



Heavy Metals Poisoning in Some Local Fish in Misurata city

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Abstract

Libya has a long coast which is more than 1970 km that is rich with different types of fishes. Fishes have a high nutritional value and people depend on them to cover their nutritional needs like proteins, minerals and vitamins. In the last years, many human activities such as nuclear and industrial wastes dropped in seas and oceans have caused high pollution with heavy metals. These pollutions are transmitted to consumers directly causing different dangerous diseases like cancers and metallic poisoning. To study this pollution, different types of fish samples have been collected randomly from local fish market in Misurata city, wet digested, and the heavy metals were determined with atomic absorption spectrometer. The results were compared with standards of WHO & FAO. The average concentrations of heavy metals (Hg, Cd, Pb, Cu, Cr, Ni, Zn, Mn, and Fe, respectively) for different types of fish were as follows: Sardine fish (*Sardinella maderensis*): 0.005, 1.58, 0.25, 0.20, 0.25, 0.56, 0.37, 0.26, 0.99 (mg/kg), Sea dog fish (*Galiorhinns galeus*): 0.007, 1.97, 0.16, 0.19, 0.35, 0.56, 0.37, 0.26, 0.59 (mg/kg), Farroj fish (*Epinehus mrgintus*): 0.004, 2.16, 0.58, 0.71, 0.46, 0.65, 0.85, 0.27, 0.77 (mg/kg), Trillia fish (*Mulhus barbatus*): 0.003, 1.65, 0.41, 0.29, 0.55, 0.45, 0.75, 0.46, 0.67 (mg/kg), Kawally fish (*Scomber japonicas*): 0.002, 0.77, 0.65, 0.19, 0.77, 0.45, 0.96, 0.45, 0.69 (mg/kg), and Rzam fish (*Auxis rochei*): 0.00, 0.00, 0.15, 0.49, 0.38, 0.29, 0.37, 0.48, 0.41 (mg/kg). this kind of works can help to assist local and state health services in their deliberations concerning such contaminants in local fish.

Key words: Fish - Heavy metals - Atomic Absorption Spectrometer – Health - Toxic.

1. Introduction

In last year's high metallic pollution occurred most of seawaters from sewage drains and petroleum ships that caused high pollution of fish with heavy metals like Mercury (Hg), Lead (Pb), Arsenic (Ar), Copper (Cu), Iron (Fe), Cadmium (Cd), Zinc (Zn), Nickel (Ni), Manganese (Mn), and Chromium (Cr) that will be if increase more than recommended by WHO & FAO carcinogenic, causing Colon cancer (Carlene, E. *et al*, 1989), the last studies showed high infected cases of toxicity with heavy metals after consumption of fish hunted from sea, so we have risk of high pollution because of domestic wastewater, industrial wastes and drains of petroleum ships (Cunningham, W. *et al*, 2004), (Bosket, E. *et al*, 2014), Lead, cadmium, copper, mercury, and nickel are toxic priority pollutants that commonly interfere with the beneficial usage of wastewater for irrigation and industrial applications (Cunningham, W. *et al*, 2004), In recent years, contamination of sea water by heavy metals is becoming major problem for aquatic life and human health (Perez M *et al*, 2003), (Cunningham, W. *et al*, 2004), Therefore, there has been constant effort to measure the impact of these metals on aquatic systems such as sea water and these researches are becoming increasingly significant owing to the biological non-degradability and chronic toxicity resulting from the accumulation of these metals in vital organs of man (FAO. (1983). FAO Fish Circ, 464: 5), The present study



attempts to analyze the level of some heavy metals (Hg, Cd, Pb, Cu, Cr, Ni, Zn, Mn, and Fe) in different types of fishes (sea dog, Farroj, Trillia, Kawally, Sardine, and Rzam) which sold in local markets in Misurata city - Libya.

2. Materials & Methods

2.1. Sample preparation

This study was conducted between January and June - November 2018. 30 Samples of different specs of fishes collected from local fish market in Misurata city. The types of studied fishes were: Farroj (*Epinephelus marginatus*), Sea dog (*Galiorhinus galeus*), Trillia (*Mulhus barbatus*), Rzam (*Auxis rochei*), Kawally (*Scomber japonicus*), and Sardina (*Sardinella maderensis*). All samples were analyzed in triplicates and the average was taken. The samples need to be brought into clear solution for analysis by the Atomic Absorption Spectrometer. For this reason, the samples were first digested with chemicals where the organic matrix was destroyed and left the element into a clear solution. "Wet Digestion" method has been used in the present study. 0.50 gr of dried sample is treated with 5 ml mixture of HCl: H₂SO₄: HNO₃ (1:1:1) and then digested on electric hot plate at 90°C and the temperature of this mixture was gradually increased to 120°C until brown fumes appeared, indicating completion of oxidation of organic matter. The organic matrix was destroyed and left the elements into clear solution, after cooling the clear solution was filtered into 10 mL volumetric flask and completed to the mark with de-ionized water, and a blank digestion solution was made for comparison.

2.2. Sample Analysis

Atomic absorption measurements were made using a Shimadzu AA-7000 with Deuterium lamp (D2-lamp) background correction and hollow cathode lamps. Air-acetylene flame was used for determination of all the elements. The AMA254 Advanced Mercury Analyzer is used to determine mercury content.

3. Results and Discussion

All the reagents used were of the analytical purity (Merck, Germany). The working solutions were prepared immediately before the analysis from the basic solution with 1000 mg L⁻¹ concentration for all metals. For the preparation of standard solutions high purity Milli-Q water was used. The glassware and polyethylene containers used for analysis were washed with tap water, then soaked over the night in 10 % HNO₃ solution, rinsed several times ultra-pure water to eliminate absorbance due to detergent.

Analysis of all fish samples indicated their contamination by some heavy metals residues, exhibiting a wide array of hazardous impacts on human health. Beyond certain limits, all metals turned to be toxic to human body. This could be applied to essential minerals like Fe; Zn and Cu, as well as non-essential metals and metalloids like Pb and Cd compounds. The concentrations of heavy metals in analyzed samples are reported in Table (1).

**Table (1) Mean concentration of heavy metals in fish samples**

Fish type	Mean concentration of heavy metals (mg/kg)								
	Hg	Cd	Pb	Cu	Cr	Ni	Zn	Mn	Fe
Sardina	0.005	1.58	0.15	0.20	0.25	0.56	0.37	0.26	0.99
	0.92	0.32		1.43	0.15	0.32	14.45	2.10	3.84
Sea Dog	0.007	1.97	0.16	0.19	0.35	0.54	0.56	0.37	0.59
	0.53	0.08		0.58	0.64	0.72	5.39	1.48	2.94
Farroj	0.004	2.16	0.58	0.71	0.46	0.65	0.85	0.27	0.77
	0.44	0.12		2.44	0.42	0.26	18.29	1.88	2.34
Trillia	0.003	1.65	0.41	0.29	0.55	0.45	0.75	0.46	0.67
	1.37	0.17		1.52	6.28	0.31	32.13	5.29	6.23
Kawally	0.002	0.77	0.65	0.19	0.77	0.45	0.96	0.45	0.69
	0.31	0.017		0.11	1.16	0.05	1.16	1.60	2.74
Rzam	ND	ND	0.15	0.49	0.38	0.29	0.37	0.48	0.41
				2.10	0.65	0.11	2.73	1.76	4.59

In average, cadmium was the metal detected at highest levels in all fish samples (0.00 – 2.16 mg/kg). The increase of cadmium level in human body could cause serious problems in kidney and liver, vascular and immune sys. The next major element detected in our samples was iron (0.41 -0 .99 mg/kg). Iron is an essential element and is crucial for the building up of red corpuscles, which in turn are essential for formation of hemoglobin, the oxygen-carrying pigment in red blood cells. It is also used against anemia, tuberculosis and disorder of growth. In average, lead, copper, chromium, nickel, and manganese have almost the same concentrations (0.35, 0.32, 0.46, 0.49, and 0.38 mg/kg) but their concentrations are lower than zinc (0.64 mg/kg). Zinc as an important constituent in promoting growth and regulation was sufficiently found in most of the samples. It is very important for nerve function, male fertility, stimulation of vitamins and formation of red and white corpuscles, healthy function of the heart and normal growth. The copper contents in fish samples were less than the FAO-permitted level of 30 mg/kg (Perez M et al, 2003), Mercury is found in all fish samples in low concentrations (0.002 – 0.007 mg/kg). Intoxication by elemental mercury or by methyl mercury is revealed primarily by changes in behavior and by neurological signs. Specific sensory symptoms are also prominent in human methyl mercury poisoning. Methyl mercury may induce alterations in the normal development of the brain of infants and may, at higher levels, induce neurological changes in adults. Children exposed to methyl mercury prior to birth may experience negative effects on their mental development. Heavy metal concentrations had the following order: Cd > Fe > Zn > Ni > Cr > Mn ~ Pb ~ Cu > Hg. All elements levels indicated significant differences between the fish samples. Sardinia fish, however, is the most polluted among the other types of fish. The distribution of concentrations of element in each fish sample are shown in Figure 1. Exposure of fish to elevated levels of heavy metals induces the synthesis of metallothioneine proteins (MT), which are metal binding proteins. Fishes are known to possess the metallothioneine proteins. Metallothioneine proteins have high affinities for heavy metals and in doing so, concentrate and regulate these metals in the liver (Perez M. et al,2003), Metallothioneine proteins bind and detoxify the metal ion (Perez M et al,2003).



4. Conclusion

The present study revealed that the heavy metal contamination in different types of fish from local market in Misurata region. Based on the fish sample analysis the concentration of Cd recorded higher in all samples. The level Pb, Zn, and Cu does exceed the acceptable levels for Libyan food regulations. The level of the heavy metal concentration in fish samples follows order: Cd > Fe > Zn > Ni > Cr > Mn > Pb > Cu.

5. Recommendations

1. Stop draining waste water in the sea
2. Making new recycling waste water stations in all coastal cities
3. Improve the ecology preventing offices to improve eco-wariness
4. Monitor the illegal ships that drain waste water in sea water
5. Control in all fish markets to stop pollution in ecology
6. Improve the health awareness in peoples

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التسمم بالمعادن الثقيلة في بعض الاسماك المحلية في مدينة مصراتة

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الملخص

ليبيا لديها شاطئ طويل حوالي 1970 كم غني بأنواع مختلفة من الاسماك, والاسماك لها قيمة غذائية عالية ويعتمد عليها البشر في تغطية احتياجاتهم الغذائية كالبروتينات, المعادن والفيتامينات الذائبة بالدهون. بالسنوات الاخيرة الكثير من النشاط البشري كالفيايات النووية والصناعية تلقى بالبحار والمحيطات مما سبب تلوث عالي بالمعادن الثقيلة, وتلك الملوثات تنتق مباشرة للمستهلكين مسببة عدة أمراض خطيرة مثل السرطان والتسمم المعدني عدة عينات من الاسماك جمعت عشوائيا من الاسواق المحلية بمدينة مصراتة , هضمت الاسماك بالتجفيف الرطب للكشف عن المعادن الثقيلة بمطياف الامتصاص الذري. قورنت النتائج بالمواصفات الدولية بمنظمة الصحة العالمية والمنظمة الدولية للغذاء والزراعة . مستوى تركيز المعادن الثقيلة (Hg , Cd , Pb , Cu ,Cr , Ni , Zn , Mn, Fe) على التوالي لمختلف الاسماك كالتالي سمك السردين (ملجم/كجم) 0.005, 1.58, 0.25, 0.20, 0.25, 0.56, 0.37, 0.26, 0.99 (ملجم/كجم) سمك الفروج (ملجم/كجم) 0.004, 0.007, 1.97, 0.16, 0.19, 0.35, 0.56, 0.37, 0.26, 0.59 (ملجم/كجم) سمك التريليا (ملجم/كجم) 0.003, 1.65, 0.41, 0.29, 0.002, 0.77, 0.65, 0.19, 0.77, 0.45, 0.55, 0.45, 0.75, 0.46, 0.67 (ملجم/كجم) وسمك الرزام 0.96, 0.45, 0.69, 0.00, 0.00, 0.15, 0.49, 0.38, 0.29, 0.37, 0.48, 0.41. وهذا البحث العملي يعزز الاصحاح البيئي لمثل هذه الملوثات بالاسماك.

الكلمات مفتاحية: السمك , المطياف الذري , المعادن الثقيلة , الصحة , التسمم .