Heavy Metal Contamination of Soil and Surface Water in the Arufu Lead-Zinc Mining District, Middle Benue Trough, Nigeria*

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Abstract

This paper is aimed at investigating the nature of heavy metals dispersion in soil and surface water around the Arufu lead-zinc mine, Middle Benue Trough, Nigeria. Rock samples from mine pits and adjoining outcrops as well as water samples from mine pits and adjacent streams were collected and analyzed. Also analyzed were soil samples collected from mine waste and adjoining areas as well as from a forest to serve as control. All samples were analysed for Fe, Zn, Mn, Cu, Pb, Cr, As, Cd and Ag, using atomic absorption spectrophotometer (AAS). Organic Matter (OM) content of the soil samples, and the pH of both soil and water samples were also determined. The results show that the OM content of soil was generally low (4 ± 1.1%) and both soil and water samples were characterized by moderate pH values of 6.30 to 8.00 and 5.60 to 7.80 respectively. Furthermore, soils developed over bedrock show normal (background) levels of heavy metals, while soils developed over mine waste are enriched in Zn (181 ± 83 mg/kg); Pb (40 ± 28 mg/kg) and Cd (3 ± 2 mg/kg). Also, water samples from mine ponds are enriched in Pb (0.02 – 0.10 mg/l) and Cd (0.02 – 0.04 mg/l). The sources of these heavy metals are most probably sulphides in the mine waste. Tailing and mine pits may therefore represent point sources of heavy metal contaminants and should therefore be reclaimed to prevent further contamination.

1 Introduction

For more than a century, the Benue Trough of Nigeria has been an area of considerable economic interest, primarily because of its Pb-Zn mineralization. More than twenty mineralized occurrences are localized in the 600 km long northeast-southwest trending belt of slightly deformed Cretaceous sediments. Arufu is one of the districts with the localized occurrences of the Pb-Zn mineralization and as far back as 1910; the inhabitants mined the ore for cosmetic purposes. Modern small-scale mining by various foreign and indigenous mining companies has been intermittent since 1921 (Pargater, 1959). At present, the mines are abandoned due to the exhaustion of ore reserves without any proper management of the mines and tailings.

According to Jung (2001), this mine waste could generate point source of heavy metal pollution in the local environment as elements are released to the biosphere at a higher rate than would occur by the natural weathering of underlying parent materials (Kelepertsis and Bibou, (1991); Pouyat, et al. (1995); Chen, et al. (1997); Wong, (1996). At Arufu, water from mine ponds is used for domestic and agricultural purposes. Besides, the mine waste together with adjoining land is being cultivated for food crop such as tubers, cereals, vegetables, legumes, etc. It is, therefore, most probable that the people may be accumulating some of these heavy metals through contaminated food and water to levels that could lead to phytotoxic effects (Mills, 1995).

This study therefore, attempts to investigate the degree of heavy metal contamination of soil and water in Arufu Pb-Zn mining district, Middle Benue Trough, Nigeria. Results from this research will serve as possible guide for better understanding of the quality of food and water as well as the health status of the inhabitants.

2 Study Area Description

Arufu mining district of Middle Trough, Nigeria is located between longitudes 9°10 and 9°20E and latitudes 7°40 and 7°45N (Fig. 1). The area which is undulating lies roughly 200-300 m above sea level. Laterite scarps which have resulted from prolonged dissection of former laterite sheets are dominant features in the area. Many small seasonal streams including Rivers Pii, Kutaji, Kiri and Ubaver, that are all tributaries of River Benue control the drainage in the area. The streams are structurally controlled and generally join to form a dendritic drainage pattern.

The area is characterized by the tropical wet-dry climate and the rainfall is generally moderate,
about 100-120 cm per annum. The annual temperature ranges from 30 – 35°C and the relative humidity is in the order of 30-60% (Iloeje, 1981). The vegetation in Arufu is the savannah wood type, typified by tall grass, shrub and a few trees ranging in height from 3-6 m.

3 Geology of Study Area

The Arufu mining district is within the Benue Trough (Fig. 1). The Benue Trough is about 600 km long and 80-90 km wide. It contains up to 5000 m thick of slightly deformed Cretaceous sediments and volcanic rocks (Olade, 1975). Detailed geological mapping of the study area (Pargater, 1959; Reyment, 1965) shows that it is underlain dominantly by Cretaceous sediments comprising shales, sandstones, and limestone. The sediments are intruded by diorite and granites (Fig. 1). There are also the quaternary sediments represented by the alluvial deposits found along stream courses as well as laterite scarp. The sediments are highly folded and faulted into gentle pitching anticlines and domes that usually trend north-south. Faults and fractures trend north-south or northwest-southeast (Olade, 1976 and Ofoegbu, 1984).

The ore-bodies in the area are structurally controlled. The ore-bodies occur in fault zones, which served as channels for hydrothermal solutions and deposit their metallic and non-metallic minerals. The main mineralization in Arufu occurs as Pb-Zn lodes and veins along sheeted zones within carbonate host rocks (Pargater, 1959). The principal ore minerals are galena, sphalerite and chalcophyrite with minor bornite, marcasite and pyrite within a gangue of manganiferous siderite, dolomite, calcite, barite and sericite. In the supergene zone, the primary minerals are replaced by secondary minerals that include cerusite, pyromorphite, anglistite, calamine, malachite, azurite, ferric oxides and minor smithsonite (Abimbola and Akande, 1996).

4 Materials and Methods

Rock samples, surface soils at depths of 0-15 cm and water samples were collected at and around abandoned Pb-Zn mines at Arufu (Fig. 1). Bedrock samples were collected by chip sampling along the most continuous accessible outcrops. Soils samples were collected from mine waste and adjoining areas. Water samples were collected...
from mine ponds and surrounding streams. Forest soils were collected in a forest near Makurdi to serve as control samples.

The rock and soil samples were air-dried at room temperature for 72 hours. The rock samples were then crushed to minus 100-mesh and the soil samples sieved through minus 80 mesh and the resulting powders digested with 4:1 mixture of nitric perchloric acids. The resulting solutions were then stored properly into well labeled test tubes prior to analysis.

Surface water samples were collected in plastic bottles which were pre-soaked in acid washing liquid (1% HNO₃) and washed thoroughly with distilled water samples. At the sample point, the bottles were rinsed with the water before filling the bottle with the water. The water samples were then acidified with 1M HNO₃ in order that the ions remain in solution and to avoid the growth of bacteria and fungus. Samples were then stored in refrigerator prior to analysis within 24 hours.

The digested solutions and water samples were analysed for Fe, Zn, Mn, Pb, Cu, Cr, Cd, As and Ag using ASS, Bulk Scientific model 210 at University of Agriculture Makurdi. Data were assessed for accuracy and precision using a quality control system integral to the analytical procedure.

Soil pH was determined in the laboratory using Hach One-Meter model -43899 from slurry formed by a 1:1 ratio of sample to deionised water. The pH of water samples was determined in the field using pH Meter. Soil OM content was estimated from loss on ignition – LOI (Chukwuma, 1995).

5 Results

5.1 Trace Element Concentrations in Rock Samples

Heavy metals vary considerably among the different lithologies in the study area (Table 1), reflecting the varying abundance and composition of minerals in the bedrock. Thus, compared to the other units, the shales and diorites are characterised by relatively high trace element contents. Although the lowest levels of Mn (18mg/kg) and Ag (0.06mg/kg) are associated with the shale. Although the granites are relatively enriched in Pb (22mg/kg) and Cd (3mg/kg), limestone and granite have the lowest concentrations of most trace elements. Sandstones have moderate levels of trace elements, despite that they are relatively enriched in As (2mg/kg) and have the lowest Pb (6mg/kg) value.

5.2 Soil and Water Characteristics

Summary of the soil pH, OM and water pH are listed in Tables 2 and 3. Table 2 shows that soil samples are weakly acidic to alkaline with pH ranging from 6.30-8.00 with a mean value of 6.99±0.16. While the OM varied from 2-10% with mean of 4±1.3% implying that the soil contains low OM. The mean value of the water pH 6.3±1.20 and range of 5.80 to 7.60 (Table 3) indicate a weakly acidic to alkaline nature or moderate pH of the water.

5.3 Trace Metal Concentration in Soil and Water Samples

The range and mean concentration of Ag, As, Cd, Cr, Cu, Fe, Mn, Pb, and Zn in surface soil samples of the study and control areas as well as mean values common in soil (Rose, et al. 1979) are listed in Table 2. The concentrations of the trace elements in the study area are comparable to those of the control (forest soils) and are within the world mean values as quoted by Rose, et al. (1979) except for Zn (mean, 181 ± 83 mg/kg; range 18-420 mg/kg), Pb(mean, 40±28 mg/kg; range 12-130 mg/kg) and Cd (mean 3±2 mg/kg; range 1-6 mg/kg). Table 3 presents the mean and range of the concentrations of Ag, As, Cd, Cr, Cu, Fe, Mn, Pb and Zn in water samples of the study area together with acceptable limits of WHO (1993).

6 Discussion

The pH obtained for soils in the study area is comparable to that of the control (forest soils) with mean of 5.68 ± 0.25 and it is also within the world mean values (Rose, et al., 1979) indicating normal soil pH (Table 2). The relative low content of OM in soils samples from tailings (4±1.13%) as compared to forest soils (10±3%) could be attributed to the relative scarce and slow rate of biological decomposition of vegetation in the study area. This may also partly account for the moderate pH values encountered in the study area. The low OM content of the soils also implies that organometallic complexion which increases the mobility of metals in the secondary environment (Cox, 1995) is minimal in the area of the study.

The mean pH of 6.3 obtained in water samples in this study (Table 3) is slightly above the mean value of 5.9 obtained by Ofulume, et al. (2004) from water samples collected in the vicinity of the Pb-Zn mining district of Ebonyi State, lower Benue Trough. This moderate pH of the water and soil samples probably reflects some interaction with the limestone in the area. Most fresh waters are not saturated with calcium carbonate (CaCO₃) and so readily dissolve it leading to increase in pH (Hem, 1985). The waste rock and tailings with significantly reduced particle sizes result in considerable increase in carbonate dissolution.
Apart from Zn, Pb and Cd, the levels of trace elements in soils are within mean values of Rose, et al. (1979) and similar to those of the control (forest) area. However, enhanced levels of these elements are restricted to the soil samples collected from mine waste (tailings). Oxidation of sulphide minerals is known to cause the release of high level of metals from exposed tailings or mine waste (Sidenko, et al., 2007; Johnson, et al. 2000).

In the study area the source of these metals are probably from the oxidation of exposed sulphide minerals such as galena and sphalerite from mine wastes which are then leached into soils during heavy precipitation (Chen, et al., 1997; Romero, et al., 2007). These sulphide minerals are associated with the Pb-Zn mineralization in the Arufu mining district (Abimola and Akanda, 1996). Similar conclusions have been reached in other mining districts of Benue Trough by Adiuku-Brown and Ogezi (1991) and Chukwuma (1995). Fisher (1998) and Kelepertisis and Bibou (1991), have also reached similar conclusions from the study of Pb-Zn mining districts.

Levinson (1974), Thornton and Plant (1980), Cox (1995) are of the opinion that lithology is one of the major controls on the levels of variability of trace elements in the soils and that the portion of any area characterized by high content of a given trace element is usually very small. The higher levels of trace elements in soil samples relative to the parent materials (Tables 1 and 2) could be attributed to modifications by soil forming processes such as leaching, podzolization and accumulation by OM, colloids and Fe-Mn oxides (Harter, 1992). These processes are known to control the level and distribution of trace elements in the soils and are

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**Table 1 Trace Element Composition of Rocks from the Study Area**

<table>
<thead>
<tr>
<th>Rock</th>
<th>Fe</th>
<th>Zn</th>
<th>Cu</th>
<th>Mn</th>
<th>Pb</th>
<th>Cd</th>
<th>Cr</th>
<th>As</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biotite Granite</td>
<td>18.00</td>
<td>31.00</td>
<td>11.00</td>
<td>36.00</td>
<td>22.00</td>
<td>5.00</td>
<td>0.20</td>
<td>0.20</td>
<td>0.10</td>
</tr>
<tr>
<td>Diorite</td>
<td>31.00</td>
<td>64.00</td>
<td>14.00</td>
<td>45.00</td>
<td>13.00</td>
<td>2.00</td>
<td>0.60</td>
<td>0.30</td>
<td>2.00</td>
</tr>
<tr>
<td>Sandstone</td>
<td>28.00</td>
<td>47.00</td>
<td>6.00</td>
<td>33.00</td>
<td>6.00</td>
<td>2.00</td>
<td>0.40</td>
<td>2.00</td>
<td>0.20</td>
</tr>
<tr>
<td>Limestone</td>
<td>15.00</td>
<td>61.00</td>
<td>4.00</td>
<td>30.00</td>
<td>13.00</td>
<td>2.00</td>
<td>0.80</td>
<td>0.30</td>
<td>0.20</td>
</tr>
<tr>
<td>Shales</td>
<td>32.00</td>
<td>35.00</td>
<td>7.00</td>
<td>18.00</td>
<td>21.00</td>
<td>3.00</td>
<td>1.00</td>
<td>0.40</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Table 2 Mean ± Sd and Range of Values of Chemical Analysis of Soil Samples in the Study Area with the Ranges of their Mean Abundance

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Arufu (Tailings) (n=40)</th>
<th>Forest Soil* (n=40)</th>
<th>General mean abundance*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (mg/kg)</td>
<td>164 ± 44 (32 - 274)</td>
<td>171 ± 24 (120 – 300)</td>
<td>1-2%</td>
</tr>
<tr>
<td>Zn (mg/kg)</td>
<td>181 ± 83 (18 – 420)</td>
<td>85 ± 15 (25 – 150)</td>
<td>36 – 100</td>
</tr>
<tr>
<td>Mn (mg/kg)</td>
<td>140 ± 52 (10 – 300)</td>
<td>120 ± 21 (90 – 200)</td>
<td>300 – 400</td>
</tr>
<tr>
<td>Pb (mg/kg)</td>
<td>40 ± 28 (12 – 130)</td>
<td>20 ± 9 (7 – 31)</td>
<td>17 – 30</td>
</tr>
<tr>
<td>Cu (mg/kg)</td>
<td>20 ± 14 (4 – 60)</td>
<td>34 ± 16 (20 – 50)</td>
<td>20 – 50</td>
</tr>
<tr>
<td>Cd (mg/kg)</td>
<td>3 ± 2 (1 – 6)</td>
<td>2 ± 0.5 (0.1 – 3)</td>
<td>0.1 – 0.5</td>
</tr>
<tr>
<td>As (mg/kg)</td>
<td>3 ± 0.8 (1 – 5)</td>
<td>2 ± 0.5 (1 – 3)</td>
<td>5 – 10</td>
</tr>
<tr>
<td>Cr (mg/kg)</td>
<td>2 ± 0.3 (0.08 – 3)</td>
<td>42 ± 18 (20 – 60)</td>
<td>40 – 50</td>
</tr>
<tr>
<td>Ag (mg/kg)</td>
<td>0.3 ± 0.1 (0.08 – 3)</td>
<td>0.2 ± 0.04 (0.1 – 0.3)</td>
<td>0.2 – 0.5</td>
</tr>
<tr>
<td>Om (L01)%</td>
<td>4 ± 1.13 (2 – 10)</td>
<td>10 ± 3 (5 – 20)</td>
<td>-</td>
</tr>
<tr>
<td>pH</td>
<td>6.99 ± 0.16 (6.30 – 8.00)</td>
<td>6.68 ± 0.25 (5.80 – 7.60)</td>
<td>6.50 – 8.50</td>
</tr>
</tbody>
</table>

Table 3 Mean ± SD and Range of Value of Selected Elements in Water Samples alongside WHO (1993) Standard

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Water samples (n = 10)</th>
<th>WHO (1993) standard limit for drinking water (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (mg/l)</td>
<td>0.09 ± 0.02 (0.02 – 0.20)</td>
<td>0.30</td>
</tr>
<tr>
<td>Zn (mg/l)</td>
<td>1.5 ± 0.50 (0.80 – 2.30)</td>
<td>5.00</td>
</tr>
<tr>
<td>Mn (mg/l)</td>
<td>0.04 ± 0.01 (0.03 - 0.05)</td>
<td>0.05</td>
</tr>
<tr>
<td>Pb (mg/l)</td>
<td>0.05 ± 0.01 (0.02 - 0.10)</td>
<td>0.05</td>
</tr>
<tr>
<td>Cu (mg/l)</td>
<td>0.08 ± 0.02 (0.05 - 0.10)</td>
<td>1.00</td>
</tr>
<tr>
<td>Cd (mg/l)</td>
<td>0.03 ± 0.01 (0.02 - 0.04)</td>
<td>0.005</td>
</tr>
<tr>
<td>As (mg/l)</td>
<td>0.02 ± 0.005 (0.1 - 0.30)</td>
<td>0.05</td>
</tr>
<tr>
<td>Cr (mg/l)</td>
<td>0.02 ± 0.001 (0.01 - 0.03)</td>
<td>0.05</td>
</tr>
<tr>
<td>Ag (mg/l)</td>
<td>ND</td>
<td>0.001</td>
</tr>
<tr>
<td>pH</td>
<td>6.3 ± 1.20 (5.6 – 7.8)</td>
<td>6.5 – 8.5</td>
</tr>
</tbody>
</table>
known to depend on one or a combination of such soil properties like pH, water content (drainage), soil biology, redox potentials, salinity, soil grain size among others (De Bustamante, 1990).

The concentrations of Ag, As, Cd, Pb and Zn in soil were found to be enriched within the mineralized bedrock and to a lesser extent over diorites and shales. Whereas the soils that developed over barren limestone were characterized by low values but decreasing their ability to dissolve metals (Cox, 1995; Howard, 2006). Most metals are known to be soluble in acidic environments (Cox, 1995; Siegel, 2002). This study has revealed the weakly acidic to alkaline nature or moderate pH of both soil samples (pH 6.3-8.0) and water samples (pH 5.8 – 7.6) (Tables 2 and 3) which most probably reflect some interaction with the limestone in the area. Thus waste rock and tailings where particles size has been significantly reduced result in a considerable increase in surface area and promote increase in carbonate dissolution. Under the weakly acidic to alkaline conditions in this area, in-situ leaching and migration in waters (hydromorphic distribution) is less effective. Clastic dispersion by man, wind and water is probably most effective in the distribution of elements in soil and water samples of the study area. This corroborates the views of Yung, et al. (2001).

The enhanced values of Pb (0.10 mg/l) and Cd (0.03 mg/l) are mainly associated with water samples from mine ponds (Fig. 2). This indicates that these pollutants are most probably released into the mine ponds during the occasional acidic conditions caused by the oxidation of the sulphide minerals associated with the Pb-Zn mineralization in the study area. However, such conditions would most likely accelerate the dissolution of carbonates downstream thereby increasing the pH of waters but decreasing their ability to dissolve metals (Kabata-Pendias and Pendas, 2000; Florea, et al. 2005). The environmental significance of this process is that heavy metals in surface soil and water of the study area could easily be removed from the solution and rendered less mobile and unavailable to the biosphere. In order words the bioavailability of heavy metals could be restricted to mine ponds and soils developed on tailings. The indiscriminate application of inorganic fertilizer in the area could however cause large-scale dissolution and mobilization of contaminants (Agbenin, 1998) thereby heightening the potential for their dietary exposure to consumers.

Adiuku-Brown and Ogezi (1991) and Ofulume, et al. (2004) reported higher mean values of Pb (1.12 and 0.7 mg/l) and Cd (1.00 and 0.2 mg/l) in water sample from Zurak and Ishiagu Pb-Zn mining districts of Upper and Lower Benue Trough respectively. This difference may partly be related to the low pH of waters in these mining districts as against the high pH values obtained in this study. Pb is generally a metabolic poison and enzyme inhibitor. It can cause brain damage and metal retardation to children at high levels (Warren, 1972; Christensen, 1995). Cadmium on the other hand is extremely toxic and can cause hypertension if ingested in large doses (Keller, 1981; Jensen, et al., 2003; Stoica, et al., 2000).

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Fig. 2 Distribution of (a) Pb and (b) Cd in Mines and Streams in the study Area.

7 Conclusion and Recommendations

Results of the study tends to suggest that, mining activities and processing of ores are possible sources of some trace metal pollution of surface soils (Zn, Pb and Cd) and surface water (Pb and Cd) in Arufu mining districts. Low contents of heavy metals in the water samples are probably due to low solubility of the metals under low OM content of the soil and moderate pH of water caused by limestone dissolution. However, enhanced levels of these trace metals are restricted to tailings and mine ponds with acidic environment caused by the weathering of sulphides associated with the Pb – Zn mineralization. It would be recommended that investigations be carried out to determine the effects of these pollutants on livestock and human health in the area. The mine
waste (tailings) should be reclaimed and the mine ponds sealed with limestone bedding to prevent further contamination of the area.

References


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