Mine Water Environ (2013) 32:97–107
DOI 10.1007/s10230-013-0220-1

TECHNICAL ARTICLE

Metal Loadings and Alkaline Mine Drainage from Active and Abandoned Mines in the Ivo River Basin Area of Southeastern Nigeria

Ifeanyichukwu Clinton Ezekwe · Ahamefula Sunday Ezekwe · George Nwabuko Chima

Received: 17 May 2012 / Accepted: 20 February 2013 / Published online: 9 March 2013

Abstract Discharges from 11 active and abandoned mines were investigated in the Lokpaukwu-Ishiagu mining areas of Nigeria. The discharges had very high concentrations of TDS, hardness, chloride, calcium, conductivity, turbidity, and unacceptable levels of some metals. A conservative estimate is that nearly 33 million L of untreated circum-neutral-alkaline drainage and effluents find their way into the Ivo River watershed annually, including about 710,000 kg of dissolved solids and 586 kg of potentially toxic metals. These discharges exceed national (FEPA) and international (EU, WHO, and USEPA) permissible standards for domestic water use and discharge into aquatic sources, and national groundwater protection standards for permitted concentrations of toxic substances in industrial effluents. Our study also revealed that wetlands that serve as sinks for this mine drainage become sources of continuous polluted recharge to both surface and groundwater. We recommend that a task force be established to investigate the environmental operations of mining companies in Nigeria, that mine sites be closely monitored by state agencies, and that host communities receive environmental education.

Keywords Ishiagu-Lekwesi-Lokpaukwu · Mining effluents · Untreated discharge · Water quality

Introduction

Mine drainage quality is controlled by geochemical processes involving ore deposit geology, overburden mineralogy, hydrogeology, climate, mining methodology, and discharge location. Neutral or alkaline mine drainage (NAMD) can result from a relatively low level of sulphide minerals, a deoxygenated sulphide environment, the presence of highly reducing or alkaline influent water, neutralization of acid by carbonate or basic silicate minerals, and the neutralization of acid by naturally highly alkaline groundwater (Banks et al. 2002). Other reactions that contribute to the formation of NAMD include the oxidation of other sulfides, dissolution of host rock minerals, precipitation and dissolution of iron hydroxide and hydroxysulfate, co-precipitation and adsorption of dissolved metals, precipitation and dissolution of iron sulfate, gypsum precipitation and dissolution, and CO_2 degassing (Iribar 2004; Nordstrom and Alpers 1999).

The concentration of metals in alkaline mine drainage decreases as metals are precipitated in wetlands and onto streambeds (Binning and Baird 2001; Younger 2000). However, the concentrations of metals in such sediments can be a major problem in aquatic environments since many organisms spend most of their lifecycle living on or in sediments (Alam and Sadiq 1993; Chima et al. 2010). Lead–zinc and aggregate mining has been going on for more than half a century in the Lokpaukwu, Ishiagu, and Lekwesi areas of the Ivo River Basin of southeastern Nigeria. Untreated mine dewatering effluents and process water are freely discharged into the environment, and industrial and mining wastes are discharged into water bodies and wetlands in this area with little regard for national and international regulations or industrial best practices. The assimilative capacities of the wetlands are not considered. Soil and water pollution associated with metal mining in the area (Aroh et al. 2007; Duruibe et al. 2007; Ezekwe et al. 2012a, b; Nwaugo et al. 2007; Obiekezie et al. 2006) and accumulation of metals in sediments (Chima et al. 2010) and in staple crops (Onyedike and

I. C. Ezekwe (✉)
Department of Geography and Environmental Management, University of Port Harcourt, Port Harcourt, Nigeria
e-mail: clidnelson@yahoo.com

A. S. Ezekwe · G. N. Chima
Abia State University, Uturu, Nigeria

Nwosu 2008) have been documented, yet no systematic attempt has been made to estimate the basin-wide quantity of discharges from mining and metal loadings from mining sources, and to explain the geochemical interactions generating NAMD in the area. Public institutions fail to emphasize monitoring of mining operations for environmental impacts. This study was an attempt to create a regional understanding of NAMD and an awareness of basin-wide discharges of untreated mine drainage and potentially dangerous metal loadings.

Study Area

The Ivo River is the major tributary of the Ezeaku River of the Cross River Basin in southeastern Nigeria. The Ivo River drains an area of over 450 km^2 and supports an estimated population of less than half a million. The Cross River Basin itself is a part of the Lower Benue Trough, which is underlain by the oldest sedimentary sequences of southern Nigeria (Fig. 1) and is characterized by a series of folds, mafic/felsic intrusives, basaltic lavas, and a narrow zone of lead–zinc mineralization running from Ishiagu through Abakililki in southeastern Nigeria to Zurak in northern Nigeria. Major towns in the Ivo River Basin include Ishiagu, Lokpauku, Lekwesi and Lokpanta (Chima et al. 2010). The Lokpaukwu, Lekwesi, and Ishiagu mining areas extend over 450 km^2 within latitudes 5° 51′N and 5° 59′N and longitudes 7° 24′E and 7° 40′E (Fig. 2).

The study area has a tropical climate with a marked wet and dry season. The rainy season lasts from April to October, and is characterized by heavy storms, surface flow, soil leaching, and extensive sheet-wash, while the dry season prevails through the remaining months of the year.

Fig. 1 Map of Nigeria showing the study area at the southern tip of the Benue Trough (outline after Uma and Onuoha 1989; relief location map of Nigeria by Uwe Dedering)

The rainy season has two maxima, peaking in July and September. Mean annual climatic figures include 1,750–2,000 mm for rainfall, up to 1,750 h of sunshine, 80 kg cal/cm^2 of solar radiation, 26.5–27.5 °C for temperature; 70 % for relative humidity, and 1,450 mm of evapotranspiration (Ezekwe et al. 2012a, b).

Lead–zinc mineralization in the study area occurs as galena-sphalerite complexes in association with quartz, iron, calcium, and magnesium carbonates, pyrites, chalcopyrites, barites, fluorite, limestone, and related minerals. Olubambi et al. (2008) studied the geology and mineralogy of these lead–zinc ores and concluded that they are characteristic hydrothermal vein deposits of a complex sulphide ore with siderite, sphalerite, galena, quartz, and traces of pyrite and copper-bearing minerals. The sphalerite occurs as ferrous sphalerite, while the hard rocks mined for construction aggregates are predominantly porphyritic and ophitic dolerite sills containing about 87 % plagioclase-pyroxene and over 11 % calcite and accessory minerals including iron oxide, chlorite, quartz, and hornblende (Reyment 1965). These hard rocks intruded country rock made up of transgressive–regressive sedimentary sequences of Albian-Turonian age, which are mainly calcareous shales, calcareous and micaceous siltstones, sandstones, and thin-bedded limestones (Cratchley and Jones 1965; Petters 1978).

Mines have been active in this area for over 60 years. Hard rock aggregates and lead–zinc ores and related minerals are mined by private businesses through concession agreements issued to them by the Federal Government of Nigeria. While the Nigerian government plays the role of administrator-regulator, the concession holders act as owner-operators.

Materials and Methods

Discharges from 11 active and abandoned mines were measured using the ‘time-volume’ method (float method and timed container fills) from piped discharges (Chartiers Greenway 2009), while chemistry (pH, temperature, alkalinity, sulphate, conductivity (EC), turbidity, salinity, chloride, phosphate, nitrate, sulphate, Ca, Mg, Fe, Mn, Zn, Pb, and Cd) of discharges and standing pools were measured in two seasons with field devices and laboratory analysis using standard methods (APHA 1995 Brown et al. 1970; Rainwater and Thatcher 1960). Water sampling for physico-chemical analysis was done in both the rainy and dry season, although some sites could not be sampled twice due to access restrictions. Two samples of water were taken at each sampling point for physico-chemical and metals analysis. Water samples were collected with new 1 L plastic containers pre-rinsed with dilute nitric acid and

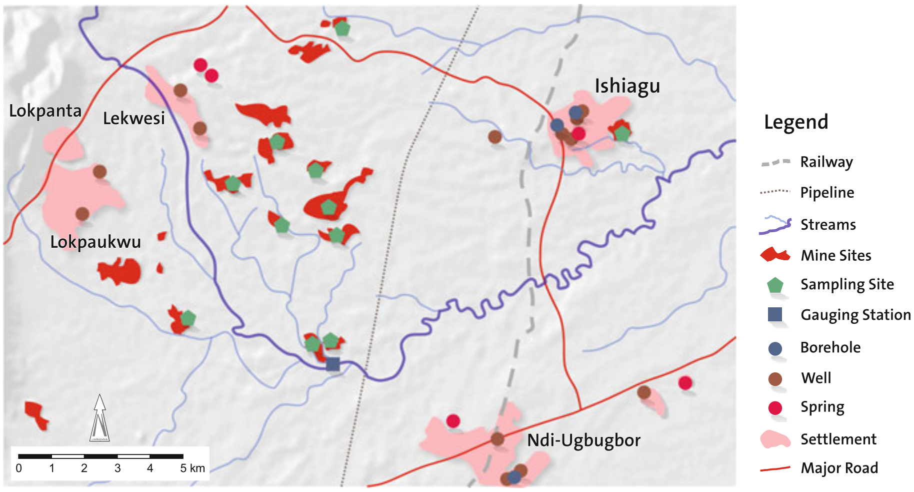

Fig. 2 Study area showing mining sites and gauging station

rinsed three to four times with the water sample before being filled to capacity and labelled. Metal analysis samples were treated with 2 mL of nitric acid (100 %, trace metal grade, Fisher Scientific) to stabilize the oxidization states of the metals. The samples were placed in ice-packed coolers and stored below 4 °C prior to laboratory analysis.

Discharges from abandoned mines were monitored weekly during the rainy season, between July and Octo. 2007, when the mines filled with water and overflowed. Discharges at active mine were measured monthly during the period of Jan. 2007 to Feb. 2008. Overall, 16 abandoned mine discharges and 12 active mine discharges were recorded within the study period and reported as average discharges. The instantaneous load of metals and other dissolved constituents were calculated by multiplying mine discharge at the time the sample was collected by the concentration of each metal in mg/L (Davis et al. 1999).

Metals were analysed by atomic absorption (AA) spectrophotometry using a Perkin-Elmer and Analyst 100 AA spectrophotometer (detection limit $\geq$0.01 mg/L). All manipulations were done under controlled conditions to avoid contamination and all experiments were carried out in duplicate. Measurements of pH, temperature, EC, turbidity, and salinity were done in situ, using a Horiba water checker (model U-10) after calibrating the instrument with the standard Horiba solution. Total dissolved solids (TDS) were measured with a Lovibond cm-21 Tintometer, while total alkalinity, hardness, Ca, and Cl^- were determined by titration. Phosphate, nitrate, and sulphate were determined using the stannous chloride, brucine, and turbidimetric methods, respectively, while Mg concentration was determined by calculation (APHA 1995). Geochechemical modelling was carried out to ascertain distribution of mineral species and their saturation indices using PHREEQC (Parkhurst and Appelo 2011).

Results and Discussion

Mines in or near Ishiagu

Physiochemical parameters of mine effluents from aggregate quarries located in or near Ishiagu were evaluated (Table 1). Sulphate, Cl^-, Ca, Mn, and Pb were elevated during the dry season while hardness, alkalinity, phosphate,

Table 1 Seasonal variation in mine water parameters at the Crush Rock and Bilwadan sites in Ishiagu; all concentrations in mg/L

Parameter	Wet season	Dry season	Dry season Bilwadan
pH	7.63	7.15	8.35
Temperature, °C	30	33.8	30.8
Eh, mv	−51	−43	−71
Turbidity NTU	9	89	3
Salinity (%)	1.4	7.6	0.1
EC, uS/cm	2,960	13,200	290
TDS	3,150	9,240	205
Alkalinity	175	120	120
Hardness	576	480	105.6
Cl^-	8.9	630	1.3
$N–NO_3^-$	0.04	0.04	0.18
SO_4^{-2}	27.1	80.3	11.5
PO_4^{-3}	0.37	0.12	0.06
Ca^{+2}	134.7	153.9	25.4
Mg^{+2}	58.3	23.3	10.3
Fe	3.98	1.22	0.9
Mn	0.21	0.51	BDL
Zn	BDL	BDL	BDL
Pb	BDL	0.1	0.03
Cd	0.05	0.033	0.01

Table 2 National and international environmental and drinking water standards

	Interim effluent limitation guidelines in Nigeria for all industries (FEPA 1991)		Maximum permitted concentrations in industrial effluents for protection of groundwater (FEPA 1991)	WHO standards (1993)	EU standards (1998)	USEPA drinking water standards
	Discharges into surface water	For land application				
pH	6–9	6–9	–	NA[a]	NA	6.5–8.5
Temperature, °C	<40 °C[e]	<40 °C	–	–	–	–
Turbidity	–	–	–	NA[b]	NA	5
EC	–	–	–	250	250	–
TDS	2,000	2,000	–	NA	NA	500
Hardness	–	–	–	NA[c]	NA	–
Cl^-	600	600	–	250	250	250
$N{-}NO_3^-$	20	–	–	50	NA	10
SO_4^{-2}	500	1,000	–	500	250	250
PO_4^{-3}	5	10	–	–	–	–
Ca^{+2}	200	–	–	–	–	–
Mg^{+2}	200	–	–	–	–	–
Fe	20	–	–	NA[d]	0.2	0.3
Mn	5	–	–	0.5	0.05	0.05
Zn	0.1	–	–	3	NA	5.0
Pb	<1	–	0.05	0.01	0.01	0.015
Cd	<1	–	0.01	0.003	0.005	0.005

NA not applicable or not available (either no guideline or not mentioned); all concentrations in mg/L, *turb* turbidity in NTU, *EC* electrical conductivity in uS/cm

[a] Desirable: 6.5–8.5

[b] Desirable: <5 NTU

[c] Desirable: 150–500 mg/L

[d] Desirable: 0.3 mg/L

[e] Within 15 m of outfall

Fe, Mg, and Cd were elevated during the rainy season. Nitrate was below 0.05 mg/L during both seasons.

High concentrations of EC, TDS, Cl^-, Ca, and sulphate, especially in the rainy season, may be related to deep-seated mobilisation of NaCl and $CaSO_4$ from brines and evaporite deposits that are characteristic of the study area (Awalla and Ezeigbo 2002; Offodile 2002). Offodile (2002) reported that NaCl made up 81 % of TDS from the Enyigba-Ameri Pb–Zn mines located within the same axis of mineralization but about 60 km away from the study area. Metal concentrations ranged from 3.98 mg/L for Fe, 0.51 mg/L for Mn, and 0.05 mg/L for Cd. Zinc was below detectible limits (<0.01 mg/L).

All of the measured parameters apart from alkalinity, pH, Pb, and Ca exceeded drinking water standards (EU 1998; USEPA 2012; WHO 1993). Also, TDS and Cl^- in the dry season exceeded Nigeria's FEPA (1983) guidelines for industrial effluents discharge on land and water while Cd and Pb concentrations exceeded the FEPA (1991) maximum permitted concentration of toxic substances in industrial effluents for the protection of groundwater; see Table 2.

The lake at the abandoned Bilwadan mine was only sampled during the dry season due to access restrictions. The results were similar to those of water samples from the aggregate mine discharges, although with much lower concentrations due to dilution. However the Pb concentrations were elevated (0.03 mg/L), which suggests communication with groundwater and polluted recharge and discharge (Fig. 2) from the Pb–Zn mine area or zones of Pb–Zn mineralization. It is also presumably a source of metal mobilisation during the rainy season.

Mines at Lokpaukwu and Lekwesi

The Consolidated Contractors Company (CCC) and Crushed Stone mines are active aggregate quarries located at Lokpaukwu and Lekwesi, respectively (Table 3).

Table 3 Seasonal variation in mine water at the CCC and Crush Stone sites in Lekwesi and Lokpaukwu; all concentrations in mg/L

Parameter	Dry season	Wet season	Wet season Crushstone
pH	7.38	8.22	7.8
Temperature, °C	36.1	28.3	27
Eh, mv	47	−67	−58
Turbidity NTU	31	31	60
Salinity (%)	1.4	0.1	0.2
EC, uS/cm	2,930	293	252.8
TDS	3,150	207	126.4
Alkalinity	130	100	96
Hardness	7,680	144	268.8
Cl^-	210	4	49
$N–NO_3^-$	0.09	0.444	0.59
SO_4^{-2}	141.9	32.6	17.2
PO_4^{-3}	0.06	0.45	0.31
Ca^{+2}	2,309	38.5	23.1
Mg^{+2}	466.6	11.7	51.3
Fe	0.75	0.94	1.04
Mn	0.04	0.08	0.32
Zn	BDL	BDL	BDL
Pb	BDL	BDL	BDL
Cd	0.32	0.28	0.098

Temperature, EC, salinity, alkalinity, TDS, hardness, SO_4^{-2}, Cl^-, Ca, Mg, and Cd showed higher dry season values, while pH decreased from 8.22 to 7.38, and redox potential increased, from −67 to 47 mV. High concentrations of SO_4^{-2} do not necessarily correlate with pyrite dissolution, since gypsum and other sulphate minerals are likely precipitating during the dry season and dissolving during the rainy season (Rose and Cravotta 1998).

This trend is similar to the mine effluent from the aggregate quarry at Ishiagu apart from a reversal in seasonal characteristics of Mg, Mn, and Ca. Also, all parameters exceed drinking water standards except for alkalinity and Fe. A very high concentration of Cl^-, Ca, and Mg was observed during the dry season. Concentrations of ion species were higher at the CCC quarry than at the aggregate quarry at Ishiagu. The wet season samples from the Crush Stone quarry at Lekwesi were similar to the samples collected at CCC Lokpaukwu, with slightly lower concentrations of all parameters except for Mg, Mn, and Ca.

The Lekwesi mines could not be sampled during the dry season due to restrictions by the mine operators. The dry season TDS, Ca, and Mg concentrations at the CCC mines exceeded the FEPA (1983) guidelines for discharges to surface water and land, while the Cd exceeded the FEPA (1991) maximum permitted concentration of toxic substances in industrial effluents. The high Ca and Mg concentrations are indicative of dissolution and mobilisation of gypsum and carbonate rocks, which are common in the country rock.

The Mayo and Amikol Pb–Zn Mines at Ihetutu

The Mayo Mines are only active during the dry season. The Amikol pool is an abandoned mine that, on preliminary investigation, very closely resembled the Mayo standing pool. Based on this determination, its chemistry was not included in this study, although its discharge was considered. These mines are located in the Ihetutu hills in the Ishiagu part of the study area.

Effluents from the Mayo mines were sampled during the dry season while mining was ongoing, while the standing pool in the mine pit was sampled during the rainy season when the mines were flooded and subsequently overflowing (Table 4). The mine effluents had very high concentrations of Cl^-, Mg, and Ca, due to the mobilisation of NaCl from the brines and evaporate deposits that are characteristic of this study area and the dissolution of gypsum (Awalla and Ezeigbo 2002; Offodile 2002).

Difference in parameters between effluents and the standing pool could be due to dilution from precipitation and overland flow. Acidic runoff and mobilisation of nutrients from the swampy catchment and nearby farms could be increasing nitrate concentrations and decreasing pH.

Table 4 Seasonal variation in mine water parameters at the Mayo Pb–Zn site Ishiagu; all concentrations in mg/L

Parameter	Dry season	Wet season
pH	7.2	6.93
Temperature, °C	35.5	32.8
Eh, mv	−70	−7
Turbidity, NTU	30	11
Salinity (%)	3	0
EC, uS/cm	5,270	255
TDS	11126.2	180
Alkalinity	124	32
Hardness	29,920	105.6
Cl^-	1155	1
$N–NO_3^-$	0.17	0.63
SO_4^{-2}	27.2	21.2
PO_4^{-3}	0.13	0.04
Ca^{+2}	9,234	1115
Mg^{+2}	700	18.7
Fe	2.43	0.24
Mn	0.78	0.49
Zn	1.07	0.06
Pb	0.24	BDL
Cd	BDL	BDL

TDS and Zn (and Cl$^-$, Mg, and Ca in the dry season) exceeded the FEPA (1983) guidelines for discharges into surface water bodies and land while Pb exceeded the FEPA (1991) permitted concentration of toxic substances in industrial effluents for the protection of groundwater (Table 2).

Unu Pond and Ugwuajirija Wetlands

The Unu and Ugwuaji wetlands are located in the heart of the lead–zinc mining area very close to the abandoned Greenfield and Geominex mines. The Unu pond is a receptor of run-off and discharges from the Ihetutu and Ugwuajirija mines. Physico-chemical analysis of discharge and pool (Table 5) from these sites showed similar seasonal trends to the Greenfield samples apart from reverses in seasonal patterns for alkalinity, phosphate, and iron.

The Ugwuajirija swamp is closer to the Amikol and Mayo mines and receives direct discharge and runoff from them. It was, however, only sampled in the rainy season as it usually dries up during the dry season. It shows a similar trend to the standing pool at the Mayo mines, although with higher concentrations. It also closely resembles the rainy season samples of the Unu pond, signifying runoff and/or recharge. This position is tenable as it receives direct discharge of untreated mine effluents.

Table 5 Seasonal variation in mine water parameters in Unu Pond and Ugwuaji Wetlands (Ishiagu); all concentrations in mg/L

Parameter	Dry season	Wet season	Wet season (Ugwuaji Swamp)
pH	7.76	7.14	7.54
Temperature, °C	30.9	31.4	33.1
Eh, mv	−63	0	−37
Turbidity, NTU	14	89	3
Salinity (%)	0	1.4	0.1
EC, uS/cm	192	28.3	473
TDS	136	257.6	333
Alkalinity	184	250	52
Hardness	682	432	211.2
Cl$^-$	1	24.8	8.9
N–NO$_3^-$	0.55	0.17	0.52
SO$_4^{-2}$	6.3	70.1	48.7
PO$_4^{-3}$	0.05	0.52	0.07
Ca^{+2}	15.4	119.3	23.1
Mg^{+2}	7.2	32.7	37.3
Fe	1.28	1.87	BDL
Mn	0.33	0.76	0.38
Zn	BDL	0.03	0.12
Pb	BDL	0.04	BDL
Cd	BDL	BDL	BDL

In the Unu ponds, Mn exceeded the EU limits in the wet season and both the WHO and EU regulatory limits during the dry season, while the EU limits where exceeded during both seasons in the Ugwuajirija swamp. EC exceeded the WHO and EU limits in the dry season in the Unu pond while Fe, Mn, and Pb exceeded both the WHO and EU standards in the Unu dry season samples (Table 2).

The Unu pond and the Ugwuajirija swamp are located in the recharge areas of both surface and ground water systems as both the Ivo River system and wells around the central and south-eastern parts of Ishiagu depend on them for recharge (Ezekwe et al. 2012a). They are therefore important in the hydrogeopollution cycle of the study area. The Ugwuajirija swamp is also a drinking and irrigation water source, especially for rice farmers, and sustains the abundant wildlife in the wetlands around the mines (Ezekwe et al. 2012a, b). Uptake of metals by plants and animals in the food chain poses a grave health risk to man.

Greenfield Abandoned Mines

The abandoned Greenfield mines are located in the same area as the Ihetutu mines in the Ugwuaji section. There are two of them, about 200 m apart, but due to similarities in physico-chemical conditions discovered during our preliminary investigation, the chemistry of the smaller northern pool was not considered in this study, though it was part of

Table 6 Seasonal variation in mine water parameters in Greenfield sites; all concentrations in mg/L

Parameter	Dry season	Wet season
pH	7.39	7.30
Temperature, °C	33.5	28.4
Eh, mv	−52	−6
Turbidity, NTU	28	27
Salinity (%)	2.7	0
EC, uS/cm	4086.3	196
TDS	2,043	138
Alkalinity	26.83	44
Hardness	1,480	91.2
Cl$^-$	980	0.09
N–NO$_3^-$	0.1	0.44
SO$_4^{-2}$	25	3.0
PO$_4^{-3}$	0.04	0.08
Ca^{+2}	980	19.2
Mg^{+2}	48	10.5
Fe	1.23	3.15
Mn	0.49	0.1
Zn	BDL	BDL
Pb	BDL	BDL
Cd	BDL	BDL

Table 7 Correlation matrix of water quality parameters between mine sites and surface/groundwater discharge areas during the wet season

	Is	Lo	Ih	Iv@ A	Iv @ OI	Iv @ OIE	Ug	Un	Ez
Is	1								
Lo	0.35	1							
Ih	0.37	**0.98**	1						
Iv@ A	0.49	0.35	0.26	1					
Iv @ OI	0.59	0.55	0.44	**0.81**	1				
Iv @ OIE	0.27	0.58	0.5	**0.67**	**0.8**	1			
Ug	0.46	**0.64**	0.54	**0.69**	**0.91**	**0.67**	1		
Un	0.12	0.41	0.25	**0.66**	**0.84**	**0.67**	**0.88**	1	
Ez	0.56	0.59	0.48	**0.71**	**0.96**	**0.77**	**0.88**	**0.81**	1

Bold values indicate strong correlations

Is Ishiagu Crush Rocks quarry; *Lo* Lokpauku CCC quarry; *Ih* Ihetutu mine (Mayo); *Iv@ A* Ivo River at Amagu Ishiagu; *Iv @ OI* Ivo River at Okue Ishiagu; *Iv @ OIE* Ivo River at Okpanku Ikoli Enugu State; *Ug* Ugwuajirija mine (Greenfield); *Un* Unu salt marsh; and *Ez* Eziator quarry Bilwadan

the discharge analysis. Seasonality and trends are readily observed from the Greenfield samples (Table 6). The close resemblance of the dry season samples from the Greenfield mines to the mine effluents from the Ihetutu Pb–Zn mines reflect similar geology and probably groundwater recharge. The Greenfield and Ihetutu mines are located at a higher elevation than their surroundings (Ezekwe et al. 2012a), which indicates that precipitation as a dilution factor, though minimal, is more important than surface runoff.

Manganese and EC exceeded the EU standards in both seasons, while Cl^- and Fe only surpassed the EU and WHO limits during the dry season (Table 2). The water is classified as brackish (Todd 1980), indicating not only neutral-alkaline mine drainage but saline drainage into the Ivo River basin. A comparison of water quality parameters between these discharge sources and the Ivo River (Tables 7 and 8) yielded very strong correlations (0.65–0.98), indicating direct or subtle impacts on the Ivo River from these contaminant sources.

An earlier report on this mine from a 2002 investigation reported acidic conditions while another study of the same mine around 2005 reported a pH above 8 (Aroh et al. 2007). A comparison of that study and our research indicates a tenfold increase in Cl^-, Ca^{2+}, Mg, hardness, TDS, and EC, with a marked decrease in pH (8.1–7.3), alkalinity, and SO_4^{-2}. The long period of inactivity may have masked pyritic compounds from sustained weathering (Aroh et al. 2007), and possibly caused a reversal in chemistry, inducing precipitated metals to go back into solution. Also, ferrihydrites [$Fe(OH)_3$)] precipitated from the reaction in Eq. (1) may be coating calcium carbonate and greatly slowing down the neutralization process. Gypsum ($CaSO_4 \cdot 2H_2O$) formation can also consume alkalinity and remove SO_4^{-2} from solution (Rose et al. 1995).

$$\begin{aligned} & FeS_2 + 4CaCO_3 + 3.75\ O_2 + 3.5\ H_2O \\ & \quad = Fe(OH)_3 + 2SO_4^{-2} + 4Ca^{+2} + 4HCO_3^-. \end{aligned} \tag{1}$$

Geochemistry of Discharges

The decreasing alkalinity, Fe, and SO_4^{-2} content of the Bilwadan pool compared to the Crush Rock effluents could be related to geochemical consumption of calcium carbonate and exhaustion of pyrite in the presence of a decreasing oxygen supply (Eh, −43 to −71) for pyrite oxidation (Lambert et al. 2002). The dissolution of calcite produces alkalinity in excess of acidity and raises the pH above 6.4, where bicarbonate (HCO_3^-) is the dominant dissolved carbon dioxide species.

Geochemical modeling of these samples using PHREEQC (Parkhurst and Appelo 2011) revealed the following order of carbon-oxide dominance, $HCO_3^- > CO_2 > CaHCO_3^+ > MgHO_3^+$. The Bilwadan abandoned mines had $PbSO_4$, $CaSO_4$, $PbCO_3$, Mn_3O_4, MnO_2, $Mn(OH)_2$, $Fe(PO_4)_2 \cdot 8H_2O$, and $FeCO_3$ as dominant species, leading to the precipitation of $Fe(OH)_3$(a), Fe_2O_3, and $Ca_5(PO_4)_3OH$; the Crush Rock samples yielded $PbSO_4$, $CaCO_3$, $Mg(CO_3)_2$, $CaSO_4 \cdot 2H_2O$, MnO_4, and $MnCO_3$ as the dominant species, with similar supersaturated species as the Bilwadan sample.

Batch reaction calculations mixing all groundwater or effluent samples from the active mines yielded the following distribution of species molality: OH^- (3.6×10^{-6}), H^+ (4.7×10^{-8}), $C_{(4)}$ (3.7×10^{-3}), Cl^- (2.5×10^{-4}), $Fe_{(2)}$ (1.1×10^{-5}), $Fe_{(3)}$ (6.1×10^{-5}), Mg (2.4×10^{-3}), $Mn_{(2)}$ (3.8×10^{-6}), P (1.2×10^{-5}), and $S_{(6)}$ (2.8×10^{-4}). Dominant dissolved species include oxygen, hydrogen and carbon dioxide as gases, and MnO_2, $FeSO_4 \cdot 7H_2O$, MnOOH, $Mn(OH)_2$, and Mn_3O. $Fe_3(PO_4)_2 \cdot 8H_2O$(−0.62) and $FeCO_3$(0.23) tended towards equilibrium while $Fe(OH)_3$(a), FeOOH, and Fe_2O_3 were precipitated out of solution. Batch reaction mixing of the abandoned mine sources yielded the following molalities: OH^- (3.9×10^{-7}), H^+ (5.2×10^{-8}), $C_{(4)}$ (2.2×10^{-3}), Cl^- (4.1×10^{-3}), Ca (4.3×10^{-3}), $Fe_{(2)}$ (2.61×10^{-5}), $Fe_{(3)}$ (2.3×10^{-5}), Mg (9.7×10^{-4}), $Mn_{(2)}$ (5.8×10^{-6}), NO_3 (2.6×10^{-5}), P (3.8×10^{-6}), Pb (6×10^{-8}), Zn (4.81×10^{-7}), and $S_{(6)}$ (3.1×10^{-4}). Precipitates from abandoned mines are similar to that from active mines, in addition to the presence of Mn_3O_4, $Ca_5(PO_4)_3OH$, and MnOOH minerals. That is to say that most minerals that remain dissolved under groundwater conditions, especially Mn-based minerals like hausamannite and manganite, precipitate out of solution upon exposure to the atmosphere. These reaction leads to the dissolution of some ferric- and sulphur-based minerals and oxy-hydroxides and hydro-oxides of Zn and Mn.

Table 8 Correlation matrix of water quality parameters between mine sites and surface/groundwater discharge areas during the wet season

	Is	Lo	Le	Ay	Iv@ A	Iv @ O	Ugm	Un	Ugs	Ih
Is	1									
Lo	0.5336	1								
Le	0.3624	**0.9007**	1							
Ay	0.2686	**0.8308**	**0.6978**	1						
Iv@ A	0.3364	0.5504	0.4593	**0.7027**	1					
Iv@ O	0.3669	**0.692**	**0.7515**	0.594	**0.6064**	1				
Ugm	0.545	**0.9784**	**0.8797**	**0.894**	**0.6585**	**0.7388**	1			
Un	0.4452	**0.8806**	**0.7576**	**0.7124**	**0.7038**	0.5586	**0.8537**	1		
Ugs	0.5501	**0.97**	**0.8609**	**0.9016**	0.5792	**0.6524**	**0.9845**	**0.8026**	1	
Ih	0.5493	**0.9572**	**0.8397**	**0.9236**	**0.6566**	**0.677**	**0.9888**	**0.813**	**0.9942**	1

Bold values indicate strong correlations

Is Ishiagu Crush Rocks quarry; *Lo* Lokpauku CCC quarry; *Le* Amita/Lekwesi Crush Stones quarry; *Ay* the Ayaragu Mkt well; *Iv@ A* Ivo River at Adia bridge; *Iv @ O* Ivo River at Okpanku Ikoli (Enugu); *Ugm* Ugwuajirija mine (Greenfield); *Ugs* Ugwuajirija swamp; *Un* Unu salt marsh; and *Ih* Ihetutu mine (Mayo)

Alkaline earth carbonates such as calcite, dolomite, ankerite, and magnesite typically react to produce elevated Ca, Mg, and HCO_3^- concentrations. Elevated Cl^-, Ca, and Mg concentrations, TDS, and EC along with low concentrations of metals, SO_4^{-2}, and alkalinity, negative Eh, and high pH is an indication of silicate, sulphide, and/or carbonate dissolution. The high pH at these mines could be accounted for by the significant volume of mine waste and large scale presence of carbonate minerals, particularly dolomite and siderite, coupled with increased exposure of these carbonates by the mining process (Aroh et al. 2007). The dissolution of silicate minerals, such as feldspar, kaolinite, and chlorite, which are also very common in the study area, would also have consumed some acidity (Rose and Cravotta 1998).

Dissolution of pure siderite ($FeCO_3$) followed by precipitation of $Fe(OH)_3$ generates no net alkalinity; however, if siderite is exposed to H^+ and the reaction proceeds in stages, with some CO_2 exsolution to the gas phase, then some neutralization may temporarily take place (Rose and Cravotta 1998). However, most siderite is actually a solid solution containing some Ca, Mg, and Mn in addition to Fe. Dissolution of siderite can produce elevated concentrations of Mn in groundwater, and, to the extent that siderite contains Ca and Mg in solid solution, its dissolution will contribute some net alkalinity (Rose and Cravotta 1998). Also, the precipitation of Fe^{3+} as iron hydroxide effectively scavenges metals from water through sorption, and increases pH; in neutralized geochemical environments, many contaminants, including Mn, As, and Zn, are effectively scavenged through a suite of metal precipitation, co-precipitation, and adsorption reactions (Cheng et al. 2009).

From the menu of trace metals and major ions observed in the water and the compositional complexity of the observed sulphides in the rocks, it can be deduced that the weathering of these sulphide-bearing rocks, greatly facilitated by mining, accounts for the elevated ions in the water samples (Akabzaa et al. 2009). According to Plumlee et al. (1999), the following reactions can generate these ions under typical surface weathering conditions:

$$\begin{aligned}&(\mathrm{Fe,Me})\mathrm{S}_2 + 5/2\mathrm{O}_2 + 2\mathrm{H}^+ \\ &\quad = \mathrm{Fe}^{2+}\mathrm{aq} + \mathrm{Me}^{2+}\mathrm{aq} + 2\mathrm{SO}_4^{2-} + \mathrm{H}^+ \end{aligned} \tag{2}$$

$$2\mathrm{Fe}^{2+}\mathrm{aq} + 1/2\mathrm{O}_2 + 2\mathrm{H}^+ = 2\mathrm{Fe}^{3+}\mathrm{aq} + \mathrm{H}_2\mathrm{O} \tag{3}$$

$(Fe,Me)S_2$ could be pyrite, chalcopyrite, bornite, or arsenopyrite. The oxidation of Fe^{2+} to Fe^{3+} would enable the aggressive oxidation of other metal sulphides with a metal to sulphide ratio <1. This is the most likely dissolution mechanism for sphalerite and other minerals identified in this study.

The combination of acid-producing and -consuming reactions discussed above would typically cause metals, sulphates, and bicarbonates to go into solution, and transform others into stable constituents in sediments (Akabzaa et al. 2009).

Mine Discharge and Metal Loadings

The composite discharge of nine mines (Greenfield 1 and 2, Amikol, Mayo, Unu, Geominex, Ugwuaji swamp, Crushstone, and CCC) to the Unu stream was calculated based on the average (2.3 L/s) of the weekly discharge measurements during the 4 month overflow period (July–October) when this section of the Ivo River Basin floods, most of the mines are abandoned due to uncontrollable water problems, and the mines begin to overflow into the environment. This was multiplied by the number of seconds in 4 months (123 days) of continuous discharge in the Unu sub-basin to produce an approximate annual discharge in the sub-basin, totalling 24,442,560 L/year.

The effluent discharge was directly measured monthly at the Crush Rock Industries site in Ishiagu by timed container fills. The annual discharge (8,409,600 L/year) was calculated by multiplying the average of these measurements (0.4 L/s) by the approximate time of discharge, assuming a 16 h daily operation (taking shut-downs and other downtime into consideration).

The instantaneous load of a water quality parameter is derived by multiplying parameter concentration by the stream discharge at the time the sample was collected. It was impossible, however, to obtain precise time-based parameter loading since the average parameter concentration and average discharge had to be estimated in the absence of continuous data. We therefore used average monthly water quality data and average monthly stream discharge data (Davis et al. 1999).

The annual dissolved load for the area was therefore calculated by multiplying the sum of the mean TDS load for the four abandoned mines and two active mines during both seasons (2,753 mg/L) (from Tables 2, 3, 4, 5), the cohort of nine mines discharging into the Ivo River system via the Unu stream, and the annual load from the Unu stream. This totalled 605,613 kg/year. For the Crush Rock mines, the total dissolved discharge load, estimated from the values in Table 1 was 104,195 kg of TDS per year. The total metal load from the abandoned and active mines was similarly calculated to be 557.3 kg.

Therefore, the Unu system, was calculated to discharge about 557 kg of metals, 605,613 kg of dissolved solids, and 24,442,560 L of circumneutral untreated mine water annually into the Ivo River basin. For the Crush Rock mines, the total metal loadings totalled about 25.7 kg of metals per year. Note that the Bilwadan mine was not included in these estimates because it belongs to a different sub-basin (Fig. 2). An extension of the used cohort could have the Bilwadan discharging more than 10 kg of metals into the Ivo River Basin annually, increasing the total discharge of metal from these varied sources to at least 586 kg of metals in a year. Thus, the mean yearly polluted discharge into the Ivo River basin from mining could exceed 32,852,160 L of untreated circumneutral drainage with over 709,808 kg of dissolved solids and 586 kg of metals.

Conclusions and Recommendations

Findings from this study revealed pH and concentration characteristics similar to those found in groundwater and surface water sources at limestone, dolomite, bituminous, and anthracite coal mines in Pennsylvania, USA (Cravotta et al. 1990; Brady and Hornberger 1990). Studies have shown that AMD typically decreases slowly with time following the cessation of mining as sulphides are consumed by weathering reactions (Rahn et al. 1996; Brady and Hornberger 1990); this may also be the case with some of the abandoned mines in this study.

Dissolution of minerals like sphalerite, calcite, and galena, the major constituents of ore and aggregate minerals in the study area, have resulted in circumneutral mine waters with sulphate as the dominant anion and significant but relatively low concentrations of zinc and other ecotoxic metals such as lead and cadmium (Nuttall and Younger 2000). Although the pH results in relatively low metal concentrations in the water column, metals may be precipitated out in wetlands and on to streambeds (Akabzaa et al. 2009; Binning and Baird 2001; Nuttall and Younger 2000). Sediment pollution is considered by many regulatory agencies to be one of the largest risks to the aquatic environment since many organisms spend the major portion of their lifecycle living on or in sediments (Alam and Sadiq 1993; Chima et al. 2010). Precipitated or sorbed metals can therefore enter into the food chain, through bioaccumulation. Although sediments are sinks, trace metals may also re-enter the water column by physical, chemical, and biological processes. In this way, the sediment serves as a buffer and may keep metal concentrations in water and biota above background levels long after their input has ended (Binning and Baird 2001; Chima et al. 2010).

Mine effluents from the active and abandoned mines contain very high concentrations of TDS, hardness, chloride, calcium, EC, turbidity, and low (though) unacceptable levels of metals, and are finding their way untreated into the environment of the study area. We used unconventional indirect methods to estimate contaminant discharges into the Ivo River basin because of access restrictions. Our study indicated that nearly 33 million L of untreated circumneutral-alkaline drainage and effluents find their way into the Ivo River watershed yearly, including about 710,000 kg of dissolved solids and 586 kg of potentially toxic metals.

Discharges from both abandoned and active mines exceed national (FEPA) and international (EU, WHO, and USEPA) permissible standards for domestic water use and discharge into aquatic sources (Table 2). Although mine water is not intended for domestic use, it is a fact that local farmers use this water for irrigation and sometimes for drinking purposes (Ezekwe et al. 2012a, b). Concentrations of Pb are also above standards for the protection of groundwater from industrial effluents, while in some seasons, concentrations of TDS, Zn, Cl^-, Mg, and Ca exceeded national guidelines for discharging effluents into surface water bodies and on to land.

Correlation analysis of water quality from discharge sources and the Ivo River indicate direct or indirect impacts on the Iwo River watershed from mining sources and surface and groundwater sources in the study area. The Unu and Ugwuajirija wetlands especially occupy a very significant place in the hydrogeopollution cycle of the study area as they receive direct discharges from the mines and are in turn a source of continuous polluted recharge to both surface and groundwater resources. Both the Ivo River system and wells around the central and southeastern areas of Ishiagu are recharged from these wetlands (Ezekwe et al. 2012a). The wetlands are also a source of drinking and irrigation water for rice farmers and sustain the abundant wildlife around the mines, necessitating their comparison with drinking water standards (DWS). Uptake of metals by plants and animals in the food chain potentially poses a health risk to the local population.

Although an environmental impact assessment is required by the Nigerian Federal Government for granting mining licenses, activities of mining companies in the study area reveal that environmental regulations and recommendations are typically ignored. We suggest that the government in Nigeria establish a task force to investigate the environmental operations of mining companies and that the state environmental agencies ensure compliance with established regulations to forestall an impending ecological disaster in the mining areas. Also, environmental education of host communities would allow citizens to understand the impacts of mining activities to their health and their environment and would encourage them to become watch dogs for their environment.

Acknowledgments We thank Mrs. Catherine I. Clinton-Ezekwe of Clinton Davidson Concepts, U. J. Ikoro, and Uyi Hanson of the Institute of Pollution Studies, University of Science and Technology, Port Harcourt for their field and laboratory support; Prof M.A Ijioma of Abia State University for encouragement and intellectual support, and Prof O. Nwaugo and Mr. Kentus Obiye for financial assistance. Also, we wish to thank Prof. Dr. habil. Christian Wolkersdorfer for assisting us with the plotting of the figures in this article.

References

Akabzaa TM, Banoeng-Yakubo BK, Seyire JS (2009) Impact of mining activities on water resources in the vicinity of the Obuasi Mine. West Afr J Ecol 11:129–139

Alam IA, Sadiq M (1993) Metal concentrations in Antartic sediment samples collected during the Trans-Antartica 1990 expedition. Marine Pollut Bull 26:523–527

APHA (American Public Health Association), (1995) Standard methods for the examination of water and waste water, 19th edn. APHA-AWWA-WPCF, Washington DC, USA

Aroh KN, Eze CL, Abam TKS, Gobo AE, Ubong IU (2007) Physicochemical properties of pit-water from ishiagu lead/zinc (Pb/Zn) mine as an index for alkaline classification of the mine drainage. J Appl Sci Environ Manag 11(4):19–24

Awalla CO, Ezeigbo HI (2002) An appraisal of water quality in the Uburu-Okposi area, Ebonyi State, South Eastern Nigeria. Water Res 13:33–39

Banks D, Parnachev VP, Frengstad B, Holden W, Vedernikov AA, Karnachuk OV (2002) Alkaline mine drainage from metal sulphide and coal mines: examples from Svalbard and Siberia. Geol Soc Lond Sp Publ 198:287–296. doi:10.1144/GSL.SP.2002.198.01.19.2002

Binning K, Baird D (2001) Survey of metals in the sediments of Swartkops river estuary Port Elizabeth South Africa. Water SA 27(4):461–466

Brady KB, Hornberger RH (1990) The Prediction of Mine Drainage Quality in Pennsylvania. Water Pollut Control Assoc 23(5):8–15

Brown E, Skougslad MW, Fishman MJ (1970) Methods for collection and analysis of water samples for dissolved minerals and gases. Techniques for Water Resources Investigations, USGS, Book 5, Reston, VA, USA

Chartiers Greenway (2009) Evaluation of mine discharges from abandoned coal mines in the lower chartiers creek watershed and restoration plan for large mine discharges to lower chartiers creek. http://www.Chartiersgreenway.net/amd_body.htm

Cheng H, Hu Y, Luo J, Xu B, Zhao J (2009) Geochemical processes controlling fate and transport of arsenic in acid mine drainage (AMD) and natural systems. J Hazard Mater 165:13–26

Chima GN, Ezekwe IC, Ijioma MA, Opuene K (2010) Preliminary assessment of metals in active stream and lake bottom sediments in the Ivo River Basin, South East Nigeria. Int J Appl Environ Sci 5(6):803–812

Cratchley RC, Jones JP (1965) An interpretation of the geology and gravity anomalies of the Benue Valley, Nigeria. Overseas Geol Surv Geophys 1:1–26

Cravotta CA, Brady KBC, Smith MW, Bean RL (1990) Effectiveness of alkaline addition at surface mines in preventing or abating acid mine drainage part 1, geochemical considerations. In: Proceedings, 1990 Mining and Reclamation Conference and Exhibition, Charleston, WV, USA, West Virginia Univ, Morgantown, WV, USA, pp 221–226

Davis AD, Webb CJ, Sorensen JL (1999) Bio-indicator evaluation of water quality impacts from inactive and abandoned mines in the Bear Butte Creek Basin of the Black Hills. SME Annual Meeting, Preprint 99–114, Denver, CO, USA

Duruibe JO, Ogwuegbu MOC, Egwurugwu JN (2007) Metal pollution and human biotoxic effects. Int J Phys Sci 2(5):112–118

European Union (1998) Drinking Water Standards. Council Directive 98/83/EC on the Quality of Water Intended for Human Consumption. Adopted by the Council, on 3 Nov. 1998. http://www.lenntech.com/applications/drinking/standards/eu-s-drinkingwater-standards

Ezekwe IC, Odu NN, Chima GN, Opigo A (2012) Assessing regional groundwater quality and its health implications in the Lokpaukwu, Lekwesi and Ishiagu mining areas of southeastern Nigeria using factor analysis. Environ Earth Sci 67(4):971–986. doi:10.1007/s12665-012-1539-9

Ezekwe IC, Odubo E, Chima GN, Onwuchekwa IS (2012b) Groundwater occurrence and flow patterns in the Ishiagu mining area of Southeastern Nigeria. Front Earth Sci 6(1):18–28. doi:10.1007/s11707-011-0203-0

FEPA (1991) Guidelines and standards for environmental pollution in Nigeria. Federal Environmental Protection Agency, Abuja

FEPA (Federal Environmental Protection Agency) (1983) Effluents limit for discharge into surface water. Federal Environmental Protection Agency, Abuja

Iribar V (2004) Origin of neutral mine water in flooded underground mines: an appraisal using geochemical and hydrogeological methodologies. In: Jarvis AP, Dudgeon BA, Younger PL (eds) Proceedings, International mine water association symposium, Newcastle upon Tyne (University of Newcastle), vol 1, pp 169–178

Lambert DC, Dzombak DA, Aljoe WW (2002) Evaluation of natural amelioration of acidic deep mine discharges in the Uniontown Syncline, Pennsylvania. Proceedings, WV surface mine drainage task force symposium. http://wvmdtaskforce.com/proceedings/00/PDzombak.PDF

Nordstrom DK, Alpers CN (1999) Geochemistry of acid mine waters. In: Plumlee GS, Logsdon MJ (eds) The environmental geochemistry of mineral deposits. Rev Econ Geol (l 6A). Soc Econ Geol, pp 133–160

Nuttall CA, Younger PL (2000) Assessment and experimental passive treatment of zinc-rich net alkaline mine waters, Nent Valley, UK. In: Rozkowski A, Rogoz M (eds) Proceedings, 7th international mine water association congress, Ustron, Poland, pp 456–463

Nwaugo VO, Obiekezie SO, Etok CA (2007) Post operational effects of metal mining on soil quality in Ishiagu, Ebonyi State. Int J Biotechnol Allied Sci 2(3):242–246

Obiekezie SO, Okereke JN, Anyalogbu E, Okorondu SI, Ezejiofor TIN (2006) Underground water quality of rock mining in Ishiagu, Ebonyi State Nigeria. Estud Biol 28(63):61–71

Offodile ME (2002) Groundwater study and development in Nigeria. Mecon Services Ltd, Jos

Olubambi PA, Ndlovu S, Potgieter JH, Borode JO (2008) Mineralogical characterization of Ishiagu (Nigeria) complex sulphide ore. Int J Miner Process 87:83–89

Onyedike GO, Nwosu GU (2008) Lead, zinc and cadmium accumulation in root crops from mineralized galena-sphalerite mining areas and environment. Pak J Nutr 7(3):418–420

Parkhurst DL, Appelo CAJ (2011) User's guide to PHREEQC (version 2.18.5570)-a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. USGS Water Resources Investigations Report 99–4259, Washington DC, USA

Petters SW (1978) Stratigraphic evolution of the Benue trough and its implications for the upper cretaceous paleogeography of West Africa. J Geol 86:311–322

Plumlee GS, Smith KS, Montour WH, Ficklin WH, Mosier EL (1999) Geologic controls on the composition of natural eaters and mine waters draining diverse mineral deposits types. In: Filipek HL, Plumlee SG (eds) The environmental geochemistry of mineral deposits, part B: processes, techniques and health issues, soc of economic geologists. Littleton, CO., USA, pp 373–409

Rahn PH, Davis AD, Webb CJ, Nichols AD (1996) Water quality impacts from mining in the Black Hills, South Dakota, USA. Environ Geol 27:38–53

Rainwater FH, Thatcher LL (1960) Methods for collection and analysis of water samples. USGS water supply paper 1454, Reston, VA, USA

Reyment RA (1965) Aspects of the geology of Nigeria. Ibadan Univ Press, Ibidan

Rose AW, Cravotta CA III (1998) Geochemistry of coal mine drainage. In: Brady KBC, Smith MW, Schueck J (eds), Coal mine drainage prediction and pollution prevention in Pennsylvania, Department of Environmental Protection, Harrisburg, PA, USA. www.dep.state.pa.us/dep/deputate/minres/districts/cmdp/chap01.html

Rose AW, Phelps LB, Parizek RR, Evans DR (1995) Effectiveness of lime kiln flue dust in preventing acidic mine drainage at the Kauffman Surface Coal Mine, Clearfield County, Pennsylvania. In: Proceedings, annual meeting of the American society for surface mining and reclamation, Gillette, Wyoming, vol 1, pp 159–171

Todd DK (1980) Groundwater hydrology. John Wiley & Sons, Etobicoke

Uma KO, Onuoha KM (1989) Ground water resources of the lower Benue trough Southern Nigeria. In: Ofoegbu CO (ed) The structure and evolution of the Benue trough. Friedr Vieweg und Sohn, Braunschweig/Wiesbaden, pp 77–90

USEPA (US Environmental Protection Agency) (2012) Drinking water regulations and health advisories. Office of water EPA 822-S-12-001, US Environmental Protection Agency, Washington, DC, USA

WHO (1993) Guidelines for drinking-water quality, 2nd edn. World Health Organization. Geneva

Younger PL (2000) The adoption and adaptation of passive treatment technologies for mine waters in the United Kingdom. Mine Environ 19:84–97