

Quantification of Metal Residues (Cadmium, Lead and Mercury) from Sarda Sarda in the Region of NOSY FALY (Ambanja) and RAMENA (Diégo II)

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Abstract— As part of the national program for monitoring chemical contaminants in the environment, three trace metals (cadmium, lead and mercury) were quantified in twenty fish species most consumed by the population of the DIANA region, notably *Sarda sarda*. These fish were landed at two sites: RAMENA and NOSY FALY, between December 2024 and January 2025. The samples were analyzed by dispersive energy X-ray fluorescence. The average concentrations observed are as follows: cadmium varies from 0.005 ± 0.001 mg.kg⁻¹ to 0.082 ± 0.07 mg.kg⁻¹, the concentration of lead varies from 0.016 ± 0.004 mg.kg⁻¹ to 0.092 ± 0.008 mg.kg⁻¹, and that of mercury is below the detection limit. The measured concentrations remain below the limit values set by European regulations (Cd: 0.05 – 1.00 mg.kg⁻¹, Pb: 0.3 – 1 mg.kg⁻¹, and Hg: 0.5 – 1 mg.kg⁻¹).

Keywords— Cadmium, EDXRF, Mercury, DIANA Region, Lead.

I. INTRODUCTION

For a few years, the consumption of seafood, and more particularly fish, has been at the heart of the news regarding elements or components beneficial to health, such as essential fatty acids, notably the long-chain polyunsaturated fatty acids of the omega-3 family, proteins, as well as vitamins A, D and E and minerals [1]. Indeed, a 150 g portion of fish can provide about 50 to 60 percent of the daily protein needs of an adult [2]. Extensive research has demonstrated the potential of fish consumption in preventing cardiovascular disease and coronary heart disease [3,4], stroke [5], certain types of cancer [6,8], depression [9,10], as well as certain neurodegenerative diseases [11,12]. Nevertheless, fish can also be a major contributor to exposure to various environmental contaminants [13,14]. Heavy metals, such as mercury and cadmium, are a group of toxic substances that accumulate in fish tissues and are transmitted through the food chain to humans [15]. Repeated incidents of human poisoning by mercury, cadmium and lead in industrialized countries have highlighted environmental pollution as one of the most pressing challenges of our time. The industrial and technological revolution of the 21st century has been accompanied by a significant increase in the release of these substances, whether natural or synthetic, into the environment, with direct or indirect impacts on human and environmental health.

The DIANA region, in the fisheries sector, plays a crucial role in the economy, not only for export but also as a source of employment and income for many families, and a source of protein for a large part of the population. The marine areas are among the most abundant in the DIANA region and are home to considerable flora and fauna. Their fishery resources, which

are essential for food security and development in the DIANA region, are currently threatened by overexploitation that worsens the effects of pollution, harming the survival of certain species.

Numerous studies have been conducted to assess the concentration of trace metals in fish tissues, such as liver, kidney, stomach, skin, gills, bones, muscles and spleen [15,16]. Muscle is systematically analyzed due to the implications it has for human consumption and health risks. The liver is often favored, given the concentration of various contaminants present at levels higher than those of muscle. It plays a crucial role in the storage of contaminants, their redistribution, as well as in detoxification or transformation.

II. METHODOLOGY

A. Presentation of the study sites

The samples were taken in the district of ANTSIRANANA II of the region DIANA, more precisely in the rural commune of RAMENA and the rural commune of Nosy Faly (Ambanja District). RAMENA is located north of Madagascar, with a longitude of 49° 20' 44 E and a latitude of 12° 14' 76 S. Nosy Faly is located at the extreme northeast of the district of Ambanja, with a longitude of 48° 29' 16 E and a latitude of 13° 20' 41 S, 35 km northeast of the city of AMBANJA.

B. Sampling

The samples were collected from twenty individuals of *Sarda sarda*, a commonly consumed species. This includes 10 samples of fresh tuna from RAMENA and 10 samples of tuna from NOSY FALY, thus totalling 20 samples. The samples were taken during the period of December 2024, with the exception of the RAMENA tuna samples which were

collected in January 2025. The sampling was carried out randomly. The selection of batches to be taken was done at random, regardless of date or location. The samples are preferably taken at the distribution level. The collected samples are placed in polyethylene bags, which are then sealed and labelled. The fresh samples are then sent to the analysis laboratory in insulated boxes by express transport. In the laboratory, fish are thawed at room temperature in their sachet and dissected under a hood.

C. Fish studied

Like tuna and mackerel, bonito is a member of the scombrid family of pelagic fish that live in schools in the upper water layers of the sea. Its reproduction is faster than that of its larger tuna cousins. It rarely measures more than 70 to 80 centimeters and weighs between 3 and 4 kg, but can reach a weight of 7.6 kg [17].

- Name in: French; Bonite; Atlantic Bonito;
- Malagasy: Djaodary.
- Habitat: they are found in the northern parts of Madagascar (Nosy Faly and RAMENA).



Fig. 1: Djaodary

D. Methods and analytical technique used

This study was carried out at the Laboratory of Nuclear Physics and Environmental Physics (LPNPE) of the University of Antananarivo in Madagascar. The elemental analysis was conducted using an Amptek EXP-2 energy dispersive X-ray fluorescence spectrometer, which includes the following:

- Excitation source: X-ray tube with silver anode (Ag), operating at 40 kV and 100 μ A,
- Detector: Si-PIN cooled by the Peltier effect, offering an energy resolution of 180 eV FWHM at 5.9 keV,
- Collimators: multilayer collimation system to improve the signal/noise ratio,
- Filters: 500 μ m aluminum (Al) filter to reduce low energy radiation.

This technique is simple, more sensitive, faster and is one of the most commonly used for the determination of ETM in biological tissues. The acquisition of spectra was carried out with the DPP-MCA software (Amptek, version 1.0.0.12), according to the following parameters:

- Acquisition time: 200 seconds per sample,
- Number of channels: 2048,
- Amplification gain: 12.5.

Spectra processing and quantitative analysis were performed using the XRS-FP2 (Amptek) software, using the fundamental parameters algorithm to convert spectral intensities into elemental concentrations. The calibration of the system was carried out using a series of single-element and multi-element reference standards.



Fig. 2. X-ray fluorescence spectrometer device (Amptek EXP-2) used for sample analysis.

E. Sample preparation

The preparation of samples was carried out according to a standardized protocol aimed at obtaining homogeneous and representative specimens for analysis by ED-XRF:

- **Drying:** The samples underwent calcination at 450°C for 30 minutes in a muffle oven to remove organic matter, which reduces matrix effects that may interfere with spectrometric analysis.
- **Grinding:** The calcined samples were finely ground using a mortar and an agate pestle to avoid any metal contamination. The grinding was continued until obtaining a homogeneous powder with a particle size of less than 50 μ m.
- **Sieving:** The resulting powder was sieved through a 50 μ m mesh nylon sieve to ensure the particle size uniformity of the final sample.
- **Packaging:** A mass of 4,00 g of each sieved sample was taken using an analytical balance and placed in a high-density polyethylene sample holder, equipped with an ultralight support film 4 μ m thick.

For each series of analyses, a certified reference sample was prepared according to the same protocol in order to validate the analytical method.

Metal elements are found in natural environments at relatively low concentrations, on the order of mg/kg. As part of this study, the sampling methods, of sampling, packaging and analysis of the samples followed strict protocols to avoid any contamination. The treatments applied to the samples as well as the measurements were validated by the analysis of reference materials and doped matrices.

III. RESULTS AND DISCUSSIONS

The results of these analyses indicate that they contain metal traces (Cadmium, Lead and Mercury) from Sarda sarda in the area of NOSY FALY (Ambanja) and RAMENA (Diégo Suarez).

A. Levels of trace metals in the liver of Sarda sarda studied.

The liver is recognized for its roles in storage and regulation of elements [18, 19]. It plays a role in the distribution, detoxification and transformation of contaminants, and is the preferred target for organic mercury [20]. Table 1 illustrates the average concentration of metal traces in the liver of *Sarda sarda* studied.

TABLE 1: Average concentration (n=5) of metal traces in the liver of *Sarda sarda* analyzed

	Ramena	Nosy Faly
Cd (mg.kg⁻¹)	0,031 ± 0,005	0,082 ± 0,07
Pb (mg.kg⁻¹)	0,092 ± 0,008	0,054 ± 0,008
Hg (mg.kg⁻¹)	< LD	< LD

From table 1, we observe that cadmium is present at the RAMENA site as well as at the Nosy Faly site. It is indeed striking to note that high values are detected in places apparently not very polluted: at RAMENA and at Nosy Faly. Indeed, Moukrim et al. proposed that these high levels of Cd are probably attributable to the phenomenon of Upwelling [21]. The most significant concentrations of Cd found in liver samples are explained by the function of the liver, which is an organ of accumulation and detoxification. Cadmium levels in the liver of *Sarda sarda* in our study are lower than those reported by Hernandez et al : 0.3 mg.kg⁻¹ [22], Canli et al. : 3 mg.kg⁻¹ [23] and by Canli et al. : 4.8 mg.kg⁻¹ [24]. Our results are similar to those reported by El Morhit et al. [25].

Pb concentrations may increase as the food chain progresses, as is the case for mercury in its methylated form [26]. Lead levels in the liver of *Sarda sarda* from both sites are noted. It is noted that the RAMENA site exhibits 0.092 ± 0.008 mg.kg⁻¹, while the Nosy Faly site displays 0.054 ± 0.008 mg.kg⁻¹. Data available in the literature indicate that lead levels in the liver of *Sarda sarda* range from 0.3 mg/kg to 39.4 mg/kg [27], [28]. Pb contamination is mainly due to urban and industrial liquid discharges, as well as pollution caused by car traffic [29].

Mercury (Hg) levels in the liver indicate a recent ingestion of mercury by the body. The liver also has a crucial function in mercury accumulation and metabolism in fish [30, 31, 32]. We observe that the concentration of mercury in the liver of *Sarda sarda* from the RAMENA and Nosy Faly sites is lower than the detection limit.

B. Average concentrations (n=5) of metal traces in the gills of *Sarda sarda* analyzed

The gills represent one of the first interfaces between water and the organism. Due to their crucial role in extracting life-sustaining elements directly from their environment, the gills also serve as an initial site for adsorption and accumulation of metals. The interaction with the external gill surface and the rate of assimilation depend on the chemical properties of the metals [19] as well as physiological factors such as the ventilation rate. Concentrations of trace elements in the gills generally reflect the composition of the environment over a short period [18], especially in case of point pollution. Metal traces are first accumulated in the gills, which act as temporary target organs, before being transferred to digestive organs such as the liver, kidneys and intestine [33]. Table 2

illustrates the average concentration of metal traces in the gills of *Sarda sarda* analyzed.

TABLE 2: Mean (n=5) concentration of metal traces in the studied *Sarda sarda* gills

	Ramena	Nosy Faly
Cd (mg.kg⁻¹)	0,016 ± 0,001	0,011 ± 0,003
Pb (mg.kg⁻¹)	0,049 ± 0,002	0,049 ± 0,005
Hg (mg.kg⁻¹)	< LD	< LD

Table 2 presents the levels of Cd in the gills of *Sarda sarda* from different sampling sites. Mean concentrations vary significantly between sampling sites, such as Ramena (0.016 ± 0.001 mg.kg⁻¹) and NOSY Faly (0.011 ± 0.003 mg.kg⁻¹). Hernandez et al. and El Morhit et al. [28], [25] reported comparable Cd concentrations (0.06 and 0.08 mg.kg⁻¹ respectively). On the other hand, the levels of Cd observed in the gills of *Sarda sarda* in the Mediterranean [23], [24] exceed our results. No difference in lead concentration was observed in the gills between RAMENA and NOSY FALY sites (0.049 mg.kg⁻¹). The results of our study are significantly lower than those reported by Hernandez et al. (0.5 mg.kg⁻¹) [28] and El Morhit et al. (18.8 mg.kg⁻¹) [25]. Regarding RAMENA and NOSY FALY, the very low levels of mercury in the gills of *Sarda sarda* indicate that water in direct contact with fish contains little or no mercury, and therefore no recent intake of total mercury is noted.

C. Average (n=5) metal trace contents in the studied *Sarda sarda* pulpits.

The chairs, in addition to the liver, represent the most essential organs from a toxicological point of view because of their crucial role in the processes of metabolism and accumulation. By crossing the intestinal or branchial walls, metals enter the blood stream where they bind to haemoglobin. The metals are then transported to target tissues. The pulpits and the liver are especially noteworthy among these organs. Table 2 presents the average concentration of metal traces in the *Sarda sarda* chairs that were studied.

TABLE 3: Mean concentration (n=5) of metal traces in the studied *Sarda sarda* chairs

	Ramena	Nosy Faly
Cd (mg.kg⁻¹)	0,006 ± 0,001	0,005 ± 0,001
Pb (mg.kg⁻¹)	0,023 ± 0,005	0,016 ± 0,004
Hg (mg.kg⁻¹)	< LD	< LD

< LD: lower than the detection limit.

Table 3 illustrates the distribution of mercury in muscle. The observed values are below the detection limit in the two studied sites. The concentration of lead in tissues between the RAMENA site (0.023 ± 0.005 mg.kg⁻¹) and the NOSY FALY site (0.016 ± 0.004 mg.kg⁻¹) is noted. The results of our study are not very comparable to those reported by Adil CHAHID et al. (0.016 mg.kg⁻¹ to 0.023 mg.kg⁻¹) [34] [35]. The cadmium levels in *Sarda sarda* muscle in our study are similar to those mentioned by Chahid et al. [36] [37].

IV. CONCLUSION

Cadmium, lead and mercury are present in all

environmental compartments and have become an international concern due to their toxicity to the organism and the environment. That is why these three metals and their harmful effects are the subject of increasingly detailed studies. This research provides new knowledge that is crucial not only for understanding site contamination, but also more generally for assessing the risks associated with consumption of certain fishery products. We have demonstrated that the average cadmium content in the analyzed products ranges from 0.005 0.001 mg.kg⁻¹ to 0.082 0.07 mg.kg⁻¹, the concentration of lead fluctuates between 0.016 0.004 mg.kg⁻¹ and 0.092 0.008 mg.kg⁻¹, while that of mercury is below the detection limit. All samples analyzed have average concentrations of Cd, Pb and Hg that remain below regulatory limits. Therefore, the Sarda sarda from the DIANA region does not represent any risk for consumers of this species.

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REFERENCES

- [1] Storelli, M.M., *Potential human health risks from metals (Hg, Cd, and Pb) and polychlorinated biphenyls (PCBs) via seafood consumption: Estimation of target hazard quotients (THQs) and toxic equivalents (TEQs)*. Food and Chemical Toxicology, 2008. 46: p. 2782–2788.
- [2] F.A.O. *Consulté le 08 aout 2015. La situation mondiale des pêches et de l'aquaculture 2014*. 2014; Available from: <http://www.fao.org/3/a-i3720f/i3720f01.pdf>.
- [3] Daviglius, M.L., et al., *Fish consumption and the 30-year risk of fatal myocardial infarction*. N Engl J Med, 1997. 336(15): p. 1046-53.
- [4] Kris-Etherton, P.M., W.S. Harris, and L.J. Appel, *Fish consumption, fish oil, omega-3 fatty acids, and cardiovascular disease*. Circulation, 2002. 106: p. 2747-2757.
- [5] He, K., et al., *Fish consumption and incidence of stroke: a meta-analysis of cohort studies*. Stroke, 2004. 35(7): p. 1538-42.
- [6] Hirose, K., et al., *Dietary factors protective against breast cancer in Japanese premenopausal and postmenopausal women*. Int J Cancer, 2003. 107(2): p. 276-82.
- [7] Norat, T., et al., *Meat, fish, and colorectal cancer risk: the European Prospective Investigation into cancer and nutrition*. J Natl Cancer Inst, 2005. 97(12): p. 906-16.
- [8] Astorg, P., Couthouis, A., Bertrais, S., Arnault, N., Meneton, P., Guesnet, P., Alessandri, J. M., Galan, P. & Hercberg, S., *Association of fish and long-chain n-3 polyunsaturated fatty acid intakes with the occurrence of depressive episodes in middle-aged French men and women*. Prostaglandins Leukot Essent Fatty Acids, 2008. 78: p. 171-82.
- [9] Timonen, M., et al., *Fish consumption and depression: the Northern Finland 1966 birth cohort study*. J Affect Disord, 2004. 82(3): p. 447-52.
- [10] Huang, T.L., et al., *Benefits of fatty fish on dementia risk are stronger for those without APOE epsilon4*. Neurology, 2005. 65(9): p. 1409-14.
- [11] Morris, M.C., et al., *Consumption of fish and n-3 fatty acids and risk of incident Alzheimer disease*. Arch Neurol, 2003. 60(7): p. 940-6.
- [12] Llobet, J.M., et al., *Concentrations of arsenic, cadmium, mercury, and lead in common foods and estimated daily intake by children, adolescents, adults, and seniors of Catalonia, Spain*. J Agric Food Chem, 2003. 51(3): p. 838-42.
- [13] Usero, J., et al., *Heavy metals in fish (Solea vulgaris, Anguilla anguilla and Liza aurata) from salt marshes on the southern Atlantic coast of Spain*. Environ. Int., 2003. 29: p. 949–956.
- [14] Storelli, M.M., *Potential human health risks from metals (Hg, Cd, and Pb) and polychlorinated biphenyls (PCBs) via seafood consumption: estimation of target hazard quotients (THQs) and toxic equivalents (TEQs)*. Food Chem Toxicol, 2008. 46(8): p. 2782-8.
- [15] Buggiani, S.S. and C. Vannucchi, *Mercury and lead concentrations in some species of fish from the Tuscan coasts (Italy)*. Bulletin of Environmental Contamination and Toxicology, 1980. 25(1): p. 90-92.
- [16] Wharfe, J.R. and W.L.F. Van Den Broek, *Heavy metals in macroinvertebrates and fish from the lower Medway estuary, Kent*. Marine Pollution Bulletin, 1977. 8(2): p. 31-34.
- [17] F.A.O., *Consulté le 03 aout 2015. Fisheries and Aquaculture Department*. 2015.
- [18] Kalay, M. and M. Canli, *Elimination of Essential (Cu, Zn,) and Non-Essential (Cd, Pb) Metals from Tissues of Freshwater Fish Tilapia zilli*. Turkish Journal of Zoology, 2000. 24: p. 429-436.
- [19] Wepener, V., J.H.J. Van Vuren, and H.H. Du Preez, *Uptake and distribution of a copper, iron, and zinc mixture in gill, liver and plasma of a freshwater teleost, Tilapia sparrmanii*. Water SA 2001. 27(1): p. 99-108.
- [20] Havelkova, M., et al., *Comparison of mercury distribution between liver and muscle – A biomonitoring of fish from lightly and heavily contaminated localities*. Sensors, 2008. 8: p. 4095-4109.
- [21] Moukrim, A., et al., *Assessment of the Trace Metal Levels in Two Species of Mussels from the Agadir Marine Bay, South of Morocco*. Bull. Environ. Contam. Toxicol., 2000. 65: p. 478-485.
- [22] Hernandez-Hernandez, F., et al., *Heavy metal concentrations in some marine organisms from the Mediterranean Sea (Castellon, Spain): Metal accumulation in different tissues*. Scient. Mar, 1990. 54(2): p. 113-129.
- [23] Canli M. and Altı G., *The relationships between heavy metal (Cd, Pb, Cu, Fe, Zn, Cr) levels and the size of six Mediterranean fish species*. Environmental pollution 2003. 121 p. 129-136.
- [24] Canli, M., M. Kalay, and O. Ay, *Metal (Cd, Pb, Cu, Fe, Zn, Cr, Ni) Concentrations in tissues of a Fish Sardina pilchardus and a Prawn Penaeus japonicus from three Stations on the Mediterranean Sea*. Bull. Environ. Contam. Toxicol., 2001. 67: p. 75-82.
- [25] El Morhit, M., D. Belghity, and A. El Morhit, *Contamination métallique de Pagellus acarne, Sardina pilchardus et Diplodus vulgaris de la côte atlantique sud (Maroc)*. 2013.
- [26] Miquel, G., *Les effets des métaux lourds sur l'environnement et la santé, in Rapport Office Parlementaire d'évaluation des choix scientifiques et technologiques (Dir.)*, Editor. 2001, rapport Sénat Rapport Office Parlementaire d'évaluation des choix scientifiques et technologiques (Dir.).
- [27] El Morhit, M., Fekhaoui, M., El Abidi, A., Yahyaoui, A., *Contamination métallique des muscles de cinq espèces de poissons de l'estuaire du bas Loukkos (Côte Atlantique Marocaine)* ScienceLib, 2012. 4(2111-4706).
- [28] Hernandez-Hernandez, F., et al., *Heavy metal concentrations in some marine organisms from the Mediterranean Sea (Castellon, Spain): Metal accumulation in different tissues*. Scient. Mar, 1990. 54(2): p. 113-129.
- [29] Benbrahim, S., et al., *Etude des facteurs influençant la répartition géographique et temporelle de la contamination des côtes atlantiques marocaines par les métaux lourds : cas du mercure, du plomb et du cadmium*. Mar. Life, 2006. 16: p. 37-47.
- [30] Mieiro, C.L., et al., *Mercury Organotropism in Feral European Sea Bass (Dicentrarchus labrax)*. Arch Environ Contam Toxicol 2010.
- [31] Drevnick, P.E., et al., *Mercury toxicity in livers of northern pike (Esox lucius) from Isle Royale, USA*. Comp Biochem Physiol C Toxicol Pharmacol, 2008. 147: p. 331-338.
- [32] Elia, A.C., et al., *Antioxidant responses and bioaccumulation in Ictalurus melas under mercury exposure*. Ecotoxicol Environ Saf, 2003. 55: p. 162-167.
- [33] Alkaa, Y., et al., *Diagnostic écotoxicologique des populations de la sardine (Sardina pilchardus) pêchée le long des zones côtières atlantiques allant de Safi à Cap Blanc*.
- [34] Chahid A., Hilali M., Benlhachemi A., Bouzid T. 2014. "Contents of cadmium, mercury and lead in fish from the Atlantic sea (Morocco) determined by atomic absorption spectrometry". Food chemistry, 147: 357-360.
- [35] Chahid A., Hilali M., Benlhachemi A., Kadmiri I.M., Bouzid T. 2014. "Concentrations of heavy metals in muscle, liver and gill of Sardina pilchardus (Walbaum, 1792): Risk assessment for the consumers". Journal of Environmental and Occupational Science, 3(1):47-52.
- [36] Chahid A., Hilali M., Benlhachemi A., Bouzid T. "Heavy metals content of canned tuna fish: estimated weekly intake". Moroccan Journal of Chemistry 3 (1), 152-156.

- [37] Adil CHAHID, (2016). "*Quantification des éléments traces métalliques (cadmium, plomb et mercure total) de certains produits de la pêche débarqués dans la zone Essaouira-Dakhla : Evaluation des risques sanitaires*", Thèse de Doctorat, Chimie fondamentale et Appliquée, University Ibn Zohr, p 83 et 84.