POTENTIAL THREATS OF SOME HEAVY METALS IN WATER RESOURCE AROUND FOUR MAJOR QUARRY SITES IN ABAKALIKI AND ITS ENVIRONS

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ABSTRACT

Quarrying a general name for all forms of solid mineral extraction from their resident rocks provides mankind with wealth that sustained the growth of civilization and higher standard of living. The immense gain of quarrying activities notwithstanding, the environmental impacts are quite enormous. There has been an increased concern as to the safety of water resources, following reported cases of the occurrence of heavy metals in water bodies especially around the quarry sites which by nature are injurious to human health. This paper in response to this, examined the occurrence of heavy metals in water resources (i.e stream, ponds, lakes, and river) in and around four quarry sites in Abakaliki capital territory and its environs. The study was carried out in four major quarrying sites in the four local government areas that make up Abakaliki capital territory and its environs. Water samples were obtained and analyzed using Atomic Absorption spectrometer. The result showed there were heavy concentrations of iron, cadmium, lead and zinc in all the sample sites than the maximum permissible limits of Nigerian industrial standard (NIS) and WHO standards. While copper and arsenic were high in some and low in some than the permissible limit of NIS and WHO standards in some sample sites. The implication of the result on the management and use of water resources in the study area were identified and discussed. Recommendations were made as to how to mitigate discussed. Recommendations were made as to how to mitigate the effects of the high concentrations of the heavy metals.

KEYWORDS: Quarrying, Heavy Metals, Pollutants and Mitigation

Introduction

Quarrying activities can result in heavy metals contamination in water resources within an environment. Heavy metals also occur naturally but rarely at toxic levels. Potentially contaminated water may occur at areas in or around quarrying waste piles and tailings (USDA and NRCS, 2000).

Excess heavy metal accumulation in water is toxic to human and other animals. Exposure to heavy metals is normally chronic (exposure over a longer period of time), due to food chain transfer. Acute (immediate) poisoning from heavy metals is rare through ingestion or dermal contact but is possible. Chronic problems associated with long-term heavy metals exposure are: lead pb mental lapse, cadmium affects kidney, liver and GI tract and arsenic causes skin poisoning, affects kidney and central nervous system (USDA and NRCS, 2000).

Environmental pollution by heavy metals, even in low concentrations and the long term cumulative health effects that go with it, is of major health concern all over the world. For instance bioaccumulation of lead (pb) in the human body interferes with proper functioning of the mitochondria thereby impairing respiration as well as causing constipation, swelling of the brain, paralyses and could eventually lead to death (Oluyemi, Feujil, Oyekunte and Ogunfowokan, 2008).

Heavy metals occur naturally in the system with large variations in concentrations. In modern times anthropogenic sources of heavy metals, i.e pollution from the activities of human have introduced some of these heavy metals into the ecosystem. The presence of heavy metals in the environment is of great ecological significance due to their toxicity at certain concentrations, translocation through food chains and non-biodegradability which is responsible for their accumulation in the biosphere (Aekola, Salami, and Lawal, 2008).

It has long been recognized that extraction of rock materials can adversely affect the quality, level and flow characteristics of water resources (Mineral Industry Research Organization, MVRO, 2012).

One impact of quarrying is to bring to the surface large quantities of minerals that are un- suitable in weathering environment. For instance, rain water runoff may react with sulphide minerals in waste rock and tailings to form sulphuric acid (H_2So_4).

Such acidic runoff can pollute streams and rivers for many kilometers, killing or diminishing plants and animals (Whitehead 2007). Runoff from quarries may also enhance levels of metals such as arsenic, copper, lead, iron, cadmium, cyanide and nickel which may pollute water resources, poisoning fish, plants and drinking water resources.

It has been established by Phil-Eze (1983) that Abakaliki has a potential water deficit extending for over months, which commences in mid-January. This water problem result from constraints imposed greatly by the topography and geology of the underlying rock-shale (impervious and with very low porosity 0-10%) and inaccessibility respectively (Chima, 1984).

According to Elechi (1983), the greatest source of health problem in Abakaliki is the scarcity of water and the low quality of the available amount. He asserted that guinea worm which is prevalent in the area is as a result of poor water quality and quantity. Although the problem of water to some extent have in recent times been solved by the opening up of boreholes, but the boreholes become dry during the dry season. Quarrying activities that can result in the release of toxic acid and heavy metals, that will destroy the vital chemical nutrients of the soil, cause erosion and silting, dewatering etc has serious water scarcity implication for an agrarian area already faced with acute water deficit.

The study is aimed at assessing the potential threat of the concentration of some heavy metals in water resources around four major quarrying sites in Abakalki capital territory and its environs, the effect of the concentration and the mitigation measures.

Material and methods

Sample and preparation

This study is basically an intense field work conducted in the study area (Abakaliki capital territory and its environs). Reconnaissance survey was carried out in the course of this study to identify the relevant issues that must be considered in designing the study methodology. The significant outcome of the reconnaissance survey was the identification of the quarry sites, their locations, and the affected water bodies and nearby cultivable farmlands in the study area. To justify the socio-economic impact of quarrying industry, a control (i.e a reserved area) was chosen. While selecting the control site, certain factors such as the absence of quarrying activities and the distance away from the quarry industries, were taken into consideration. The study made an attempt to compare between the area affected by quarrying activities and the non -quarrying area -the control site. During the reconnaissance survey, the researcher found out that the socio-economic source of livelihood, agro-climatic condition and infrastructural development before the commencement of quarrying activities were the same in the quarry and control sites. There are no quarrying activities in the control site.

Using purposive sampling method four (4) major quarrying sites were selected. These quarrying sites are: Iboko Igbeagu site (popularly known as the sharon site) in Nkpuma Ezzaegu village Onunwafor, Odemigbo, Nwagbakoro and Ahalugo villages in the Ezza North L.G.A. Ezza Inyimagu (Achinwangboko) quarry site, in the military cantonment territory in Nkwagu, Abakaliki L.G.A and the Enyadilogu quarry site in the Ndiebor village in the Ebonyi L.G.A. The control area, New Layout Quarters, though located in Abakaliki L.G.A is about 8km away from the closest quarry sites, Sharon.

Table 1: Names of sample sites and their abbreviation

S/N	Name	Abbreviation
1	New layout (Control)	NL
2	Umuaghara	UM
3	Enyadilogu	EN
4	Archinwamgboko	ARC
5	Sharon	SH
6	Crushing sampled site 1	CRS. 1
7	Crushing sampled site 2	CRS. 2

Accordingly water samples from the 4 major quarry and the control sites were analyzed in the study area. Water samples were collected with the assistance of a laboratory technician at designated points, with swam water cans, rinsed severely with distilled water. The cans were cocked to avoid trapping of air bubbles and transported to laboratory. In the laboratory the water samples were kept in the fridge for 24 hours before been analyzed.

Metal Analysis

Cloud point extraction (CPE) was used for the simultaneous pre-concentration of cadmium copper, lead and zinc after the formation of a complex with 1 – (2-

thiazolylazo) -2- naphthol (TAN) and later analysis by flame atomic abosorption spectrometry (FAAS) using octylphenoxypolyethoxyethanol (Triton X-114) as surfactant. The chemical variables affecting the separation phase and the viscosity affecting the detection process were optimized. At pH, preconcentration on only 50ml of sample in the presence of 0.05% Triton X-114 and 2 x 10 -5 mol 1-1 TAN permitted the detection of 0.099, 0.27, 1.1 and 0.095ng ml-1 cadmium, copper, lead and zinc respectively. The enhancement factors were 57.7, 64.3, 55.6 and 63.7 for cadmium, copper, lead and zinc respectively. The proposed method has been applied to the determination of cadmium, copper, lead and zinc in water samples and a standard reference material (SRM).

Iron was determined by using phenathronic method. A curette was filled with each water sample plus 0.5% orhophenamhroline solution (1:10 dilution). From a standard curve, the concentration of iron in the sample was determined. Arsenic was determined spectrophotometrically using 2-(5-beomo-2-pysidylago) -5-diethylaminophenol nitrogen arsenic ingestion can cause reverse toxity through ingestion of contaminated food and water.

Result

Results of the heavy metals analyzed in the study area are shown in Table 1 below. The heavy metals were selected based on their possible impact on water quality and aquatic organisms, and for easy interpretation. The heavy metals are, lead (pb), cadmium (Cd), Zinc (Zn), copper (Cu), Arsemic (As) and Iron (Fe)

Discussion

Table 2: Concentration of heavy metal in the quarrying and control sites

Metals	Iboko Igbeagu (SH)	Umuaghara (UM)	Ezza Inyimagu (Archi nwamgboko) (ARC)	Enyadilogu (EN)	New layout Control site (NL)
Lead (mg/l)	0.075	12.20	5.80	7.85	0.075
Cadmium (mg/l)	0.012	0.029	0.050	0.16	0.012

Zinc (mg/l)	4.85	11.15	5.26	6.80	4.85
Copper (mg/l)	0.005	0.95	1.40	1.090	0.005
Arsenee (AS) Mg/l	0.10	0.040	0.028	0.26	0.10
Iron (Fe) Mgl	1.45	16.50	11.68	18.60	1.45
	6.402	40.869	24.218	34.526	6.402

Table 2 shows sum total of concentration of all the heavy metals in each quarrying site and the control site. Except for the Sharon quarrying site, all other quarrying sites show higher concentration of heavy metals than the control site. This is an indication that quarrying activities unlock heavy metals inundated beneath the earth surface in rock masses into the surrounding water bodies.

A look at Table 2 also reveals a comparatively quantitative disparity of the heavy metals concentration among the quarrying sites. In ascending order sharon site has 6.402 mg/l Archinwamgboko 24.218 mg/l, Enyadilogu site 34.526 mg/l and Umuaghara quarrying site 40.868 mg/l. The Sharon quarrying site is the oldest and the 1st quarrying site in Abakaliki and its environs, followed by Archinwamgboko, then Enyadilogu site and lastly Umuaghara site. This may imply that the newer a quarrying site, the more the heavy metals are unlocked into the surrounding water bodies.

Table 3: Heavy metals concentration level in the quarrying site compared with the control site

Water	**Water samples**				**Mean ±**	**Standard deviation**	**Control water sample**
	SH	UM	ARC	EN			
Lead (mg/l)	0.075	12.20	5.80	7.85	6.481	4.361	0.075
Cadmium	0.012	0.029	0.050	0.16	0.06275	0.058	0.012

(mg/l)							
Zinc (mg/l)	4.85	11.15	5.26	6.80	7.015	2.496	4.85
Copper (mg/l)	0.028	0.95	1.40	1.090	0.8745	0.51895	0.028
Arsenic (As) (mg/l)	0.010	0.040	0.028	0.026	0.026	0.01068	0.010
Iron (Fe) (mg/l)	1.45	11.50	11.68	18.60	12.0575	6.6186	1.45

The result in Table 3 generally revealed that the mean concentrations for most of the metals including the toxic ones as lead (Pb), cadmium, copper, arsenic etc were all found to be very high relative to those of the control site.

Among the toxic heavy metals, lead (Pb) (6.481 mg/l), cadmium (0.06275 mg/l), Zinc (Zn) (7.015 mg/l), copper (0.8663) and iron (Fc) (12.0575) recorded worrisome mean concentrations. Even lead, cadmium, and iron at mean concentrations of 6.481mg/l, 0.06275 mg/l and 12.057 mg/l respectively cannot be simply glossed over, since the least of these concentrations surpassed the allowable limits in water by regulatory agencies like Nigerian Industrial Standard and World Health Organization maximum permissible limit.

Excess of iron, through food intake causes rapid, hypertension and drowsiness. Fe also imparts a bitter taste to water and a brownish colour to laundered clothing and plumbing fixtures. The maximum allowed concentration of iron in drinking water according to NIS (2007) is 0.3 (mg/l).

Table 4: Concentration ranges and means of Heavy Metals in water samples from the quarry sites compared with the mean concentration of WHO and Nigerian Industrial Standard

Metals	**Mean**	**Standard Deviation**	**Range**	**Maximum permissible limit (WHO)**	**Maximum permissible limit (NIS)**
Lead	6.481	4.361	0.075- 12.20	0.05mg/l	0.01 mg/l

Cadmium (mg/l)	0.06275	0.058	0.012-016	0.01 mg/l	0.003
Zinc	7.015	2.496	4.85 – 11.15	15.0 mg/l	3 mg/l
Copper	0.8663	0.51895	0.025-1.40	2.0 mg/l	1 mg/l
Arsenic	0.026	0.01068	0.010-0.040	0.05 mg/l	0.01 mg/l
Iron	12.057	6.6186	1.45-18.60	3.0 mg/l	0.3 mg/l

Table 4 above shows that in all the collected water samples, concentration of iron is above the permissible limit. The concentration level of iron in all the sites ranges from 1.45 (mg/l) in SH to 18.70(mg/l) in EN with a mean of 13.6(mg/l).

Copper normally occurs in drinking water from Cu pipes, as well as from additives design to control algal growth. While copper's interaction with the environment is complex a research shows that most Cu introduced into the environment is, or rapidly becomes, stable and results in a form which does not pose a risk to the environment. Copper is an essential trace element but toxic to plants and algae at moderate levels.

The water copper content of our study area range from 0.028 (mg/l) in SH site to 1.43 (mg/l)in ARC site, It has an average of 0.90 (mg/). Among all the sample sites only the ARC and EN sites with 1.43 (mg/) and 1.090 (mg/) copper level respectively, are higher than the NIS (2007) permissible limit of 1.0 (mg/), The rest of the sites, except SH site with 0.028 (mgl) are less but very close to the maximum permissible limit of NIS (2007) of 1.Omg/1. The fact is that the sites (except SH site) are within the permissible limit and copper concentration is high in the quarry sites than at the control site.

Cadmium occurs naturally in ores together with zinc, lead and copper. Water contaminated with cadmium, can lead to increase uptake of cadmium by crops and vegetables grown for human consumption. The uptake process of soil cadmium by plants is enhanced at low pH. Cadmium is present in most food stuffs, but concentrations vary greatly and individual intake also varies considerably due to differences in dietary habits

The cadmium concentration level in our water samples is generally high, higher than the Nigerian industrial Standard (NIS) maximum permissible limit of 0.003 (mg). Cadmium concentration level range from 0.012 (mp/) at SH site to 0.l6 (mg/) at the EN site and has an average of 0.48 (mg/l). This very high level of cadmium can be picked up in place of zinc by aquatic plants and through food chain transferred to the inhabitants of Abakaliki and environs. This can result in the disruption of homeostatic levels in the people and the availability of excess Cd. and other metals when Cd induces metallothonein activities in them. Excess Cd can also result i in kidney malfunction (NIS, 2007).

Arsenic ingestion can cause severe toxicity through ingestion of contaminated food and water. Plants can be affected through direct poisoning for example arsenic soil content reduces bryophyte diversity. Ingestion of arsenic causes diarrhea, vomiting and cardiac abnormalities (Viessman and Hammer, 1985).

Apart from the SH sample site with As 0.01 (mgl), all other sample sites have their As concentration level above the maximum limit of NIS - 0.01 (mg/). Arsenic range from 0.01 (mgl) at SH site to 0.04 (mg/|) at UM site and has an average of 0.23 (mg/l).

Because of size and change similarities, lead (Pb) can substitute for calcium and included in bone. Children are especially susceptible to lead because developing skeletal system require higher level of calcium. Lead that is stored in bone is not harmful, but if high levels of calcium are ingested later, the lead in the bone may be replaced by calcium and, mobilized. Once free in the system, lead may cause nephrotoxicity, neurotoxicity and hypertension. WHO's limit for lead (Pb) is 0.0Img/l. All the areas of quarrying and crushing activities have lead (pb) water content far above WHO standard limit. The water lead content range from 0.075 mg/l at the SH site to 12.20mg/l at at the Umuaghara quarry site.

There is a significant difference in the quantity of water content of lead (Pb) between the controlled sampled area (NL) and the other sample areas of quarrying activities. This is an indication that quarrying activities release enormous quantity of lead (Pb) into surrounding water bodies. Lead content is its lethal stage.

Zinc occurs naturally in water (about 70mg/l) in crustal rocks (Greany, 2005). Water- soluble zinc that is located in soils can contaminate ground water. Many foodstuffs contain concentrations of zinc. Zinc is a trace element essential for human health. Zinc may increase the acidity of water and some fish can accumulate zinc in their bodies, when they live in Zn contaminated water ways. When Zn enters the bodies of these fish, it is able to biomagnify up the food chain. Algae communities are less diverse in acidic water containing high zinc concentration, and mine drainage stress and decrease their primary production.

The concentration level of Zn in our study area range from 4.85mg/l in SH and to 115mg/1 in UM, with an average of 5.14mg/. The NIS for Zn is 3,O mg/l. In all the quarry sites the water Zn concentration level is above the NIS (3.0 mg/l) permissible standard limit.

Of all the heavy metal examined iron was found to be the most abundant metal in quarrying sites in Abakaliki and its environs, with an average value of 13.09 mg/l. This is acceptable because it has been reported that iron occurs at high levels in Nigeria Soil (Asaolu, S.S., K.O. Ipnimoroti, O. Olaofe and C.E. Adeeyinwo, 1997, Asaolu, S.S. and O Olaofe 2004, and Nwajei, G.E. and P. O. Gagophien 2000).

Clean and safe drinking water, unarguably the natural resource most precious to humanity, is threatened by the impacts of quarry activities across the globe. The risk of an operating quarry site releasing wastes into drinking water resources is ever-present (Aimee and Alexander, 2004). Pollution of drinking water, rivers, ponds, streams etc and loss of vegetation are common ecological impacts of modern quarry industries .There is an adverse health effects onto those living near, down-streams or downwind from supplies. Many watersheds used for drinking water are impacted and threatened by metal pollution, polluted by runoff from abandoned quarry pits (Aimee and Alexander, 2004). In our study area – Abakaliki and its environs from the laboratory analysis, interviews, and observations, quarrying activities releases a lot of pollutants through runoff into the surface water bodies.

Discharged water from quarry pits containing salts of heavy metals like iron, zinc, copper, arsenic etc contributes to the acidity of receiving water (UNEP, 2008). These salts hydrolyze to release acid. The acidic quarry pit water – acid mine drainage, has so many effects. Acidic water is very corrosive. Corrosive acidic water from the sites is a problem to water treatment plants and pipes. Very high dissolved oxygen and the presence of some heavy metals like iron and zinc, in our area of study, enhance water corrosiveness. Rapidly moving water such as mountain, streams, tend to contain a lot of dissolved oxygen than stagnant water. Water flowing over rocks is also more oxygenated. Apart from the fact that runoffs in our area of study pass through rocks, they flow fast because all the quarry sites are located on high lands. Water bodies around quarry sites are therefore oxygenated and are therefore very corrosives. Interviewed Abakaliki Water Board Workers said that leakages from pipes and broken down water treatment plants is the result of the severe irregular pipe borne water supply in Abakaliki capital territory and its environs.

Field investigation of some residents revealed that due to the breakdown of the water treatment plants and leakages, there was no pipe borne water supply for more than nine (9) months in the year 2016.

Water acidity affects aquatic plants and animals especially their reproductive capacity. Strong acidity (low pH) can even lead to death of aquatic organisms (Navean, 2012). Amphibians are particularly vulnerable to pollutants (Mesner and Greiger, 2000). Oral interview with some people in Abakaliki, revealed that catching of fish and frogs, the main occupation of some people, is a thing of the past. Today, very few people if any are engaged in the catching of fish and frogs. This may not be unconnected with the high acidic discharged quarry waters and runoff over quarried rocks into streams of the study area.

Through informal interview and field observation, we observed that the near absence of pipe borne water made the people in Abakaliki its environs, living near quarry sites, to depend on quarry hard and polluted water trapped in pits for drinking, bathing, washing and other domestic purposes especially in the dry seasons, when most sources of water are dry or not good enough for domestic use.

Ebonyi State in general and Abakaliki and its environs in particular are known for water deficit problem (Phil-Eze 1983, Chime, 1984 and Njaduara, 2006). With the heavily polluted surface water resources, water related crisis is worsened. The people seems to in between the much campaign against dreaded guinea worm infested man-made water pond (Okpuru) and the deadly heavy metal ladened chemically poisoned surface water resources. The state government made frantic efforts to supply the study area with pipe borne water, but to no avail. The quarry activities which seem to put food on the tables of the indigenes by way of employment is rather compounding their problems through reduced farm yields, contaminated crops and poisonous surface water. The people may unconsciously be dying in their numbers without knowing the cause.

Mitigation measures

The importance of quarrying activities notwithstanding, some damage to the environment is inevitable in the cause of mineral exploitation and the only option left is to apply some remedy to the damage. The remedy or compensation vary and depend on the type, extent and magnitude of damage, which can be permanent or redeemable with time, as the causative factor is withdrawn.

Two remediation methods for water as pointed by UNEP (2010) can be applied these are (i) the passive treatment and (ii) the active treatment remediation methods. The passive treatment involves the use of natural process to improve the quality of incoming water with minimal operation and maintenance requirements. These processes are chemical, biological and physical in nature. The chemical removal processes are by oxidation, reduction, coagulation, absorption adsorption, hydrolysis and precipitation. The physical removal processes include gravity, aeration, and dilution. While the biological processes include, biosorption, biomineralization, bioreduction, alkalinity generation.

Active treatment on the other hand is a scheme. It is a plant or a machine through which polluted quarry water flows and oxidation, mixing with alkali and sedimentation processes take place in different parts of the plant. The end result is the precipitation of metals at one end and at another end the outflow of water. Oxidation is done with Fe2+ while the akali mixture is with NaOH and $Ca(OH)_2$. Although the active treatment is more effective and reliable, they are very expensive.

In summary according UNEP (2010), possible techniques for quarry water prevention include dry covers, water covers, selective diversion of surface water, inundation, alkaline addition, alkaline injection, coating/encapsulation, biocides and separation of sulphides.

Conclusion

Extraction of mineral resources (ie quarrying) is the backbone of most economics in developed and developing countries of the world. However, the great danger resulting from the exploitation, such as abandoned water filled pits, biodiversity loss, the release of toxic heavy metals deeply locked in rock masses and the accompanying heavily polluted water resources, all of health rick to quarry workers and neighbouring communities, deserve urgent attention. Emphasis should shift from the much generated income to the safety of the workers first and then the nearby communities. From the onset water diversion channels should be created to prevent the mixing up of the acid mine drainage from the other usable surface water resources

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