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Impact Of Marine Pollution by Heavy Metals

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ABSTRACT

Environmental pollution and its hazards are the most important problems of societies and living creatures. On the other hand, increased population with the development of technology and production can cause a lack of attention to environmental safety Industrialization leads to the pollution of ecosystems. Therefore, recognition of pollutants and prevention of their environmental sources, their marine environmental effects and prevention methods; also, filtration of industrial waste water and education of instructions for environmental protection is vital works to control and protect against pollutants. The most basic property of heavy metal is that they are bioavailable and are indestructible having toxic effects on living organisms when they exceed a certain concentration limit Heavy metals may affect organisms by accumulating in their bodies or by transferring to the next trophic level of the food chain and toxicity has proved to be a major threat as several health risks are associated with it. The objective of this study was to determine the heavy metals concentrations and distribution in the water from the beach opposite the Al-zawia refinery, and to provide insight into the source of heavy metals and their harmful effects on environment and living organisms[1].

Keywords: Heavy metals; the Marine Environment Pollution; human health, , fish Contamination; Toxicity.

1. INTRODUCTION

Heavy metal is a general collective term which is applied to the group of metal and metalloids, many of them have biotoxic effects due to which they became harmful. These metals are released into environment by both natural and arthropogenic sources such as mining and industrial activities. Urban sewage and industrial effluents are the main factor for the pollution by heavy metals. Heavy metals refers to any metallic element that have relatively high density and is toxic or poisonous even at low

concentration. Heavy metal is collective term which is applied to the group of metals and metalloids with atomic density greater than 4g/cm3 or 5 times or more greater than water [1].

Fish is a rich source of nutrients, however, its nutritional value may be affected by the environment in which it exists. The threat of toxic and trace metals in the environment is more serious than those of other pollutants due to their non-biodegradable nature. This is coupled with their bio-accumulative and biomagnification potentials. Within the aquatic habitat fish cannot escape from the detrimental effects of these pollutants. Heavy metal toxicity as a result of fish consumption can result in damage or reduced mental and central nervous system function, lower energy levels, and damage to blood composition, lungs, kidneys, bones, liver and other vital organs. Long term exposure may result in slowly progressing physical, muscular, and

Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Allergies are not

uncommon and repeated long term contact with some metals or their compounds may even cause cancer. Heavy metal toxicity is a chemically significant condition when it does occur. If unrecognized or inappropriately treated, toxicity can result in significant illness and reduced quality of life which can ultimately result in death. Recommended strategies to combat this menace involves environmental legislation, holistic planning, technological measures to improve the quality of waste discharges and environmental monitoring programs.

Objective: The aim of this study Provide information about heavy metals pollution. The characteristics of Mercury(Hg), Cadmium (Cd), Lead (Pb) and Nikel(Ni), and their implications on human health and marine life was demonstrate, distribution in seawater, sediments in aquatic life in LIBYA. These metals have hardly biological effect in the human where their toxic effect causes malfunctioning of the body system. In this study, several properness were measured the distribution of heavy metals (Pb, Ni, Cd, and Hg) in the sea water of Al-zawia Refinery. The concentration of heavy metals was measured using atomic absorption spectroscopy (AAS) instrument. Heavy metals concentrations were found to decrease in sequence of Pb > Hg > Ni > Cd. Results showed that heavy metal concentrations

in the marine surface water generally exceed the criteria of international marine water quality. Constant monitoring of the seawater quality is needed to record with a view to minimize the risk of health of the population and the detrimental impacts on the aquatic ecosystem.

1.1.EFFECT OF HEVY METALS ON AQUATIC LIFE

Fish is high in omega-3 and protein that the human body needs to stay healthy. However, potentially dangerous heavy metals are absorbed into the body tissues of fish that are transferred to humans on consumption of this affected fish. Good quality of food for human consumption can only be produced in an environment free from contamination and pollution. Fish are of great economic importance, but are affected immensely by various chemicals including heavy metals directly or indirectly in different ways. Fish, an important source of food for humans is also a key component in many natural food webs. Fats, fat-soluble vitamins and protein is obtained from fish. The high quality protein from fish is better for human health than that in meat and poultry. Fish consists of (15 – 24)% protein; (1 – 3)% carbohydrate; (0.1 – 22)% lipid; (0.8 – 2) % inorganic substances and (66 – 84)% water [1]. Each of these is important for human health, growth and intelligence. Fish play an important role as it is an important source of trace minerals and calcium. It also provides calories, nutrients such as fat, vitamins (B complex and D), elements

such as, phosphorus, sodium as well as trace elements. Fish may easily absorb pollutants from the ambient water and from their food and then deposit them in the tissue through the effects of bioconcentration and bioaccumulation. In this regard, heavy metals have long been recognized as an important pollutant due to their toxicity and ability to accumulate in marine organisms. Some of the identified toxic metals are arsenic, beryllium, cadmium, chromium, cobalt, tin, zinc, copper, iron, lead, manganese, aluminum, mercury, nickel and selenium [2].

1.2. SOURCES OF HEAVY METALS POLLUTION

Heavy metals differ widely in their chemical properties, and are used extensively in electronics, machines and the artifacts of everyday life as well as in high-tech applications. As a result, they are able to enter into the aquatic environment and food chains of humans and animals from a variety of anthropogenic sources as well as from natural sources [3]. The main sources of contamination include; mining wastes, landfill leaches, municipal wastewater, urban runoff, and industrial waste waters particularly from electroplating, electronic and metal finishing industries. Bradl [10] divided the transport of heavy metals in the marine environment into three parts:

1.3.Heavy Metals Diffusion

Heavy metals are transferred into the atmosphere and are transported by wind over vast distances, depending on their state (gaseous, vapor

or particulate). The atmosphere is a major route for the transport of heavy metals to the open oceans [11].

Diffusion of metals by living organisms also plays a role in the total transport. Generally, the greater part of metal load emitted into the environment is transported by water.

2.EFFECTS OF HEAVY METALS ON HUMAN HEALTH

Heavy metals such as cadmium, mercury, lead, and arsenic pose a number of hazards to humans, these metals are also potent carcinogenic and mutagenic [13]. Heavy metal toxicity can result in damage or reduced mental and central nervous system function, lower energy levels, and damage to blood composition, lungs, kidneys, liver and other vital organs. Long term exposure may result in slowly progressing physical, muscular, and Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Allergies are not uncommon and repeated long term contact with some metals or their compounds may even cause cancer [14].

The contamination chain of heavy metals almost always follows a cyclic order ie. Industry → Atmosphere → Soil → Water → Foods → Humans. Therefore concern about exposures, intakes and absorption of heavy metals by humans are increasing day by day in developing world. In recent years, the pollution of the aquatic environment with heavy metals has become a worldwide problem. Toxic pollutants, such as heavy metals originating from direct atmospheric deposition,

geologic weathering, or through the discharge of industrial waste products deposited in marine sediments as a sink. Due to their potential toxic effect and ability to bioaccumulation in aquatic ecosystems, the investigation of distribution and pollution degree of heavy metals in coastal area has attracted more public concerns recently. The potential sources of heavy metal pollution in the aquatic environment are industrial wastes and mining. To shorten the discharge of trace metals into aquatic system, a number of preventive actions are being applied, but existence of these metals in water system are even found nowadays. Heavy metals including both essential and non-essential elements have ecotoxicological effect to the living organism. Although metabolic activities in organisms necessitates some metals like iron, copper, manganese, zinc etc. but lead, nickel, cadmium, mercury, chromium, arsenic are marked as hazardous due to their toxic nature to the environment. Concentrations of heavy metals in the aquatic ecosystems are generally monitored by analyzing their accumulation in water, sediments, and associated biota. Usually level of accumulated metals in water are found considerably lower than sediment and biota. Marine fishes of the polluted area are acting as a pathway to carry away heavy metals to human beings. However, it is important to assess and track the abundance of these heavy metals in coastal ecosystem.

3.HEAVY METALS REMOVAL

Many processes for the removal of heavy metals from water and wastewater have been investigated. Coagulation and precipitation are the processes that have been reported to be most effective in the removal of heavy metals. In order to protect the human health, plants, animals, soil and all the compartments of the environment, proper and careful attention should be given to remediation technologies of heavy metals. Most physical and chemical heavy metal remediation technologies require

handling of large amounts of sludge, destroy surrounding ecosystems and are very expensive [19] (Figure 1). Biochemical detection method is also developed at a rapid rate, in which, enzyme inhibition method, immunoassay method and biochemical sensor applications are particularly prominent. Compared with traditional methods, biochemical detection method is more convenient, fast and economical, and is more suitable for instant detection of heavy metal ions on site. In recent years, there are more and more studies combining biochemical detection technology with intelligent systems, which also provides a great possibility for online monitoring on heavy metal environment. Nevertheless, along with the unceasing change of water environmental pollutants on a globe scale, the detection methods on heavy metal pollution in water environment need to be continuously updated to meet the practical application need in

contemporary scientific research and detection[5].

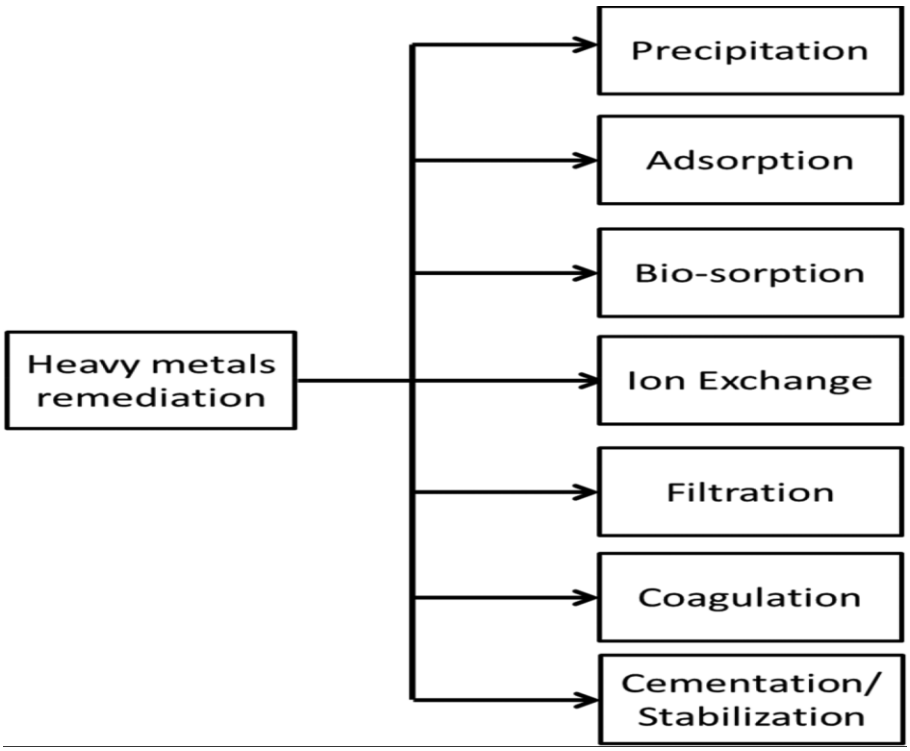


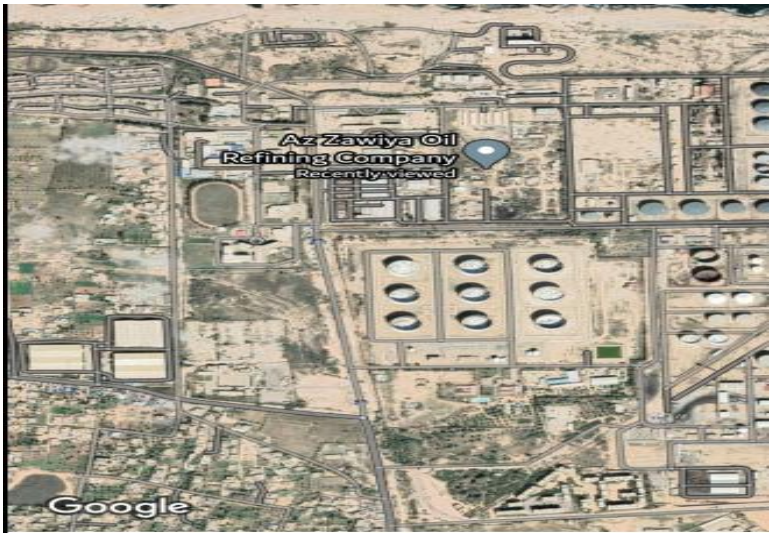
Figure 1. Mechanisms of heavy metals removal [20].

4. MATERIALS AND METHOD

4.1.Study site

All the study samples were taken from the beach opposite the Zawiya refinery and at various distances, Figure 2 shows the location of the study on Google map.

Figure: 2 shows the location of the study site.



4.2.Sample collection method:

All the water samples were collected by the method of the samples collected and placed in bottles containing polyethylene with a capacity of 1 liter with screw caps of the same material, and they were placed in basins containing concentrated nitric acid for a period of 24 hours, then they were washed with distilled water twice, then were immersed in a mixture of Nitric acid and concentrated hydrochloric acid in a ratio of 1: 2, then washed well and several times with distilled water, and then each sample was filtered using filter paper with a diameter of 0.25 μm, and two drops of concentrated nitric acid were added to it to adjust the acidity (PH), where it was less than 2, The samples were then sealed well. Then the samples were placed in an ice container to maintain the temperature of the samples at 4 degrees Celsius, and then they were transported to the laboratory, where they were placed in a refrigerator at a temperature of 4 degrees Celsius.

4.3.Steps of the experiment

After collecting and preserving samples, they were analyzed in the laboratories of the Libyan Oil Institute in Tripoli. Where the concentration of heavy elements in the samples was measured by the atomic absorption device, except for mercury, whose concentration was measured by the mercury analyzer, and the experiment steps were as follows:

1- Preparation of standard solutions of heavy elements using the dilution law: $(M_1V_1) = (M_2V_2)$

Where: (M_1V_1) is the initial concentration and volume of samples;
and (M_2V_2) is the final volume and concentration of samples.

2- Preparing samples of heavy elements for measurement:

All samples were injected directly into the lead, cadmium and nickel atomic absorber. As for the element nickel, it was injected into a mercury analyzer. The results are as shown in Table 1.

4.4.. Description of study area

For surface water sampling, 7 sampling points were chosen at the coast of marine

These sites were chosen, because they receive considerable namounts of waste water from industrial areas as well as from ship. The details of concentration values of sampling are shown in Table 1.

Table 1: Concentration of heavy metals in water samples.

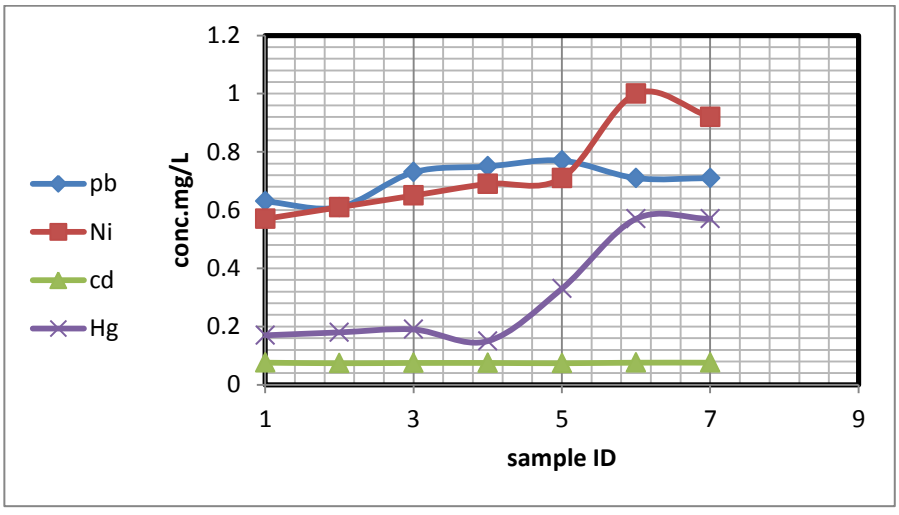
Sample ID	pb	Ni	cd	Hg
1	0.63	0.57	0.076	0.17
2	0.61	0.61	0.074	0.18
3	0.73	0.65	0.075	0.19
4	0.75	0.69	0.075	0.15
5	0.77	0.71	0.074	0.33
6	0.71	1	0.076	0.57
7	0.71	0.92	0.076	0.57

5. R ESULTS AND DISCUSSION

5.1. Determination of heavy metals in sediments

regulates the concentration of dissolved metals in the sea water. Concentration of heavy metals in the water sample of the beach opposite the Al-zawia Refinary in Figure 2 which reflects the order of

metal concentration of the present study as follows: Pb > Hg > Ni > Cd. The average concentration of Pb, Hg, Ni, and Cd, in the water of near of the beach opposite the Al-zawia Refinary shown in Figure 3 which are 0.701 mg/L, 0.308 mg/L, 0.735 mg/L, 0.064 mg/L, , respectively, Whereas maximum limits of these metals permissible in drinking water recommended by WHO/FEPA are, pb, 0.16 µg/L, and Cd= 0.003 µg/L . Cadmium naturally exists in Soil and rocks of some extend. Besides, anthropogenic activities like unsafe use and handling of Ni–Cd batteries, industrial activities, waste treatment plant, as well as agricultural fertilizer are the source of cadmium load to the sea . Residual discharge of produce water from gas processing plant, metallurgical activities (Ship breaking) and also other industrial activities are responsible for increase in cadmium.



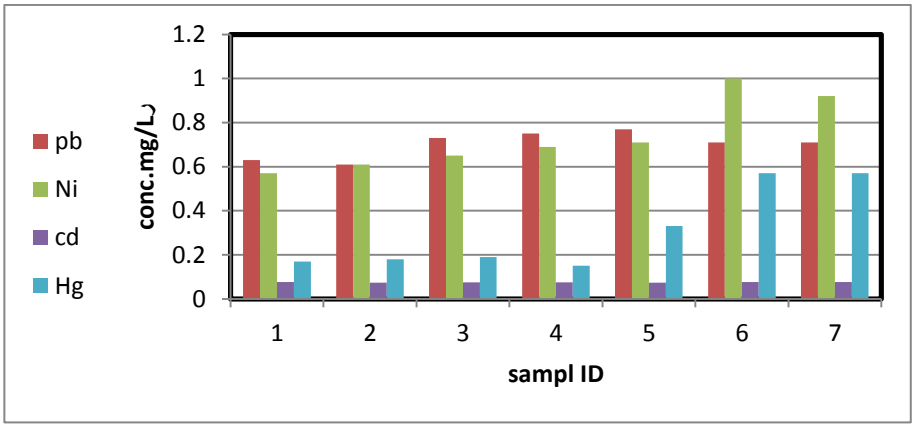


Figure3 and 4: measured concentration of heavy metals in different water samples.

5.2. Pollution assessment

Due to consequences of variations in analytical procedures between studies and the presence of an unknown natural background in the water, it is difficult to make an overall assessment of the degree of metal contamination.

5.2.1. Density

Density of water is greatly affected by temperature compared to salinity. Average density of sea water was found 1.02 g/mL that is slightly lower than world average value that is 1.025 g/mL.

5.2.2. Total dissolved solids

Total dissolved solids (TDS) is the measure of extent of solid materials dissolved in water. If the TDS level is high, especially due to dissolved salts, many forms of aquatic life are affected. The salts act to dehydrate the skin of animals.

5.2.3. Temperature

Temperature plays an important role in water. It affects the rate of chemical reactions, the metabolic rates of organisms, as well as the distribution of aquatic organisms throughout aquatic system. The temperatures determine the solubility of dissolved oxygen (DO) in water. There were significant differences in the temperature of water over the study period. The water temperature generally ranged from 22.5 to 30.5°C.

5.2.4. Dissolved oxygen

Oxygen in water is measured as DO. Oxygen enters the water through photosynthesis in aquatic plants or from the transfer of oxygen between the air and water (waves, turbulence, currents, etc.). Fast-moving water, lower temperature, and lower salinity all result in the availability of more DO. WHO (1993) recommended a concentration of DO of 5 mg/l or above.

5.2.5. Electric conductivity

Electric conductivity (EC) is an indication of the amount of salts dissolved in water. It is also defined as the amount of ions (positive and negative) in water, and the water's ability to pass an electrical current. Electrical conductivity is a useful indicator of the salinity, total salt content in a water sample.

5.2.6. Acidity (pH)

Many chemical and biological processes in the water are affected by

lower pH value. A pH reading below 6.5 generally considered as being acidic may cause problems of heavy metal toxicity.

5.2.7. Salinity

On average, seawater in the world's oceans has a salinity of about (0.035 g/mL) [22]. Seawater is not uniformly saline throughout the world, as mixing occurs with fresh water run-off from river mouths or near melting glaciers, as a result seawater can be substantially less saline.

6. CONCLUSION

From the present study, it was observed that the accumulation of heavy metals is found to be high in the surface water of the beach opposite the Al-zawia Refinary mainly due to the land-based activities in general. Most attention should be given to control industrial discharge input into the coastal environment, especially discharge from gas production plant and ship breaking yard plays important role in water quality

parameters studied in this research. In the near future, management practices and Government policy should be employed for regulating contamination of the beach opposite the Al-zawia Refinary controlling effluent discharge from nearby industries which is required to protect the marine ecosystem.

7.RECOMMENDATIONS

The presence of heavy metals in aquatic ecosystems is a threat not only to the inhabitants of the ecosystems but also to the well-being of humans. To combat this menace, the following measures are suggested:

1. Environmental legislation: Environmental laws should be enforced to ensure that the aquatic environments are protected from exposure to toxic substances and from the risk associated with the use of chemicals.

2. Anthropogenic activities should be regulated to ensure that heavy metals are net released into aquatic environments (either directly or indirectly).

3. Holistic Resource Planning; This approach should ensure that relationships among land use, development, water flow, water quality, and aquatic ecosystems are considered prior to any land use designation. Technological measures to improve the quality of waste discharges and to lower both water demands and effluent loading should be implemented in response to environmental and water use concerns.

4. Environmental monitoring programs should be set up and implemented to monitor chemicals in water, sediment, and organisms which would help to identify potential ecosystem problems and to track existing problems.

5. Compensatory measures such as fish hatchery operation can produce young fishes that heavy metals contaminated habitats can no longer produce, and;

6. Environmental sustainability education needs to be incorporated into the curricula of schools and universities, while awareness creation on environmental pollution needs to be given the seriousness it deserves.

REFERENCES

1- "Heavy metals distribution and contamination in surface water of the Bay of Bengal coast", M.R. Hasan1§, M.Z.H. Khan1§*, M. Khan2, S. Aktar2, M. Rahman2, F. Hossain2 and A.S.M.M. Hasan3, Hasan et al., Cogent Environmental Science (2016), 2: 1140001.

2- "Heavy Metal Concentration of Sea Water and Marine Organisms in Ennore Creek, Southeast Coast of India", C. Suresh Kumara*, M. Jaikumarb, Robin R.S.c, P. Karthikeyanc, C. Saravana Kumard., The Journal of Toxicology and Health. Photon 103 (2013) 192-201.

3- "Heavy Metal Impact On Aquatic Life And Human Health An Over View" ,Dr. Alkesh I. Shah.

4- "Environmental Contamination by Heavy Metals" ,Vhahangwele Masindi and Khathutshelo L. Muedi.

5- Advances in the Effect of Heavy Metals in Aquatic Environment on the Health Risks for Bone,Li Jun-Jie1, Pang Li-Na1,*, Wu Shan2, Zeng Meng-Da1, IOP Conf. Series: Earth and Environmental Science 186 (2018) 012057.

6- "Heavy Metals Contamination in Fish: Effects on Human Health", Isangedighi Asuquo Isangedighi, Gift Samuel David*, Journal of Aquatic Science and Marine Biology, Volume 2, Issue 4, 2019, PP 7-12

7- "Heavy Meatls Pollution And It's, Effect On Environment And Human Health ",*Vani Sharma and Padma Singh, Vol. 6, Issue, 12, pp. 7752-7755, December, 2015

8- "Heavy Metal Removal By Coagulation With Seawater Liquid B ittern ", By G. M. Ayoub,1 Member, ASCE, L. Semerjian,2 A. Acra,3 M. El Fadel,4 and B. Koopman5.

9-(Lenntech, 2004).

10-(Huton and Symon, 1986; Battarbee *et al*., 1988; Nriagu and Pacyna 1988; Niragu, 1989; Garbarino *et al*., 1995; Hawkes, 1997).

11-(Rainbow, 2007; Wang & Rainbow, 2008)

12-(Christophoridis, Dedepsidis, & Fytianos, 2009; Feng et al., 2011; Gao & Chen, 2012; Larrose et al., 2010; Liu et al., 2011; Sundaray, Nayak, Lin, & Bhatta, 2011; Varol, 2011; Yang et al., 2012).

13-(Gumgum, Unlu, Tez, & Gulsun, 1994).

14-(Dural & Bickici, 2010; Kumar, Rita, & Mukherjee, 2011; Kumar, Senthilkumar, Priya, Mukhopadhyaya, & Saha, 2010; Paller & Littrell, 2007).

15-(Storelli et al., 2015).

16-(E.C., 2001; USFDA, 1993).

17-(Camusso, Vigano, & Balestrini, 1995).

18-(Namminga & Wilhm, 1976).

19-(Jones & Murray, 1984; Moore, 1978; Wangersky, 1986; Yeats & Campbell, 1983).

20-(World Health Organization, 2003).

21-(HELCOM, 2007).

22-(Anthony, 2000).