رقم البحث (13)

DETERMINATION OF SOME HEAVY METAL POLLUTANTS IN WATER AND ORGANS OF SOME FISH SPECIES FROM NILE RIVER DYMIATTA BRANCH

BY

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ABSTRACT

Mean concentration of lead, cadmium and mercury in muscles and organs of some common species of fish Tilapia nilotica , Clarias lazera and Bagerus bayad)from Nile riiver were investigated using atomic absorption spectrophotometric method .

The mean concentrations of lead in the muscle , kidney and liver tissues were in the ranges of 0.5–0.8mg /kg , 0.6–0.9mg / kg , and 0.5– 0.7mg / kg respectively, while that of the surrounding waters were between 0.013 and 0.062 mg/l .Levels of cadmium concentrations in the muscles were in the range of 0.1–0.2 mg /kg; in the kidney tissues, 0.4–0.5 mg /kg and in the liver tissues 0.2–0.3 mg / kg .While the mean levels of cadmium in the surrounding water were between 0.004and 0.008 mg /l . The levels of mercury in fish tissues were 0.3–0.5 mg /kg in the muscles , 0.5–0.6mg /kg in the kidney and 0.3–0.4mg /kg in the liver, whereas 0.0050–0.0021 mg/l were the mean concentrations in the surrounding water . From the results, it was observed that the levels of these metals in the fish samples were higher than that obtained in the surrounding water.

The distribution of lead, cadmium and mercury in the fish tissues investigated showed significant variations with respect to muscles and the organs .The kidney tissues had higher concentrations of the metals compared to the liver tissues, which is in turn higher than that in the muscles. This indicates that the kidney of fish is a better bio-accumulator of heavy metals than the liver and the muscle tissues. The accumulation patterns of heavy metals

contaminants in fish depend on uptake and elimination rate.The implications of these contaminants beyond the **World Health Organization (WHO, 2002)** permissible limits were discussed .

INTRODUCTION

Human body has need for approximately (70) friendly trace elements, but there are twelve poisonous heavy metals , such as lead , mercury , aluminum, arsenic, cadmium, nickel , chromium, etc, that acts as poisonous interference to the enzyme system and metabolism of the body. Heavy metals overload will be a detriment to the natural healing functions of the body **(Kakulu et al , 1987, Elson and Haas ,2003).**

Heavy toxic metals are trace metals that are bio-accumulate in fish five hundred times than their levels in water. They are some times passed up the food chain to humans**, (Fergosson 1990)** . These metals include mercury, lead, arsenic, cadmium, aluminum and copper (metallic and ionic form).

Most heavy metals have no beneficial function to the body and can be highly toxic **(fergosson,1990).** They are taken into the body via inhalation, ingestion and skin absorption. If they enter and accumulate in body tissue faster than the body's detoxification pathways can dispose of them, a gradual buildup of these toxins will occur. Overtime levels of bio-accumulation can reach toxic concentration levels **(khaled et al,1978, proti,1989; prusty,1994).**

Heavy metals were present in our environment in minute concentrations until recent centuries that industrialization brought in technological advances such as the use of metals in medicine as silver–mercury tooth amalgam, lead based paints and leaded gasoline **(seddek,et al 1996).**

Pollution of rivers streams flowing through agricultural areas where pesticides, fungicides, etc may have been applied, and industrial districts where they may have been metal waste deposits, All these present varied and difficult problems due to drainage into our different water bodies. Effluents discharged into rivers which may affect aquatic environment**. Moriber (1974)** found that drinking water contaminated by wastes from mines producing cadmium; lead and zinc resulted in ricket-like diseases.

Fish is often at the top of the aquatic food chain and may concentrate large amount of these metals from the surrounding water up to (5000) folds **(Nweodozie,1998).**

Lead is known to cause the disease called plumbism. Lead accumulate in aquatic biomass, they are concentrated and passed up the food chain to human consumers. Lead is also known to damage the brain the central nervous system, kidneys and liver **(Ademoroti, 1996a).**

Cadmium is of even greater concern because of its harmful effects on plants, animal and man. Cadmium cause **itai-itai disease**; this disease is known to damage the joints, cause bones to soften and the body to shrink while the affected person dies a painful death **(Ademoroti, 1996a).**

Mercury gets into the body through the respiratory and gastrointestinal tract and is distributed into the liver and kidney. It is also accumulated in nervous tissues. The alkylated mercury (alkyl-Hg) accumulates in central nervous system (CNS) tissues. It is toxic to the glial cells mostly Schwann cell production of myelin, neuropsychotic, severe developmental CNS abnormalities in foetus and prolonged action potentials. Fish intake is the major source of exposure to mercury, mainly in the form methyl mercury, which it accumulates from the surrounding waters **(McKinney and Rogers , 1992) .**

Studies shows that fish accumulate these heavy metals from the surrounding water bodies there by leaving a health risk if taken as food **(Proti, 1989; Prusty, 1994; US. DPHHS, 2005) .**

Nile river is a major source of water and fish supply for the inhabitants in Dymiatta Governorate. Mechanic workshops, car wash, battery charging fabric of dyeing ,etc are common source of pollution to the River all over its course **(Seddek,et al 1996).** Also, people at some villages dump their waste indiscriminately in the river . These activities may have impact on the water body, thereby introducing some of these heavy metals in to the water, which is subsequently ingested and absorbed by the fishes. The present study investigates the levels of these metals(Pb, Cd and Hg) in some common species of fish so as to determine their suitability as seafood to the inhabitants.

MATERIALS AND METHODS

The following studies were conducted to determine the heavy metal concentrations in different fish species .Sixty Tilapia nilotica, **(60)** Clarias lazera and **(36)** Bagerus bayad fish samples as well as **(12)** water samples were collected allover the experiment from three localities in the Nile river at Delta, Egypt from November **(2003)** to February **(2004).**

Three localities were identified infront of Al-Zarka city, Kafr Al-Shennawy village and Faraskor city to collect the samples .

Collection of water samples:

Three water samples were collected monthly from the afore mentioned three localities allover the four months **(12 totals).** The technique of sampling was conducted according to the recommendations of American Public Health Association **(A.P.H.A. 1985)** as follows:

Three clean polyethylene bottles, each of one liter capacity were used. The samples were taken at depth of half meter from the water surface to avoid floating materials. The bottle was immersed to the required depth and filled with the water samples. Each sample was labelled to identify the source, site and date of sampling. Each sample was acidified by adding 3ml of concentrated nitric acid (analytical grade). The samples were transferred to the laboratory and stored in the refrigerator until the metal analysis was conducted.

Collection of fish samples:

Three pool samples from different localities**(5)**Tilapia niloticas**,(5)** Clarius lazera and**(3)** Bagerus bayad each were collected monthly from the aforementioned localities of Nile river. Three fish species were collected and identified morphologically. The fish samples were catched by fisherman using fish nets. The collected different species of fish samples were warpped separately in acid washed polyethylene bags, identified and, then transferred to the laboratory in an ice box and kept frozen till the metals analysis was conducted .

METAL ANALYSIS

Determination Of Heavy Metals In Water Samples

Preparation of water samples:

The preparation of water samples for heavy metals analysis was conducted according to , **(Polprasert 1982) .**

The collected water samples were filtered through 0.45 micromembrane filters .One hundred ml of the filtrate measured and was collected in clean glass bottles, preserved by 0.3 ml of

nitric acid, and kept till the metals analysis was performed .

Preparation of blank sample :

To chick the traces of metals that may be present in the nitric acid and the deionized water used in the prepared samples,3ml of the used nitric acid was added to 3ml of the used deionized water in clean screw capped tube and kept in the refrigerator until metal analysis was conducted .

Atomic absorption spectrophotometer analysis technique for water samples :

Analysis of filtrated collected water samples was conducted according to the methods of **(medina , et al ,(1986)** by using Perkin Elmer atomic absorption spectrophotometer model 2380 equipped with MHS–10 hydride generation system . Instrumental analysis of lead and cadmium were conducted by air acetylene flow rate(5.5/1.1 1/m)flame atomic absorption spechophotometry , whereas flamless technique (cold vapor technique) using nitrous oxide gas in flow rate (1.2 1/m) was used for detecting mercury . Hydride generation system using mixture of sodium borohydride 3% in sodium hydroxide 1% as reductant agents, was used for detecting mercury . Addition of 0.5% of potassium cyanide to the previous reductant agents to avoid interfering effects of foreign transition metals was conducted during the detection of mercury **(Abdallah , et al. 1993)** . The detection limits used in estimation of lead and cadmium were 0.01ppm and 0.001ppm , while that of mercury was 0.001ppm .

The concentrations of heavy metals in water samples were calculated and recorded in **Table(1) .**

Determination Of Heavy Metals In Fish

Preparation of fish samples for analysis :

The fish samples were prepared for heavy metals analysis according to the procedure described by **(Greig , et al . 1982)** as follows :

Five grams from dorsal and caudal peduncle muscles of each fish samples , as well as one gram of liver and kidney were taken as follows :

Each fish sample was individually skinned at the place of dorsal and tail muscles using clean ,plastic forceps and scalpel. Pool muscle samples were taken as previously mentioned and homogenized using glass morter. Five grams from each pool homogenized sample was transferred into acid washed screw capped digestion tube with polyethylene stopper ,aswellas1 gm liver and kidney each pool sample were prepared incised by scalpel into fine pieces, then placed into the previously acid washed, screw capped digestion tubes.

To each tube ,10ml of concentrated nitric acid (analytical grade) were added and thoroughly mixed and kept at room temperature over night . The mixture was then heated in water bath at 70 °c for 6 hours . The mixture was cooled at room temperature . Few drops of hydrogen peroxide (30%) were added (4–5drops) to each tube and returned back to the water bath till clear solution was obtained .

To dilute the digested tissues, deionized water was added to the digestion tube up to 15ml, and filtered through 0.45 m micropore membrane filter. The clear filtrate of each sample was kept in screw capped tube in refrigerator to avoid evaporation until the analysis was carried out .

Atomic absorption spectrophotometer analysis technique for fish tissues :

Analysis of the digested filtrated fish tissue samples was conducted according to **(Medina, et al.1986)** corrected and recorded in **Tables (3,4and 5)**

Rate of recovery

Known amount of each metal (20 mg) was added to a known weight of a pool fish muscle sample as well as another plan sample from the same fish muscles was prepared and used as control. The two samples were digested , diluted and filtrated by the same method used in preparation of the fish samples of the study, then subjected to heavy metals analysis technique. The detected results were corrected according to the rate of recovery obtained . The percentage of recovery rates were 91.1%,89.2%and92.0% for lead, mercury and cadmium, respective.

RESULTS AND DISCUSSION

From the results in **Table (1)**, the mean concentrations of lead, mercury and cadmium in water samples were ranged from 0.031 mg/l–0.038 mg/l ,0.0010 mg/l–0.0021 mg/l and 0.004 mg /l–0.009mg/l respectively. Mean lead and mercury values were within the permissible limits (100%) of samples as recommended by **World Health Organization (WHO, 1981)** for portable and drinking water whereas 40% of water samples had cadmium over the permissible limits. This is may be due to the effluents from mines allover the course of the river. The results in **Table (2)** show that the mean levels of lead in the muscle, kidney and liver of various fish species ranged from 0.5–0.8, 0.6–0.9 and 0.5–0.7 mg / kg respectively .

These values were higher than that of the surrounding waters, this is due to the fact that fishes bio–accumulate heavy metals over time. The mean levels of lead in fish muscles and organs of different species were within the permissible limits as recommended by **(WHO,1981)**. These values may reach dangerous trend if the sources of these metals are not checked. As it is known that lead is toxic and may damage the brain, the central nervous system , kidney , liver and the reproductive system when it exceed the tolerable limit in humans **(Ademoroti,1996a)**. Waste products from the use of chemicals, leaded gasoline and other lubricants like diesel oil which are spilled here and there specially as car wash is located along the river course may be responsible for the presence of lead in the river water **Table (1).**

Table (1) : Mean concentrations of heavy metals (mg/l) of water samples

Metal	Locality			
	Value	**Al-zarka site**	**Kafr-Al-Shenawy site**	**Faraskor site**
Lead	**Min.**	0.013	0.016	0.015
	Max.	0.062	0.057	0.059
	Mean.	0.031	0.037	0.038
	S . E .	± 0.004	±0.003	±0.007
Cadmium	**Min.**	0.005	0.004	0.005
	Max.	0.009	0.008	0.008
	Mean.	0.008	0.006	0.007
	S . E .	0.003	0.002	0.002
Mercury	**Min.**	0.0016	0.0010	0.0013
	Max.	0.0018	0.0014	0.0021
	Mean.	0.0017	0.0013	0.0018
	S . E .	±0.0008	±0.0003	±0.0007

Table (2) : concentrations of lead (mg/kg wet weight) in tissues of some selected fish species

Fish species	Mean concentration of lead (mg/kg)		
	In muscles	In kidney	In liver
Clarias lazera	0.66± 0.001	0.75 ± 0.001	0.73 ± 0.001
Tilapia Nilotica	0.56 ± 0.001	0.63 ± 0.001	0.56 ± 0.001
Bagerus Bayad	0.87 ± 0.001	0.97 ± 0.001	0.74 ± 0.001

All values are mean values of triplicate determinations ± SD.

Table (3) :concentrations of cadmium (mg/kg wet weight) in tissues of some selected fish species .

Fish species	Mean concentration of cadmium (mg/kg)		
	In muscles	In kidney	In liver
Clarias lazera	0.26 ± 0.00	0.45 ± 0.01	0. 32 ± 0.001
Tilapia Nilotica	0.13 ± 0.00	0.43 ± 0.01	0. 26 ± 0.001
Bagerus Bayad	0.29 ± 0.00	0.57 ± 0.01	0. 33 ± 0.001

All values are mean values of triplicate determinations ± SD.

Table (4) : concentrations of mercury(mg/kg wet weight) in tissues of some selected fish species

Fish species	Mean concentration of mercury (mg/kg)		
	In muscles	In kidney	In liver
Clarias lazera	0.45 ± 0.01	0.53 ± 0.01	0. 35 ± 0.01
Tilapia Nilotica	0.34 ± 0.01	0. 56 ± 0.01	0.34 ± 0.01
Bagerus Bayad	0.56 ± 0.01	0.69 ± 0.01	0. 46 ± 0.01

All values are mean values of triplicate determinations ± SD.

Table (5) : Frequency distribution of heavy metals in water samples from different localities in Nile river

Heavy metals	Permissible limits ppm	Within permissible limit %	Over permissible limit %
Lead	0.05	100%	-
Mercury	0.01	100%	-
Cadmium	0.005	60%	40%

According to the guide line values recommended by W.H.O. (1981) & U.S.E.P.A. (1979)

Table (6) : Frequency distribution of heavy metals in fish tissue samples from different localities in Nile River

Heavy metals	Permissible limits ppm	Within permissible limit%	Over permissible limit%
Lead	1.0	100%	-
Mercury	0.5	100%	-
Cadmium	0.1	100%	-

Permissible limits were established according to the recommendation of Egyption General Authority of Standardization and Quality Control (1991) .

From the results **Table(3)** , it can be observe that the levels of cadmium in the muscle , kidney and liver of the fish are in the range of 0.13–0.29 mg/kg, 0.43–57 mg/kg and 0.26–0.33 mg/kg respectively. These values are also higher than the cadmium contents in the surrounding waters but are within the permissible limits of **(WHO,1981)**. These results may be due to the untreated effluents of mines and chemical industries drained in the river which can rise the load of cadmium in the river. The obtained mean levels of cadmium in fish still below the permissible limits. Cadmium wastes washed into aquatic bodies accumulate in aquatic biomass, leads to its concentration and pass up to the food chain causing health hazard to humanbeing.

Table(4) reveals that the results of mercury concentration in the muscle, kidney and liver of the common fish used in this study clarify that the amount of mercury in the range of 0.34–0.56, 0.52-0.69 and 0.34–0.46 mg/kg respectively. These values were also higher than levels in the surrounding waters but within the recommendation of **Egyptions General Authority of Standardization and Quality Control(1991)** for food and potable drinking water**..**

The levels of these metals in the fish samples were higher than that obtained in the water samples. This could be attributed to the metals being lipophilic (methyl mercury); they reside and accumulate in fatty tissues as well as the mercurial pesticides originated from Al-Serw agricultural drain which pore 72000 cupic meters of untreated water of agricultural activities to the river stream **(Al-Safy et al.2001)** beside the industrial activities allover the river course. Heavy metals enter fishes not only by ingestion but also through dermal absorption and respiration. When these chemicals are taken in by the fish , they bio–accumulate, bio-magnify, and remain in the fish till they are caught and use as food by humans or eaten by predatory fish Bagerus Bayad , which are eventually eaten by humans. In our study lead and mercury obtained in Tilapia Nilotica and Clarias Lazera were aggread with those detected by **Seddek et al.(1996) in Assiut Governorate** whereas cadmium levels detected in Tilapia Nilotica and Clarias Lazera in Assiut were over the obtained concentrations in our study and were above the permissible limits. recommended by the **Egyptions General Authority of Standardization and Quality Control 1991).**

On this ground , one can suggest that the use of these fishes for the preparation of seafood for consumption in risky. However, high consumption of fish will pose health hazard to the communities around the river since they depend solely on the river as a source of drinking water and fish. More over, the distribution of lead , cadmium and mercury in the fish showed significant variations with respect to the muscle and the organs . The kidney had higher concentration of the metals as compared to the liver, which is in turn higher than that in the muscle. This indicates that the kidney of fish is a better bio-accumulator of heavy metals than the liver and the muscle .

CONCLUSION

Pollution of Nile river still suffers from continous untreated industrial, agricultural and sewage pollution which adversely affect its aquatic environment .Nile river is the main source of drinking water and aquatic creatures specially fish acts as a source of health hazard to the Egyptians . Recycling of industrial effluents as well as hygienic desposal and treatment of agricultural and sewage wastes from the origin will decrease the hazards caused by heavy metals . Regular monitoring of the levels of industrial wastes specially toxic heavy metals poured in the Nile river .

There is significant variability in the concentrations of these metals in the muscle and organs of the fish . The accumulation patterns of heavy metals contaminants in fish depend on uptake and elimination rate . Studies have shown that omnivorous fish accumulate these metals (Pb ,Cd and Hg) from surrounding waters, whereas the bio-accumulation and bio-magnification of metals in carnivorous fish(Bagerus Bayad and cat fish) is due to its predatory habitate in food consumption .

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الملخص العربي

- نظرا لأهمية نهر النيل فرع دمياط كمصدر هام لمياه الشرب والأسماك فى محافظة دمياط, ونظرا للتلوث المستمر الذى يئن منه نهر النيل على طول مجراه, فقد قمنا بهذه الدراسة لمعرفة قيم بعض الملوثات مثل المعادن الثقيلة في مياه و بعض أسماك النهر.
- تم تقدير مستويات المعادن الثقيلة (الرصاص, الكادميوم و الذنبق) في عضلات و أحشاء بعض أنواع الأسماك (البلطي النيلي, القراميط و أسماك قشر البياض) باستخدام طريقة الامتصاص الذرى الكروماتوجرافي.
- تراوحت متوسطات قيم الرصاص في أنسجة كل من العضلات، الكلى والكبد للأسماك محل الاختيار بين (٥,- ٨, مجم/كجم)، (٦,- ٩,مجم/كجم) و (٠٥,- ٧, مجم/كجم) على التوالى.
- جاء متوسط قيمة الرصاص في مياه نهر النيل في مواقع تجميع العينات بين (٠١٣,- ٠٦٢, مجم/ لتر).
- أما متوسطات قيم الكادميوم في عضلات الأسماك المختلفة فكانت بين (١, - ٢, مجم/كجم) بينما كانت في أنسجة الكلى بين (٠٤, - ٥, مجم/كجم) و أخيرا في أنسجة الكبد بين(٠٢, - ٣, مجم/كجم)، في حين جاء متوسط قيمة الكادميوم في عينات المياه بين (٠٠٤, - ٠٠٨, مجم/ لتر).
- جاءت مستويات الذنبق في عضلات الأسماك بين(٠٣,- ٥, مجم/كجم)، (٥,- ٦, مجم/كجم) في أنسجة الكلى ، (٣, - ٤, مجم/كجم) في أنسجة الكبد, بينما مستواه في عينات المياه كانت بين (٠٠٥, - ٠٠٢١, مجم/ لتر).
- أظهرت النتائج أن المستوى التراكمي للمعادن الثقيلة في عينات أنسجة الأسماك أعلى من مستواها في عينات المياه كما أظهرت النتائج تباين بين مستويات الرصاص, الكادميوم و الذنبق في أنسجة العضلات, الكلى و الكبد, وكذا بين الأنواع المختلفة من الأسماك.
- كذلك تبين أن أنسجة الكلى احتوت على أعلى التركيزات للمعادن الثقيلة عن مستوياتها في أنسجة الكبد و العضلات كما تبين أن أنسجة العضلات احتوت على النسب الأقل من المعادن الثقيلة عنها في باقي الأحشاء.
- كذا أظهرت النتائج أن قيم المعادن الثقيلة جاءت الأعلى في الأسماك المفترسة (قشر البياض و القراميط) عنها في الأسماك الرمية (البلطي النيلى).
- فيما يتعلق بالمسموح به فقد ثبت من الدراسة أن مستويات المعادن الثقيلة في أسمك نهر النيل اقل من الحد الأدنى للمسموح به للاستهلاك الآد مى كما جاء في تعليمات منظمة الصحة العالمية, في حين تبين أن (٤٠٪) من عينات المياه احتوت على عنصر الكادميوم بقيم أعلى من الحد المسموح به عالميا.
- مما سبق يتضح أن ارتفاع مستوى بعض المعادن الثقيلة بنهر النيل يدق ناقوس الخطر مما يحدونا إلى التحرك السريع لمنع إلقاء الملوثات المختلفة بصفة عامة و الصناعية منها بصفة خاصة حفاظا على صحة الإنسان المصري.