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Tin Concentrations and Human Health Risk Assessment for Children and Adults in Seafood and Canned Fish commonly consumed in Bayelsa State, Nigeria

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ABSTRACT: Tin is a naturally occurring element in the environment, and the most important dietary intake is from tin-plates steel cans used for food packaging. The objective of this paper is to evaluate the tin concentrations and human health risk assessment of children and adults in seafood and canned fish (Sardine and Mackerel) obtained from Bayelsa State, Nigeria using the Thermo-Elemental Atomic Absorption Spectrometer (S4-71096 model) after mixed-acid digestion. Data obtained reveal tin concentrations (mean ± SD, mg/kg) in seafood in the order of fresh water fish (0.99 ± 0.07) > salt water fish (0.98 ± 0.16) > salt water–Blood Clam (0.75 ± 0.022) > fresh water- Clam (0.17 ± 0.12) > fresh water-Prawn (0.06 ± 0.01) > salt water shrimp (0.02 ± 0.01) respectively, tin concentrations in the brands of canned fish were significantly higher than the concentration in seafood ($p < 0.05$). However, the mean concentrations of tin in the seafood and brands of canned fish were lower than the standard guideline limits set by regulatory bodies (200 mg/kg - 250 mg/kg). The health risk exposure assessment revealed that the values of all the samples were lower than the provisional maximum tolerable daily intake (PMTDI) of tin. The target hazard quotient (THQ) values of tin for both children and adults in all the samples were also lower than the reference dose (RfD). The health risk index (HRI) values of the seafood and the brands of canned fish for both children and adults were less than 1.0, which indicates that there are no adverse effects at the moment. However, the HRI values of the brands of canned fish were higher than the seafood for children and adults. Hence, assessment of tin in seafood and canned food could be periodically assessed by Nigerian food and drug regulatory organizations for efficient policy regulations.

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Tin is a trace metal found in the environment as a component of soils (Burec-Drewniak *et al.,* 2013), rocks (Lehmann, 2021), air (Yilmaz *et al.*, 2009), air and water (Ahmed *et al.*, 2013). Tin and its compounds may be released from the burning of waste and fossil fuel (Ayeni *et al.*, 2013), smelting and refining processes (Chirikura *et al.*, 2010), particulate matter in the air (Yilmaz *et al.*, 2009), roads and agricultural activities (anthropogenic, sources) (Irzon *et al.*, 2018). The environmental menace of tin and its compounds lies in the fact that, they are relatively immobile and as such they can easily bind to sediments in water and soil. Also, they are not biodegradable but can transform from one form to another. For example, organotin compounds bind to soil, sediments and particulate material in water and may be degraded by sunlight and bacteria into inorganic tin compounds and could persist for years. As a result of their persistence in the ecosystem, tin and its compounds may be absorbed into the tissues of plants, animals, and humans via biomagnifications within the food chain and this may pose a threat to the ecological community (ATSDR, 2005).Humans are exposed to tin and its compounds such as organotin via ingestion of seafood, juice or other liquids products distributed in tin-lined cans, especially unlacquered tin - lined cans that contain up to 100 ppm of tin (Graf, 2000). Also, the concentration of tin increases if the food is stored in

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open tin cans (Suhendan, 2010; Islam *et al.*, 2010). It has been reported that Tributyltin (TBT) is a common contaminant in fish and shellfish (Cornelis *et al*., 2003). Young children residing near hazardous waste site can be exposed to tin and its compounds via pica play, or ingestion of canned foods, juices, and beverages (ATSDR, 2005). Higher levels of exposure to tin and its compound have been reported to cause toxic effects such as eye irritation, respiratory irritation, gastrointestinal effects, and neurological problems (JECFA/WHO, 2001; Boogaard *et al*., 2003). Generally, the major route of exposure to tin and its compounds are inhalation (breathing), oral (eating and drinking), and dermal (skin contact or absorption). However, the route of exposure to tin and its compounds in this study was via oral ingestion. Since humans are exposed to tin compounds daily via household products such as toothpaste, perfume, paints, polymer, canned foods and drinks, and seafood (fish and shellfish), it is imperative to determine the concentrations of tin in seafood (fresh and salt water fish and shellfish) and different brands of canned fish and assess the risk of exposure of children and adults via consumption. The objective of this study is to evaluate the tin concentrations and assess the human health risk of children and adults who consume seafood and canned fish (Sardine and Mackrel) obtained from Bayelsa State, Nigeria.

MATERIALS AND METHODS

Sample Collection: Salt water (SW) fish bonga shad (*Ethmalosafimbriata*) and shellfish shrimp (*Penaeusmonodom)* and blood clam (*Tegillarcagranosa*) were purchased from local fishermen on the River Nun, at Sangana axis, Akassa. The fresh water (FW) fish (*Synodontisbudgetti*), and shellfish prawn (*Microbrochiumfelicinum)* and clam (*Galatea paradoxa)* were purchased from local fishermen on the River Nun, at Igbomatoru axis. While five different brands of commonly consumed canned sardine (Costa, Tropical sun, Sarah, Titus and Mega) and Mackerels (Geisha, Costa, Dinor, Estus and Super gold) were purchased from a supermarket in Yenagoa. All the above sample sources are in Bayelsa State, Nigeria.

Sample Preparation: The edible tissues (muscle) of the saltwater fish, freshwater fish, clam, and shellfish and the canned fish products (Sardines and Mackerel) were washed thoroughly with distilled water, oven dried between 80-100^{0}C to a constant weight. Thereafter, each sample was crushed with laboratory mortar and pestle and sieved to uniform particle size.

Sample Digestion and FAAS Analysis: Sample digestion was carried out using the method described by Markmanuel *et al* (Markmanuel *et al*., 2020; 2021). Briefly, one (1) gram of each sample was digested with 20 mL solution of HNO_3/H_2SO_4 of about 3:1 v/v and 2mL of $HClO_4$. The digests were cooled and diluted with 20 mL of distilled water, stirred and filtered into 100 mL volumetric flasks, and distilled water was added to make up to the mark. Tin concentrations in each digest were analyzed with a Thermo-Elemental Atomic Absorption Spectrophotometer (S4-71096 model). The digests and FAAS analysis were all performed in triplicates and the results were expressed on a dry weight basis.

Exposure Assessment Model: Adults and children exposure to tin for the freshwater, seafood and the different brands of canned fish were assessed via oral ingestion using the United States Environmental Protection Agency (USEPA) models. These include the Tolerable Daily Intake (TDI) mg/kg-bw/day, Target Hazard Quotient (THQ) and Health Risk Index (HRI) (mg/kg-bw/day), commonly known as the non-carcinogenic risk assessment (USEPA, 2001; 2016).

Tolerable Daily Intake (TDI): The Tolerable daily intake (TDI) is the daily maximum amount of a contaminant an individual may be exposed to over a lifetime without unacceptable risk of health effects. TDI (mg/kg-bw) can be expressed according to equation 1.

$$TDI\ (mg/kg\text{-}bw/day) = \frac{IR \times MC}{BW} \ldots\ldots 1$$

Where; IR is the daily ingestion rate of the seafood and canned fish products for adults (0.3 mg/kg/person/day) and for children (0.15 mg/kg/person/day). BW is the average body weight (60 kg for adults and 25 kg for children (USEPA, 2002; Manual *et al*., 2011).

Target Hazard Quotient (THQ): The target hazard quotient (THQ) is the ratio between human exposures to contaminants or toxicants and the oral reference dose which indicates the estimation of non-carcinogenic risk effects. THQ values of tin in the seafood and brands of canned fish were assessed based on USEPA regional risk-based concentration table (USEPA, 2011) and was expressed according to equation 2.

$$THQ = \frac{EF \times ED \times IRMC}{RfD \times BW \times ATn} \times 10^{-3} \ldots\ldots\ldots 2$$

Where EF is the exposure frequency (365 days/year). ED is the exposure duration (70 years for adults and 10 years for children), IR and MC have been expressed in equation (1), RfD is the oral reference dose for tin (mg/kg-bw/day). The oral reference dose expresses a daily exposure of a contaminant or toxicant to human population (including vulnerable subgroups such as children, pregnant women, and the elderly) that is likely to be without an appreciable risk of deleterious effects during their lifetime. The RfD (mg/kg-bw/day) for tin is 0.20, ATn is the average exposure for non-carcinogenic (EF × ED) 365 days × 70 years for adults, and 365 days × 10 years for children which are equivalent to 25550 days and 3650days respectively while 10^{-3} is the conversion factor unit.

Health Risk Index (HRI): HRI defines the health risk of non-carcinogenic adverse effects due to exposure to contaminants or toxicants. It is expressed as the ratio of tolerable daily intake of tin (TDI) in the seafood and the brands of canned fish, and the oral reference dose (RfD) of tin as expressed in equation 3.

$$HRI = \frac{TDI}{RfD} \ldots\ldots\ldots\ldots\ldots 3$$

If the lower range of acceptable risk distribution of HRI values defined by a single constraint on the 95th percentile is < 1.0. This indicates that the exposed population is safe and is unlikely to experience adverse health effects. However, when the HRI value is >1.0, it implies that the exposed population will likely experience potential non-carcinogenic effects (Adeel and Riffat, 2014; Adowei *et al*., 2020).

Data Analysis: The statistical analysis for mean, standard deviation, standard error, range, and confidence interval from the concentrations of tin in the seafood and brands of canned fish from the triplicate analysis was performed using SPSS Microsoft Excel. The invariability of the data obtained from this study was subjected to a one-way analysis of variance (ANOVA) to uncover the variations between the means of samples at 95% confidence level and to identify precisely which sample varied significantly from the others. Variation between samples were considered statistically significant when $p < 0.05$ and insignificant when $p > 0.05$ respectively. The results of the mean values of tin concentrations were employed for the evaluation of health risk exposure assessment.

RESULTS AND DISCUSSION

Mean Concentrations of Tin in Seafood and Brands of Canned Fish: The mean concentrations (mg/kg) of tin in the seafood and brands of canned fish are displayed in Table 1. One way ANOVA, variance analysis of the results revealed that tin concentrations in the seafood were significantly different ($p < 0.05$) compared to the concentration of tin in the brands of canned fish. This could be attributed to the leaching of tin from tin cans during production or storage because the fish products are preserved in liquid media, especially acidic media (tomato sauce) (ATSDR, 2005; Ghoul *et al*., 2020). Also, tin concentrations were significantly different ($p < 0.05$) among the different brands of canned fish investigated.

Table 1: Mean concentrations (mg/kg dry wt. basis) of tin in seafood and brands of canned fish obtained from Bayelsa State, Nigeria**.**

Samples	Statistics		
	Mean+SD	**Range**	**Standard Error (SE)**
FW–Fish	0.99±0.07	0.91–1.04	0.04
FW–Prawn	0.06±0.01	0.06–0.07	0.00
FW–Clam	0.17±0.12	0.03–0.24	0.07
SW–Fish	0.98±0.16	0.79–1.08	0.09
SW–Shrimp	0.02±0.01	0.01–0.02	0.00
SW–Blood Clam	0.75±0.22	0.51–0.93	0.12
Costa Sardine	4.97±0.16	4.82–5.13	0.09
Titus Sardine	11.98±0.04	11.94–12.01	0.02
Tropical Sun Sardine	9.22±0.09	9.15–9.32	0.05
Mega Sardine	8.08±0.05	8.05–8.13	0.03
Sarah Sardine	8.03±0.11	7.91–8.13	0.06
Costa–Mackerel	5.98±0.04	5.93–6.01	0.03
Super Gold Mackerel	3.59±0.02	3.58–3.61	0.01
Geisha–Mackerel	6.02±0.14	5.93–6.19	0.09
Dinor–Mackerel	10.71±0.02	10.69–10.72	0.01
Estus–Mackerel	4.12±0.09	4.01–4.17	0.05

FW - Freshwater; SW - Saltwater

Tin concentrations in the seafood (fresh and saltwater species) were in the order of FW- Fish > SW-Fish > SW-Blood Clam > FW-Clam > FW-Prawn > SW-Shrimp with mean ± SD of 0.99±0.07 mg/kg, 0.98±0.16 mg/kg, 0.75±0.022 mg/kg, 0.17±0.12 mg/kg, 0.06±0.01 mg/kg and 0.02±0.01 mg/kg, respectively. The slight variation observed in the seafood species could be due to the bioavailability of tin to each species in the aquatic ecosystem, the mode of feeding, as well as the capacity of each species to accumulate tin in its tissues (Markmanuel *et al*., 2020; 2021). As indicated in Table 1, the concentrations of tin in the canned fish Sardine were in the order of Titus > Tropical Sun > Mega > Sarah > Costa. Titus ranked the highest with a mean value of 11.94±12.01 mg/kg and Costa ranked lowest with a mean value of 4.97±0.16 mg/kg. Meanwhile, the highest mean concentrations of tin in Mackerel canned fish were found in Dinor with a mean value of 10.71±0.02 and the lowest value was recorded in Supergold with a value of 3.59±0.02 mg/kg. Thus, the mean concentrations of tin in Mackerel canned fish were in the order of Dinor > Geisha > Costa > Estus > Supergold.

The observed difference in the concentrations of tin in the canned fish (Sardine and Mackerel) in the different brands could be attributed to factors such as pH, oxygen content, and temperature of the canned fish during packaging and storage. As reported in literature low pH increases the concentrations of tin, especially in unlacquered tin cans, an increase in temperature will also influence bacterial and fungal growth while exposure to air can also enhance the leaching of tin from the tin-coat into the food can, especially stannous fluoride and chloride (ATSDR 2005, Blunden and Wallance, 2003). Generally, the concentrations of tin in the seafood and brands of canned fish in this study were lower than the standard guidelines values of 200 mg/kg and 250 mg/kg recommended by JECFA/WHO (2006) and EU (2006).

However, the values of tin in this study were higher than the mean value of tin in canned Tuna reported by Ghoul *et al.*,(2020) and Grazyna *et al*., (2020). Tin has no known biological function in living organisms, but rather it is easily absorbed and immobile, hence it accumulates in living tissues and interferes with iron and copper metabolism.

For instance, it affects semen and cytochromeP450 and decreases their effectiveness (Westrum and Thomassen, 2002). Therefore, excessive consumption of canned fish should be discouraged because data from literature also revealed that those who depend on a high percentage of their diet from canned foods will be more exposed to high levels of tin compared to those who depend on fresh foods (ATSDR, 2005, WHO, 2005).

Risk of Exposure Assessment: The risk of exposure pathway of tin to children and adults in this study was via oral ingestion of seafood (freshwater fish and shellfish) and brands of canned fish. The exposure risk assessment models employed are tolerable daily intake (TDI), target hazard quotient (THQ), and health risk index (HRI). The results are presented in Tables 2, 3, and 4.

Table 2: Tolerable daily intake (mg/kg-bw/day) for children and adults via ingestion of seafood and brands of canned fish from Bayelsa State, Nigeria.

Samples	TDI (mg/kg-bw/day)	
	Children	**Adults**
FW – Fish	5.96 E $^{-03}$	4.97E $^{-03}$
FW – Prawn	4.00E $^{-04}$	3.33E $^{-03}$
FW – Clam	1.00E $^{-03}$	8.33E $^{-03}$
SW – Fish	5.88E $^{-03}$	4.90E $^{-03}$
SW – Shrimp	1.20E $^{-04}$	1.00E $^{-04}$
SW – Clam	4.50E $^{-03}$	3.75E $^{-03}$
Costa – Sardine	2.98E $^{-03}$	2.48E $^{-02}$
Titus – Sardine	7.19E $^{-02}$	5.99E $^{-02}$
Tropical – Sardine	5.53E $^{-02}$	4.61E $^{-02}$
Mega – Sardine	4.85E $^{-02}$	4.04E $^{-02}$
Sarah – Sardine	4.82E $^{-02}$	4.02E $^{-02}$
Costa – Mackerel	3.59E $^{-02}$	2.99E $^{-02}$
Supergold – Mackerel	2.16E $^{-02}$	1.79E $^{-02}$
Geisha – Mackerel	3.61E $^{-02}$	3.01E $^{-02}$
Dinor – Mackerel	6.43E $^{-02}$	5.36E $^{-02}$
Estus – Mackerel	2.47 $^{-02}$	2.06E $^{-02}$
Standard guidelines		
JECFA/WHO (2001)	2.0	
EVM (2003)	0.22	

The tolerable daily intake (TDI) is the total amount of nutrient substances ingested from food and food products (e.g seafood, canned fish, meat) that is considered adequate for a daily requirement of 97-98% healthy individual during a lifetime without unacceptable health effects. A tolerable daily ingestion rate of 0.3 mg/kg/person/day for adults and 0.15 mg/kg/person/day for children were considered adequate and safe via the ingestion of tin in the seafood and brands of canned fish. The results in Table 2 shows that the tolerable daily intake of tin in the seafood and brands of canned fish for both children and adults were lower than the established provisional maximum tolerable daily intake (PMTDI) of 2 mg/kg-bw/day by JECFA/WHO (2001) and 0.22 mg/kg-bw/day guideline value established by EVM (2003).The TDI values obtained in this study are similar to the value obtained by Ghoul *et al*., (2020) and Grazyna *et al*., (2020). The TDI of tin for children and adults in the seafood was lower than the TDI of the different brands of canned fish. A high intake of tin can result in the development of gastrointestinal effects such as diarrhea and vomiting.

However, the effects depend on the concentration of tin in the food rather than the dose ingested on a body weight basis (JECFA/WHO, 2006). Therefore, a daily ingestion rate of 0.3 mg/kg/bw/daily for adults and 0.15 mg/kg-bw/daily for children used in this study based on the concentrations of tin in the seafood and the different brands of canned fish were considered safe at the moment, but concentrations above these levels may pose risk to consumers.

Table 3: THQ values of tin for children and adults via the ingestion of seafood and brands of canned fish from Bayelsa State, Nigeria.

Samples	Children	Adults
FW – Fish	2.98E-05	2.48E-05
FW – Prawn	2.00E-06	1.67E-05
FW-Clam	5.00E-06	4.17E-05
SW – Fish	2.94E-05	2.45E-05
SW – Shrimp	6.00E-07	5.00E-07
SW – Clam	2.25E-07	1.88E-05
Costa – Sardine	1.49E-04	1.24E-04
Titus – Sardine	3.59E-04	2.99E-04
Tropical – Sardine	2.77E-04	2.31E -04
Mega – Sardine	2.42E-04	2.02E-04
Sarah – Sardine	2.41E-04	2.01E -04
Costa – Mackerel	1.79E-04	1.49E-04
Supergold – Mackerel	1.08E-04	8.99E-04
Geisha – Mackerel	1.81E-04	1.51E-04
Dinor – Mackerel	3.21E-04	2.68E-04
Estus – Mackerel	1.24E-04	1.03E-04

The target hazard quotient (THQ) was employed in this study to determine the potential non-carcinogenic health risks of children and adults ingesting seafood and brands of canned fish in Bayelsa State. The THQ defines the ratio of a determined dose of a pollutant to the oral reference dose (RfD). As indicated in Table 3, the THQ values for tin in the seafood and different brands of canned fish for both children and adults were all lower than the oral reference dose (RfD) (0.20 mg/kg-bw/day) for tin. This implies that the exposed population (children and adults) from Bayelsa State is unlikely to be experiencing a non-carcinogenic risk of adverse health effects at the moment. The THQ values in this study were also lower than the minimal risk level (MRLs) of 0.3 mg/kg/day for inorganic tin (stannous chloride) and 0.0003 mg/kg/day organotin (tributyltin) (ATSDR, 2005).

Table4:HRI (mg/kg-bw/day) of tin for children and adults via the ingestion of seafood and brands of canned fish from Bayelsa State, Nigeria.

Samples	HRI (mg/kg-bw/day)	
	Children	Adults
FW – Fish	2.98E-02	2.49E-02
FW – Prawn	2.00E-03	1.67E-03
FW–Clam	5.00E-03	4.17E-03
SW – Fish	2.94E-02	2.45E-02
SW – Shrimp	6.00E-04	5.00E-04
SW – Clam	2.25E-02	1.88E-02
Costa – Sardine	1.49E-01	1.24E-01
Titus – Sardine	3.59E-01	2.99E-01
Tropical – Sardine	2.77E-01	2.31E-01
Mega – Sardine	2.42-01	2.02E-01
Sarah – Sardine	2.41E-01	2.01E-01
Costa –mackerel	1.78E-01	1.49E-01
Supergold –mackerel	1.08E-01	8.99E-02
Geisha – Mackerel	1.81E-01	1.51E-01
Dinor – Mackerel	3.21E-01	2.68E-01
Estus – Mackerel	1.24E-01	1.10E-01

The THQ values of tin in the canned fish were lower than the value reported by Grazyna *et al.*,(2020) while the THQ value of tin in the seafood were also lower than the values reported by Markmanuel *et al.*,(2021) of some heavy metals in seafood. However, it is imperative to note that, the THQ values of the brand's canned fish were higher than the THQ values of the seafood. Therefore, excessive consumption of these brands of canned fish should be discouraged.The human health risks of non-carcinogenic adverse effects due to exposure to tin via oral ingestion of seafood and brands of canned food for children and adults were assessed based on the health risk index (HRI). It was evaluated as the ratio of the tolerable daily intake (TDI) of tin in the seafood and canned fish and the RfD of tin. As shown in Table 4, the HRI values of tin in the seafood and brands of canned fish for both children and adults were < 1.0. This indicates that the exposed populations are unlikely to experience non-carcinogenic adverse health effects due to tin exposure via the ingestion of seafood. Also, the HRI values for the different brands of canned fish (Sardines and Mackerels) were all < 1.0. However, canned fish posed the highest risk with $p < 0.05$ compared to the seafood. This implies that excessive consumption of canned fish may pose a potential health risk with respect to tin concentrations in the canned fish from this study. The HRI values of tin in the different brands of canned fish obtained from this study, are higher than the values of tin and other metals in canned Tuna reported by Ghoul *et al.*,(2020) and Sobhanarddkani (2017).Therefore moderate consumption of canned fish products is recommended.

Conclusion: This study evaluated tin concentrations for children and adults via the consumption of seafood and different brands of canned fish (Sardine and Mackerel). Data obtained shows that, the mean concentrations of tin in the seafood and the different brands of canned fish were lower than the recommended standard limits of regulatory bodies. Also, the human health risk assessment revealed that the TDI, THQ, and HIR values of tin in the seafood and brands of canned fish were also within the safe limits of regulatory bodies.

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