MERCURY CONCENTRATIONS IN CRASSOSTREA MADRASENSIS (PRESTON) FROM COCHIN BACKWATER

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Abstract

In this study, the concentrations of mercury in the oyster *Crassostrea madrasensis* (Preston) and sediment collected from Cochin Backwater were monitored from eight different stations. Mercury was analysed by cold vapour absorption in a mercury analyser. The levels of mercury in the oyster samples ranged from 15 to 48 ppb for smaller size and 7.0 to 37.0 ppb for larger size group, whereas the concentrations of mercury in the sediment samples were higher than in the oyster. The concentrations of mercury in sediment samples ranged from 31 to 144 ppb. However, the concentration of mercury in smaller size oyster was higher than that in the larger size oyster. The concentrations of mercury in the oyster and sediment samples were higher in summer than in monsoon. Generally, higher concentrations were observed in sediment followed by the smaller and larger size oysters during the study period.

INTRODUCTION

TRACE metals as a group among the major pollutants of the aquatic environment are toxic to organisms and human life. In the 1960's, 41 people died and a further 70 became seriously ill after eating fish caught in Japan's Minamata Bay, which had been contaminated by mercury released in industrial wastes. By 1975, mercury poisoning had been confirmed in 798 people and was suspected in another 2800 (WHO & UNEP, 1986). Better knowledge of the present levels of trace metals in the aquatic environment apparently play a major role in pollution studies. Local pollution sources are generally responsible for high levels of metals in Cochin Backwater (Sankaranarayanan et al., 1978; Venugopal et al., 1982; Rajendran and Kurian, 1986: Unnikrishnan Nair and Balakrishnan Nair, 1986).

Cochin is one of the most highly industrialised and densely populated areas in Kerala. Mercury is known to be discharged into Cochin Back-

water by a paper mill and other chemical manufacturing factories situated in and around Cochin. Levels of mercury in sediments and biota have received much more attention than other matrices. Sediments can act as a reservoir for trace metals which can under appropriate conditions such as intensive circulation, mixing of the water mass, salinity, bioactivity, be released from the sediments at a later time into the water. Further, sediments are the vast reservoirs for the storage of mercury and they have the seat of the chemical transformations of the compounds (Craig, 1981). Hence, sediment analysis will provide a good indication of gradients of the contamination provided the mineralogical composition is also taken into consideration. The aquatic organisms can accumulate quite high concentrations of heavy metals which might be harmful to either the animal or its predator, including man.

With this in view, sampling stations have been established in the backwaters and barmouth with some stations set close to urban and industrial areas in order to assess the general pattern of the concentrations of mercury in sediment and the oyster and the existing maximum pollution in the study area.

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MATERIALS AND METHODS

Cochin Backwater is situated on the southwest coast of India $(9^{\circ}50' \text{N}-10^{\circ}\text{N}-76^{\circ}20'\text{E})$. Six major rivers discharge freshwater into the Vembanad Lake. Of these Periyar opens in the northern region (Cochin Backwater), where-Muvattupuzha, Meenachil, Manimala, as Pamba and Achankoil Rivers have their exit in the southern part. Eight sampling stations were selected for the collection of sediment and the oyster Crassostrea madrasensis. Surface sediment samples were collected using van Veen grab from February-September 1986. The oysters were collected from rocks/piles near the stations from March to September 1986. Two different size groups of the oysters (30-50 mm and 100-120 mm) were collected for the analysis of mercury. The samples were analysed immediately after they were brought to the laboratory. The method of AOAC (1975) was followed for the digestion process. Weighed wet sample was taken in the oxidation flask followed by the addition of a cold mixture of concentrated HNO₃ and H₂SO₄ in the ratio of 4:1 (V/V) and heated. When the mixture started to darken a little of the distilate was allowed to run from the reservoir to the flask until the solution ceased to darken and fumes of H_2SO_4 were evolved. The solution was then allowed to cool and the contents and distillate in the reservoir were transferred into

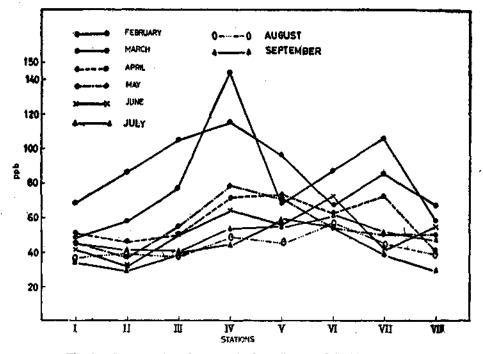
a volumetric flask and made upto 25 ml with redistilled water. Mercury content was analysed using a mercury analyser (ECIL) by cold vapor AA Technique. The pipette analysis method was followed for grain size analysis (Krumbein and Pettijohn, 1938).

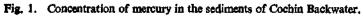
RESULTS

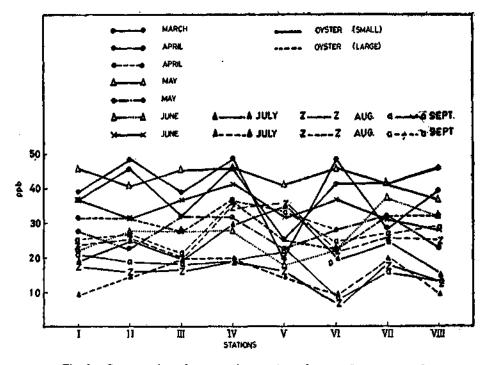
The concentrations of mercury in sediment samples of Cochin Backwater are shown in Fig. 1. The lowest and the highest concentrations of mercury were 31 ppb at stations II and VIII and 144 ppb at station IV respectively. Station IV always showed higher values of mercury during the study period. Higher concentrations of mercury were observed in the Ernakulam Channel (I to IV) than in the barmouth stations, a gradual decrease in concentration of mercury was prevalent from February to July representing the pre-monsoon and monsoon periods.

The sediments of the study area have variable grain size composition. According to the lithological classification of Shepard (1954), silty clay are predominantly prevailing in the sediments of all stations, sand-silt-clay, clayey silts, sandy silts and silts followed with decreasing frequency. Sand and silty sand are also present in negligible quantity.

The ranges of concentrations of mercury in the oyster of Cochin Backwater were from 15 to 48 ppb in small size group and 7 to 37 ppb in larger size group (Fig. 2). The smaller size oysters always exhibited higher concentrations of mercury than the larger ones. At all the stations, minimum concentrations of mercury were observed for both the sizes in July. As observed in the sediments, the concentrations of mercury in oysters also decreased from March to July. However, in the study area, the decrease and increase in concentrations of mercury were intermittent. It is interesting









to note that the mean concentrations of mercury in sediments were higher, followed by smaller and larger size oysters (Fig. 3),

DISCUSSION

Cochin Backwater is considered a polluted area owing to the discharging of the wastes from urban areas and industries and a point source of mercury input from the effluents of a chemical complex situated on the banks of the River Periyar. There is also a known discharge from a paper mill containing mercury. The results obtained in the present study showed the increased values of mercury at Station IV (Fig. 1) which seems to be the most locally polluted area of Cochin Backwater. for Vellar Estuary (0.18-0.58 ppm); backwater (0, 13-0.48 ppm) and mangrove (0.18-0.43 ppm) by Kumaraguru (1980); for Kastela Bay (0.01-8.51 ppm) by Stegnar et al. (1980) and for the Gulf of Venice (0,10-7.55 ppm) by Angela et al. (1980). When compared to the higher values reported for Gknnekleirfjorden, Norway (90-350 ppm) by Skei (1978); for Agano River sediments (150 ppm) and Minamata Bay, Japan (630 ppm) by Matida and Kumada (1969), we could draw a conclusion that in the mercury concentrations in Cochin Backwater are far safer and could be considered as relatively unpolluted, but only contaminated. The low values observed in the present study could be due to continuous agitation of the surface sediments caused by frequent transport

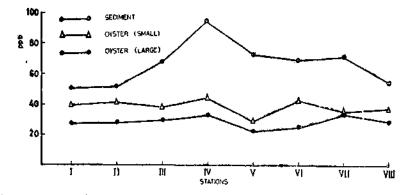


Fig. 3. Mean concentrations of mercury in sediments and two sizes of the oyster C. madrasensis.

The concentrations of mercury in sediment ranged from 31 to 144 ppb in Cochin Backwater. No published results in this region regarding contamination are available for comparison. However, the observed mercury values in sediments were lower than the values reported for Fyris River mouth (2.4 ppm) by Axelesson and Hakkanson (1972); for Ottawa and Ridean River sediments (0.28 and 0.2 ppm respectively) by Oliver (1973), for Lattave Estuary (0.32 ppm) by Cranston (1976); for Vellar Estuary (100-330 ppb) and backwater (125-275 ppb) by Kumaraguru *et al.* (1977); of ships, fishing vessels and other boats in the backwater.

The concentrations of mercury in the backwater showed no marked difference among the stations of the study area. However, the stations III and IV showed similar patterns in fluctuations of concentrations of mercury. Even between these two stations, the station IV showed pronounced variation in March (Fig. 1). In the barmouth stations, the magnitude of fluctuations are not high. The influence of rivers could be one of the reasons for higher concentrations of mercury at stations III and IV. Towards Station VII, the concentration decreased which could be due to precipitation and flocculation of mercury happening at different places of the backwater. However, during summer months, comparatively higher concentrations of mercury were observed. It is known that significant changes occur as a result of the salinity difference and sedimentation plays a major role in removing much of the pollutant load to the sediment (HMSO, 1977).

From the results of the present study, it could be seen that fine sediments are associated with higher concentrations of mercury. The sand predominantly occurring at stations VI and VII showed comparatively lower values (Fig. 1). This is in confirmity with the results obtained for the Gulf of Venice by Angela *et al.* (1980); for Kastela Bay by Stegnar *et al.* (1980) and for Evoikos Gulf sediments by Angelidis *et al.* (1980). The grain size of these sediments is influenced by the nature and of the materials transported by various rivers.

The concentrations of mercury in the oyster of Cochin Backwater varied from 15 to 48 ppb for smaller size and 7 to 37 ppb for larger size (Fig. 2). As observed in sediment samples, the values monitored for oyster were lower than the values reported for *Mytilus edulis* (0.434 ppm), *Cardium edule* 60.8 ppm) by Raymont (1972), for *Crassostree virginica* from the upper Delaware Bay (0.28 ppm) by Cunnigham and Trip (1973), for *Cardium edule* (0.08-0.14 ppm) and *Crassostrea gigas* (0.09-0.10 ppm) of English waters by HMSO (1977) and for *C. madrasensis* from Vellar Estuary (0.32-0.72 ppm) by Kumaraguru (1980).

The distribution pattern of mercury in oysters of the two sizes in eight stations during the present study showed that the variations are not great. However, the difference in concentrations of mercury could be due to the metal availability, physico-chemical factors, size and physiological conditions of the organisms. In the present study, pronounced difference in mercury concentrations between two size groups are obvious (Fig. 3). That the rate of accumulation decreased with increase in size of the animals *C. madrasensis* and *M. casta* was observed by Kumaraguru (1980) for Vellar Estuary. He has also suggested that accumulation of metal would be in progress even as the animal grows older and older, but the rate of accumulation would be diminished.

Phillips (1978) has suggested that the seasonal variations may be due to the variations of the wet mass of organism with season. During the present study period, comparatively low values were observed in monsoon than that in summer (Fig. 2). Sankaranarayanan et al. (1978) monitored low values of metals during May-December which was due to fresh water influx that reduced the salinity. This reduction in salinity reduced the availability of metal ions. Changes in salinity affects the basic physiological functions like filteration and feeding of bivalves. Kendall (1978) was not able to demonstrate any significant difference in mercury levels in benthic invertebrates along the salinity gradient. Denton and Burdon Jones (1981) opined that the salinity gradient might influence the concentration of mercury. Further, as observed by Riisgard (1984) for mussels from Limfjord, in the present study also, a decrease in mercury level towards barmouth was observed. Unnikrishnan Nair and Balakrishnan Nair (1986) observed high values of mercury in oysters collected near the barmouth during October-March and this period is the breeding season of the oyster. The major quantity of metals including mercury taken into the organic system is tucked away in selected sites during breeding season (Unnikrishnan Nair and Balakrishnan Nair, 1986). The uptake of metal from sediment by oyster has a close relation between the metal concentration in sediments and in oyster. Ayling (1974) suggested that this route is important and so concentration

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factor for metals in oyster should be based on and land drainages in deciding the variations the mercury level in the sediments than in ambient water. Water movement and frequent transport of ships and fishing vessels set the fine materials in suspension and brings it up within the reach of bivalves.

It is clear from the differences in the mean concentration of mercury (Fig. 3) in sediment and oyster (two sizes) at the stations that the chief role is played by Industrial discharges

in the concentrations of metal in the sediments and ovster.

Since the oyster accumulates quite high concentrations of metals it might be harmful to the animal as well as its predator including man. Hence it is imperative that concentrations of pollutants like mercury be kept under observation to ensure that unacceptable increase do not occur.

REFERENCES

ANGELA, G., R. DONAZZOLO, O. HIEKEMERLIN, L. MENEGAZZO VITTURI, A. A. ORIO, D. PAVONI, G. PERIN AND S. RABITTI 1980. Heavy metal contents in bottom sediments from the Gulf of Venice and comparisons on their nature, Ves Journees Etud. Pollutions : pp. 399-406.

ANGELIDIS, M., A. P. GRIMANIS, D. ZAFIROPOULOS AND M. VASSILAKI-GRIMANI 1980. Trace metals in the sediments of Evoikos Gulf, Greece. *Ibid.*, pp. 413-418.

1975. Official methods of analysis. Asso-AOAC. ciation of official Analytical Chemist. 12 ed.

AYLING, G. M. 1974. Uptake of cadmium, zinc, copper, lead and chromium in the Pacific oyster Crassos-trea gigas. Water Res., 8: 729-738.

AXELSSON, V. AND L. HAKANSON 1972. The relation between mercury distribution and sedimentological environment in Lake Ekoln. Report No. 14. Uppsala University, Sweden.

CRAIG, P. 1981. Biomethylation. Pollution amplified. New Scientist, 90: 694-697.

CRAIG, P. J. AND S. F. MARTON 1983. Total mercury methyl mercury and sulfide in River Carron sediments. *Mac. Pollut. Bull.*, 14: 408-411.

CRANSTON, R. E. 1976. Accumulation and distribution of total mercury in estuarine sediments. Estuar. Coastal Mar. Sci., 4: 695-700.

CUNNINGHAM, P. A. AND M. R. TRIPP 1973, Accu mulation and depuration of mercury in the Americanoyster Crassostrea virginica. Mar. Biol., 20: 14-19.

DENTON, G. R. W. AND C. BURDON-JONEA 1981. Influence of temperature and salinity on the uptake, distribution and depuration of Hg, Cd and Pb by black-slip oyster Saccostrea echinata. Ibid., 64: 317-326. 1981.

HMSO, 1977. Monitoring the marine environ-ment of the United Kingdom. Pollution Report, 2: 82 pp.

KENDALL, D. R. 1978. The role of macrobenthic organisms in Hg, Cd, Cu and Zn transfers in Georgia salt marsh ecosystem. Ph.D. Thesis, Emory University.

KRUMBEIN, W. C. AND P. J. PETTUOHN 1938. Manual of Sedimentary petrography. Appleton Centuary—Crafts, New York, 549 pp.

KUMARAGURU, A. K. 1980. Studies on the chemical and biological transport of heavy metal pollutants of copper, zinc, mercury in Vellar Estuary and the toxicity of these pollutants to some estuarine and shellfish. Ph. D. Thesis, Annamalai University, 308 pp.

, D. SELVI AND V. K. VENUGOPALAN 1977. Mercury in Vellar Estuary and its toxicity to oyster. Proc. Symp. Environ. Biol., pp. 253-264.

MATIDA, Y. AND H. KUMADA 1969. Distribution of mercury in water, bottom mud and aquatic organisms in Japan. Bull., 19 : Freshwater Fish. Res. Lab., Japan.

OLIVER, P. G. 1973. Heavy metal levels of Ottawa and Rideau River sediments. Environ. Sci. Technol., 9:135-137.

PHILLIPS, D. J. H. 1977. Use of biological indicator organism to monitor to marine and estuarine environment - A Review. Environ, Pollut., pp. 281-317.

RAFENDRAN, N. AND C. V. KURIAN 1986, Crasso-strea (Preston) — Indicator of metal pollution in Cochin Backwaters. Proc. National Seminar on Mussel Watch 1: 120-131.

RAYMONT, J. F. G. 1972. Some aspects of pollu-tion in Southampton water, Proc. Roy. Soc. London., 180:451-468.

RIISGARD, H. V. 1984. Mercury pollution in the water around Harboore Tange and Limfjord, Denmark. Mar. Pollut. Bull., 15: 129-133.

SANKARANARAYANAN, V. N., K. S. PURUSHAN AND T. S. S. RAO 1978. Concentrations of some heavy metals in the oyster *Crassostrea madrasensis* (Preston) from the Cochin region. *Indian J. Mar. Sci.*, 7:130-131.

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SHEPARD, F. P. 1954. Nomenclature based on sand-silt-clay ratios. J. Sedim. Petrol., 24: 151-158.

SKEI, J. M. 1978. Serious mercury contamination of sediments in a Norwegian semi-enclosed bay. *Mar. Pollut. Bull.*, 9: 191-193.

STEGNAR, P., I. VUKADIN, P. SMODIS, A. VAKSELJ AND A. PROBENC 1980. Trace elements in sediment and organisms from Kastela Bay. Ves Journees Etud, Pollutions., pp. 595-600. UNNIKRISHNAN NAIR, N. AND N. BALAKRISHNAN NAIR 1986. Seasonality of trace metals in *Crassostrea* madrasensis (Preston) inhabiting the Cochin Backwaters. Proc. National Seminar on Mussel Watch, 1: 6-14.

VENUGOPAL, P. K., SARALADEVI, K. N. RAMANI AND R. V. UNNITHAN 1982. Trace metal levels in the sediments of the Cochin Backwaters. Mahassagar-Bull. Natl. Inst. Oceanogr., 15: 205-214.

WHO AND UNEP, 1986. Pollution and Health, 22 pp.