Natural Zeolite Mediated Mercury Toxicity in Fish



M. K. Chaurasia and Subodh Kumar Jain* Department of Zoology Dr. H.S. Gour University SAGAR 470003 M.P. (India)

Abstract : There is no truly effective treatment of mercuralism, once it gets in to the body. In the present investigation, efforts have been made to study the role of natural zeolite stilbite for remediation of mercury toxicity. Zeolites are naturally and artificially occurring ion exchangers. Heavy metal viz. mercury takes the position of element present in the molecular sieve of zeolite in the exposure water. Thus, heavy metal becomes unavailable to fish. During the study, experimental fish were exposed to mercuric chloride, mercuric chloride + stilbite and stilbite only. Values of protein contents in the liver, kidney and gills of teleost fish *Heteropneustis fossilis* in various experimental groups indicates that the toxicity of mercury is reduced due to addition of zeolite. It is also observed that exposure of fish to stilbite only increase the protein contents in the fish tissue significantly, suggests that natural zeolites can be used not only for the remediation of metal toxicity, rather also for enhancing protein contents in the fish.

Key words : Stilbite, Mercury, Fish, Protein, Liver, Kidney, Gill.

Introduction :

According to both, the World Health Organization (WHO) and the US Environmental Protection Agency (EPA), consumption of fish and marine mammals, is the single most important source of human exposure to methyl mercury. Methyl mercury is a potent neurotoxin that concentrates at increasingly poisonous levels in the body. It can pass through the placental barrier during pregnancy causing severe neurological damage in developing fetuses. Fish dependent populations are not only exposed to mercury but their exposure is the most highly potent organic form of mercury that damages the central nervous system and can decimate fishing communities for generations.

Mercury poisoning, also known as mercuralism, is the phenomenon of toxicities by contact with mercury. Human activities like the application of agricultural fertilizers and industrial waste water disposal are examples of how humans release mercury directly in to the soil and water. Mercury toxicity is a serious problem since it does not degrade in the environment; therefore its removal is difficult. It is highly toxic particularly to children and the developing foetus, where it interferes with development, particularly the maturation process of the brain. Whatever form, mercury is in elemental, inorganic or organic, it is toxic, and there is no truly effective treatment once it gets into the human body. Chelating therapy may help but there are doubts about the effectiveness.

Fish accumulates mercury directly from food and the surrounding water which gets biomagnified in fish and fish products and constitutes an important part of human diet.

^{*} **Corresponding author :** Subodh Kumar Jain, Phone : +91-7582-237175 **E-mail :** subodhjain@sancharnet.in

Methyl mercury is a well-known human neurotoxin. The accumulation of heavy metals in different organs of fish as a whole in marine as well as freshwater has been described by several workers (Eaton, 1974; Wright, 1976; Pentreath, 1977; Edgren and Notton, 1980). It has been demonstrated that gills and gut could be important transfer route for mercury in insect nymphs (Saouter et al., 1991 and Odin et al., 1995 and 1996). Mercury accumulates in fish tissue is usually in the form of methyl mercury, while the source is usually inorganic mercury (Huckabee et al., 1979). It is that generally agreed mercury concentrations in carnivorous fish are higher than in non carnivorous species (Watras and Huckabee, 1994). Schweiger (1957) investigated the effect of mercury ions on fish and their food organism and suggested a toxic threshold concentration of 0.03 mg/litre for various species tested.

There is no truly effective treatment of mercuralism, once it gets in to the body. In the present investigation, efforts have been made to study the role of natural zeolite stilbite for remediation of mercury toxicity. Zeolites are naturally and artificially occurring ion exchangers. Heavy metal viz. mercury takes the position of element present in the molecular sieve of zeolite in the exposure water. Thus, heavy metal becomes unavailable to fish.

Zeolites are naturally occurring, finegrained materials with pronounced ion exchange properties. Small amount of zeolites increase biomass production and improves nitrogenous efficiency. They promote better plant growth by improving the value of fertilizer. They also improve water quality and filtration in aquaculture. Element present within molecular sieve of zeolite is exchanged with heavy metal of water resource. This result into nonavailability of heavy metal to fish and thus deleterious effects to fish (Jain *et al.*, 1997; Jain, 1999 and Shrivastava *et al.*, 2004). Mercury causes depletion in protein, RNA and glycogen contents (Shakoori *et al.*, 1994). In the contaminated water the sodium of zeolite is exchanged with heavy metal ions in their molecular sieve; at the same time, natural zeolite helps in protein digestion in cattle, sheep and goats (Petkova *et al.*, 1984).

The present study has been planned at assessing the protein contents of liver, kidney and gills of teleost fish *Heteropneustes fossilis* in normal conditions and under the influence of mercuric chloride, mercuric chloride+stilbite and only stilbite. This study explores the possibility of usefulness of natural zeolite stilbite for remediation of mercury toxicity and economic opportunities to fish farmers.

Materials and Methods :

Prior to experimentation, 120 healthy, specimens of teleost fish adult Heteropneustes fossilis (Bloch.) have been acclimatized for two weeks to laboratory conditions. By interpolation method, 96h LC_{50} value for HgCl₂ determined (2 mgl⁻¹ day⁻¹). Fish were divided into four equal groups. Group I served as control while group II, III and IV exposed to sublethal concentration of mercuric chloride, mercuric chloride+stilbite and only stilbite, respectively. During experimental study, sublethal concentration of HgCl₂ and equal amount of stilbite powder sprinkled into exposure water. Fishes were sacrificed after 7, 14, 21, 28 and 35 days of exposure, their liver, kidney and gill tissues were removed

s of protein content (mg/g) in the	e in various treatment groups.
Values	tissue
Table : ¹	fish

Fish	Days of	Control		Treatment groups	
anssn	Exposure		HgCl ₂	HgCl ₂ +Stilbite	Only Stilbite
	7	82.06±1.65	57.87±1.37 P<0.001	59.97±1.40 P<0.001	01 86.90±1.70 P<0.001
	14	82.19±1.65	57.08±1.38 P<0.001	60.34±1.41 P<0.001	01 86.94±1.70 P<0.001
Liver	21	82.29±1.65	58.15±1.39 P<0.001	61.30±1.42 P<0.001	01 86.12±1.70 P<0.001
	28	82.46±1.65	59.02±1.40 P<0.001	62.43±1.44 P<0.001	01 88.48±1.71 P<0.001
	35	82.53±1.65	61.02±1.42 P<0.001	63.42±1.45 P<0.001	01 89.22±1.72 P<0.001
	7	69.84±1.52	47.08±1.25 P<0.001	50.12±1.29 P<0.001	01 71.23±1.54 P<0.001
	14	69.88±1.52	48.05±1.26 P<0.001	51.00±1.30 P<0.001	01 74.51±1.57 P<0.001
Kidney	21	69.89±1.52	49.04±1.27 P<0.001	52.20±1.31 P<0.001	01 75.21±1.58 P<0.001
	28	69.98±1.52	50.15±1.29 P<0.001	53.38±1.33 P<0.001	01 76.42±1.59 P<0.001
	35	69.98±1.52	51.48±1.31 P<0.001	54.72±1.35 P<0.001	01 78.06±1.61 P<0.001
	7	63.93±1.46	44.70±1.22 P<0.001	47.67±1.26 P<0.001	01 64.85±1.47 P<0.001
	14	63.85±1.46	45.68±1.23 P<0.001	48.48±1.27 P<0.001	01 69.50±1.52 P<0.001
Gill	21	63.98±1.46	46.43±1.24 P<0.001	49.81±1.28 P<0.001	01 70.02±1.52 P<0.001
	28	64.00±1.46	47.09±1.25 P<0.001	50.73±1.30 P<0.001	01 71.03±1.53 P<0.001
	35	64.02±1.46	48.81±1.27 P<0.001	51.70±1.31 P<0.001	01 72.06±1.54 P<0.001

and processed for quantitative estimation of protein by Lowery (Folin-Ciocalteau) method. Student's 't' test was applied for statistical evaluation of data.

Results and Discussion :

According to observation table, values of protein contents in liver, kidney and gills are almost similar to those of the initial control fish. Sublethal concentration of mercuric chloride decreases the protein contents significantly. Addition of stilbite to the exposure water improves the values towards normal. When fishes were exposed to stilbite only, protein contents in the tissue increased in comparison to control.

Ram and Sathyanesan (1984) reported that mercuric chloride reduces the protein, lipid and cholesterol contents in various tissues of *Channa punctatus*. Sastry and Gupta (1978) emphasized that over all decrease in protein contents is probably due to enzyme inhibition which plays an important role in protein synthesis. Kidney lysosomes tend to accumulate mercury (Suzuki, 1977). Although Backstrom (1969) reported that despite relatively high level of methyl mercury, fishes do not show any over toxicity.

Dhanapakiam *et al.* (1998) studied the gill of mature *Channa punctatus* exposed to effluent of industrial water in the Cauvery river water for 45 days, revealed deformities and also observed that the secondary lamellae of primary filaments showed hyperplasia. Khangarot (1982) reported that gill epithelium-exhibited varying degrees of hypertrophy, the gap between the basement membrane and the epithelial layer increased in size and the lamellar capillary was dilated due to zinc toxicity in *Puntius sophore*. Liver is the most important target organ for

heavy metal toxicity (Holocombe *et al*, 1976). Decrease in soluble protein, RNA and glycogen contents and hepatic enzymes due to mercury have been reported by Shakoori *et al*. (1994).

There are a number of metal chelators which are used for the remediation of metal toxicity as reported by Graziano et al. (1985); Klavassen (1985); Chislom (1970 & 1971); Friedhein et al. (1978) and Hammond (1971). The element in the molecular sieve of zeolites is exchanged with metal ion thus the concentration of metal is decreased in the exposure water; as a result deleterious effects in the tissues are reduced (Jain, 1999, 2001; Jain and Shrivastava, 2000; Jain et al., 2003). The removal of ammonia from aqueous solution by natural zeolites has been investigated by Aral et al. (1999). Among the various cation exchangers, zeolites are preferred due to its high specificity for heavy metal cations (Sherman, 1978; Semmens and Sayfarth, 1978). In the present study, it can be concluded that natural zeolite stilbite is useful and can be used for attenuation of mercury toxicity and enhancing the protein contents in fish.

References :

- Aral N., Gunay A., Serimoglu O., Cali M. and Debik
 E. (1999) : Ammonia removal from aqueous solution by ion exchange using natural zeolite. *Fres. Environ. Bull.* 8, 344-349.
- Backstrom J. (1969) : Distribution studies of mercuric pesticides in quail and some fresh water fishes. Acta Pharmacol. Toxicol. 27(3), 3-103.
- Chislom U. Jr. (1970) : Treatment of acute lead intoxication choice of chelating agents and supportive therapeutic measurements. *Clin. Toxicol.*, **3**, 527-540.
- Chislom U. Jr. (1971) : Treatment of lead poisoning, Mod. Treat. 8, 593-611.

- Dhanapakiam P., Ramasamy V.K. and Sompooranin (1998) : A study of the histopathological changes in gills of *Channa punctatus* in Cauvery river water. J. Environ. Bio., **19(3)**, 265-269.
- Eaton J. (1974) : Chronic cadmium toxicity to blue gill (Leposmis marco chritus rafinesque) *Trans. Fish. Soc.* **108**, 729-735.
- Edgren M. and Notton M. (1980) : Cadmium uptake by fingerlings of perch (*Pera flueriatits*) studies by CD-115 nm at two different temperatures. *Bull. Env. Contam. Toxicol.* **24**, 644-651.
- Friedhein E., Graziano J.H., Popovac D., Dragaric D. and Kaul B. (1978) : Treatment of lead poisoning by 2,3-dimercaptosuccinic acid. *Lancet*, 2, 1234-1236.
- Graziano J. H., Siris E. S., LoIacono N., Silverberg S.J. and Turgeon L. (1985) : 2, 3-dimercaptosuccinic acid as an antidote for lead intoxication Clin. Pharmacal. *Ther.*, **37**, 431-438.
- Hammond P.B. (1971) : The effect of chelating agents on the tissue distribution and excretion of lead. *Taxicol Appl. Pharmacol.*, **18**, 296-310.
- Holcombe G.W., Benoit D.A., Leonard E.N. and Mckim I.M. (1976) : Long term effects of lead exposure on three generations of brook trout *Salvelinus fonlinalis. J. Fish Res. Board Can.*, 33, 1731-1741.
- Huckabee J.W., Elwood J.W. and Hildebrand S.G. (1979) : In : Accumulation of mercury in freshwater biota. (ed. Nriagu JO) : The biogeochemistry of mercury in the environment. p. 277-302.
- Jain S.K., Raizada A.K., Jain K. and Shrivastava S. (1997) : Protective role of zeolite on lead toxicity in freshwater fish. XII ISEB (21-26 Sept.) at Monopoli, Bari, Italy.
- Jain S.K. (1999) : Protective role of zeolite on short and long term lead toxicity in the teleost fish *Heteropneustes fossilis, Chemosphere.* **39(2)**, 247-251.
- Jain S.K. and Shrivastava S. (2000) : Zeolite mediated lead accumulation in fish tissue. Him. *J. Environ. Zool.*, **14**, 65-68.

- Jain S.K. (2001) : Zeolite influence on remediation of heavy metal toxicity in fish. Polish society of Humic substances, *Grunwaldzka*, **53**, 350-357, Wroclaw, Poland, 77-78.
- Jain S.K. Shrivastava R.K. and Mishra M. (2003) : Chabazite mediated remediation of mercury toxicity in fish tissue: A biochemical study. 16th international symposium on Environmental Biogeochemistry. Aomori prefecture, Japan Page 227.
- Khangarot B.S. (1982) : Histopathological changes in the branchial apparatus of *Puntius sophore* (Hamilton.) subjected to toxic doses of zinc *Acta*. *Hydrobiol.* **93(3)**, 352-358.
- Klavassen C.D. (1985) : Heavy metals and heavy metals antagonist. In: *The Pharmacological basis* of *Therapeutics*, (eds. Gilman, AG, Goddman, LS, Rail, TW, Murad F) Mc Millan, New York, p. 1605-1627.
- Odin M., Ribeyre F. and Boudou A. (1995) : Cadmium and methyl mercury bio- accumulation by nymphs of the burrowing mayfly *Hexaginia rigida* from the water column and sediment. *Environ. Sci. Pollut. Res.* **2**, 145-152.
- Odin M., Ribeyre F. and Boudou A. (1996) : Temperature and pH effects on cadmium and methyl mercury bioaccumulation by nymphs of the burrowing mayfly *Hexaginia rigida*. Arch Environ. Toxicol. **31**, 339-349.
- Pentreath R.J. (1977) : The accumulation of cadmium by the plaice *Pleuronectes plastassa* and the Thornbackary, Roja clavata, L. J. Exp. Mar. Biol. Ecol. **30**, 223-232.
- Petkova E., Venkov T. and Chushkov D. (1984) : Cited in uses of natural zeolites by Alen Dyer paper presented at Symposium held in Manchester, April 1984.
- Ram R.N. and Sathyanesan A.G. (1984) : Mercuric chloride induced changes in the protein, lipid and cholesterol levels of liver and ovary of the fish *Channa punctatus. Environ. Ecol.* 2, 113-117.
- Saouter E. Lemenn R. Boudou A. and Ribeyre F. (1991): Structural and ultra structural analysis of gills and gut of *Hexagenia rigida* nymphs in

relation to contamination mechanisms. *Tissue Cell* **23**, 929-938.

- Sastry K.V. and Gupta P.K. (1978) : Effect of mercuric chloride on digestive system of *Channa punctatus*. A histopathological study. *Environ. Res.* 16, 270-278.
- Schweiger G. (1957) : The toxic action of heavy metals salts on fish and organisms on which fish feed. *Arch. Fisch. Wiss.* **8**, 54-78.
- Semmens M. J. and Sayfarth M. (1978) : The selectivity of clinoptilolite for certain heavy metals. In: Natural zeolites occurrence, properties and use, (eds. L.B. Sand and F.A Mumpton). Pergamon Press, Elmsford, New York, pp. 517-526.
- Shakoori A.R., Iqbal M.J, Mughal A. L. and Ali S.S. (1994) : Biochemical changes induced by inorganic mercury on the blood, liver and muscles of freshwater Chinese grass carp

Ctenopharyngodon idella, J. Ecotoxicol. Environ. Noit. **4(2)**, 081-092.

- Sherman J.D. (1978) : Ion exchange separations with molecular sieve zeolites: AICLE Symposium series, 179(74), 98-116.
- Shrivastava R.K., Mishra M. and Jain S.K. (2004) : Chabazite mediated remediation of mercury toxicity in fish tissues. *Nat. Journ. Life Sc.* 1(1), 29-33.
- Suzuki T. (1977) : Metabolism of mercurial compounds. In: Toxicology of trace element, edited by R.A. Goyer, M.A. Mehlman, 1-40, New York: Joha Wiley and Sons.
- Watras C.J. and Huckabee J.W. (1994) : Mercury pollution, integration and synthesis. Lewis publishers, USA, pp.727.
- Wright D.A. (1976) : Heavy metals in Animals from the north east coast, *Mar. Pol. Bull.* 36-38.