

## Accumulation of Cadmium and Lead in the muscles of *Sardinella maderensis* and *Alosa fallax* caught from the Syrian marine waters.

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### □ ABSTRACT □

The research was conducted on *Sardinella maderensis* (Lowe, 1838) and *Alosa fallax* (Lacepède, 1803), based on their importance for local consumption as food for humans and bait in catching other fish species. Fish samples were collected from the Ras Al-Baset area north of the Syrian coast during the period between 20/October/2021 and 14/September/2022. 10g (wet weight) was taken from the muscles of 360 individuals. The concentrations of Cadmium and Lead were measured using an Atomic Absorption Spectrometer device (AAS) and flame technology. The results showed high values of Lead (0.11-1.54µg/g) and Cadmium (0.11-0.27µg/g) in *Sardinella maderensis* muscles as well as in the muscles of the *Alosa fallax* (Lead=1.46, 1.02 µg/g, and Cadmium= 0.26, 0.11 µg/g) in comparison with the cut-off values allowed by the international organizations FAO&WHO (2010), The highest values recorded were in the summer period of the studied year 2021-2022 AD.

**Keywords:** Heavy metals, Syria, *Sardinella maderensis*, *Alosa fallax*. Cadmium, Lead.

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## تراكم الكاديوم والرصاص في عضلات السردين العريض *Sardinella maderensis* والسردين القشر *Alosa fallax* المصطادة من المياه البحرية السورية

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### □ ملخص □

أجري البحث على نوعين من فصيلة أسماك *Clupeidae* هما السردين القشر والسردين العريض انطلاقاً من أهميتهما للاستهلاك المحلي كغذاء للإنسان وكذلك كطعم في اصطياد أنواع سمكية أخرى. جمعت العينات السمكية من منطقة رأس البسيط شمال الساحل السوري خلال الفترة بين 20/تشرين الأول/2021 و 14/أيلول/2022، أُخِذَ 10g (وزن رطب) من العضلات لـ 360 فرد، قيست تراكيز عنصري الكاديوم والرصاص باستخدام جهاز الامتصاص الذري (AAS) بتقانة اللهب. بينت النتائج وجود قيم مرتفعة لعنصري الرصاص (0.11-1.54 µg/g) وللكاديوم (0.11-0.27 µg/g) في عضلات السردين العريض وكذلك في عضلات السردين القشر الرصاص (1.02، 1.46 µg/g) والكاديوم (0.11، 0.26 µg/g) وذلك بالمقارنة مع القيم الحدية المسموح بها عالمياً التي وضعتها المنظمات الدولية FAO&WHO (2010)، لكلا النوعين. وسجلت أعلى قيم للعنصرين في فصل الصيف من عام الدراسة 2021-2022م.

**الكلمات المفتاحية:** العناصر الثقيلة، سوريا، السردين العريض، السردين القشر، الكاديوم، الرصاص.

حقوق النشر : مجلة جامعة تشرين- سورية، يحتفظ المؤلفون بحقوق النشر بموجب الترخيص



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## Introduction

Sardines occupy great importance among the economic fish from fishing landings on the Syrian coast and are also caught by fishermen to use as bait for catching other fish.

*Sardinella maderensis* and *Alosa fallax* are pelagic fishes, found in the Mediterranean Sea, feed mainly on zooplankton, less on phytoplankton, and spawn in spring, (Golani *et al.*, 2006).

Sardines are used as an important food rich in protein and fat. They also contain an important group of nutrients that the body needs, such as Iron, Phosphorus, Calcium, Sodium and Zinc; in addition to many vitamins, including vitamin D and omega.3. Fish are also used as bioindicators in the aquatic systems to assess latent contamination of trace elements (Kaushik and Seiliez, 2010).

Heavy metals are naturally occurring elements with high atomic weights and weight and their densities are at least five times greater than water. Their multiple industrial, domestic, agricultural, medical, and technological applications have made them to be widespread in the environment. This has raised concerns about their potential effects on human health and on the environment (Qabas, 2010). Their toxicity depends on several factors including dose, mode of exposure, chemical composition, as well as age, sex, genetics, and nutritional status of exposed individuals. Arsenic, Cadmium, Chromium, Lead, and Mercury are among public health priority minerals. These metals are systemic toxicants that are known to induce damage to many organs, even at low exposure levels. It is also classified as a human carcinogen (known or probable) according to the US Environmental Agency and the International Agency for Research on Cancer (Tchounwou *et al.*, 2012).

Lead is one of the heavy, highly toxic, and deadly chemical elements whose accumulation leads to a condition known as lead poisoning, which hurts the brain (Ziada, 2005). Also, Cadmium is a highly toxic heavy metal, as exposure to very small doses for long periods would cause chronic toxicity which is one of the most important health problems resulting from the accumulation of Cadmium in the body: kidney disease, high blood pressure, heart enlargement and anemia (Kloke, 1980; De boo, 1990).

Pollution with heavy elements has devastating effects on the aquatic environment. This pollution has led to global pollution of fish with substances harmful to health. This pollution occurs as a result of human activities, such as the use of pesticides, sewage, and agricultural and industrial remnants. The assessment of toxic and dangerous compounds accumulated in aquatic organisms gives direct information about the seriousness of pollution in the aquatic environment. Among animal species, fish are animals that cannot get rid of the harmful effects of these pollutants or elements (Alsaraj *et al.*, 2014). Concentrations of heavy metals in fish muscles increase compared to their proportions in seawater and sediments (Tariq *et al.*, 1993).

## The importance of the research and its objectives:

The importance of the research arises from knowing the content of heavy elements (Pb, Cd) in two species of economically important sardines that are consumed by living organisms, including humans.

This study aims to:

- 1: Measuring the percentage of cadmium and lead accumulations in *S. maderensis* and *A.fallax* caught from Syrian marine waters.
- 2: Evaluation of the quality of the studied area through the values of heavy metals in the muscles of *S. maderensis* and *A. fallax*.

## 2: Material and methods:

*Alosa fallax* (Figure 1) and *Sardinella maderensis* (Figure 2) were collected from Ras Al-Basit area 35.8524°N, 35.8378°E (Figure 3) using the locally used fishing nets: Gill nets (opening diameter 18 mm) and Purse nets (opening diameter 16 mm). The total number of individuals reached (180 for each species), caught during the period 20/October/2021 to 14/September/2022 AD. Ras Al-Basit is 60 km north of Lattakia, and the waters of this area are relatively clean, as there are no obvious sources of pollution.

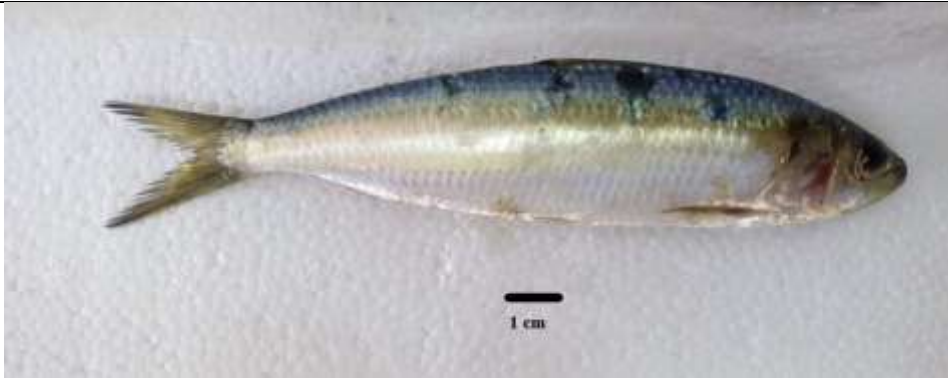


Figure (1): *Alosa fallax*, 17 cm , 14.45 g , caught from the Syrian coast on 10/19/2021



Figure (2): *Sardinella maderensis*, 24 cm, 127.72 g, caught from the Syrian coast on 10/19/2021

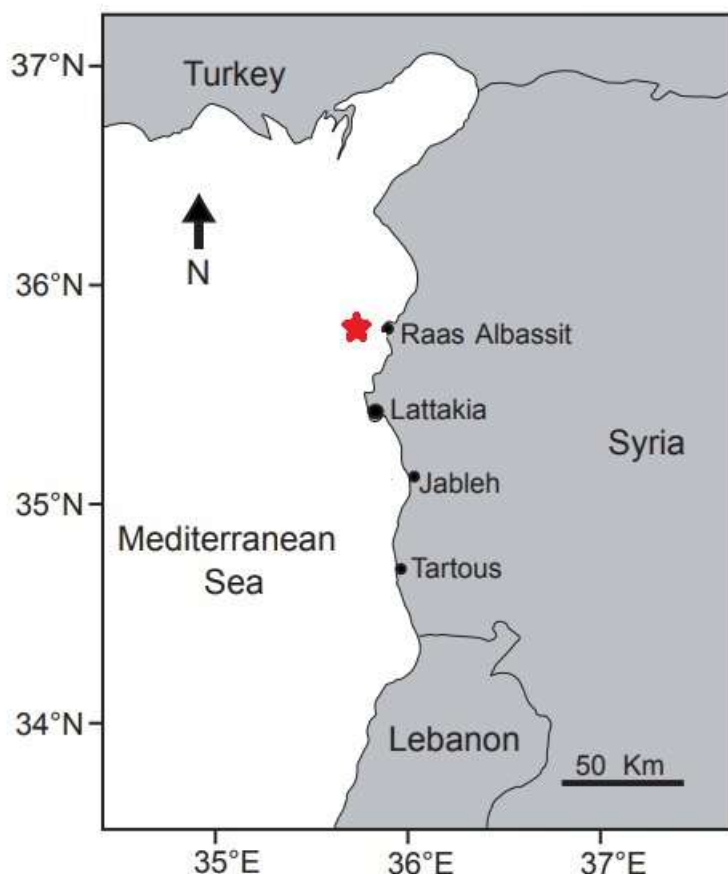


Figure (3): Sampling site, Ras Al-Baset, Lattakia, Syria.

Fish samples were sorted according to size into three groups (big, medium, and small). After that, 10 grams of muscle were taken from each fish, after removing the skin and bones from the muscles. Thus, we had four groups, each group includes three categories of samples of different sizes. The tissue samples were dried using a special dryer at a temperature of 105 ° C Twenty-four hours until the weight stabilizes (Hanson,1973). Dry weights were taken and 2 g samples were placed in 50 ml polyethylene containers for digestion according to IAEA (2006), which is based on the principle of digesting samples using 10 ml of high-purity nitric acid. The samples were left for an hour at room temperature and the tubes were gently and incompletely closed and placed in a water bath at boiling point for four hours until complete digestion. The samples were then cooled to room temperature and diluted with double distilled water to a volume of 50ml to be ready for measurement using flame technology under the analytical conditions listed in Table (1).

Table (1): Instrumental Conditions Approved for Analysis on Atomic Absorption Spectrometer (Flourea-AAS) Technology:

Bulb Type	Flame Type	Slit hole (nm)	Bulb current (mA)	Wave length (nm)	Element
HCL	Air-Acetylene	0.5	4	228.8	Cd
HCL	Air-Acetylene	0.2	10	217	Pb

Tools and devices used: Atomic Absorption Spectrometer (Varian220 type) of the High Institute of Marine Research, drying oven (Bleu M type), various glass laboratory tools, Electric mixer, 0.0001g sensitive balance.

Chemicals used: Concentrated nitric acid 65%, mineral buffers (1000mg/l).

**Statistical analysis:** Pearson correlation test was carried out using spss.

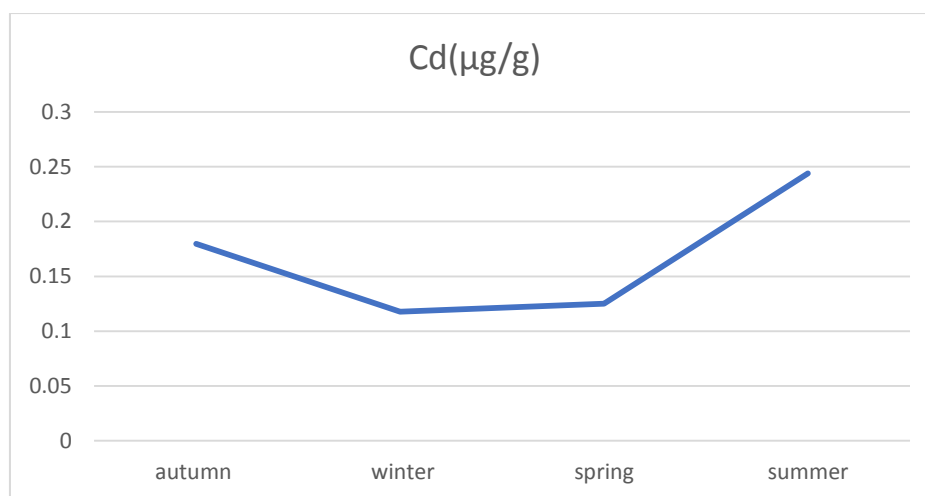
### Results and Discussion:

The results of the research on *S.maderensis* caught from the marine waters of the coast of Lattakia. that there is an increase in the concentration of Cadmium and Lead in the summer compared to the other seasons (Figures 4-5) The values of Cadmium (1.27 µg/g) and Lead (0.16 µg/g) in *S.maderensis* muscles were higher than the values permitted by the international organizations (FAO/WHO, 2010) shown in Table (4), but they were within the permissible values, according to (FAO/WHO, 2003) except the values in the summer were also higher than (FAO/WHO, 2003) .

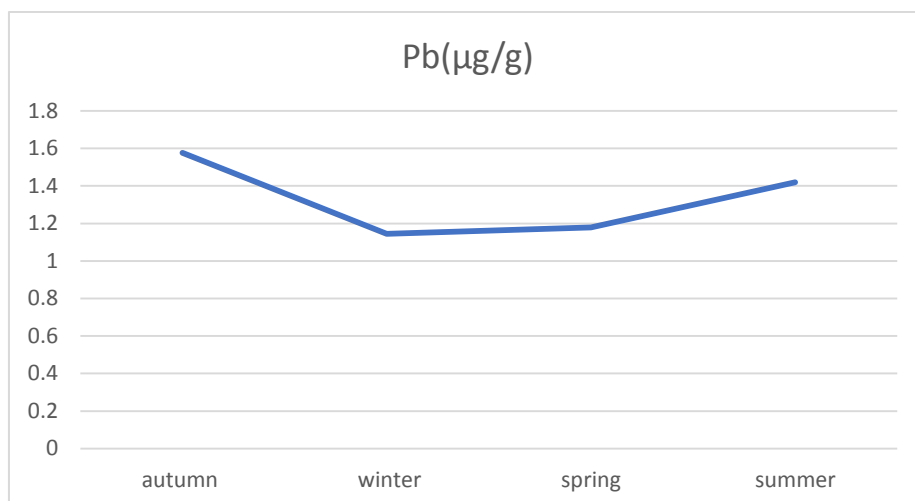
**Table (2): Seasonal concentrations of Cadmium and Lead in *Sardinella maderensis* muscles caught from Ras Al-Baset 2021-2022.**

Cd(µg/g)	Pb(µg/g)	Samples	
0.196	1.428	Large (21-26cm)	Autumn
0.178	1.364	Medium (15-20cm)	
0.165	1.281	Small (10-14cm)	
0.122	1.165	Large (21-26cm)	Winter
0.117	1.176	Medium (15-20cm)	
0.114	1.092	Small (10-14cm)	
0.131	1.225	Large (21-26cm)	Spring
0.125	1.193	Medium (15-20cm)	
0.119	1.118	Small (10-14cm)	
0.273	1.539	Large (21-26cm)	Summer
0.234	1.382	Medium (15-20cm)	
0.225	1.337	Small	
0.1666	1.2750	Asthmatic average	
0.05457	0.13672	Standard deviation	
0.11	1.54	Maximum	
0.27	0.11	Minimum	

The results revealed a strong correlation between Cadmium and Lead in the muscles of *Sardines maderensis*, ( $R= 0.933$ ).



**Figure (4): Seasonal changes of Cadmium concentrations in *Sardinella maderensis* muscles caught from Ras Al-Baseet, 2021-2022 AD.**



**Figure (5): Seasonal changes of Lead concentrations in *Sardinella maderensis* muscles caught from Ras Al-Baseet, 2021-2022 AD.**

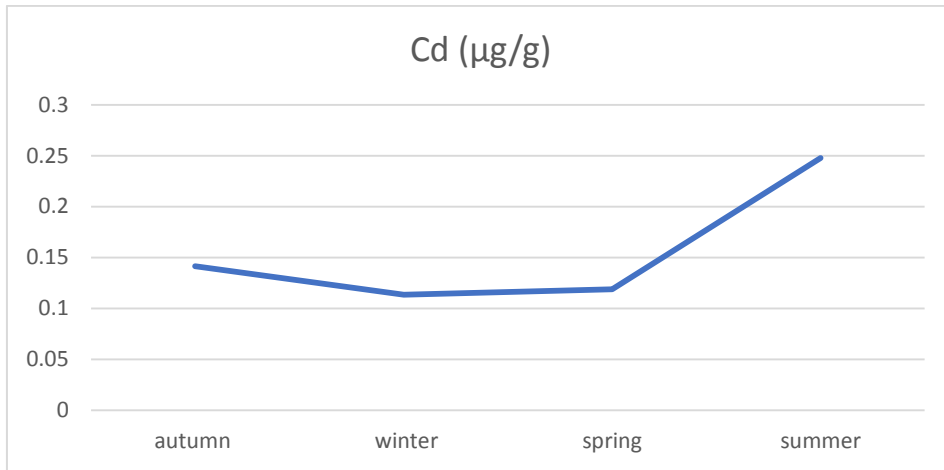
Likewise, for *A. fallax*, the values of Cadmium and Lead in the muscles (Table. 3) were higher than the internationally allowed values, except when compared with FAO/WHO(2003) where the values become acceptable in all seasons except in the summer when these values were high. There was also a rise in the concentrations of Cadmium and Lead in the summer compared to the other seasons (Fig. 6.7).

**Table (3): Seasonal concentrations of Cadmium and Lead in the muscles of *Alosa fallax* from Ras Al-Baset 2021-2022 AD. (B: Big sample, M: Medium sample S: Small sample)**

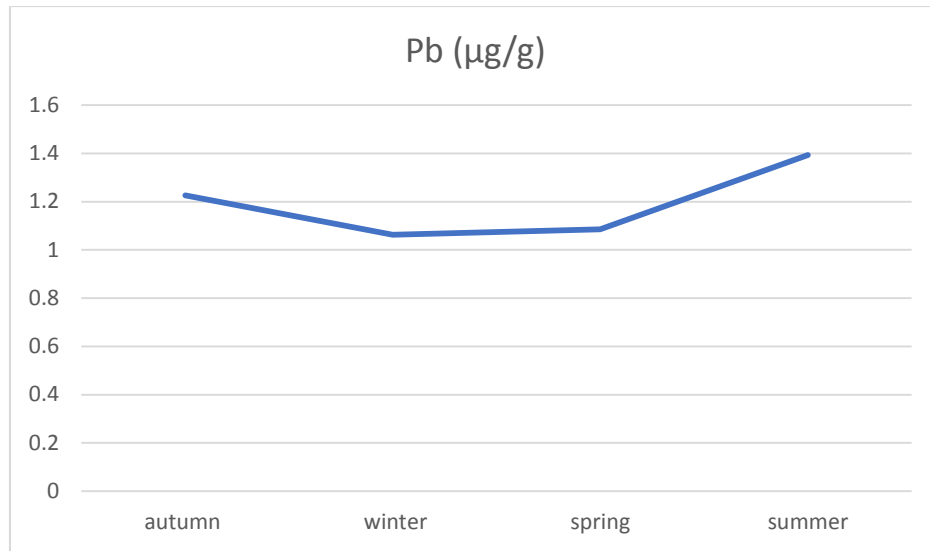
(µg/g) Cd	(µg/g) Pb	Samples	
0.152	1.358	Large (21-26cm)	Autumn
0.139	1.173	Medium (15-20cm)	
0.134	1.148	Small (10-14cm)	
0.116	1.113	Large (21-26cm)	Winter
0.113	1.057	Medium (15-20cm)	
0.112	1.018	Small (10-14cm)	
0.124	1.124	Large (21-26cm)	Spring
0.118	1.108	Medium (15-20cm)	
0.115	1.025	Small (10-14cm)	
0.258	1.459	Large (21-26cm)	Summer
0.249	1.427	Medium (15-20cm)	
0.236	1.293	Small (10-14cm)	
0.1555	1.1919	Arithmetic average	
0.05703	0.15400	Standard deviation	
0.26	1.46	Maximum	
0.11	1.02	Minimum	

The results showed that there was a strong correlation between the values of Cadmium and Lead in *Alosa fallax* muscle correlation coefficient (R= 0.897).





**Figure (6): Seasonal changes of Cadmium concentrations in *Alosa fallax* muscles from Ras Al-Basit 2021-2022 AD.**



**Figure (7): Seasonal changes of Lead concentrations in *Alosa fallax* muscles caught from Ras Al-Basit 2021-2022 AD.**

**Table (4): Internationally permissible limit values for the accumulation of Lead and Cadmium (for reference):**

References	Heavy Elements	
	Pb(µg/g)	Cd(µg/g)
FAO(1983)	0.5	0.05
FAO/WHO(1989)	0.5	0.05
WHO(1989)	2	The analysis is not done
FAO/WHO(1992)	0.5	0.05
USFDA(1993)	The analysis is not done	0.01-0.21
EU(2001)	The analysis is not done	0.1
EuropeanCommunity(2005)	0.2	0.05
FAO/WHO (2003)	1.5	0.2
FAO/WHO (2010)	0.5	0.05

Several studies were conducted on other fish species as bioindicators of Cd and Pb pollution in the Syrian coastal waters (Table 5).

**Table (5): Some studies conducted on the measurement of heavy metals for different fishes species from the Syrian coast:**

References	( $\mu\text{g/g}$ ) Cd	( $\mu\text{g/g}$ ) Pb	fish sample
(Mohamad,2000,2001,2007)	0.14- 0.075	0.41-0.28	<i>Mugil sp.</i>
Soliman <i>et al.</i> , 2021	0.26-0.12	0.26 - 0.21	<i>Siganus luridus</i>
Salah <i>et al.</i> ,2022	0.17-0.005	0.315- 0.016	<i>Siganus rivulatus</i>
(Hammoud and Salma,2016)	0.006	0.04	<i>Saprus aurata</i>
	0.021-0.006	0.78- 0.28	<i>Mulus barbatus</i>
(Sarem <i>et al.</i> ,2015)	0.091	0.043	<i>Chelon labrosus</i>
(Jaber,2018)	0.36-0.18	1.33- 1.15	<i>Lithognathus mormyrus</i>
(Akel <i>et al.</i> ,2017)	0.78 - 0.58	0.30 -11.19	<i>Boops boops</i>

In comparison with the internationally allowed limits (Table 2), all of these values indicate the pollution of the Syrian marine coastal waters with Lead and Cadmium that accumulated in the muscles of the studied fish.

Few studies have been done on sardines tendency to accumulate heavy metals in their muscles and the suitability of such fish as bioindicators (Table 6).

**Table (6): Some of the studies conducted on the measurement of heavy metals in sardines of different regions:**

Cadmium ( $\mu\text{g/g}$ )	Lead( $\mu\text{g/g}$ )	The sample	Reference
0.5	0.7	<i>Alosa fallax</i>	(Durrieu <i>et al.</i> ,2005) France
0.1	The analysis is not done	<i>Sardinella maderensis</i>	(Celina& Aroloye, 2020). Nigeria
0.02	0.05	<i>Alosa fallax</i>	(Bat <i>et al.</i> ,2017) Turkey
0.16- 0.132	0.239- 0.223	<i>Sardine sp.</i>	(Mohamad,2000,2007) Syria

We note from the table that there are differences between the studied species, and all the species differ from those dealt with in this study. This is due to what was mentioned in many studies about the factors upon which the accumulation of heavy elements in different tissues depends within fish. The difference may be due to a change in feeding pattern, food behavior and metabolism (Ogbeibu and Ezeanara,2002; Rauf *et al.*,2009) and may also due to water temperature and metabolic rates (Oguzie, 2003). The accumulation of heavy metals may vary according to age, species, sex, size, and the duration of exposure to heavy metals (Idodo-Umeh, 2002). In addition, the accumulation values of heavy metals in fish tissues vary according to metal absorption and storage rates (Kalay and Canli.2000).

The exposure of the marine ecosystem in the recent years to pollutants of different types, including oil spill incident from Baniyas oil refinery on 24/8/2021, as well as the crisis effects, that began since 2011, were the most important reasons for the high concentrations of heavy elements in living organisms, especially fish.

## Conclusions:

- The values of the concentration of Lead and Cadmium in the muscles of *Sardinella maderensis* and *Alosa fallax* caught in the Syrian marine waters of Lattakia-Ras Al-Baset 2021-2022 AD are higher than the internationally permitted limit values.
- The concentrations of Cadmium and Lead in the muscles of *Sardinella maderensis* and *Alosa fallax* had changed according to the seasons of the year (2021-2022), and were the highest in the summer compared to the other seasons..

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