JIMMA UNIVERSITY

COLLEGE OF NATURAL SCIENCE

DEPARTMENT OF CHEMISTRY

A REVIEW PAPER ON DETERMINATION OF HEAVY METALS IN LAKE WATER

A RESEARCH PAPER SUBMITTED TO THE DEPARTMENT OF CHEMISTRY COLLEGE OF NATURAL SCIENCE IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF BACHELOR SCIENCE IN CHEMISTRY

SUBMITTED BY: KASSEGN ANDARGIE

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JUNE, 2014

JIMMA, ETHIOPIA

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APPROVED BY:

NAME ____________________________________

SIGNATURE ______________________________

DATE ____________________________________

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Abstract

Heavy metal consist less than one percent of living mass organisms and their different density cause to some disorder, surface waters and also acidic rains can transfer these metal to lake via washing polluted environment.

Increased anthropogenic activities have increased the potential pollution of the lake especially the heavy metal pollution which may be toxic to human and aquatic fauna. To determine and compare heavy metal content (Pb, Cd, As and Hg) in edible tissue and gill of grey mullet. The result of heavy metal level is several times lower than arsenic and were found in range 0.01-0.02 g w.w. The concentration of heavy metal in water and their accumulation in the edible tissue of nile Tilapia fish ranged from undectable to 4.57 µg/l for copper (Cu) and also form undectable to 0.25 µg/l ror lead (Pb) but dissolved nickel (Ni) and zinc (Zn) concentration were totally undictable in water sample in lake Hawassa. The order of heavy metal concentration in fish sample were found to decrease in sequence as Zn>Cu>Cr. The levels of the heavy metal concentration were compared with permissible limit value provided by WHO.

Chapter One

1. Introduction

1.1 Background of the Study

Water pollution is a serious environmental problem in the world. Anything which degrades the quality of water is termed as pollutant [1]. Of different pollutants, heavy metal pollution of aquatic environment has become a great concern in recent years because they are very harmful as a result of their non-biodegradable nature, long biological half-life and their potential to accumulate in different body parts of organism [2].

There are various sources of heavy metals; some originate anthropogenic activities like draining of sewerage, dumpling of hospital wastes and recreational activities. Conversely, metals also occur in small amounts naturally and may enter into aquatic system through leaching of rocks, air bone dust, forest fires and vegetation [3].

The most common potential toxic elements (PTE) listed by the united stated environmental protection agency (USEPA) are mercury (Hg), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn). Depending on difference between uptake rate, detoxification rates and excretion rate of the different organisms compared. However, the general order of toxicity of heavy metals is Hg>Ag> Cu>Cd>Zn>Ni>Pb>Sn>Sun [4].

Bioaccumulation of metals reflects the amount of heavy metal ingested by the organism. The way in which the metals are distributed among the different tissues and extent to which the metal is retained in each tissue type [5].

Toxic heavy metal can cause dermatological diseases skin cancer and internal cancer (liver, kidney lung and bladder) cardiovascular diseases, diabetes and anemia, as well as well as reproductive developmental, immunological and neurological affects in the human body [6].

Heavy metals are non-biodegradable and once discharged in to water bodies, they can either be adsorbed on sediment particles or accumulated in aquatic organisms. Fish may absorb dissolved elements and heavy metals from surrounding water and food, which may accumulate in various tissues in significant amounts [7] and are eliciting toxicological effects at critical targets also, fish may accumulate significant concentration of metals even in waters in which those metals are below the limit of detection in routine water sample [8].

Fish occupies the highest trophic level in aquatic systems. Besides that, it has high economic value, thus fish are suitable as water quality indicator organism. Fish is a good bio-indictor because it has a potential to accumulate heavy metals and other organic pollutants [9]. When fish is exposed to high concentration of heavy metals in water it may take up substantial quantities of these metals [10].

The study on heavy metal contamination in water and fish is vital to assess the current status of water pollution with heavy metal and threats to human health from heavy metal pollution of the lake. The purpose of this review was to determine the presence and effects of heavy metal in lakes.

1.2 Statement of the Problem

Heavy metal is one of the most widely distributed in aquatic environment. Therefore, the concentration of heavy metal in lakes, in humans and aquatic animal is crucial in order to determine the risk of health.

At the time of the study the answer of the following question will be expected

- What are the major sources of heavy metal?
- What is the permissible concentration of heavy metal in lakes?
- What level of heavy metal is enough to toxic fish?
- What is the effect of heavy metal in aquatic organism?

1.3 Objective of the Study

1 General Objective

- To review literature on determination of heavy metal in lake and to forward recommendation for assessed literature.

1.3.2 Specific Objective

- To determine some water quality of the lake.
- To compare the level of heavy metal in lake on the assessed literatures.
- To assess whether the degree of heavy metal varies on type of lake.
- To forward possible recommendation for assessed literatures.

1.4 Significance of the Study

The review will provide to assess the level of heavy metal, or well as type of heavy metal found in the lake and effect of heavy metal in aquatic animal.

Chapter Two

2. Literature Review

2.1 Environmental Pollution

Environmental pollution is caused due to the discharge of substances or energy in to air, water, or lead that may impart acute (short-term) detriment to the quality of life. According to tokalogluasetal. (2003) and moja, (2007), the impact of pollution classified as primary and secondary. "Pollutants make because primary damage in the biological food chain that are noticeable over long periods". Environmental pollution is insidious and its harmful effects only become apparent after periods of exposure.

Water pollution has an effect on oceans and in land water bodies. During the last decider the rapid economic development of Africa has led to an increase in environmental pollution [11]. Heavy metal released in to the environment find their way in to aquatic systems as a result of agricultural practices for instance, the use of fertilizer and pesticides for the control of pests in the cultivation of coffee, cotton, tea and sugarcane and other activities such as mining and industry as well as growth of the human population have increased the discharge of the waste effluents in to lakes and rivers rendering it environmentally unstable. Consequently, aquatic organisms may be exposed to elevated level of heavy metal due to their use for anthropogenic purpose [12].

2.2 Accumulation of Heavy Metal in Fish

Fish are used as bio-indicator of aquatic ecosystem for estimation of heavy metal pollution and potential risk for human consumption [13]. Many authors have reported that metal accumulation by liver and gills occur in higher magnitude than muscle. Metal accumulation in each tissue considerably depends up on the accumulation capacity of the tissue. Gill is the main place for gas exchange in fish. In this organ, because of the short distance between blood and surrounding seawater, heavy metal ions may directly take up from the passing water [14]. The metal such as copper, zinc, iron and cobalt are essential and have important biochemical function in the organism as opposed to non-essential metals like lead, cadmium, mercury and arsenic essential metals are used either an electron donor system or function as ligand in complex enzymatic compounds. The essential traces metals are only used in trace amount of the organism and usually they are found in small concentration in the environment.

Heavy metals have an effect on different aquatic organisms but its effect is often complex and difficult to interpret. Dissolved oxygen, PH, salinity, temperature and hardness of water have been shown to be factors that influence the physiology of an organism and the rate of uptake of heavy metals.

2.3 Bio availability of Metals

Bioavailability is defined as the fraction of the total amount of a chemical substance that can be taken up by living organism within a certain time span [15]. Factors affecting metal bioavailability of complexing ligand (e.g. organic carbon, chloride, carbonate, sulfides manganese and ferrous oxide) competition by other cations for membrane adsorption sites (e.g. calcium, magnesium), PH, redox, particles sorption, sediment and soil physicochemical properties and hydrology. Hydrogen ion activity (PH) is probably is the most important factor governing metal speciation, Solubility from mineral surfaces, transport and eventual bioavailability of metal in aqueous solution. The solubility of metal hydroxide mineral increases with decreasing PH, and more dissolved metal become potentially available for incorporation in biological process as PH decreases [16].

In recent organic carbon-rich sediments, trapped interstitial fluids can commonly form a strongly reducing (anoxic) environment. Low redox potential in their environment can promote sulfate reduction and sulfide mineral deposition. During diagnosis, much of the non-silicate bound fraction of potentially toxic metals such as arsenic, cadmium, copper, mercury, lead and zinc can be co-precipitated with pyrite, form insoluble sulfides and become unavailable to biota seasonal variation in flow rates or storms that induce an influx of oxygenated water can result in rapid reaction of their anoxic sediment and there by release significant proportions of these metals.

Pyritization and/or de-Pyritization of trace metal probably can be an important process in controlling bioavailability of many trace metals, especially in the aquatic environment [17].

2.4 Effects of heavy Metals on Aquatic Animals

Growth of fish larvae and juveniles is very fast. Many environmental factors influence growth: temperature, accessible alimentary base and presence of toxicants. Under optimum conditions, at appropriate temperature and at sufficient quantities of food. The fish increase in both body length and mass. On the other hand, in the water polluted with toxicants, e.g. heavy metals, fish growth may be inhibited. Inhibition of growth is one of the most distinct symptoms of toxic action of metals on fish larvae. Therefore, fish body length and mass are indicators of environmental condition [18].

Results of a research (Begum et al 2005) showed that the highest concentration of heavy metal is in kidney and liver of ten different fish species. Contaminated sediments can threaten creatures in the benthic environment, exposing worms, crustaceans and insects to hazardous concentration of toxic chemicals. Some kinds of toxic sediments via killing the benthic organisms, reducing the food availability for larger animals such as fish. Some contaminants in the sediments are taken up by benthic organisms in a process called bioaccumulation. When larger animals feed on these contaminated organisms, the toxins are taken in to their bodies, moving up the food chain with increasing concentration in a process known as bio magnifications [19].

Low concentration of heavy metals can cause a chronic stress which may not kill individual fish, but lead to a lower body weight and smaller size and thus reduce their ability to compete for food and habitat. Toxic effect of heavy metals on soil microorganisms in situ (near the roadside of the Vilnius-kaunas-klaipeda high way) were investigated by Jadhey et al. (2010) and a negative influence of the test metals on actinomycetes, mineral nitrogen assimilating and oligonitrophilic bacteria was found [20].

Aquatic organisms, such as fish, accumulate pollutants directly from contaminated water and indirectly via the food chain. Application of chemical fertilizers containing trace of heavy metals causes contamination of fish with these metals. The effects of pesticides either organ phosphorous or chlorinated pesticides have been extensively studied and confirmed in fish. The impact of toxic materials on the integrity and functioning of DNA has been investigated (sun et al 2010) in many organisms under field conditions [21]. Several biomarkers have been utilized as tools for detection of exposure to geno toxic pollutants. Such biomarkers include presence of DNA adducts, chromosomal aberrations, DNA strand breaks and micro nuclei measurements. In fish, erythrocytes are mainly used as sentinel markers of exposure to geotaxis compounds [22].

Vinodhini et al. (2009) in common carp with exposing of fish to heavy metals showed that the concentrations of red blood cells, blood glucose and total cholesterol were significantly elevated. The level of serum iron and copper was increased. The results showed the decreased activity of vitamin C during chronic exposure to toxic heavy metals, which indicates the presence of reactive oxygen species-induced per oxidation. They suggested that the presence of toxic heavy metal in aquatic environment has strong influence on the hematological parameters in the fresh water fish common carp (cyprinuscarpio L) [23]. Hayat et al. (2001) on three species of main carps (catalcatla, Labeorohita and CirrhinaMrigala) showed that they had negative growth with weight in exposing to sub-lethal concentration of manganese for 30 days. In fish, the toxic effect of heavy metals may influence physiological functions, individual growth, reproduction and mortality. High concentration of manganese detected in the gills of various fish species showed that the main route of manganese uptake was through the gills because little absorption of this metal occurred through the gut via the food. Long-term exposure (20 days or more) to water borne cadmium at sub-lethal concentrations showed decreased growth in Juvenile and adult rainbow trout, oncrohynchusMykiss [24].

Creatures as bio monitoring organisms; during the past few decades, many species have been studied to determine their potential as a bio monitoring organism, and Mollusca have become a popular choice for heavy metal monitoring. Mollusca have a depuration mechanism to reduce heavy metal toxicity in their body. This mechanism might diminish the effectiveness of mollusks as bio monitoring organism, as the concentration of heavy metal in the Mollusca may not accurately reflect the concentration in the environment. Therefore, there is a need to evaluate the effects of heavy metal accumulation and depuration in the bio monitoring organism. Studies have shown that meretrix is able to accumulate Cu, Zn, and Pb in the natural environment and this species may be used as a bio monitoring organism [25].

While many heavy metals are nutrients at trace levels, Pb, Cd, and Hg are non-essential and recognized as important industrial hazards, causing serve toxic effects in higher animals up on acute or chronic exposure. These three elements are highly persistent and in the bivalent form stable in organic and organic complexes in biological systems [26].

In lakes, heavy metals in dissolved form are easily taken up by aquatic organisms where they are strongly bound with sulfhydryl groups of protein and accumulate their tissues. Fish absorb dissolved or available metals and can therefore serve as are liable indication of can there in aquatic ecosystem. Tench (Tincatinca) is considered a good test organism for heavy metal contamination because of its feeding behavior and bottom feeding habits [27].

Fish embryos and larvae and generally considered to be the most sensitive to environmental pollutants, thus they have been widely used as bio indicator for water quality evaluation [28].

2.5 The Review of Some Heavy Metal in Lake

2.5.1 Mercury

Mercury is the only metal known to be liquid at room temperature and with low solubility in water dissolved mercury is distributed among several chemical forms including elemental mercury, which is volatile but relatively unreactive. A number of mercuric species (Hg (II) and organic-Hg such as methyldimethyl and ethyl mercury. In general the level of total Hg and Me Hg are higher near the sediments [29].

Mercury is one of the most toxic elements among the studied heavy metal and exposure to high level this element could permanently damage the brain, kidney and developing fetus [30].

2.5.2 Copper

Copper is one of the most widely used metals. The most common copper-bearing ores are sulfides, arsenates, chloride, and carbonates [31]. It reaches aquatic systems through antoropogenic sources such as industry, mining plating operations, usage of copper salts to aquatic vegetation or influxes of copper containing fertilizers [31].

Copper is essential trace metal to plant, animal and even humans and although the concentration of copper is usually low in nature, it happens in adequate quantities for growth in all aquatic environment. "It is required for bone formation, maintenance of myelin within the nervous system. Synthesis of hemoglobin, component of key metalloelzymes, plus it forms an important part of cytochrome oxidase, and assorted other enzymes involved in the redox reaction in the cell of animals, but becomes toxic at elevated levels [32].

Although copper is important it is toxic when concentrations exceed that of natural concentration (<0.054 mole/l) [33].

The toxicity of copper in aquatic organisms is largely attributable to Cu2+ that forms complexes with other ions [34].

Acute poisoning result from ingestion of excessive amount of copper salt can lead to "nausea, vomiting stomachache and diarrhea and may produce death,

2.5.3 Lead

Lead enters the aquatic environment through erosion and leaching from soil, leads dust fallout, combustion of gasoline, municipal and industrial waste discharge, runoff of Fallout deposit from street and other surface as well as precipitation [35].

The main targets of lead toxicity are "the hematopoietic and nervous system. Several of the enzymes involved in the synthesis of heme are sensirve to inhibition by lead. Several effect of lead toxicity has been reported on the exposure of fish to lead. These include metabolism and survival decreasing in growth rate and development a deficit in behavior and learning increased mucus formation in fish and the level at 50 μg/g in the diet are associated with reproductive effects in some carnivorous fish [36].

2.5.4 Zinc

Zinc is common environmental contaminate and it is commonly found in association with lead and cadmium [37]. Major source of zinc to aquatic environment in clued the discharge of domestic waste water, manufacturing process involving metal and fallout atmosphere.

Zinc is an essential element for human, animal and certain type of plant. It is necessary for a healthy immune system, cell division and synthesis of protein and collagen which is great for wound healing and healthy skin [37].

Even though zinc is an essential element and help in hemostastically control in fish, but at high concentration resulting gill damage. Which interferes with respiration, leading to hypoxia, chronically toxic are generally extensive deterioration of liver, kidneys, heart, and muscle [38].

2.6 Speciation of heavy Metals in Bottom Sediments of Lakes

The term speciation of heavy metals in bottom sediments of natural and man-made water reservoirs refers to quantitative and qualitative differentiation of the forms of their occurrence. Speciation of metals in bottom sediments has been the subject of interest for a long time, however, the first work in which a complete scheme of operational differentiation of metal forms by sequential extraction was proposed was a paper by Tessier et al. [39].

According to the studies by kwapulinski and wiechula [40] in the sediments of the above lake the greatest amount of iron was present in the residual fraction, but in the fraction bound to the oxides they found twice as much iron as in the fraction bound to organic matter. The same were the observations of Tessier et al. [39] for fluvial Sediments in the rivers Yamaska and Saint-Francois in Canada. Moreover, the total content of iron, as well as other metals, was much greater in sediments from Canadian rivers and Goczalkowice man- made reservoir than in bottom sediments from Gorecrielake. Manganese was found in the sediments from Goreckie lake mainly in the fraction bound to carbonate [41%] and hydrated oxides (31%) less was determined in the exchangeable fraction (11%) and residual fraction (9.9%). Only 6.1% of the metal was in the fraction bound to organic matter. In the studies of the sediments in Goczalkowicereservoir, Kwapulinsk, and Wichula [40]. Observed a more homogeneous distribution of manganese among particular fractions, and the greatest amount of thesis metal in the fraction bound to oxides, while the lowest in the fraction bound to carbonates.

In the sediments from Goreckie lake, Zinc was found mostly in the fraction bound to hydrated oxides of iron and manganese (58%), considerably smaller amount of this metal were detected in the fraction bound both to carbonates (16%) and organic matter (16%), while the amounts found in the exchangeable and residual fractions were 8.6 and 1.9 %, respectively. A significant amount of zinc was found in the residual fraction and in the fraction found to organic matter, while a relatively small concentration of this metal was in the fraction bound to carbonates [40].

Nickel in sediments from Goreckil Lake was mainly found in the residual fraction (66%). Its contribution to the fractions bound to hydrated oxides of iron and manganese organic matter and carbonates were 20%, 12% and 3.8% respectively copper, likewise nickel, was mainly found in the residual fraction (83%) much fewer amounts of this metals were bound to organic matter (16%) and hydrated oxides of iron and man sanase (2.9%). Lead was found mainly in the form bound to hydrate oxides of iron and manganese (34%), then the residual fraction (34%) and bound to carbonates (21%). In smaller amount it was bound to organic matter (10%). Cadmium was present mainly in the forms bound to organic matter (43%), in lesser amount in the fraction bound to hydrated iron and manganese oxides (28%) and in that bound to carbonates (18%) and the residual one (5.9%). Chromium, in the sediments from Gorckielake, was mainly found in the residual fraction (56%) and in that bound to organic matter (38%), while in smaller amounts in the fractions bound to hydrated iron and manganese oxides (1.2%). In the vesoritis lake sediments in Greece chromium was mainly found in the fraction bound to organic matter, then in smaller amounts in the residual fraction [41].

2.7 Review of Relevant Studies in Lakes

2.7.1 Determination of Heavy Metal (Pb, Cd, As and Hg) in Black Seagery Mullet (Mugicephalur)

Stan Cheva. M. L-Makedunski and E, Petroua, (2013) studied to determine and compare heavy metal content Pb, Cd, As and Hg in edible tissue and gills of grey mullet (mogulcephalur). The results are follow.

2.7.1.1 Lead

The joint FAO (WHO) (2012) represented three times higher concentration for Pb (0.023 mg/k+-ww) for golden Muller from sinopression (Torky Black Seacoast). The result indicated that highest Pb levels were obtained in gills in grey mullet from Varna Lake

2.7.1.2 Cadmium

The obtained concentration of Cd were highest in gills from varna lake grey mullet (0.031mg kg^{-1}ww) compared to edible tissue (0.024 $mg.kg^{-1}$ww) and nesseber sampler ($p<0.001$).

2.7.1.3 Arsenic

The highest detected values of As was measured in edible tissue from nessebar (1.1mgkg^{-1}w.w) and verna lake srey mullet (0.9 mgkg^{-1}ww).

2.7.1.4 Mercury

The highest detected value of mercury was in gills of varna lake srey mullet (0.12mgk-1 ww) were as in gills in newsbeat sample was measured a twice of lower value (0.06 mg.kg^{-1}ww).

2.7.2 Determination of Heavy Metal Contents in Water Sediment and Microalgea from Lake Victoria.

In this studies the highest concentration of trace metals in general werefound in sediments sample with Zn hiving the highest mean concentration value in both winam (1.01 ppm) and mwanza gulf (0.889 ppm). The mean concentration of Pb was higher in water sample from winamgvif (0.823) ppm and the mean concentration of mercury (kg) in microalgea sample from winam gulf (0.000148ppm) was the lower trace metal vabue were determined.

2.7.3 Accumulation of certain heavy metal in the nileTitapia (orcochromsniloticus) fish species relative to heavy metal concentration in the water of lakeHawassa.

AbaynehAtaroetal, (2003) studied trace metal in fish from lake Hawassa and Ziway. The results indicated the concentration 1.03-2.78ug/g in lakeHawassa and 1.03-1.98mg/g in lake Ziway for Cu and 23.04-30.92µg/g in lake Hawassa and 26.29-30.49 µg/g in lake Ziway for Zn. The accumulation of Pb and Ni were below 1.66 and 0.99 in Tilapia fish of both lakes. SelamawitGeta (2010). Found 1.35 of Cu, 0.35 of Pb and 27.13 of Zn in the muscle of Tilapia fish from lakeZiway.

Chapter Three

3. Methodology of the Study

3.1 Study Area and Period

The study was conducted in Jimma University, which is found in Oromia Region, Jimma Town from March to June.

3.2 Methods of Data Collection

The data was collected by using internet and searching different documents

3.3 Study Design

The study used both Qualitative of quantities of data collection

3.3 Source of Information

Necessary information would collect from different journals, internet and other written documents found in Jimma University.

Chapter Four

4. Conclusion and Recommendation

4.1 Conclusion

The concentration of trace metals from water sample i.e. in blachseagreyMuller, water, sediments and microalgae from Mwanz gulf of lake Victoria, Niletilapia of lake Hawassa were determined heavy metal accumulate in different tissue of Muller fish with different magnitudes. Generally, metal accumulation in mulclewar lower than gills Cd, Hg, and As mainly accumulated in gill while the edible tissue presented lower heavy metals concentrations of Winam Gulf and Mwanzagulf the concentration of heavy metal were highest in the sediment sample. Lake Victoria basin has significant basal contamination levels that do not reach those of clearly polluted aria. However, there is need for continuous monitoring of pollution level in the lake. In lake Hawassa in fish samples, the concentration of Cu, Ni and Zn were detected in all sampling sites in the detected samples concentration of Zn>Cu>Pb>Ni. The P- value for Cu, Ni and Zn accumulation in muscle tilapia fish showed that there no variallon throughout the lake and their accumulations are lower than the FAO/WHO (for Cu and Zn), Ev /for Cu) and USFDA (for Ni) limit. Every pollution in aquatic environment which impacts physiology, development, growth or survival of fish, affects human that, of the top food chain, consul fish. The accumulation of heavy metal in the tissue of organisms can result in chronic illness and cause potential damage to the population.

Aquatic animals have often been used in bioassays to monitor water quality of effluent and surface water. The development of biological monitoring techniques based on fish offers the possibility of checking water pollution with fart responses on low concentrations of direct acting toxicants. Development of chemical and biological methods for effectively monitoring environmental levels of heavy metals in a subject of interest and a critical step in development of environmental waste management.

4.2 Recommendation

The assessment of the concentration of the heavy metals in the whole soft tissues of the fish and other microorganism has provided very valuable and comprehensive baseline information and data on the pollution status of the lake. This data can serve as a guideline for future researchers and environmental managers to identify future anthropogenic impacts of the review location with respect to the studied metals, and better assess the need for recommendation by monitoring for changes from the existing levels. The data of this research can be useful for the management and sustainable development of the studied localities as for as heavy metal pollution is concerned. To prose the unpolluted state of the lake, it remains important that allochtonousimputs from the catchment area are devoid of heavy metals and regulatory mechanism should be enforced to ensure that current trends are not exacerbated. Despite the fact that the lake are for human consumption as far as the studied metals are concerned.

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