Estimation of Some Heavy Metals Intake through Tuna Loins (*Thunnus* Sp) Produced in Côte D'ivoire

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Abstract

The aim of the present study was to measure concentrations of three heavy metals in tuna loins of four tuna species from two industries in Côte d'Ivoire during September 2011 to September 2013. Cadmium (Cd) and lead (Pb) concentrations were measured by graphite furnace atomic absorption spectrometry and Mercury (Hg) was measured by cold vapour atomic absorption spectrometry. Results showed that the concentration varied from 0.029 to 0.470 with a mean of 0.203 ± 0.103 mg/kg for Hg; from 0.002 to 0.092 with a mean of 0.015 ± 0.014 mg/kg for Cd and from 0.016 to 0.310 with a mean of 0.162 ± 0.057 mg/kg for Pb. These concentrations are lower than the maximum permissible values in European and Ivoirian regulation. The average weekly intakes of Cd, Pb and Hg per body weight values respectively 0.39; 0.97 and 1.21 not exceeded the Provisional Tolerable Weekly Intake (PTWI) established.

Keywords: Lead, Cadmium, Mercury, tuna loins, PTWI, Côte d'Ivoire

1. Introduction

Several pollutants such as heavy metals like Cadmium, lead and Mercury are cumulative toxic, stable and not easy biodegradable (Ikem and Egibor, 2005). Except for occupationally exposed individuals, food is usually the most important source of toxic trace element intake. Amongst food, fish are constantly exposed to heavy metals present in ocean and sea water. Thus, fish have been found to be good bioindicators or biosensor of heavy metal contamination in aquatic systems (Burger and *al.*, 2002, Keskin and *al.*, 2007). Amongst fish species recognized as potentially accumulating elevated metal levels, tuna is one of the most frequently consumed and commercially available groups of fish worldwide (Burger and *al.*, 2005). These pelagic organisms are high performance fish with very high metabolism rates and, thus, high food intake rates, a property that accentuates the exposure to trace elements (Kojadinovic and *al.*, 2007). Consequently, adverse human health effects may occur if this fish is consumed too often or in large enough quantities. Mercury can cause serious brain damage, including psychological disturbance, impaired hearing, loss of sight, ataxia, loss of motor control and general debilitation (Aschners, 2002). Cadmium cause impaired kidney function, poor reproductive capacity, hypertension, tumours and hepatic dysfunction (Waalkes, 2000).

Ingestion of lead causes lead poisoning which causes disturbances to the acquisition of some higher brain functions and can be the cause of intellectual delays, learning difficulties, psychomotor impairment, impaired attention, irritability, impaired sleep and even slower growth (Tanquerel, 1839). WHO and FAO have established a provisional tolerable weekly intake of body weight (PTWI) values: 7 μ g/kg for Cadmium; 5 μ g/kg for total Mercury and 25 μ g/kg for Lead (FAO, 1972; FAO, 1999; FAO, 2003).

Côte d'Ivoire through the processors and exporters of fish products has become one of the largest exporters of tuna products to the global level. The exports of products tuna boats in 2009 amounted to 24 994 tons for 135 million USD (DPH, 2009). There are 2 types of tuna products exported: Tuna finished products (canned) and semi-finished products tuna (tuna loins, tuna flakes, tuna skin and tuna pulp). The tuna loins are portions of the tuna flesh usually skinless and boneless and ready to use. Beforehand precooked in a temperature about 65°C in heart, packed and stored in a lower temperature in 0°C, the tuna loins are likened to semi-canned tuna so to products semi-finished tuna. They are intended for canning factories and for fast food. The world production of tuna loins is 34 706 tons (FAO, 2009). In Côte d'Ivoire, this sector produces 2 200 tons (DPH, 2002) and employs 70 % of women; what constitutes a livelihood for several families (Datté-Aké, 2006).

This present study aims to estimate the intake of three important toxic metals: Mercury (Hg), Lead (Pb) and Cadmium (Cd) through tuna loins produced in Côte d'Ivoire and compared with the Provisional Tolerable Weekly Intake (PTWI) established. Thus, it is expected that the results of this research will assist in acquiring information about the level of toxic metals in this region.

2. Materials and Methods

2.1. Sample Collection

Tuna loins were obtained from two industries located in Abidjan (economical capital of Côte d'Ivoire) from September 2011 to September 2013. Per sampling day, samples of about 500 g frozen tuna in a polyethylene bag were aseptically collected from each industry. Per month, the number of samples collected and analyzed depends on the importance of the tuna loins production. Quantities of 134 samples were collected from Industry A and 337 from industry B. Quantities of 370 samples were collected from specie *Skipjack (Katsuwonus pelamis)*, 57 from *Yellowfin (Thunnus albacares)*, 32 from *Bigeye (Thunnus obesus)* and 12 from *Longfin (Thunnus alalunga)*. A total of 471 samples were collected from both industries. Each sample was labeled, stored in an ice box and sent to the laboratory.

2.2. Chemical Analysis

All samples were homogenized in a food blender with stainless steel cutters, followed by digestion.

For the determination of Lead (Pb) and Cadmium (Cd), 0.5 ± 0.01 g of each samples was weighed and 5 mL of nitric acid (HNO₃) 65% and 2 mL of hydrogen peroxide (H₂O₂) 30% were added slowly in portion according to the AOAC 999.10 method (2003). The homogenate was digested in the microwave (Milestone) at 200°C during 25 min. After cooling, the residual solution was diluted with HNO₃ 0.1 M. The concentrations of cadmium and lead were determined using a Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS) (Varian, China) in different samples according to the program reported in table 1.

Step	Temperature (°C)		Ramp tin	Ramp time (s)		Hold time (s)	
	Pb	Cd	Pb	Cd	Pb	Cd	
Drying	650	350	10	10	15	15	
Atomizing	1900	1200	0	0	4	4	
Cleaning	2500	2500	1	1	5	5	

Fable 1: Lead and Cadmium GFAAS Determination: Furnace Par	ameters
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Lead wavelength: 283.3 nm; injected volume: 10µl

Cadmium wavelength: 228.8 nm; injected volume: 10µl

Mercury (Hg) was determined according to the AOAC 974.14 method (2000). About 5 mL of HNO₃ were added to 1 ± 0.1 g of the sample. The homogenate was digested in a microwave (Milestone) at 200°C during 25 min. After cooling, the residual solution was diluted in 100 mL with the solution of dilution (dilution of 58 mL of 65 % HNO₃ and 67 mL of H₂SO₄ in 1 L of bidistilled water). Mercury concentration was determined using a cold vapour atomic absorption spectrophotometer (Varian) in different samples. About 10 µL of the diluted is injected according to the following regulation: width crack, 160 µm; roaming lamp, 3 mA; wavelength, 253,7 nm.

2.3. Validation of Methods

A validation of method internal in the laboratory was made on the mode of sampling and method of analysis for verifying the analytical methodology of the contents in Mercury, Lead and Cadmium in foodstuffs according to the directive 2001 / 22 / CE. The repeatability and reproducibility tests were determined on 10 samples for each metal according AFNOR (1996).

2.4. Intake Levels Calculation

The average heavy metal weekly intake was calculated according to the following formula:

Heavy metals intake level	= (average heavy metal	content X(consumption of fish j	per pers/ body
weight)			
(µg/(week x kg bw))	$(\mu g/kg)$	(kg/week)	kg

The annual quantity of fish consumed is 18.8 kg / pers (FAO, 2012). The body weight of adult person is 60 kg

2.5. Statistical Analysis

Data were expressed as mean \pm standard deviation (SD). Data were analyzed by ANOVA at α = 0.05. Comparison of means was performed by Duncan test and difference was considered significant at p < 0.05. ADE 4 software is used for statistical analysis.

3. Results

3.1. Analytical Quality Assurance

Table 2 reports the analytical results obtained on the reference material used to assess the methods. The coefficients of variation are: 1.756 for Pb; 4.593 for Hg; 4.614 for Cd for repeatability test and 4.468 for Pb; 4.529 for Hg; 4.809 for Cd for reproducibility test.

	Mean (mg/kg)		SD (mg/kg)			RSDR (%)			
	Pb	Hg	Cd	Pb	Hg	Cd	Pb	Hg	Cd
Test 1	0.672	0.0113	0.1538	0.011	0.0005	0.0070	1.756	4.593	4.614
Test 2	0.140	0.0099	0.1514	0.006	0.0005	0.0073	4.468	4.529	4.809

Table 2: Analytical Results for Pb, Hg and Cd for Validation Methods

Test 1: repeatability test, concentration of standard solution $30\mu l$

Test 2: reproducibility test, concentration of standard solution $10 \mu l$

3.2. Influence of Different Species on Metals Concentrations

The concentrations of Lead, Cadmium and Mercury in *skipjack*, *bigeye*, *yellowfin* and *longfin* species are shown in table 3. The concentrations (mg/kg) of Lead in *skipjack*, *bigeye*, *yellowfin* and *longfin* species are respectively: 0.16 ± 0.06 ; 0.19 ± 0.06 ; 0.17 ± 0.05 and 0.17 ± 0.07 .

The concentrations (mg/kg) of Cadmium in *skipjack*, *bigeye*, *yellowfin* and *longfin* species are respectively: 0.02 ± 0.01 ; 0.01 ± 0.01 ; 0.02 ± 0.02 and 0.02 ± 0.01 . The concentrations of Mercury (mg/kg) in *skipjack*, *bigeye*, *yellowfin* and *longfin* species are respectively: 0.20 ± 0.11 ; 0.21 ± 0.09 ; 0.21 ± 0.08 and 0.17 ± 0.08 . The concentrations of Lead, Cadmium and Mercury are not significantly different in *tuna loins species (figure 1)*. The observations 1,2,3,4 correspond to tuna species respectively skipjack, bigeye, yellowfin and longfin.

Parameters	skipjack	bigeye	yellowfin	longfin	
Lead	0.16 ± 0.06	0.19 ± 0.06	0.17 ± 0.05	0.17 ± 0.07	
Cadmium	0.02 ± 0.01	0.01 ± 0.01	0.02 ± 0.02	0.02 ± 0.01	
Mercury	0.20 ± 0.11	0.21 ± 0.09	0.21 ± 0.08	0.17 ± 0.08	





Figure 1: Distribution of Heavy Metals Concentrations According to Tuna Loins Species

3.3. Influence of Different Industry on Metals Concentrations in Tuna Loins

The results obtained for the determination of Lead, Cadmium and Mercury in industry A and industry B are presented in table 4. The concentrations (mg/kg) of Lead in industry A and industry B are respectively: 0.17 ± 0.05 and 0.16 ± 0.06 . The concentrations (mg/kg) of Cadmium in industry A and industry B are respectively: 0.02 ± 0.01 and 0.02 ± 0.01 . The concentrations of Mercury (mg/kg) in industry A and industry B are respectively: 0.20 ± 0.10 and 0.20 ± 0.11 . The concentrations of Lead, Cadmium and Mercury are not significantly different in *various industries (figure 2). The observations 1 and 2 correspond to industry A and B respectively.*

Fable 4:	: A	Assessment	of Heavy	Metal in	Various	Tuna Loins	Industries	(Concentrations:	: mg/kg)
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Parameters	Industry A	Industry B	
Lead	0.17 ± 0.05	0.16 ± 0.06	
Cadmium	0.02 ± 0.01	0.02 ± 0.01	
Mercury	0.20 ± 0.10	0.20 ± 0.11	





3.4. Influence of Various Months on Metals Concentrations in Tuna Loins

The results obtained for the determination of Lead (Pb), Cadmium (Cd) and Mercury (Hg) in various months are presented in figure 3. These concentrations are higher in December; April-May and lower in June-July-August.





3.5. Chemical Properties of the Tuna Loins

The various metals concentrations of the tuna loins are given by the table 5. The results indicate that the concentration varied from 0.03 to 0.47 with a mean of 0.20 ± 0.10 mg/kg for Mercury; from 0.00 to 0.09 with a mean of 0.02 ± 0.01 mg/kg for Cadmium and from 0.02 to 0.31 with a mean of 0.16 ± 0.06 mg/kg for lead. These concentrations are lower than the maximum permissible values in European and Ivoirian regulation.

Parameters	Range	Mean	European regulation	(CCE,	Ivorian	regulation
			2006)		(MIPARH,	2010)
Lead	0.02-0.31	0.16 ± 0.06	0.3		0.3	
Cadmium	nd-0.09	0.02 ± 0.01	0.1		0.05-0.	1
Mercury	0.03-0.47	0.20 ± 0.10	0.5		0.5-1	

nd: not detectable

3.6. Estimation of Heavy Metals Intake in Tuna Loins

The average weekly intakes of Cd, Pb and Hg per kg of body weight are showed in table 6. Cd (μg /(week x kg bw)), Pb (μg /(week x kg bw)) and Hg (μg /(week x kg bw)) weekly intake values respectively 0.39; 0.97 and 1.21 not exceeded the PTWI established (μg /(week x kg bw)): 7; 25 and 3.3 for Cd, Pb and Hg respectively.

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	Average weekly	intake Maximum weekly	intake PTWI (µg/(wee	k x kg
	(µg/(week x kg bw))	$(\mu g/(\text{week x kg bw}))$	bw))	
Cd	0.09	0.55	7	
Pb	0.97	1.86	25	
Hg	1.21	2.82	5	

4. Discussion

All the results obtained for the coefficient of variation for repeatability and reproducibility test are lower than 5%. These results demonstrate the validity of methods applied. The results of the present study demonstrated that the concentrations varied from 0.03 to 0.47 with a mean of 0.20 ± 0.10 mg/kg for Mercury; from 0.00 to 0.09 with a mean of 0.02 ± 0.01 mg/kg for Cadmium and from 0.02 to 0.31 with a mean of 0.16 ± 0.06 mg/kg for lead. The lead level obtained in the tuna loins is near that Ganjavi and al. (2010) and Rahimi and al. (2005) which found in Iranian tuna cans: 0.15 mg/kg and 0.10 mg/kg. However, this lead rate is higher than that of Storelli and al. (2010) and Khansari and al. (2005) which found 0.06 mg/kg and 0.04 mg/kg values in tuna cans in Italy and Iran respectively. The mercury concentrations in tuna loins is near than the concentrations of fresh tuna (0.27 mg/kg) determinate by Koffi and al. (2007) in Côte d'Ivoire and lower than the mercury concentrations in canned tuna (0.78 mg/kg) determinate by Gerstenberger and al. (2009) in USA. The rate of Cadmium determined in this study is lower than of the aroused authors: 0.022 mg/kg (Khansari and al., 2005); 0,029 mg/kg (Ganjavi and al., 2010); 0.04 mg/kg (Storelli and al., 2010) and 0.050 mg/kg (Rahimi and al., 2010). Furthermore, the results of this study are lower than Keskin and al. (2007) which found in tuna flesh for Mercury, Lead and Cadmium in Turkey: 0.374 mg/kg; 0.228 mg/kg and 0.032 mg/kg respectively. These differences in the levels of Lead, Mercury and Cadmium could give some explanation in the differences of weight, size, behavior, housing environment and species of tuna.

No significant difference of heavy metals in various industries and various species was noted. This finding is disagreeing with the results of Besada and *al.* (2006) and Kojadinovic et *al.* (2007). These authors find a significant difference between *longfin*, *yellowfin* and *Bigeye* species from Atlantic Ocean. One possible explanation of the result of the present study is the location from which the tuna were caught. Indeed, the ivoirian industries stock up with the same French and Spanish ships. These ships go fishing in the Atlantic East-Central Ocean and land 53 % of the tunas in the fishing port of Abidjan (Oceanic Development, 2009).

The statistical comparison between the various month sampling showed that the December values as well as the April-May values were significantly higher and the June-July-August values were significantly lower. These results are similar to Sepe and *al.* (2003) which shows a significant difference between heavy metals concentrations of two seasonal variations.

The average weekly intakes of Cd, Pb and Hg per kg of body values not exceeded the Provisional Tolerable Weekly Intake (PTWI) established. These result are similar to Sepe and al. (2003); Koffi and *al.* (2007); Cardoso and *al.* (2010).

5. Conclusion

This study had for objective to measure concentrations of Lead, Mercury and Cadmium in tuna loins of *Skipjack*, *Yellowfin*, *Longfin* and *Bigeye* species from industries A and B in Côte d'Ivoire. All values of Lead, Mercury and Cadmium were lower than the limits of concentration fixed for these elements by European and Ivoirian legislation. The means concentrations of the heavy metals varied not depending on the industries and on the tuna species but depending on the various months. The average weekly intakes of Cd, Pb and Hg per kg of body values not exceeded the Provisional Tolerable Weekly Intake (PTWI) established. The data obtained in the present study do not show evidence risk for the consumer, even if the most exposed categories are taken into account. However, the present study shows that precautionary measures need to be taken in order to prevent future heavy metal pollution.

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