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Seasonal Variations of copper and lead bio-accumulation in two fish species: *Mullus barbatus* and *Siganus rivulatus* in the southern part of the Syrian Coast

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Abstract

Seasonal variations in the concentrations of two heavy metals: copper (Cu) and lead (Pb) were determined in the liver and muscles of *Mullus* the two species *barbatus* and *Siganus rivulatus fish* from the southern part of Syrian Coast. The average concentrations of the metals in the fish tissues exhibited the following order: Cu>Pb. The statistical analysis revealed a significant seasonal effect P≤0.05 for Cu and Pb measured. The highest values of the metals were recorded in dry season. The highest concentrations of heavy metals were found in liver tissue of both fish species, while the lowest concentrations were recorded in muscles tissue. The values of the metals detected in the fish muscles (the edible part) were within the permissible limits

Keywords: Heavy metals, Bio-accumulation, *Siganus rivulatus*, *Mullus barbatus*, Syrian Coast.

Introduction

Fish is one of our most valuable sources of protein food in human nutrition (Bahnasawy *et al*., 2009). In Syria the two species *Mullus barbatus* and *Siganus rivulatus* are economically and very important fish (Ulman *et al*., 2015; Saad *et al*, 2017). The aquatic system become contaminated with heavy metals released from domestic, agricultural and industrial activity which are continuously discharged into it (Bahnasawy *et al*., 2009).

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Agricultural runoff contains high concentrations of different pesticides, fertilizers and heavy metals (Weber *et al*., 2013). Fish are generally considered to be an important bioindicator of aquatic environments. Fish, which usually constituent the last ring of the food chain, is considered to be one of the important groups for transferring metals to humans (Aytekin *et al*., 2019). Seasonal Variations of heavy metals in different fish tissues has been studied by several investigators (Hammoud, 2005; Beldi *et al*., 2006; Bahnasawy *et al.,* 2009; Sarem, 2015; Mohanraj *et al*., 2021). El-Moselhy, (2003) indicated that seasonal variations in the accumulation of the heavy metals in the marine organisms were affected by several and complicated factors, such as wind, the current regime, salinity variation during different months, the impact of different pollution sources.

Therefore, this study examined the seasonal variations of heavy trace metal concentrations in *Mullus barbatus* and *S. rivulatus* from the southern part of the Syrian Coast. Two fish species studied in this work differ from each other with respect to their feeding habits.

Fish Sampling and Analysis.

Samples *M. barbatus and S. rivulatus* (Fig. 12-) were collected from the southern part of Syrian (34°59'46» N, 35°53'21» E to 35°10'11» N, 35°55'36» E). (Fig. 3) during the seasons of 2019 to 2020, to determine metal in their tissues. The fishes were immediately placed on ice in an insulated box and transported immediately to the laboratory and stored at -20 C until analyzed. Total weight and Lengths for all individual was measured with the nearest 0.1 cm and 0.1 g. Two organs (liver and sufficient amount of muscle) were dissected. The rainy digestion method was used in the analysis of heavy metals. Samples were transferred into digestion flasks and treated with 5 ml HNO3 (ultrapure, Merck) on the hot plate until the color turns into light yellow, nearly white. After this process, the samples were transferred to 25 ml flanks and added double distilled water until 25 ml. The solution was filtered by filter papers. After digestion, all the samples were analyzed for the trace metal (Cu and Pb) concentrations using a computer controlled Atomic Absorption Spectrophotometer. The accuracy of the employed method was tested with a reference material.

Figure 1: *M. barbatus* sampled from southern part of Syrian

Figure 2: *S. rivulatus* sampled from southern part of Syrian.

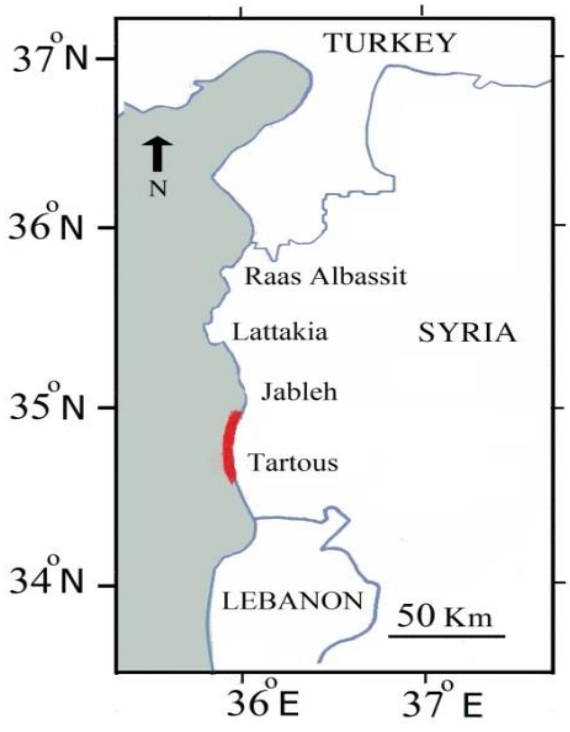


Figure. 3: Sampling sites in the southern part of Syrian Coast

Table 1: Concentration of heavy metals (µg/g rainy weight) of *Siganus rivulatus* and *Mullus barbatus* collected from the southern part of the Syrian Coast.

Sp.			**Heavy metals concentration**	
Siganus rivulatus	muscles	Season	Cu	Pb
		dry	0.729	0.0173
		Rainy	0.54	0.019
		Mean	0.626	0.0185
		± SD	0.20	0.003
		t-value	-8.48	11.18
		P	<0.001	<0.001
	liver	dry	48.5	0.11
		Rainy	32.46	0.065
		Mean	40.47	0.1
		± SD	18.20	0.09
		t-value	3.27	4.53
		P	0.01	0.004
Mullus barbatus	Muscles	dry	0.59	0.0644
		Rainy	0.51	0.049
		Mean	0.552	0.056
		± SD	0.088	0.022
		t-value	-3.07	-4.34
		P	0.028	0.007
	liver	dry	10.45	0.1745
		Rainy	7.39	0.1315
		Mean	8.92	0.153
		± SD	2.40	0.088
		t-value	-4.80	-2.04
		P	0.005	0.096

Total Heavy Metal Concentrations in *Mullus barbatus*

The metal Cu was P≤0.05 in white muscle and liver of *M. barbatus* caught from dry and rainy (table 1). The mean Cu concentration in fish muscles from Syrian coast ranges between 0.51 / µg /g in rainy season to 0.59 µg/g in dry season and 7.39 at rainy to 10.45 at dry µg/g in liver (table.1)

In *M. barbatus,* according to the t-test, level of Cu metals under investigation was significantly in the muscle and liver tissues in dry compared with rainy.

The mean pb concentration in white muscle tissues showed significant differences between seasons (table 1). The mean concentration of pb in the muscle of *M. barbatus* ranged from 0.049 µg/g and 0.0644 µg/g and show significant differences between the seasons (table 1).

The mean Pb bio accumulation of ranged from 0.131 at rainy to 0.174 at dry µg/g in liver. Pb levels in liver tissues did not show significant differences between season (table 1)

Total Heavy Metal Concentrations *Siganus* in *rivulatus*

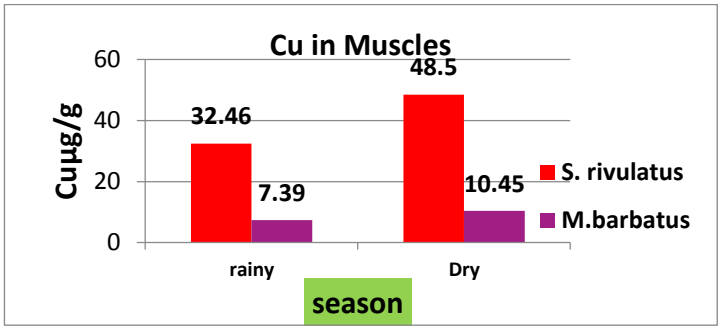
There were P≤0.05 in the metals Cu and pb accumulated in the white muscle and liver of rabbitfish caught seasonally from dry and rainy seasons.

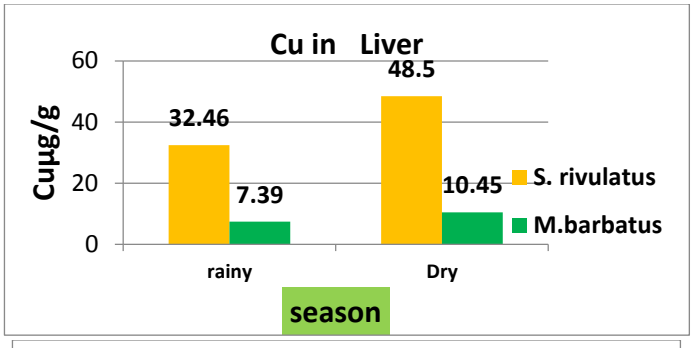
The metal Cu was P≤0.05 in white muscle and liver of rabbitfish *(S. rivulatus)* caught from dry and rainy (table.1). The mean Cu concentration in fish muscles from Syrian coast ranges between 0.54 / µg /g in rainy season to 0.729 µg/g in dry season and 32.46 at rainy to 48.50 at dry µg/g in liver (table 1)

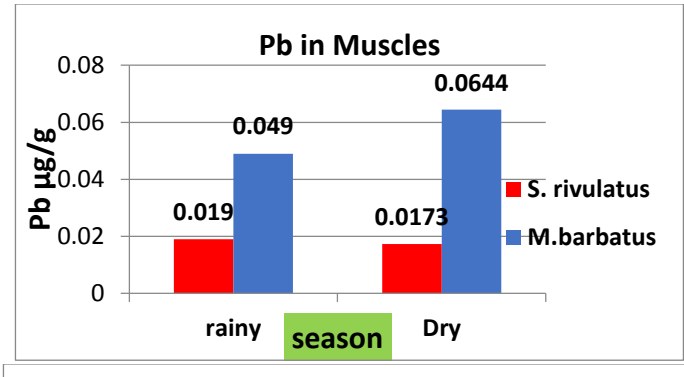
In *S. rivulatus*, according to the t-test, level of Cu metals under investigation was significantly in the muscle and liver tissues in dry compared with rainy.

The mean pb concentration in white muscle and liver tissues showed significant differences between seasons (Table 1). The mean concentration of pb in the muscle of S. *rivulatus* ranged from 0.017 µg /g to 0.019 µg/g and show significant differences between the seasons (table 1).

The mean Pb bio accumulation of ranged from 0.065 at rainy to 0.11 at dry µg /g in liver. Pb levels in liver tissues were different between seasons (table 1).







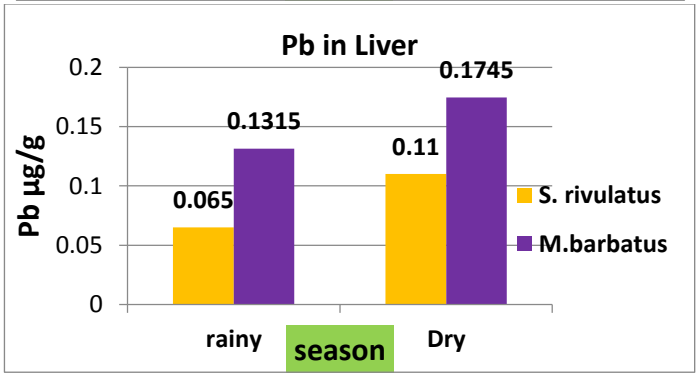


Figure 4: Heavy metals in white muscle of *S. rivulatus* and *M. barbatus* collected seasonally from the southern part of Syrian Coast.

Pb and Cu concentrations displayed the same distribution pattern in the tissues of (*M. barbatus* and *S. rivulatus*. The highest metal concentration was found in the liver while the lowest levels of the heavy metals were recorded in the muscle (Fig. 4). Metals concentrations in liver and muscle of the examined fish follow the sequence: Cu> Pb.

The liver is situated directly in the way of the blood vessels that convey substances absorbed from the digestive system. Therefore, the liver the first chance to metabolize these substances making it to be the first organ to be exposed to toxic compounds (Opute *et al*., 2016).

Muscles, in the present study, contained the lowest levels of heavy metals. This result agrees with many authors who reported that muscles are not active tissue in accumulating heavy metals. (Saad and Hammoud, 2007; Mohamed, 2008; Sarem *et al*., 2015; Hammoud and Salama, 2016). The accumulation of metals in two fish species *S. rivulatus and M. barbatus* increased in the dry season than rainy season (fig .4). This may be related to increasing human activities in these seasons (Hegazi *et al*., 2015) and an increase in the physiological activity of fish due to an increase of temperature this is confirmed by previous studies such as (Jakimska *et al*., 201; Aytekin *et al*., 2019). Similar increases in metal levels were observed during the dry season in fish from the Syrian coast. (Sarem *et al*., 2015; Hammoud and Salama, *2016*). Shreadah *et al*. (2016) found also an increase in concentration of most metals in Some Fish Species during summer which could be a result of human impact and traffic increase.

Many studies attributed high metal accumulation to the feeding habit of the fish. (Bahnasawy *et al*., 2009; Khaled, 2004). *S. rivulatus* showed a tendency to accumulate (Cu) in the liver and muscles with relatively high concentrations. Feeding habit may be one reason for metal variation in *S. rivulatus* ,which accumulated relatively high bio accumulation of Cu in the liver and muscles (Fig.4). These findings in *S. rivulatus* could be linked to feeding on phytoplankton since it is the most likely biota compartment for Cu concentration. The same results were previously recorded by Khaled (2004) in two fish species (*S. rivulatus* and *sargus sargus*) collected from EL-Mex Bay and Eastern Harbour, Alexandria, Egypt. A higher level of pb Was recorded for *M. barbatus* relative to that in *S. rivulatus* in dry and rainy season during the study (Fig.4). *M.*

barbatus is a carnivorous feed mainly on crustaceans, mollusks beside small fishes while the second is herbivorous

Conclusion

It was found that minerals accumulated (Cu and Pb) in different tissues of Mullus barbatus and Siganus rivulatus at different levels and different seasons, as the inedible parts accumulated more minerals than in the edible muscles. The values of heavy metals in the muscles (the edible parts) of *M. barbatus* and *S. rivulatus* were below recommended limits of the Food and Agriculture Organization/World Health Organization (FAO/WHO) (Cu: 30 and Pb: 0.5 µg/g ww). Therefore, fish muscles in the present study are considered safe for human consumption. It is useful to conduct future studies on the effect of heavy metals on enzyme action in the same current and other fish species in Syrian marine waters.

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التغيرات الموسمية للتراكم الحيوي لعنصري النحاس والرصاص في أنسجة نوعين من الأسماك: السلطاني الرملي ***Mullus barbatus*** والغريبة الرملي ***Siganus rivulatus*** في الجزء الجنوبي من الساحل السوري

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المستخلص

تم تحديد التغيرات الموسمية في تراكيز معدنين ثقيلين: النحاس (Cu) والرصاص (Pb) في الكبد والعضلات لنوعين من الأسماك (*M. barbatus*، و *S. rivulatus*) في الجزء الجنوبي من الساحل السوري. أظهر متوسط تراكيز المعادن في أنسجة الأسماك الترتيب التالي: Cu> Pb. أظهر التحليل الإحصائي تأثير موسمي معنوي $P \geq 0.05$ لتركيز كل من النحاس والرصاص المقاس. تم تسجيل أعلى قيم للمعادن في موسم الجفاف. تم العثور على أعلى تراكيز من المعادن الثقيلة في أنسجة الكبد لكلا النوعين، بينما سجلت أقل التركيزات في الأنسجة العضلية. كانت قيم المعادن المكتشفة في عضلات الأسماك (الجزء الصالح للأكل) ضمن الحدود المسموح بها وفق المعايير الموصى بها من قبل منظمة الصحة العالمية ومنظمة الأغذية والزراعة الدولية.

الكلمات المفتاحية: معادن ثقيلة، تراكم حيوي، سلطاني رملي، غريبة رملي، الساحل السوري.

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