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Metal Residues in Process Water Used in Seafood Processing Industries

M. P. Ashraf, M. K. Mukundan, A. G. Gopalakrishna Pillai, K. Ravindran

Central Institute of Fisheries Technology (ICAR), Matsyapuri, Post Office Cochin 682 029, Kerala, India

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Presence of inorganic contaminants in surface water continues to be one of the most important environmental issues in recent years. Certain metallic residues are toxic and dangerous pollutants if it exceed prescribed limits known as maximum admissible concentration (MAC) and are non-biodegradable by any natural phenomena (Florence 1982). They reach in man from various sources via respiration and the continental and marine food chains. Heavy metals accumulated by organisms undergo biochemical cycle in the environment during which they are transformed into various chemical species. Lead, mercury, cadmium, arsenic, chromium, selenium and nickel have occupational hazards and some of them have been linked to cancer and heart disease (Dulka and Risby 1976).

Consequent on the ban imposed on seafood imports by the European Union, Ministry of Commerce, Government of India gave a set of guidelines for approving seafood processing plants in India for export to EU. One of the requirements in this guideline is evaluation of ice and water quality based on 62 parameter test report. Central Institute of Fisheries Technology was authorised for testing and certification of ice and water of seafood processing industries in accordance with EU directive No 80/778/EEC dated 15-7-1980. The study was conducted to evaluate the suitability of water with respect to toxic and undesirable metallic residues from different sources in the east and West Coast of India for use in fish processing plants.

MATERIALS AND METHODS

A total of 46 water samples from 42 fish processing industries were analysed as part of the requirements of the EC council directive No. 80/778/EEC. The water sources were mainly from municipal supplies (50%), borewells (42%) and open wells (8%). Among the 46 samples 13 were from east coast and 33 from west coast of India. The water samples were analysed for metals As, Be, Cd, Cr, Pb, Ni, Sb, Se and V by ICP – AES, Labtam 8410 and Cu, Zn, Fe, Mn, Mn, Co, Ba, Ag by atomic absorption Spectrometer GBC 902. The Hg analyzed by cold vapor technique using Hg analyzer (ECIL 5838). The data were tabulated and

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Correspondence to: M. P. Ashraf

analyzed statistically by two way Anova available in Excel of MS Office software (Microsoft Corpn.).

RESULTS AND DISCUSSION

Of the 17 trace metals analysed, viz. Cu, Zn, Fe, Mn, Co, Ba, Ag, As, Be, Cd, Cr, Pb Hg, Ni, Sb, Se, and V, all the water samples were free from Be, As and V. The absence of Be may be due to the nature of its occurrence as Be(OH), which is insoluble in water. Throughout the world Be in water is reported to be far below the WHO and USEPA (1989) standard. Vanadium have little toxic significance because of their insignificant distribution in nature (Moore 1991)

21.2% of the samples were having either one or a combination of the following residues viz. Cd, Ni, Pb, Ag, Mn and Cu above the maximum admissible limit prescribed by the EU directive (Table 1). Pb and Ni exceeded the limit in two samples each from East Coast whereas Cd in one sample from west coast of India. All the samples, which shows higher levels of Pb were from borewells and in the case of nickel one each from borewell and from municipal supplies. Ag and Mn exceeded in two samples each and were distributed equally in west and east coast. Ag was detected in one sample each from borewell and open well while Mn was detected one each in municipal and borewell. Out of 46 samples one sample from east coast was contaminated with Mn, Cu and Ni together and their levels were respectively 72, 1627 and 72.75 µg/L.

All samples except those described were free from toxic and undesirable metallic residues and their levels were far below the maximum permissible limit. However their distribution was as follows. Among toxic residues lead and nickel have significantly higher values than Hg, Cd, Sb and Se (Table1). Water from east coast recorded higher lead and nickel concentration compared to west coast where Cd is higher. Borewell sources recorded significantly higher Pb and Ni concentration whereas municipal supplies have higher Cd concentration. Pb was detected in 19 samples out of which 2 samples exceeded the limit. Lead contamination in surface water mainly comes from anthropogenic sources (96%), particularly from combustion of leaded fuels, pyrometallurgical non-ferrous metal production and coal combustion. (Nriagu 1989; Urban etal. 1987). Lead in natural waters may be in the form of organic lead complexes originally from the fuel of ever growing automobile population and subsequent break down of tetra ethyl lead. Lead concentration in the reported 19 sample ranges from 0.008 to 185.2 µg/L. Nickel was detected in 22 out of 46 samples and three samples exceeded the limit. Nickel contamination may come from desorption of the metal to natural waters from the earth's crust after the global climatic change or from growing electroplating / steel industries (Ravindran 1999). The nickel concentration in process water ranges from 0 to 90 µg/L of which three contaminated samples showed concentrations as

90.0, 83.0 and 72.75 μg/L. Ajmal and Uddin (1986a,b) detected Ni in well waters of Aligarh to an average level of 0.015 mg/L compared to which the average Ni concentration in process water was 8.96μg/L.

Cadmium was detected in 22 samples out of these one sample exceeded the maximum admissible concentration, 15.5μg/L (Table2). The contamination of Cd in surface water is mainly from the use of phosphatic fertilizers for agricultural operations, which is reported to contain high amounts of Cd (Hutton and Symon 1986). Cd is relatively mobile in aquatic systems existing as Cd^{2+}, $Cd(OH)_2(aq)$, $Cd(OH)_4^{2-}$ and $CdCO_3$ in the form of various other organic and inorganic complexes. Most of the fish processing industries are located in coastal areas and are drawing water mainly from municipal supplies, originating from river sources, and borewells where there is a possibility of saline ingression. Ajmal and Uddin (1986a,b) found that the Cd content was below 5μg/L in the drinking water of the city of Aligarh. Chromium was reported in 7 water samples and in all the samples Cr was below the MAC ranging from 0.001 to 0.01μg/L. Not only Cr^{3+} is classified as hard acid and forms relatively strong complexes with oxygen donor ligands and also clays rapidly adsorb it and the adsorption is increased by increase of pH. Cr^{6+} is highly mobile in aquatic systems even then it is quickly immobilised in the sediments whereby the changes of Cr concentration is considerably reduced (Moore 1991).

Mercury was detected in 7 samples and all of them were within MAC, which ranges from 0.01 to 0.25 μg/L. Hg is extensively used in agricultural and industrial purposes due to its stereo specific properties. Municipal supplies have comparatively higher values (0.014μg/L) since significant portion of mercury is associated with suspended solids, which accounts for a major part of the downstream transport of Hg in rivers. In surface waters Hg exists as Hg^0, Hg^+ and $Hg^{2+}$and in well-aerated waters (Eh>0.5V) Hg^{2+} dominates whereas under reduced condition Hg^0 exist (Moore 1991). Selenium in process water was detected in 6 out of 46 samples, which ranges from 0.054 to 0.2 μg/L. Water from west coast region and open wells recorded comparatively higher values of Se. Selenium is an essential element but is toxic at high concentrations. According to Cutter (1989) dissolved selenium residues in fresh water typically ranges from < 0.1 to 5 μg/L when there are no major anthropogenic input. Se exhibits a complicated chemistry because there are 4 oxidation states viz. –2, 0, +4 and +6. Selenite (SeO_3^{2-}) and selenates (SeO_4^{2-}) are the most dominant species in fresh waters where they typically account for more than 90% of total Se in water column (Cutter 1989) and the latter are stable under alkaline oxidizing condition (Faust and Aly 1981). Selenium binds selectively to iron and aluminium sesquioxides forming relatively stable insoluble complexes. Antimony was present in three samples and their concentrations are 0.01, 0.04 and 0.06 μg/L.

Among undesirable trace elements Cu and Zn recorded significantly higher concentration compared to Fe, Mn, Co, Ba and Ag (Table 3). Cu, Zn and Co concentrations were highest in west coast region while Fe, Mn, Ba and Ag were highest in east coast. Metallic residues of copper, zinc, iron and Ba were highest in borewell sources, Co and Mn in municipal supplies and Ag in open wells. The primary sources of copper in water include domestic wastewater from both central and non centralized sources, use of copper as fungicides in agriculture practices and dumping of sewage sludge. Ajmal and Uddin (1986 a, b) reported that residues of copper in hand pump water sources from the city of Aligarh ranged from 4 to 83 µg/L compared to 1 to 15 µg/L in running water of Aligarh university campus. When oxygen in sediment water interface approaches zero it causes reduction of Mn^{4+} to soluble Mn^{2+}which is then transported upwards in the water column (Moore 1991). Cobalt exists in fresh water as Co^{2+} ions, $CoCO_3$, $Co(OH)_3$, CoS and cyanocobalamine Vit B_{12}. Municipal sources are mainly from rivers which receives wastes from lands, and there is a possibility of contamination with phytoplankton and other organisms that metabolise Vitamin B_{12}.

Copper was detected in 28 out of 46 samples of which one sample was rejected due to the presence of Cu above the permissible limit (1627µg/L) and the remaining samples ranges from 0.25 to 188 µg/L. Copper shows a pronounced tendency to form complexes with organic and inorganic ligands. Being an intermediate receptor between hard and soft acids copper forms relatively insoluble complexes with sulfides. Manganese was detected in 27 samples of which three were above MAC. After Al and Fe, Mn is having highest environmental flux. In aqueous systems Mn^{2+} (manganous) and Mn^{4+}(manganic) states are more important. The manganese concentration ranged from 0 to 392.5 µg/L and the samples showing concentrations above the MAC were 72.75, 77.75 and 392.5 µg/L.

Zinc was present in 37 samples, which ranged from 3.0 to 595 µg/L. Under aerobic condition Zn^{2+} is the predominant species at acidic pH, but is replaced by $Zn(OH)_2$ at pH 8-11and $Zn(OH)_3^-/Zn(OH)_4^{2-}$ at pH >11(Vymazal 1985). Zinc readily binds with many organic ligands particularly in the presence of N or S donor atoms. Stability constant for Zn/humic acid ranges from 2.3 to 5.9 implies the fate of zinc will vary in waterways. Ajmal and Uddin(1986a,b) noted that the concentration of zinc in stagnant water was appreciably higher than that of running water. This was likely due to dissolution of zinc from plumbing materials. Silver is 69th most abundant elements in nature and 37 samples were detected with silver, which ranges from 0.25 to 16.75µg/L. The principal species of Ag in water is Ag^+, occurs in number of forms including AgCl, Ag_2S etc. Sorption is the dominant process controlling the fate of Ag in surface waters. Lin etal (1988) observed that Ag is more or less immobile in the presence of sulphide complexes.

Iron was detected in 18 samples that ranged from 3 to 150 µg/L. The samples from east coast recorded at an average 30 µg/L compared to west coast (14.53 µg/L). Borewell water recorded double the amount of iron

Table 1. Details of water samples exceeded maximum admissible concentration (MAC) as per EEC directive No. 80/778/EEC

Metals exceeded the MAC	Total No of samples	No of samples					Concentration µg/L
		East Coast	West Coast	Municipal Supplies	Bore Well	Open Well	
Pb	2	2	0	0	2	0	152& 185
Ni	2	2	0	1	1	0	83 & 90
Ag	2	1	1	0	1	1	17 &13
Cd	1	0	1	1	0	0	15
Mn	2	1	1	1	1	0	392 & 77
Cu, Mn &Ni	1	0	1	0	1	0	1627, 72 &72 resp.

Table 2. Concentration of toxic metals in µg l^{-1} in processing water.

Metal	Conc. Range µg/L	Average	Average				
			East Coast	West Coast	Municipal Supplies	Bore Well	Open well
Cd	0-15.50	1.135	1.028	1.177	1.402	0.950	0.333
Cr	0- 0.02	0.001	0.001	0.001	0.001	0.002	0.000
Hg	0- 0.25	0.011	0.000	0.016	0.014	0.008	0.020
Ni	0- 90.0	8.966*	16.346	6.059*	7.870*	11.423	1.000
Pb	0-185.2	11.90*	29.86*	4.826*	4.924*	21.713*	0.000
Sb	0-0.06	0.002	0.003	0.002	0.000	0.002	0.020
Se	0-0.20	0.009	0.005	0.0106	0.007	0.003	0.067
LSD at 5% level		6.426	21.021	3.017	4.561	13.66	1.163

*Significant at $\alpha=0.05$

Table 3. Distribution of undesirable metal residues in µg L^{-1} in process water

Metal	Conc. Range µg/L	Average	Average East Coast	West Coast	Municipal Supplies	Bore Well	Open well
Fe	0- 150	19.71	30.000	14.53	13.354	27.330	5.333
Mn	0- 392	15.99	32.423	9.863	27.141	5.838	2.000
Cu	0-1627	60.08*	17.538	68.92*	26.598	94.538	0.000
Zn	0- 595	68.99*	25.519	82.17*	47.848	96.735	2.750
Co	0- 548	20.18	4.119	23.82	34.675	2.114	0.000
Ba	0- 0.30	0.036	0.040	0.031	0.022	0.053	0.000
Ag	0- 16.75	2.287	2.923	2.064	1.543	2.344	7.917
LSD at 5%	-	46.940	.38.582	63.490	35.723	99.817	8.157

*Significant at α=0.05

content than in municipal supplies. The major industrial cities located along the east coast of India may be a reason for high amounts Fe in these samples. Iron is almost always detected in finished drinking water obviously due to it abundance in the earth's crust. Ajmal and Uddin(1986 a,b) detected higher levels of Fe in hand pump water than municipal supplies. In most surface waters Fe^{3+} predominates under aerobic condition. The oxidation-reduction cycles (Moffet and Zika 1987), adsorption of phosphate over iron (Armstrong et al 1987), complexation with sulphates (Moore et al 1988) controls the fate and transport of iron in surface waters. Cobalt was detected in 27 samples and ranges from 0 to 548 µg/L. Except one sample all other samples had values less than 100 µg/L. The average cobalt content in west coast region is 23.82 and that of east coast is 4.12µg/L. Municipal supplies recorded 34.67µg/L and that of borewell is 2.11µg/L. The barium is reported in 13 samples which ranges from 0.006 to 0.3µg/L. The samples from borewell and east coast have recorded moderately higher barium concentration. The environmental chemistry and its biological fate are little known and its principal form in fresh water is Ba^{2+} (American Water Works Association 1988).

Lead in surface waters arises mainly from anthropogenic sources like automobile emission from ever growing automobile population. Cadmium contamination in surface water comes mainly from phosphatic fertilisers used in agricultural operations, which is reflected in municipal water supplies drawing water mainly from river sources. Nickel in surface water may be due to the desorption of the metal to natural waters from the earth's crust after the global climatic change as well as from growing elctroplating / steel industries. Based on the study it was found that out of the total 46 sources only 13.04% of samples were contaminated with toxic metal residues and 7.0% samples with undesirable trace elements. These water sources can be exploited for fish processing after necessary treatments. The study provides strong experimental evidence for compulsory quality assessment of process water as well as drinking water with respect of metallic residues.

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REFERENCES

Ajmal M, Uddin R (1986a) Quality of drinking water in the Aligarh Muslim University Campus, Aligarh, India with respect to heavy metals. Environ Monit Assess 6:195-205.

Ajmal M, Uddin R (1986b) Studies on heavy metals in the ground waters of the City of Aligarh, UP (India). Environ Monit Assess 6:181-194.

Armstrong DE, Hurley JP, Swackhamer DL, Shafer MM. (1987) Cycles of nutrient elements, hydrophobic organic compounds, and metals in Crystal lake. In: Sources and fates of aquatic pollutants. eds R.A. Hites and S.J. Eisenreich, 491-518. American Chemical Society. Washington.

American Water Works Association (1988) A review of solid solution interactions and implications for the control of trace inorganic materials in water treatment. J American Soc Water Works Assoc 80:56-54

Cutter GA (1989) Fresh water systems. In: Ihnat M (ed) Occurrence and distribution of selenium. CRC Press. Boca Raton, FL, p243-262

Dulka JJ, Risby TH (1976) Ultra trace metals in some environmental and biological systems. Anal Chem 48:640

Faust ID, Aly OS (1981) Chemistry of natural waters. Butterworth, Woburn. Mass

Florence TM (1982) Speciation of trace elements in waters. Talenta 29:345-364

Hutton M, Symon C (1986) The quantities of cadmium, lead, mercury and arsenic entering the UK environment from human activities. Sci Total Environ 57:129-150

Lin Y, Bailey GW, Lynch AT (1988) Metal interactions at sulfide mineral surfaces. III. Metal affinities in single and multiple ion adsorption reactions. USEPA, EPA/600/D-88/247, Athens, GA p45

Moffett JW, Zika RG (1987) Reaction kinetics of hydrogen peroxide with copper and iron in seawater. Environ Sci Technol 21:804-810

Moore JW (1991) Inorganic contaminants of surface water. Springer-Verlag, New York

Moore JN, Ficklin WH, Johns C (1988) Partitioning of arsenic and metals in reducing sulfidic sediments. Environ Sci Technol 21:804-810.

Nriagu JO (1989) A global Assessment of natural sources of atmospheric trace metals. Nature 338:47-49

Ravindran K(1999) Quality assessment of water used in seafood processing industries. Presented at National workshop on Development and use of reference material (DUREM 2) organized by Central Pollution Control Board, New Delhi, India 10-12 February 1999

Urban NR, Eisenreich SJ, Gorham E (1987) Al, Fe, Zn and Pb in bog waters of Northeastern North America. Canadian J Fish Aquat Sci 44: 1165-1172

US Environmental Protection Agency (1989) Drinking water health advisories. Rev Environ Contam Toxicol 107:1-184

Vymazal J (1985) Occurrence and chemistry of zinc in fresh waters- its toxicity and bioaccumulation with respect to algae: A review. Part 1: Occurrence and chemistry of zinc in fresh waters. Acta Hydrochim Hydrobiol 13:627-654