

# Assessment of the Presence of Trace Metal Elements (Hg, Pb, Cd) in Six Species of Fish Landed at the Artisanal Fishing Port of Boulbinet Republic of Guinea

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## Abstract

Aquatic organisms on the Guinean coast are exposed to environmental contaminants including trace metals (TMEs), such as mercury, cadmium and lead, which accumulate in fish tissues and transfer up the food chain to the consumer. The objective of this study is to evaluate the presence of these chemical contaminants in the main species of fish landed at the fishing port of Boulbinet. Trace element analyses were carried out by atomic absorption spectrometry at the Regional Centre for Research in Ecotoxicology and Environmental Safety (CERES-Locustox). This work made it possible to identify two (2) of the three (3) trace metal elements in the six species of fish collected at the artisanal fishing port of Boulbinet. The determination of the demersal and pelagic species studied shows respectively minimum and maximum averages between (0.01 to 0.057 mg/kg) and (0.011 to 0.032 mg/kg) for lead on the one hand and (0.153 to 0.278 mg/kg) and (0.160 to 0.275 mg/kg) for cadmium on the other hand in fish muscle. All these observations show that the bioaccumulation of the trace elements studied varies from one species to another. However, for all six species, an accumulation of trace metals was observed in the muscles of individuals of these six species, with concentrations below the accepted standards for lead and above those for cadmium. Future studies should continue to develop biomarkers for different groups of contaminants and use them in key fish species, at sensitive stages of their life cycle, by combining different multi-stress experimental approaches with field monitoring studies. Given the limited data available on such an important subject, it is desirable to conduct more studies before concluding definitively.

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## Keywords

Metal Traces, Fish, Port

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### 1. Introduction

The marine environment is an immense reserve of energy, mineral and biological resources, and forms the basis of the diet of the vast majority of the population. However, it is under constant threat from various sources of pollution that threaten to reduce its economic potential and have harmful repercussions on human health [1].

In Guinea, the coastal area covers 15% of the total surface area, *i.e.*, 36,200 km<sup>2</sup>, of which around 70% is at a depth of between 0 and 40 m, giving easy access to geological resources. On the whole, it is characterised by the presence of sandy beaches, vast expanses of plains with lush vegetation of mangrove forests that constitute spawning grounds, hatcheries and niches for a varied range of species of fish, shrimp, mollusks, etc. [2].

Fishing is one of the most important sectors of the national economy, generating more than 10,000 direct jobs and providing 40% of animal protein intake. It is an important link in the primary sector, contributing 6% of the nominal GDP in 2018. In 2004, the sale of licenses and fines in the fishing sector brought in more than 13 billion Guinean francs, or nearly 5 million US dollars, to the public purse.

In coastal and estuarine environments, organisms have to cope with variations in environmental factors such as salinity, turbidity and oxygen availability. These natural factors are compounded by anthropogenic disturbances. Estuaries and coastal zones can be considered the most degraded environments to have been affected by human settlement for centuries [3].

These anthropogenic processes are often the source of various organic and inorganic pollutants that contribute to the pollution of these hydrosystems [4] [5].

Estuaries and coastal areas are generally considered to be essential nurseries for many species of marine fish [6] [7], sites where high densities of juveniles are found and explained by the presence of trophic conditions favourable to growth and the existence of refuges from predation [8].

The lack of concern in the past about discharges of highly toxic products into the coastal environment is attributed to the assumption that the oceans are receptacles of infinite dilution and/or removal. Today, this concept is no longer accepted. We talk about an environment's capacity to accept, and we define discharge or concentration standards or guide values.

The most insidious and permanent threat of chemical pollution to Guinea's marine environment comes from diffuse pollution from industrial zones, sea-ports, navigation areas and thermal power stations. In particular, the dredging carried out during port construction and periodically to remove sediments that

have accumulated in the channels and docks has a number of effects on the environment. They lead to an increase in turbidity following the resuspension of anoxic underlying sediments [9]. For some years now, the consumption of seafood, and more specifically fish, has been in the spotlight for its health-boosting elements and components, such as essential fatty acids, mainly long-chain polyunsaturated fatty acids from the omega-3 family, proteins, vitamins A, D and E and minerals [10].

However, fish are also a sometimes major contributor to exposure to certain environmental contaminants [11] [12]. Trace metals (TMEs), such as mercury, cadmium, lead and persistent organic pollutants (polychlorinated biphenyls, polybrominated diphenyl ethers, dioxins, etc.) represent a group of toxic substances that accumulate in the tissues of fish and are transferred along the food chain to humans [13].

Many marine organisms accumulate contaminants in very high concentrations in their tissues. Their use in monitoring aquatic pollution originated 35 years ago in studies on the abundance of radionuclides in marine ecosystems [14].

The impact of trace elements on health depends on their chemical species, their concentration, their bioavailability and their passage through food chains.

Some trace elements are necessary for the growth of living organisms, but often in small quantities. They are known as “essential” and their absence can lead to deficiencies. At high concentrations, they can be harmful to organisms. They are involved in metabolic reactions or biochemical reactions such as oxidation-reduction or hydrolysis. These are trace elements such as copper (Cu), iron (Fe), manganese (Mn) and zinc (Zn) for plants and animals. Cobalt (Co), chromium (Cr) and selenium (Se) are only present in animals, while molybdenum (Mo), a micro-nutrient, is involved in biochemical or metabolic reactions in plants [15]-[17].

Other elements such as arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg) and antimony (Sb) are not essential for living organisms. They have no biological function and produce only toxic effects. They generally have a much lower concentration threshold to be toxic [15] [16] [18] [19]. As well as being toxic to living organisms, these trace elements can lead to deficiencies in essential elements, through competition for the active sites of molecules that are important in the physiology of organisms (Walker *et al.*, 1996) [20]. Throughout the world, fish are used as indicators of environmental and ecological changes in estuarine environments [21]-[23].

As the concentrations measured are generally high, they are not subject to much risk of accidental contamination. In addition, they represent the fraction that is bioavailable to marine organisms.

The aim of this study is to assess the levels of environmental contamination of the area by toxic metallic elements using sentinel fish, many of which are consumed by the local population. We will discuss the results of the fish targeted to assess the quality of our coastline. Our outlook is also aimed at identifying future needs in this field of research.

## 2. Materials and Methods

### 2.1. Choice of Sentinel Species

A sentinel species is one that can be used to trigger an alert when a situation poses a risk to the environment or human health. It can be defined as an organism whose changes in known characteristics can be measured in order to assess the extent of environmental contamination and its implications for human health, and thus provide early warning of its implications [24].

The selection of species to be studied as a priority was based on:

- their accessibility and appreciation by Guinean households
- their wide geographical distribution and abundance off the Guinean coast
- their lifestyle and biological characteristics (whether they are benthic or pelagic, their relative sedentary nature, whether they belong to the fatty fish/lean fish groups, etc.), making it possible to discern the environmental and biological factors affecting bioaccumulation.

The particular importance attributed to the first criterion led to the selection of six species likely to be present in all the zones. These are: *Dentex congoensis*, *Galeofdes decadactylus*, *Sardinella aurita*, *Ethmalosa fimbriata*, *Pseudotolithus senegalensis* and *Decapterus punctatus*.

#### 2.1.1. *Dentex congoensis* PoII, 1954

This is the smallest dentate, measuring just over 20 cm in length. Its jaws are those of the genus *Dentex* and the spines on its dorsal fin are “normal”. Its body is almost vermilion-red, with no distinctive markings. The species is coastal and common in the African tropical Atlantic, where it can be trawled on sandy-muddy bottoms at depths of 50 to 200 m.

Available information on feeding indicates that juveniles are detritus feeders and adults omnivores with a more or less pronounced carnivorous tendency depending on the size the species can reach. [25]-[29] indicate that juveniles are detritivores and adults omnivores with a more or less pronounced carnivorous tendency depending on the size the species can reach. *Penaeus notialis* reaches fairly large sizes at sea. As a result, it probably has a varied diet with a marked carnivorous tendency.

#### 2.1.2. *Galeoides decadactylus* (Bloch, 1795)

It is very common on the western coasts of America, from Cabo Blanco to Angola. It is abundant down to 35 m on soft bottoms (mud and sand). It seems to reproduce all year round, with “flushes” at the beginning and end of the swimming winter. Individuals reach maturity at 13 - 14 cm, *i.e.* after one year. In 1974 Congo, SAMBA also noted that *Galeoides decadactylus* avoided oxygen-poor areas. Young individuals are mainly concentrated in the deepest part of the distribution area, while the largest individuals are found closer to the coast [30]. This was also observed by CAVERIVIERE in Côte d’Ivoire in 1982 [31].

#### 2.1.3. *Sardinella*

*Sardinella* are 25 to 30 cm long. They are pelagic species of the continental shelf,

frequenting coastal waters and the edge of the shelf, *i.e.* around 150 m. The species *Sardinella aurita* is widely distributed in tropical and subtropical waters of the North and South Atlantic, and is also thought to exist in the western Pacific. Young *S. aurita* remain in nurseries until they reach maturity, when they join the stock of adults that migrate offshore following the movements of cold waters. *Sardinella aurita* predominates during the cold hydrofological season, from December to May, when the trade winds bring cold, salty water up to the coast. Sardinella are caught using purse seines and beach nets. They are used for consumption (canning and fermenting), for making fishmeal and as bait by the tuna fleet.

Studies of the diet of sardinella have shown that these species have a very broad food spectrum. Like most Clupeidae, they feed mainly on plankton [32]-[35].

Size-related variations are significant in *Sardinella aurita*. Analysis of stomach contents showed that crustaceans and molluscs are eaten more by adults, while juveniles tend to target inorganic detritus and various terrestrial debris. This variability in the diet of *S. aurita* supports the hypothesis of segregation by size, with young individuals living close to the coast and frequenting estuaries, and adults living further back from the shore [36].

#### **2.1.4. *Ethmalosa fimbriata* (Bowdich, 1825)**

*Ethmalosa* is a very coastal West African species. It swims up estuaries and enters lagoons during the dry season. It appears to reproduce all year round, although there are “flushes” in spring, summer and autumn. It reaches a length of 45 cm and a weight of 1 kg.

*Ethmalose* is planktonophagous, although it used to be considered a “limnivore” [37]. This is because “all stomach inventories reveal sand or mud” or “mud-grazing microphage” [38]. These implicit characterisations of the diet can be explained by the fact that sand and unidentified organic matter can make up a large proportion of stomach contents [39] [40]. However, this phenomenon appears to be linked to flood seasons when the water content of suspended particles is high.

Furthermore, BAINBRIDGE did not find a significantly high proportion of benthic organisms in the stomach contents; it is therefore assumed that the diet of *Ethmalose* is planktonophagous.

#### **2.1.5. *Pseudolithus senegalensis* (Valenciennes, 1833)**

This is a coastal species found on muddy, sandy or rocky bottoms at depths of between 15 and 70 m. It is fairly common from Senegal to Angola, but rarer in Mauritania. It reaches 90 cm in length. *Pseudolithus senegalensis* are active predators, hunting the swimming part of the vagile fauna of the coastal population, and mainly the small shrimp, *Palaemon hastatus aurivillius*.

#### **2.1.6. *Decapterus rhonchus* (E. Geoffroy Saint-Hilaire, 1817)**

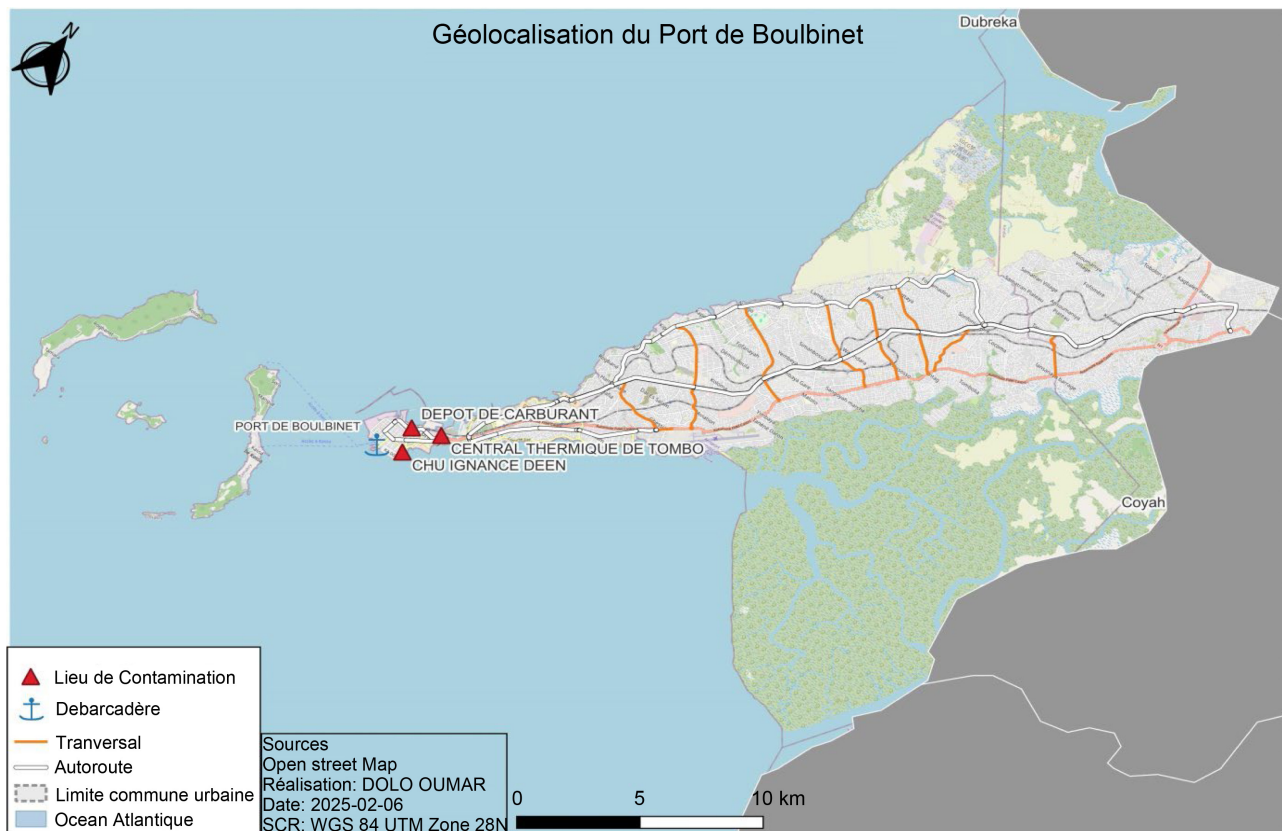
The term “horse mackerel” covers several species of the Carangidae family, which share the general shape of their bodies, reminiscent of mackerel. It is a coastal pelagic species of fairly small size (25 to 35 cm long), which can reach lengths of 60 and 70 cm respectively.

## 2.2. Presentation of the Study Area

Conakry like showing in the (Figure 1) is a peninsular city with coordinates 9°32'14" North, 13°40'14" West. Its coastline is the main collector of run-off water for the whole of Conakry. Sources of pollution are mainly urban in origin. Urban pollution is made up of all the wastewater from various domestic and collective uses (health centres, schools, markets, etc.), mining operations and other activities. This wastewater is laden with detergents, grease, solvents, organic debris, faecal germs, paints, glues, waste oils, etc. and is discharged directly, without prior treatment, through the city's network of sewers along the coast. Rainwater carries with it all the organic, chemical, mineral and suspended solids it encounters, from car traffic, soil erosion and so on.

It was chosen for this study because of its proximity to the industrial port, the fuel depot and the Ignace Deen University Hospital Centre.

This site, where fish products are landed in the commune of Kaloum, is a crossing point between the coast and the islands of Loos.



**Figure 1.** Showing the map of the coastline of the city of Conakry of the Republic of Guinea.

## 2.3. Sampling

Three sampling campaigns were carried out at the artisanal fishing port of Boulbinet. The fish were sampled when the fishermen's boats arrived on shore. With the agreement of the fishermen, who agreed to sell part of their catch, the fish were

collected and bagged by species and by individual in sterile, labelled plastic bags. The fish were then placed in a cool box containing ice packs and transported to the laboratory. A total of nine (9) individuals of each fish species were sampled, with three (03) individuals per species and per campaign. The total lengths measured ranged from 21.9 to 23.3 cm, with an average of  $22.25 \pm 1.59$  cm.

## 2.4. Research Framework

Trace element analyses were carried out at the Centre Régional de Recherche en Ecotoxicologie et Sécurité Environnementale (CERES-Locustox), which is accredited ISO/CEI/17025 v 2017 by the West African Accreditation System (SOAC) under Convention No. SOAC-ES190007.

## 2.5. Apparatus and Principle of Operation

Atomic absorption spectrophotometry (AAS) is a method of dosing exclusively metallic elements. Monochromatic electromagnetic radiation is sent to the population of atoms to be dosed in the vapor state. These atoms will absorb some radiation. The measurement of  $I_0$  and  $I_t$  makes it possible to know the concentration of the element to be measured. Light of a specific wavelength for a given mineral is emitted by the lamp and passes through the atomization chamber to be monochromatized (transformed into light of a single frequency) in the monochromator. The optical signals from the monochromator enter the detector to be transformed into electrical signals that are transmitted as spikes on a paper screen or spectrogram. This first peak represents the initial amount of light coming from the lamp. Then, the mineralized sample is introduced into the atomization chamber which is heated by a flame Generated by the mixture of air and acetylene to atomize mineral elements at a temperature of about  $2300^\circ\text{C}$ . After the elements are atomized, they absorb some of the light coming from the lamp. The rest of the light passes successively through the monochromator and the detector to give electrical signals in the form of peaks on the screen or on a paper spectrogram. The difference between the height of the peak formed by the initial light and the height of the peak formed after the absorption of light by the atoms of the mineral, called the extinguisher, is proportional to the concentration of the mineral in the sample. To reduce errors due to working conditions, standard solutions of different concentrations of the element to be determined are analyzed alongside the sample. Knowing the extinctions caused by the different standard solutions, a calibration curve makes it possible to determine exactly the extinction caused by the atoms of the mineral to be determined in the sample.

### 2.5.1. Mercury Principle

The homogeneous samples (0.2 - 1) are mineralized by wet process (acid attack). They are then heated to a boil in a closed system where temperatures will vary. The mineralized tubes will be stripped of their contents and then thoroughly washed with dilute nitric acid (0.1 N) in order to collect all the inorganic mercury in 50 ml vials. The mineralized sample is sucked up and mixed with stannous

chloride in the reactor. Subsequently, the  $\text{Hg}^{2+}$  ions are reduced to elemental mercury Hg by stannous chloride ( $\text{SnCl}_2$ ) and then carried by carrier gas (in this case, argon) into the atomic absorption spectrometer cell. Absorption is at 253.7 nm and is proportional to the concentration of mercury.

### 2.5.2. Principle of Cadmium and Lead Determination

Homogeneous samples (0.2 - 1 g) are mineralized by wet process (acid attack). The determination of metals (Cd, Pb) is based on measurement by graphite furnace atomic absorption spectrophotometry.

### 2.5.3. Calibration and Reference Materials

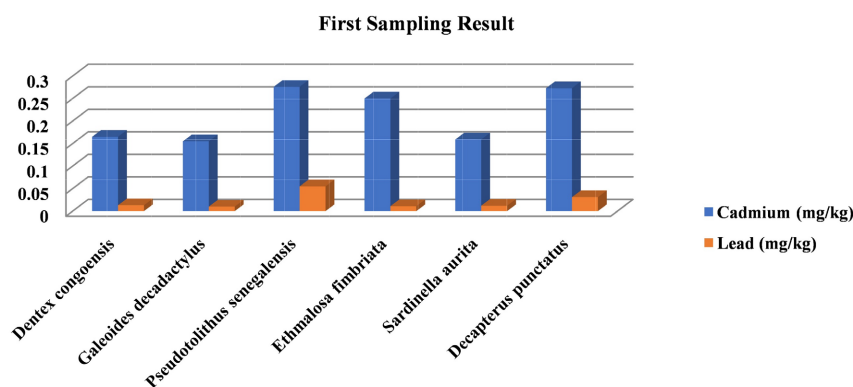
Standard solutions used for calibration should be accompanied by a certificate making them traceable to their origin. Where possible, reference materials (RMs) used for internal quality control should be traceable to certified reference materials (CRMs).

### 2.5.4. Validation of the Acid Attack Protocol

In this section, to validate the effectiveness of the  $\text{HNO}_3$  attack protocol, blanks and a reference material certified for trace metal analysis were analyzed under the same conditions as the fish samples. The analysis revealed that all blanks used in the analysis of the samples were free of contamination. The overlap rate obtained between the measured and certified values of the certified reference material is correct, as these values are between 90% and 109%. This allows us to validate the protocol and the results obtained during this study.

## 3. Results and Discussion

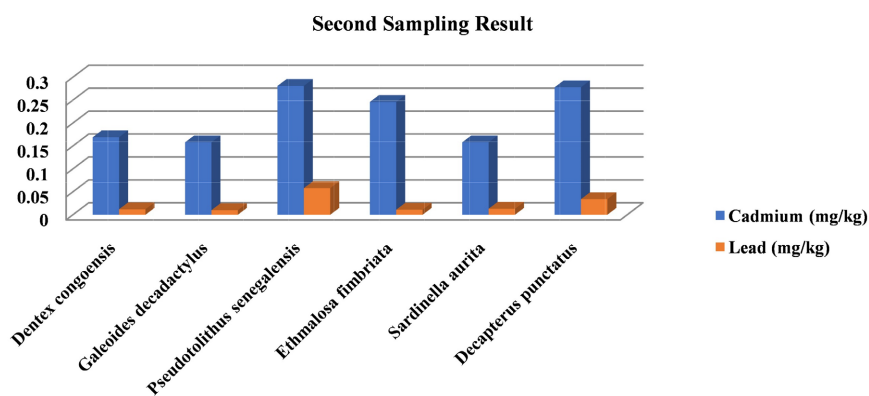
The results of this study are showing on the (Figures 2-5).



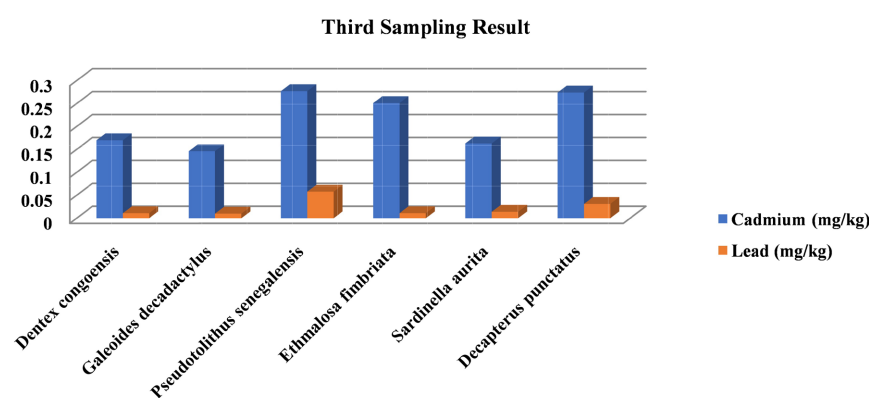
**Figure 2.** First sampling campaign.

This work revealed the content of two of the 3 metallic trace elements in the six species of fish sampled at the artisanal fishing port of Boulbinet.

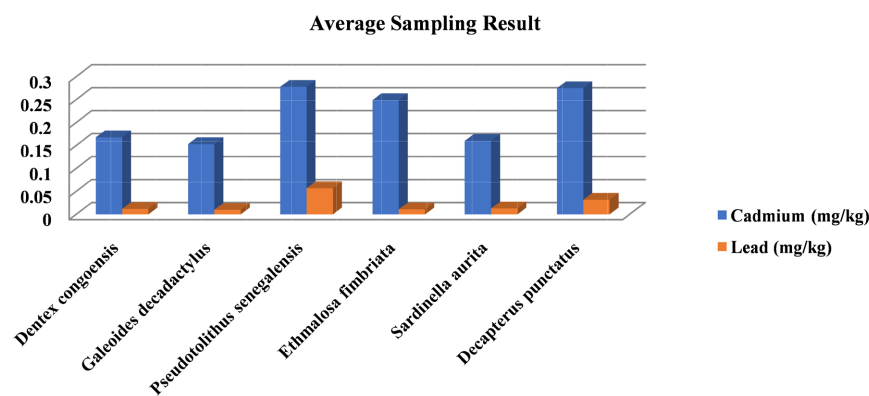
It should be noted that it was not possible to measure mercury because the concentrations were below the detection limit in the muscles of these fish. The low levels in fish muscle tissue could be explained by the fact that trace metals are



**Figure 3.** Second sampling campaign.



**Figure 4.** Third sampling campaign.



**Figure 5.** Average sampling results.

found in much greater quantities in the liver than in muscle tissue. This is because muscle is not a target organ for the accumulation and sequestration of trace elements [41].

This work made it possible to measure the levels of two of the three trace metals in the six species of fish sampled at the Boulbinet artisanal fishing port.

It should be noted that it was not possible to measure mercury levels because the concentrations were below the detection limit in the muscles of these fish.

In our study, *Decapterus punctatus* and *Pseudotolithus senegalensis* were the species with the highest concentrations of lead and cadmium, respectively, while the lowest concentrations were found in the muscles of *Galeoides decadactylus*. Taken together, these observations show that the bioaccumulation of the trace elements studied varies from one species to another.

A comparison of the sampling results indicates a relatively high concentration of cadmium compared to lead. The demersal species with the highest concentration of lead and cadmium is *Pseudotolithus senegalensis*, followed by *Dentex congoensis* and finally *Galeoides decadactylus*. On the other hand, the least exposed pelagic species is *Ethmalosa fimbriata*, followed by *Sardinella aurita* for lead and *Sardinella aurita* followed by *Ethmalosa fimbriata* for cadmium. It follows that, despite a lower trophic level, the measurements taken did not reveal any clear difference in the response to contamination between pelagic and demersal fish. The differences in concentrations between fish species living in the same habitat could therefore be explained by the feeding zone, as mentioned in the study conducted by Mr Z. Kljakovic Gaspic's team in 2002 [41] on hake (*Merluccius merluccius*), a semi-pelagic fish, and mullet, a coastal fish. This indicates that cadmium and lead contamination is very low, contrary to the conclusions of other studies conducted on Mediterranean fish.

The trace element levels in the demersal and pelagic species studied show minimum and maximum average concentrations ranging from (0.01 to 0.057 mg/kg) and (0.011 to 0.032 mg/kg) for lead, and (0.153 to 0.278 mg/kg) and (0.160 to 0.275 mg/kg) for cadmium in fish muscle tissue.

However, for the fish studied, lead accumulation was found in the muscles of individuals of these six species, with concentrations below the maximum levels permitted by Regulation (EU) (0.2 mg/kg) for the consumption of fresh fish. On the other hand, cadmium accumulation was detected above the maximum levels set by Commission Regulation (EU) 2021/1323 of 10 August 2021 on maximum levels of cadmium in certain fish species (0.1 mg/kg). The low levels in muscle tissue in fish could be explained by the fact that trace metals are found in much higher quantities in the liver than in muscle tissue. This is because muscle is not a target organ for the accumulation and sequestration of trace elements [42].

#### 4. Conclusions

This study addresses the issue of assessing the effects of pollution in coastal environments using fish as a biological model. An approach was developed by analyzing trace metals in order to obtain information that would both indicate an organism's exposure to chemical contaminants and assess the effects of this exposure on the health of individuals. For the pelagic and demersal fish species sampled, the measurements taken did not reveal any clear difference in the response to contamination between the two classes. However, the presence of lead and cadmium in the tissues is therefore evidence of exposure.

The differences in cadmium concentrations, which are relatively higher than

those of lead, could explained by the fact that fish can regulate the concentrations of inorganic forms of metals in muscle tissue and, in this case, the concentrations do not exceed regulatory or recommended limits even when the fish have been caught in lakes or ponds contaminated with metal or in marine environments exposed to metal contamination [43].

The relevance of this study lies in the environmental situation, which is worsening day by day, despite some efforts to limit the population's exposure to these pollutants. It is clear that even though industrialisation has not reached a very high level compared to developed countries, coastal pollution is an inevitable problem, particularly in the city of Conakry, where the country's industries are concentrated. Indeed, port transport activities, the discharge of ballast water from oil tankers on the high seas, the infiltration of crude oil and/or oil spills from fuel depots directly into the sea are among the major sources of contaminant emissions. In addition, effluent discharges from hospitals, hotels, industries and crafts, which are evacuated into urban networks without prior treatment, as well as conventional domestic wastewater, are another significant source of emissions.

Although analyses show that heavy metal accumulation in these edible marine species is evident, the results of our studies suggest that monitoring procedures should not be based solely on measuring contaminant levels in fish muscle tissue. Measuring levels in other organs such as the gills, liver, kidneys and bones also appears essential for assessing the effects of chemical contaminants. Given the limited data available on such an important subject, further studies should be conducted before reaching a definitive conclusion.

## Recommendation

Future studies should continue to develop biomarkers for different groups of contaminants and use them in key fish species at sensitive stages of their life cycle, combining different multi-stressor experimental approaches with field monitoring studies.

## Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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