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Review

The Implications of AMD Induced Acidity, High Metal Concentrations and Ochre Precipitation on Aquatic Organisms

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Abstract

Acid mine drainage (AMD) is a legacy left behind by abandoned and active mines that affects all environmental media. Contamination of water resources by AMD presents significant challenges to aquatic ecosystem stability and on the abundance and diversity of aquatic species. Aquatic organisms react and are affected differently by these conditions. Several studies have reported on how AMD affects aquatic organisms with most of these studies focusing on a specific group of organisms or characteristic of the water. This review paper presents a holistic view on how aquatic organisms cope with, and are affected by the high acidity, high heavy metals content and precipitation of oxides of iron and aluminium which are characteristic of AMD contaminated freshwater ecosystems. Mechanisms of tolerance and the effects of high acidity, high heavy metals content, and precipitates of oxides of iron and aluminium on diatoms, algae, fish, and amphibians are discussed. The paper concludes by discussing the implications of AMD contamination of aquatic environments on the United Nations Sustainable Development Goals (SDGs) and recommendations on possible future prospects.

Keywords: diatoms, fish, amphibians, SDGs, metal and acid tolerance

Introduction

Acid mine drainage (AMD) is a low pH, high conductivity, high metals, and sulphate ion concentration liquid formed by the oxidation of sulphide minerals in pyrite-bearing mine wastes. The generation of AMD has been associated mostly with coal and gold mining but mining of other sulphidic metal ores such as tin, silver, copper, and iron are also known to generate AMD [1-3]. A series of studies [4-9] have reported on AMD generation and the microbes involved in the process with all these studies indicating that AMD forms when sulphide-rich mine wastes get exposed to oxygen-rich conditions. Sulphur containing minerals associated with the generation of AMD according to Li et al. [10] and Chopard et al. [11] include pyrite (FeS_2), arsenopyrite (FeAsS), chalcopyrite ($CuFeS_2$), galena (PbS), gersdorffite (NiAsS), pyrrhotite, and sphalerite

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(ZnS). A complex series of biotic and abiotic reactions (Equations 1-4) involving these minerals are responsible for AMD generation which starts with the oxidation of pyrite (FeS_2) and ends with the formation of free protons (H^+), sulphate ions (SO_4^{-2}), and the precipitation of iron hydroxide (Equations 1-4).

$$2FeS_2(s) + 7O_2 + 2H_2O \rightarrow 2Fe^{+2} + 4SO_4^{-2} + 4H^+ \quad (1)$$

$$2Fe^{+2} + ½O_2 + 2H^+ \rightarrow 2Fe^{+3} + H_2O \quad (2)$$

$$2Fe^{+3} + 6H_2O \leftrightarrow 2Fe(OH)_3 (s) + 6H^+ \quad (3)$$

$$14Fe^{+3} + FeS_2(s) + 8H_2O \rightarrow 2SO_4^{-2} + 15Fe^{2+} + 16H^+ \quad (4)$$

The prevailing environmental conditions and the microorganisms present play a significant role in the generation of AMD. Wolkersdorfer et al. [12] for example showed that pH conditions below 3.5 slow down, whereas the presence of iron (Fe) and sulphur (S) oxidising bacteria like *Acidithiobacillus thiooxidans* accelerates the oxidation of Fe^{2+} to Fe^{3+} (Equation 3). Microorganisms identified as playing a major role in AMD generation based on geomicrobiological studies include acidophilic and Chemolithotrophic bacteria or Archaea species but Méndez-GarcÍa et al. [5] in their study indicated that bacteria belonging primarily to the phyla Proteobacteria, Nitrospirae, Actinobacteria, Firmicutes, and Acidobacteria are the main players. Van Hille et al. [4] on the other hand, highlighted mesophilic and moderate thermophilic iron and sulphur oxidizing bacteria as the most encountered in AMD environments.

Acid mine drainage occurs in most abandoned and active mines and may remain a long-term environmental challenge in these environments because abandoned mines continue to generate highly acidic and metal-rich AMD many years after their closure. Freshwater ecosystems remain the most vulnerable environmental media to AMD contamination because most of the AMD generated in mines, both treated and untreated, are discharged into surrounding surface water bodies. The flow of AMD into streams and reservoirs affects water quality, causes long-term biotic impairment through direct toxicity, and alteration of aquatic habitats [13]. Global environmental concerns on the impacts of AMD on aquatic ecosystems is reflected in the growing body of literature on the subject [14-19]. Several studies have delved into the effect of AMD on aquatic ecosystems and the resources therein. Whereas these studies have looked at the overall effects of AMD on these ecosystems, water bodies contaminated by AMD display three common characteristics: low pH, high metals concentrations and bioavailability, and the formation of ochre which are precipitates of Fe and Al.

Data from studies [14, 17, 20-25] focusing on surface water resources affected by AMD have reported a water pH range of 8.4 (alkaline) to 1.6 (extremely acidic). The concentrations of metals including arsenic (As), cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb), mercury (Hg), and zinc (Zn) among others in AMD and AMD impacted water bodies have also been widely reported [26-32]. The concentrations of these metals in the AMD are influenced by the geochemistry of the orebodies, the processes involved in extracting the metals from the orebodies, and beneficiation of the mined metals. Ochre describes materials containing between 3 – 30% or Fe or Fe-rich ore minerals found around mines [33] and are formed when the prevailing pH condition in the water are between 3.5 and 4.3 [34]. These Fe rich minerals according to Máša et al. [35] could include jarosite precipitate (($NaKH_3O^+$) $Fe_3(SO_4)_2(OH)_6$), ferrihydrite ($Fe_5HO_8.4H_2O$), goethite (α-FeOOH), schwertmanite ($Fe_8O_8(OH)_6SO_4$) or usually mixtures of these. Ochre formation is a common occurrence is AMD contaminated water bodies where the ochre makes the water turbid and may also coat sediments [36].

These three characteristics of AMD contaminated waterbodies affects all groups of organisms present in these ecosystems. This review focuses on the impacts of low pH, high metals concentrations, and ochre in AMD impacted surface water bodies on the community structure and physiological processes of various groups of aquatic organisms in the water body in an endeavour to understand their implications on environmental sustainability. It also looks at the tolerance of these organisms to these water characteristics and the factors that influence the extent to which organisms may be affected by them. The review concludes by looking at the challenges that these impacts may pose on the realisation of the United Nations Sustainable Development Goals (SDGs).

Effects of AMD on Receiving Water Bodies

Published data from around the world demonstrates a wide variation in the characteristics of AMD affected water bodies (Table 1). AMD induced changes observed in water bodies include lowering of pH, increase in sulphate and metallic ion concentrations, electrical conductivity (EC), TDS, turbidity, redox potential (Eh) biological oxygen demand (BOD), and chemical oxygen demand (COD) [14, 37]. The concentrations of heavy metals in these water bodies (Table 1) are mostly above the maximum concentrations stipulated in the WHO drinking water quality standards. In addition to the increase in mobility of heavy metals, the reduction in acidity of water bodies caused by AMD may also cause the precipitation of hydroxides of Fe and Al (ochre) out of solution when the water pH is between 3.5 and 4.3 [38]. The ochre makes the water turbid and may also coat aquatic plants with consequences [36]. Acid mine drainage also lowers the buffering capacity of water by neutralizing CO_3^{-2} and HCO_3^- ions to form carbonic

Table 1. Characteristics of AMD contaminated water bodies from different mines and areas.

Country & Name of Mine	Type of mine	pH	EC/	SO_4	Al	Fe	Zn	Cu	Pb	Mn	Sources where published
			μScm^{-1}			mg/l					
South Africa Blesbokspruit	Gold	6.3	1040		-	-	0.34	0.29	2.53	-	[24]
Tanzania Bulyanhulu Gold Mine	Gold	7.5	-	48.78	-	3.2	1.26	-	-	-	[41]
Brazil	Coal	3.8	-	5846	219	1314	83.7	0.05	0.0008	23.8	[42]
USA Appalachians mines West Virginia	Coal	3.6	520	865	4.79	12.4	-	-	-	2.07	[43]
Zimbabwe Mazowe Iron Duke Mine	Iron pyrite	3.6	3762	3986	-	10.89	-	-	-	-	[44]
Spain Iberian pyrite belt	Pyrite	4.8	1094	474	0.37	129	11.59	11.41	-	5.75	[22]
Swaziland Ngwenya Iron Ore Mine,	Iron ore	7.5	298	22.3	-	0.34	-	0.07	-	0.3	[20]
Malaysia Pahang	Tin	3.8	0.116	-	-	-	5.3	5.07	0.01	-	[45]
Italy SW Sardinia,	Lead-Zinc	7.6	-	330	-	0.25	342	0.04	<0.01	0.09	[46]
Macedonia Zletovo	Lead-Zinc	5.1	-	-	-	0.3	1.5	139	0.18	46	[47]
Zimbabwe Bindura Trojan Nickel mine	Nickel	8.4	1524	650.5	-	0.34	-	-	-	-	[44]
Australia Mount Morgan mine	Gold-Copper	2.7	-	5950	-	74	10	45	0.6	46	[48]
Cyprus Lefka	Copper	1.6	-	12186	-	-	10.3	106	-	10.5	[49]
Cajamarca, Peru		3.32			14.8	9.3	2.1	1.6	-	1.8	[50]

acid (H_2CO_3) which readily breaks down into water and CO_2(g), reducing the amount of dissolved inorganic carbon available for photosynthesising producers, phytoplankton and periphyton [36, 39]. The high concentrations of sulphates of Ca and Mg in the water bodies and the level of dissolved salt contribute to an increased load of TDS and EC and consequently high salinity in AMD contaminated waters [40].

Effect of Acidity on Various Organisms

Different organisms have different pH range within which their physiological and biochemical processes function at optimum levels and so changes in water pH tends to affect the abundance and diversity of aquatic organisms. Results from studies on the effect of acid conditions on organisms in freshwater ecosystems show that acidity has huge implications on their physiology and biochemistry with different organisms reacting differently to this condition

Diatoms

Diatoms dominate the group of organisms described as phytoplankton which are an important prey for Zooplankton. They therefore constitute a significant link in aquatic food chains. A significant positive correlation between diatomic populations and pH was reported by Saelam and Kulabtong [51] which may be justified by the unavailability of nutrients when pH values are low. According to Fu et al. [52], inorganic carbon is rapidly dissolved under acidic conditions reducing its availability to photosynthesizing organisms. Different authors including Duarte-Santos et al. [53], Zhang et al. [54], and Morales et al. [55] have therefore indicated that only organisms that can compete for dissolved organic carbon are commonly found in AMD contaminated environments.

Acidic conditions could affect the diatomic cell directly and indirectly. Due to the high acidity in AMD contaminated waterbodies, Fe intake by the diatomic cell is reduced which may result in a decrease in the amount of carbohydrates stored in diatoms according to Shi et al. [56]. This has been attributed to the fact that the Fe chelating properties of the protein 2A (ISIP2A) which functions as a phytotransferrin is pH sensitive [57-58] and so reduced pH affects the amount of Fe that diatoms can absorb. This may be a direct effect of acidity on diatoms. Reduced uptake of Fe by diatoms in turn affect their metabolic iron quota with implications on photosynthesis, respiration, and the synthesis of amino acids, and lipids, among others. Gao et al. [59] and Huysman et al. [60] have also indicated that reduced Fe has a substantial effect on diatomic cell division with consequences on their population in acidic waters. These effects are indirect consequences of acidity. Another highlighted effect of water acidity on the diatomic population is the reduction in silica production which affects the buoyancy of diatoms. Though this has been reported in marine environments mostly, it is likely to occur in freshwater ecosystems as well. According to Petrou et al. [61], silica plays an important role in the ability of diatoms to float in water and also influences the rate at which they sink but increased acidity reduces silicification in diatoms with a consequent loss in their ballast and ability to swim. Studies by Pančić et al. [62] also show that the silicified cell makes diatoms unpalatable for grazers like protozoans and so depletion of the silica wall renders them vulnerable to predators. Dissolved silica is also required by these organisms for reproduction as it is necessary for DNA replication and cell wall formation [63]. Deficiency in silica in acidic waters could therefore also affect the abundance of these organisms in AMD impacted waters.

Another effect of acidity on the diatomic cell is the expansion of the cellulolytic cell walls. This has been attributed to the high H^+ present in AMD contaminated waters which may weaken the hydrogen bonds of the cellulose strands in these cell walls, causing uncontrolled cell expansion [64-65]. Despite these negative impacts, there are also some benefits associated with acidic waters for diatoms. For example, reduced surface binding of metals on the cell wall due to low acidity observed by Capasso and Pinto [66] in diatoms residing in acidic waters causes less metals to be absorbed thus decreasing their toxicity to the organism. However, the toxicity of anions like arsenite, arsenate, selenite and selenate may increase.

Algae

Tolerance of algae to acid conditions has been attributed to their ability to generate alkalinity through the assimilation of NO_3^- and inorganic carbon [67-68], and to reduce proton influx while increasing their efficiency in pumping out protons from the algal cell [69]. Algae also circumvent the depleted inorganic carbon in acidic environments by being highly motile in acid environments, migrating to areas where they can access light and CO_2 required for photosynthesis [65]. Despite this acid tolerance, an overall decrease in algal population has been reported in AMD contaminated water bodies and this has been attributed to the detrimental effects of acidity on these organisms. According to Yadav et al. [70] the internal pH range of cyanobacteria is 7.1-7.5 whereas externally, they can thrive in environments with pH values of between 5 and 10. Increased acidity in environments inhabited by cyanobacteria could result in cell wall biosynthesis, solute transfer and reduction in growth [71].

Bacteria

Bacteria commonly identified in AMD affected waters include the acidophiles and those that utilize various chemical elements as a source of energy. *Thiobacilli* was believed to be the dominant bacterial species in acidic environments but recent techniques in microbial analyses have enabled the identification of several other species. *Proteobacteria, Nitrospira, Firmicutes, and Acidobacteria*, are some of the bacterial species that have been identified in AMD contaminated waters. Most of these bacterial species are chemolithotrophic and are therefore able to oxidize the Fe and S compounds present in the AMD contaminated water. These bacterial species are able to survive in this extreme acid environments because of their highly impermeable cell membrane caused by increased production of cyclopropane fatty acids under acid stress conditions that accords them the capacity to restrict proton influx into their cytoplasm [72]. According to Guan et al. [73], the reduced permeability of bacterial cells in acid tolerant microbes is caused by the tough structure of the monolayer, the bulky isoprenoid core, and a unique lipid composition. Some species are also known to alter the size of membrane channels according to prevailing conditions to maintain pH homeostasis. Species like the *acidocaldarius* and *T. acidophilum* are also able to remove excess protons from the cytoplasm that reduces the effect of high acidity on these organisms. Removal of protons is facilitated by the efflux of protons by proton pumps including the H^+ -ATPase symporter antiporter and secondary transporter [74]. Guan et al. [73] and Liu et al. [75] have also highlighted the synthesis of alkali products from urea and arginine and the formation of a biofilm by some bacterial species to neutralize acidity. Details of these can be found in Guan et al. [73] and Liu et al. [75]. Because most bacterial species are neutrophiles, low acid conditions present in AMD contaminated environments present significant challenges to their survival. Studies by Lear et al. [76] indicate that the structure of bacterial communities in AMD impacted water bodies is driven by the pH of the water. Whereas pH has been reported to retard the growth of certain organisms, the growth of Fe-oxidizing bacteria is stimulated. Studies on the acidification of oceans also show that increased acidity enhances bacterial removal of dissolved organic carbon due to increased respiration in the bacterial cell. James et al. [77] associated this to enhancement of extracellular enzyme activity of bacteria in acidic environment.

Benthic Macroinvertebrates

These are bottom dwelling invertebrates that colonise lakes, streams and ponds among others and are visible with the naked eye. They include insects, crustaceans, worms, and molluscs. Macroinvertebrates play an important role in aquatic ecosystems as vital food sources for aquatic and terrestrial predators [78-79]. This pivotal position of theirs in aquatic food webs means that any negative impacts brought about by AMD can affect the overall ecosystem health. A strong relationship exists between water acidity and benthic macroinvertebrate community. *Odonata, Ephemeroptera,* and *Plecoptera* have been reported to disappear in AMD impacted waters whereas species like the molluscs and crustaceans which require calcium ion for the formation of their shells are restricted to water with pH values above 5.5. Macroinvertebrate communities in AMD contaminated streams become dominated by acid-tolerant species like chironomids, tubificids, baetids and simulids, while sensitive species such as mayflies and caddisflies, are excluded [38]. Svitok et al. [80] for example observed that invertebrate diversity decreased along a gradient of decreasing pH and increasing concentrations of dissolved metals in streams affected by AMD. Among the benthic macroinvertebrates, those that are found in the streambed are less affected by pH because they are more influenced by sediment chemistry than the chemistry of the stream water [81].

Fish

Fish are also sensitive to high acidity and their tolerance range for acidity varies. Jerneloev [82] in their study found the pH tolerance range of fish including eel, pike, grayling, minnow, roach, perch and whitefish to be 4.5-3.5, 5.5-4.5, 5.8-4.8, 5.8-5.2, 5.8-5.2, 5.5-4.5, and 5.8-4.8 respectively. These ranges are in alignment with results of studies on the effect of acidity on fish communities by Tremblay and Richard [83] which indicated that most fish would survive within a pH range of 4.5-6.7 with a pH of between 5-5.5 being the break point for most fish species. Hogsden and Harding [36] also indicated that in water bodies where pH<5, few or no fish are found with more than 70% of the variation in species richness and abundance of fish recorded in AMD affected waters being caused by pH. According to Burggren and Bautista [84], fish have the ability to regulate their acid-base balance to maintain an appropriate pH of their bodily fluids. This is associated with their ability to take up HCO_3^- in the chloride cells to neutralize protons. Modification in fish spawning habits has also been cited as an acid tolerance mechanisms by Jermeloev [82] in the Japanese fish *Tribolodon hakoniensis*. Even though fish can regulate the pH of their bodily fluids, high acidity in water bodies present a challenge to these organisms.

According to Kwong et al. [85], the primary effect of low water pH (4-4.5) on fish include a decrease in plasma Na^+ level due to the inhibition of active uptake of Na^+ coupled with an increased rate of passive Na^+ losses. High mortality, increased permeability of the integumental epithelium of the gills to various ions, reduced feeding and growth and disturbances in haematology, fluid volume distribution and circulatory function have all been reported as consequences of high water acidity on fish [23, 86-90]. In the juveniles and adults of *Oreochromis niloticus*, behavioural and morphological changes that included accelerated operculum movement, erratic swimming, gasping, peeling of the skin, bleeding of the dorsal fin, bending of the caudal fin, and the occurrence of slimy mucus on the gills and skin were also observed when water pH was between 4 and 5 [91]. The critical velocity of some fishes has also been shown to be influenced by water pH [92]. Kwong et al. [85] have reported an increase in the number and turnover of ion-transporting cells (ionocytes), and elevated mucus production whereas Kim et al. [87] highlighted a substantial increase in blood plasma cortisol concentration, lower liver glycogen and whole-body lipid content as a reaction of fish to high acidity. Kim et al. [90] in their study looked at the effect of acidity on the respiratory, ion regulation, and the immune and reproductive system and found that fish exposed to low acid (pH<5) conditions experience immune and reproductive system failures which were associated with alterations of various physiological features caused by the high acidity.

Amphibians

The reports on the effect of acidity on amphibians are conflicting with some indicating that they can tolerate acidic conditions in water and only begin to show acid induced negative effects when the pH of the water accommodating them drops to below 4, and others indicating that acid conditions affect all stages of amphibian life negatively [93]. A report by Buehler [94] in the New Scientist Indicates that the Australian scarlet-sided pobblebonk frog can thrives in acidic conditions that are deadly to other frogs by drawing dissolved calcium through their gills which neutralises the acid [94].

The tolerance of amphibians to acidity varies with species, and age of the amphibian. Farquharson et al [93] have reported on the acid tolerance of the embryos of different frogs and salamanders and their review indicates that most frogs will tolerate a pH of between 3.5-4.8, with the salamander embryos displaying a higher tolerance range of between 4.2 and 5.6. Amphibian larvae can withstand acid conditions better than the embryos and only display acid stress when the pH of the water drops to 4 and below. The embryos are most vulnerable to environmental chemical pollutants because amphibian fertilization is external whereas the adults are less affected since they spend most of their time on land [95]. Between a pH of 4-5, the embryos of frogs are reported to develop completely but the egg capsule becomes opaque and shrunken due to several morphological changes that include failure of the perivitelline space to expand, inhibition of the hatching enzyme, and changes in the egg capsule. The embryos also curl within the egg coat and may fail to hatch under acidic conditions [96]. Absence of hatching in the embryos of frogs (*C. xerampelina* and *P. edulis*) was also observed in studies by Farquharson et al [93] at pH below 4.5. However, in other species such as *C. xerampelina*, hatching was reported to increase with a decrease in pH [93] indicating that the effect of pH on the hatching of amphibian embryo varies with species.

Though some of these effects may not be lethal to the embryo, it may have an implication on their ability to survive and compete in the environment. The larvae are also affected negatively with loss of Na^+ at low pH reported, which may also affect the osmotic potential of the epithelial cells of the larvae [97]. Under very low acid conditions, the gills of amphibian larvae and especially the integument is damaged according to Meyer et al. [98], but the larvae of *L. cooloolensis* have shown no such vulnerability in other studies carried out by Meyer et al. [99]. These difference was however attributed to increased mucus secretion as a result of the acid conditions which has also been reported in fish by Kwong et al. [85]. The implications of this on the vulnerability of the larvae to pathogens needs to be investigated.

Inhibition of larval growth due to low pH has also been reported by Pierce and Montgomery [97]. The effects of acid conditions on tadpoles include poor feeding which results in death, corked tails, and loss of pigmentation and other morphological abnormalities according to Farquharson et al. [93] and Devi et al. [100]. Adult amphibians are however less affected by acidification because they spend more time on land [95]. The results of studies by Farquharson et al. [93] also showed that the toads were less susceptible to acid conditions compared with the frogs. This may also highlight species specific response to acid conditions. Studies carried out by Leuven et al. [101] show that amphibians like *Rana arvalis, Triturus helveticus* and *Triturus alpestris* populations are highest in moderately acid waters, whereas for other species of amphibians, pH above 5 is most suitable. The physiological effects of high acidity on amphibians contribute towards the decline in their abundance in acidic environments.

Effects of Metals on Aquatic Organisms

Results of studies on the effect of metals on aquatic organisms are less contradictory relative to those on the effects of acidity with most of them highlighting negative effects which may include decline in population structure, disruption of the endocrine system and various physiological processes. Hong et al. [102] in their study presented some significant details on the toxicity of heavy metals on aquatic organisms. The effects of metals in AMD contaminated water on aquatic organisms are caused by their interference with several biochemical processes. Organisms which have been exposed to heavy metals for prolonged periods however seem to have developed tolerance for these pollutants. The mechanisms of heavy metal tolerance vary with species.

Metals and Diatoms

Several studies on the effects of metals on diatoms and the tolerance of diatoms to metals have been undertaken possibly because of the ecological significance of diatoms and the potential of metals to affect their population. Their response to heavy metals vary with Marella et al. [103] highlighting three centric forms and more than ten (10) pennate forms as being metal tolerant, and two each of the centric and pennate forms as being metal sensitive. Details of these can be found in Biswas and Choudhury [104]. In diatoms, low concentrations of metals like Cu, Cd Co, and Zn are required for various enzyme systems but at higher concentrations, these metals could present significant damaging effects [103, 105-109]. Luİs et al. [110] have shown that high metal concentrations results in a reduction in cell number and cell size which affect diatomic growth rate. Once inside the diatomic cell, Pinto et al. [111] have indicated that metals could cause membrane depolarization and cytoplasmic acidification which could affect homeostasis. The formation of metal-protein complex inside the diatomic cell is a tolerance mechanism but it negatively affects reproduction, respiration and nutrient assimilation [112]. Metal stress also causes changes in diatomic cell outline and striation pattern which results in the production of teratological forms that may in turn be affected by pollutants [113]. Teratological deformation in diatoms have for example been associated with Cu, Cd and Zn contamination [114]. Details of the effects of metals on diatoms have been covered in Salma et al. [115]. Metals effects on diatoms could also be indirect. An example is the formation of precipitates with phosphorus in water, reducing the availability of phosphorus [116], which in turn limits the productivity of organisms that may require this nutrient.

Metals and Algae

The tolerance of algae to high concentrations of metals has been associated with mechanisms that include their ability to keep these metals outside the cell through the production of chelating compounds, removal of the metal ions from the cell by ATPase pumps, the synthesis of proteins that are able to protect them from the metals, extracellular binding of metals, precipitation of metals, internal detoxification, metal exclusion and transformation [67, 111, 117-118]. According to Novis and Harding, [119], the chelating compounds produced by the algae form a complex with the metals keeping them outside the cell. Some algal species have acquired metal-detoxifying genes which are involved in biotransformation and detoxification of certain heavy metals. Though high metal concentrations may not be lethal to some species, they are affected in various ways. In situations where the algae are able to tolerate high concentrations of heavy metals, the metals accumulate in the cytoplasm and may be transferred along the different trophic levels.

Generally, four different effects of heavy metals on algae have been reported in Falasco et al. [120]; disappearance of the most sensitive taxa and growth of the tolerant ones, reduction in algal biomass, alterations in community structure, and disappearance of teratological forms. High metal concentrations also cause cytotoxicity and structural changes in algae that affect their physiological processes. Arsenite for example was shown to alter the photosynthetic elements of *Chlamydomona acidophila* with the mitochondria also significantly affected [121]. This could contribute to the reduction in algal biomass observed in AMD affected streams. In general, cyanobacteria require significantly higher concentration of metals than non-photosynthetic organisms, since they perform oxygenic photosynthesis [70]. Cyanobacteria safeguard metallic homeostasis by various methods, including membrane alterations, transfer pump activation or inactivation, biotransformation, and sequestration [122]. Huertas et al [123] have indicated that tolerance mechanisms of cyanobacteria to heavy metals include excretion of heavy metal ligands like siderophores and extracellular polymeric substances, production of metallothionein and induction of metal transporters.

Metals and Benthic Macroinvertebrates

The response of benthic macrophages to contaminants have been widely studied and results indicate that these organisms vary in their sensitivity to contaminants. Responses of benthic macroinvertebrates to metal contamination is related to several factors among which are how they get exposed to the metals and their trophic status and physical position on the streambed [81]. Generally metal contamination has been reported to reduce species richness, density growth and production of benthic macroinvertebrates [124-125]. The effects of heavy metals on macroinvertebrates vary with taxa but the predators are mostly affected. Lower abundances of scrappers shredders, collectors and predators have been recorded in areas with high heavy metal concentrations in studies carried out by Clements [126] with the predators being the most sensitive to high metal concentrations. According to Osikemekha and Ovie [127] and Alric et al. [125], these organisms accumulate heavy metals in their gut which Freund and Pretty [128] and Clements [126] have indicated could affect predatory prey interactions and fish communities respectively. Macroinvertebrates documented as being very sensitive to heavy metals include Ephemeroptera, Plecoptera, and Trichoptera species whereas Trichoptera are known to be tolerant [129]. In a study by bat et al [130], Cu was more toxic to *Hyale crassipes* than Cd and Zn with 96-hr LC50 values of 0.06 mg/l, 0.23 mg/l, and 0.52 mg/l for Cu, Cd and Zn. These observations highlight the fact that effects of metals on benthic macroinvertebrates are metal and species specific.

Metals and Fish

Metal effects on fish have been widely reported possibly because of the role of fish in human diet and the dependence of several communities in the vicinity of water resources on fish as a source of protein and income. Fish occupy a high trophic level in the aquatic ecosystem and so they accumulate heavy metals from various sources including food, water, and sediments [131]. The response of fish to metal pollution varies with age and species of fish with the larvae being less tolerant to metals than the embryo since embryos have protective hard chorion layers and a perivitelline fluid that can impede the entry of metals [132-133]. Metal toxicity results in the development of oxidative stress through the stimulation of reactive oxygen species (ROS) production in the cells of fish, which stimulates the synthesis of antioxidant enzymes as a physiological protective mechanism to deal with and mitigate the negative impacts of metals. These tolerance mechanisms do not completely shield the fish from metals.

The effects of metals on fish however depend on the fish species, the organ where the metal accumulates, as well as the metal in question (Table 2). In a study carried out by Hossain et al [134] on different fish in Bangladesh, metal accumulation in fish tissue generally followed the order Fe>Zn>Cu>Cr>Mn>Co>Hg>Ni >Pb>As. In another study by Mehana [135] a similar pattern (Fe>Zn>Pb>Cu>Cd>Hg) was observed. Bawuro et al. [136] also reported a metal bioaccumulation pattern of Zn>Cu>Pb>Cd, whereas Moodley et al, [137] reported a pattern of Fe>Al>Zn>Mn>Cu>Cr>As>Se >Pb>Cd. These studies highlight the variability in the accumulation of metals by fish species but despite these variations, fish seem to have a high bioaccumulation potential for Fe, Zn, and Cu as these metals showed high concentrations in the fish in most of the studies.

The distribution of absorbed metals in the fish organs also varies. Lead, Cd, Cr and Cu in edible fish from a polluted river in Pakistan displayed organ concentrations patterns of liver>kidneys>gills>muscles [138]. A similar organ metal accumulation pattern was obtained by El-Moselhy et al. [139] in Egypt and by Bawuro et al [136] in Nigeria indicating that the flesh/muscles which is most widely consumed seems to accumulate the least amount of metals. Studies have also been carried out to determine the preference of different metals for different fish organs. In their study on the bioaccumulation of different metals by organs of different fish species Garai et al [140] reported different preferences for different metals with Cr, Ni, preferring the kidneys, Pb preferring the gills and kidneys, Zn, the gills and liver, and Hg, As, and Cu displaying different preferences based on fish species. Hossain et al. [134] also reported the accumulation of different metals by different species and found huge variability as shown in Table 2.

Toxicity of heavy metals to fish is usually evaluated by determining the amount of toxicant that can kill 50% of the exposed fish individuals within a specified time. This is referred to as LC50. Shahjahan et al. [143] have published details of the effects of heavy metals on fish physiology. According to their report, LC50 values for various metals range from 14.14 mg/l for *Catla catla* to 89.00 mg/l for *Clarias gariepenus*. A statistical evaluation of the 96 hour LC50 data published by Shahjahan et al [143], Shuhaimi-Othman [144], Li et al. [145], Ambreen and Javed [146], IIiopoulou-Georgudak and Kotsanis [147] De Smet and Blust [148] and Shat and Altindag [149] is presented in Table 3. These analyses show that the heavy metal tolerance limits for different fish species differs. Among the fish species studied, LC50 values for most metals in *Rasbora sumatrana* were very low indicating the sensitivity of this species to heavy metals. Mean LC50 values for the presented metals followed the order Pb, >Zn>Cr>Cu>Ni>As>Cd >Hg highlighting the toxicity of Ni, As and Cd to most fish species. A similar pattern of LC50 values was also reported for *Cyprinus carpio* by Stefania et al. [150].

In addition to fish species, age, and metal type, the effect of heavy metals on fish is also influenced by exposure duration, water chemistry, and other environmental factors. Among the effects of metals commonly reported in fish embryo and larval stages are reduced survival, reduced, and delayed hatching, stunted growth rate, skeletal deformities, vascular system abnormalities, reduction in pigmentation, and eye anomalies [143, 151-154]. Increased levels of red blood cells, and increase in glucose and cheolesterol were also observed in Carp by Narayanan [155] after exposure to metals. Histopathological changes were observed in *C. punctatus by* Javad et al. [156] due to heavy metal exposure. Chromosomal aberrations have also been reported in fish exposed to metals. According to Neeratanaphan et al. [157] and Neeratanaphan et al. [158], centric fragmentation, centromere gap, single chromatid gap, fragmentation, deletion, and polyploidy were some of the chromosomal aberrations reported in *Esomus metallicus e*xposed to metals in an AMD contaminated site. Some of the reported effects of metals on some fish species are shown in Table 4. It is however not all negative. Exposure of fish to metals could also be beneficial. Pre-exposure of fish to Cu

Table 2. Pattern of accumulation of different metals by different fish species.

Metal	Pattern of accumulation in different fish species
Cd	*Clarias gariepinus >Hampala macrolepidota> Hemibagrus nemurus >Osteochilus hasseltii> Pangasius micronemus> Hemibragus wyckii*
	Notopterus notopterus> Barbonymus schwanenfeldii >Puntioplites bulu, Cyclocheilichthys apogon> Barbonymus gonionatus> Tachysurus maculatus, Chitala chitala
Cr	*Otolothoides pama > Lates calcarifer > Anabas testudineus> Ctenopharyngodon Idella > Apocryptes bato > Polynemus paradiseus > Cirrhinus reba > Aristichthys nobilis*
Cu	*Liza parsia > Tenualosa ilisha > Polynemus paradiseus > Liza tade > Stolephorus commersonii*
Fe	*Aristichthys nobilis > Ctenopharyngodon Idella > Polynemus paradiseus > Otolothoides pama > Gibelion catla > Cirrhinus reba > Apocryptes bato > Mystus gulio > Oreochromis mossambicus > Labeo calbasu > Harpadon nehereus > Ompok pabda > Labeo rohita > Anabas testudineus > Lates calcarifer*
Hg	*Harpadon nehereus > Gibelion catla > Lates calcarifer > Otolothoides pama > Polynemus paradiseus > Cirrhinus reba > Labeo rohita > Mystus gulio > Ctenopharyngodon idella > Aristichthys nobilis > Oreochromis mossambicus > Apocryptes bato > Anabas testudineus > Ompok pabda > Labeo calbasu*
Ni	*Hampala macrolepidota > Pangasius micronemus > Osteochilus hasseltii > Hemibagrus nemurus > Clarias gariepinus > Barbonymus gonionatus > Puntioplites bulu > Cyclocheilichthys apogon > Hemibragus wyckii > Tachysurus maculatus > Barbonymus schwanenfeldii >Notopterus > Chitala chitala*
Pb	*Anabas testudineus > Apocryptes bato > Cirrhinus reba > Aristichthys nobilis > Labeo rohita > Gibelion catla > Mystus gulio > Labeo calbasu > Ctenopharyngodon Idella > Ompok pabda > Polynemus paradiseus > Lates calcarifer > Oreochromis mossambicus > Otolothoides pama > Harpadon nehereus*
	Liza parsia > Liza tade > Tenualosa ilisha > Polynemus paradiseus > Stolephorus commersonii
	Pangasius micronemus> Hampala macrolepidota > Hemibragus wyckii > Puntioplites bulu > Chitala > Barbonymus gonionatus > Notopterus > Clarias gariepinus > Barbonymus schwanenfeldii > Hemibagrus nemurus > Cyclocheilichthys apogon > Tachysurus maculatus > Osteochilus hasseltii
Zn	*Cirrhinus reba > Labeo rohita > Mystus gulio > Oreochromis mossambicus > Ctenopharyngodon Idella > Apocryptes bato >Labeo calbasu > Otolothoides pama > Anabas testudineus > Harpadon nehereus > Gibelion catla > Lates calcarifer > Aristichthys nobilis > Ompok pabda > Polynemus paradiseus*
	Liza parsia > Liza tade > Tenualosa ilisha > Polynemus paradiseus > Stolephorus commersonii

Source: [141-142, 134]

Table 3. Lethal concentrations of various heavy metals and the species have the lowest and highest LC50 values.

Metal	96-hr LC50 mg/l							Number of samples
	Mean	Median	Range	Minimum		Maximum		
				Value	Species	Value	Species	
As	38.24±5.6	32.00	74.90	14.10	*Catla catla*	89.00	*Clarias gariepenus*	15
Cd	8.96±1,9	5.48	30.30	0.10	*Rasbora sumatrana*	30.40	*Poecilia reticulata*	26
Cu	29.21±25.8	0.13	567.99	0.01	*Rasbora sumatrana*	568.00	*Pomatoschistus microps*	22
Cr	58.79±6.7	40.58	146.16	18.20	*Cirrhinus mrigala*	164.36	*Oreochromis nilitica*	30
Fe	33.23±18.3	16.00	115.74	1.46	*Poecilia.* reticulata	117.20	*Salmo trutta*	6
Hg	0.50±0.11	0.41	1.11	0.10	*Rare minnow*	1.21	*Channa punctatus*	12
Ni	32.06±10.8	15.62	172.27	0.83	*Rasbora sumatrana*	173.10	*Poecilia reticulata*	19
Pb	120.54± 39.2	7.57	473.57	0.53	*Rasbora sumatrana*	474.10	*Chanos chanos*	19
Zn	49.38±13.2	31.37	212.73	0.17	*Poecilia reticulata*	212.90	*Labeo rohita*	19

modulates the negative effects of chlorinated insecticide, endosulfan whereas preexposure to Cd modulates the toxic effect of deltamethrin and endosulfan in fish kidney and liver though the opposite was true for gills [159].

The effects of metals on fish also vary depending on the cocktail of metals present. Accumulation of Ni, Pb and Cr in fish studied by Sauliutė and Svecevičiu [160] showed that accumulation increased when a cocktail of metals was present than when single metals was present in the water where the fish was found. These synergistic effects however vary with fish species. The effect of a mixture of metals on the gills of *C. punctata* was studied by Pandey et al. [159] and they found significant negative biochemical and morphological effects on the gills. 96-hr LC50 values in studies by Ambreen and Javed [146] on the effect of a mixture of metals on *Tilapia niloticus* showed that this fish is more vulnerable to a mixture of cadmium and cobalt (mean 96-hr LC50 value = 37.93) compared to a micture of lead/cadmoim (mean 96-hr LC50 value = 49.16) and Cobalt/lead (mean 96-hr LC50 value = 62.68). These effects were also noticed in the various fish organs. According to Liu et al. [75] the interactive effects of metal mixtures on fish decrease as the number of metals in the mixture increases with Ambreen and Javed [146] indicating that mixtures of metals are more toxic to fish than individual metals.

Metals and Amphibians

Amphibians are not as appealing a protein source as fish and are also not occupying a prominent position in food webs and food chains. They may therefore not be triggering a lot of interest except to zoologist and conservationists. Studies on the effects of metals on amphibians are therefore limited and the few which have been reported present conflicting observations. Flynn et al. [170] revealed that metals have little impact on amphibians but AmphibiaWeb [171] has a different view as they have indicated that chemical stressors such as metals and acidification have generally contributed to the global decline of amphibian populations. Studies like those of Hill et al. [172] and Akinsanya et al. [173] have highlighted the sensitivity whereas studies by McCrary and Heagler [174] have highlighted the tolerance of amphibians to metals.

Mechanisms of heavy metal tolerance in amphibians include decreased metals uptake, metal speciation, increased excretion and redistribution of metals to less sensitive target sites [175]. According to Flynn et al. [170], amphibian tolerance to heavy metals may be associated to their ability to eliminate the metals from their bodies rather than osmoregulation. Exposure of these organisms to heavy metals in early life according to Flynn et al. [170] may also increase their ability to tolerate metals at a later stage in life.

Amphibians are exposed to AMD both while they are on land and in water. According to Putshaka et al [176] and Guerriero et al [177] the effect of heavy metals on toads is influenced by the affinities of the various metals to various tissues in the toad, the rates of metal uptake and deposition and the excretion rate of the metals from the toad body. Generally, Anuran amphibians are characterised by a permeable skin and eggs that lack a protective shell. The tadpoles are microphagous in their feeding and so always ingest sediments which are known to accumulate metals. Amphibians, like fish, also accumulate metals in different organs. Mahmood et al. [178] for example reported accumulation of Cu, Co, Mo, Cr and Cd in the livers of *Pelophylax ridibundus*.

Exposure of some amphibians to metals or metalloids is reported to induce the synthesis of stress proteins such as heat-shock proteins (HSP) and metallothionein

Table 4. Effects of some metals in fish species.

AMD pollutant	Fish species affected	Effect	Author(s)
AMD effluent from a coal mine	freshwater fish (*Channa punctata*)	• Fusion of primary and secondary gill lamellae, • Profuse mucous secretion on the surface epithelium of the gill lamellae, • Cellular necrosis, • Gradual decrease in Total erythrocyte count (TEC) total leukocyte count (TLC), and Haemoglobin (Hb) • DNA fragmentation in kidney	[161]
Al and Zn	Common carp (*Cyprinus carpio*)	• Gill tissue necrosis. • Impairment of the excretory function of gills • Higher concentrations of ammonia in the blood • Damage to parenchymatous tissues (kidney, liver, spleen • Higher aluminium and iron content, and • Enhanced activity of transaminases in blood plasma	[162]
As	rainbow trout (*Oncorhynchus mykiss*)	• Slower feeding rate, • Reduced food conversion efficiency, • Liver cell abnormalities, • Faecal matter changes.	[163]
Cd	rosy barb (*Puntius conchonius*), catfish (*Clarias lazera*), common carp (*Cyprinus carpio*)	• Decrease in hepatosomatic index • Hypoglycaemia • Decreased haematocrit levels • Renal damage	[164-165]
Cu	Catfish *(Heteropneustes fossilis),* rainbow trout (*Oncorhynchus mykiss)* and North African catfish (*Clarias lazera),*	• Decreased muscle and live glycogen • Decrease in muscle and liver total protein • Affects sense of smell, alteration in appetite, reduced awareness of surroundings • Reduced sperm and egg production	[166]
Fe	Mrigal (*Chirrhinus mrigala),* catla (*Catla catla),* roho labeo (*Labeo rohita)*, atlantic salmon (*Salmo salar*) and rainbow trout (*Oncorhynchus mykiss)*	• Prolonged stress and reduced growth in juveniles, • Decrease feeding rate	
Mn	Sucker head (*Garra gotyla gotyla*)	• Decreased total erythrocyte count • Oxidative damage	[167]
Ni and Zn	Mozambique tilapia (Oreochromis mossambicus). common carp (Cyprinus carpio)	• High glutathione-s-transferase (gst) enzyme activity and • Low heat shock protein (hsp) • Protein concentrations • Sublethal stress and increased rbc coun	[168]
Pb	Nile tilapia (*Oreochromis niloticus*)	• Degeneration of gill filaments and pavement cells • Increased mucus secretion • Decrease in calcium and phosphorus weight percentages • Decrease in hepatosomatic index	[169] [165]

(MTs), which are involved in protection against metal toxicity [179]. Therefore, the amphibian population in habitats severely contaminated by metals from AMD may remain unchanged suggesting that amphibians are capable of sensing and avoiding extreme degrees of contamination [180]. However, some negative outcomes have been recorded in amphibians exposed to metals. In most of these studies, the embryos and tadpoles are more vulnerable compared to the adults

Among the negative effects of metals on amphibians reported are delays in metamorphosis [172], chromosomal aberrations where Tengjaroenkul et al. [181], Intamat et al. [182] and Intamat et al. [183] reported single chromatid gap, single chromatid break, centromere gap, fragmentation and deletion in frog *(F limnocharis*) as a result of exposure to As and Cd from a gold mine whereas Boonmee et al. [184] reported more than 10 different aberrations as a result of exposure of *F. limnocharis* to Cd. Uptake of metals by cells of amphibians especially frogs generally result in alterations of cellular morphology including irregular shaped hepatocytes, discontinuous glomeruli characterised by dead or ruptured cells, and cytoplasmic depositions as was observed in *E cyanophlyctis* by

Mahmood et al. [178]. Studies by Khattab et al. [185] on the effect of several metals on the Egyptian toad (*Sclerophrys regularis)* showed that mono nucleation and nuclei lesions of red blood cells positively correlated with Mn, Fe and Cr whereas Fe positively correlated with kidney shape and vacuolated nuclei. Positive correlation between helminth infection in the green frogs and heavy metal concentration have been reported by De Donato et al. [186]. Studies by Eisler [187] indicate that Cd, Co, Pb, Ni and Zn present more challenges to amphibians than Fe and Mn. The adverse effects of Cd in toad (*Bufo arenarum*) were however reported to be counteracted by Zn. According to Flyaks and Borkin [188], the toxicity of heavy metals to *Rana hexadactyla* follows the order Ag>Cu>Hg>As>Zn>Co>Fe>Pb>Cr. This pattern is contrary to what has been mentioned in other papers which have highlighted the toxicity of Pb. Details of biochemical and histopathological changes in Indian frog caused by metal contamination can also be found in Jayawardena et al. [189]. Bird et al. [190] have however highlighted that the effect of metals on amphibians depends on the combination of metals present. Some of these effects are presented in Table 5. The information presented in Table 5 indicates that the effects of metal exposures in amphibians may result in the development of various unusual patterns of behaviour in these organisms. These indicate that amphibians, contrary to what was reported earlier by Flynn et al. [170] do display negative outcomes as a result of metal exposure.

Ochre

Whereas studies of the effects of acidity and heavy metals on aquatic organisms are widely reported, the effects of ochre on organisms are scarce. The few studies reported however highlight some negative effects due to the impact of ochre on the water as a habitat. Up to 50% decrease in the biomass of algae in areas with ferric hydroxide deposits have been reported which indicate that the precipitation of ochre may have a negative effect on diatomic population. The ochre found in AMD contaminated waters also affects algal biomass with up to 50% decrease in the biomass of algae in areas with ferric hydroxide depaosits. Heavy metals form precipitates with phosphorus in AMD impacted waters which reduces the availability of phosphorus [116] further limiting algal productivity and consequently their biomass. Bray et al. [195] also observed a decrease in algal biomass in a river basin affected by AMD which he attributed to nutrient limitation of reactive phosphorus. Generally low algal biomass in AMD contaminated water bodies has been associated with inhibited nitrogen uptake rates and nitrification [196], metal precipitates, and low organic carbon inputs [197]. Despite these challenges faced by algae in AMD impacted streams and rivers, many unicellular and filamentous algae such as *Ulothrix, Stigeoclomium, Chlamydomonas*. In addition to the effects of metals, low macroinvertebrate richness and abundance in AMD contaminated water bodies has been associated with the disruption of habitats, nursery sites and refugia caused by the accumulation of ochre on streambeds.

The accumulation of ochre on gill surfaces and streambed sediments create barriers for migratory fish species, thus reproductively isolating them from fish in unimpacted headwaters [198]. Hogsden and Harding [36], observed this effect of ochre on rainbow trout (*Oncorhynchus mykiss*) eggs in AMD contaminated streams. Amphibians especially the tadpoles are also significantly affected by ochre. Studies by Efimov et al. [199] revealed that ochre causes water turbidity which affects the feeding patterns and consequently the growth and survival of tadpoles. Schorr et al. [200] also reported significant decline in aquatic salamander population whereas Sasaki et al. [201] reported a decline in species richness and population of Amphibians in an AMD affected rivers. Whereas the effects of acidity and high metal concentrations are physiological and biochemical, the effects of ochre are mostly indirect and usually physical.

Table 5. Effects of some metals in amphibians.

AMD pollutant	Amphibian species affected	Effect	References
Cd	*Triturus carnifex*	Alteration of adrenal gland activity	[191]
	Pelophylax bergeri	Skin metallothionein and heat shock protein (HSP) activations	[192]
Cu	*Rana ridibunda*	Increased permeability of the skin to copper	[193]
Zn, Cu and Cd	*Proteus anguinus and Necturus maculosus*	Increased synthesis of metallothioneins (MTs)	[194]
As	*Rana pipiens*	Decreased tadpole swimming speed.	[6]
As and Cr	*Pelophylax bergeri*	Elevated levels of arsenic and chromium in the skin and testes of adult males beyond acceptable levels	[177]

Factors Influencing Toxicity of AMD Impacted Streams on Aquatic Organisms

Buffering Capacity of the Water Body

The ability of a water body to resist changes in pH is referred to as its buffering capacity and it is influenced by the soil and bedrock through which the water flows especially if these rocks contain bicarbonate and carbonate compounds according to Grochowska [202]. Hagens et al [203] also indicated that decaying organic substances originating from the decomposition of plant materials can contribute towards the buffering capacity of water bodies indirectly through their effect on the carbon dioxide content of the waterbody. Water with a high buffering capacity is important for aquatic life because it protects aquatic organisms from the negative effects that may arise because of increased acidity and rapid pH changes. The buffering capacity of water bodies enables a fixed pH range to be maintained which may minimize the effect of high acidity in AMD on stream water pH and consequently the effects on aquatic organisms.

Metal Speciation

Metal speciation plays a significant role in metal bioavailability and toxicity [204]. Divalent ionic cadmium (Cd^{2+}) for example has been reported to be the most bioavailable species at moderately acidic to neutral pH. Both arsenite and arsenate are present in AMD environments but arsenate which is the less toxic form predominates because of the presence of ferric Fe [205]. As (III) and Cr (VI) for example are more mobile and soluble than As(V) and Cr (III) respectively according to Wang et al. [206], and so they can be taken up by aquatic species. The toxicity of various metals species is presented in Table 6. The most available form of most elements is the free hydrated form according to Stefania et al. [150]. The results from toxicokinetic and toxicodynamic studies indicate that the free metallic ionic species of As, Cd, Cr, and Pb for example are more toxic than their organic or inorganic compounds, while for Ni, it is the water-soluble Ni compounds comprising oxides and sulphides that exert more toxicity than the free ionic form. Various factors including, pH, redox potential, hardness, and ionic strength of the medium, valence state of the metal, organic matter [207] availability of complexing ligands and particle surfaces for adsorption [208] interact to determine metal toxicity levels of these metal species to biota. These findings all indicate that the species in which these metals are present in AMD will determine the extent to which aquatic biota may be affected.

Water pH

The mobility and solubility of most metals is dependent on pH with bioavailbility increasing as the acidity of the environment increases [216-217]. Under acidic conditions, Fe, Al, Cd, Cr, Cu and Pb are more likely to be released while Zn and Hg are more likely to be released under neutral conditions and Mn released under alkaline conditions. Studies by Magalhaes et al. [218] have indiated that some metals can be less toxic at low pH and more toxic in alkaline conditions or the pH may have no influence on metal toxicity. Niyogi et al. [219] associated low toxicity at low pH conditions to the fact that H^+ may protect against metal uptake, while at higher pH conditions, there is reduced competition with H^+, resulting in more available metal ions for uptake, even if there is a low concentration of the

Table 6. Toxicity of some metal species.

Heavy metal	Less toxic species	More toxic species	References
Arsenic (As)	$C_5H_{11}AsO_2$ $(CH_3)_3AsO$ $C_4H_{12}As^+$	As^{3+}	[209]
Cadmium (Cd)	$CdPO_4$ CdOHCl	Cd^{2+} CdOH+ CdOHCl	[210-211]
Chromium (Cr)	Cr (III) CrO_4 Cr_2O_7	Cr (VI)	[212]
Lead (Pb)	-	Pb^{2+} C_3H_9Pb $C_6H_{15}Pb$	[213]
Mercury (Hg)	Hg^0, Hg^{2+} Hg^{2+}	(CH_3Hg^+), $((CH_3)_2Hg)$.	[214]
Nickel (Ni)	Ni^{2+}	NiS NiO	[215]

metal available in the aquatic environment. When the acidity of water bodies drop to very low levels, Fe and Al toxicity increases.

Redox Potential (Eh)

Redox reactions can result in the mobilization or immobilization of metals, depending on the metal species and the prevailing microbial environment [220]. Under oxidizing conditions and above pH 5.5, metals such as Cr, Cu, Hg, Mn, and Fe react with water to produce low solubility oxides and hydroxides. In the case of Fe, for example, in conditions of low oxygen concentration and pH<7, the solubility increases by promoting soluble cations such as Fe^{2+} instead of Fe^{3+} [221]. Martİnez and Motto [222] have reported that redox potential (Eh) and pH are generally considered the most important factors controlling As speciation and consequently its toxicity because their mobility and toxicity in AMD are largely dependent on their redox speciation. Studies by Cai et al [223] show that redox conditions together with a weak buffering system can accelerate the acidification of a waterbody which may have further consequences on the acidification of the water by AMD.

Complexing Ligands

The presence and concentration of inorganic ligands such as hydroxides, carbonates, chlorides, organic ligands such humic and fulvic acids, and nutrients are important in controlling the mobility and toxicity of many metals [224-226] and buffering capacity of water bodies [202, 227]. Complexation reactions with hydroxyl, carboxylate, cyano- and amino groups in the ligands have been observed to reduce the accumulation and toxicity of metals in rainbow trout (*Oncorhynchus mykiss*) [228], in bivalve molluscs [229], and in the crustacean *Hyalella azteca* [230]. However, studies on Cd have shown that the presence of organic ligands increases its bioavailability in mussels and fish by facilitating the diffusion of the hydrophobic compound in the lipid membrane [231]. Methylation of metals has been reported as one of the mechanisms which generally increases toxicity of some metals such as Hg and Pb. The methylation process makes these metals more lipid soluble, thus facilitating their transport across lipid barriers such as the cell membrane or blood-tissue barriers such as the blood-brain barrier, blood-testis barrier, and blood-placenta barrier. For instance, viability of spermatozoa, reduced egg production and low survival rate of frys have been observed in the fish species *Barbus graellsii* (barbels) and *Alburnus alburnus* (bleaks) due to methylmercury exposure [232], while, histological analysis of *Clarias gariepinus* (catfish) showed degeneration of hepatocytes, decreased cytoplasm/nucleus ratio and a proliferation of macrophages [232].

Implications of AMD Stream Contamination on Sustainable Development Goals

As a universal call to action in 2015, the United Nations adopted 17 Global Goals also known as the Sustainable Development Goals (SDGs) in an endeavour to end poverty, protect the planet and ensure that all people enjoy peace and prosperity around the globe. These Goals are integrated and among the 17 goals, about eight (8) of them (SDGs 3, 6, 7, 11, 12, 13, 14, 15) address issues of safe environments. AMD generated in mining environments has strong impacts on the realisation of some of the United Nations Sustainable Development Goals (UN SDGs) [233]. SDG3 for example speaks to the idea of ensuring that member countries promote well-being and healthy living conditions for all people at all ages, with Target 9 of SDG3 requiring countries to substantially reduce the number of deaths and illnesses caused by the contamination of air, water and soil and hazardous chemicals by 2030. AMD contains several contaminants that compromise the quality of water in streams and rivers where it is disposed and surrounding soils into which it seeps. The health of humans and other animals may be compromised by exposure to these contaminants through various pathways that include ingestion of food irrigated with the water from AMD contaminated sources, drinking water from the AMD contaminated stream, and bathing and swimming in AMD contaminated streams. Algae that tolerate high concentrations of heavy metals present a risk to aquatic food chain as these metals may be transferred along the different trophic levels. Fish occupy a higher trophic level in the aquatic ecosystem and so they accumulate heavy metals from various sources including food, water, and sediments [131]. The ingestion of fish harvested from AMD contaminated streams is therefore a potential source of exposure to these contaminants.

SDG 6 aims at ensuring the availability and sustainable management of water and sanitation for all people with Target 3 of this SDG spelling out that countries should by 2030 have improved water quality through pollution reduction, elimination of the dumping and minimization of the release of hazardous chemicals and materials, substantially reducing the proportion of untreated wastewater and increasing recycling and safe reuse. SDG 12 addresses sustainable production and consumption patterns with Target 4 laying out that by 2030 member countries should have significantly minimized the adverse impacts on human health and the environment through ensuring environmentally sound management of chemicals and wastes, their release to air, water, and soil, in accordance with agreed international frameworks. Introduction of AMD unto the environment presents a significant pollution challenge to the realization of both these SDGs directly and indirectly.

For SDG2 which speaks to erasing hunger to be met, the quality and safety of food consumed in various communities need to be guaranteed. The challenges faced by mining communities because of AMD contamination of water bodies compromise the provision of contaminant free food to communities and therefore affect the realisation of SDG2. Quality education cannot be provided or realised if people are unhealthy, or hungry. The mining sector therefore also indirectly affects the realisation of SDG4 which speaks to the provision of quality education. More efforts need to be made to control the contamination of surface water bodies by AMD as this will go a long wat towards contributing to the realisation of more than 5 other SDGs.

Future Prospects

Considering the wide-ranging effects of AMD contamination on the aquatic ecosystem, efforts need to be harnessed to control its spread into aquatic resources. Preventive control measures for AMD formation include oxygen barriers, and alkaline amendments [234-235]. However, prevention of AMD formation is not always practical or possible. Predicting AMD formation through chemical characterization of mine wastes could enable an evaluation of the geochemical stability and acid producing potential of waste rock samples. This technique, according to Dold [236] could mitigate the problem of AMD but these tests are carried out off-site and therefore present inherent limitations in that they may not reflect the actual biological and geochemical processes that occur at the mine sites. In addition, accurate prediction of AMD is a challenge, given the multifaceted processes that lead to AMD generation. Acidity is caused by the high sulphur content in the AMD. Efforts to recover this sulphur to come up with low grade sulphuric acid that can be used for various purposes could be harnessed. There are efforts to recover metals from AMD. More needs to be done in this area so that these pollutants could be recovered from the AMD and contaminated water bodies. There are also efforts to make use of ochre in the dye industry. All these efforts need to be harnessed to ensure that mine AMD discharged into streams and rivers meet recommended standards of water quality for intended uses.

Conclusion

AMD is a significant and costly environmental impact of the mining industry worldwide which extends well beyond the boundaries of the mining activities, especially when discharges to waterbodies are considered. Though aquatic organisms have developed mechanisms of tolerance to the harsh environment presented by AMD, AMD contamination of water bodies decreases reproductive ability and increases developmental abnormalities of aquatic organisms which lead to reduced survivorship and fecundity, which in turn leads to reduced species richness through elimination of sensitive and less tolerant species and promotion of pollution tolerant ones. This has the domino effect up the ecosystem by causing the reduction of the food sources available for animals at the top of the food chain. The goal for water quality should therefore aim at not only neutralising AMD-contaminated waters by increasing pH, but also decreasing the concentration of available toxic heavy metals. Several methods to rehabilitate AMD contaminated water have been studied and implemented, albeit with success and limitations. In the face of persistent problems presented by AMD, there is an urgent need to implement long-term, cost-effective, and eco-friendly green technologies for a more effective restoration strategy. To this end, phytoremediation is a technology with great potential to alleviate the effects of AMD. However, the choice of hyperaccumulating plant species for use in phytoremediation will need to be identified through extensive research activities so that a suitable plant species with a high tolerance, adaptability to high metal levels and ability to hyperaccumulate heavy metals in their tissues in specific AMD environments can be identified. With the advances in molecular biology and genetic engineering techniques, innovative approaches are needed in developing suitable transgenic plants which are well tested, safe, and efficient in removing heavy metals from AMD contaminated water. Future studies will, therefore, need to integrate both biological and physicochemical approaches for a more effective clean-up of the environment.

Conflicts of Interest

The authors declare no conflict of interest in relation to this manuscript.

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