Bioaccumulation Assessment of Trace Metals by Three Main Demersal Fish from Algerian Coast

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Abstract In this study, the level of bioaccumulation of some trace metals (Cu, Zn, Hg, and Ni) by three demersal fishes of the Algerian coast (the red mullet "*Mullus barbatus*", the European hake "*Merluccius merluccius*", and the common pandora "*Pagellus erythrinus*") in relation to their biochemical composition (proteins, lipids and carbohydrates) was estimated. Thirty individuals of each fish species separated into two size classes were collected at different sites during an oceanographic survey along the Algerian coast in the summer of 2013. The specimens were dissected to obtain fish tissue samples from the muscles, liver, and gonads. A difference in the bioaccumulation of the metals analyzed between the three species of fish in relation to sex, size, and organs was revealed. Therefore, a difference in the biochemical composition of the three organs (muscle, liver, and gonads) of the three fishes has been revealed. In addition, significant correlations between Carbohydrates—Zinc, Proteins—Copper and Proteins—Nickel, respectively, were unveiled. However, the lipid level showed no significant correlation with all analyzed metals. Nevertheless, the three fishes (red mullet, European hake, and common pandora) from Ghazaouet and Bou-Ismail bays showed high concentrations on the trace metals analyzed compared to other areas.

Keywords Red mullet · European hake · Common pandora · Bioaccumulation · Trace metals · Biochemical composition

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1 Introduction

One of the anthropogenic impacts on the marine environment is the contamination of the various matrices of this environment by inorganic pollution, in particular trace metals, which are transported from the continental environment to the marine environment by natural water courses and discharges of urban and industrial wastewater. In the marine environment, these trace elements undergo several processes: dissolution and dispersion in the water, complexation and precipitation in the marine sediment, digestion and bioaccumulation by many marine species. Regarding their persistence in the environment, cumulative potency in the food web and toxicity, trace metals are considered a hazardous pollutant to the aquatic environment and organisms. Among these organisms, the most commonly used are bivalves (mussels, oysters) and fishes. In fact, biomonitoring using species from different taxonomic groups with distinct ecological niches or feeding trophic levels enables a fuller assessment of the extent of any contamination [1], and makes it possible to obtain information concerning the geographic and temporal variations of this contamination in the natural environment.

The objective of this study was to evaluate the contamination levels of some trace metals in three marine fishes from the same trophic levels of a food web, representative the main benthic resources in fishing areas along the Algerian coast, with great commercial value: the Red mullet "*Mullus barbatus*", the European hake "*Merluccius merluccius*" and the Common pandora "*Pagellus erythrinus*".

2 Materials and Methods

2.1 Study Area

The Algerian coast along the southwestern side of the Mediterranean Sea is 1300 km long and receives several rivers, the most important being Seybousse, Lekbir, and Soumam on the east, Yesser, Harrach, and Mazafran in the center and Chelif, Tafna on the west (Fig. 1). Algeria's population increased by 95% over the last thirty years with 22 million inhabitants in 1985, 33 million in 2005, and 40.4 million in the end of 2015 [2].

About 45% of this population is concentrated on a very narrow strip of the littoral, especially in industrial and harbor zones, such as Algiers, Annaba, Arzew, Oran, and Skikda [3].

This situation exerts great pressure on the coastal marine ecosystem, and the worsening conditions can be observed on large sections of the coast, particularly in the gulfs close to the biggest agglomerations, such as Algiers, Oran, and Annaba [4].

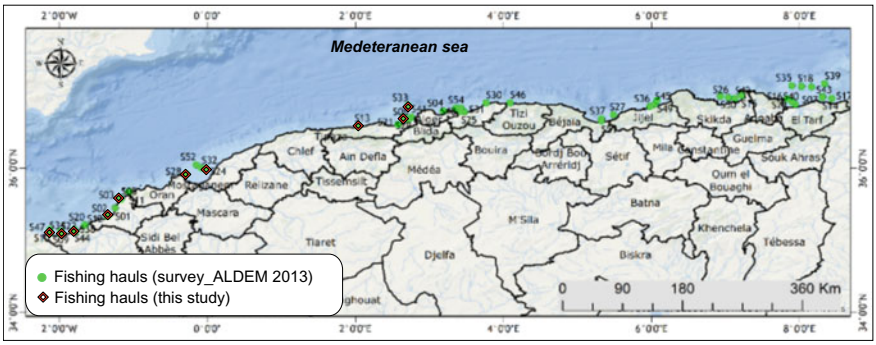

Fig. 1 Location of Algerian coast and fishing grounds along this coast

2.2 Choice of Species

In this study, we chose the red mullet "*Mullus barbatus*", the European hake "*Merluccius merluccius*", and the common pandora "*Pagellus erythrinus*" as indicators of biological species because they respond to several characteristics including abundance, accessibility, longevity, as well as a size facilitating manipulations. Therefore, the choice of these fish species is interesting, because they constitute important links in the food chain, and are highly appreciated by a large population.

2.3 Fish Sampling

Fish samples were collected during an oceanographic survey by a research vessel "Grine Belkacem" during the summer of 2013, in 10 fishing hauls along the Algerian coast (Fig. 1).

A total of 30 specimens per sample in each fishing haul were collected. They were fished by bottom trawl (using standard net GOC 73) following the Mediterranean International Bottom Trawl Survey (MEDITS) protocol. The samples were separated by size and sex, and dissected to remove muscle, liver, and gonads. All samples were placed in glass pillboxes previously rinsed with nitric acid, diluted several times with distilled water, and frozen at (−18 °C) on board. In the laboratory, they were freeze-dried and crushed to powder.

2.4 Analysis of Trace Metals

0.5 g dry biota samples were put into a Teflon vessel with a concentrated acid (7 ml HNO_3). The samples were digested in a hot plate at 120 ° C for nickel, zinc, and

copper and at 90 °C for mercury, between 2h30 and 3 h. In the case of mercury, 1 ml of (K2Cr2O7, 5%) potassium dichromate, (50 g for 500 ml to 10%) was added. The quality of chemical analysis and the accuracy of the data was checked with a blank sample and biota reference material (IAEA-407). The results indicate a good agreement between the certified and analytical values for all metals analyzed. The analysis was achieved by graphite furnace atomic absorption spectrometer (AAS) for copper, zinc, and nickel, while mercury was analyzed by AAS cold vapor.

2.5 Biochemical Analysis

Proteins analysis was carried out according to the "Kjeldahl" method", which is done in three steps: sample digestion or mineralization, distillation of ammonia, and titration of ammonia.

Lipids are insoluble in water and soluble in organic solvents. The extraction of the lipids is performed by the Soxhlet method. It is a gravimetric method, since the sample is weighed at the beginning and at the end of the extraction. Total soluble sugars were determined by the method of [5]. The total carbohydrates are determined by Spectrophotometry at 485 nm. A calibration curve was made from a glucose solution.

2.6 Statistical Analysis

The correlation analysis and Principal Component Analysis (PCA) were used to determine the variation between the four trace metals analyzed in the different organs and between the analyzed metals and biochemical composition levels. Both correlation and PCA were performed using the statistical software package STATISTICA version 6.1 for Windows.

3 Results and Discussion

3.1 Trace Metals Levels

The results showed that the concentrations of zinc are clearly distinct from the other elements (Ni, Cu, and Hg) at very high levels. In fact, for Zn and Cu, the concentrations are higher in the gonads than in the muscle and liver. While, for Hg, the concentrations in gonads are the lowest, the highest concentrations are showed in muscle and liver. In the case of Ni, the concentrations are approximately similar in the three organs (Table 1).

Table 1 Average concentrations of trace metals in organs of the three fishes. (dry weight)

Fish	Organ	Zn (μg/g)	Hg (μg/g)	Ni (μg/g)	Cu (μg/g)
Red mullet	Muscle	31.99 ± 0.7	0.11 ± 0.02	15.13 ± 0.31	5.31 ± 0.21
	Liver	144.59 ± 5.3	0.13 ± 0.02	17.29 ± 0.43	6.53 ± 0.14
	Gonads	190.20 ± 9.1	0.03 ± 0.02	17.23 ± 0.36	9.82 ± 0.23
European hake	Muscle	33.77 ± 1.2	0.13 ± 0.02	7.69 ± 0.14	3.16 ± 0.11
	Liver	67.98 ± 3.2	0.13 ± 0.02	5.29 ± 0.17	4.32 ± 0.12
	Gonads	191.01 ± 8.1	0.10 ± 0.02	5.30 ± 0.21	5.20 ± 0.15
Common pandora	Muscle	34.29 ± 1.8	1.12 ± 0.02	12.14 ± 0.24	2.54 ± 0.32
	Liver	118.20 ± 6.8	0.25 ± 0.02	14.50 ± 0.25	3.28 ± 0.28
	Gonads	227.45 ± 8.9	0.04 ± 0.01	11.17 ± 0.23	6.63 ± 0.27

For the red mullet, the bioaccumulation of zinc and nickel is preferentially done in the gonads, while mercury bioaccumulates mainly in the liver. The immature class seems to be the most bioaccumulative, and it appears that the mercury levels are low in the females during spawning.

For the common pandora, the results show pronounced bioaccumulation of all analyzed trace metals in the liver and gonads compared to the muscle. Compared to sex, it seems that females accumulate trace metals more than males.

For the European hake, the liver appeared to be the most accumulating organ of the analyzed trace metals (Hg, Ni, and Zn). Thus, immature individuals bioaccumulate the three trace metals more than the mature ones. However, both sexes bioaccumulate these trace metals in a similar way.

3.2 Carbohydrates, Lipids, and Proteins Levels

The highest level of lipids is observed in the liver of the red mullet, that of carbohydrates is in the liver of the pandora, while the protein level does not show significant differences between the organs for the three fishes (Table 2).

3.3 Relationship Between Trace Metals and Biochemical Composition

3.3.1 Correlation

The relationships found between trace metals and biochemical composition were reported in Table 3. The results showed that only Zn had a positive significant corre-

Table 2 Average levels of carbohydrates, lipids, and proteins in organs of the three fishes (in %)

Fish	Biochemical component	Muscle	Liver	Gonads
Red Mullet	Carbohydrates	0.7	2.9	2.6
	Lipids	36.0	20.0	32.5
	Proteins	13.6	9.4	3.8
European Hake	Carbohydrates	0.9	0.7	5.1
	Lipids	33.3	59.6	16.6
	Proteins	14.8	4.9	6.6
Common pandora	Carbohydrates	3.1	5.5	5.1
	Lipids	9.1	8.9	12,8
	Proteins	15.0	14.3	13.6

Table 3 Matrix of correlation

	Zn	Hg	Ni	Cu	Carbohydrates	Lipids	Proteins
Zn	1,00						
Hg	– 0,47	1,00					
Ni	0,12	0,03	1,00				
Cu	0,69	– 0,56	0,46	1,00			
Carbohydrates	0,70	0,05	0,07	0,06	1,00		
Lipids	– 0,35	– 0,39	0,13	0,13	– 0,82	1,00	
Proteins	– 0,42	0,42	– 0,62	– 0,62	0,11	– 0,51	1,00

The values in red indicate that the correlation is significant.

lation with the carbohydrates level. Two other metals (Ni and Cu) had negative significant correlations with the proteins level.

The values in red indicate that the correlation is significant

3.3.2 Principal Components Analysis

The Principal Components Analysis (PCA) shows that the two main components represent 72.15% of the total variance (Fig. 2). Thus, the first axis that represents 38.68% of the total variance is well defined negatively for Zn, Cu, and positively for Hg and proteins. The second major component, accounting for 33.87% of the variance, is positively correlated with the element Hg and lipids but negatively with carbohydrates.

Based on this analysis, it was found that:

European Hake accumulates high concentrations of Hg and protein in muscles, high concentrations of Ni and lipids in the gonads and high concentrations of Zn, Cu in the liver. Red Mullet accumulates high concentrations of Zn and Cu in the gonads and liver and high concentrations of Ni, lipids in the muscles.

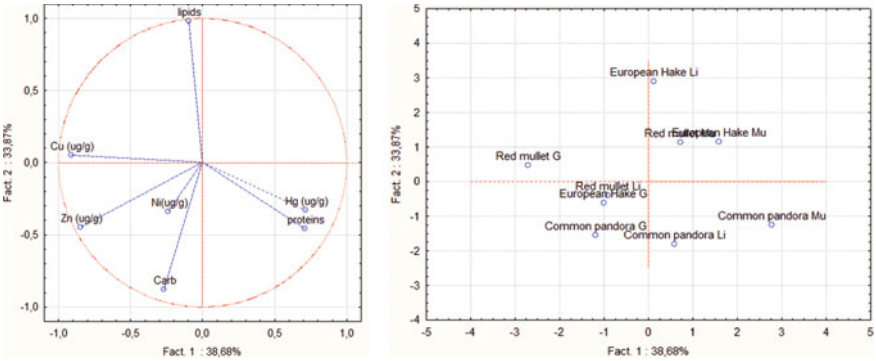

Fig. 2 Projection of trace metals and fish organs on the factorial plans (1x2) and (1x3)

Common pandora accumulates high concentrations of Zn and Cu in the muscles and high concentrations of carbohydrates in the gonads and liver.

4 Conclusion

The results show that the concentrations of zinc in the different organs of three fishes are the highest compared to the other metals (Ni, Cu, and Hg). For the common pandora, a high bioaccumulation level of three metals (Zn, Ni, and Hg) in the liver and gonads compared to the muscle was showed. However, in relation to gender, females accumulate more than males. For the red mullet, bioaccumulation of Zn, Ni, and Cu occurs preferentially in the gonads, while Hg essentially bioaccumulates in the liver. For the European hake, the liver appeared as the greatest accumulating organ of the analyzed metals (Hg, Ni, and Zn).

Thus, immature fish bioaccumulates these metals more than the mature ones. However, both sexes bioaccumulate these metals in the same concentrations. On the other hand, the bioaccumulation of zinc had a high significant correlation with the protein levels in the three organs of the three fishes. That of mercury had a significant correlation with the carbohydrates and lipids. Then, nickel had a significant correlation with protein levels in the Hake, carbohydrates levels in the Red mullet, and lipids levels in the Common pandora, while the bioaccumulation of copper is independent of the biochemical composition for the three organs of three fishes.

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