

Available Online

JOURNAL OF SCIENTIFIC RESEARCH www.banglajol.info/index.php/JSR

J. Sci. Res. 8 (1), 93-100 (2016)

A Quantitative Analysis of Chromium and Zinc in Water and Raw Milk in Chittagong, Bangladesh

S. Akther^{1*}, S. M. S. Shahriar², H. M. Zakir², M. K. Alam¹

¹Department of Food Processing and Engineering, Chittagong Veterinary and Animal Sciences University, Khulshi, Chittagong-4225, Bangladesh

²Department of Applied Chemistry and Chemical Engineering, Rajshahi University, Bangladesh

Received 28 August 2015, accepted in final revised form 12 October 2015

Abstract

The concentration of selected heavy metals (chromium and zinc) was detected and estimated in water and raw milk collected from Chittagong City of Bangladesh. A total of 25 water samples and 20 raw milk samples were collected from different farms situated in 10 locations of Chittagong, Bangladesh. Chromium content in water was obtained in the range from $0.2 \ \mu g/L$ to $13 \ \mu g/L$. The highest level of chromium content in water was 13.068 $\ \mu g/L$. The content of chromium in raw milk was obtained in the range from $2 \ \mu g/L$ to 17 $\ \mu g/L$. The highest level of chromium in milk was 17.062 $\ \mu g/L$. Chromium concentrations in water and milk were below the maximum allowed limit. The concentration of zinc in water was 1.024 mg/L. The concentration of zinc in raw milk was in the range from 0.6 mg/L to 0.9 mg/L. The highest concentration of zinc in water was 1.024 mg/L which is around the toxicological guidance value of zinc.

Keywords: Chromium; Zinc; Water; Milk.

©2016 JSR Publications. ISSN: 2070-0237 (Print); 2070-0245 (Online). All rights reserved. doi: <u>http://dx.doi.org/10.3329/jsr.v8i1.24776</u> J. Sci. Res. **8** (1), 93-100 (2016)

1. Introduction

Chromium (Cr) and zinc (Zn) is a naturally occurring element found in food products of both plant and animal origins. These are regarded as essential trace element in humans and animals, taking part in various metabolic processes. Cr an essential element is usually present in food in the trivalent form; the hexavalent form of Cr is toxic and not normally found in food [1]. Cr(VI) has been reported to be toxic and carcinogenic to humans owing to its oxidizing potential and easy permeation of biological membranes [2]. In living organisms, Cr is present in the more stable trivalent state, and its essential biological

^{*} Corresponding author: <u>shireen_cvasu@yahoo.com</u>

activities are due to the complexes known as "biologically active Cr" (glucose tolerance factor or GTF) [3]. Cr is a component of enzymes which control glucose metabolism and synthesis of fatty acids and cholesterol, and its deficiency leads to severe impairment of glucose tolerance, which finally leads to diabetes and atherosclerotic disease [4]. Insufficiency of Cr is caused mainly by its insufficient supply with food products. The recommended daily intake proposed for Cr by the US RDA is 50–200 µg/day for a 60-kg person [5]. These levels are not usually reached in the industrialized countries where Cr deficiency is perhaps the principal trace element deficiency, particularly in people above the age of 35. As a result, it is referred to as geriatric nutrient [6]. According to literature data, daily Cr intake in European countries ranges from 22 µg to 146 µg, but in most of them it is under 100 μ g, and in the USA it is as low as 23 to 62 μ g [7]. On the other hand, Zn is a trace element that is essential for human health. Zn constitutes about 33 µg/g of an adult body mass and it is essential as a constituent of many enzymes involved in several physiological functions, such as protein synthesis and energy metabolism [8]. Too much Zn can still cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anaemia. Zn can be a danger to unborn and newborn children. When their mothers have absorbed large concentrations of zinc the children may be exposed to it through blood or milk of their mothers. To assess the dietary intake of Cr and Zn with food it is necessary to know their content in different groups of food products. Cr and Zn contents in fruits, vegetables and dairy products are relatively low, but their consumption is high, which make their contribution to Cr and Zn intake significant [2]. However, scientifically reliable data on the Cr and Zn contents in different foods and agricultural products are still insufficient [9]. Water, milk and dairy products make an important contribution to the supply of Cr and Zn for the human diet. The aim of the present study is to determine the concentration of Cr and Zn in water and cow's milk available in market in Chittagong city corporation area of Bangladesh.

2. Experimental

2.1. Sample collection

Total 25 and 20 samples of water and raw milk were collected from 10 different locations during March-April, 2014 in Chittagong area of Bangladesh which are listed in Table 1.

2.2. Sample preparation

 HNO_3 was used for the dilution and mineralization of water samples. 100 mL of each representative water sample was transferred into Pyrex beaker containing 10 mL of conc. HNO_3 . The sample was boiled slowly and then evaporated on a hotplate to the lowest possible volume (about 20 mL). The beaker was allowed to cool and another 5 mL of conc. HNO_3 was added. Heating was continued with the addition of conc. HNO_3 as necessary until digestion was complete. The sample was evaporated to dryness and then cooled, followed by the addition of 5 mL HCl solution (1:1 v/v). The solution was

warmed and 5 mL of 5M NaOH was added, and then filtered through Whatman No. 42 filter paper. The filtrate was transferred to 100 mL volumetric flask, diluted upto the mark with deionized water and then subjected to elemental analysis.

For the milk samples, 5 mL of milk was pipetted into the 200 mL cylindrical flask. Conc. HNO_3 (10 mL) and H_2SO_4 (3 mL) as well as milk were heated at 120°C for 4 h. After heating 1 mL of 20% H_2O_2 was added and heated the mixture at 200°C for 8 min. The final digested sample was diluted to 50 mL with deionized water and then filtered through Whatman No. 42 filter paper. The filtered solution was then used for the elemental analysis.

Sample Code		Location				
Water	Milk					
W-1	M-1	Anwara				
W-2	M-2					
W-3	M-3	Patiya Pourashava				
W-4	M-4					
W-5	M-5	Hathazari				
W-6	M-6					
W-7	M-7	Raozan				
W-8	M-8					
W-9	M-9	Sitakunda (north west)				
W-10	M-10					
W-11	M-11	Chandanaish				
W-12	M-12					
W-13						
W-14	M-13	Mirsharai				
W-15	M-14					
W-16						
W-17	M-15	Halishohor				
W-18	M-16					
W-19						
W-20	M-17	Bondor				
W-21	M-18					
W-22						
W-23	M-19	EPZ				
W-24	M-20					
W-25						

Table 1. Locations of sample collection.

2.3. Analytical methods and instrumentation

Cr and Zn in water and milk samples were determined according to previously described methods [10,11]. The samples were analyzed in a laboratory with a quality assurance schemes by using "Analytikjena Atomic Absorption Spectrophotometer, model: ZEEnit700P, Germany".

2.4. Measurement of different variables

Exposure estimates have been compared with health-based toxicological reference values (e.g. heavy metals have been compared with acceptable daily intakes ADI).

2.5. Data analysis

The concentrations of Cr and Zn in water and raw milk were determined by using ASpect LS 1.2.0.0, Analytik Jena AG 2011-2012 system software. Statistical analysis was performed by using SPSS statistical software of version 14. All values were expressed as mean \pm standard deviation (SD).

3. Results and Discussion

Atomic absorption spectrophotometer (AAS) was calibrated with Cr concentrations at 5 ppb, 10 ppb, and 15 ppb respectively for the calibration of the AAS. The AAS was also calibrated with Zn concentrations at 0.40 ppm, 0.80 ppm, and 1.20 ppm respectively. The results of water sample analyses are given in Table 2. The content of Cr in water was obtained in the range from 0.2 μ g/L to 13 μ g/L. The highest level of Cr in water was 13.068 μ g/L. Cr concentration in water was below the maximum allowed limit. The concentration of Zn in water was in the range from 0.01 mg/L to 1 mg/L with the highest concentration being observed was 1.024 mg/L. The concentration of Cr and Zn in raw milk are given in Table 3. The content of Cr in milk was obtained in the range from 2 μ g/L to 17 μ g/L. The highest level of Cr in milk was 17.062 μ g/L. The concentration of Zn in raw milk was in the range from 0.6 mg/L to 0.9 mg/L and the highest concentration was 0.984 mg/L.

The maximum allowable limit of Cr in water according to United State Environmental Protection Agency (EPA) is 0.1 mg/L or 100 μ g/L [12]. The Codex Alimentarius Committee considered the level of Cr is 0.05 mg/L or 50 μ g/L for water and health-related certain substances [13]. The Secondary Maximum Contaminant Level of Zn in water according to United State Environmental Protection Agency (EPA) is 5 mg/L [12] and according to Codex Alimentarius the toxicological guidance value of Zn is 0.3-1 mg/kg body weight [14]. In this study, the Cr content in all the samples was found under maximum permeable limit. The maximum concentration of Cr in raw milk (17.062 μ g/L) is below the safe limit for Cr in water and health-related certain substances. The highest concentration of Zn in water (1.024 mg/L) is around the toxicological guidance value of zinc.

In several countries, similar studies were previously reported concerning heavy metals as is the case in the current study. In surface waters in the USA, levels up to 84 μ g/L have been found [15]; in central Canada, surface water concentrations ranged from 0.2 to 44 μ g/L (National Water Quality Data Bank (NAQUADAT), Inland Waters

Directorate, Environment Canada, 1985). In the Rhine, Cr levels are below 10 μ g/L [16], and in 50% of the natural stream waters in India the concentration is below 2 μ g/L [17].

	Concentration in				
Sample no.	Cr (µg/L)	Zn (mg/L)			
sumple no.	$(mean \pm SEM)$	$(\text{mean} \pm \text{SEM})$			
	n=3	n=3			
W-1	1.882 ± 0.0003	0.524 ± 0.0015			
W-2	0.604 ± 0.0050	1.024 ± 0.0013			
W-3	1.033 ± 0.0008	0.832 ± 0.0007			
W-4	0.614 ± 0.0008	ND			
W-5	0.512 ± 0.0006	0.442 ± 0.0010			
W-6	1.098 ± 0.0004	0.015 ± 0.0008			
W-7	2.112 ± 0.0015	0.016 ± 0.0006			
W-8	4.232 ± 0.0030	0.826 ± 0.0012			
W-9	0.947 ± 0.0009	0.429 ± 0.0005			
W-10	0.854 ± 0.0012	ND			
W-11	3.122 ± 0.0012	1.006 ± 0.0006			
W-12	1.342 ± 0.0010	0.085 ± 0.0010			
W-13	5.622 ± 0.0022	ND			
W-14	8.245 ± 0.0045	0.634 ± 0.0008			
W-15	0.896 ± 0.0028	0.084 ± 0.0012			
W-16	ND	0.224 ± 0.0007			
W-17	0.287 ± 0.0017	0.205 ± 0.0005			
W-18	6.438 ± 0.0060	0.064 ± 0.0004			
W-19	3.232 ± 0.0017	0.322 ± 0.0007			
W-20	0.697 ± 0.0004	0.084 ± 0.0004			
W-21	1.872 ± 0.0033	ND			
W-22	9.523 ± 0.0086	0.109 ± 0.0006			
W-23	13.068 ± 0.0098	0.566 ± 0.0010			
W-24	ND	0.342 ± 0.0006			
W-25	1.456 ± 0.0015	0.435 ± 0.0008			

Table 2. Concentration of chromium and zinc in water

ND = Not detectable

In general, the Cr concentration in groundwater is low (<1 μ g/L). In Netherland, a mean concentration of 0.7 μ g/L has been measured, with a maximum of 5 μ g/L [18]. In India, 50% of 1473 water samples from dug wells contained less than 2 μ g/L [17]. In groundwater of the USA, levels up to 50 μ g/L have been reported [15]; in shallow groundwater, median levels of 2–10 μ gL have been found [19]. Most supplies in the USA contain less than 5 μ g/L. In 1986, levels in 17 groundwater supplies and one surface water supply exceeded 50 μ g/L. Approximately 18% of the population of the USA are exposed to drinking-water levels between 2 and 60 μ g/L and <0.1% to levels between 60 and 120 μ g/L [15]. In Netherland, the Cr concentration in 76% of the supplies was below 1 μ g/L and of 98% below 2 μ g/L [20]. A survey of Canadian drinking-water supplies gave an overall median level of Cr as 2 μ g/L, with maxima of 14 μ g/L (raw water) and 9 μ g/L (treated water) [21]. Cocho *et al.* reported that normal cow milk contains 5-15 μ g/L of Cr [22].

98 Chromium and Zinc in Water and Raw Milk

In natural surface waters, the concentration of Zn is usually below 10 μ g/L, and in groundwaters, 10-40 μ g/L [23]. In tap-water, the Zn concentration can be much higher as a result of the leaching of Zn from piping and fittings [24]. The most corrosive waters are those of low pH, high carbon dioxide content, and low mineral salt content. In a Finnish survey, 67% of public water supplies, the median Zn content in water samples taken upstream and downstream of the waterworks was below 20 μ g/L; much higher Zn concentrations were found in tap-water, the highest being 1.1 mg/L [25]. Even higher Zn concentrations (up to 24 mg/L) were reported in a Finnish survey of water from almost 6000 wells [26].

	Concentration			
Sample no.	$Cr (\mu g/L)$	Zn (mg/L)		
Bumple no.	$(mean \pm SEM)$	$(mean \pm SEM)$		
	n=3	n=3		
M-1	6.016 ± 0.0015	0.984 ± 0.0012		
M-2	5.014 ± 0.0008	0.826 ± 0.0041		
M-3	4.625 ± 0.0012	ND		
M-4	7.116 ± 0.0023	0.728 ± 0.0022		
M-5	5.348 ± 0.0022	0.904 ± 0.0034		
M-6	6.316 ± 0.0010	0.711 ± 0.0016		
M-7	10.452 ± 0.0011	0.920 ± 0.0052		
M-8	ND	0.684 ± 0.0046		
M-9	8.254 ± 0.0028	ND		
M-10	12.045 ± 0.0016	0.832 ± 0.0058		
M-11	ND	0.801 ± 0.0046		
M-12	2.854 ± 0.0014	0.588 ± 0.0055		
M-13	8.482 ± 0.0026	0.942 ± 0.0064		
M-14	11.624 ± 0.0058	0.785 ± 0.0048		
M-15	5.033 ± 0.0008	ND		
M-16	6.614 ± 0.0008	0.905 ± 0.0082		
M-17	17.062 ± 0.0086	0.769 ± 0.0085		
M-18	6.342 ± 0.0048	0.824 ± 0.0050		
M-19	3.868 ± 0.0082	0.916 ± 0.0085		
M-20	6.134 ± 0.0030	0.774 ± 0.0065		

Table 3	Concentration	of	Cr	and	Zn	in	raw	milk

ND = Not detectable

Zn concentrations in cow milk ranges from 2–6 mg/L [27]. Pechova *et. al.* reported that Zn level in cow milk is 3.855 ± 0.814 mg/L [28]. Only a few studies on the content of Zn in cow milk have been published to date, and the factors affecting its concentration in milk have not been described thoroughly. Zinc in cow milk primarily binds to casein and, to a small extent, citrate. Almost 90% of Zn binds to casein in mature milk, in contrast to just 60% in the colostrums [29]. In casein, Zn binds primarily to colloid calcium phosphate of casein micelles [30].

4. Conclusion

The purpose of this study was to focus on concentration of selected metals in water and raw milk. In this study, it was found that in both water and raw milk concentrations of Cr and Zn were within the maximum limit. Comparative study of the present work with those of relevant works done in other countries revealed similar levels of metals in water and raw milk. Further studies are necessary to evaluate the contents of "essential" and "toxic" heavy metals on a greater number of samples to confirm the absence of possible toxicological risks.

Acknowledgments

The authors are thankful to the department of Applied Chemistry and Chemical Technology, Faculty of Food Science and Technology, Chittagong Veterinary and Animal Sciences University, Bangladesh and UGC (University Grant Comission) for financial support and necessary facilities.

References

- 1. L. Noel, J. -C Leblanc, and T. Guerin, Food Addit. Contam. **20**, 44 (2003). http://dx.doi.org/10.1080/0265203021000031573
- 2. I. Schonsleben, M. Wilplinger, and W. Pfannhauser, in Determination of the Trace Element Chromium in Various Foodstuffs - *Proc. Euro Food Chem*. (Vienna, 1995) VIII, pp. 665–669.
- 3. R. A. Anderson, Total. Environ. 17, 13 (1981). <u>http://dx.doi.org/10.1016/0048-9697(81)90104-2</u>
- 4. R. Cornelis and B. Wallaeys, Chromium revisited, *in*: Trace Element Analytical Chemistry in Medicine and Biology, eds. P. Brätter et al. (Walter de Gruyter, Berlin, New York, 1984) **3**, pp. 219–233.
- 5. Food and Nutrition Board, Committee on Dietary Allowances, Recommended Dietary Allowances, 1989, 10th edition (Washington DC. National Academy Press, 1989).
- C. J. Mateos, M. V. Aguillar, and M. C. Martinez-Papa, J. Agric. Food Chem. 51, 401 (2003). <u>http://dx.doi.org/10.1021/jf025574x</u>
- 7. R. V. Cauwenbergh, P. Hendrix, H. Robberecht, and H. Deelstra, Zeitschrift Lebensmittel-Untersuchung und Forschung **203**, 203 (1996). <u>http://dx.doi.org/10.1007/BF01192863</u>
- P. C. Onianwa, A. O. Adeyemo, O. E. Idowu, and E.E. Ogabiela, Food Chem. 72, 89 (2001). http://dx.doi.org/10.1016/S0308-8146(00)00214-4
- Z. Gyori, and J. Prokisch, J. Agric. Food Chem. 47, 2751 (1999). http://dx.doi.org/10.1021/jf980781b
- I. Al-Saleh and N. Shinwari, Biolog. Trace Element Res. 83, 91 (2001). http://dx.doi.org/10.1385/BTER:83:1:91
- J. M. Llobet, G. Falcoa, C. Casas, A. Teixidoa, and J. L. Domingo, J. Agric. Food Chem. 51, 838 (2003). <u>http://dx.doi.org/10.1021/jf020734q</u>
- United State Environmental Protection Agency (EPA) 816-F-09-004, (2009).http://water.epa.gov/drink/contaminants/upload/mcl-2.pdf
- 13. Codex Alimentarius Commission, Joint FAO/WHO Food Standards Programme, 31st session (Geneva, switzerland, 2008).
- 14. Codex Alimentarius Commission, Joint FAO/WHO Food Standards Programme, 5th session (The Hague, The Netherlands, 2011).
- 15. Office of Drinking Water, Health Advisory-chromium (EPA, Washington, DC, US, 1987).

100 Chromium and Zinc in Water and Raw Milk

- 16. RIWA, Composition of the Water of the Rhine in 1986 and 1987 (Amsterdam, 1989).
- 17. B. K.Handa, Adv. Environ. Sci. Technol. 20, 189 (1988).
- W. Slooff, Integrated Criteria Document Chromium. Bilthoven (National Institute of Public Health and Environmental Protection, Neatherland, 1989) Report no. 758701002.
- S. J. Deverel and S. P. Millard, Environ. Sci. Technol. 22, 697 (1988). <u>http://dx.doi.org/10.1021/es00171a013</u>
- A. W. Fonds, A. J. V. Eshof, E. Smit, Water Quality in the Netherlands, (National Institute of Public Health and Environmental Protection, Bilthoven, Netherlands, 1987) Report No. 218108004.
- J. C. Méranger, K. S. Subramanian, and C. Chalifoux, Environ. Sci. Technol. 1979, 13, 707. <u>http://dx.doi.org/10.1021/es60154a009</u>
- J. A. Cocho, J. R. Cervilla, M. L. Goldar, and J. R. Fdez-Lorenzo, Biolog. Trace Element Res. 32(1-3), 105 (1992). <u>http://dx.doi.org/10.1007/BF02784593</u>
- C. G. Elinder, L. Friberg, G. F. Nordberg, and V. B. Vouk, Handbook on the Toxicology of Metals, 2nd edition (Amsterdam, Elsevier Science Publishers, 1986) pp. 664-679.
- 24. J. O. Nriagu, Zinc in the environment, Part I, Ecological cycling (John Wiley, New York, 1980).
- 25. L. Hiisvirta, Vatten 1986, 42, 201 (1986).
- 26. P. Lahermo, The Geochemical Atlas of Finland, Part 1, The Hydrogeochemical Mapping of Finland Geological Survey of Finland, Espoo, Finland, 1990).
- S. O. Knowles, N. D. Grace, T. W. Knight, W. C. McNab, and J. Lee, Anim. Feed Sci. Technol. 131, 154 (2006). <u>http://dx.doi.org/10.1016/j.anifeedsci.2006.04.015</u>
- A. Pechova, L. Pavlata, R. Dvorak, and E. Lokajova, Acta Vet. Brno. 77, 523 (2008). <u>http://dx.doi.org/10.2754/avb200877040523</u>
- 29. R. L. Kincaid, J. D. Cronrath, J. Dairy Sci. **75**, 481 (1992). http://dx.doi.org/10.3168/jds.S0022-0302(92)77784-4
- F. V. Silva, G. S. Lopes, J. A. Nobrega, G. B. Souza, and A. R. A. Nogueira, Acta Pt B-Atom Spectr. 56, 1909 (2001). <u>http://dx.doi.org/10.1016/S0584-8547(01)00313-5</u>