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## EVALUATION OF HEAVY METALS CONTENT IN FRESH AND CANNED SARDINES PRODUCED IN SOME MEDITERRANEAN COUNTRIES.

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### ABSTRACT

Most heavy metals which bio-accumulate in fishes do not have any biological significance or beneficial use, but due to the presence of heavy metal, fish can pose a health risk to consumers. The present investigation was carried out to evaluate the Concentrations level of mercury (Hg), cadmium (Cd), and lead (Pb) in Sardines available in the Libyan market and produced in different countries of the Mediterranean region. All collected samples were analyzed by graphite furnace atomic absorption spectrometry after microwave assisted digestion, for detection of their contents of heavy metal residues to evaluate their quality according to standard legislations. The obtained results indicated concentrations for lead and mercury ranges from (0.0070 - 0.0125) and (0.0 - 0.0095) mg/kg respectively. It was observed that the levels of Lead and Hg in all different samples were within the permissible limits according to the standards of the World Health Organization and the European Union. Cadmium was not found in all samples.

تقييم المعادن الثقيلة في السردين المنتج في بلدان مختلفة من منطقة البحر الأبيض المتوسط  
وفاء الهادي الذيب<sup>1</sup> بسمة الهادي الذيب<sup>2</sup> عمر احمد القايدي<sup>3</sup>

الملخص:

معظم المعادن الثقيلة التي تتراكم بيولوجيًا في الأسماك ليس لها أي أهمية بيولوجية أو استخدام مفيد، ولكن نظرًا لوجود المعادن الثقيلة، يمكن أن تشكل الأسماك خطرًا صحيًا على المستهلكين. تم إجراء هذا البحث لتقييم مستوى تركيزات الزئبق، الكاديوم والرصاص في السردين المتوفر في السوق الليبي والمنتج في بلدان مختلفة من منطقة البحر الأبيض المتوسط. تم تحليل جميع العينات التي تم جمعها بواسطة مطياف الامتصاص الذري لفرن الجرافيت بعد الهضم بمساعدة الميكروويف، للكشف عن محتوياتها من بقايا المعادن الثقيلة لتقييم جودتها وفقًا للنشريات القياسية. أشارت النتائج المتحصل عليها إلى أن تركيزات الرصاص والزئبق تتراوح بين (0.007-0.0125) و (0.0 - 0.0095) مجم / كجم على التوالي. نلاحظ أن مستويات الرصاص والزئبق في جميع العينات المختلفة كانت ضمن الحدود المسموح بها وفقًا لمعايير منظمة الصحة العالمية والاتحاد الأوروبي. لم يتم العثور على الكاديوم في جميع العينات.

### INTRODUCTION

The pollution of marine ecosystems is a worldwide problem, and the situation is aggravated by the ability of these ecosystems to concentrate and accumulate some metals within the food chains (Jinadasa *et al.*, 2010). The molluscs, crustaceans, cephalopods, fish and others seafood are an important part of the human diet that can be naturally rich or contaminated with some heavy metals (García, *et al.*, 2016; Yi *et al.*, 2017). Fish can

concentrate very high levels of these contaminants, sometimes exceeding authorized limits. This bioaccumulation is closely related to the place of some fish species at the top of the aquatic food chain (Chahid *et al.*, 2014). Fish are a significant source of proteins, vitamins, minerals, and omega-3-polyunsaturated fatty acids whose benefits an important role in the prevention of most cardiovascular pathologies. But the polluted water from industrial and domestic waste water leads to fish contaminated by toxic metals (Olmedo *et al.*, 2013). Heavy metals like cadmium (Cd), mercury (Hg) and lead (Pb) can interfere with biological systems and have

inappropriate interactions with different intracellular structures. They are highly toxic to marine organisms and human, even at very low concentrations due to bioaccumulation (Ungureanu and Mustatea, 2022). Absorbed mercury in humans becomes more toxic due to its prolonged half-life. Its interaction is not limited with various enzymes and proteins, it has a great affinity with thiol group in proteins and can cause damage and dysfunction of the central nervous system (CNS) (Jyothi and Farook, 2020). Cd and Pb are extremely harmful to humans, and excessive amounts may harm the kidneys and induce chronic toxicity signs such as decreased organ function, infertility, hypertension, tumors, and hepatic malfunction (Khansari *et al.*, 2005). Lead exposure is associated with neurodevelopmental effects which can impact brain function, and lower intelligence quotient, delayed growth, hearing loss, impaired fertility, and adverse pregnancy outcomes. Because of neurodevelopmental effects, fetuses, infants, and children are the most sensitive to lead exposures (Dahiya *et al.* 2005). Levels of heavy metals in fish and canned fish samples have been widely reported in the literature (Tarley *et al.*, 2001; Mol, 2010; Kumar *et al.*, 2013; Halabi 2015; Popovic *et al.*, 2018; Mehoul *et al.*, 2019; Kowalska *et al.*, 2020; Alcalá-Orozco *et al.*, 2021; Rakib *et al.*, 2021; Islam and Mustafa, 2022; Bufarwa *et al.*, 2022 Aljabryn, 2022, Kasmí *et al.*, 2023).

Data or information on the heavy metal content in canned fish is important to ensure safe consumed fish for human consumption. The Aim of the present study was the determination of heavy metals levels cadmium (Cd), mercury (Hg) and lead (Pb) in fresh and canned Sardines produced in different countries of the Mediterranean region.

**MATERIALS AND METHODS**

• **Sample collection**

Six (6) different Sardines Samples were random collected from the Libyan Market to determine the levels of heavy metals cadmium (Cd), mercury (Hg) and lead (Pb). The Sardines samples include one fresh and five canned Sardines produced in Libya, Malta, Morocco, Tunisia and Spain. The commercial name and Country are summarized in Table (1).

**Table (1): Fresh and canned Sardines.**

SS-1	Alkhoms	Libya
SS-2	Delamaris	Malta
SS-3	Flash	Morocco
SS-4	Nour	Tunisia
SS-5	Calvo	Spain
SF-1	Fresh	Sabratha

• **Procedure used**

The sardine samples were dried at 110 °C until they

attained constant weight. 5.0 mL of nitric acid and 5.0 mL of sulfuric acid was added to 5g of Fish samples in 50.0 mL beaker. After the reaction is complete, the samples were heated up in heat block at 60 °C for 30 minutes, cooled down and then added 10 mL of nitric acid. After drying, the temperature was then raised 150 °C. After cooling, hydrogen peroxide was added until it become clear, and then transferred to the 50.0 mL volumetric flask and completed with di-ionized water. The determination of heavy metals concentration was performed using the PerkinElmer® AAnalyst 800 atomic absorption spectrophotometer (DSL, 2023).

**RESULTS AND DISCUSSION**

Samples of fresh and canned Sardines were analyzed for lead (Pb), Cadmium (Cd) and mercury (Hg) contents, and summarized in Table (2).

**Table (2): Heavy metals concentrations in Sardines.**

	Concentrations in [mg/kg]					
	Cd		Pb		Hg	
	WHO 0.1	EU 0.05	WHO 0.2	EU 0.3	WHO 0.5	EU 0.5
	Experimental		Experimental		Experimental	
SS-1	0.0		0.0093		0.0002	
SS-2	0.0		0.0110		0.0002	
SS-3	0.0		0.0125		0.0001	
SS-4	0.0		0.0070		0.0001	
SS-5	0.0		0.0081		0.0	
SF-1	0.0		0.0088		0.0095	

The World Health Organization has established as the safety permissible limits for heavy metal quantity from eating fishes a weekly, maximum dosage, commonly known as Provisional Table Weekly Intake (PTWI), per kg of body weight. Taking an average human body weight for an adult of approximately 75 kg, we can calculate the quantity per person/per week (Report of experts, 2004). Therefore, these limits are given in µg/person/week and are the following:

Hg: 5 µg/(kg.p.w.) = 375 µg/person/week  
=0.375 mg/person/week

Cd: 7 µg/kg.p.w. =525 µg/person/week  
= 0.525 mg/person/week

Pb: 25 µg/kg.p.w.=1,875 µg/person/week  
= 1.875 mg/person/week.

Furthermore the EU Regulation1881/2006/EU has established the following maximum concentration limits in fish tissues for Hg, Cd, Pb and these are 0.5 mg/kg, 0.05 mg/kg and 0.30 mg/kg, respectively.

The study revealed that the average concentrations of lead and mercury in the examined samples of canned and fresh sardines were 0.0093 ± 0.00188 mg/kg and mercury 0.0017± 0.00383 respectively. It was observed

that the levels of Lead and Hg in all different samples were within the permissible limit according to the WHO and EU Standards.

## CONCLUSION

Aim of the present study was the determination of heavy metals levels in fresh and canned Sardines produced in different countries of the Mediterranean region. Six (6) different Sardines Samples were random collected from the Libyan Market to determine the levels of heavy metals cadmium (Cd), mercury (Hg) and lead (Pb). The Sardines samples include one fresh and five canned Sardines produced in Libya, Malta, Morocco, Tunisia and Spain. The determination of heavy metals concentration was performed using the PerkinElmer® AAnalyst 800 atomic absorption spectrophotometer in Delta Technical Services (DSL) company Tripoli Libya. The study revealed that the average concentrations of lead and mercury in the examined samples of fresh and canned sardines were  $0.0093 \pm 0.00188$  mg/kg and mercury  $0.0017 \pm 0.0038$  respectively.

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