

HEAVY METAL CONTENT IN YELLOWFIN TUNA *THUNNUS ALBACARES* (BONNATERRE) OF LAKSHADWEEP SEA

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Abstract: Tissue samples of fresh, dried and canned Yellowfin Tuna (*Thunnus albacares*) from Agatti Island of Lakshadweep were subjected to analysis of metals (cadmium, cobalt, chromium, nickel, lead, aluminium and mercury) using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) and Mercury analyser. Analysis revealed that the metals have different levels of accumulation - Cd: 0.007-0.387 $\mu\text{g g}^{-1}$, Co: 0.007-0.173 $\mu\text{g g}^{-1}$, Cr: 0.166-0.373 $\mu\text{g g}^{-1}$, Ni: 0.014-0.081 $\mu\text{g g}^{-1}$, Pb: 0.042-0.346 $\mu\text{g g}^{-1}$, Al: 10.69-24.29 $\mu\text{g g}^{-1}$ and Hg: 0.109-0.471 $\mu\text{g g}^{-1}$. The concentration of Co, Cr, Ni and Pb were comparatively higher in smoked and canned tuna rather than in fresh tuna. During processing of tuna, mercury content decreases while the content of other metals increases. Concentration of toxic metal such as Cr in all samples was well above the permissible limits (0.1-0.15 $\mu\text{g g}^{-1}$) proposed by the World Health Organization, while remaining metals were below the limits. Due to the high accumulation of all heavy metals, it is advisable to avoid liver and gill of tuna from consumption.

Key words: Tuna, masmin, canned tuna, Agatti, chromium, mercury, WHO

1. INTRODUCTION

Contamination of many ecosystems arises from both anthropogenic sources of pollution and natural weather conditions. During the past few decades, the natural aquatic systems are extensively contaminated with metals released due to anthropogenic activities. Many studies have proved beyond doubt that metals are stable and persistent environmental contaminants in aquatic system and posing threat to aquatic organisms in particular and to the whole ecosystem in general (Kojadinovic et al., 2007). Since the toxic metals are non-biodegradable, they tend to accumulate in various vital organs and tissues of the biota. Therefore, even trace amounts of these metals can lead to long-term toxic effects, due to their transfer through the food chain, and the resultant bioaccumulation.

Metal concentration in fish tissues reflects past or present exposure and incorporation occurs

mainly through the gills, skin or by food. Fishes are widely used to evaluate the health of aquatic ecosystems because pollutants accumulated in the food chain are responsible for adverse effects in the aquatic systems. There has been increasing concern over the concentration of metals in edible fishes since they form major part of human diet (Kojadinovic et al., 2007). Heavy metals can be classified as potentially toxic (aluminium, arsenic, cadmium, lead, mercury), probably essential (nickel, vanadium, cobalt) and essential (copper, zinc, selenium). Among the metals, mercury (Hg) needs special attention for its ability to cause serious health problems in various life forms. Mercury is a toxic heavy metal released into the environment from both natural and anthropogenic sources and it can cause neurological effects at low dose levels. Many nations have considerable concern over the presence of high levels of toxic elements in fishes. There are instances where fish catches are banned from human

consumption as the total mercury content in their body exceeded the maximum limits (0.5 mg kg^{-1}) recommended by the Food and Agriculture/World Health Organisation (FAO/WHO, 1972).

Tuna was recognised as a predator, able to concentrate large amounts of heavy metals. The ingestion of food is an obvious means of exposure to metals, not only because many metals are natural components of foodstuffs, but also because of environmental contamination and contamination during processing (Voegborlo et al., 1999). The presence of heavy metals, particularly mercury, in the environment has been a matter of concern since their toxicity has been documented unequivocally. The tuna abundant in the territorial waters of Lakshadweep islands is used extensively for domestic consumption as well as for export. An appraisal is hence necessary to evaluate the concentration of heavy metals in fresh and processed tuna from Lakshadweep waters, so as to understand the present condition of the ecosystems and to compile the baseline data for future monitoring. The present study was therefore carried out in view of the scarcity of information about the metal levels (Cd, Co, Cr, Ni, Pb, Al and Hg) in the body organs (gill, liver, muscle and skin) of fresh, smoked (masmin) and canned yellowfin tuna, *Thunnus albacares* from Lakshadweep Archipelago.

2. MATERIALS AND METHODS

2.1. Sample collection

Five numbers of yellowfin tuna, *Thunnus albacares* were collected from the Agatti waters (latitude $10^{\circ}48'$ - $10^{\circ}52'$ N; longitude $72^{\circ}10'$ - $72^{\circ}12'$ E), during March-April, 2012. Total lengths were measured and no significant differences were found among specimens ($P > 0.05$). Traditionally processed (smoked and sun dried) tuna (masmin) and canned tuna were collected from "Masmin packaging unit of Agatti Island" and "Tuna processing unit of Minicoy" of Lakshadweep Development Corporation Ltd, respectively.

2.2. Determination of metal concentration

Fresh tuna samples collected were immediately brought to the laboratory and the tissues were dissected out using stainless steel dissection instruments to remove liver, gills, skin and muscle of each fish. Body organs, masmin and canned tuna (five samples each) were cut into small pieces and dried in microwave oven at 70°C for 15 minutes (after opening each can, oil was drained

off). Metal concentrations were determined by following the method of Turkmen et al. (2005). Concentrations of metals except Hg were determined by using Inductively Coupled Plasma Optical Emission Spectrometer (Software - WinLab 32) (Perkin Elmer, Optima 2100DV). Total mercury was determined by a Coleman Mercury Analyzer (MAS-50B) according to the method of cold vapour described by Hatch & Ott (1968). The precision of the analytical procedure was checked by analyzing standard reference materials of commercially available standards (Merck KGCA, 64271 Damstadt, Germany, ICP-Multielement standard solution IV, 23 elements in nitric acid). All acids and chemicals used were of analytical reagent grade. Metal concentrations were calculated in microgrammes per gramme dry weight ($\mu\text{g metal g}^{-1} \text{ d.w.}$).

2.3. Statistical analysis

One way ANOVA was employed in the assessment of variation in metal concentration among body organs and processed tuna. Pearson Correlation Coefficient was employed to find out the relationship between the concentrations of various metals with various tissue types and processed samples using SPSS 16.0.

3. RESULTS AND DISCUSSION

Concentrations of metals (Cd, Co, Cr, Ni, Pb, Al and Hg) in the body organs (gill, liver, muscle and skin) of fresh, smoked and canned yellowfin tuna, *Thunnus albacares* from Lakshadweep Archipelago are given in Table 1. Total metal concentrations recorded were in the range Cd: 0.007 - $0.387 \mu\text{g g}^{-1}$, Co: 0.007 - $0.173 \mu\text{g g}^{-1}$, Cr: 0.166 - $0.373 \mu\text{g g}^{-1}$, Ni: 0.014 - $0.081 \mu\text{g g}^{-1}$, Pb: 0.042 - $0.346 \mu\text{g g}^{-1}$, Al: 10.69 - $24.29 \mu\text{g g}^{-1}$ and Hg: 0.109 - $0.471 \mu\text{g g}^{-1}$. In general, our results were in agreement with those reported by other authors (CIFA 1992; Voegborlo et al., 1999). Dhaneesh et al. (2012a) & Dhaneesh et al. (2012b) reported a concentration range of Cd (0.01 - $0.61 \mu\text{g g}^{-1}$), Co (0 - $0.07 \mu\text{g g}^{-1}$), Ni (0.04 - $0.56 \mu\text{g g}^{-1}$) and Pb (0.08 - $0.55 \mu\text{g g}^{-1}$) in marine organisms, except tuna from Lakshadweep waters. While comparing to the previous reports from the same locality (Dhaneesh et al., 2012a, b), concentration of Co was increased while that of Cd, Ni and Pb was decreased in the current study. One way ANOVA revealed that the level of each metal in fresh and processed samples was varied significantly ($F_{(6, 35)} = 71.53$, $P < 0.05$). According to Pearson Correlation, cobalt was positively correlated to nickel ($r = 0.955$) and lead (r

= 0.995) at 0.01 level, whereas nickel was positively correlated to chromium ($r = 0.857$ at 0.05 level), cobalt ($r = 0.955$) and lead ($r = 0.974$) at 0.01 level.

Samples	Cd ($\mu\text{g g}^{-1}$)	Co ($\mu\text{g g}^{-1}$)	Cr ($\mu\text{g g}^{-1}$)	Ni ($\mu\text{g g}^{-1}$)	Pb ($\mu\text{g g}^{-1}$)	Al ($\mu\text{g g}^{-1}$)	Hg ($\mu\text{g g}^{-1}$)
Gill	0.039±0.004	0.009±0.004	0.239±0.047	0.021±0.003	0.063±0.013	13.466±0.29	0.471±0.058
Liver	0.387±0.029	0.01±0.005	0.221±0.0	0.021±0.005	0.042±0.021	20.59±0.424	0.141±0.016
Skin	0.387±0.029	0.007±0.005	0.207±0.021	0.025±0.009	0.048±0.019	24.29±0.363	0.196±0.021
Muscle	0.007±0.002	0.009±0.006	0.166±0.01	0.014±0.007	0.047±0.023	10.69±0.498	0.109±0.015
Masmin	0.085±0.014	0.151±0.064	0.373±0.061	0.081±0.006	0.343±0.011	17.19±0.342	0.086±0.011
Canned tuna	0.068±0.013	0.173±0.011	0.245±0.014	0.065±0.008	0.346±0.012	15.96±0.625	0.085±0.009
FAO/WHO standard reference	0.0-0.2	-	0.1-0.15	-	0-1.5	-	0.5

Table 1. Concentrations of metals ($\mu\text{g metal g}^{-1}$ d. w.) in the body organs of fresh, smoked (masmin) and canned yellowfin tuna, *T. albacares* were significantly varied ($P < 0.05$). Concentration of Co, Cr, Ni and Pb were comparatively higher in processed tuna rather than fresh tuna

Concentration of Cd was lower in muscle ($0.007 \mu\text{g g}^{-1}$) and higher in liver ($0.387 \mu\text{g g}^{-1}$) which was above the maximum permissible limit ($0.2 \mu\text{g g}^{-1}$) suggested by FAO/WHO (1976). Cadmium may accumulate in the human body and may induce kidney dysfunction, skeletal damage and reproductive deficiencies (Commission of the

European Communities, 2002). Cobalt concentrations in all the samples analysed ranged from 0.007 to $0.173 \mu\text{g g}^{-1}$. The processed tuna samples showed higher cobalt level than that in fresh tissues. Cobalt is beneficial for humans because it is part of vitamin B₁₂. Exposure to high levels of cobalt can result in lung and heart effects and dermatitis (Agency for Toxic Substances and Disease Registry, 2004). Chromium concentrations in all samples were higher than the maximum permissible limit ($0.15 \mu\text{g g}^{-1}$). The processed tuna however showed highest chromium accumulation ($0.373 \mu\text{g g}^{-1}$ in masmin and $0.245 \mu\text{g g}^{-1}$ in canned tuna) and found least in muscle tissues ($0.166 \mu\text{g g}^{-1}$). Chromium (III) is an essential nutrient that helps the body use sugar, protein and fat but chromium (VI) is carcinogenic (Institute of Medicine, 2002). Excessive amount of chromium (III) may cause adverse health effects (Agency for Toxic Substances and Disease Registry, 2004). There is no upper tolerable intake level for chromium according to the Institute of Medicine but the recommended intakes of chromium for females and males of 9-70 years old is 21-25 and 25-35 $\mu\text{g/day}$, respectively (Institute of Medicine, 2002).

Nickel concentration was higher ($0.081 \mu\text{g g}^{-1}$) in masmin (smoked and dried tuna) followed by canned tuna ($0.065 \mu\text{g g}^{-1}$) and least in muscle tissue of fresh tuna ($0.014 \mu\text{g g}^{-1}$). Nickel can cause respiratory problems and it is carcinogenic (Agency for Toxic Substances and Disease Registry, 2004). The upper tolerable intake level (UL) of nickel for children (1-3 years old) and males/females (14-70 years old) is 0.2 and 1 mg/day, respectively (Institute of Medicine, 2003). Concentration of Pb was found to be higher in canned tuna ($0.346 \mu\text{g g}^{-1}$) and masmin ($0.343 \mu\text{g g}^{-1}$) but lower than the maximum permissible limit ($1.5 \mu\text{g g}^{-1}$; FAO/WHO, 1976), which agrees well with the values reported by other authors (CIFA, 1992; Voegborlo et al., 1999; Dhaneesh et al., 2012b). Soldering is a recognised source of lead contamination of food during canning process. Furthermore, it is known that various types of fish were found to be contaminated with this metal. Therefore, the monitoring of lead concentration in canned fish is important for human health (Voegborlo et al., 1999). The maximum concentration of Pb which is permitted in prepared foods specifically intended for babies or young children is $200 \mu\text{g kg}^{-1}$ (FAO/WHO, 1976). Lead is known to induce reduced cognitive development and intellectual performance in children and increased blood pressure and cardiovascular disease in adults (Commission of the European Communities, 2002). Although, marine food does not significantly contribute to the chronic lead body burden, the

monitoring of lead concentration in the diet is essential since fish of various types were found to be contaminated with lead in addition to cadmium and mercury.

Aluminium is not considered to be an essential element for humans. Exposure to aluminium has been concerned in dialysis dementia, Parkinson disease and Alzheimer's disease. Concentration of aluminium was found maximum in skin and liver (24.29 and 20.59 $\mu\text{g g}^{-1}$ respectively) and minimum in muscle (10.69 $\mu\text{g g}^{-1}$). It is far higher than the fish species from Iskenderun Bay, northern east Mediterranean Sea, Turkey in which it was in the range 0.02–5.41 $\mu\text{g g}^{-1}$ dry weight (Turkmen et al., 2005). The permissible aluminium dose for an adult is quite high (60 mg per day) (World Health Organization, 1989). The concentration of mercury in the tuna fish samples analysed varied from 0.085 to 0.471 $\mu\text{g g}^{-1}$. Higher concentration of mercury was in gill of fresh tuna (0.471 $\mu\text{g g}^{-1}$) and lower in dried (0.086 $\mu\text{g g}^{-1}$) and canned tuna (0.085 $\mu\text{g g}^{-1}$) respectively. All the samples have concentrations below the limit (0.5 $\mu\text{g g}^{-1}$) recommended by the FAO/WHO (1972) and CIFA (1992). Mercury may induce alterations in the normal development of the brain of infants and at higher levels may induce neurological changes in adults (Commission of the European Communities, 2002). Mercury also has toxicity effect on the kidney, the developing fetus and it is a possible human carcinogen (Occupational Safety and Health Administration, 2004).

The levels of toxic metals in the tuna samples of Lakshadweep Sea are not much high when compared to some other areas of the world. Among the body organs, the metal levels were higher in the gills and liver while least in muscle. The concentration of Co, Cr, Ni and Pb were comparatively higher in smoked and canned tuna rather than fresh tuna. As a consequence of its known toxicity, as well as that of Pb and Cd and of the serious contamination of foods that occurs from time to time during commercial handling and processing, most countries monitor the levels of toxic elements in foods. The Joint Food and Agriculture Organisation/World Health Organisation (FAO/WHO) Expert Committee on Food Additives has suggested a provisional tolerable intake of $400 \pm 500 \mu\text{g Cd}$ per week for man; the quantity of Hg to be tolerated in human food is 0.3 mg per week and, for Pb, a weekly intake of 3 mg (FAO/WHO, 1972). But the present analysis indicated that all the metals except mercury present in the muscle of tuna have increased 5-15 times during processing, while the level of Hg decreased through processing.

The results of this study showed significant differences in the metal concentrations among fresh and processed tuna of Lakshadweep Archipelago. Though estimates of the amount of toxic metals consumed in the diet are difficult to obtain, the levels of Cd, Co, Cr, Ni, Pb, Al and Hg in the fresh, smoked and canned yellowfin tuna, *Thunnus albacares* is not plausible to constitute a significant health hazard. The notable finding from this study is the decrease of mercury level in tuna and increase of other metals such as Co, Cr, Ni and Pb during processing to masmin and canned tuna. The level may be reduced by more careful handling practices and processing of raw materials. Due to the high accumulation of all metals, it is advisable to avoid liver and gill of tuna from consumption. Further studies are necessary to estimate the metal levels in human milk, blood and urine for the confirmation of bioaccumulation of toxic metals through food chain from various fin and shell fishes of this island ecosystem.

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