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83. HEAVY METALS IN COMMERCIALLY PROCESSED MOLLUSCAN PRODUCTS IN RELATION TO QUALITY

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ABSTRACT

Heavy metals (Hg, Cu, Zn, Cd, Fa, Mn, Pb and Sn) were determined in several brands of three commercially processed canned and frozen molluscan products - mussels, clams and oysters Concentrations of Hg, Cu, Zn, Cd, Pb and Sn were well below the recommended maximum concentrations in clams and mussel products. However, copper and zinc were higher in oyster products: Overall mean concentrations being 56.88 and 178.6 ppm respectively. Products in Aluminium cans were better in quality compared to the products in traditional tin cans. Impact of heavy metals on the safety and evaluation of colour and flavour for product for acceptability are discussed Depuration studies have been suggested to remove heavy metals from molluscs.

INTRODUCTION

Study of the levels of heavy metal residues (e. g. mercury, cadmium, lead, copper, zinc, arsenic etc) in seafoods has assumed importance in recent years, in view of their possible toxic effects on humans through the food chain. Among the various aquatic organisms benthic filter feeding molluscs are noted for their ability to concentrate these metals from water and sediments to a very high level. As a result of industrialisation there is an increasing build up of these metals in the coastal waters. There is, therefore, growing concern throughout the world with the impact of pollutants on the quality and safety of the consumer from the aquatic resources. Heavy metals can also cause problems in certain fishery products from offensive colour and flavour. Nitta (1972) attributes green discolouration of oysters to copper and zinc pollution either in solution or from sediments. Levels of heavy metals in molluscs had been studied by various workers (Brookers and Rumsby 1965; Bertin and Goldberg 1972; Bryan 1973; Bryan et al; 1977; Topping 1973; Eustace 1974; Ratkowsky et al 1974; Eisenbery and Topping 1984; Khristoforova, et. al 1984). Heavy metal levels in canned seafoods also been determined by a few workers (Hall 1974: Sanchez etc al; 1980; Yamomoto et al 1980: Suddendorf et al 1981; Mauro et al 1981). However, in India work on the occurrence of heavy metals in seafoods is rather scanty. Bhat et al (1965) have determined certain metals in oysters from the Bombay region. Somayajulu and Rama (1971) have determined mercury in sea foods collected from coastal waters off Bombay. Zingde et al; (1976) and Sankaranarayanan et al (1978) have also studied the levels of certain heavy metals in molluscs from the Goa and Cochin region respectively. Lakshmanan and Nambisan (1983) have studied the distribution and seasonal variation of certain trace metals in three bivalve molluscs from Cochin waters.

The objective of the present studies was to monitor the levels of toxic heavy metals (viz. Hg, Cu, Zn, Fe, Mn, Pb Cd and Sn) in canned and frozen molluscan products on a commercial scale and to evaluate their quality with respect to heavy metal levels and sensory criteria and to suggest measures to remove heavy metals from them. With canned foods in particular, shelflife assessment is often made by monitoring the building up of metals especially tin and iron during storage.

MATERIAL AND METHODS

Canned molluscan products were procured from retail outlets in Cochin and a few canned mussel samples processed in the Central Institute of Fisheries Technology, Cochin. The species comprised oyster, *Crassostrea madrasensis* and green mussel, *Perna viridis* (Linnaeus). Frozen clams (*Meretris casta* and *Villorita*

cyprinoides) and mussel (*Perna viridis)* were obtained from fish processing factories located near Quilon. About 20% of the samples were purchased from retail cold storages. A total of seventyfive samples comprising thirty canned products and fortyfive frozen samples were examined for toxic heavy metals and qualities of taste and smell. The soft tissues of various fishery products were homogenised in a glass mortar and subjected to wet digestion using concentrated HNO_3 and concentrated H_2SO_4 mixture (AOAC 1975). The metals were then determined by Flame Atomic Absorption Spectrophotometer. Mercury was estimated by cold vapour technique in a Mercury Analyser (ECIL Model MA 5800) after digesting the sample in in Bethge's apparatus using Con, HNO_3 and Con. H_2SO_4 (4: 1 v/v). Glass distilled water and Analar Reagent Grade chemicals were used in the study.

Three experiments of 48 h duration were performed for depuration with the clam, *Meretrix casta* and oyster, *Crassostrea madrasensis*. Clams for the study were collected from Quilon and oyster from Cochin region. The live animals were immediately transferred into a perspex tank containing filtered seawater (25%). in static condition. In one experiment with the oyster, chelating agent (EDTA) was introduced in the depuration tank at 100 ppm level. The metal levels in the soft parts of the animals were determined immediately after catch and after 48 h depuration.

Sensory evaluation of the canned products and frozen products after cooking were performed by a taste panel team. Emphasis was given to the colour and flavour of the products.

RESULTS AND DISCUSSION

a) Canned Products:. The levels of various heavy metals, viz. Hg, Cu, Zn, Fe, Mn, Ca, Pb and Sn in different brands of canned oyster, *C. madrasensis* and the mussel, *P. viridis* are presented in Table 1. The data showed that the toxic metals like Hg, Pb and Cd were below the permitted limits Indian Standards for heavy metals in canned fishery products are : Hg =0.5 pmm, As=1 ppm, Cu=10ppm, Pb=5ppm, Zn=50 ppm. anb Sn=250 ppm US-FDA permits a maximum of 1.0 ppm Hg in seafood and Australian Authority 2 ppm Cd in shellfish in 90% of the canned products. About 10% of the canned oysters had cadmium content above the permitted

TABLE 1. *Heavy metals in canned Oyster,* Crassostrea madrasensis *and mussel,* Perna viridis *(Linnaeus). Mean and range of values in *ppm (Original weight basis)*

Name of species and type of pack	*Metals*							
	*Hg	Cu	Zn	Fe	Pb	Cd	Mn	Sn
Oyster								
(C. madrasensis)								
Tin cans								
1. Canned in oil	70.7	62.64	195.83	245.22	4.465	3 375	4.983	42
	65-78	58.64-68 0	164.56-227.6	221.7-264.47				
2. Canned in tomato sauce	102.5	68.64	201 98	386.50	4.563	3.155	8.075	50
	90-120	66.20-71.34	178.84-235.86	325.44-342.36				
Aluminium cans								
3. Canned in brine	101.6	46.59	163.60	77.89	0 5125	1.580	5.035	Nil
	98-112	43.41-53.50	142.6-183.73	57.72-109.4				
4. Smoke oyster in oil	89	54.81	154.86	69.40	Nil	1.165	4.123	Nil
	86.4-98	52.51-59.15	141.30-183.7	51.11-98.40				
Mussel								
(P. viridis)								
Canned in oil (Tin can)	45.9	4.12	34.48	320.965	1.99	0.308	8.823	62
	27-57.6	2.46-5.35	17.47-42.06	196.70-488.79				

* Mercury content is expressed in ppb; since the variations were not wide, only mean vaiues are given for Pb, Cd, Mn & Sn.

TABLE 2. *Heavy metals in three commercially frozen molluscan products; viz.' two species of clams and a mussel (Mean and range of values in *ppm wet weight).*

Species & Grade (Count/lb)	Metals *Hg	Cu	Zn	Fe	Cd	Pb	Mn
Clams							
1. *meretrix sp.*							
200-300	24.58	8.54	16.88	97.59			
	19-35	6.86-9.89	13.77-19.82	77.20-121.62	0.188	1.301	4.358
	21.65	5 25	12.17	92.75			
300-500	16.6-28	4.32-6.50	10.16-14.25	81.76-106.85	0.179	1.580	5.044
	15.75	4.43	11.55	84.60			
500-700	11-22	4.12-5.30	10.44-13.84	59.5 -108.44	0.239	2.539	3.99
	6.0	4.28	12.86	87.4			
700-1000	Traces-14	3.91-4.58	11.47-14.03	63.9 -102.5	0.473	1.750	4.566
	5.0	3.58	10.09	61.32			
1000-1500	Traces-11.3	3.04-4.59	8.59-12.04	54.10- 79.2	0.577	2.494	2.828
2. *Villorita sp*							
200-300	29.63	4.31	44.50	544.37			
	22-38	4.09-5.11	41.86-47.18	403.95-768.38	0.395	1.560	10.33
300-600	22.48	4.80	40.9	515.50			
	18-29	4.32-506	39.50-46.26	384.89-768.80	0.301	0.878	10.56
	20.30	4.51	31.91	435.4			
700-1000	15.2-26	4.20-4.84	25.85-36.50	291.6-688.32	0.737	2.225	9.35
3. *Mussel*							
Perna viridis	27.46	1.59	10.81	17.05			
Smaller size	23.0-36.5	1.47-1.68	8.90-12.14	14.40-19.70	1.192	0.686	2.41 6
	48.90	2.36	14.04	59.86			
Larger size	40.6-65	1.37-3.86	9.35-16.85	24.43-158.30	0.437	1.132	3.051

* Mercury is expressed in ppb: since the variations were not wide, only mean values are given for Cd, Pb & Mn.

TABLE 3. *Heavy metal levels in canned molluscan products showing discolouration and metallic flavour*

Product	Metal content in ppm Cu	Zn	Fe	Mn	Sensory Evaluation Colour	Flavour
1. *Oyster* (Tin can)	> 60	> 190	> 250	> 5	Normal	Metallic taste
2. *Oyster* (Aluminium can)	> 40	> 150	> 65	> 5	Green	Metallic taste
3. *Mussel*	> 5	> 35	> 300	> 10	Normal	Metallic taste

limit of 2 ppm. The mean mercury content of canned oysters and mussels were 92 and 46 ppb respectively. Lead was below the limit (5 ppm) in all the products and was nil or in traces in aluminium canned products. All the canned mussel products were safe with respect to their heavy metal content. However, copper and zinc were higher in all the oyster products, overall mean concentrations being 56.88 and 178.6 ppm respectively. Oyster products in aluminium cans contained lesser quantity of Cu, Zn and Fe compared to tin cans and Pb, Cd and Sn were either nil or traces. There was a high build up of iron and tin content in the products canned in the traditional tin containers. Thus, there was an average increase of around 324% iron content in these products compared to aluminium cans.

The sensory evaluation of the products showed that 15% of the mussel products had a metallic flavour. However, 33.3% of oyster products developed metallic flavour and 10% of the sample had green discolouration. The metal levels in the discoloured/off flavoured products are given in Table 3. From the result it seems that Cu and Mn do play a major role in the development of metallic flavour.

The high levels of Cu and Zn observed in the present study in all the oyster products are not abnormal. Higher values have been reported by other workers. Sankaranarayanan et al (1978) have reported copper and zinc concentration in oyster, *C. madrasensis* ranging from 70 to 205 µg/g and 2450 to 12500 µg/g respectively. Zingd et al (1978) have reported values for zinc in *Crassostrea* sp. varying between 323 to 2800 µg/g compared to the above:

Compared to the above results, the present findings indicate lower concentration for these metals. The raw materials for the canned oyster products were collected mainly from Tuticorin where Pillai et al (1986) have reported levels of copper and zinc in fresh oyster from the same area which are comparable with the present observation.

b) Frozen products, A total of 45 frozen mussels/clams have been examined during the present study. The distribution of heavy metals in various size grades of the molluscs are given in Table 2. The important observation is that none of tne products had toxic heavy metals above the permissible limits. The highest concentrations of mercury observed in the various species were 35 ppb in *M. casta* 38 ppb in *Villoritta* sp. and 65 ppb in *P. viridis*. The other two highly toxic metals, Cd and Pb were also very low in these samples; the mean values can be seen from Table 2. Few samples of frozen *Villorita* contained 10 ppm Mn in their meat. Based on heavy metal levels in these products, it can be presumed that 100% of the products are safe and acceptable to the consumer.

The distribution of the metals in various size grades of the clams indicated that the

TABLE 4. *Depuration of heavy metals by the clam,* M. casta *and oyster,* C. madrasensis *in filtered seawater (Salinity = 25% and FS containing EDTA (100mg / litre).*

Mean metal content in ppm.

		M. casta		
Clams from bed		After 48h depuration in seawater		
		I	II	
Cu	7.65	3.56	4.66	
Zn	13.40	8.59	8.89	
		C. madrasensis		
Oyster from bed		After 48h depuration in seawater		After 48h depuration in FS-EDTA medinm
Cu	43.80	43.23		28.60
Zn	892.00	743.00		497.00

concentration of various metals increased with size. In the mussel also larger size showed higher values than smaller size groups (Table 2). The higher levels of metals in larger size groups may be attributed to bioaccumulation of these metals. However, this trend was not conspicuous in the case of Cd, Pb and Mn.

Depuration of metals by clams and Oysters:- The results of the depuration studies are given in Table 4. Only, the values for copper and zinc are presented in the table; iron could not be estimated. The concentrations of Cu and Zn in the tissue declined in both clams and oysters. Mean Cu and Zn concentrations in the clam, *M. casta* declined from 7.65 to 4.106 ppm & 13.40 to 8.73 ppm respectively. In the oyster, the mean Zn concentration (ppm) in filtered seawater was 743 Vs. 497 in seawater containing EDTA in the 48 h depuration period compared to the background level of 892 ppm. Copper did not leach out from the oyster in the filtered seawater media; however, significant amount of copper was depurated in seawater containing EDTA. Copper content of oysters in the EDTA-Seawater mediums was 28.60 ppm Vs. 43.80 ppm before depuration.

Results of the depuration studies seemed to be encouraging. However, detailed investigations are required before any conclusion is drawn from the limited information.

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