]. However, the uptake is affected by so many factors including soil texture, pH, Eh, CEC, organic matter content, Fe-Mn-Al-oxides and hydroxides, presence of other metals, amount and rate of fertilizer and biocide applications as well as plant species, parts, cultivars and age [27,28] accounting for the variable relationship between soil heavy metal contents and plant.

A Stepwise multiple linear regression analysis was applied in the study to find the dominant factors influencing metal uptake in plants and to also predict metal levels in plants. A step-by-step procedure was used to obtain the best fit regression equation. The independent variable was always total metal content in the surface soils. The regression equation was calculated using statistical package for the social sciences (SPSS). At each stage the significance of the equation was tested by the Coefficient of determination (r^2) and probability ($P < 0.05$). The equation was considered significant for r- squared values ≥ 0.50 at $P< 0.05$. The result of the linear multiple regressions are presented in Table 5. It can be seen that total metal concentrations in surface soils are the main factor affecting those in plants. Other factors that contributed to the prediction of heavy metal concentrations in plants in this study are pH and clay content.

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Table 5: Result of Step Wise Multiple Regression Analysis.

Plant Type	Multiple Regression Equation	r^2
Cassava leaves	(Cu) P = 211.28 + 0.081 (Cu) S+ 41.977pH- 3.202 clay	0.888
Pineapple leaves	(Pb) P = 84.599 + 0.014 (Pb) S+ 14.577pH + 2.104 clay	0.858
Cassava tubers	(Ni) P = 3.234 + 0.008 (Ni) S-0.745 clay	1
Cocoyam tubers	(Cu) P = 9.309 + 0.013 (Cu) S-1.912 clay	1

Note: (Cu) P = Copper concentration in plants (mg/kg dry Wt),

(Cu) S = Copper concentration in surface soil (mg/kg),

(Pb) P = Lead concentration in plants (mg/kg dry Wt).

(Pb) S = Lead concentration in surface soil (mg/kg).

(Ni) P = Nickel concentration in plants (mg/kg dry Wt).

(Ni) S = Nickel concentration in soil (mg/kg).

r^2 = Coefficient of determination.

Environmental Implications

The distribution of heavy metals in soils from the three mine locations under study reveals enhanced concentrations of metals in surface soils (0-30cm depth) than in subsurface soils (30-60cm depth). This implies that surface soils (agricultural soils) in the areas have higher metal enrichment even when compared with soils from the control areas. This enhanced concentration of metals could be attributed to mine drainage in the areas and contents of heavy metals in surface soils among others.

The locations of the three mine areas are rural communities and a good percentage of the inhabitants are farmers, therefore agriculture is their main occupation. Land is intensively cultivated, and animals are reared for food production. These animals feed directly from the locally grown crops and these metals are ingested into their systems from these unwashed crops. There is the possibility that shallow crop feeders will accumulate these metals more than the deep feeders since surface soils have metal concentrations than the subsurface soils. Although animal tissues from the study area locations were not sampled due to limited resources, it is likely that animals in the area may be accumulating heavy metals through feeding on crops grown on contaminated soils which may have some health implications on the animals, though this may not result in direct increasing intake in humans. Contamination of useable water is more direct way of ingestion by human being [3].

Residents of the area under study feed from crops grown on the soils and use water from the mines. The long-term metal exposures by regularly feeding on locally grown crops from within and around the mine sites can give rise to health related problems in both animals and human beings in the vicinity of the mine areas.

Conclusion

Heavy metal contaminations of soils and plants in the vicinity of three barite mines in cross River State, Nigeria were investigated and the results of each of the mines were compared between sites. It was revealed that agricultural soils were contaminated by heavy metals that are mostly sourced from mine waste materials. Although the degree and extent of contamination varied with each mine sites, the dispersion of metals may be controlled by factors such as the distance from the mines, prevailing wind in the area and possibly the geology. The degree of contamination was assessed by comparing heavy metal contents in soils with acceptable standards and also with results from the control areas. The main source of contamination was attributed to be from mine waste materials that were abandoned without proper cover system and metals have been continuously released by wind or drainage from the source to the surrounding environment.

Analysis of metals in plants from the study areas indicated that leaves; cassava and pineapple leaves tend to accumulate higher metal concentrations than the cassava and cocoyam tubers. This was observed in all the sampled plants from the three mine locations. It is very obvious that high levels of heavy metals in soils around the mines and in the mine dump materials will continuously migrate and disperse into agricultural soils. As a result, soils and plants in the vicinity of the mines will continue to be contaminated.

Recommendation

The timely environmental reclamation of the mine sites using techniques such as revegetation, neutralization of soil acidity and enhancement of metal adsorption using clay materials, is hereby recommended. If implemented can lead to adequate loss of heavy metals from the mine and dump sites.

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