

Environmental Pollution by Heavy Metals in the Aquatic Ecosystems of Egypt



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Abstract

Contamination with heavy metals is one of the most serious problems in the aquatic environments. In Egypt, Environmental pollution with heavy metals is one of the biggest problems that face human being. Metals are natural trace components of the aquatic environment, but their levels have been increased due to industrial wastes, geochemical structure, agricultural and mining activities. There are certain heavy metals such as As, Cd, Cu, Pb, Ni and Zn are common pollutants and came from different natural and anthropogenic sources. Metals are partitioned among the various aquatic environmental compartments (water, suspended solids, sediments and biota) and can occur in dissolved, particulates or complex form. Metals have been reported to affect cellular organelles and induced toxicity & carcinogenicity. The aim of this review is to provide up to date information about metals pollution status, sources, distribution in seawater, sediments in aquatic biota in Egypt and to explore potential ecological risk index methods for heavy metals in sediments

Keywords: eavy metals; Pollution; Marine Environment; Contamination; Toxicity

Introduction

Pollution is considered as one of the most serious problems that faces human societies in the whole world especially in the developing countries. Though produced by man himself and his activities, it has deleterious effects on human's environments and resources [1,2]. So, pollution and its effects are considered as one of man's greatest crimes against himself. Pollutants may cause primary damage, with direct identifiable impact on the environment, or secondary damage in the form of minor perturbations in the delicate balance of the biological food web that are detectable only over long time periods [3-5].

Aquatic habitats, especially the freshwater ecosystems, are more subjected to pollution than other environments, because of water use in industrial processes as well as discharge of effluents from industry and urban development's [6,7]. Most aquatic ecosystems can cope with a certain degree of pollution, but severe pollution is reflected in a change in the fauna and flora of the community, which suffer such pollution. River Nile is the principal freshwater resource for Egypt, meeting nearly all demands for drinking water, irrigation, and industry [8]. Contamination of the river Nile and its tributaries with heavy metals may have devastating effects on the ecological balance of

the aquatic environment and the diversity of aquatic organisms. It is well known that the level of heavy metals in the water and sediment of some parts of the river Nile is higher than the limits set by the Egyptian General Authority for Standards and Quality Control [9].

The Egypt's northern Delta Lakes include Lake Edku, Lake Borollus, Lake Manzala, and Lake Mariut. These Lakes are situated on the Mediterranean Coast of the Delta and cover about 6% of the non-desert surface area of Egypt. The Lakes are an important natural resource for fish production in Egypt. Until 1991, these Lakes have always contributed more than 40% of the country's total fish production, but at present this has decreased to less than 12.22% [10]. Tilapia species including *Oreochromis niloticus*, *Oreochromis aureus*, *Sarotherodon galilaeus* and *Tilapia zillii* ranked first followed by *Clarias gariepinus* in the fish production of the Lakes. However, pollution with heavy metals has been reported in water, sediment and fish species collected from these lakes [11,12].

The Egyptian coastline extends 3000 km along the Mediterranean Sea and Red Sea beaches in addition to the Gulf of Suez and Gulf of Aqaba. Unfortunately, most of the Egyptian

coastal zones along the Mediterranean Sea are subjected to intense discharges of pollutants from numerous anthropogenic activities [13]. Some of the Egyptian coastal areas of (especially in front of the large cities) receive different types of pollution sources [14]. In coastal ecosystem, metals exist in either dissolved state in the water column or get deposited on the sediment bed, depending upon the nature of the chemical species and physicochemical factors like pH, conductivity, salinity and organic matter [15-17]. Following industrialization, unnatural quantities of metals such as Cd, Cu, Pb, Ni and Zn have been released, and continue to be released into the aquatic environment through storm water and wastewater discharges.

Heavy metals are of high ecological significance since they are not removed from water as a result of self-purification, but accumulate in reservoirs and enter the food chain [18]. The elevation of metal levels in a reservoir is shown mainly by an increase of their concentrations in the bottom sediment. Accordingly, sediments represent one of the ultimate sinks for heavy metals discharged into the environment [19,20].

Natural and Anthropogenic Sources of Heavy Metals

Table 1: Potential industrial and agricultural sources for metals in the environment [24].

| Metal | Sources |
|---------|--|
| Fe | Pigments and paints; fuel; refineries; textile. |
| Mn & Zn | Batteries and electrical; pigments and paints; alloys and solders; pesticides; glass; fertilizers; refiners; fuel. |
| Pb | Batteries and electrical; pigments and paints; alloys and solders; pesticides; glass; fertilizer; refiners; fuel; plastic. |
| Cd | Batteries and electrical; pigments and paints; alloys and solids; fuel; plastic; fertilizers. |
| Ni | Batteries and electrical; pigments and paints; alloys and solids; fuel; catalysts; fertilizers. |
| Cu | Batteries and electrical; pigments and paints; alloys and solid; fuel; catalysts; fertilizers; pesticides. |
| Cr | Pigments; fertilizers; textile. |

Heavy metals enter the aquatic ecosystem from both natural and anthropogenic sources. Entry may be as a result of direct discharges into both fresh and marine ecosystems or through indirect routes such as dry and wet deposition and land run-off [21]. Important natural sources are volcanic activity, continental weathering and forest fires. The contribution from volcanoes may occur as large but sporadic emissions due to explosive volcanic activity or as other low continuous emissions, including geothermal activity and magma degassing [22]. The anthropogenic sources include; mining effluents, industrial effluents, domestic effluents and urban storm-water run-off, atmospheric sources e.g. burning of fossil fuels and petroleum industry activities (Table 1).

Anthropogenic inputs, geochemical structure and mining of metals create potential sources of heavy metals pollution in the aquatic environment. Heavy metals are natural constituents of rocks and soils and enter the environment as a consequence

of weathering and erosion [23]. Under certain environmental conditions, heavy metals may accumulate to a toxic concentration and cause ecological damage. Heavy metals pollutants are conservative and often highly toxic to biota. They have been shown to be an important group of toxic contaminants because of their high toxicity and persistence in all aquatic system. As, Cd, Cu, Hg, and Zn are the five metals with most potential impact that enter the environment in elevated concentrations through storm water and wastewater discharges as a consequence of agricultural and industrial activity. Zn and Cu are used in small amounts as fertilizers in some soils deficient in these elements, while As, Cd, and Hg are constituents of some fungicides also used as an algacide; and Cd and Zn occur as contaminants of phosphatic fertilizers. Because of, the concentration of potentially toxic substances in sea water are extremely low and vary considerably in space and time so that their determination is difficult and the obtained data are of doubtful practical interest.

For most heavy metals, anthropogenic emissions are more than or equal to natural emissions. The combustion of leaded petrol in automobiles, for instance, is responsible for the widespread distribution of lead in the world [24]. As, Cd, Cu, Hg and Zn are five metals with most potential impact that enter the environment in elevated concentrations as a consequence of agricultural activity [25].

Delta and Mediterranean coast of Egypt

The River Nile from Aswan to El-Kanater Barrage receives wastewater discharge from 124 point sources, of which 67 are agricultural drains and the remainders are industrial sources. The total amount of wastewater discharged into the main stem of River Nile has been estimated to be 2628 million cubic meters per year, of which the industrial wastewater constitutes 15% [26]. Large parts of the Nile Delta suffer from severe coastal erosion, although adequate protection and mitigation measures have been considered. Most of the coastal lagoons “lakes” are however in crisis, suffering from the excessive discharge of industrial, agricultural and domestic sewage flow [27].

Along the Mediterranean coast of Egypt, there are eight coastal governorates. These are from west to east Matruh, Alexandria, Behaira, Kafr El- Sheikh, Damietta, Daqahliya, Port Said, and North Sinai. The enormous urban population and adjacent agricultural areas, all contribute to the pollution load reaching coastal waters. These derived either directly from coastal cities discharge points; the Rosetta branch of the River Nile, the Mahmudiya and Nubariya irrigation canals, drainage canals discharged directly to the sea, such as “El-Tabia and El-Ummun”, or from coastal lagoons “lakes” Maryut, Idku, Burullus and Manzala [28].

Alexandria governorate coastal zone receives a large amount of metal pollution from the principle industries of this region include fertilizers, agrochemicals, pulp, paper, power plant, food processing, detergents, fibres, dyestuffs, textile, and building

and partitioning are dilution, dispersion, sedimentation and adsorption/desorption, nonetheless some chemical processes could also occur. Thus speciation under the various soluble forms is regulated by the instability consists of the various complexes and by the physico-chemical properties of the water (pH, dissolved ions, Eh and temperature [39].

Soils and sediments contain some toxic heavy metals bound within the structural lattice of the crystalline minerals as primary constituent. Metals in this form are un-reactive and only slowly become available over geologic times as the result of natural mineral weathering. The metals fixed within the lattice of minerals are the dominant constituents. Between the readily available and unavailable forms of metals in sediments are a number of chemical forms which are potentially available. Most of metals present in sediments fall into this category. Metals in these potentially available forms may possibly be mobilized to more readily bio-available forms as a consequence of relatively mild physico-chemical changes in sediments and surface waters [23].

Gibbs [20] suggested four groups of heavy metal associations in aquatic solid substances (including suspended matter as well as sediments). They can be characterized by the following bonding processes:

- i) Adsorptive bonding;
- ii) Co-precipitation by hydrous iron and manganese oxides;
- iii) Complexation by organic molecules and
- iv) Incorporation in crystalline minerals. This categorization includes all main types of metal associations in both natural and polluted water systems.

Levels of Heavy Metals in Different Environmental Compartments

Concentration of Metals in Water

Saeed and Shaker [11] evaluated the concentrations of heavy metals including (Fe, Zn, Cu, Mn, Cd and Pb) in water samples collected from northern Delta Lakes (Edku, Borollus and Manzala). Water from Lake Manzala showed greater concentrations for the most of the metals studied than those reported for Lake Edku and Lake Borollus. Recorded levels above the international permissible limits in water were found in Lake Manzala for (Fe, Mn, Cd and Pb) and for (Mn and Pb) in Lake Borollus.

Hamed et al [38] studied the impact of land-based activity on the distribution of mercury and tin in surface seawater samples from the Egyptian Mediterranean beach during May 2010. The authors found that Nile Delta, Port Said and Alexandria beaches, which are the most industrialized areas in the Egyptian Mediterranean Sea, showed high levels of mercury in water compared to other studied sites. Alexandria beach showed the

absolute greatest concentration of tin in water (1.23 lg/l), while the least concentration was recorded at Port Said area (0.23 lg/l).

Heavy metals concentrations; Fe, Cu, Cd, Pb, Zn, Cr, Mn, Hg and Ni were determined in water collected from six areas at Assiut Governorate on river Nile, Egypt [40]. The results revealed that Zn, Cu and Fe concentrations were the highest in water followed by Mn, Cr, Pb, Cd, Ni and Hg in areas under investigation.

Ghani [4] assessed the pollution status of Marsa Matrouh Beaches, North West coast of Egypt by estimating levels of V, Al, Sn, As, and Se in seawater. Health risk assessment was also concerned. The decreasing trend of metals was observed in water as $Al > Sn > As > V > Se$. The levels of dissolved V, Se and as were lower than the typical natural trace element concentration of seawater while, Al surpassed. Dissolved Sn concentration was higher than the background concentration (0.01 lg/l) but it is still lower than the toxic concentration for organisms.

Sharaf & Shehata [41] assessed the concentration of heavy metals in water samples collected from two sites (Temsah Lake and Suez Canal, Egypt) represent polluted and unpolluted sites respectively. The results showed that, the levels of the heavy metals (Pb, Cd, Co, Mg and Zn) in the polluted area have reached harmful limits recorded globally.

Concentration of Metals in Sediment

Heavy metal (Fe, Mn, Zn, Ni, Co, Cr, Cu, and Cd) distribution and concentration in the sediments of the Egyptian coast of Aqaba Gulf have been assessed [34]. Obtained results found large heavy metals fluctuations along the studied area. Moreover, highly significant correlations among Fe, Cu, Ni, and Co heavy metals and their similar lithogenic origin beside their input sources were pointed out. Cd was the only metal that showed moderate pollution for Geoaccumulation index (Igeo) as well as it exceeded the primary and the secondary criteria of China State Bureau of Quality and Technical Supervision CSBTS and the threshold effect level of the Canadian guidelines (TEL).

In sediment samples collected from northern Delta Lakes (Edku, Borollus and Manzala), Mn (in Lake Edku) and Cd (in Lake Manzala) recorded higher values than the sediment quality guidelines [11]. Surficial sediment samples have been collected from the Egyptian Mediterranean beach during May 2010 to study the impact of land-based activity on the distribution of Hg and Sn [38]. The highest mean value of Hg in sediments (14.938 ng/g) was found in Sinai Beach and Sn (1.414 lg/g) was at Alexandria beach. While, in sediments samples collected from six areas at Assiut Governorate on river Nile, Egypt, the order of accumulation was $Fe > Zn > Mn > Cu > Ni > Pb > Cd > Cr > Hg$ [40].

The pollution level with certain heavy metals (Fe, Mn, Zn, Cr, Ni, Pb, Cu, and Cd) in sandy sediment samples collected from eight sites along the Egyptian Red Sea coast have been evaluated [14]. The results of the partitioning study showed that the average concentrations of the heavy metals analyzed in

investigated sediment exhibited the following decreasing order Fe > Mn > Zn > Cr > Ni > Pb > Cu > Cd.

Ghani [4] assessed the pollution level in Marsa Matrouh Beaches, North West coast of Egypt by estimating levels of V, Al, Sn, As, and Se in sediments samples. Pollution load index (PLI) recorded values >1 indicate progressive deterioration of the sediment quality. Enrichment factor (EF), contamination factor (CF) and geoaccumulation index (Igeo) demonstrated that most of the sediment samples were moderately to heavily contaminated by Sn which surpassed the threshold limit value (TLV).

Concentration of Metals in Aquatic Fauna

The bioaccumulation of heavy metals including (Fe, Zn, Cu, Mn, Cd and Pb) in Nile tilapia (*Oreochromis niloticus*) organs (muscle, gills and liver) collected from northern Delta Lakes (Edku, Borollus and Manzala) have been evaluated [11]. Gills and Liver of *O. niloticus* contained the highest concentration of the heavy metals detected. The edible part of *O. niloticus* showed higher levels of Cd (in Lake Edku and Manzala) and Pb (in Lake Manzala).

The concentrations of Fe, Mn, Zn, Cu, Pb and Cd in the soft tissues of the bivalve (*Donax trunculus*) in the Egyptian coastal waters along the Mediterranean Sea, were determined by El-Serehy et al [42]. Obtained results revealed that the concentrations of Cd and Pb in the soft tissues of the edible bivalve *D. trunculus* were above the maximum acceptable concentrations for human consumption proposed by FAO/WHO, EU. Moreover, estimation of concentration factor (Cf) for the studied metals in the soft tissues of the edible bivalve *D. trunculus* recorded high accumulation rates of Cd and Cu.

Heavy metals concentrations; iron (Fe), copper (Cu), cadmium (Cd), lead (Pb), zinc (Zn), chromium (Cr), manganese (Mn), mercury (Hg) and nickel (Ni) were determined in fish muscles of *Clarias gariepinus* collected from six areas at Assiut Governorate on river Nile, Egypt by Omar [40]. The results revealed that Zn, Cu and Fe concentrations were the highest in muscles, followed by Mn, Cr, Pb, Cd, Ni and Hg. While metal bioaccumulation in the muscles of the eight fish species collected by Ghani [4] from Marsa Matrouh Beaches, North West coast of Egypt was in the decreasing order of Al > Sn > V > Se, while As was not detected in all species. Calculated metal pollution indices (MPI) were lower than 1 except in *Saurida undosquamis* with 1.43 indicating that it is safe for human consumption.

Sharaf & Shehata [41] assessed the concentration of heavy metals in tissues of the snail *cyclope neritea* from two sites of the study area (Temsah lake and Suez canal) represent polluted and unpolluted sites respectively. Lead in tissue of the snail reached 7.93 ppm while Cadmium and cobalt reached 3.08 ppm and 10.36 ppm respectively. Meanwhile Magnesium and Zinc concentrations reached 12.6 ppm and 12.60 ppm respectively. The results showed that, the levels of the heavy metals (Pb, Cd,

Co, Mg and Zn) in the polluted area have reached harmful limits recorded globally.

Ecological Risk Assessment of Heavy Metals

The assessment of the potential risk of heavy metals contamination was proposed as a diagnostic tool for water pollution control purposes as a result of the increasing content of heavy metals in sediments and their subsequent release into the water, which could threaten ecological health. Many methodologies have been developed to assess ecological risks of heavy metals. However, most of them are suitable only for ecological assessment of a single contaminant (e.g., Geoaccumulation index method and Enrichment factor). In reality, many kinds of heavy metals usually accumulate simultaneously and cause combined pollution. Hakanson [43] developed the potential ecological risk index, which introduced a toxic response factor for a given substance and thus can be used to evaluate the combined pollution risk to an ecological system [44]. On the other hand, mean Sediment Quality Guidelines (SQG) quotient (mSQGQs) has been developed for assessing the potential effects of contaminant mixtures in sediments. Mean SQGQ have been calculated most frequently with SQGs derived with empirical approaches, such as the effects-range-low (ERM), probable effect level (PEL) values, in which measures of adverse effects were associate with, but not necessarily caused by specific chemicals.

Contamination factors (CF) and Pollution load Index (PLI) are calculated for heavy metals in sediment by the equation introduced by Hakanson [43]. Individual Contamination factors are calculated based on the following formula:

$$C_f = \frac{M_x}{M_b}$$

Where, M is the concentration of the target metal and Mb is the concentration of the metal in the selected reference background, Cf is defined according to four categories as follows: Cf < 1 low contamination factor 1 < Cf < 3 moderate contamination factor 3 < Cf < 6 considerable contamination factor Cf > 6 very high contamination factor.

Then pollution load index (PLI) for each site can be evaluated as indicated **Pollution load index (PLI) =**

$$(C_{f_1} \times C_{f_2} \times \dots \times C_{f_n})^{1/n}$$

Where, n is the number of metals and CF is the contamination factor. The contamination can be calculated from; The PLI value >1 is polluted whereas PLI value <1 indicates no pollution [45,46].

Potential ecological risk index method advanced by Swedish scholar Hakanson [43], is an approach to evaluate the heavy metal contamination from the perspective of sedimentology according to the characteristics of heavy metal and its environmental behavior. It not only considers heavy metal level in the soil, but also associates ecological and environmental

effects with toxicology, and evaluates pollution using comparable and equivalent property index grading method [47]. According to this method, the potential ecological risk coefficient E_r^i of a single element and the potential ecological risk index RI of the multielement can be computed via the following equations:

$$C_f^i = \frac{C_s^i}{C_n^i}$$

$$E_r^i = T_r^i \times C_f^i$$

$$RI = \sum_{i=1}^n E_r^i$$

where C_s^i is the pollution coefficient of a single element of “ i ”; C_n^i is the measured level of sedimentary heavy metal; T_r^i is the background level of sedimentary heavy metal; C_f^i is the toxic response factor for the given element of “ i ”, which accounts for the toxic requirement and the sensitivity requirement.

Twenty surficial sediment samples from different selected stations along the Egyptian Mediterranean Sea were collected to determine the status of heavy metals distribution and their ecological risk assessment in the studied area [28]. The results revealed that Fe had the highest mean value (243–38045 μgg^{-1}) followed by Mn (17–1086 μgg^{-1}), and a lower concentrations were found for Co (0.43–26.39 μgg^{-1}) and Cd (0.04–0.47 μgg^{-1}). Risk assessment showed that Cd had the highest ecological risk ($E_r = 21.52$), followed by Pb ($E_r = 3.01$), while Zn had the lowest risk ($E_r = 0.23$). Both the ecotoxicological index method and the potential ecological risk index (RI) suggested that the combined ecological risk of the studied metals was low.

Toxicity of Heavy Metals

In biological systems, heavy metals have been reported to affect cellular organelles and components such as cell membrane, mitochondrial, lysosome, endoplasmic reticulum, nuclei, and some enzymes involved in metabolism, detoxification, and damage repair [48]. Metal ions have been found to interact with cell components such as DNA and nuclear proteins, causing DNA damage and conformational changes that may lead to cell cycle modulation, carcinogenesis or apoptosis [49,50]. Several studies have demonstrated that reactive oxygen species (ROS) production and oxidative stress play a key role in the toxicity and carcinogenicity of metals such as arsenic [51,52], cadmium [53], chromium [54], lead [51,55], and mercury [56]. Because of their high degree of toxicity, these five elements rank among the priority metals that are of great public health significance. They are all systemic toxicants that are known to induce multiple organ damage, even at lower levels of exposure. According to the United States Environmental Protection Agency (U.S. EPA), and the International Agency for Research on Cancer (IARC), these metals are also classified as either “known” or “probable” human carcinogens based on epidemiological and experimental studies showing an association between exposure and cancer incidence in humans and animals.

Heavy metal-induced toxicity and carcinogenicity involves many mechanistic aspects, some of which are not clearly elucidated or understood. However, each metal is known to have unique features and physic-chemical properties that confer to its specific toxicological mechanisms of action. The entrance of certain metals into the nucleus can enhance the synthesis of RNA that codes for metallothioneins. Metallothioneins (MT) are peptides found mainly in the cytosol, lysosomes and in the nucleus, low molecular weight peptides, high in the amino acid cysteine which contains a thiol group (-SH). The thiol group enables MTs to bind heavy metals. Metallothioneins can be induced by essential and non-essential metals in aquatic organisms (mollusks, crustaceans). The MT induction is leading to changes in several biochemical processes that have the potential to be used as biomarkers of exposure and evaluation of pollution in the marine environment [57].

Marine and estuarine species commonly used for toxicity testing are: rotifers (*Brachionus plicatilis*), crustaceans copepods (*Acartia tonsa*), brine shrimps (*Artemia salina*), mysids (*Mysodopsis bahia*), bivalves oysters and mussels (*Crassostrea gigas*, *Mytilus edulis* or *Mytilus galloprovincialis*). These marine species are selected on the basis of their availability at low cost, ease of handling in laboratory tests and ecological importance. These marine species are generally supported by the American Society for Testing and Material (ASTM), the U.S. Environmental Protection Agency and International Organization for Standardisation (ISO) (American Society for Testing and Materials [58,59]).

Toxicological studies dealing with heavy metal pollution in aquatic organisms must take into account the interactions among metals that may influence uptake, accumulation and toxicity. Some interactions are antagonistic, such as between mercury and selenium. The toxicity of Hg is ameliorated by Se in vertebrates. Cadmium and selenium also show interactions [61,62]. Studies with heavy metals found interactions of iron (Fe) with mercury (Hg) in the bivalve *Mercenaria mercenaria*. Low concentrations of Se reduce Hg uptake in *Mytilus edulis* [42,63]. Copper (Cu) and Manganese (Mg) interactions may have special significance regarding phytoplankton growth [64].

Conclusion

There are many mechanisms for preventing pollution and mitigating long-term adverse effects. Thus, national legislation and international conventions provide considerable protection from both land- and sea-based sources of pollution. Economic forces can be used to control pollution, either via governmental intervention in the form of taxation or through corporate environmentalism. The main goal of toxicological and ecotoxicological studies is to ensure that heavy metal pollution from anthropogenic pollution do not give rise to adverse effects on living organisms. Ultimately, these studies must focus on measuring levels of pollution that may induce irreversible ecological changes to aquatic ecosystems. Ecotoxicological

studies with heavy metal pollution must consider the differences in bioavailability among aquatic organisms. The physiological state (e.g. nutritional state) of the aquatic organism has been shown to have a very marked influence on the uptake, distribution and adverse effects of heavy metals. Similarly, environmental factors, such as salinity, oxygen and temperature, may influence permeability and urinary excretion rates of heavy metals in aquatic organisms.

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