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COPPER AND LEAD AS ENVIRONMENTAL POLLUTANT AND THEIR ELEMENTAL TOXICITY – A REVIEW

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ABSTRACT
Pollutants are substances in the environment with potential objectionable effects leading to impairment of the welfare of environment, interfering with the quality of life that may eventually result to the organisms being affected. The aim here was to give summary of the review of the toxicity of Copper and Zinc as pollutants in the environment, be it air, water or soil, which may be poisonous and will cause harm to living organisms in the polluted environment. The elemental concentration of sediment therefore and its bioavailability not only depends on anthropogenic and lithogenic sources, but also on organic matter, physical (textural) characteristics as well as mineralogical composition and depositional environment of sediments. Copper causes toxicity and hazards in flora, fauna and human beings. It causes a disease called 'Wilson's disease. Excessive exposure to Cu may cause haemolysis, hepatotoxic and nephrotoxic effects. Mucosal irritation, corrosion, widespread capillary damage, hepatic and renal damage and central nervous system irritation are some of the dysfunctions consequent to Cu exposure. Among the various means through which lead toxicity occurs are; the ionic mechanism and the oxidative stress. Several studies indicated that oxidative stress in living cells is caused by the imbalance between the production of free radicals and the generation of antioxidants to detoxify the relative intermediates or to repair the resulting damage.

Keywords: Heavy Metals, Copper, Lead, Toxicity, Environment.

INTRODUCTION

Heavy metals in the environment

Heavy metals are metallic elements whose relative density is high and are toxic and poisonous even at low concentration or element that in aqueous solution displays cationic behaviour or that can form an oxide which is soluble in acids (Nagajyoti *et al*., 2010). These are group of metals with atomic density greater than 4 g/cm^3 or 5 times or more than water. The chemical properties of heavy metals are the most influencing factors than their density because the ability of heavy metals to become bioavailable or attach itself depends on the kind of chemical properties it possess (Nagajyoti *et al*., 2010). Generally, heavy metals do not degrade except only in insignificant rates, it can however be transformed from one form to another. Degradation, as a nuclear process, rarely occurs among the stable elements (heavy metals) (Federal Research in Progress 2004). Increased metal concentrations in sediment is best explained by the sorption of metals onto organic matter and Fe/Mn oxy hydroxides which usually tend to be higher in the fine-grained part of the sediment due to formation of surface coating and by the absorption of metals into primary and secondary minerals. Metals are therefore higher in clay than in sand, under the same metal concentration in a given environment, due to difference in specific surface area (Song, Choi, Lee, & Jang, 2014). In this regard, grain size may be described as a major player in the absorption and distribution of heavy metals in sediment indicating connection between the specific surface area and grain size since metal distribution depends also on grain size (Song *et al*., 2014). Elemental concentrations are highly depended on the grain size of the sediment (Gao *et al*., 2012). The following heavy metals were considered in this study; Copper (Cu), Zinc (Zn), Nickel (Ni), Cadmium (Cd) and Lead (Pb).
Some heavy metals (Cu, Zn, Ni and others) are referred to as essential metals because they are useful to plants and animals alike. The availability of heavy metals in the medium varies. The essential metals play a biochemical and physiological functions in plants and animals. The non-essential metals however, are metals that have no single significance in biological system. These may include; Cd, Hg, Pb and others. This lack of biological function makes them extremely toxic when they find their ways into biological systems. Their toxic effects sometimes manifest even small dosage.

Source of copper in the environment.

Copper is an essential trace element which is required in small amounts (5-20 micrograms per gram (μg/g) by most animals including human for carbohydrate metabolism and the functioning of more than thirty enzymes. The formation of haemoglobin and haemocyanin also requires the presence of copper as well as the oxygen-transporting pigments in the blood of vertebrates and shellfish (Maduabuchi *et al*., 2006). It is also required in the synthesis of chlorophyll (a photosynthetic pigment in plants). However, copper concentrations that exceed 20 micrograms per gram (μg/g) can be toxic. Copper is regarded as one of the earliest known toxic metals (Shrivastava, 2009). It has been known to humans for at least 6000 years (Okocha and Adedeji, 2012). It is placed in d-block in the modern day periodic table with melting point of 1083.0 ± 0.1 °C (Shrivastava, 2009). Copper is used in alloys, tools, coins, jewellery, food and beverage containers, automobile brake pads, electrical wiring and electroplating reflect (Okocha and Adedeji, 2012; Shrivastava, 2009). To discern the ecological as well as biological effects of Cu toxicity in the environment, it is imperative to understand its chemistry (Shrivastava, 2009). It is widely distributed in the environmental media because it is naturally emitted. Emission of copper from human activities are substantial, Figure 1. Most copper released from human activities comes from disposal of coal ash residue and spreading of municipal and industrial wastes on land.

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Table 1 Summary of physical and chemical properties of copper.

Property	Copper
Atomic/ molecular weight	63.546
Colour	Reddish
Physical state	Solid
Melting Point °C	1083.4
Boiling Point °C	2567
Density g/cm^3	8.92
Odour.	None
Odour threshold: Water/Air	No data
Taste	No
Taste Threshold	No data
Solubility	
Water (g/100mL)	Insoluble ($CuSO_4$ 14.3 @ 0 °C
Organic Solvent	"$CuSO_4$ solution in methanol, slightly soluble in ethanol
Vapour pressure, mm Hg	10 (1870 °C)
Autoignition temperature	No data

Adopted from Alberta Environmental Protection, 1996.

Mechanism of copper toxicity in biota.
To understand the ecological and biological effects of Cu toxicity in the environment, the knowledge of its chemistry is very crucial (Shrivastava, 2009). The use of Cu to kill algae, fungi and molluscs is another evidence that, in certain amount of concentration, it is highly toxic to aquatic organism. In fact, copper is one of the most toxic metals to aquatic organisms and ecosystem (Okocha and Adedeji, 2012). Copper causes toxicity and hazards in flora, fauna and human beings. It causes a disease called 'Wilson's disease. Excessive exposure to Cu may cause haemolysis, hepatotoxic and nephrotoxic effects. Mucosal irritation, corrosion, widespread capillary damage, hepatic and renal damage and central nervous system irritation are some of the dysfunctions consequent to Cu exposure (Shrivastava, 2009). Aquatic organisms may experience lethal effects of Cu either directly or indirectly. Organisms within the same or different species can exhibit differing sensitivity to elevated Cu levels. While some organisms bioaccumulate and store Cu, others actively regulate its levels (Okocha and Adedeji, 2012). The toxicity of Cu on aquatic animals is caused by impairing osmoregulation and ions regulation in the gills. Although the long-term toxicity of copper has not been well studied in humans, it is however infrequent in normal population not having some hereditary defect in copper homeostasis (Okocha and Adedeji, 2012). A respiratory disorder called 'Vineyard sprayer's lungs' is developed by workers involved in use of fungicides containing copper sulphate where interstitial pulmonary lesions and nodular fibro-hyaline scars may occur (Shrivastava, 2009). Figure 2 shows the source, pathways and interactions between Cu and organisms.

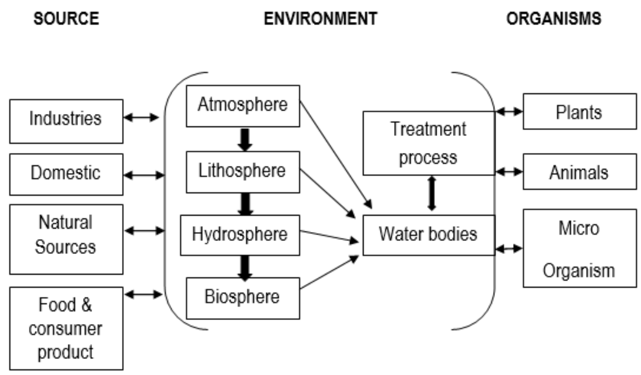

Figure 1 Copper pollution: Source, pathways and interaction with organisms. Adopted from Shrivastava (2009)

Sources of lead in the environment.
The discovery of the use of lead (Pb) could be traced as far back as 6000 years ago (Hernberg *et al*., 2000). Lead is a divalent cation which has strong binding capability to sulfhydryl groups on protein (Needleman, 2004) and is one of the three most toxic elements (Moattari, Rahimi, Rajabi, Derakhshan, & Keyhani, 2015). Elemental lead is an odourless, silver-bluish-white metal which is soft, highly malleable, ductile, and insoluble in water and a poor conductor of electricity. Much of its toxicity can be attributed to disruption of enzymes and proteins especially in the Central Nervous System (CNS) (Needleman, 2004). Lead has the ability to mimic or compete with calcium (Ca). For more than a century ago, the clinical toxic effects of Pb have been discovered which include the central (CNS) and the peripheral nervous system (PNS), Kidney, haematological effect as well as defect in the outcome of pregnancy. There is virtually no biological activity and or enzyme that is not affected by the presence of high Pb concentration (Hernberg *et al*., 2000). The permissible limits/safety limits of Pb vary across the globe but often do not exceed 1.0mg/L (Moattari *et al*., 2015). Lead mainly source of pollution is industrial processes, food, smoking, drinking water and domestic sources. Other sources of Pb includes gasoline and house paint, plumbing pipes, storage batteries, mining and smelting and incineration of wastes. It is an extremely toxic heavy metal with no biological function (Jaishankar *et al*., 2014)

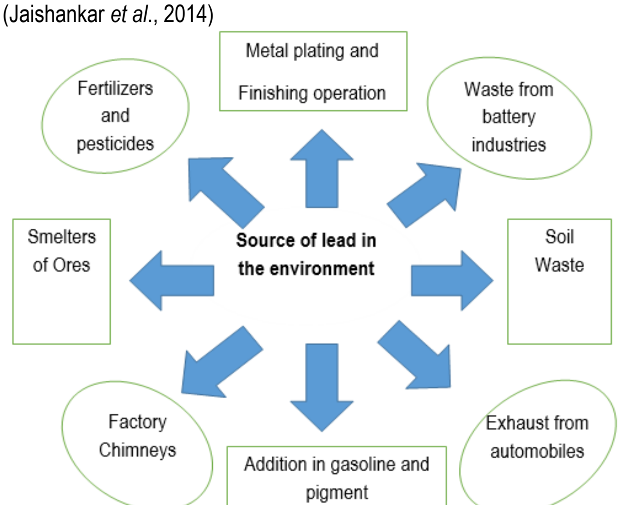

Figure 2 Sources of lead. Adopted from Jaishankar *et al*.(2014).

Mechanism of lead toxicity
Lead exerts its toxicity on living cells through several ways. The fact that lead does not have any biological function to the benefit of living cells leaves it with only a function of adversity (Jaishankar *et al*., 2014). Among the various means through which lead toxicity occurs are; the ionic mechanism and the oxidative stress. Several studies indicated that oxidative stress in living cells is caused by the imbalance between the production of free radicals and the generation of antioxidants to detoxify the relative intermediates or to repair the resulting damage (Mathew, Tiwari & Jatawa, 2011; Nehi Wadhwa, Blessy & Mathew, 2012). The ionic mechanism occurs mainly due to the ability of lead ions to replace other bivalent cations like Ca^{2+}, Mg^{2+}, Fe^{2+} and monovalent cations like Na^{+}, which will consequently alter the biological metabolism of the cell (Flora, Mittal, & Mehta, 2016). Significant changes occur as a result of this mechanism of lead toxicity such as, cell adhesion, inter and intra-cellular signalling, maturation, apoptosis, protein folding, enzyme regulation, ionic transportation and release of neurotransmitters (Jaishankar *et al*., 2014).

General sources of heavy metals in the environment
Heavy metals in the environment originate from numerous source, to include but not limited to, atmospheric deposition, improper stacking of the industrial solids waste, mining activities, sewage, irrigation farming, use of fertilizers and pesticides and other natural sources (Sörme & Lagerkvist, 2002, Klang et al., 2013, El Nemr, El-Said, Khaled, & Ragab, 2016;). The heavy metals from atmosphere are mainly embedded in the gas and dust generated by energy, metallurgy, transport and production of construction materials. These metals exist in the atmosphere in the form of aerosol and deposit to the soil through natural sedimentation and precipitation. It is believed that emission in the air may be the greatest source of heavy metal pollution that eventually contaminates the aquatic ecosystem through atmospheric fallout (Mohammed, Kapri, & Goel, 2011). Many reports of fine particles of these metals being carried by wind have been published, from lead pollution in a downtown Central Sweden to chromium in Nanjing of China (Jiang & Zhang, 2014). Automotive transport and other means of transports like railways, seaways, have caused significant contamination of heavy metals in the environment.

Significant amount of heavy metals is also generated from natural deposition and raining sedimentation to add to the pool of heavy metals in the soils (Chen, 2002).
Sewage also contributes immensely to the loading of heavy metals in the soils. Industrial mining, sanitary sewage, chemical wastewater, wastewater treatment plant (WTP) and several other factors fall under this category of sewage. Sewage water from household, business settings, drainage system, sewage water through pipelines are all source through which heavy metals are recovered (Sörme & Lagerkvist, 2002). There is again the solid waste which comprise complex composition of materials. When a waste is piled and left, heavy metals tend to move easily under the facilitation of sunlight, rain and washing. This spread to the surrounding environment, water and soils. Solid wastes can therefore widen the scope of heavy metal contamination when there is water and wind to facilitate (Su *et al*., 2014).

Agriculture is another major contributing source in generating heavy metals. Long term application of fertilisers and pesticides to the soil result in heavy metal contamination. Many pesticides are organic compounds while a few are organic-inorganic compound or pure mineral. Heavy metals are the most reported pollutants in fertilisers. Compound fertilisers consist of heavy metals mainly from master materials and manufacturing processes (Tafesse, 2014). Distinctively, contamination of heavy metals in urban soils is essentially from emission from transport (exhaust, particles formed by weathering street, tire wear debris particles and so on.), wastes from industries (power plants, metallurgical industry, coal combustion, automobile repair plants, chemical plants, etc.), household garbage, building and weathered particles of sidewalk and precipitation in the atmosphere, etc. the major sources of contamination in agricultural soils however, include the automobile exhaust, impact from city, sewage sludge, smelting minerals, waste treatment, fertilisers and pesticides, etc. (Montagne *et al*., 2007).
Poultry Farms: poultry farms generate livestock manure which is also a ubiquitous source of heavy metals. In this case, the amount of the elements found are usually as a result of the quantity added to the animal feeds which could be Zn or Cu or any other element to enrich the food for a desired outcome (Al Akeel, 2013).

Heavy metals can originate from the parent materials (The lithogenic source of heavy metals) which consists of rock or unconsolidated drift material which, by way of weathering and pedogenesis, forms the mineral skeleton of the soil. Weathering involves the chemical decomposition of minerals to form new (secondary) minerals and release of some of their constituent elements in soluble form through chemical reactions between the products of weathering. Some part of the mineral will not be decomposed chemically, it will remain as residue and any metal retained in it are not likely to become soluble and available to plants for a long time. In addition to concentrations of major and trace elements, the mineralogical composition of the soil derived from its parent material also determines its texture composition (percentages of sand, silt and clay-sized particles) and has a major influence on the physical and chemical properties of soils. Chemical property that enables the soil to adsorb cations and anions is perhaps the most important soil chemical property and is directly linked to the type and amount of secondary minerals including clays, the soil pH and redox condition, carbonate and hydrous oxides of Fe and Mn. This phenomenal capacity of adsorption by the soil will have a profound effect on the bioavailability of metals (Alloway, 1995; Mohammed *et al*., 2011). Black Shales for example, including bituminous and oil shales, have high organic matter and clay contents to which heavy metals and other trace elements are significantly embedded. Coals are also found to be closely related to black shales in being formed from organic-rich sediments in shadow reducing environments. Heavy metals are also released from when limestone and sulphide ore minerals undergo dissolution and oxidation during weathering. The metal becomes dispersed in the residual soil/or leached into groundwater. Another form of sedimentary rocks in the form of phosphorites contained high concentration of phosphate minerals, mainly apatite. The phosphorites have been found to be enriched in a number of heavy metals. Other parent material that are considered reservoir of heavy metals are; ultrafamic rocks, sedimentary ironstones and metallogenic mineralization (Al Akeel, 2013)

Conclusion
Toxicity and persistence of heavy metal pollution due to intense human activities around estuarine areas have attracted serious

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public attention. Adsorption of heavy metals on sediment is an important process that controls dissolved metal concentration, bioavailability as well as toxicity in natural environment. The ecotoxicity and mobility of an element in the environment depend strongly on their specific chemical forms or metal binding as a result, the biogeochemical pathways and toxic effects of these elements can best be studied on the basis of the species. Total metal extraction is a poor method of obtaining information regarding bioavailability, mobility and toxicity of heavy metals because these properties depend on the chemical forms of binding between the metals and the solid phase. One of the important properties of heavy metals that make them standout from many other environmentally toxic pollutants is the fact that they are non-biodegradable and can enter into biological system resulting to severe harmful effects. Heavy metal toxicity lowers energy levels and damage the functioning of the brains, lungs, kidneys, liver, blood composition and other organs. Gradual degenerative processes of physical, muscular and neurological functions become eminent after a long-term exposure. Diseases such as Alzheimer, Parkinson, multiple sclerosis and muscular dystrophy are likely to manifest. The toxicity level of a few heavy metals can be just above the background concentration that are present in the environment.

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