Metallic trace elements in sea fish of Morondava and the sanitary risks

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ABSTRACT

There is risk for the contamination of trace elements in food to human (and/or animal) health. As a part of the national monitoring plan for chemical contaminants in the Marine Environment, four metallic trace elements (arsenic, cadmium, total mercury and lead) are analyzed in eight species of sea fish from Morondava at the West coast of Madagascar. They are classified harmful as far as human health and marine environment are concerned. Fish samples are analyzed by Energy Dispersive X-Ray Fluorescence (EDXRF). Cadmium concentrations in muscle meats are under the WHO/FAO standard of 0.05 $mg.kg^{-1}$. Thus, concerning cadmium, all fish meats present no risk for human consumption. But, cadmium contents are higher in bronchitis than in bones of six species of fish. For *Sphyraena fosteri* and *Polydactylus sextarius*, total mercury contents are higher than WHO/FAO standard of 0.5 $mg.kg^{-1}$. The concentrations of arsenic, ranging from 3.4 to 19.4 $mg.kg^{-1}$, in muscle meats of fish for all species exceed WHO/FAO limit value of 0.1 $mg.kg^{-1}$. The human body can inactivate and eliminate much of the amount of arsenic; but even if the arsenic in sea food is found in its less toxic organic form, on long term it may accumulate in the kidney, liver and skin. Concerning lead, its concentration is more than the WHO/FAO guideline (0.2 $mg.kg^{-1}$) and the European Union maximum limit (0.3 $mg.kg^{-1}$). Higher concentration is 1.4 $mg.kg^{-1}$. Heavy metals are considered the most toxic to humans and animals even at low concentrations, among other harmful effects, neurotoxic and carcinogenic actions are the most common ones.

Keywords: arsenic, cadmium, mercury, lead, sea fish, EDXRF, Madagascar.

1. INTRODUCTION

Madagascar is the fourth largest island in the world located in the Eastern Africa. Fishing is with the mining sector and tourism, one of the three main economic sectors of this country. It is a vital activity. Unfortunately, it is threatened by the release of naturally occurring toxic chemicals such as metals. Domestic, industrial and anthropogenic activities are mainly the source of natural aquatic systems contamination of heavy metals [1,2]. Although certain metals are essential to the metabolism of living beings (arsenic, chromium, copper, iron, nickel, zinc), they become toxic beyond a certain concentration. Other metals, such as cadmium or lead, are not necessary for life and are toxic [3]. However, fishery products are most often used for human and very often for animal consumptions of food. They may contain large amounts of these metals which have a negative impact on the quality of food [4]. The present work tackles the study the problem of contamination of Morondava sea fish from Morondava on the west coast of Madagascar. Its objectives are to determine the levels of arsenic, cadmium, lead and mercury in different fish species.

2. MATERIALS AND METHODS

2.1. Sampling site and sampling protocol

Sampling was carried out at Morondava, in western coast of Madagascar, at the edge of the Mozambique Channel (20° 17' 05" S, 44° 15' 16" E) during 12-15 November 2017.

Eight (08) sea fish species such as *Gazza minuta* (Toothpony), *Gymnosarda unicolor* (Dogtooth tuna), *Upeneus taeniopterus* (Finstripe goatfish), *Sphyraena fosteri* (Bigeye barracuda), *Polydactylus sextarius* (Blackspot threadfin), *Herklotsichthys quadrimaculatus* (Bluestripe herring), *Chirocentrus dorab* (Dorab wolf-herring), *Euthynnus affinis (*Kawakawa) were collected. Figure 1 shows the photos of eight species of fish from the Morondava Sea.

Figure 1. Photos of eight species of fish from the Morondava Sea

They were stored in a cooler containing refrigerant (ice cubes) and transported to INSTN-Madagascar laboratory for analysis.

2.2. Analysis protocol

2.2.1. Fish preparations

Fish scales were peeled off with a tool. Then, the viscera, roes and eggs were removed from the belly of the fish. Then fish were washed and rinsed thoroughly to clean it. The muscles, bones and bronchitis of fish were separately dried in an oven at 85 °C for 48 hours and grinded.

2.2.2. X-ray Fluorescence Metals Analysis

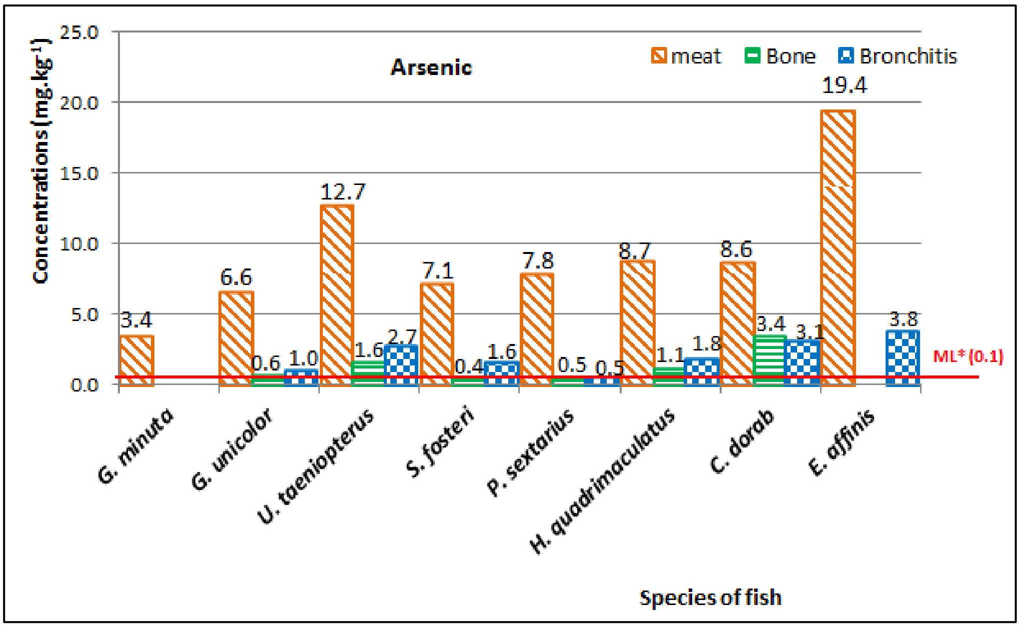
The metals were measured using a SPECTRO XEPOS Energy Dispersive X-ray Fluorescence spectrometer. The results are expressed in $mg.kg^{-1}$ of dry weight.

3. RESULTS AND DISCUSSION

Multielemental analysis of the toxic chemical elements in the eight species of Morondava sea fish shows the presence of the four elements: arsenic (As), cadmium (Cd), mercury (Hg) and lead (Pb).

3.1. Arsenic

Arsenic concentrations in the muscles, bones and bronchitis of fish species are illustrated in Figure 2.



***ML: Maximum Limit**

Figure 2. Arsenic concentrations in muscles, bones and bronchitis of fish species

The concentrations of arsenic in fish muscles, ranging from 3.4 to 19.4 $mg.kg^{-1}$, are higher than the World Health Organization/Food and Agriculture Organization (WHO/FAO) standards of 0.1 $mg.kg^{-1}$ [4, 5]. *Euthynnus affinis* and *Upeneus taeniopterus* fish have the highest concentrations of 19.4 $mg.kg^{-1}$ and 12.7 $mg.kg^{-1}$ respectively. High arsenic content could come from crops irrigated with arsenic-rich water, industrial processes. At high concentrations, it can be harmful for humans and animals.

Arsenic has no known biological function in human body. It may be in inorganic or organic form. Inorganic compounds (such as those present in water) are very toxic. Its inorganic form can damage DNA and it is carcinogenic. But organic compounds (such as those in seafood) are less harmful to health [6]. Arsenic organic form is mainly less toxic and accumulates in the exoskeleton of invertebrates and in the liver of fish [7].

3.2. Cadmium

Cadmium is a relatively rare element emitted into the air, earth and water by human activity. Figure 3 shows cadmium concentrations in muscles, bones and bronchitis of fish species.

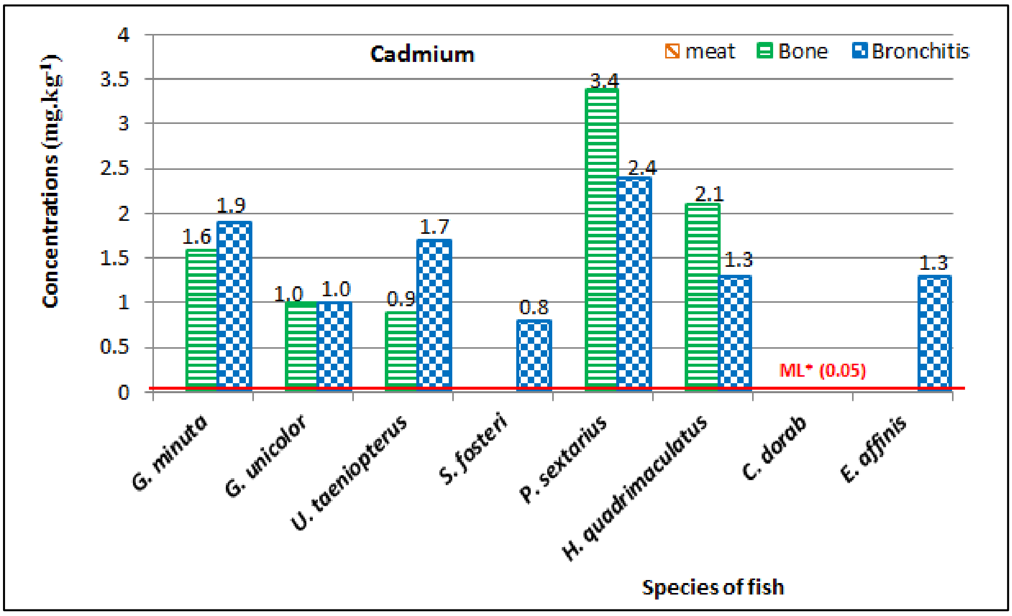


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Figure 3. Cadmium concentrations in muscles, bones and bronchitis of fish species

Cadmium concentrations in muscle meats are not detected, below the detection limit of 0.3 $mg.kg^{-1}$. They are of course lower than the WHO/FAO standards and European Union (EU) maximum limit of 0.05 $mg.kg^{-1}$ [5,8] Cadmium levels are the lowest in muscles fish. This may be due to the fact that cadmium has no biological role in living organisms [9]. Thus, there is no risk in term of cadmium. The concentrations of cadmium are higher in bronchitis than in fish species, with the exception of those in *Polydactylus sextarius* and *Herklotsichthys quadrimaculatus*. In this case, these concentrations are in the range of 0.8 to 2.4 $mg.kg^{-1}$.

3.3. Mercury

Mercury occurs naturally in the environment and exists in a large number of forms. Like lead or cadmium, mercury is a constituent element of the earth, a heavy metal. It is considered by WHO to be one of the ten chemicals or groups of chemicals of very high concern for public health. Mercury concentrations in muscles, bones and bronchitis of fish species are given in Figure 4.

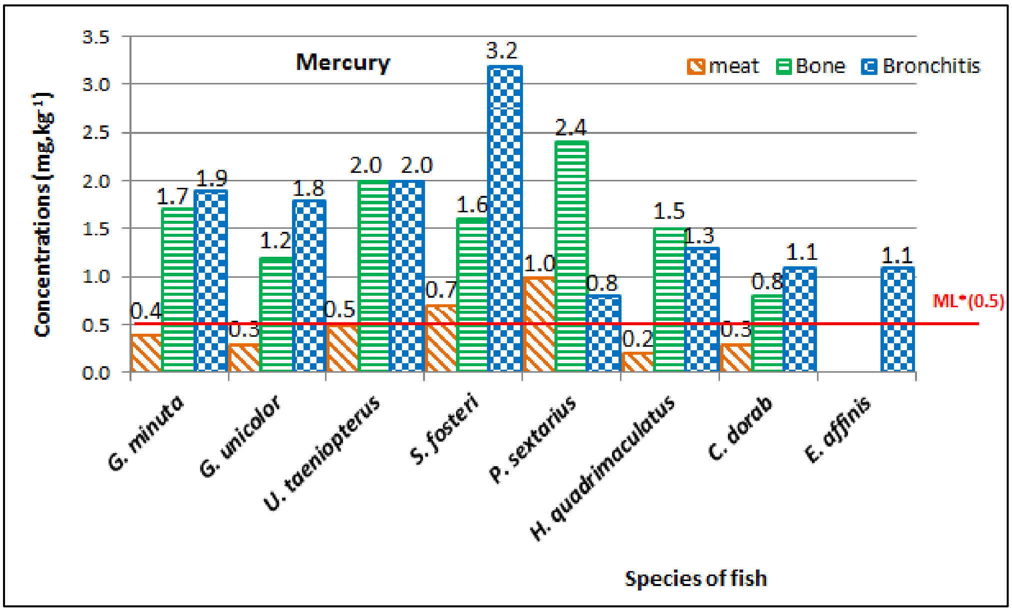

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Figure 4. Mercury concentrations in muscles, bones and bronchitis of fish species

The contents of mercury in *Sphyraena fosteri* and *Polydactylus sextarius* do not respect WHO/FAO standard of 0.5 mg.kg^{-1} [10]. High concentrations of mercury in bronchitis of all species are observed. The concentrations vary from 0.8 to 3.2 mg.kg^{-1}. The maximum level (3.2 mg.kg^{-1}) corresponds to *Sphyraena fosteri*. Toxicity mainly affects brain, kidney, endocrine and cell cycle functions.

3.4. Lead

Lead (Pb) is as a potent environmental pollutant. Its toxicity is very important due to its great concern for human health. Figure 5 shows the lead levels in the muscles, bones and bronchitis of fish species.

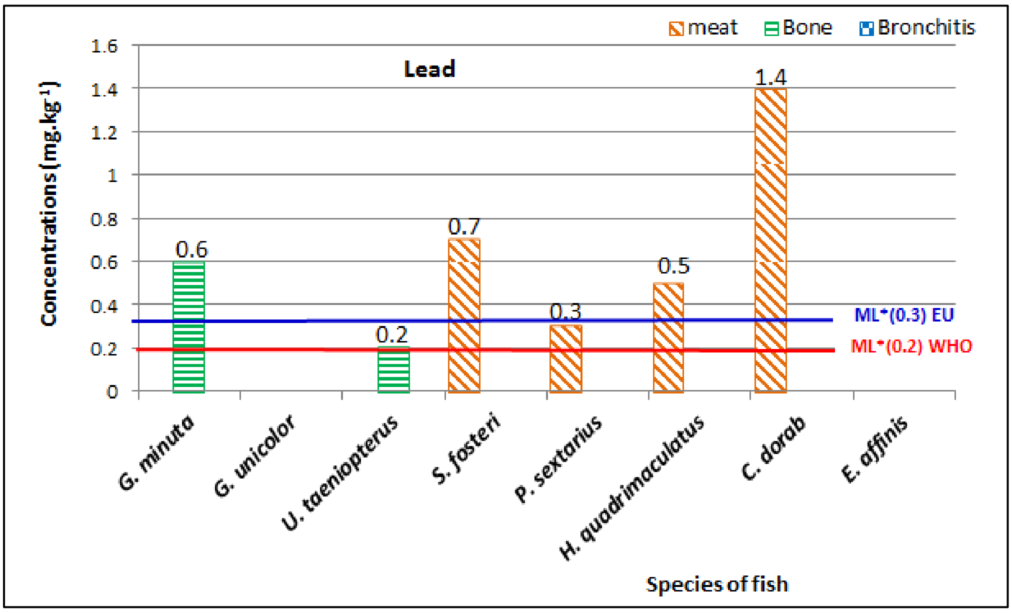

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Figure 5. Lead levels in muscles, bones and bronchitis of fish species

Lead levels in the muscles of *Sphyraena fosteri, Polydactylus sextarius, Herklotsichthys quadrimaculatus and Chirocentrus dorab* fish are 0.7 $mg.kg^{-1}$; 0.3 $mg.kg^{-1}$; 0.5 $mg.kg^{-1}$and 1.4 $mg.kg^{-1}$ respectively. These levels exceed 0.2 $mg.kg^{-1}$ of WHO/FAO standard [4] in the fish and three of these levels are greater than or equal to 0.3 $mg.kg^{-1}$ of EU maximum value [11]. Therefore, they may be dangerous for consumers [12].

The traffic of adulterated petroleum products on the lagoon system is not negligible with regard to pollution by lead, because these petroleum products are dumped into the lake voluntarily or accidentally during the transportation [13]. Organic lead is not completely eliminated from gasoline. The inorganic lead of petrol traffic is more toxic than the lead inorganic compounds [14]. A level of 1.4 $mg.kg^{-1}$ is lethal for fish. This elevated level can be attributed to anthropogenic sources especially from paints and leaded gasoline which spill from boats. Lead can enter the human body in three ways: by inhalation, by ingestion and by the dermal route. Lead diffuses rapidly through the bloodstream into various organs such as the brain, highly calcified tissues (teeth and bones) [15]. Fish and people are primarily exposed to lead by food ingestion and breathing. Lead accumulates in the muscles and bones.

4. CONCLUSION

The present work shows that X-ray Fluorescence technique, particularly, Energy Dispersive X-Ray Fluorescence EDXRF) is able to analyze heavy metals in fish species from the sea of Morondava. The results show that four metallic trace elements (As, Cd, Hg and Pb) pollute the eight species of sea fish in comparison with the standards recommended by WHO/FAO and EU. Cadmium levels in muscle meats are below the WHO/FAO and EU standards. The highest concentrations of cadmium are in bronchitis of fish species, with the exception of those in *Polydactylus sextarius* and *Herklotsichthys quadrimaculatus*. The highest concentration of lead (1.4 $mg.kg^{-1}$) accumulates in fish muscles and bones. Primary sources include discharge from paints and leaded gasoline spilled from boats.

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REFERENCES

[1] Velez D, Montoro R., "Arsenic speciation in manufactured seafood products", J Food Prot. 61: 1240-1245, 1998.

[2] Conacher H, Mes J., "Assessment of human exposure to chemical contaminants in foods", Food Addit. Cont. 10:5-15, 1993.

[3] Cédric Fisson, "Qualité des eaux de l'estuaire de la Seine", Fascicule 3.2 : 20, 2014.

[4] OMS/FAO, "Norme générale pour les contaminants et les toxines présents dans les produits de consommation humaine et animale" CODEX STAN 193-1995 Adoptée en 1995. Révision : 1997, 2006, 2008, 2009. Amendement : 2010, 2012, 2013, 2014, 2015.

[5] OMS/FAO, "Liste provisoire des principales espèces de poissons faisant l'objet d'un commerce international (y compris propositions concernant des concentrations maximales de plomb dans différentes espèces de poissons)", Trente-septième session, La Haye, Pays-Bas, 2005.

[6] Edmonds J.S., Francesconi K.A., "Arsenic in seafoods: human health aspects and regulations", Marine Poll. Bull., 26, 665-674, 1993.

[7] Axelle Leufroy, "Spéciation de l'arsenic dans les produits de la pêche par couplage HPLC/ICP-MS. Estimation de sa bioaccessibilité en ligne et applications à d'autres éléments traces métalliques d'intérêt". Thèse de Doctorat, 2012.

[8] Règlement (UE) N° 488/2014 de la commission du 12 mai 2014 modifiant le Règlement (CE) N° 1881/2006 en ce qui concerne les teneurs maximales en cadmium dans les denrées alimentaires, Journal officiel de l'Union européenne, 2014.

[9] V. M. Muinde, E. K. Nguu, D. O. Ogoyi and P. M. Shiundu, "Effects of Heavy Metal Pollution on Omega-3 Polyunsaturated Fatty Acids Levels In Tilapia Fish from Winam Gulf of Lake Victoria". The Open Environmental Engineering Journal, Vol. 6, 29, 2013.

[10] OMS/FAO, "Evaluation de certains additifs alimentaires et des contaminants : mercure, plomb et cadmium, Sixième rapport du Comité mixte FAO/OMS d'experts des Additifs alimentaires", Genève, 14p, 1972. URL : http://www.asef-asso.fr/production/mercure-peut-on-encore-consommer-du-poisson-la-synthese-de-lasef/

[11] Règlement (UE) 2015/1005 de la commission du 25 juin 2015 modifiant le règlement (CE) n° 1881/2006 en ce qui concerne les teneurs maximales en plomb dans certaines denrées alimentaires, Journal officiel de l'Union européenne, L 161/1, 2015.

[12] M. Öztürk, G. Özözen, O. Minareci, and E. Minareci, "Determination of heavy metals in fish, water and sediments of Avsar dam lake in Turkey", Iran. J. Environ. Health. Sci. Eng., vol. 6, no. 2, pp. 73-80, 2009.

[13] Kamilou Ouro-Sama, Hodabalo Dheoulaba Solitoke, Kissao Gnandi, Komlan Mawuli Afiademanyo and Essô Joseph Bowessidjaou, "Evaluation et risques sanitaires de la bioaccumulation de métaux lourds chez des espèces halieutiques du système lagunaire togolais", VertigO - *la revue électronique en sciences de l'environnement*, Vol.14 Nº2, septembre 2014. URL: http://journals.openedition.org/vertigo/15093.

[14] Alassane Youssao et al, "Evaluation de la bioaccumulation du plomb dans les espèces animales marines et identification des sources de contamination métallique par une analyse multiélémentaire en métaux (Al, Cd, Cr, Cu, Pb) dans les eaux côtières du Bénin", Int. J. Biol. Chem. Sci. 5(1) : 188-195.

[15] V. M.C Laperche, et al.. "Guide méthodologique du plomb appliqué à la gestion des sites et des sols pollués". Rapport final BRGM/RP-52881-FR, 2004.