

*Research Article*

## **Studies on toxic elements accumulation in shrimp from fish feed used in Bangladesh**

**B. Q. Shamshad\*, R.K. Shahidur and R.C. Tasrena**

Chemistry Division, Atomic Energy Centre, Dhaka-1000, Bangladesh.

\*Author to whom correspondence should be addressed, email: [mumu3222@yahoo.com](mailto:mumu3222@yahoo.com)

---

### **Abstract**

This article focuses on the trace element content of fish feed and shrimp sampled from aquaculture ponds in Bangladesh which were determined using a Flame Atomic Absorption Spectrometer (FAAS), Cold Vapour-Atomic Absorption Spectrometer (CV-AAS) and the Hydride Generation-Atomic Absorption Spectrometer (HG-AAS). Analytical methods combining closed digestion, followed by determination with HG-AAS, CV-AAS and FAAS was developed for study of Arsenic, Cadmium, Lead and Mercury concentration at very low levels in fish feed. The method has detection limits of 0.1 µg/g, 0.1 µg/g, 0.1µg/g, and 0.03 µg/g for As, Cd, Pb and Hg respectively. Oyster tissue and lobster hepatopancreas (TORT-2) reference standards were used in trace element recovery and method validations. The range of elemental concentrations (mg/kg diet, dry wt.) of fish feed were: As 0.14-0.91, Cd <0.1-2.1, Pb <0.1-8.57 and Hg was found to be below the detection limit (<0.03). The results show that the elemental concentrations (mg/kg wet wt.) of arsenic, cadmium, mercury, lead and chromium in shrimp from aquaculture sources were below the detection limit and were low compared with maximum limits for contaminants in shrimp set by the EU.

**Keywords:** AAS, toxic metals, fish feed, shrimp, contamination, food safety.

---

### **Introduction**

Tannery and poultry waste are often used as a cheap sources of fish feed in Bangladesh. Use of these feedstocks may, therefore, theoretically lead to the accumulation of toxic contaminants in

cultured fish and present a food safety risk. Toxic metals are of particular concern as these are used in tanneries, dye producers, textile dyeing and paper and pulp mills [1].

Potentially toxic metals such as arsenic (As), cadmium (Cd) and lead (Pb) may accumulate in fish because of dietary exposure or absorption through the gills [2]. Increased levels of As, Cd and Pb in food may constitute a food safety risk. Ingestion of As may induce peripheral vascular diseases and skin disease such as hyperkeratosis [3]. Intake of Pb can cause damage to the central and peripheral nervous system and memory deterioration [4]. Both Cd and Pb can cause kidney damage [5] and long-term exposure to Cd may cause skeletal damage, which may result in fractures [6]. Therefore, threshold values for certain toxic metals in fish for human consumption and in fish feed have been established by the European Commission (EC 2002). The specific aim of this study was to assess the concentration of toxic metals in fish feed and associated food safety risks of Pb, Cd, As and Hg in fish which are fed with enriched toxic metal content. The article also describes the establishment of a method to determine toxic metals in fish feed and shrimp samples by AAS.

## Material and Methods

Twelve samples of shrimp and twelve samples of feed were collected from different aquaculture sites in Bangladesh. One kilogram of each fish sample was collected and the head was removed from the flesh with a stainless steel knife. The samples were washed with deionised water and excess water removed with tissue paper and then each aliquot was air-dried for 2 hours. 500 gm of shrimp sample was ground in a kitchen blender until a smooth mass was obtained while the feed was dried at 105°C in an oven and then ground with an agate mortar. A portion of 1.0g of ground sample was transferred directly to the flasks of the microwave oven (CEM MARS 5) and 6 ml of suprapure nitric acid was added. The heating program employed was the one proposed in the user's manual. The following three steps temperature program was applied: 180°C with a ramping time 10min; holding time 15 min; and cooling time 10 min. For quality control, analytical blanks and certified reference materials were included namely, oyster tissue and TORT-2 from the National Institute of Standards and Technology and National Research Council Canada, respectively. Recovery was within 10% of the certified values. In shrimp digested samples, As, Cd, Pb, and Hg concentration were measured by Atomic Absorption Spectrometer (Varian, Duo AA 240FS), in Flame- (FAAS), Cold Vapor-(CV-AAS) and Hydride Generation-Atomic Absorption Spectrometric mode (HG-AAS). The limit of quantification was determined as ten times the standard deviation of twenty replicate analyses of the calibration blank.

High purity deionised water ( $18 \text{ M cm}^{-1}$ ) obtained with a Bransted Water purification plant (Bransted series 1090 ), Suprapure nitric acid (Merck, Germany), Sodium borohydride (Acros Organics, USA), Potassium Iodide (Merck, Germany), Hydrochloric acid (Merck, Germany), were used throughout the work. The working standard solution was prepared by diluting a stock solution containing  $1000 \text{ mg L}^{-1}$  of single element AAS grade standard with ultra pure water.

## Results and Discussion

### *Optimization of analytical conditions*

Analytical conditions for determination of trace amounts of Pb, Cd, Hg by AAS have been optimized in our previous study [7]. Here, optimization of analytical conditions for determination

**Table 1. Concentration of Arsenic, Lead, Cadmium and Mercury (mg/kg wet weight) in shrimp feed.**

Sample ID	Arsenic	Lead	Cadmium	Mercury
FF 1	0.48	8.57	<0.1	<0.03
FF2	0.67	2.75	<0.1	<0.03
FF3	0.54	5.50	2.10	<0.03
FF4	0.21	3.70	<0.1	<0.03
FF5	0.14	2.57	<0.1	<0.03
FF6	0.14	<0.1	<0.1	<0.03
FF7	0.56	4.87	<0.1	<0.03
FF8	0.39	2.17	<0.1	<0.03
FF9	0.65	2.50	<0.1	<0.03
FF10	0.91	3.17	<0.1	<0.03
FF11	0.70	1.44	<0.1	<0.03
FF12	0.36	2.12	<0.1	<0.03
EU Max level	4.0	5.0	0.5	0.1
Mean	0.45	3.58	-	-
Range	0.14-0.91	<0.1-8.57	<0.1-2.1	<0.03

of As in shrimp and shrimp feed have been discussed. Various operating parameters e.g. flow rate of sample, NaBH<sub>4</sub>, HCl, and concentration of NaBH<sub>4</sub> and HCl were optimized individually while the other parameters were kept at their optimum values to obtain a maximum As net intensity. The other experimental parameters investigated were KI reaction time and acidity of sample solution. As a result of this investigation, 3M Hydrochloric acid (HCl) was chosen as the acidic reaction medium with flow rate 7 ml/min. The effect of Acid concentration in sample solution on sensitivity has been studied, while KI reaction time, HCl, NaBH<sub>4</sub> conc. were kept at 3.5h, 5M, 0.6%, respectively and HCl, NaBH<sub>4</sub> flow rate at 1 ml/min.

Effect of KI reaction time on sensitivity has also been studied. It is observed that sensitivity is increased with time and it gives maximum absorbance after 2 h which indicates that complete reduction of As (V) to As (III) occurred after 2 hours and after that there was no change in absorbance. It was also found to be stable even up to 24 h.

### ***Toxic metals in feed and shrimp***

This paper only includes non-essential metals which contribute to our diet through seafood consumption (e.g. arsenic, cadmium, mercury, and lead). It is important to consider that their toxicity depends on their chemical form.

### ***Arsenic (As)***

Among different chemical forms, both inorganic and organic, inorganic arsenic compounds are the most toxic, particularly As<sub>2</sub>O<sub>3</sub>. The mean arsenic content in shrimp feed that is mostly used in Bangladesh was 0.45 mg/kg wet weight and the range was from 0.138 to 0.909 mg/kg (Table 1). Arsenic concentration in shrimp feed didn't exceed the European Union (EU) maximum level of 4 mg/kg feed.

Since toxic metals may accumulate in shrimp through feed, levels of toxic metals in seafood is a great concern. From this point of view, some farm shrimp are checked periodically for their toxic

metals levels. However, the level of As in most of the shrimp samples was found to be below detection limits (0.1 mg/kg).

**Table 2. Concentration of Arsenic, Lead, Cadmium and Mercury (mg/kg wet weight) in shrimp samples.**

Sample ID	Arsenic	Lead	Cadmium	Mercury
F 1	<0.1	<0.1	<0.1	<0.03
F2	<0.1	<0.1	<0.1	<0.03
F3	<0.1	<0.1	0.12	<0.03
F4	<0.1	<0.1	<0.1	<0.05
F5	<0.1	<0.1	<0.1	<0.03
F6	<0.1	<0.1	<0.1	<0.06
F7	<0.1	<0.1	<0.1	<0.03
F8	<0.1	<0.1	<0.1	<0.03
F9	<0.1	<0.1	0.14	<0.03
F10	<0.1	<0.1	<0.1	<0.03
F11	<0.1	<0.1	<0.1	<0.03
F12	<0.1	<0.1	<0.1	<0.03
EU Max level	-	0.5	0.5	1.0

#### ***Cadmium (Cd)***

Cadmium is one of the contaminants that health authorities are most concerned about, due to the long biological half-life in humans. The cadmium concentration in shrimp feed was less than 0.1 mg/kg, in most cases, with the exception of one case (2.1 mg/kg) and the EU maximum level for cadmium in fish/shrimp feed is 0.5 mg/kg.

The level of Cd in most of the cases was found to be below detection limits with the exception in two cases but these two cases did not exceed the permissible limit set by EU (0.5 mg/kg) for shrimp.

#### ***Lead (Pb)***

Lead can be adsorbed from air, food and water. Food and water account for approximately 70% of the total lead intake in adults. The mean lead in shrimp feed was 3.58 mg/kg and the range was <0.1(DL) to 8.57 mg/kg (Table 1). In one case, the lead concentration in shrimp feed was found to be around 2 times higher than the EU maximum level for lead in fish/shrimp feed which is set at 5.0 mg/kg. However, the mean lead content in feed is low compared to the maximum level of 5.0 mg/kg set by the EU.

The level of Pb in most of the shrimp samples was found to be below detection limits (0.1 mg/kg) and also below permissible limits (Table 2). EU has set the maximum limit for Pb in shrimp at 0.5 mg/kg.

#### ***Mercury (Hg)***

Mercury occurs naturally in the marine food chain, both as organically bound mercury (e.g. methyl mercury) and inorganic bound mercury. It is the organic form that is most toxic and gives rise to concern. The mercury content in shrimp feed was lower than the quantification limit for the analytical method (0.03mg/kg). The EU has a maximum level for mercury in feed of 0.1 mg/kg.

The level of Hg in most of the shrimp samples with a very few exceptions was also found to be below detection limits (0.03 mg/kg) and also low compared with permissible limits (Table 2) set by EU for Hg in shrimp as 1.0 mg/kg.

## **Conclusion**

Mercury and cadmium concentration were generally low and for most of the feed and shrimp samples were below detection limits. Though maximum concentration in feed was 8.57 and 0.909 mg/kg for lead and arsenic respectively, the levels of these two metals were below detection limits in the most analyzed shrimp samples. These results indicate that consumption of shrimp which are produced in aquaculture farms seems not to constitute a food safety problem with respect to As, Pb, Cd and Hg.

## **References**

1. Bartone C.R and Benavides L., (1997). Local Management of Hazardous Wastes from Small-Scale and Cottage Industries. **Waste Management and Research** 15, 3-21.
2. Hollis L., Hogstrand C. & Wood C.M., (2001). Tissue-Specific Cadmium Accumulation, Metallothionein Induction and Tissue Zinc and Copper Levels During Chronic Sublethal Cadmium Exposure in Juvenile Rainbow Trout. **Archives of Environmental Contamination and Toxicology** 41, 468-474.
3. WHO (2001). Arsenic and Arsenic Compounds. Environmental Health Criteria, Vol. 224 World Health Organization (WHO), Geneva.
4. Verity M.A., (1995). Nervous system. In: Metal Toxicology (eds RA Goyer, CD Klaassen & MP Waalkes) Academic Press, San Diego, pp. 199-235.
5. Goyer R.A. and Cherian G., (1995). Renal effects of metals, In: Metal Toxicology (eds RA Goyer, CD Klaassen & MP Waalkes) Academic Press, San Diego, pp. 389-412.
6. Alfven T., Elinder C.G., Carlsson M.D., Grubb, A. Hellstrom, L., Persson, B. Pettersson, C., Spang, G., Schutz, A. and Jarup, L. (2000). Low-Level Cadmium Exposure and Osteoporosis. **Journal of Bone and Mineral Research** 15, 1579-1586.
7. Shamshad B. Q. and Sohela A., (2007). **Journal of Bangladesh Academy of Sciences** 31, 191-196.