



Occurrence and distribution of heavy metal in arable soils around lead–zinc mining sites of Abakaliki, Southeast Nigeria

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Abstract

This study involved the geochemical assessment of the occurrence and distribution of heavy metals in available agricultural soils and stream sediments in the lead–zinc mining areas of Abakaliki, Southeastern Nigeria. A total area of about 794.2 km² was assessed, with major communities covered including Enyigba, Mkpuma Akpatakpa, Ameka, Amorie, Amanchara and Alibaru where active and abandoned mines are located. One hundred and sixteen soil/stream sediments were collected and subjected to geochemical analysis using the atomic absorption spectrophotometric method. The result shows concentration of Cd > Pb > As > Zn > Cu > Ag > Hg > Cr, especially in the areas close to the active mines. The contamination percentage of metal in samples shows Cd (40.51%), Pb (36.20%), As (23.27%), Zn (17.24), Cu (8.62%) and Cr (0%). This implies that arable soils around the mining areas are not suitable for food crop production as biomagnification can occur in the food chain. The consumption of food produce in these areas can lead to potential health risk as they accumulate. However, the Mkpuma Akpatakpa and Ameka areas show higher distribution of these metals than the Enyigba and Amanchara areas. Seasonal analysis shows a decreased concentration of chemical constituents in the rainy season relative to the dry season except for Cd, Cr and Hg.

Keywords Geochemical · Mineralization · Mine waste · Chemical constituents · Food crops

Introduction

The effects of mineral deposits' weathering and degeneration may be deleterious on soil and water quality due to soil–water interaction (Obasi and Akudinobi 2019b; Loska and Wiechula 2003; Lucassen et al. 2002). This may not only lead to challenges in sustainable water quality; pollutants and contaminants from mining sources constitute a major threat to human health, aquatic lives, land use and agriculture, and other aspects of ecosystem imbalance (Zhiyuan et al. 2014; Yousefi et al. 2017). Obasi (2017) noted that soils and environmental degradation problem are obvious in mining areas. Many authors including (Vanek et al. 2005; Akoto et al. 2008) have shown that the major pathways for heavy metals are by sedimentation of particles and by the sorption of dissolved metals from surface water or ground-water seepages in contact with stream sediments. Kishe and

Machwa (2003), and Lech et al. (2007) noted that geochemical stream sediment surveys are employed almost invariably for reconnaissance studies in drainage basins, because if properly collected, these stream sediments represent the best composite materials from catchments areas upstream from sampling sites. Therefore, by sampling and analysing stream sediments and soils, it is possible to recognize geochemical anomalies within a catchment area and trace them to their source.

Geochemical soil survey, according to the dictionary of Earth Science Ailsa and Michael (1999), is the process of collecting and analysing unconsolidated soil sediments in order to locate geochemical anomalies in the underlying rock and to use these to find ore bodies. In weathering environments, many minerals, particularly sulphide minerals, are unstable and will break down as a result of oxidation or other chemical reactions, and this is the underlying rationale behind stream sediments and soil geochemical surveys (Aus-IMM 2011). Their breakdown often results in dispersion of both ore and indicator elements in solution, in run-off and in ground water for relatively long distances within the drainage basin (Levinson 1974; Al-Momani 2009).

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Oti and Nwabue (2013), Chibuikwe and Obiora (2014), and Obiorah et al. (2016) have shown that plants' intake of heavy metals in mining areas can have adverse effects on man. Kamau (2001), Asaah et al. (2006), Ezech et al. (2007), Dikinya and Areola (2010), Li et al. (2014), Hari-kumar and Jisha (2010), Casper et al. (2004); Mendoza et al. (1996), Nriagu and Pacyna (1988), Obasi and Akudinobi (2019a), Obiorah et al. (2018), and Alexakis (2016) have evaluated the concentration of heavy metals in soils and sediments in mining areas in different parts of the world. These works have shown that mining activities have effects on the surrounding soils in the areas.

Rural communities of Enyigba, Mkpuma Akpatakpa, Ameka, Amorie, Amanchara, Agbaja and Alibaruhu where active and abandoned mines are located comprise the lead–zinc mining areas of Abakaliki. These communities are endowed with lead–zinc mineralization which occurs as lodes and veins (Obiorah et al. 2016; Obasi and Akudinobi 2015; Obasi 2017; Obasi et al. 2018a, b; Obasi and Akudinobi 2019a, b). The mineralization in the area has facilitated small-scale mining in the area with the consequent random citing of excavations and waste dumps, and

unplanned disposal of mine wastes (see Fig. 1). All these affect the hydrogeochemistry of the area. Also, these are agrarian communities with peasant farming as their major occupation. The villagers cultivate the farmlands in the rainy season and the river banks and alluvial plains in the dry season. The purpose of this work, therefore, is to establish the concentration and distribution of Pb, Zn, Cu, Cd, Hg, Cr, Ag and As in the soils/sediments of the mining areas of Abakaliki. Emphasis shall be placed on qualitative assessment of various soils in the area. Hence, providing valuable information in this regard may constitute a vital planning tool to healthcare providers and agro-allied industries on possible bioaccumulation of heavy metals in the food chain.

Geology and physiography

Geologically, the study area is underlain by the Asu River Group. The sediment is a product of the earliest documented marine transgression in Nigeria (Obage 2009; Nwajide 2013). According to Kogbe (1976), the group consists largely of olive-brown sandy shales, fine-grained micaceous



Fig. 1 Cases of discharge of mine waste into agricultural lands in the study area

sandstones and micaceous mudstones. Bluish-grey or olive-brown shales, which weather to a rusty brown colour, are also present. Nwachukwu (1975) described the sediments as structurally folded, particularly in the southern area of Abakaliki with fold axes stretching in the NE-SW direction. Locally, the shales are fissile at Enyigba, Amanchara and Mkpuma Akpatakpa area, while the indurated, hard and baked facies are prominent in the Abakaliki urban. Lead–zinc mineralizations (veins and lodes) were observed variously at Mkpuma Akpatakpa, Ameka, Enyigba, Amorie, Ekweburu Village and Agbaja. The area is mainly drained by the Ebonyi River and other tributaries like River Ewe, River

Ogbogbo and Ikenyi River. All these rivers have major flow in the N-S direction in the tabular plain of the area (Fig. 2).

Material and method

Sample collection and preparation

A total of one hundred and sixteen (116) stream sediments and soil samples were collected in two seasons, fifty-eight (58) from each season, at various locations from the major tributaries and distributaries of Ebonyi River (which controls the

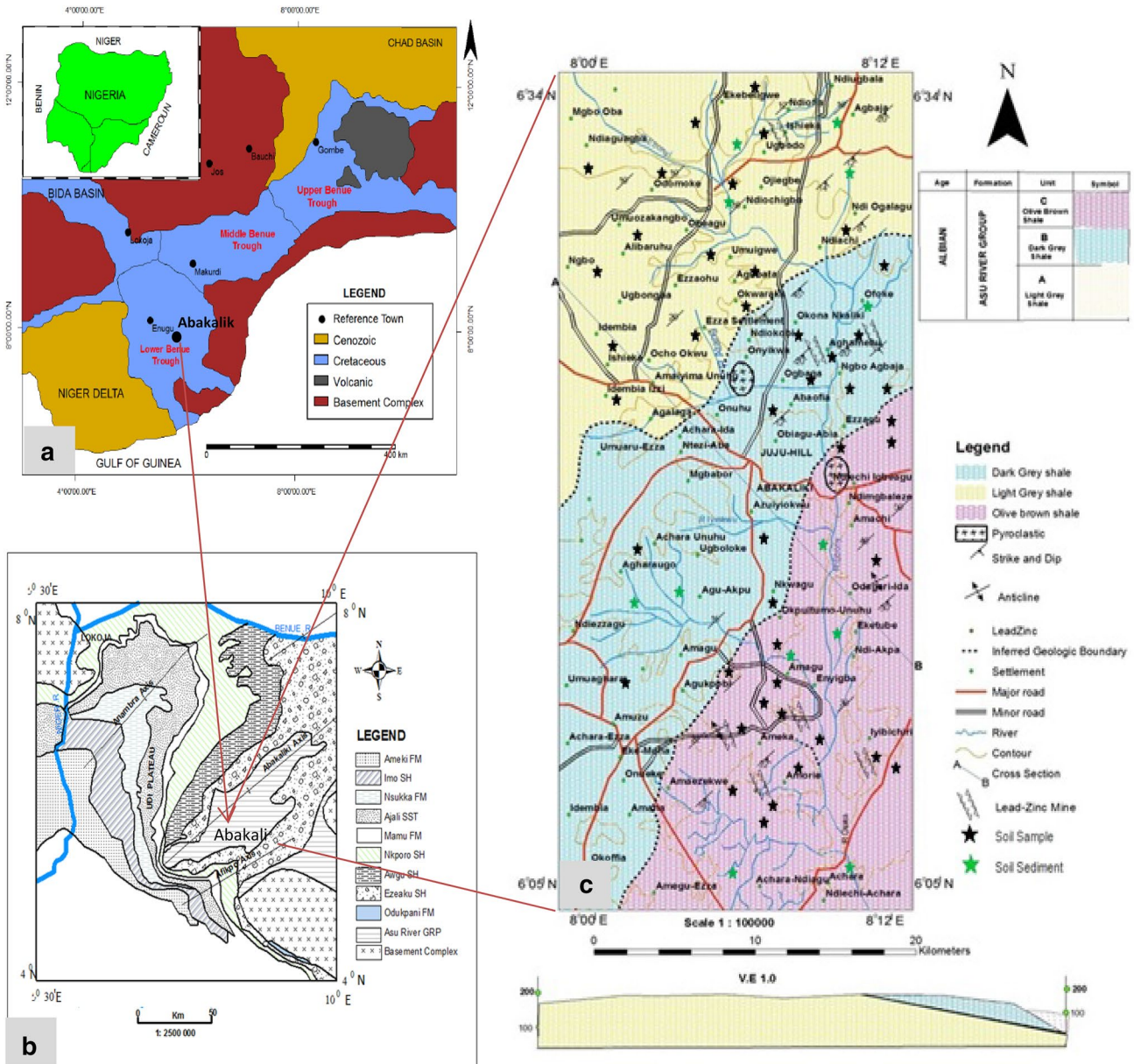


Fig. 2 a Geologic map of the lower benue trough (LBT) (Zaborski 1998), b stratigraphic settings of the LBT (modified from Nwajide 2013) and c geological map of the study area showing dominant rock types and sample locations

drainage of the area), mine sites and agricultural farmlands (Fig. 2). Pretest systematic sample preparation was done for each soil sample analysed, including drying, screening and digestion. At the point of collection, the soil was dug about 10 cm to avoid undue concentration from top soil. Since the sediments were damp, they were firstly dried and disaggregated prior to sieving. The samples were laid out in pre-numbered evaporating dishes and sun-dried for three days. Each sample was disaggregated and homogenized by the use of agate pestle and mortar. Ukpong (1991) noted that for sediments from Benue Trough, the optimum grain size to achieve best geochemical contrast is 120mesh. The nylon screen was used to avoid contamination. After screening, 2.0 g of each sample was weighed for digestion. The samples were digested by using aqua regia, which was prepared by the mixture of HNO₃ and HCl in the ratio 1:3. The heavy metal analysis was conducted using Varian AA240 atomic absorption spectrophotometer in line with American Public Health Association (APHA) (2005) specification. Electrical conductivity (EC) and pH were carried out using electrical conductivity meter (DDS 307 model) and pH meter (Hanna model H1991300), respectively.

Laboratory analysis

Laboratory analysis for the concentration of As, Cr, Zn, Ni, Pb, Cu, Hg, Cr, Cd and Mn²⁺ was done using fast sequential (FS) (Varian 2400 AA) atomic absorption spectrophotometer. Agilent FS2400AA has an accuracy level of 99.8%, precision of 97.6% and detection limit of 0.0003 ppm. All sampling steps and data analysis were performed according to standard methods for water and wastewater APHA (1995).

Data analysis

Microsoft Excel and Suffer 11 software were used to show the distribution of the contaminants in the area. The results were discussed and compared with the World Health Organization (WHO) standards for water quality with respect to the associated health risk.

Results and discussion

The results of geochemical analysis of soils/stream sediments are shown in Table 1, while Table 2 is a statistical summary with average abundance.

Concentration and distribution of various elements

Zinc (Zn)

Zinc is well dispersed in the study area, and all the samples recorded concentrations for zinc. The concentration of zinc

ranged from 6.01 to 203 mg/kg, with a mean concentration of 48.07 mg/kg, from the dry season samples, while concentration of rainy season samples ranges from 0.08 mg/kg to 186 mg/kg. The standard deviation is 29.81. It also has a geochemical background value that has been set at 70 mg/kg in the Earth's crust and 90 mg/kg for shale (Table 2). The highest concentrations of zinc were recorded at the areas around Enyigba, Ameka and Mkpuma Akpatakpa, where active mining is ongoing (Fig. 3a). This result shows higher concentrations in soils of the derelict mines than stream sediments in the area. The lowest concentration was recorded in River Abe Odomoke.

The distribution and transport of zinc in water, sediments and soils are dependent upon the species present and characteristics of the environment, especially pH, redox potential (Eh), salinity, nature and concentrations of complexing ligands, cation exchange capacity, and the concentration of zinc (Mcqueen 2008; Gundersen and Steinnes 2003). Sorption is the dominant reaction, resulting in the enrichment of zinc in suspended and bed sediments (ATSDR 2005; Environmental Protection Agency (EPA) 1979). Natural background of total zinc concentration is usually from 10 to 300 mg/kg dry weight in soils (Buchauer 1973). ATSDR (2005) stated that increased levels of zinc in soils can be attributed to natural occurrence of zinc enriched ores (as in the study area), anthropogenic sources including the disposal of zinc wastes from metal manufacturing industries and coal ash from electric utilities, sludge and fertilizer or even through abiotic and biotic processes. Toxicity in human may occur if zinc concentration in water approaches 400 mg/kg. This is characterized by symptoms of irritability, muscular stiffness, pain, loss of appetite and nausea. Zinc appears to have a protective effect against the toxicities of both cadmium and lead (Alloway 1995; Fergusson 1990).

Copper (Cu)

From the result, copper was observed in nearly all the locations except in Umuoze-Okoha and Ikenyi, and it was well dispersed. Copper has a mean concentration of 13.40 mg/kg and a range of 126 mg/kg for the dry season samples, while rainy season samples range from 0.16 to 115.17 mg/kg, with mean value of 15.49 mg/kg, and the standard deviation is 1.08. Copper is more concentrated at Ameka and Aghamegu (Fig. 3b). Geochemical background value was set as 55 mg/kg in Earth's crust and 50 mg/kg in shale. The high concentrations of copper can be attributed to the mining activities and the chemical behaviour of copper. The movement of copper in soil is determined by the physical and chemical interactions of copper with soil components (Andrews and Sutherland 2004). Tyler and McBride (1982) noted that most copper deposited in soil from the environment and sludge disposal will be strongly adsorbed and remains in the upper

Table 1 Result of geochemical constituents for stream sediments/soil samples (mg/kg) analysed

S/N	LOCATION	Dry season										Rainy season									
		P ^H	EC	Zn	Cu	Pb	Cd	Cr	Hg	Ag	As	P ^H	EC	Zn	Cu	Pb	Cd	Cr	Hg	Ag	As
		1	Egwudinagu	7.39	457	18.89	28.19	4.120	0.00	0.00	0.00	0.00	0.00	8.02	37	1.80	28.19	4.120	0.00	0.00	0.00
2	Umuezekoha	6.75	64	9.29	5.520	5.810	0.00	15.08	0.00	0.00	0.0	6.28	48	5.120	5.520	5.810	0.00	15.08	0.00	0.00	0.0
3	Ikenyi	3.33	918	10.43	1.260	23.63	6.60	37.97	1.00	0.370	0.00	4.48	11.8	22.71	1.260	23.63	6.60	37.97	1.00	0.370	0.00
4	Igbuhoatum	3.34	27.8	16.62	4.110	36.27	0.250	31.12	1.00	0.240	0.00	4.12	17.8	36.59	4.110	36.27	0.250	31.12	1.00	0.240	0.00
5	Okaria Nkaliki	6.68	88.3	6.58	4.260	49.23	7.070	7.960	0.00	0.230	0.00	4.19	10.7	107.0	4.260	49.23	7.070	7.960	0.00	0.230	0.00
6	Mkpuma Akpatakpa	3.32	910	120.59	102.66	65.47	7.670	13.65	1.00	0.640	0.00	3.26	12.10	107.58	102.66	65.47	7.670	13.65	1.00	0.640	0.00
7	Aghamegu	4.41	94	121.35	1.660	6.640	0.00	2.00	0.00	0.170	0.00	6.92	11.11	0.810	1.660	6.640	0.00	2.00	0.00	0.170	0.00
8	Abofia	4.89	98.2	52.16	54.21	27.23	0.390	13.44	1.00	0.560	0.00	6.12	18.48	31.31	54.21	27.23	0.390	13.44	1.00	0.560	0.00
9	Ohoke	5.48	29.8	26.65	10.60	0.520	0.000	2.100	0.10	0.050	0.00	7.48	13.62	10.90	10.60	0.520	0.000	2.100	0.10	0.050	0.00
10	Ebonyi River, Ndiegu	6.56	172.4	21.77	4.70	0.000	0.20	0.60	0.00	0.000	0.10	4.01	10.82	33.80	4.70	0.000	0.20	0.60	0.00	0.000	0.10
11	Ameka 1	6.69	385	109.31	115.17	67.20	1.620	51.00	28.0	0.210	0.10	2.26	13.1	105.01	115.17	67.20	1.620	51.00	28.0	0.210	0.10
12	Ameka 2	3.26	107.8	108.09	102.68	56.01	1.500	49.26	31.2	1.210	0.10	2.58	11.2	96.80	102.68	56.01	1.500	49.26	31.2	1.210	0.10
13	Enyigba 1	9.87	137.4	42.78	96.21	27.93	1.610	0.00	29.0	1.7	2.09	3.42	10.3	84.73	96.21	27.93	1.610	0.00	29.0	1.7	2.09
14	Amegu 1	6.24	120.2	14.96	32.61	31.21	0.080	12.04	8.10	0.010	0.00	5.21	32.8	52.08	32.61	31.21	0.080	12.04	8.10	0.010	0.00
15	Amegu 2	6.18	102.1	29.14	32.61	20.00	0.100	8.120	1.00	0.010	0.00	6.18	34.5	52.08	32.61	20.00	0.100	8.120	1.00	0.010	0.00
16	Ameri Salt lake	8.26	92	103.9	40.12	74.05	0.310	25.60	1.00	0.570	0.00	6.77	13.8	50.70	40.12	74.05	0.310	25.60	1.00	0.570	0.00
17	Akpara River, Enyigba	6.22	120	18.90	31.98	60.07	10.21	1.650	1.00	0.150	1.00	7.29	9.4	2.90	31.98	60.07	10.21	1.650	1.00	0.150	1.00
18	Elimwobvu, Enyigba	6.17	86	21.52	4.180	29.60	0.00	1.30	0.00	0.010	0.00	6.88	21.7	15.18	4.180	29.60	0.00	1.30	0.00	0.010	0.00
19	Ameri	6.33	192	22.64	1.260	1.490	0.220	2.940	0.00	0.00	0.00	6.71	20.3	17.66	1.260	1.490	0.220	2.940	0.00	0.00	0.00
20	Amorie	6.69	388	17.62	1.010	10.00	0.00	1.410	0.00	0.000	0.00	5.20	10.6	9.810	1.010	10.00	0.00	1.410	0.00	0.000	0.00
21	Ndiefi	8.67	96	9.60	0.160	0.600	0.00	1.410	0.00	0.000	0.00	6.87	8.13	5.680	0.160	0.600	0.00	1.410	0.00	0.000	0.00
22	Ugbodo road, Egwudinagu	7.69	27	12.73	1.10	1.800	0.00	7.100	0.00	0.00	0.00	6.89	20.1	9.10	1.10	1.800	0.00	7.100	0.00	0.00	0.00
23	Egwudinagu	8.25	38	23.43	2.10	0.280	0.000	0.900	0.00	0.00	0.00	6.59	11.4	14.90	2.10	0.280	0.000	0.900	0.00	0.00	0.00
24	Ojiegbe	7.53	209	15.08	1.340	0.000	0.200	0.000	0.00	0.00	0.00	7.18	12.1	9.030	1.340	0.000	0.200	0.000	0.00	0.00	0.00
25	Amanchara	4.06	78.6	48.97	1.820	10.05	4.100	1.400	1.00	0.710	0.00	4.89	27.16	18.91	1.820	10.05	4.100	1.400	1.00	0.710	0.00
26	Nwofe rd, Amanchara	7.19	278	15.18	1.660	5.230	0.00	1.600	0.00	0.00	0.00	5.86	13.4	11.06	1.660	5.230	0.00	1.600	0.00	0.00	0.00
27	R. Awumini, Ndiechi	6.99	112	17.78	6.700	0.010	0.500	0.100	0.00	0.060	0.00	8.21	10.86	12.90	6.700	0.010	0.500	0.100	0.00	0.060	0.00
28	Nwofe	5.62	118	35.05	0.700	5.200	0.000	0.110	0.00	0.000	3.00	6.74	9.8	26.30	0.700	5.200	0.000	0.110	0.00	0.000	3.00
29	Abandoned Pb-Zn Amanchara	4.32	282	29.63	56.68	10.01	5.60	5.120	0.00	0.060	0.00	4.41	39.2	21.96	56.68	10.01	5.60	5.120	0.00	0.060	0.00
30	Ndiegbala	6.25	152	13.47	2.030	0.300	0.400	2.800	0.00	0.000	3.80	6.92	10.4	6.740	2.030	0.300	0.400	2.800	0.00	0.000	3.80
31	Mkpuma Akpatakpa 1	3.33	920	101.32	12.06	48.67	16.46	12.03	0.00	0.770	0.00	2.52	36.4	99.90	12.06	48.67	16.46	12.03	0.00	0.770	0.00
32	Mkpuma Akpatakpa 2	2.98	813	96.74	9.26	19.04	8.360	10.16	0.00	0.240	0.00	3.40	48.1	89.51	9.26	19.04	8.360	10.16	0.00	0.240	0.00
33	Ndiagu Obovu	6.42	148	18.85	12.10	3.80	0.00	1.09	0.00	0.00	0.00	8.92	17.8	4.560	12.10	3.80	0.00	1.09	0.00	0.00	0.00
34	R. Abe, Ndiagalegu	6.46	272	25.12	3.400	20.70	0.40	9.500	0.00	1.30	0.00	6.63	11.01	21.03	3.400	20.70	0.40	9.500	0.00	1.30	0.00

Table 1 (continued)

S/N	LOCATION	Dry season											Rainy season										
		pH	EC	Zn	Cu	Pb	Cd	Cr	Hg	Ag	As		pH	EC	Zn	Cu	Pb	Cd	Cr	Hg	Ag	As	
		35	Agubata	6.68	232	23.62	6.990	10.01	0.00	1.080	0.00	0.02	0.00	8.11	13.21	1.980	6.990	10.01	0.00	1.080	0.00	0.02	0.00
36	Ngele Akpu, Oyege	8.29	72	13.95	1.260	1.420	0.000	10.32	0.00	0.220	0.00	6.46	9.2	5.010	1.260	1.420	0.000	10.32	0.00	0.220	0.00		
37	River Abe, Obeagu	7.26	274	26.77	1.120	9.940	0.070	12.70	1.00	0.010	0.00	6.01	8.08	21.24	1.120	9.940	0.070	12.70	1.00	0.010	0.00		
38	River Abe, Odomoke	8.10	26.8	6.01	0.210	7.120	0.260	4.170	1.00	0.600	0.00	7.48	10.06	2.220	0.210	7.120	0.260	4.170	1.00	0.600	0.00		
39	Ekebiligwe	6.78	342	86.30	1.120	10.60	0.00	1.00	0.00	0.000	0.00	8.27	11.40	0.080	1.120	10.60	0.00	1.00	0.00	0.000	0.00		
40	Ndiaguebe	9.00	27	6.83	1.160	29.09	0.00	23.86	0.00	0.660	0.00	6.26	10.02	27.75	1.160	29.09	0.00	23.86	0.00	0.660	0.00		
41	Eketabe	6.88	231	96.16	4.410	26.29	0.450	0.00	0.00	0.700	0.00	5.71	9.06	80.68	4.410	26.29	0.450	0.00	0.00	0.700	0.00		
42	River Akpara, Enyigba	4.10	827	90.28	2.50	13.90	0.00	9.00	0.00	0.500	0.00	4.83	29.5	87.41	2.50	13.90	0.00	9.00	0.00	0.500	0.00		
43	Agalegu	3.48	542	103.00	7.40	44.70	2.90	2.50	0.00	1.600	29.80	4.98	44.6	81.30	7.40	44.70	2.90	2.50	0.00	1.600	29.80		
44	Mbabo	4.18	241	103.55	7.10	21.80	2.80	9.10	0.00	7.70	31.20	5.29	56.98	93.20	7.10	21.80	2.80	9.10	0.00	7.70	31.20		
45	River Akpara, Agalegu	6.89	268	56.13	6.610	27.06	0.00	11.87	0.00	0.970	19.00	6.81	29.02	22.66	6.610	27.06	0.00	11.87	0.00	0.970	19.00		
46	Alibaru	6.18	37	60.76	0.600	3.910	0.010	6.610	0.00	0.740	0.00	5.12	28.1	30.56	0.600	3.910	0.010	6.610	0.00	0.740	0.00		
47	River Ogorube, Ngbo	7.25	48	15.71	1.120	5.06	0.00	0.500	0.00	0.020	0.00	8.76	21	6.980	1.120	5.06	0.00	0.500	0.00	0.020	0.00		
48	River Ogbogbo, Izzi	5.68	281	84.20	28.81	34.41	0.110	8.120	0.00	0.00	1.00	6.71	13.01	45.10	28.81	34.41	0.110	8.120	0.00	0.00	1.00		
49	River Atang Ndiokabi	5.78	301	83.19	6.920	28.17	0.00	4.110	0.00	0.760	20.10	6.42	19.2	36.61	6.920	28.17	0.00	4.110	0.00	0.760	20.10		
50	Agbaja	8.18	56	17.20	5.700	1.540	0.00	11.30	0.00	0.210	0.00	8.99	17.2	10.01	5.700	1.540	0.00	11.30	0.00	0.210	0.00		
51	Mgbabor	8.26	97	19.36	6.120	2.310	0.010	4.800	0.00	0.00	8.80	9.28	9.81	4.650	6.120	2.310	0.010	4.800	0.00	0.00	8.80		
52	Otere Offie	7.41	92	23.24	1.820	1.980	0.020	5.00	0.00	0.00	25.0	9.98	6.44	9.270	1.820	1.980	0.020	5.00	0.00	0.00	25.0		
53	Idembia	7.28	108	21.13	3.610	4.440	1.700	0.00	0.00	0.030	0.00	5.69	26.1	10.08	3.610	4.440	1.700	0.00	0.00	0.030	0.00		
54	Umuaghara	6.66	128	47.11	3.080	3.110	0.00	0.030	0.00	1.30	0.00	5.21	10.08	21.39	3.080	3.110	0.00	0.030	0.00	1.30	0.00		
55	Agharugha	6.89	27	26.90	3.010	5.140	0.000	10.21	0.00	0.46	0.00	5.69	18.02	28.09	3.010	5.140	0.000	10.21	0.00	0.46	0.00		
56	Idembia	7.29	47	14.51	2.110	7.850	0.00	8.520	0.00	0.00	0.00	8.27	2.16	4.640	2.110	7.850	0.00	8.520	0.00	0.00	4.640		
57	Ameka 3	2.98	929	202.00	6.080	65.20	5.920	0.010	0.00	4.10	19.00	3.26	14	142.0	6.080	65.20	5.920	0.010	0.00	4.10	19.00		
58	Enyigba 3	3.43	816	203.00	3.300	56.20	2.300	0.400	0.00	0.300	19.00	2.91	29	186.0	3.300	56.20	2.300	0.400	0.00	0.300	19.00		

Table 2 Summary of statistical analysis with average abundance of heavy metals

Metals	Maximum conc.		Min conc (mg/kg)		Mean conc (mg/Kg)		Variance (mg/kg)($x - \bar{x}$)		SD	Average abundance Levinso (1974)	
	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy		Earth's crust	Shale
	Zn	203	186	6.01	0.08	48.07	37.16	5.45	-5.46	29.81	70
Cu	206.99	115.17	0.00	0.00	13.40	15.49	-1.05	1.04	1.08	55	50
Pb	74.3	74.05	0.00	0.00	18.49	19.71	-0.61	0.61	0.37	12.5	20
Cd	8.25	16.46	0.00	0.00	1.08	1.56	-0.24	0.24	0.06	0.15	0.3
Cr	28.32	51	0.00	0.00	9.00	8.20	0.4	-0.4	0.16	100	73
Hg	6.03	31.2	0.00	0.00	0.37	1.83	-0.73	0.73	0.53	N/A	N/A
Ag	30.29	7.7	0.00	0.00	3.14	0.52	1.31	-1.31	1.72	N/A	N/A
As	56	19.00	0.00	0.00	11.19	1.21	5.09	-4.89	23.91	1.8	10

layers of soil. In general, copper is mostly adsorbed to organic matter, carbonate minerals, clay minerals or hydrous iron and manganese oxides (Callahan et al. 1979; Fuhrer 1986). Apart from the fact that the distribution of copper in soils is less affected by pH than other metals, it binds to soil much more strongly than other divalent cations (Gerritse and Van Driel 1984). Tyler and McBride (1982), in a study of competitive adsorption and leaching of metals in soil columns of widely different characteristics, showed that copper eluted much more slowly and in much lower quantities than Zn, Cd and Ni from two mineral soils and not at all from peat soil, which contained the greatest amount of organic matter. Hermann and Neumann-Mahlkau (1985) demonstrated that copper shows a pronounced solubility in the oxidizing environment, than in the reducing environment, possibly due to the formation of sulphides.

Lead (Pb)

Lead–zinc deposits are the major source of lead in the environment. Other sources in dust and soil include lead that falls to the ground from the air and deterioration of products of lead-based paint from buildings (ATSDR 2007). Landfills in industrial areas are also potential sources, as they may contain waste from lead ore mining or other industrial activities such as battery production (Denaix et al. 2001). Deposits of lead-containing dust from the atmosphere (in industrial areas) and wastewater from industries handle raw materials that contain lead (primarily iron and steel industries and lead producers), urban run-off and mining piles (Finster et al. 2004). This analysis shows high dispersion for lead in the study area. A mean concentration of 18.49 mg/kg with the range of 0.00–74.3 mg/kg, for the dry season samples, was recorded for lead, while the result of rainy season samples ranged from 0 to 74.05 mg/kg, with mean concentrations of 19.71 mg/kg. The standard deviation is 0.37. The maximum concentration was recorded in samples around the Ameka and Mkpuma Akpatakpa mining area (Fig. 3c). Geochemical background value was set as 12.5 mg/kg in Earth's crust and

20 mg/kg in shale. The occurrence of lead zinc ores (galena) in the study area notwithstanding the chemical behaviour of lead contributes to its higher values in the soils of the area. Studies by ATSDR (2007) showed that once lead falls onto soils, it sticks strongly to soil particles and remains in the upper layer of soil. Lead is immobilized by ion exchange with hydrous oxides or clays or by chelation with humic or fulvic acids in the soil (Olson and Skogerboe 1975). Reddy et al. (1995) have also concluded that the mobility of lead will increase in environments having low pH due to the increased solubility of lead under acidic conditions. Both studies showed that the accumulation of lead in most soils is primarily a function of the rate of deposition from the atmosphere. High concentrations of lead are retained strongly in soil, and very little is transported through run-off to surface water or leaching to groundwater except under acidic conditions EPA (1986) and NSF (1977), noted.

Cadmium (Cd)

Cadmium can be released to the atmosphere through metal production activities, fossil fuel combustion and waste materials incineration. Cadmium can also accumulate in soils due to atmospheric deposition and direct application methods such as the use of phosphate fertilizer and sewage sludge disposal. Geochemical analysis indicates concentrations of cadmium with a range of 8.25 mg/kg, with mean concentration of 1.08 mg/kg for the dry season samples, while rainy season samples ranged from 0.00 to 16.46 mg/kg with mean concentrations of 1.56 mg/kg. The standard deviation is 0.06. This indicates very high concentration, especially for the Ameka and Mkpuma Akpatakpa mining areas (Fig. 3d) when compared to the geochemical background value of 0.15 mg/kg on the Earth's crust and 0.3 mg/kg in shale. ATSDR (2007) noted that high concentration of cadmium is commonly associated with the occurrences of zinc, lead and copper ores. This is the case of the study area. Garvey et al. (2013) and Harrison et al. (1981) also noted that in soils, physical and

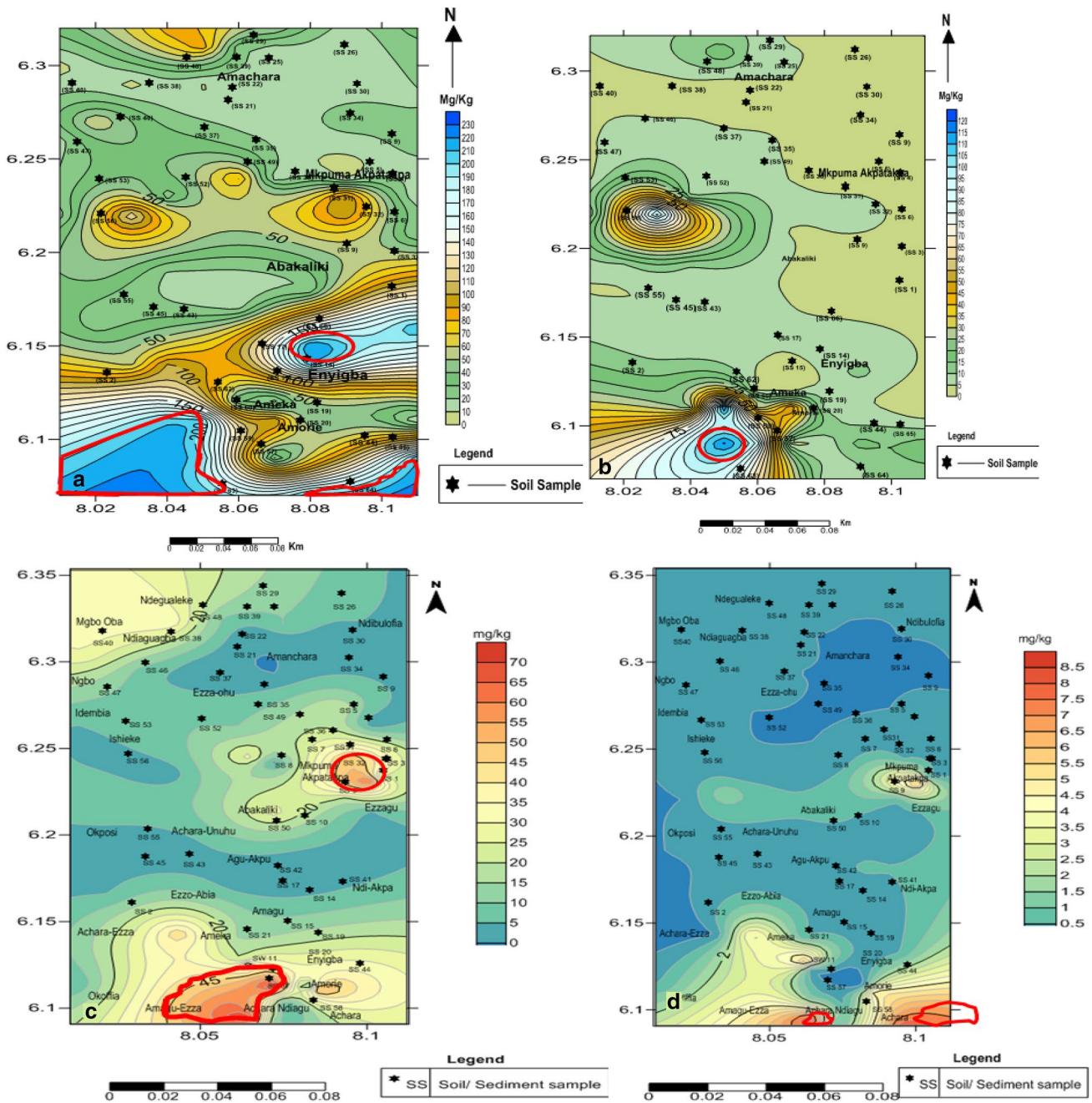


Fig. 3 Contoured distribution of **a** zinc, **b** copper, **c** lead and **d** cadmium in dry season samples analysed with areas of high concentrations as highlighted

chemical factors like pH, oxidation–reduction reactions, formation of complexes and the availability of organic matter are affected by the mobility of cadmium. Low pH (acidity) increases the availability of cadmium (Elinder 1992). Generally, cadmium is more immobilized in soils. This is because it binds strongly to organic matter (Autier and White 2004). Studies by Kamau, (2001) and Elinder (1985) showed that while soluble forms may migrate in

water, it is relatively nonmobile in insoluble complexes or adsorbed to sediments. Although cadmium may be released into the air as particles and vapour, the net flux to soil will be positive as cadmium will eventually deposit onto soils. Harrison et al. (1981) also observed that cadmium may precipitate as insoluble cadmium compounds or form complexes or chelates by interaction with organic matter.

Chromium (Cr)

Chromium was evenly distributed in the study area. The mean concentration of Cr is 9.00 mg/kg with a range of 0.00–28.32 mg/kg for the dry season samples, while rainy season samples range from 0.00 to 51.87 mg/kg with mean of 8.20 mg/kg. Higher concentrations were observed around the mines than other areas (Fig. 4a). Geochemical background value was set as 100 mg/kg in Earth's crust and 73 mg/kg in shale.

Although chromium occurs naturally in rocks, animals, plants and soil, where it exists in combination with other elements to form various compounds, ATSDR (2012) indicated that anthropogenic activities like the manufacture of chromium-based products, leather tanning and the burning of natural gas, oil or coal can release chromium in the environment. (Ashley et al. (2003) noted that the movement of chromium in soil is dependent upon the speciation of chromium, which is determined by the redox potential and the pH of the soil. Researches by Barnhart (1997) and Robson (2003) have noted that in most soils, chromium will be present predominantly in the chromium (III) oxidation state. This form has very low solubility and low reactivity, resulting in low mobility in the environment. Many researchers including James et al. (1997), Balasoio et al. (2001), Jardine et al. (1999) and Robson (2003) have studied the solubility and mobility of chromium. James et al. (1997) noted that chromium (VI) may be present in soil as CrO_4^{2-} and HCrO_4 under oxidizing conditions and Sahuquillo et al. (2003) demonstrated a leachability study comparing the mobility of several metals including chromium and showed that chromium had the least mobility of all of the metals studied. Balasoio et al. (2001), Jardine et al. (1999) and Robson (2003) have supported previous data findings that chromium is not very mobile in soil, especially in the trivalent oxidation state. Leachability investigations by Sheppard and Thibault (1991) carried out in a period of 4 years in a sandy loam also showed that chromium mobility is low while Jardine et al. (1999) emphasized that in deeper soil where anaerobic conditions exist, chromium (VI) will be reduced to chromium (III) by S^{-2} and Fe^{+2} present in soil.

Mercury (Hg)

Low concentration of mercury was observed in the study area. Only few samples around Abakaliki area showed the presence of Hg while the rest showed low concentrations (Fig. 4b). The mean concentration of mercury is 0.37 mg/kg with the range of 0.00–6.03 mg/kg for the dry season samples, while rainy season samples ranged from 0.00 to 8.1 mg/kg. Its maximum concentrations were recorded at the Amanchara and the Ameka mining areas. The accumulation of mercury in the environment is due to the weathering of

minerals in rocks and soil from exposure to climatic forces and from volcanic activity, and ATSDR (2012) noted that human activities such as mining and burning of fossil fuels have resulted in its additional release to the environment. In soils and surface waters, mercury can exist in two states: mercuric (Hg^{+2}) and mercurous (Hg^{+1}) (Meili 2013). Temperature controls the vaporization of mercury from soils, with emissions from contaminated soils being greater in warmer weather when soil microbial reduction of Hg^{+2} to the more volatile elemental mercury is greatest (Lindberg et al. 1991). Sato and Sada (1992) and WHO (1990, 1991) noted that atmospheric deposition of mercury from both natural and anthropogenic sources has been identified as an indirect source of mercury to soil and sediments. This is correct as mercury is released to cultivated soils through the direct application of inorganic and organic fertilizers (e.g. sewage sludge and compost), lime and fungicides containing mercury (Andersson 1979). In their view, Glass et al. (1991) suggested that the concentration of mercury in the atmosphere is due to its long resident time in the atmosphere. They estimated the residence time in the atmosphere to range from 60 days to 2 years. Mercury concentration can also increase by the release of volatile forms in water or soil, but most mercury is adsorbed to soil and sediment (EPA 1984; Meili 2013). Mercuric mercury usually forms various complexes with chloride and hydroxide ions in soils (Boske et al. 2004; Andersson 1979).

Silver (Ag)

From the result obtained, silver was not evenly distributed compared to the heavy metals in the study area. Many samples showed the absence of silver for the two seasons. Maximum concentration of 30.29 mg/kg and 7.7 mg/kg and mean concentration of 3.14 mg/kg and 0.52 mg/kg were recorded for the dry and rainy seasons, respectively. The mining regions of Mkpuma Akpatakpa and Enyigba showed higher concentrations (Fig. 4c). Silver has a standard deviation of 1.72.

Mining processes and the weathering of silver-bearing rocks and ores like chalcopyrite, galena and siderite are the major sources of silver in soils and the environment. ATSDR (1990) also indicated that rain can also release large amounts of silver into the environment. Apart from the weathering of ores which deposits silver in the study area, other factors which affect the mobility of silver in soils are drainage (silver tends to be removed from well-drained soils); oxidation–reduction potential and pH conditions (which determine the reactivity of iron and manganese complexes which tend to immobilize silver); and the presence of organic matter (which complexes with silver and reduces its mobility) (Boyle 1968). Although the environmental fate of silver are not well studied and characterized, silver and its compounds

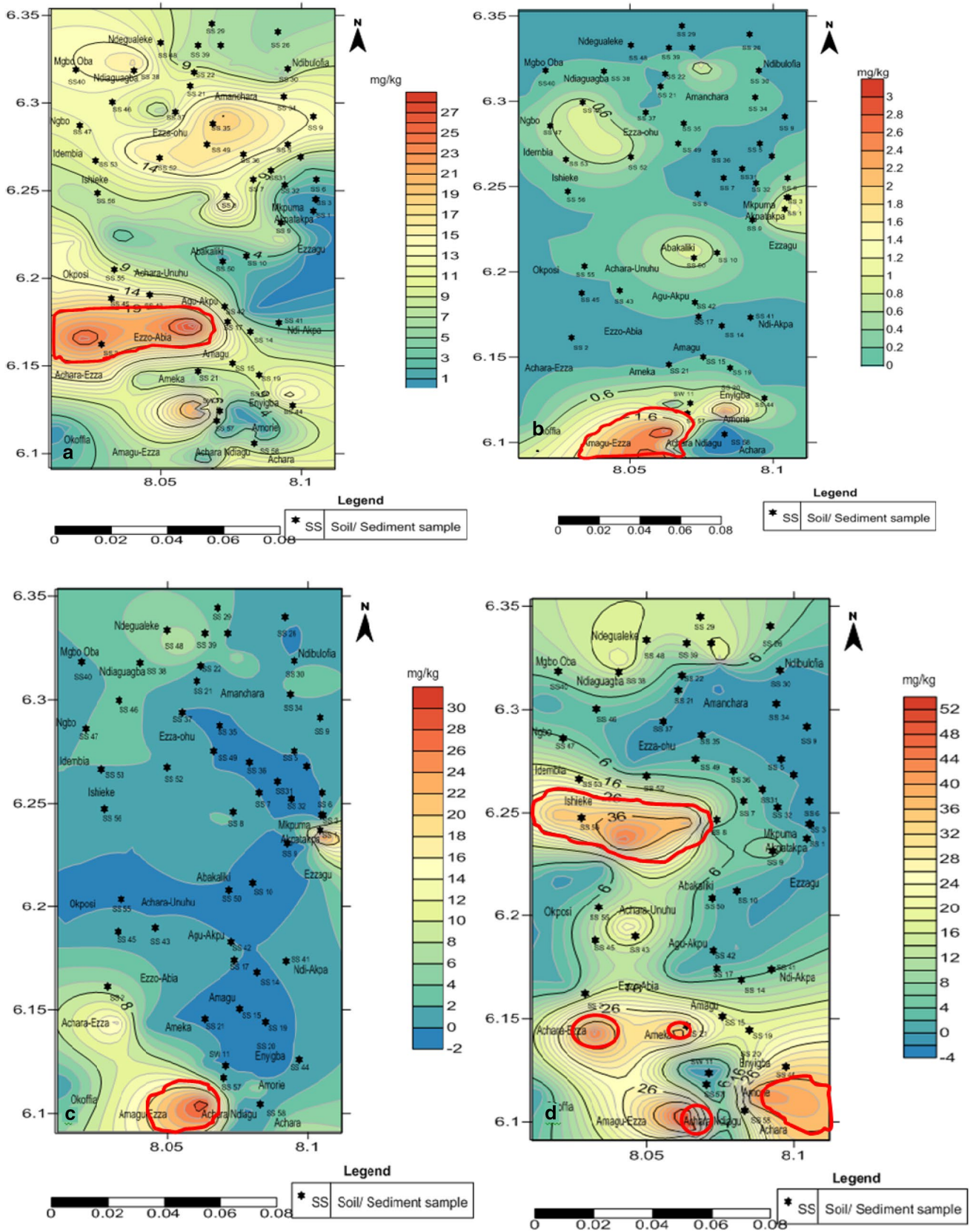


Fig. 4 Contoured distribution of **a** chromium, **b** mercury, **c** silver and **d** arsenic in dry season samples is analysed with areas of high concentrations as highlighted

are transported in the air, water and soil and are partitioned between these media (ATSDR 1990; Dissanayake et al. 1983). The transport and partitioning of silver in surface waters and soils are influenced by the particular form of the compound. However, according to Lindsay and Sadiq (1979), under oxidizing conditions the primary silver compounds would be bromides, chlorides and iodides, while under reducing conditions the free metal and silver sulphide would predominate.

Arsenic (As)

The result of geochemical analysis showed that arsenic was dispersed in the study area (Fig. 4d). Many of the samples locations show high concentrations of arsenic. It has a maximum concentration of 56 mg/kg with mean concentration of 11.19 mg/kg for the dry season samples, while rainy season samples showed very low concentration values of 0.00 mg/kg (in most places)—19.0 mg/kg with mean concentration of 1.21 mg/kg. The standard deviation is 23.91. Geochemical background value was set as 1.8 mg/kg in Earth's crust and 10 mg/kg in shale. This result indicates very high contamination for the area, especially in the mining fields of Ameka and Enyigba.

Major sources of arsenic in the environment are exploitation and processing of minerals and ores that contain copper or lead. Environmental and physical forces including leaching may transport arsenic into subsurface soil (Moore et al. 1988). However, EPA (1982), Pantsar-Kallio and Manninen (1997) and Welch et al. (1988) noted that under oxidizing conditions, leaching does not transport arsenic to great depth in the soil profile. Sanok et al. (1995) also affirmed that arsenic is largely immobile in agricultural soils; therefore, it tends to concentrate and remain in upper soil layers indefinitely. Natural or anthropogenic particles of arsenic form insoluble complexes with iron, aluminium and magnesium oxides in soil surfaces, and in this form, arsenic is relatively immobile (Merwin et al. 1994).

Conclusion

The geochemical assessment of soils and stream sediments in the mining areas of Abakaliki, Southeastern Nigeria, was carried out in all communities where active and abandoned mines are located: Enyigba, Mkpuma Akpatakpa, Ameka, Amorie, Amanchara, Agbaja and Alibaru. One hundred and sixteen soil/stream sediments were collected and subjected to geochemical analysis using an atomic absorption spectrophotometric method. The study showed high concentration and percentage contamination of $Cd > Pb > As > Zn > Cu > Ag > Hg > Cr$. This implies that arable soils around the mining areas (about 5 km radius) are not suitable for

food crop production as biomagnification can occur in the food chain. Hence, agricultural activities should be concentrated in safe areas to minimize the risk of potential health hazards. This work showed that the discharge of mine wastes and gangues in mining areas has effects on the available arable soils in mining areas. This can also serve as pointers for mineral exploration in mining areas. This assessment shows higher distribution of metals in the Mkpuma Akpatakpa and Ameka areas than the Enyigba and Amanchara areas. Solid minerals with high composition of Cd, Pb, As and Zn can be harnessed in the area.

Compliance with ethical standards

Conflict of interest I state clearly, that I have no conflict to declare.

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