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Comparative Concentrations of Heavy metals and Metallic Oxidesin Sediments and Galena using MP-AES and XRF Methods

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Abstract

Micro Plasma Atomic Emission Spectroscopic was used tostudy andanalyze heavy metals. Their mean concentration showed that Pb(136.08 ± 23.56 mg/kg) was highest followed by Fe(129.5 ±87.47 mg/kg) and the least Cr (0.047 ± 0.39mg/kg) showed the trend asPb >Fe >Zn > Cu > Cd > Mn > Co > As > Ni > Cr, in sediment samples. While in Galena showed Pb (718.23 ± 88.29 mg/kg) was also higher followed by Cu (8.44 ± 7.59mg/kg) andCd (0.0014 ± 0.0015 mg/kg) showed the lowest with trend asPb > Cu > Fe > Zn > Co > As > Ni > Mn > Cr > Cd. This does not comply with the previous studies which stated that Iron appear to be higher in Nigerian soil (Milam, 2014) credibly because Galena is an ore of Lead and should not be surprise why Lead is higher in Galena and also in sediments around the mining area. X-ray fluorescence was used to analyzed metallic oxides of SO_2 (65.86%/wt) as highest,followed by Al_2O_3(16.2 %/wt)Oxides in sediments with trend of SiO_2> SO_3 > Al_2O_3> Fe_2O_3> K_2O > P_2O_5 > N_2O > MgO> ZnO > SrO > Cr_2O_3, while SiO_2 (42.11 %/wt.)Showed highest concentrationfollowed by SO_3 (34.81 %/wt) while Cr_2O_3 showed least inGalena mineral with trend ofSiO_2> SO_3 > Al_2O_3> Fe_2O_3> K_2O > P_2O_5 > N_2O > MgO> ZnO > SrO > Cr_2O_3.The heavy metals levels are high at the Galena mining vicinityand their effects polluted the drinking water with adversehealth risks hence, adequate diagnosis should preserve life.

Keywords:*Galena, Sediment, Heavy metal,Metallic Oxides,Concentrations*

Introduction

Mined Galena deposits release ions typically during the crushing of ore and gangue (waste) materials which resulted to increase in surface area of material exposed to weathering processes. Certain types of mineral deposits exposed at the earth's surface released sufficient concentrations of heavy metals that are considered pollutants such as arsenic released from the weathering of

arsenical pyrite. Scattering of these ions occurred, especially the oxidations of sulfide minerals, which are often present in form of heavy metals and metallic oxides in ore deposits, which enhance the mobility of oxides and heavy metal cations in the soil sediments. For example, the oxidation of pyrite (FeS_2) produces ferric hydroxide solids, sulfate, and hydrogen ions by means of a reaction of the following type:(Gordon *et al*., 1999)

$$FeS_{2(s)} + \frac{15}{4} O_{2(g)} + \frac{7}{2} H_2O_{(l)} \rightarrow Fe(OH)_{3(s)} + 2\,SO_{4(aq)} + 4\,H^+_{(aq)}$$

Materials and Methods

Sampling

Samples were collected from the identified points in the mining area at five different locations in Nahuta village in Alkaleri Local Government of Bauchi State. Samples of soil sediments associated to Galena (Kohl) mining area, are collected by using the methods described by (Samuel and Maina, 2010).

Digestion methods for preparation of MP-AES

Method involves in sample preparation procedure relating to the acid digestion of sediments, sludge, and soils was used. A short description of this digestion procedure was given below. Initially, 10 cm^3 of 1:1 HNO_3 was added to 1.00 g of soil sample in a 25 x 150 mm glass digestion tube. The samples were then heated to 95 ± 10 °C for about 15 minutes. When cool, 5 cm^3 of HNO_3 was added and heat was applied for another 30 minutes. The digests were again allowed to cool, before 2 cm^3 of distilled water and 3 cm^3 of 30% H_2O_2 was added and heated to 95 ± 5 °C. After the digests were cooled again, another 1 $cm^3$of 30% H_2O_2 was added. Heating continued until the sample volumes reduced to approximately 5 cm^3. The digests were then allowed to cool again before being diluted to 50 $cm^3$with distilled water. Prior to analysis, the soil digests were further diluted tenfold. The 2% moisture content given in the certificate of analysis of the sample was incorporated into the calculation on specific intensities that would analyzes metals contents present. (Stefan *et al*., 2014)**.**

X-Ray Fluorescence Analysis of Galena

Powdered galena of about 2g was accurately measured as samples from mine site and it was separately placed in crucibles and taken to furnace then it was heated for 30 minutes at 970^{0c} which removed moisture and other impurities. The content was then allowed to cool and 1g of the galena was weighed and mixed in a platinum crucibles with 8 small spatula spoon of X-Ray

Flux crystals containing 80% lithium tetraborate, 20% lithium meta-borate was added with 1cm^3 4% lithium bromated solution in a platinum crucible. The crucible together with the content was empty into platinum mold which was placed inside XRF burner or fusion machine (XRF Scientific VFD 4000) as adopted by (Karl and Andy, 2012).

Connected sources of Oxygen, Acetylene and compressor sources was applied to the machine at 4bar, 0.8bar and 6bar pressures respectively. The compressor bottom nozzle was open to discharge water contaminants, and then XRF burner was switch on and regulated that made the fused beat within 15 minutes. Crucible contents was drained into the oppositely placed platinum mold automatically after frequents shaken by the machine which was allowed to cool for 10 minutes. The fused glass galena samples or pellets was made from the burner, which was removed and placed in a XRF detector machine that automatically detected the compositions of the sample metallic oxides with their respective concentrations in percentage on the computer screen attached to the machine, as the machine was programmed as reference curve of fine galena composite as adopted by (Karl and Andy, 2012).

Results and Discussions

Table 1 Comparatives compositions of Metals and Oxides using MP-AES and XRF

Metals	MP-AES Sediments (mg/kg)	MP-AES Galena (mg/kg)	Oxides	XRF of Sediments (%wt)	XRF of Galena (%wt)
Co	0.4546	0.4462	Na_2O	0.5102	0.6296
As	0.4408	0.3582	K_2O	2.26	1.3154
Fe	129.4572	6.3828	Fe_2O_3	3.0472	2.113
Ni	-0.0016	0.0062	MgO	0.5746	0.511
Cr	0.0466	0.0036	Cr_2O_3	0.004	0
Zn	18.134	3.1752	ZnO	1.5384	0.1314
Cd	0.099	0.00142	CaO	0.5878	0.2274
Cu	14.8706	8.4386	SrO	0.0112	0.0264
Pb	81.6528	287.298	SiO_2	65.864	42.10662
Mn	0.7888	0.0978	Mn_2O_3	0.0282	0.015
Al	N/D	N/D	Al_2O_3	16.215	15.7698

P	N/D	N/D	P_2O_5	0.4382	1.2272
S	N/D	N/D	SO_3	7.9806	34.8056
Cl	N/A	N/A	Cl	0.1436	0.5948
Ti	N/A	N/A	TiO_2	0.7962	0.5272

Key

N/A = Not Available N/D = Not Determined

XRF Compositions of Metallic Oxides in Sedimentsand Galena

Table 1 showed the highest mean percentage of SiO_2 oxides (65.86 %) in sediment while Galena showed (42.11 %)Galena followed by the second highest mean concentrations of.SO_3 showed(34.811 %) in Galena compared to sediment (7.981 %) In the same trend Cr_2O_3. Showed the least concentrations of sediments (0.004%) and Galena (0 %) respectively.

Other metallic oxidespresent include Na_2O showed 0.51 % in sediment and 0.62% in Galena , K_2O showed 2.26 wt % in sediment and 1.32 wt % in Galena, while Fe_2O_3showed 3.05 wt % in sediment and 2.11 wt % in Galena and MgO showed 0.57 wt % in sediment and 0.51 wt % in Galena. ZnO showed sediment(1.54 wt%) compared to Galena(0.131 wt %), CaO showed sediment (0.59 wt %) and Galena (0.22 wt %). SrO showed sediment(0.11 % and Galena(0.026 wt %), Mn_2O_3showed sediment (0.028 wt% and Galena (0.015 wt %). Also Al_2O_3showedsediment (16.22 wt % and Galena (15.77 wt %), while P_2O_5showed sediment (0.44 wt %) and Galena (1.23 wt %) respectively Finally TiO_2showed sediment(0.80 wt %) compared to (0.53 % wt) presented in Galena.

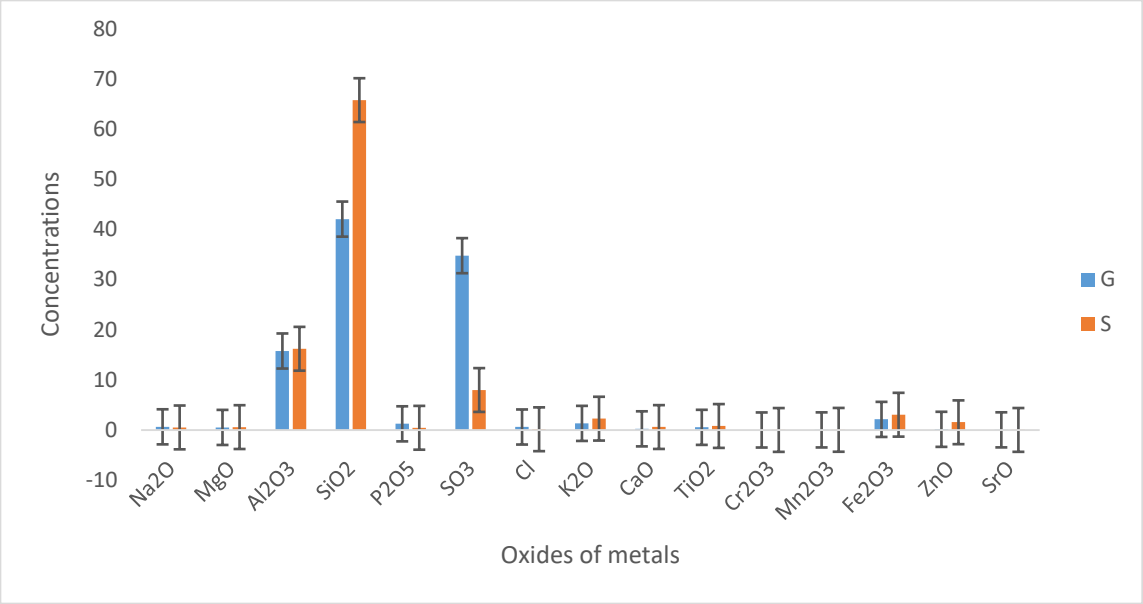

Fig 1 Mean Concentrations of Heavy metals in Sediments and Galena using XRF

Figure 1 showed illustrativemean trend from higher percentage compositions of metallic oxides in sequenceto the lowest composition of the oxides in both sediments andGalena analyzed in theorder of;SiO_2>SO_3> Al_2O_3> Fe_2O_3>K_2O > ZnO>TiO_2> CaO > MgO > Na_2O > P_2O_5>Mn_2O_3>SrO >Cr_2O_3respectively.

Metallic oxides analyzed showed that sedimentscontain high percentage concentrations of oxides of metals than Galena mineraldue to high deposition of chemical weathered constituents of ores of Galena and their close associations of minerals present in the soil sediments than in the Galena mineral.

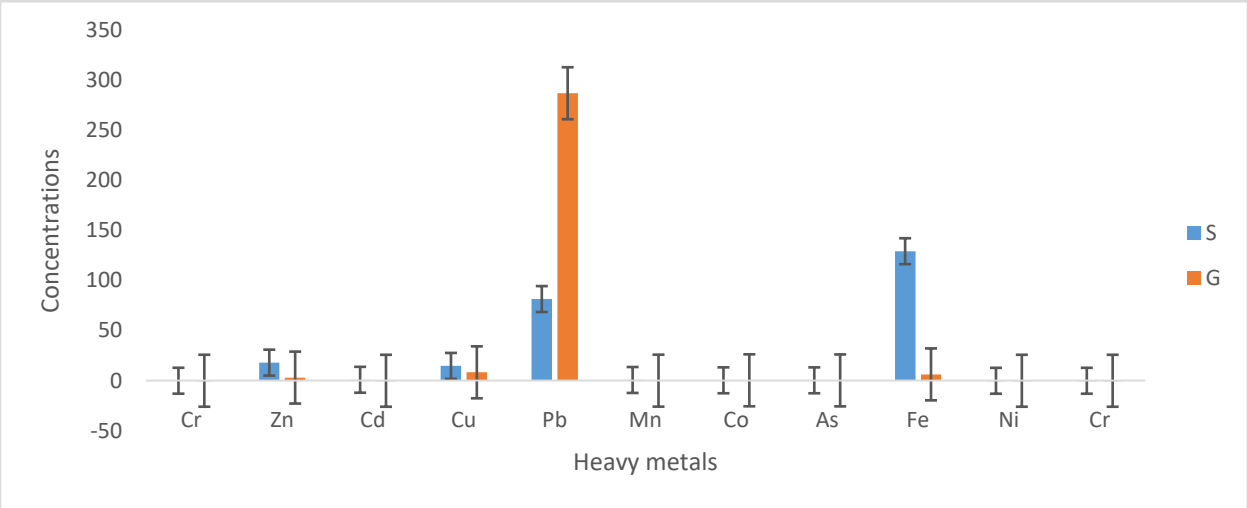

Fig 2Mean Concentrations of Heavy metals in Sediments and Galena using MPAES

Comparative Compositions of Heavy metals in Sediments and Galenausing MPAES

Figure 2 showed mean concentrations of Pb in Galena minerals revealed higher values with 718.228 ± 88.29 mg/kg compared to mean concentrations of Pb in sediments with 136.08 ± 23.56 mg/kg. Fe showed the second highest heavy metal withvalues of:129.457 ± 87.47 mg/kg insediment which was higher compared to the concentration of Fe in Galena mineral with only 5.86 ± 11.638 mg/kgusing MP-AES analysiswhich was contrary to Fe = 0.03 mg/kg, as reported by (Khan *et al*., 2008) also the leastmean concentration of heavy metal was shown byCr metal with 0.0466 ± 0.39 mg/kg in sediment compared to 0.036 ± 0.0154 mg/kg in Galena mineral.

Others are Arsenic in sediments has mean of 0.440 ± 0.084 mg/kg compared to mean concentration of 0.358 ± 0.051 mg/kg in Galena mineral. Mean composition of Zinc showed 18.134 ± 13.75 mg/kg in sediments compared to Zn = 0.02mg/kg, As = 0.10mg/kg as reported by (Khan *et al.*, 2008), and Manganese metal has mean concentration of 0.788 ± 0.642 mg/kg compared to Zn with 3.175 ± 1.85 mg/kg in Galena, but the elemental sulphur was not available in MP-AES analysis for comparative analysis. Heavy metals showed Co(0.45± 0.266 mg/kg) in sediment while Galena showed Co (0.446 ± 0.121 mg/kg, As(0.44 ± 0.082 mg/kg) in sediment while compared to As(0.358 ± 0.051 mg/kg) in Galena. Ni(0.0488 ± 0.178 mg/kg) was present in sediment compared to Ni (0.0962 ± 0.0249 mg/kg in Galena which was synonymous to Ni was 0.050 – 0.120 mg/kg as reported by (Adedokun *et al*,. 2016), Cd(0.099 ± 0.133 mg/kg) in sediment compared to Cd(0.0014 ± 0.0015 mg/kg) in Galena which was lower than Cd (0.27 mg/kg) reported by (Oluwole *et.al*,.2013)., and Cu(14.87 ± 23.56 mg/kg) in sediment have higher concentrations in their sediments as compared to Galena mineral with 8.438 ± 7.585 mg/kg as exposed by MP-AES analysis.

Conclusion

Analysis showed that the concentrations of heavy metals are more pronounce in sediments than they appear in the Galena mineral in either oxides, minute crystals or dissolved ions. It also indicated that metallic oxides analyzed using XRF showedSO_2 with the higher mean composition of65.86 wt % in sediments while the composition in Galena mineral showed SO_2 with only 2.11

wt% . The trend of decreasing order metallic oxides concentrations in sediments showed;SO_2 (65.8 %)> Al_2O_3(16.2 %)> SO_3(7.98 %)> Fe_2O_3(3.04 %)>K_2O(2.26 %)> ZnO(1.5 %)> TiO_2(0.79)> CaO (0.58%)> MgO (0.57%)> Na_2O(0.51%)> P_2O_5(0.43%)> Mn_2O_3(0.02%)> SrO(0.011%)> Cr_2O_3(0.004%)respectively. However, mean composition of metallic oxides in Galena mineral showed the trend of SiO_2> SO_3> Al_2O_3> Fe_2O_3> K_2O > P_2O_5> N_2O> MgO> ZnO> SrO > $Cr_2O_3$with percentages compositions of 42.11 % > 34.8 % > 15.7 % > 2.1 % > 1.3 % > 1.2 %> 0.64 % > 0.51 %> 0.13 % > 0.02% > 0 % respectively. The oxides determined in both sediments and Galena mineral showed fluctuated valuescompared to values of oxides analyzed in coal by (Usman *etal*., 2016) showedSiO_2(45.67%)>Al_2O_3(14.85%)>SO_3(12.02%)>CaO(11.81%)>Fe_2O_3(8.56%)>MgO(4.01 %)>P_2O_5(0.43%)>K_2O(0.38%)> Na_2O(0.17%) respectively.

Heavy metals analyzed using MPAES showed Sediment composition trend in the following sequence of Pb> Fe >Zn> Cu> Cd >Mn> Co > As > Ni > Cr with concentrations of 136.08 mg/kg > 129.5 mg/kg> 18.14mg/kg> 14.69mg/kg > 0.90mg/kg> 0.79 mg/kg > 0.45 mg/kg >0.44 mg/kg > 0.049mg/kg> 0.047mg/kg respectively. While Galena showed a trend of heavy metals concentrations as; Pb >Cu >Fe >Zn> Co> As >Ni > Mn >Cr >Cd with concentrations of 718.23 mg/kg > 8.44 mg/kg > 5.98mg/kg > 3.18mg/kg> 0.45 0.36 mg/kg > 0.25mg/kg>0.15 mg/kg >0.098 mg/kg >0.0014 mg/kg

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