ANALYSIS OF SEAWATER QUALITY ON THE ORAN COAST USING PHYSICO-CHEMICAL PARAMETERS AND TRACE METALS (FE, MN, NI) AND THEIR IMPACT ON *CHELON LABROSUS* (RISSO, 1827) FISH

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Abstract. The Oran coastline in Algeria is a region particularly affected by human activities. This area faces significant environmental concerns in the Mediterranean due to the pressures exerted by urban, industrial, agricultural, and port traffic discharges. Therefore, it is essential to conduct a water quality assessment based on physico-chemical parameters and the measurement of certain trace metals in order to understand their impact on *Chelon labrosus* a species highly valued by the local population. This research is part of an environmental monitoring mission aimed at studying parameters to detect and assess pollution levels in water and in *Chelon labrosus*. The aim of the study is to spatially evaluate the physico-chemical parameters and the concentration of trace metal elements in the water of the Oran coast, as well as the levels of these elements in the various organs of Thick-lipped grey mullet. The results of water quality assessment in the Oran coast have revealed that the general trend in the levels of the parameters analysed shows a deterioration. These results indicate a slight risk, as some parameters exceed international seawater quality standards. Analyses of trace metal elements reveal the presence of these pollutants both in the water taken from the sampling site and in the fish species caught. The highest concentration in seawater was observed for nickel, followed by manganese and finally iron, with values of 0.74 mg/l, 0.56 mg/l and 0.47 mg/l respectively. Compared with the concentration of iron, manganese and nickel found in the water sampled at the sampling site, the levels of these elements in the *Chelon labrosus* are significantly higher, at 1.94 mg/kg, 1.71 mg/kg and 1.09 mg/kg respectively.
Keywords: *thick-lipped grey mullet, trace metal elements, water quality assessment, Oran coastline*

Introduction

The Mediterranean Sea is rich in marine resources. Its unique marine ecosystem of warm temperate waters is characterized by exceptional biodiversity. For millennia, its marine species have been a source of sustenance for mankind and the driving force behind the region's national economies. However, population growth and increased demand for marine resources are leading to concerns about the decline of ichthyological species and the impoverishment of local marine diversity as a whole (Belhoucine, 2012).

In addition to the potential overexploitation of marine resources, pollution, eutrophication, urban development, and habitat degradation are some of the anthropogenic threats facing Mediterranean marine species (Caddy, 1993; Aydoğan and İncekara, 2017; Pal et al., 2018). Among these, marine pollution stands out as one of

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today's most pressing problems. It is often attributed to various anthropogenic activities, such as industrial, agricultural, or domestic practices, and includes different forms of contaminants (hydrocarbons, pesticides, trace metallic elements, etc.) (Aydoğan et al., 2017; Pal et al., 2018). Aquatic environments are particularly affected by metal pollution (Rodrigue et al., 2016). Elements like iron (Fe), nickel (Ni), and manganese (Mn) are considered essential trace elements for living organisms. but can become dangerous if they exceed a certain threshold in the organism (Richir, 2016). Iron (Fe), nickel (Ni) and manganese (Mn) are considered essential trace elements for living organisms but can become dangerous if they exceed a certain threshold in the organism (Richir, 2016). This chemical contamination can represent a toxicological risk and affect marine life and its diversity. Various studies have shown that, in aquatic species, these xenobiotics cause reproductive system disturbances, behavioral changes, disruption of energy metabolism and the appearance of mutagenic or carcinogenic effects (Meyer, 2003). Humans can also be affected by this type of contaminant, which can represent a great risk to their health (Merhaby et al., 2018; Diop et al., 2019; Karikari et al., 2020). In Algeria, pollution is mainly generated by the discharge of untreated industrial and urban wastewater (Taleb, 2007; Grimes et al., 2010). Petrochemical, chemical, iron and steel and agri-food activities are mainly concentrated on Algeria's coastal strip (Grimes et al., 2010). Given this importance, our present study focuses on estimating the state of water quality on the Oran coast, based on monthly monitoring of physico-chemical parameters in the coastal waters of Oran Bay, and on assessing the quantity of trace metal elements (Fe, Ni and Mn) in the organs (liver, gonads and muscle) of a teleost fish *Chelon labrosus* (Risso, 1827) caught on the Oran coast. Our choice fell on thick-lipped grey mullet, a species which is among the most consumed by the Oranese population, for which it is essential to carry out a regular follow-up in order to have an idea on the danger or not as for the consumption of this pelagic species. but can become dangerous if they exceed a certain threshold in the organism (Richir, 2016). Iron (Fe), nickel (Ni) and manganese (Mn) are considered essential trace elements for living organisms but can become dangerous if they exceed a certain threshold in the organism (Richir, 2016). This chemical contamination can represent a toxicological risk and affect marine life and its diversity. Various studies have shown that, in aquatic species, these xenobiotics cause reproductive system disturbances, behavioral changes, disruption of energy metabolism and the appearance of mutagenic or carcinogenic effects (Meyer, 2003). Humans can also be affected by this type of contaminant, which can represent a great risk to their health (Merhaby et al., 2018; Diop et al., 2019; Karikari et al., 2020). In Algeria, pollution is mainly generated by the discharge of untreated industrial and urban wastewater (Taleb, 2007; Grimes et al., 2010). Petrochemical, chemical, iron and steel and agri-food activities are mainly concentrated on Algeria's coastal strip (Grimes et al., 2010). Given this importance, our present study focuses on estimating the state of water quality on the Oran coast, based on monthly monitoring of physico-chemical parameters in the coastal waters of Oran Bay, and on assessing the quantity of trace metal elements (Fe, Ni and Mn) in the organs (liver, gonads and muscle) of a teleost fish *Chelon labrosus* (Risso, 1827) caught on the Oran coast. Our choice fell on thick-lipped grey mullet, a species which is among the most consumed by the Oranese population, for which it is essential to carry out a regular follow-up in order to have an idea on the danger or not as for the consumption of this pelagic species. The main objective of this study is to demonstrate the state of the marine environment of the Oran coast and its level of pollution, particularly with regard to certain metals such as iron (Fe), manganese (Mn) and nickel (Ni). This research also aims to assess the

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concentrations of these pollutants in *Chelon labrosus* (Risso, 1827), a species that is widely consumed and appreciated by the local population. By providing a detailed assessment of coastal water quality and contamination levels in this species, we hope to provide crucial information for marine resource management and food security in the region.

Material and methods

Overview of study areas

Algeria has an extensive coastline in the heart of the Mediterranean. From an ecological point of view, its coastline is rich and diverse. Its long coastline alternates between rocky shores, sandy beaches and wetlands (Benzohra and Millot, 1995). The Bay of Oran, with latitude 35º43' North and longitude 00º 38' West (*Fig. 1*), is located in north-west Algeria and south-west of the Mediterranean and belongs to the coastal chain of the Tel Septentrional (Djebel Murdjadjo and Djebel Khar) (Leclaire, 1972). The Oranese coastline is a set of landforms whose shaping depends directly or indirectly on the actions of the sea. It includes the coastline, of which beaches and cliffs are a part; the latter differ from one area to another (Leclaire, 1972). The Oran coastis bordered by cliffs, particularly at Cap Falcon (Boutiba, 2007).

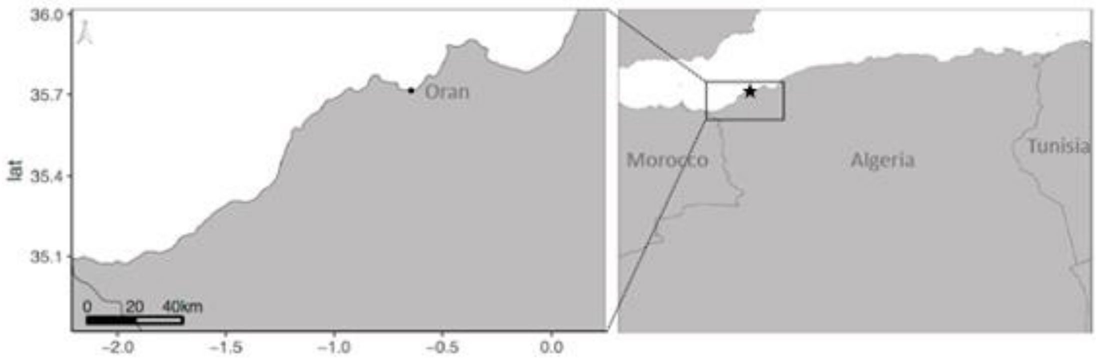

Figure 1. *Location of study site: Oran coast (Tabeche et al., 2021)*

The Oranese coastline is under heavy attack from the nuisances of the civilized world: industrial activities, intensive tourism and massive urbanization, with the corollary of ever-increasing levels of pollution from domestic sources (Kerfouf et al., 2010).

Sample collection and processing

To carry out this study, fish sampling was conducted monthly between January 2017 and December 2017 along the coast of Oran. The samples were collected around this site, located at 35.7623578°N, 0.7885159°W. In total, we collected 110 individuals of *Chelon labrosus* (Risso, 1827). The total length of the individuals captured was between 25.7 cm and 53.6 cm, and their weight between 104.9 g and 1,300 g. We collected 41 males, 49 females, and 20 individuals whose sex could not be determined. Thick-lipped grey mullet were mainly caught by small-scale fishermen using nets, which are commonly used in the region for artisanal fishing. The samples were processed in the laboratory immediately after collection, minimising the time between capture and analysis. *Table 1*

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summarises the number of thick-lipped grey mullet individuals caught each month during the sampling period. After biometric measurements, the fish were dissected to remove muscle, liver and gonads. Fish sampling was accompanied by seawater sampling at the same time. Seawater sampling was carried out in accordance with the technical recommendations of Rodier et al. (1996), using polyethylene bottles, previously washed and rinsed with distilled water, then transported to the laboratory in the cooler to be stored at +4°C until analysis. Temperature, pH, electrical conductivity (σ) and hardness (TH) were measured using a multi-parameter instrument (WTW Multi 340i). Other physico-chemical parameters were analyzed in the laboratory using standardized methods and techniques. We used the U.V. Spectrophotometer SECOMAN Anthélie Light® for the determination of ammonium, nitrates and chlorides, using specific characterization kits for each substance.

Table 1. *Monthly Catch of Chelon labrosus (Risso, 1827) Along the Oran Coast in 2017*

	Total	Sex		
		Male	**Female**	**Unidentified sex**
Jan	15	7	6	2
Feb	10	1	6	3
Mar	12	2	4	6
Apr	8	0	7	1
May	9	6	2	1
Jun	10	6	2	2
Jul	5	2	3	0
Aug	4	1	3	0
Sep	12	10	2	0
Oct	5	0	4	1
Nov	12	2	6	4
Dec	8	4	4	0

Trace metal analysis (Fe, Ni and Mn)

Prior to the analysis of metals in the various organs studied, the samples had been mineralized (Chiffoleau et al., 2001). This stage consists in destroying organic matter with HNO_3 acid. The sub-samples were oven-dried at 60° C until a constant weight was reached (72 h), then ground. 0.2 g of dried sample for each replica was mineralized in 4 ml of HNO_3 at room temperature overnight, then placed in an oven at 90°C for 3h. The mineralization was then filtered using Wattman filter paper. ETMs determination was performed using a Perkin Elmer AAnalyst 100 – version 1.10 5s70 flame atomic absorbance spectrophotometer, operated via a computer for result processing. The assays were conducted at Sonatrach, in the laboratory of the GNL1 / Z (Liquefied Natural Gas 1 Arzew) complex.

Test blanks were used to check that the samples had not been contaminated during analysis. These negative controls were treated using the same protocol as the other samples, to check the validity of the method by guaranteeing that the compounds detected in the samples did not originate from contamination during analysis.

The reliability of the protocol described above was also validated using a homogenized standard sample, known as an intercalibration sample, supplied by the International Atomic Energy Agency (I.A.E. A 1995). In our case, the fish sample was coded 140/TM. To detect possible contamination in the seawater, the samples underwent a simple acid digestion, in accordance with procedure 3030E of the Standard Methods for the

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Examination of Drinking and Waste Water (APHA, AWWA and WCPF, 1999). A 10 ml water sample is first acidified, then placed in a test tube to which 0.5 ml of nitric acid has been added, the test tubes containing these samples are then placed in a heating block at a temperature of 105°C under a fume hood for a period of 2 hours, without allowing boiling. After cooling, these samples were diluted to 10 ml with distilled water. Seawater samples were measured using the same procedure and the same apparatus for the determination of ETMs in fish is the Perkin Elmer precisely AAnalyst 400 flame atomic absorbance spectrophotometer.

Statistical treatment and data analysis

All the data was compiled in Excel files according to the matrices studied, and then processed using SPSS software. To compare the average concentrations of trace metals as a function of several parameters (physico-chemical parameters of the water, organs, periods). An analysis of variance (ANOVA) was applied to test the significance of the differences between the parameters (2 groups).

Other statistical analyses, such as the Pearson test and principal component analysis (PCA), were also used. The Pearson test was used to assess the correlations between the various parameters, while the PCA was used to summarise the structure of the data described by the quantitative variables, identifying correlated or uncorrelated factors between these variables.

Results and discussions

Spatial variation of physicochemical parameters of the sampling site

Several physicochemical parameters were the subject of our study including temperature T°, hydrogen potential, electrical conductivity, TH, chlorides, nitrites, nitrates and ammonium, as well as trace metal elements iron, manganese and nickel. The results of the analyzes obtained are represented as follows:

Physical parameters

The analysis of the temperature in *Figure 2* shows overall a small variation between months, they vary depending on the sampling periods, they oscillate between 19.5°C and 25°C during the year. Subtle fluctuations in water temperature reflect seasonal climate changes in the region. Water temperature is a major ecological element which has significant ecological repercussions: it influences many aspects of the ecosystem such as: density, viscosity, solubility of gases in water, dissociation of dissolved salts, as well as the biogeochemical processes taking place in the oceans and the sea. These interactions are complex and can be exacerbated by factors such as trace metal element pollution, (McCauley et al., 2022), on the other hand, the physiology of marine organisms is also closely linked to the temperature of sea water, with effects on their metabolism, growth and reproduction (Pörtner and Farrell, 2008). PH is a very important factor in the study of water chemistry. It is a major factor affecting the availability of nutrients and trace metal elements to plants and animals (APHA, 1995; Gehan and Elsayed, 2015). The values observed in our study range between 6.78 and 7.55, pH mainly in the neutral to slightly alkaline range. Compared to Algerian normative values (> 6,5 et < 8,5). In literature, a natural pH between 6.5 and 8.5 characterizes waters where life develops optimally (Bendjama, 2014).

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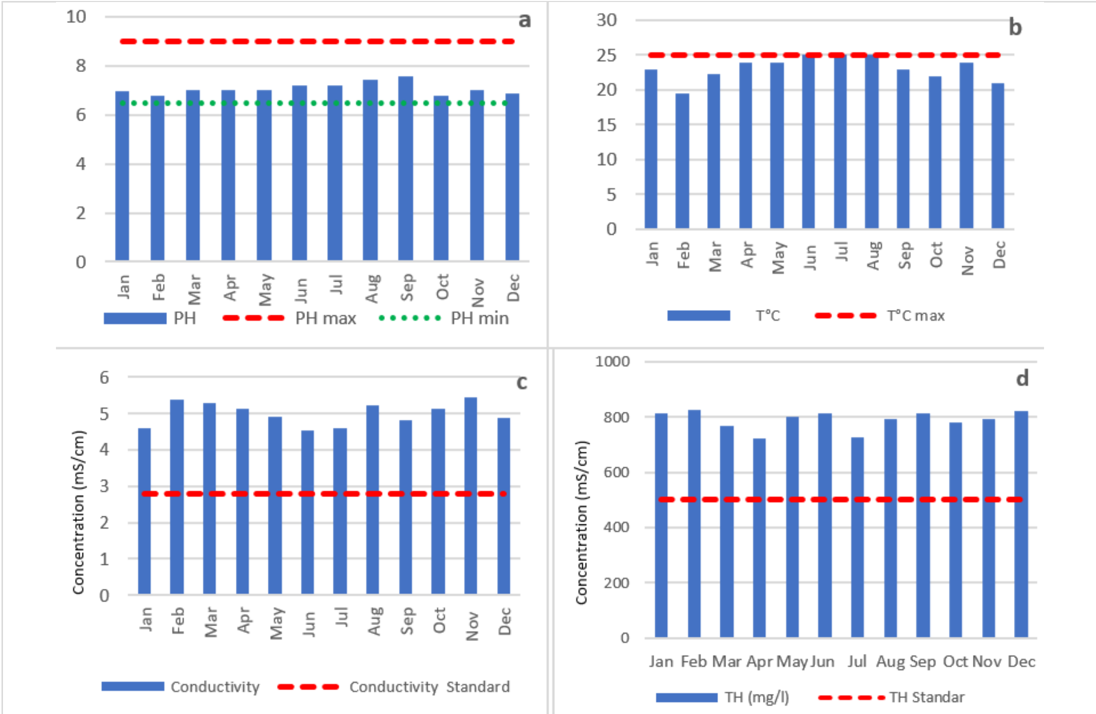

Figure 2. *Representation of the Spatial Evolution of Physical Parameters. (a) pH, (b) Temperature, (c) Conductivity, (d) Total Hardness*

The conductivity of seawater is an essential parameter for evaluating its quality and composition. In our study the conductivity value varies between 4.6 mS/cm and 5.43 mS/cm with an average of 4.99 mS/cm. We observe that these values exceed the standard established by the WHO, which is 2,800 mS/cm (*Figure 2*). These values likely indicate the presence of high quantities of ions or contaminants in the water. This could be due to the significant human activities carried out in this area, especially the discharge of wastewater and industrial effluents as in the case of the study carried out by Avnish et al. (2010). In addition, the location of the Oran coast specifically Ain Turk is a village located near urban areas.

Total Hardness (TH) expresses the hardness of water. The latter is particularly due to the presence of calcium and magnesium salts (Rejsek, 2002). In *Figure 2*, the water hardness results obtained throughout the year show a variation between 721.9 mg/l and 820 mg/l during the entire sampling period, these variations are much greater than the WHO standard (2011). According to Batvari et al. (2016), Environmental factors such as pH, temperature, salinity, hardness, nutrients, organic matter, organic carbon and environmental conditions of the marine ecosystem influences the bioavailability and bioaccumulation rate of metals.

Chemical facies

Chemical facies in water describe the composition and characteristics of water based on its chemical properties. In this work we measured nitrates (NO_3^-), nitrites (NO_2^- -), ammonium (NH_4^+) and chloride (Cl^-) are shown in *Figure 3*.

Concentrations of chloride ions (Cl^-) show a fluctuation over the year, ranging from 321.4±0.2 mg/l to 498.9 ±0.09mg/l. There is no universally established toxic threshold

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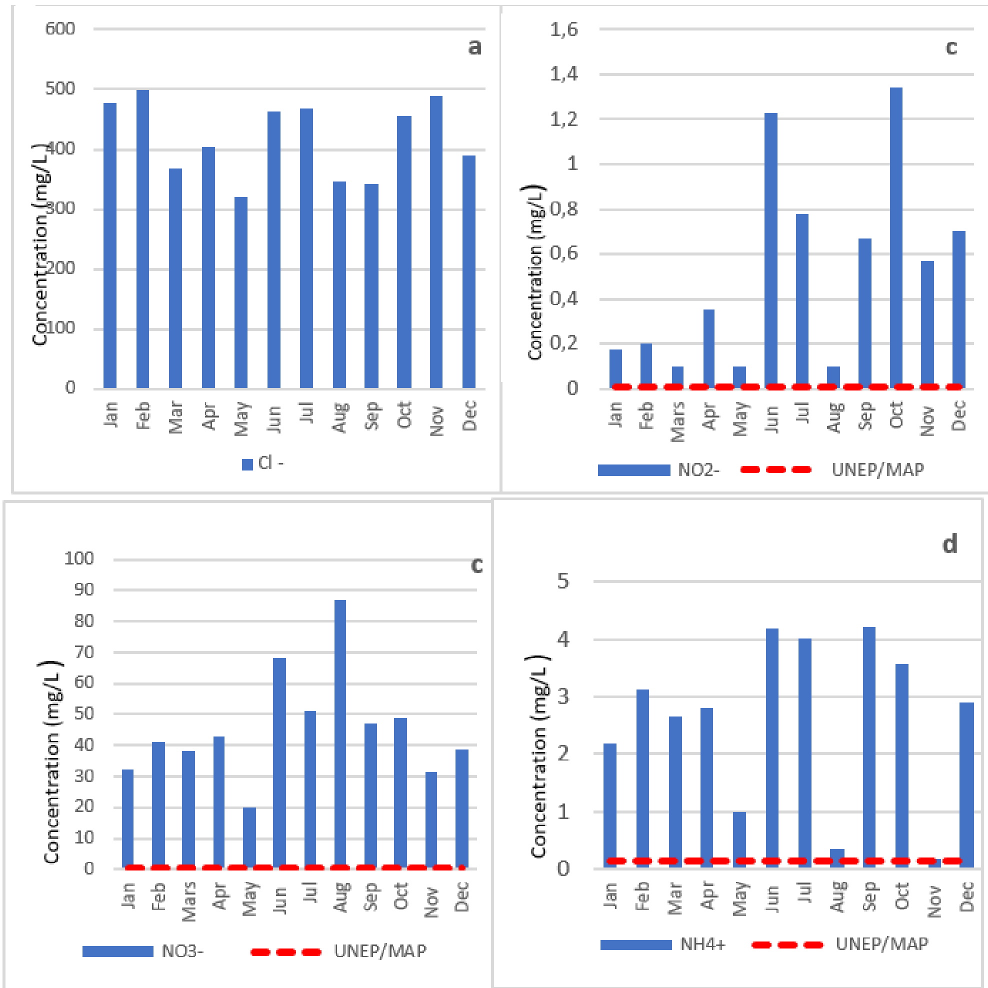
for chloride in marine waters. According to EPA 440/5-88-001, the limit value for chloride in fresh water is much lower, with toxic thresholds for aquatic life generally around 230 mg/l to 860 mg/l. The concentrations measured in *Figure 3a* are well below the toxicity thresholds for freshwater and drinking water. According to Gouaidia (2008), chloride is a good indicator of pollution.



UNEP/MAP: Mediterranean Information System on Environment and Sustainability

Figure 3. *Representation of the Spatial Evolution of Chemical Facies. (a) Chloride (Cl^-), (b) Nitrites (NO_2^-), (c) Nitrate (NO_3^-), (d) Ammonium (NH_4^+)*

The results for nitrite ion (NO_2^-) levels vary from 0.1 mg/l to 1.34 mg/l (*Figure 3b*), and these variations are generally temporal. These NO_2^- levels are very high compared with the standards set by the United Nations Environment Programme. This increase in (NO_2^-) probably indicates the presence of toxic substances (Costa and Castro, 2007). High nitrite concentrations often indicate the presence of toxic substances. Nitrites are particularly harmful to young fish. A concentration of more than 3 mg/l NO_2^- is considered critical (Lisec, 2004).

Nitrate ion (NO_3^-) concentrations ranged from 19.7±0.1mg/L to 87±0.098mg/l. All the values recorded during the year of sampling are relatively very high and well above the limits prescribed by UNEP/MAP. This is a sign of pollution. According to UNEP/MAP,

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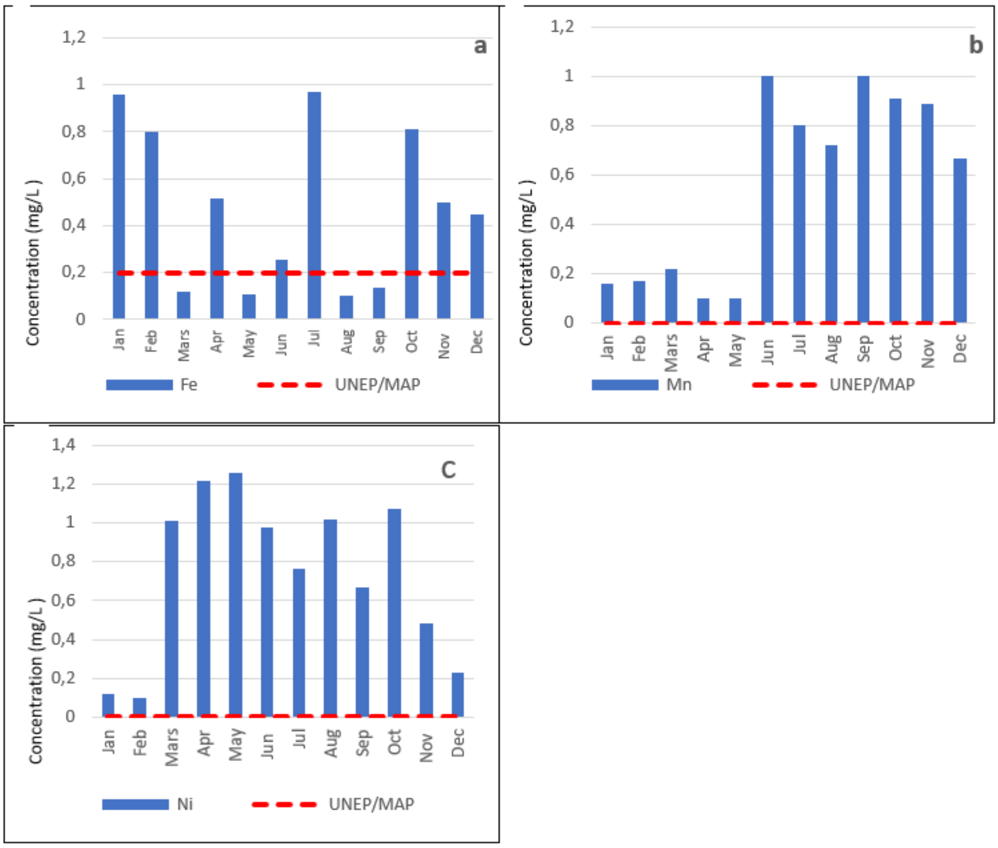
nitrate concentrations in the Mediterranean can vary widely, but are generally in the order of 0.1 to 10 µM (0.9 to 0.14 mg/L) depending on the area. Higher concentrations, above 1 µM (0.14 mg/L), may be indicative of pollution or anthropogenic inputs. These values (NO_3^-) and (NO_2^-) are not without danger for fish, as water containing nitrites can be considered suspect or even toxic for fish, even at low doses, according to Vissin et al. (2010).

Examination of the *Figure 3c* shows that the concentration of ammonium ions (NH_4^+) is 40 times higher than the UNEP/MAP limit of 0.14 mg/l. However, in surface waters, ammonium can have several origins, such as plant organic matter in watercourses, animal or human organic matter, and industrial waste (fertilisers, textiles, etc.) (Rodier et al., 2005). Given that the Oran coast is a major hub for maritime traffic and is home to a high population density, high concentrations of certain chemical parameters may indicate pollution, particularly near urban and industrial areas, as confirmed by UNEP/MAP.

Spatial evolution of metallic trace elements in seawater from the sampling site

The results of analyses of the trace metals studied (Fe, Mn and Ni) in the seawater of Oran coast during the study period (January 2017 - December 2017) are shown in *Figure 4*. It can be seen that the values measured for the three heavy metals (Fe, Mn and Ni) show very strong fluctuations over time.



UNEP/MAP: *Mediterranean Quality Status Report 2017* et EPA *National Recommended Water Quality*

Figure 4. *Representation of the Spatial Evolution of Metallic Trace Elements in Seawater Samples. (a) Concentration of Iron (Fe), (b) Concentration of Manganese (Mn), (c) Concentration of Nickel (Ni)*

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Values for January, February, July, October, November and December show iron (Fe) concentrations above the 0.2 mg/l threshold recommended by UNEP/MAP, while March and May and August and September are below the recommended threshold, respectively 0.011±0.12mg/l 0.10±0.16mg/l 0.13±0.22mg/l and 0.138±0.2mg/l. Our results are close to those found by Benadda,2019. ANOVA revealed a statistically significant difference between groups (f = 7.36428, p = 0.0093).

Manganese (Mn) concentration values are of the same order of magnitude throughout the year. The maximum values are 1± 0.12 mg/l in June and September 1± 0.09mg/l, the lowest levels in April and May are 0.1 ± 0.09 mg/kg and 0.1 ±0.074mg/l respectively. Manganese (Mn) concentrations far exceed the dose permitted by UNEP/MAP. The two-group ANOVA analysis showed a statistically significant difference between the groups, with an F value of 5.07741 and a p value of 0.029274, indicating significance at $p < 0.05$.

Iron and manganese are elements that occur naturally in the constituents of the earth's crust, crystalline rocks and sedimentary rocks. They can therefore have both natural and industrial sources (Achour et al., 2017). Previous studies, in particular those carried out by Debieche (2002); Khelfaoui et al. (2012); Kerboub and Fehdi (2014); and Achour et al. (2015) report the presence of metallic elements in both groundwater and surface water, with iron and manganese being omnipresent.

Relatively high concentrations of nickel (Ni) were detected throughout the sampling year. The highest level in May was 1.25 ± 0.091 mg/l, compared with 0.09 ± 0.025 mg/l in February. Nickel concentrations tend to be higher in the warmer months than in the cooler months. These levels also exceed the dose threshold established by UNEP/MAP, which is 0.00001 mg/l. This high Ni content results in an F value = 5.80207 and a p value = 0.02007. The p value is less than 0.05, indicating statistical significance.

Statistical study of the different compartments

In order to highlight possible relationships that could exist between the physicochemical parameters of the environment and the ETMs contents, a Pearson correlation matrix was established in conjunction with a Principal Component Analysis (PCA) using the software SPSS 2.

Intra-relationships between variables

The results obtained from the Pearson correlation analysis and their significance levels with respect to the physicochemical parameters studied and the metallic trace elements in water are given in *Table 2*.

Table 2 shows the Pearson correlation matrix applied to the eleven samples, the following observations emerge:

T° shows an average correlation with pH (r = 0.621), Ni water (r = 0.573) and a negative correlation with Conductivity (r = -0.64).

pH presents a negative correlation with Fe water (r = -0.52).

Conductivity shows no correlation with any variable.

TH correlates negatively with Ni water (r = -0.538)

Cl^- presents a positive correlation with Fe water (r = 0.798) and a negative correlation with NO_3^- (r = -0.555).

NO_2^- shows a positive correlation with NH4+ (r = 0.620) and Mn water (r = 0.746).

NO_3^- presents a positive correlation with Ni water (r = 0.524).

NH_4^+ does not show any correlation with any variable.

No significant correlation between Fe water and the other variables.

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Table 2. *Pearson Correlation Coefficient Matrix for Trace Metals and Physicochemical Parameters in Seawater.*

Correlation	T°	pH	Conduct	TH	Cl^-	NO_2^-	NO_3^-)	NH_4^+	Fe_water	Mn_water	Ni_water
T°	1,000										
pH	,612*	1,000									
Conduct	-,064	,036	1,000								
TH	-,435	-,016	-,214	1,000							
Cl^-	-,188	-,466	-,261	,020	1,000						
NO_2^-	,060	-,045	,123	-,020	,401	1,000					
NO_3^-	,321	,107	,138	,098	-,55*	-,309	1,000				
NH_4^+	-,214	,027	-,038	-,089	,205	,620*	-,353	1,000			
Fe_water	-,261	-,521	-,434	-,193	,798**	,264	-,459	,270	1,000		
Mn_water	,298	,475	,248	,115	,124	,746**	-,238	,266	-,081	1,000	
Ni_water	,573*	,239	,417	-,538	-,519	,066	,524	-,052	-,496	,026	1,000

* Correlation is significant at the 0.05 level (2-tailed), ** Correlation is significant at the 0.01 level (2-tailed). T°: Temperature,pH: Potential of Hydrogen,Conduct: Conductivity, TH: Total Hardness, Cl^-: Chloride, NO_2^-: Nitrite,NO_3^-: Nitrate,NH_4^+: Ammonium, Fe_water: Iron in water,Mn_water: Manganese in water,Ni_water: Nickel in water

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Mn water shows no significant correlation with the other variables.

Ni water presents no significant correlation with the other variables.

The correlation between water temperature and pH can be explained by variations in the ability of water to dissolve atmospheric CO_2, which affects the balance between CO_2, bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) in seawater, thus influencing the pH (Hoegh-Guldberg and Bruno, 2010).

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The strong correlation between water temperature and nickel concentration in water may be due to the increased solubility of nickel in water at varying elevated temperatures, due to thermodynamic dissolution processes.

A correlation between chlorides and iron in water may be due to complex geochemical interactions between ions in seawater (Byrne et al., 1988). The same goes for the correlation of Nitrates (NO_3^-) and ammonium (NH_4^+) is explained by an assignment to biogeochemical processes in seawater, such as denitrification and biological nitrogen fixation, which can influence the relative concentrations of these ions (Dalsgaard et al., 2005).

Factor analysis

This type of analysis is used to understand the relationship between variables (physicochemical parameters and trace metal elements) and to define their characteristics.

In our study, the eigenvalue graph makes it possible to distinguish four factors (4) representing 80.49% of the total variance, which is sufficient to identify the main variations in environmental pollution.

In our study, the eigenvalue graph (*Figure 5*) makes it possible to distinguish four factors (4) representing 80.49% of the total variance, which is sufficient to identify the main variations in environmental pollution. The factor F1 represents 32.40% of the total variance and shows moderately positive loadings in T°, pH, NO_3^- and Ni_water. Strongly negative in Cl^- and Fe water.

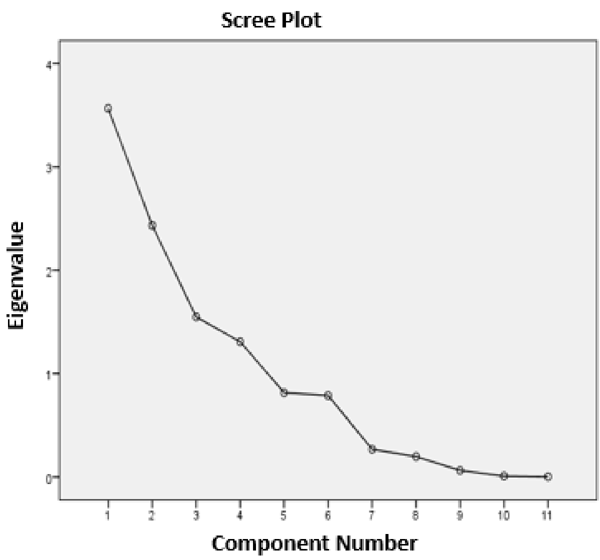

Figure 5. *Eigenvalue graph*

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The F2 factor accounts for 22.12% of the total variance. It shows positive and high charges in NO_2^- and positive and moderate charges in T°, pH and NH_4^+.

The F3 factor describes 14.07% of the total variance and presents positive and high loadings in TH.

The factor F4 presents 11.88% of the total variance and shows positive and moderate loadings in T and pH, and negative in Conductivity.

Factors F1, F2 and F3 seem to be linked by common variables (like NO_2^-, NH_4^+, Conduct, etc.) (*Table 3*).

Table 3. *Represents the connections between variables-Factors*

	Component			
	F1	**F2**	**F3**	**F4**
T°	,583	,416	-,290	,585
pH	,565	,430	,355	,463
Conduction	,383	,265	-,015	-,748
TH	-,194	-,276	,878	-,006
Cl^-	-,835	,151	-,205	,145
NO_2^-	-,356	,835	,045	-,186
NO_3^-	,692	-,283	-,016	-,058
NH_4^+	-,394	,559	,002	-,227
Fe_water	-,832	,010	-,413	,190
Mn_water	-,014	,855	,392	,065
Ni_water	,756	,290	-,445	-,201
Valeurs propres	3.65	2,434	1,548	1.30
Variance%	32,408	22,127	14,074	11,888
Cumulative %	32,408	54,535	68,609	80,496

T°: Temperature, pH: Potential of Hydrogen, Conduct: Conductivity, TH: Total Hardness, Cl^-: Chloride, NO_2^-: Nitrite, NO_3^-: Nitrate, NH_4^+: Ammonium, Fe_water: Iron in water, Mn_water: Manganese in water, Ni_water: Nickel in water

Principal component analysis reveals that different factors contribute to the total variance in water quality data, highlighting positive relationships between temperature and pH with water quality (Li et al., 2016) (*Figure 6*).

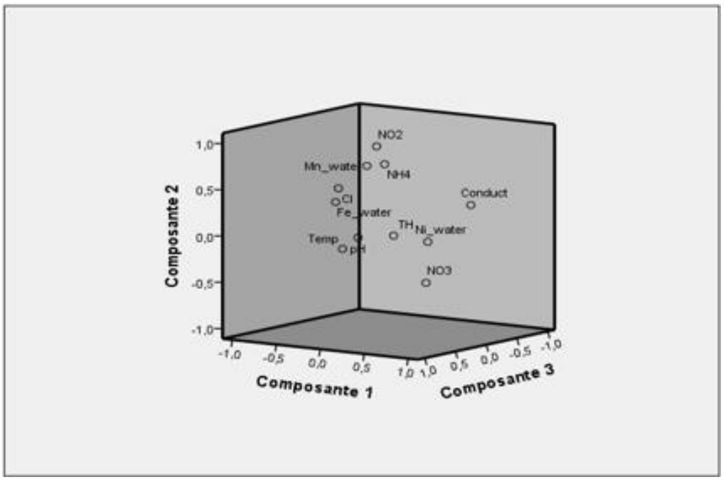

Figure 6. *Plot of the component matrix*

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Fish compartment

Intra-relationships between variables

The mean levels of trace metallic elements (Fe, Mn and Ni) in *Chelon labrosus* (Risso, 1827) studied on the Oran coast are shown in *Figure 7*.

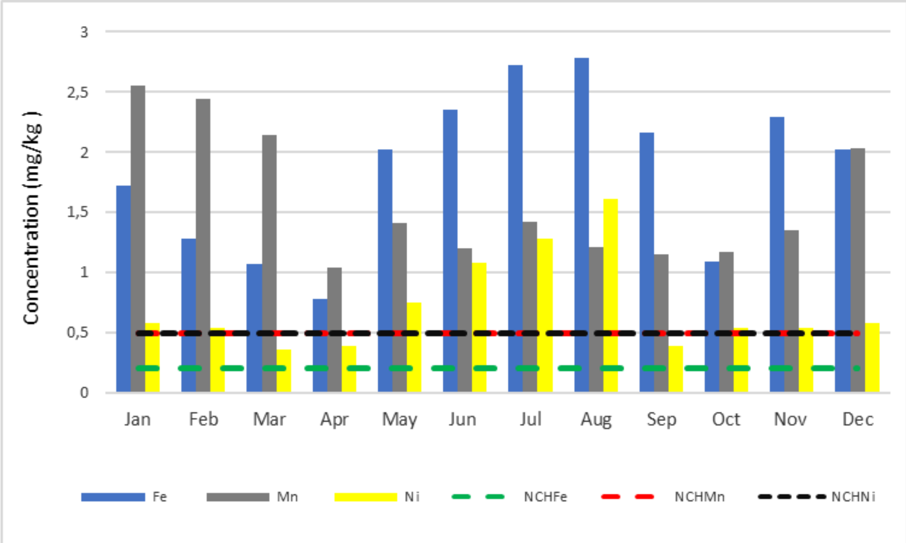

Figure 7. *Representation of the Spatial Evolution of ETMs in Chelon labrosus (Risso, 1827): Iron (Fe), Manganese (Mn), and Nickel (Ni) Levels). NCHFe (WHO: World Health Organization), NCHMn (0,5; WHO/FAO: General Standard for Contaminants and Toxins in Food and Feed. WHO/FAO), NCHNi (Guidelines and Standards for Environmental Pollution Control in Nigeria)*

Iron levels found ranged from 0.77± 0.01 to 2.78± 0.009 mg/kg (*Fig. 7*) and are above the normative limit set by WHO (0.2 mg/l). Very low in December (0.03 mg/l), the highest differences recorded between the months of the year were in the hot months of May, June, July and August, respectively 2.01±0.04mg/kg, 2.35±0.02mg/kg, 2.72±0.07mg/kg, 2.78± 0.009 mg/kg compared with the rest of the year. Statistical analysis applied to the data showed a very large significant difference between the concentration of ETMs in fish and the limit ($p \leq 0.001$). No significant differences were recorded between the months during the year.

Manganese levels found ranged from 1.03± 0.009 to 2.55± 0.01 mg/kg (*Fig. 7*), well above the WHO limit of 0.1mg/l. The highest values were recorded in January, February and March respectively: 2.56± 0.01 mg/kg, 2.44 ± 0.06 mg/kg and 2.14± 0.04 mg/kg. A significant difference was recorded in winter (January, February and March) and autumn (November and December) compared with the rest of the year. On the other hand, there was a very large significant difference between the concentration of ETMs in fish and the limit ($p \leq 0.001$).

Nickel concentrations ranged from 0.36 ± 0.008 to 1.61 ± 0.09 mg/kg (*Fig. 7*), with levels frequently exceeding the FEPA normative limit of 0.5 mg/kg. The highest concentrations were observed during the summer months: May (0.75 ± 0.03 mg/kg), June (1.08 ± 0.06 mg/kg), July (1.28 ± 0.04 mg/kg), and August (1.61 ± 0.04 mg/kg), in contrast to the other months of the year. Conversely, nickel concentrations in March and

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April were 0.36 ± 0.01 mg/kg and 0.39 ± 0.03 mg/kg, respectively, not exceeding the FEPA threshold limit. A significant difference was observed between the sampling months throughout the year. On the other hand, a significant difference was found between the concentration of ETMs in the fish and the limit ($p \leq 0.001$).

The concentrations of the three metals are in descending order: Fe > Mn > Ni.

These levels of Fe, Mn and Ni could come from its diet, as it is an omnivorous fish, according to Coudre et al. (2021). Thick-lipped grey mullet ingest plants and mud rich in diatoms, and also supplement their diet with small invertebrates. Diatoms are known for their ability to accumulate and concentrate certain trace metals (ETMs) in their cells (Navarro and Barra, 2017). These ETMs enter the body either by ingestion through the food chain or by inhalation (Diagne, 2012).

Statistical study of the different compartments

Variation of mean concentrations of ETMs in the organs of Chelon labrosus (Risso, 1827) *as a function of month*

Figure 8 shows graphs of changes in iron (Fe), manganese (Mn) and nickel (Ni) concentrations in the muscles, liver and gonads of thick-lipped grey mullet fish over the months. This analysis provides an understanding of the distribution of these metals in the various organs of the fish.

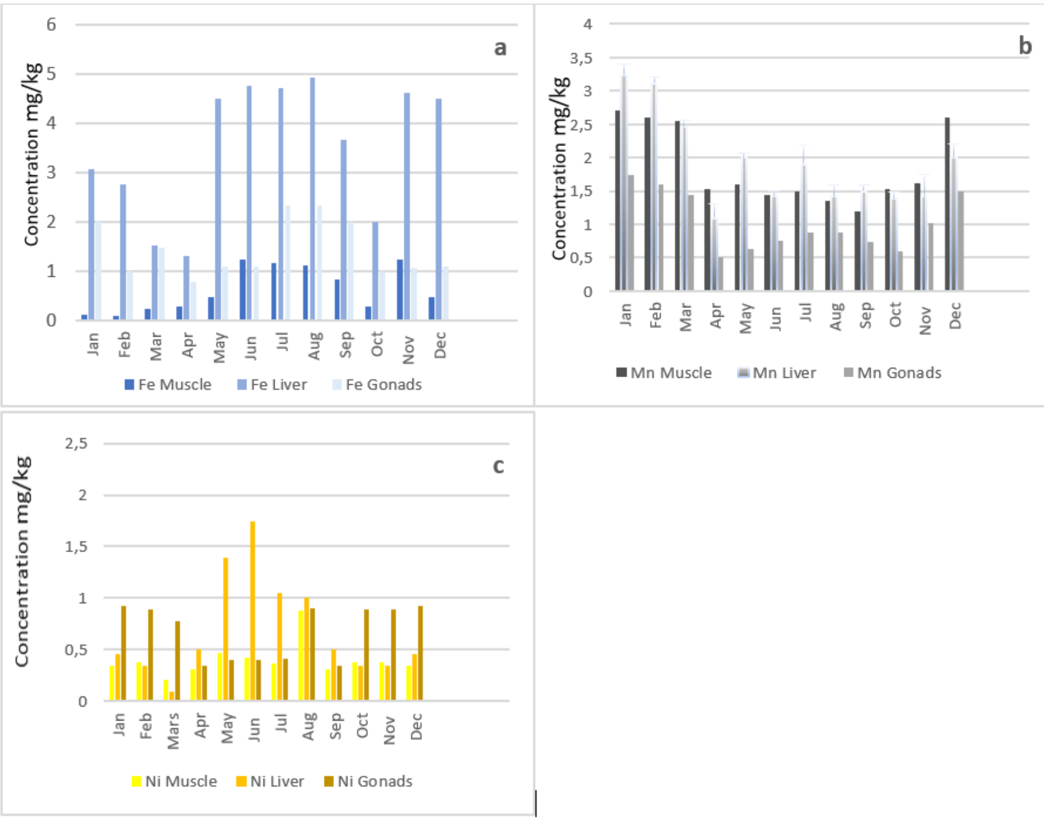

Figure 8. *Representation of the Spatial Evolution of Metallic Trace Elements in the Organs of Chelon labrosus (Risso, 1827) as a Function of Month: (a) Concentration of Iron (Fe), (b) Concentration of Manganese (Mn), (c) Concentration of Nickel (Ni)*

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Muscle

Concentrations of iron, manganese and nickel in muscles vary over the year. Significant fluctuations were observed: Iron concentrations vary from 0.098 ±0.16 to 1.22±0.12 (mg/kg), manganese from 1.2±0.22 to 2.7±0.21 mg/kg, and nickel from 0.31±0.08 to 0.87±0.17 mg/kg. These fluctuations are significant, with values generally higher for manganese than for iron and nickel. This increase in June for iron and manganese, followed by a decrease in July, could be linked to environmental and dietary factors influencing the accumulation of these metals in fish muscle tissue (El Morhit, 2013).

Liver

In the liver, concentrations of iron, manganese and nickel also showed monthly variations. Iron varies from 1.3±0.062 to 4.92±0.093 mg/kg, manganese from 1.09±0.22 to 3.23±0.17 mg/kg, and nickel from 0.35±0.01 to 1.75±0.28 mg/kg. Peaks can be observed, as in August for iron and nickel. These fluctuations could be associated with metal storage and detoxification processes in this vital organ, highlighting the importance of the liver in regulating metal contamination (El Morhit, 2013).

Iron remains the main metal contaminant and shows a wide distribution in the liver. This metal tends to concentrate easily in the liver. The low level in muscle is significant because muscle is an organ of metabolisation (El Morhit et al., 2013; Dione et al., 2018).

Gonads

Concentrations of iron, manganese and nickel in the gonads show variations throughout the year. Iron varied from 0.766±0.062 to 2.316±0.022 mg/kg, manganese from 0.5±0.09 to 1.74±0.101 mg/kg, and nickel from 0.34±0.06 to 0.92±0.062 mg/kg. The gonads showed intermediate levels of these metals, with variations that could be linked to reproductive and sexual maturation processes. Significant differences were observed between months, highlighting a possible differential accumulation of these metals in the reproductive organs of fish. These variations could have implications for the reproduction and health of fish populations (El Morhit, 2013; Bouhadiba, 2017; Dione et al., 2018).

The ANOVA test shows a significant difference ($p < 0.05$) between organs for all trace metal elements.

All the BCF have values greater than 1, as shown in *Table 4* which explains why there is a bioconcentration of the trace element and therefore its transfer from the biotope to the organism.

Table 4. *Table shows the trace element bioconcentration factors in Chelon labrosus (Risso, 1827) muscles*

ETMs	BCF
Fe	4.06
Mn	30.05
Ni	1.47

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Trace element bioconcentration factors in Chelon labrosus (Risso,1827)

A Pearson correlation matrix was established in conjunction with a Principal Component Analysis (PCA) in order to detect and establish relationships between the various parameters, in order to highlight any relationships that might exist between the three trace metal levels in the sampling medium and the ETMs levels in fish.

Table 5 shows the Pearson correlation matrix applied to the twelve samples:

Mn_water shows a significant and positive correlation with Fe_fish (r = 0.566).

Mn_water shows a positive correlation with Fe_fish (r =0.566) and a negative correlation with Mn_fish - (r =-0.539).

Mn_fish and Ni_water are significantly negatively correlated (r = -0.725).

Ni_fish and Fe_fish show a significant positive correlation (r = 0.753).

Table 5. *Matrice des coefficients de corrélation de Pearson pour les paramètres des métaux traces dans l'eau de mer et les poisons*

Correlation	Fe_water	Mn_water	Ni_water	Fe_fish	Mn_fish	Ni_fish
Fe_water	1,000					
Mn_water	-,081	1,000				
Ni_water	-,496	,026	1,000			
Fe_fish	-,183	,566**	-,087	1,000		
Mn_fish	,357	-,539	-,725**	-,255	1,000	
Ni_fish	-,074	,327	,215	,753**	-,284	1,000

* Correlation is significant at the 0.05 level (2-tailed).** Correlation is significant at the 0.01 level (2-tailed). Fe_water: Iron Concentration in Water,Mn_water: Manganese Concentration in Water, Ni_water: Nickel Concentration in Water, Fe_fish: Iron Concentration in Fish,Mn_fish: Manganese Concentration in Fish,Ni_fish: Nickel Concentration in Fish

The literature states that manganese (Mn) and iron (Fe) can interact in aquatic systems and in organisms. A significant positive correlation between Mn_water and Fe_fish suggests that the presence of manganese in water could facilitate the accumulation of iron in fish.

According to Rudnicki et al. (2014) the concentrations of Mn and Fe in sediments may be linked to their levels in fish tissue, due to mechanisms of co-accumulation or competition between these metals during uptake.

A negative correlation could be explained by biological regulatory mechanisms or competitive interactions with other metals. According to Yılmaz (2010) cited that competition for binding sites on transport proteins can influence the accumulation of specific metals in fish tissues, which could explain the negative correlation observed between Mn_water and Mn_fish.

The significant negative correlation between Ni_water and Mn_fish could be explained by competition between these two elements for uptake in fish, as has been observed in other bioaccumulation studies (Mason et al., 2016).

The significant positive correlation between Ni_fish and Fe_fish indicates that these two metals may be co-accumulated in fish tissues, potentially due to similar transport mechanisms or biochemical regulations (Kamunde et al., 2002).

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Factor analysis

In our study, the eigenvalue graph distinguishes two factors (2) representing 71.48% of the total variance, which is sufficient to identify the main variations in environmental pollution.

The F1 factor accounts for 44.04% of the total variance and shows positively high loads in Fe_fish (0.700), Ni_fish (0.692), and strongly negative loads in Mn_fish (-0.808). Factor F2 accounts for 27.24 % of the total variance. It shows positive and significant loads in Fe_water , Ni_water , Fe_fish.

This *Table 6* resulted in a component matrix plot (*Fig. 9)* which highlighted two groups.

Table 6. *shows the links between variables and factors*

	Component	
	F1	**F2**
Fe_water	-,490	,507
Mn_water	,677	,354
Ni_water	,568	-,740
Fe_fish	,700	,621
Mn_fish	-,808	,379
Ni_fish	,692	,433
Variance Total	2,643	1,646
Variance%	44,042	27,442
Cumulative %	44,042	71,484

Fe_water: Iron Concentration in Water,Mn_water: Manganese Concentration in Water, Ni_water: Nickel Concentration in Water, Fe_fish: Iron Concentration in Fish,Mn_fish: Manganese Concentration in Fish,Ni_fish: Nickel Concentration in Fish

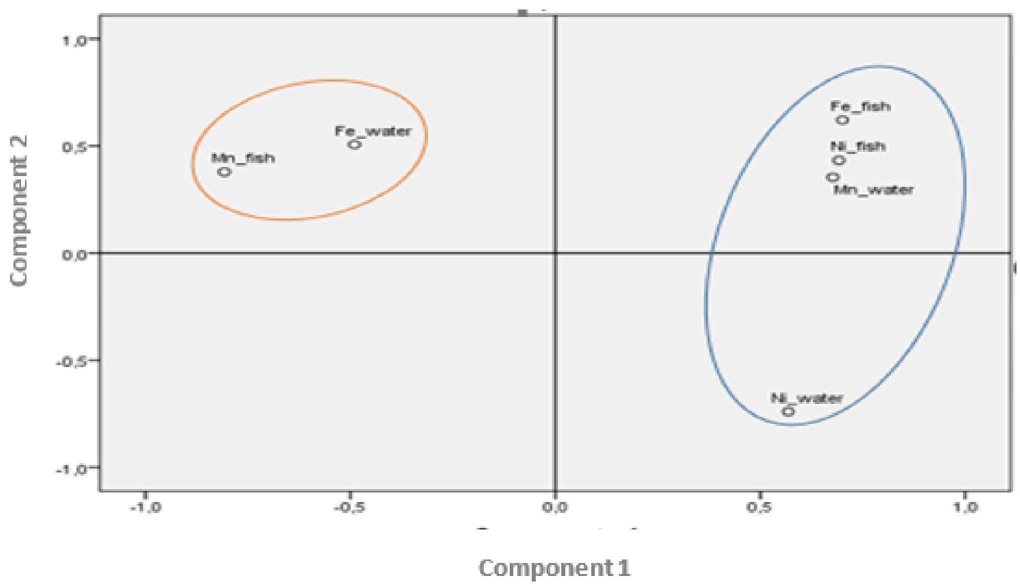

Figure 9. *Plot of the component matrix*

Group 1: variables strongly associated with F1 Fe_fish, Ni_fish , Mn_water, Ni_water
Group 2: variables associated with F2 Mn_fish, Fe_water.

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Group 1 includes Fe_fish, Ni_fish and Mn_water and shows a positively strong association, suggesting that the presence of Mn in the water could favour the accumulation of Fe and Ni in fish, in agreement with the observations of simultaneous bioaccumulation in other studies (Burger et al., 2007). Group 2 shows a relationship where the Fe concentration in the water (Fe_water) could influence the regulation or accumulation of Mn in fish (Mn_fish), although the relationship is complex. This observation is compatible with homeostatic regulation mechanisms and competitive interactions between metals, already discussed and cited by Watanabe et al. (2008) and Papagiannis et al. (2004).

These observations are in line with the existing literature on the interactions and regulation of metals in aquatic ecosystems, offering prospects for effective environmental management measures.

Conclusion

Marine pollution has been a major global problem for over twenty years. Today, the seriousness of the threat to the seas and oceans is driving governments to actively seek solutions. As the last link in the food chain, humans are directly threatened by the toxicity of trace metals, posing a permanent danger to the food chain and public health. This study focuses on coastal and marine pollution on the Oranese coast, analysing the physico-chemical parameters of seawater and the level of metal pollution, particularly in *Chelon labrosus* (Risso, 1827) fish. Our results indicate slight chemical pollution and contamination by trace metals, with concentrations exceeding the thresholds recommended by the World Health Organisation (WHO). The levels of trace metals found in the organs of the fish studied are generally higher than WHO standards for human consumption, posing a health risk for populations that consume these fish in excess.

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