ISSN 1112-9867

Available online at

http://www.jfas.info

TRACE METAL CONCENTRATIONS IN SURFACE WATER AND PORE WATER SEDIMENT OF COASTAL AQUACULTURE PONDS, BANGLADESH

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Received: 30 December 2018 / Accepted: 19 April 2019 / Published online: 01 May 2019 ABSTRACT

This study investigates contamination of surface water and pore water sediment by trace metals at the three coastal fish farms of Noakhali district in Bangladesh using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) standards were used as the baseline for the evaluation of surface water pollution and contamination of the sediments respectively. Cr and Cd concentrations in the surface water exceeded the reference limit, but there was no metal contamination of the pore water sediment. The average trace metals concentrations in both surface water and pore water sediment respectively showed similar trends Cr> Pb > Cu> Zn > Cd. All the metals studied exhibit negative I_{geo} values and CF<1 indicating uncontaminated sediment quality. The results of this study indicate that surface water of aquaculture ponds may be a possible source of trace metals which could be of health concern.

Keywords: Surface water, Pore water sediment, Contamination, Trace metals, Noakhali district

Author Correspondence, e-mail: nstusaiful34 @mail.com doi: http://dx.doi.org/10.4314/jfas.v11i2.13



1. INTRODUCTION

In recent years, multifarious scientific research conducted on the toxicity of trace metals in the environment, redundancy, and persistence helps to draw attention universally [1-3]. Study of the metals concentration in aquatic environment is to ensure regular monitoring program, but the concentrations in sediment and biota also attain a substantial level [4]. Several anthropogenic factors are responsible for the trace metal pollution, and different studies showed that industrial activities played a prominent role in the amplification of metal concentrations resulting in serious environmental problems [5]. Unauthorized sources of pollution such as laundry services and dumping of waste although in small scale often causes severe problems in the aquatic environment. On the other hand, agricultural run-off brings pesticide and fertilizers with inorganic anions and trace metals into the water bodies.

Fish feed plays a vital role in aquaculture and is considered a good source of protein and vitamins for a healthy growth, but there could be traces of metals and other contaminants. The sources of trace metals in commercially available fish feed are associated with unclean water sources mostly influenced by industrial activities such as tannery operations and the use of different types of additives and feed colorant [6, 7]. Some of the media reported the use of tannery and poultry waste in the fish feed formulation so as to minimize production cost and reduce expenditure. Farmers in the present study area utilize the fish feeds, which may contain levels of trace metals [8]. Most of the trace metals are reported to be toxic to humans, plants and animals [9, 10]. Trace metals easily aggregate in the water and sediment and can exceed toxic limit when the ambiance condition is changed [11-14]. Elevated levels of trace metal contaminated fishes has been reported [17]. Thus, in aquatic ecosystem, trace metal contaminations may have detrimental effects [18, 19].

Though trace metal study is of vital importance considering the health implications, not much scientific research has been carried out in Bangladesh so far especially in relation to the coastal aquaculture [20-22]. Furthermore, considering that fishes ingest and uptake metals through food and water which depends on concentration and availability [23]. The presence of metals in water and pore sediment will directly influence the levels in fishes. Therefore, this

study is aimed to evaluate trace metal concentrations (Cr, Cu, Zn, Cd, and Pb) in surface water and pore water sediment of fresh water fish culture ponds and to assess the extent of contamination. The world health organization standard for aquaculture water quality [24], toxicity reference limit for sediments [25] are used as the baseline.

2.0 EXPERIMENTAL

2.1 Site Selection

This study was conducted between the month of August to November 2015 at three different coastal fresh water fish farms named Globe Agro Production Ltd (GAPL), Bismillah Agro Production Ltd (BAPL) and Suborno Agro-based Initiative (SABI) indicated as S1, S2, and S3 respectively on the map of Noakhali district of Bangladesh (Fig.1). Different fish species named Catla (*Jubilion catla*), Magur (*Clarius batrachus*), Rui (*Labro rohita*), Shing (*Heteropneustes fossilis*), and Tilapia (*Tilapia mossumbica*) were commercially cultured in these fish farms for a duration of 120 to 300 days in a year.



Fig.1. Sampling Location of different ponds under different coastal fish farms of Noakhali district

2.2 Samples collection

Total of 48 surface water and pore water sediment samples were collected from 8 ponds (P1 to P8) (Table 1) based on the type of culture and cultured species. The samples were diagonally collected from the ponds in triplicate. Sediment samples were collected using single core sampler and the samples were then sub-sampled 0-3 cm thickness using stainless knife. Sub-sampled sediments were poured in to labelled plastic bottle and were immediately transported to the laboratory using ice box. Water samples were acidified using conc. HNO₃ (Analytical grade) to prevent metals adherence to the container surface. In the laboratory, samples were transferred into clean centrifuge tube and were centrifuged (2000 rpm, 15 min) at room temperature to collect clear supernatant (pore water) and appropriate dilution was made using distilled deionized water. Surface water samples were collected using Van Dorn water sampler and were transferred to clean sampling bottles for analysis.

Hatchery	Ponds No.	Types of Ponds
GAPL	P1	Culture
	P2	Brood
BAPL	P3	Nursery
	P4	Culture
	P5	Brood
SABI	P6	Nursery
	P7	Culture
	P8	Brood

Table 1. Hatchery and Type of ponds

2.3 Quality control

All plastic wares were previously soaked in 5% HNO_3 for at least 24 hr, rinsed with doubled deionized water and dried. Appropriate quality control and quality assurance were followed to ensure reliable and reproducible result. All the reagents used are pure and analytical grade, and the results obtained were expressed as the 95% confidence interval of the mean. The

certified values from certified reference materials used in this analysis showed a good agreement with recoveries ranging between 95% and 105%.

2.4 Determination of trace metals

Surface water and pore water sediment (50 ml each) were taken in separate flask and 5 ml concentrated HNO₃ (Analytical grade) was added and the mixture was heated for 10 mins to reach volume of 20 ml and allowed to cool. The digestion was completed when the mixture became colorless. Moreover, the appearance of brown fumes also indicated the completion of digestion process. The resulting solutions were filtered using Whatmann 0.42µm filter paper. Metal concentrations were determined using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (SPECTRO MS, SPECTRO GmbH, Germany). The metal standards prepared were checked with Standard reference material (SRM) from National Bureau of Standards (NBS, USA). The ICP-MS operational conditions were adjusted in accordance with the manufacturer's guidelines to yield optimal determination [26].

2.5 Assessment of pore water sediment contamination

2.5.1 Calculation of Geo-accumulation index

Geo-accumulation index (I_{geo}) was calculated using the following equation described by [27,28].

$$I_{geo} = \log_2 \left(Cn / 1.5Bn \right) \tag{1}$$

Where, Cn is sediment concentration, Bn is geochemical background value of a metal in shale [29] and 1.5 is the background matrix correction factor. The classification of pore water sediment in this study was carried out using Table 2 below;

I _{geo} value	Class	Contamination levels
< 0	0	Practically clean
0 to 1	1	clean to moderate
1 to 2	2	moderate
2 to 3	3	moderate to high
3 to 4	4	high
4 to 5	5	high to very high
5 <	6	very high

Table 2. Geo-accumulation index for the pore water sediment [30]

2.5.2 Calculation of contamination factor

Contamination factor (CF) was calculated using the following equation according to [31].

$$CF = Cn \ sample \ / \ Bn \ shale \tag{2}$$

Where, Cn is the concentration in sediment, Bn is geochemical background value of a metal in shale [29]. The evaluation of contamination factor of the pore water sediment was made with reference to Table 3 below;

Cf value	Degree of Contamination
<1	Minute
1 to 3	Medium
3 to 6	Considerable
≥6	Very high

 Table 3. Classification of contamination factor [32].

2.5.3 Statistical analysis

The means and standard deviations were calculated using IBM-SPSS Statistics for windows (IBM, USA). Pearson correlation matrix was computed using PAST statistical software where values at (p < 0.05) were considered significantly different [33].

3.0 RESULTS AND DISCUSSION

3.1 Metal concentrations in surface water

Table 4 present the mean and standard deviation of trace metal concentrations in surface water of the studied sites. The average trace metal concentrations in water samples from the study sites decreased in the following trend Cr> Pb> Cu> Zn> Cd. The mean Cr concentration of 1.26 ± 0.07 mgL⁻¹ was higher than 0.1 mgL⁻¹ considered as maximum permissible limit in waste water for agriculture and aquaculture [24]. The elevated concentration of Cr in the aqua culture ponds (Fig 2a) could be linked to the abundant chrome tanning industries in Bangladesh which were reported to affect both surface and underground water sources [34, 35].

The mean concentration of Zn and Cu in the surface water were $0.12\pm0.06 \text{ mgL}^{-1}$ and $0.19\pm0.12 \text{ mgL}^{-1}$ which were below WHO standard limits of 2.0 mgL⁻¹ and 0.2 mgL⁻¹ respectively as shown in Table 4. Both Zn and Cu are useful elements for aquatic organisms [36]. Zn concentrations were below the reference limit at all the sampling locations (Fig. 2c). Rahman et al., [37] reported similar result for Zn in Bangshi river water, Bangladesh. However, elevated concentrations of Cu above the reference limit were obtained at P3, P4, P5 and P7 (Fig. 2b) which could be much associated with industrial activities and automobile sources [38]. Furthermore, source of Cu could be from the nearby agricultural land. Cu is used as an agent for control of livestock and poultry diseases, and in Fertilizer and feed additives [39]. Higher Cu concentration is a threat to human health as copper aggravates gastrointestinal disorder [40].

Sample type	Sample site	Cr	Cu	Zn	Cd	Pb
Surface water	P1	1.27±0.06	0.09±0.10	0.21±0.11	0.05 ± 0.02	0.38±0.04
	P2	1.20 ± 0.07	0.18 ± 0.07	0.08 ± 0.02	0.06 ± 0.08	0.41 ± 0.05
	P3	1.31 ± 0.04	0.22 ± 0.08	0.12 ± 0.10	0.09 ± 0.04	0.39 ± 0.05
	P4	1.32 ± 0.08	0.21 ± 0.05	0.16±0.11	0.11 ± 0.05	0.35 ± 0.08
	P5	1.29 ± 0.06	0.26 ± 0.14	0.11 ± 0.04	0.10 ± 0.06	0.37 ± 0.04
	P6	1.24 ± 0.06	0.14 ± 0.05	0.07 ± 0.04	0.08 ± 0.05	0.38 ± 0.07
	P7	1.26 ± 0.05	0.28 ± 0.07	0.11 ± 0.07	0.09 ± 0.06	0.40 ± 0.04
	P8	1.25 ± 0.08	0.15 ± 0.05	0.08 ± 0.05	0.07 ± 0.04	0.36 ± 0.04
	Mean	1.26 ± 0.07	0.19 ± 0.12	0.12 ± 0.06	0.08 ± 0.06	0.38 ± 0.06
	Recovery (%)	99.09±7	97.21±2	95.92±7	101.88 ± 5	105.06 ± 8
	WHO, 1989	0.1	0.2	2.0	0.01	5.0
Pore water sediment	P1	1.31 ± 0.10	$0.19{\pm}0.08$	0.38 ± 0.44	0.08 ± 0.04	0.40 ± 0.10
	P2	1.25 ± 0.04	0.35 ± 0.04	0.18 ± 0.06	0.09 ± 0.03	0.41 ± 0.04
	P3	1.35 ± 0.05	0.46 ± 0.45	0.16 ± 0.04	0.15 ± 0.07	0.41 ± 0.06
	P4	1.34 ± 0.09	0.25 ± 0.03	0.22 ± 0.12	0.16 ± 0.05	0.36 ± 0.10
	P5	1.35 ± 0.03	0.23 ± 0.25	0.25 ± 0.13	0.12 ± 0.01	0.39 ± 0.02
	P6	1.32 ± 0.07	0.17 ± 0.13	0.22 ± 0.17	0.15 ± 0.09	0.41 ± 0.05
	P7	1.32 ± 0.09	0.29 ± 0.17	0.15 ± 0.07	0.12 ± 0.10	0.44 ± 0.08
	P8	1.28 ± 0.05	0.36 ± 0.18	0.12 ± 0.08	0.14 ± 0.06	0.43 ± 0.07
	Mean	1.32 ± 0.06	0.28 ± 0.26	0.21 ± 0.08	0.13 ± 0.05	0.41 ± 0.06
	Recovery (%)	99.09±7	97.21±2	95.92±7	101.88 ± 5	105.06 ± 8
	USEPA,1999	26	16	N.A.	0.6	31

Table 4. Trace metal levels in surface water (mgL⁻¹) and pore water sediment (mgkg⁻¹)

(mean \pm SD), n = 3, NA = Not available.

Cd is a toxic metal and its presence in the aquatic ecosystem indicates contamination. The mean concentration of Cd was 0.08 ± 0.06 mg/L which exceeded the WHO aquaculture water standard level of 0.01 mgL⁻¹ (Fig 2d). The lowest value of Cd of 0.05 ± 0.12 mgL⁻¹ was observed at P1 and the highest concentration was 0.11 ± 0.06 mgL⁻¹ obtained at P4. High concentrations of Cd in the surface aqua culture water may be linked to metal processing industries and other anthropogenic influences [41]. The mean concentration of Pb in the surface water was 0.38 ± 0.06 mgL⁻¹ which was below WHO standard aquaculture limit of 5.0 mgL⁻¹. The Pb concentrations at all the sample locations studied were below the reference limit (Fig. 2e).



Fig.2. Comparison of mean concentrations (mgL⁻¹) of trace metal in surface water (Dot line indicates aquaculture water standard) [24]

3.2 Metal concentration in pore water sediment

The mean concentrations of trace metals in the pore water sediment were higher than the observed values in surface water. This agrees with the literature findings that 30 to 98% of the metal loads are deposited in sediments compared to surface water [42-44]. However, the

observed trend of the studied metals in pore water sediment was similar to those of surface water. The level of trace metals in sediment determines the quality of the water [45]. In this study, Cr concentration in pore water sediment was higher than other metals which could be associated with the fish feed. The presence of hexavalent Cr from tanneries is much related to the high Cr concentration in fish feed which ultimately increases the concentration level in the sediment [22, 9]. A study conducted on metal levels in the sediment of aqua culture in the northwest Bangladesh and Southern China showed Cr concentrations of $63.05 \pm 6.92 \text{ mgkg}^{-1}$ and 21.9 ± 6.47 mgkg⁻¹ respectively [22, 46]. These values are higher than Cr concentration of 1.32 ± 0.06 mgkg⁻¹ obtained in the present study which is lower than maximum permissible value of Cr in sediment [25].

Cu is necessary for good health, but excess intake can cause health complications [47]. The highest concentration of Cu (1.32±0.06 mgkg⁻¹) in pore water sediment in all the studied ponds was found at P3 situated near agricultural land. Mean concentration of Cu in the present study 0.28±0.26 mgkg⁻¹ is much lower than USEPA maximum permissible values of 16 mgkg⁻¹ in sediments [25], and is lower than values obtained in coastal water ponds of 8.41 $\pm 2.31 \text{ mgkg}^{-1}$ from Southern China [46].

Table 5. Comparison of trace metal accumulation (mgkg ⁻¹) in pore water sediment with the	
reported values in the literatures	

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Sample area	Cr	Cu	Zn	Cd	Pb	References	
Noakhali	1 32+0 06	0 28+0 26	0 21+0 08	0 13+0 05	041+006	Present	
(Bangladesh)	1.52±0.00	0.20±0.20	0.21±0.00	0.15±0.05	0.11±0.00	work	
Mymensingh	63 05+6 02		208+31 38	0.000±0.01	1/1 8/1+1 00	[22]	
(Bangladesh)	05.05±0.92	-	200-51.50	0.009±0.01	14.04-1.77		
Southern	21.0 ± 6.47	0 11 10 21	260 + 192	0.12 ± 0.02	22.5 ± 10.0	[46]	
China	21.9 ± 0.47	0.41±2.31	309 ± 102	0.13 ± 0.03	52.3 ± 10.9	[40]	
Sunderban			40.0 ±16.7	0.01 ± 0.02	1.81 ± 1.00	٢/٩٦	
(India)	-	-	40.9.±10.7	0.01 ± 0.02	4.04 ± 1.99	[40]	
Bioshere	80 5+13 4	12 9+4 2	28 2+7 4	_	_	[/]0]	
reserve (Iran)	00.5±15. 4	12.7-7.2	20.2±7.4			[47]	
Astatic ponds	8 50+ 5 51	1/1 30+5 9	63 //+26 /	1.15 ± 0.77	20 35+8 6	[50]	
(Poland)	0.50 ± 5.51	17.30±3.7	03.77-20.4	1.15-0.77	20.33 ± 0.0	[30]	

Although Zn plays a vital role in the physiological and metabolic process, it can be toxic at higher concentrations. Sediments release Zn when water environment is changed [51, 52]. The practice of aquaculture depends mainly on the application of fish feed which might be a potential source Zn pollution. The average value of Zn in the present study was 0.21 ± 0.08 mgkg⁻¹ which is much lower compared to other values reported from other aquafarms in the literature (Table 5). This could be due to lower stocking density followed in the present study [22].

The mean Cd concentration of 0.13±0.05 mgkg⁻¹ obtained in this study is lower than Cd maximum permissible value of 0.6 mgkg⁻¹ [25]. The reported Cd value is similar to that of coastal water ponds in Southern China, but slightly higher than other reported values. The mean concentration of Pb is 0.41±0.06 mgkg⁻¹, this is much lower than Pb maximum permissible value of 31 mgkg⁻¹ in sediment [25], and significantly lower than the reported values from the literature.

3.3. Indices of pore water sediment contamination

3.3.1 Geo-accumulation index (I_{geo})

The range of I_{geo} values for Cr, Cu, Zn, Cd and Pb were -6.7 to -6.6; -8.6 to -7.2; -10.2 to -8.55; -2.5 to -1.5 and -6.4 to -6.1 respectively (Fig. 3). The Igeo values of all metals were very low (Igeo <0) implying that there is no trace metal contamination of sediment in the present study area.



Fig.3. Geo-accumulation index of trace metals in pore water sediment

3.3.2. Contamination factor (CF)

The mean CF values of Cr, Cu, Zn, Cd and Pb were 0.015, 0.006, 0.002, 0.421 and 0.02 respectively which are in descending order of Cd > Pb > Cr > Cu > Zn (Fig. 4). The results indicates a very low degree of contamination (CF <1) in the pore water sediment and therefore have no potential risk.



Fig.4. Contamination factor of trace metals in pore water sediment

3.4. Correlation matrix

The source and passage of these elements may be known by correlation matrix [53]. Metals which show positive correlation may be from the same pollution sources [54]. Table 6 shows the results of correlation study in which metals in the surface water showed significant

positive correlation (p < 0.05) between Cr-Zn (0.54) and Cr-Cd (0.68). However, significantly negative correlation (p < 0.05) was observed between Cr-Pb (0.73); Cu-Cd (0.75) and Cd-Pb (0.57). In pore water sediment, significant negative correlation (p< 0.05) was formed between Cu and Zn (0.67) indicating dissimilar source of the metals.

	Surface water					Pore water sediment				
	Cr	Cu	Zn	Cd	Pb	Cr	Cu	Zn	Cd	Pb
Cr	1.00					1.00				
Cu	0.33	1.00				-0.15	1.00			
Zn	0.54	-0.25	1.00			0.19	-0.67	1.00		
Cd	0.68	-0.75	-0.08	1.00		0.51	-0.18	-0.51	1.00	
Pb	-0.73	0.04	-0.45	-0.57	1.00	-0.41	0.33	-0.47	-0.20	1.00

Table 6. Pearson's correlation coefficients among trace metal concentrations (mgkg⁻¹)

Values >-0.5 or < -0.5 are significantly correlated.

4. CONCLUSION

The levels of trace metals in aquatic environment indicate the state of pollution. The concentrations of trace metals in the coastal aquaculture ponds were determined. Cr and Cd concentrations in the surface water were found to exceed the reference guideline which could be linked to the fish feed and other agricultural practices. This indicates pollution of the surface water with toxic metals which could be transferred to the fish and subsequently the consumers. The pore water sediment contained trace metals at concentrations below the reference values, signifying absence of contamination due to the selected metals. This is further justified by the results of Igeo and CF which confirmed that pore water sediment of the aquaculture ponds was not contaminated. The findings of this study could be served as a guide for monitoring the levels of toxic trace metals in the abundant and increasing aquaculture farming.

5. ACKNOWLEDGEMENTS

The authors grateful to Abdul Matin for his assistance in sampling and to the Forensic Analysis Department, Rab HQ, Bangladesh for providing research facilities.

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How to cite this article:

Palash Md A, Islam Md S, Bayero AS, Sani S, I. B. Koki. Trace metal concentrations in surface water and pore water sediment of coastal aquaculture ponds, Bangladesh. J. Fundam. Appl. Sci., 2019, *11*(2), 729-747.