OPEN ACCESS Freely available online

ISSN: 2155-9546
Journal of Aquaculture Research & Development

Research Article

Bioaccumulation of Minerals and Heavy Metals in *Crassostrea madrasensis* (Oyster) from Vellar Estuary, Parangipettai Southeast Coast of Tamilnadu

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ABSTRACT

Heavy metal pollution from human activities has emerged as a global threat, with many metals released untreated into aquatic zones where they accumulate in organisms. In India's Vellar estuary, the oyster *Crassostrea madrasensis* provides food and income for local communities, while filtering water. This study analyzed oyster tissue to determine levels of five heavy metals and five essential minerals, assessing potential human health risks and the estuary's ecosystem health. Atomic absorption spectroscopy revealed manganese at 11.0121 µg/L, 10 times higher than lead. Calcium was most abundant among minerals at 371.7 µg/L. All metals and minerals were within safe levels for human consumption according to UN Food and Agriculture Organization standards. However, as a breeding ground for commercially valuable species, periodic monitoring of accumulation is recommended to safeguard ecosystem and community health. Though currently deemed safe, heavy metals persist and accumulate, posing eventual health threats. This biomarker species indicates water quality and, through bioaccumulation and biomagnification up the food chain, can forewarn of risks before dangerous contamination levels are reached. Regular testing can detect rising trends to trigger preventative measures, rather than reaction after irreversible impacts occur. Thereby, oysters help sustain environmental and economic vitality.

Keywords: Heavy metals, Minerals, *Crassostrea madrasensis*, Spectroscopy, Bio accumulation

INTRODUCTION

Heavy metals occur in nature and are essential to life, but they can become toxic through accumulation. In recent years heavy metals are agglomerating in the biosphere through industrialization and urbanization [1]. Anthropogenic activities like mining, smelting procedure, steel industry, iron industry and agriculture as well as domestic activities are also a part of the polluting environment [2]. Industries like the chemical industry, paper industry, storage battery factories and companies releasing hydrocarbon and detergents are the main source of heavy metals [3]. Improper metal disposal gets ingested into the living tissues through drinking/eating/breathing [4]. Direct disposal of the effluents into the ocean has become a major concern as they cause the sediment to be polluted by heavy metals [5]. Recent studies show that the environment including both sediments bed and water columns come across heavy metal's contamination [6-8]. High level of metals are being brought into surface waters through the strong upwelling and bottom sediments by the downwelling process [9-12]. Sediments provide habitats for many marine organisms in turn in which the polluted habitat affect the entire ecosystem [13]. The marine benthic organisms feed on these sediments which get accumulated in them and eventually leads to bio availability [14-19]. However, heavy metals cannot fix in sediment forever. This sediment acts as both carriers and potential sources for

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Received: 08-Dec-2023, Manuscript No. JARD-23-24281; **Editor assigned:** 11-Dec-2023, Pre QC No. JARD-23-24281(PQ); **Reviewed:** 25-Dec-2023, QC No JARD-23-24281; **Revised:** 01-Jan-2024, Manuscript No. JARD-23-24281(R); **Published:** 08-Jan-2024, DOI: 10.35248/2155-9546.24.15.830

Citation: Justin AA, Sangamesh U, Ananthan G (2024) Bioaccumulation of Minerals and Heavy Metals in *Crassostrea madrasensis* (Oyster) from Vellar Estuary, Parangipettai Southeast Coast of Tamilnadu. J Aquac Res Dev. 15:830.

metals in the aquatic environment [20]. In recent years, estuarine sediment contamination is receiving an increasing attention from the scientific community, as it is a major source of healthy ecosystem [21]. A Biotic community which feeds on these sediments have higher levels of metal content in their digestive organs like the gut and stomach [22]. Accumulation or toxicity of cationic metals such as cadmium, lead, nickel, zinc, and copper to benthic organisms has been correlated with pore water concentrations of the metals [23-29]. Oyster is a filter feeder, cultured in estuaries and offshore areas and occupies an important part in global shellfish consumption [30,31]. They feed by extracting algae and various types of food particles like suspended materials, sediments, detritus, microorganisms, etc., by filtering massive amounts of seawater through their gills [32]. Restoration of oyster reefs in bays and estuaries has been confirmed that oysters can absorb up to 10 times more nitrogen and mineralization of phosphorous and living oysters and their shells as sites of nitrification and denitrification [33-35]. Sediment can release trace metals into the overlying seawater and be absorbed by algae and further absorbed by oysters from the contaminated seawater and food they have ingested [36]. Consequently, the bioaccumulation of trace metals may cause various toxic effects on oysters, namely, toxicity associated with growth, development, health, etc. [37]. On behavioural response of oysters, researchers have started a monitoring study called Asia Pacific Mussel Watch Program (APMW), which aims to monitor marine pollution [38]. A recent study has been proved that oysters can be used as an ecological tool to trace heavy metals [39]. Therefore, they are called as bio marker because they can accumulate heavy metals and indicate the heavy metal pollution level [40]. As a result, of bioaccumulation the most common exposure route to the metal for the human population is consumption of large piscivorous fish, sources of which are the productive coastal, estuarine, and shallow continental shelf fisheries [41]. They cause a serious threat to human health, natural ecosystems, and living organisms because of their toxicity and bioaccumulation characteristics [42,43]. This negative effect is one of the evident by not only affecting the aquatic species diversity but also exposing human beings to these xenobiotics directly through the food chain, with potential danger to human health [44]. The present study was aimed to determine the concentration of heavy metals like Ni, Pb, Cr, Cd, Mn in water, sediment and *Crassostrea madrasensis* from the Vellar estuary [44-50].

MATERIALS AND METHODS

Study area

Vellar estuary is bar-build estuary located in Parangipettai, Cuddalore district, Southeast coast of India, latitude 10° 06'E and longitude 79°27' N. Vellar river originates from Kalrayan hills and travels 480 km runs through Salem, Cuddalore and Parangipettai (formerly known as Porto Novo) where its open into the Bay of Bengal. Vellar estuary joins with Coleroon estuary and forms a complex Killai backwater estuarine system that supports Pichavaram mangroves [51-55]. Length of the estuary is 16 km, width of the estuary mouth is 600 m, Average depth of the estuary is 2.5 m, and the nature substratum of sand is made of clay, silt and a mixture of both during the period of observation. Coastal currents are tidal, and wind driven towards the north during March-September and towards the south during November-January. Waves are predominantly from southeast (100-1601) during southwest monsoon (June-September) and northeast (80-901) during northeast monsoon (November-February) [56]. Biotic community of the estuary comprises of Bivalves, Gastropods, and polychaetes, etc. [57-61].

Sample collection

The Oyster *Crassostrea madrasensis* is widely distributed all over the Indian backwater ecosystem. Oyster samples were collected during the lowest low tide time at 0.5 m depth by hands-on training method in January 2021, post-monsoon season. The size of the oyster was approximately about 2.5 cm to 5 cm in length. The oysters were collected in zip-lock covers and transferred to the laboratory.

Moisture content

Tsuyoshi Yoda method was followed to calculate the moisture content [62]. Weight of the samples measured in grams. Samples were kept in a Muffle furnace at 625°C for 6 hrs, weighing the sample mass up to fourth decimal point. Water content of the sample is determined by the following equation.

$$\text{Moisture content}(\%) = 100 - 100 \times \frac{\text{Dried mass}}{\text{Initial mass}}$$

Extraction of heavy metals and mineral's from oyster

Minerals and heavy metals were extracted by using Jayaprabha method [63]. Homogenize the sample and make it to a powder form. Add 1 gm of the powdered sample with 20 ml of nitric acid and leave it for overnight digestion. Add 10 ml of perchloric acid and nitric acid in a 4:1 ratio and make the solution complete dry by heating it at 100°C. Dilute the residue with a 4:1 ratio of de-ionized water and nitric acid then filtered it with No 1 Whatman filter paper.

Extraction of heavy metals from sediment

Heavy metals from sediments were extracted by using Moon [64]. Sediment samples were collected from the same place where oyster was collected. A dry and clean Peterson grab was used to collect the sediments. Prepare the sample sediment to dry circumstance with the help of hot plate. Grind the dry sediments using Pestel motor, take 1 gm of fine powdered sample add 20 ml of nitric acid and leave it for overnight digestion. Evaporate the solution and add another 20 ml of Nitric acid followed by Perchloric acid in a ratio of in 4:1 and make the solution into complete dryness by heating it under 100˚C in hotplate. Dilute the residue with 10%, 10 ml Nitric acid, filter the solution with No 1. Whatman paper.

Extraction of heavy metals from water

Robert method was used to extract the heavy metals from water

[65]. Water samples were collected from the bottom in Polypropylene Erlenmeyer Flask from the same place the animal and sediments were collected. Adjust pH of water to 4 ± 1 by adding 5% Nitric acid drop by drop. Divide one liter of the sample into four equal aliquots (250 ml each) and transfer them into a separate funnel. Add 2.5 ml of the APDC solution and 10 ml of MIBK solution into the sample water. Shake the separatory funnel for 5 mins and leave it for 10 mins without any disturbance, drain off the aqueous layer and collect organic layer. Add another 5 ml of MIBK solution shake it and leave it for 5 mins and collect the solution. Combine the organic layers and add 1 ml of 50% nitric acid into the solution shake vigorously to decompose the dithiocarbonate. Add two aliquots of 1 ml distilled water, allow the phase to separate and collect the aqueous layer make up to 25 ml. Metals were observed by Atomic Absorption Spectroscopy (AAS).

RESULTS

Moisture content

The Amount of moisture content present in the oyster, *Crassostrea madrasensis* is 88%, during post monsoon season (January to march).

Amount of heavy metals present in *Crassostrea madrasensis*

The concentration of heavy metals (Cd, Mn, Pb, Ni, Cr) present in the *C. madrasensis* is shown in Table 1 and Figure 1. The average concentration of metals during the January period is 4.67 µg/l. Manganese has a higher amount of metal concentration than remaining metals i.e., 11.121 µg/l, and Lead has the lower concentration i.e., 0.2149 µg/l. Sequential order of metal concentration in *Crassostrea madrasensis* is Mn(11.121)>Cr(10.908)>Ni(0.8472)>Cd(0.2848)>Pb(0.2149)was observed.

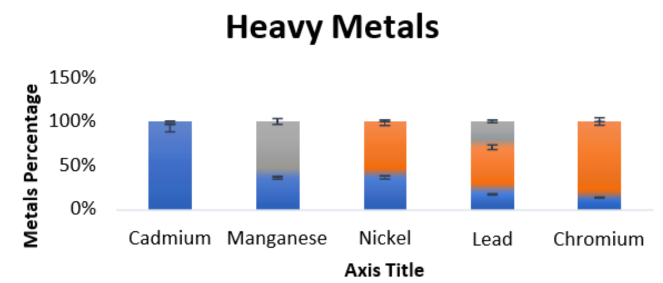

Figure 1: Show heavy metals concentration **Note:** (■)-Concentration; (■)-Heavy metals of *C. madrasensis*; (■)-Heavy metals Water.

Amount of minerals present in Crassostrea madrasensis: The concentration of Minerals (Zn, Ca, Mg, Fe, Cu) was present in the sample Crassostrea madrasensis is shown in Table 2 and Figure 2. The average concentration of metals during the January period is 130.03 µg/l to 4.3023 µg/l. Calcium has present in higher (371.7 µg/l) concentration than remaining metals and Copper has the lowest concentration (4.3023 µg/l). Minerals were observed the following order of Ca(371.7)>Mg(124.2)> Fe(112.79)>Zn(37.16) and>Cu(4.3023).

S.no.	Cadmium	Manganese	Nickel	Lead	Chromium
Heavy metals in Oyster	0.2848 µg/l	11.121 µg/l	0.8472 µg/l	0.2149 µg/l	10.908 µg/l
Heavy metals in Sediments	0.0119 µg/l	0.1009 µg/l	1.4166 µg/l	0.6555 µg/l	66.49 µg/l
Heavy metals in Water	0.01 µg/l	19.246 µg/l	0.0341 µg/l	0.3596 µg/l	0.0976 µg/l

Table 1: Show heavy metal concentrations.

Minerals	Concentration
Zinc	37.16 µg/l
Calcium	371.7 µg/l
Magnesium	124.2 µg/l
Iron	112.79 µg/l
Copper	4.3023 µg/l

Table 2: Show minerals concentrations.

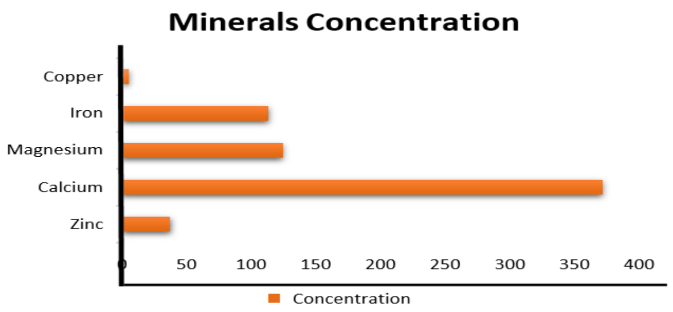

Figure 2: Show heavy minerals concentration of oyster. **Note:** (■)-Concentration

Amount of heavy metals present in Sediment sample: Concentration of heavy metals such as Cd, Mn, Pb, Ni, and Cr in the sediments are showed in Figure 1 and Table 1. Average concentration of metals during the January period is 13.73498 µg/l. Chromium have highest value of 66.49 µg/l and Cadmium have least value of 0.0119 µg/l were observed using Atomic Absorption Spectroscopy(AAS). Based on metals concentration followed by Sequence order Cr(66.49)>Pb 1.4166)>Ni(0.6555)>Mn(0.1009)>Cd(0.0119) was observed.

Amount of heavy metals present in water sample: Concentrations of metals measured in the water samples are presented in Figure 1 and table 1. The metal concentration of (Cd, Mn, Pb, Ni, and Cr) in the estuarine water varied. Metals were observed in the order of Mn(19.24)>Pb(0.341)>Cr (0.0976)>Ni(0.03596)>Cd(0.01). Manganese has a higher amount of metal concentration than remaining metals i.e., 19.246 mg/l and Cadmium has the least value of 0.01 µg/l observed using Atomic Absorption Spectroscopy (AAS).

DISCUSSION

In this study the level of anthropogenic contamination of heavy metals like Cd, Mn, Pb, Ni and Cr in seawater, sediments, soft tissue of *Crassostrea madrasensis* and natural deposition of minerals like Zn, Ca, Mg, Fe and Cu were examined during the post monsoon season in the speciemen *C. madrasensis* from the inter-tidal zone of vellar estuary. Every day they purify 50 gallons of water and make the environment eco-friendly to other organisms likes sponges, hydroids, bryozoans, barnacles, mussels, limpets, clams etc. Mussel watch programs were initiated to monitor environmental conditions and they purify water [66]. In the present study the moisture content of the oyster is approximately 88% which is similar to the study conducted by Hosoi M, et al [67]. The distribution of heavy metals in both sediments and water samples exhibited comparative patterns. The result indicates that the accumulation of heavy metals is higher t in the sediment sample rather than in water sample. This can be clarified that the sediment acts as a reservoir for the contaminant and dead matter descending from the ecosystem above. The highest value for the metals in the Vellar estuary was recorded in the pre monsoon period and lowest one recorded in the post monsoon this indicates the relatively high concentration of heavy metals during monsoon season coincide principally with decreasing rate of organic matter decomposition due to the low temperature was noticed in sediments [68]. A comparison of heavy metals in the present study value resemblance with concentration of heavy metals in sediments reported by Magesh NS et al, [69]. Pb and Mn concentration is much lesser when compared to Raj SM et al, but Mn, Pb, and Ni concentration be situated in a similar range in sediments reported by Magesh NS [69,70]. Cd level in sediments sample found in this study are higher than the Sundaray and it is worth mentioning here that cadmium is non-essential element for animals and human beings. Sediment from Sundarban wetland ecosystem display Cd level closer to Vellar ecosystem [71,72]. In water column Nesakumari et al, proved that the presence of cadmium in pulicat lake. During the post monsoon period concentration of Cd is 0.38 mg/l [73]. Kottuli wetland sediments were analysed by Harikumar PS et al, absorbed chromium mean value which is 1.71 mg/kg, but the present study shows 66.49 µg/l [74]. It is significant to mention that Cr is the only metal to have the highest sediment value observed during this study period. Subsequently, Kumar V et al, shows 2.01 mg/l of chromium in water but velar estuary have 0.0976 µg/l which shows that chromium concentration is highly accumulated in the sediment rather than in water [75]. To, comparing the present results with the Adyar estuary reported by Rubalingeswari N et al [76]. The values of Cr, Pb, Mn and Ni are lower most in concentration than the Adyar estuary because Vellar river channel are non-polluted channel due to this reason it's showing lower sediment metal concentration. Kamalakannan et al, metal investigation report from Pulicat Lake shows 8.32 mg/l of lead mean value were observed in post monsoon period, which represent the amount of metal absorption in sediment getting increased frequently [77]. The bioaccumulation of essential mineral like Zn, Cu, Mg, Fe, and Ca concentration from the *C. madrasensis* were ordered by Ca was followed by Mg>Fe>Zn>Cu. Ca is an essential nutrients help form a shell for gastropods and to get bone hardness for other animals. The present study in Vellar indicates higher concentration magnesium (124.2 µg/l) and copper (4.3023 µg/l) than the earlier study. This might be the result of anthropogenic interruption recorded the enrichment of copper (1.773 ± 0.03 µg g-1) and magnesium (0.976 ± 0.025 µg g-1) [78]. Periyasamy N et al, studied calcium level from bivalves (315.2 mg/g) [79]. But in the present study it was recorded to 371.7 µg/l. Fe and Zn concentration is lesser but higher Cu values were detected by Chinnadurai S et al, Laxmi Priya S et al [80,81]. Shanmugam N et al determined the bioaccumulation of minerals such as Magnesium, Iron, Zinc and Copper concentration in body parts [82]. The bivalves take up metals from solution and organic matters, but oysters *Crassostrea rhizophorae* are particularly recommended as bio-monitors given their strong accumulation patterns for many metals [78]. Table 2 compares the data collected in this study with similar data for species of the genus *Crassostrea* from Brazil [83]. They reported that the values of zinc level from the tissue were found to be 307 mg g-1 in tissue. The values were relatively lower than the present study. Oyster from Parangipettai zone, are used as a food source by the local communities. The order of heavy metals concentration in seawater and animal *C. madrasensis* from the velar estuary was specimen<water<sediment, respectively. It can be concluded that marine organisms especially

Oysters are good indicator for both essential and toxic metals pollution. In oyster metals can be uptake by different type of mechanisms and this mechanism may get affected by various physiological and environmental factors [84,85]. Concentration of heavy metals and minerals levels in C. *madrasensis* at vellar estuary may be related to one or both of the following mechanism: 1) the availability of different metal to the animal varies with different seasonal period and the animal involves different uptakes and retention mechanism for the same metal at different season. Therefore, the order of metal accumulation in the animal where Mn was followed by Cr>Ni>Cd>Pb. This order may be due to variation in the level of discharged metals in the estuary and the chemical changes of metals before being taken up by the inspected animal. In concordance with the present study, similar findings have been reported by various authors like Shulkin VM et al. [86-89]. The heavy metal accumulation in the Oyster has been analyzed and it was reported that the concentration of the cadmium, is comparatively higher than that of the present study in vellar estuary. Similar metal like Cd, Pb and Mn concentrations were reported from Kesavan K et al, from vellar estuary in Parangipettai, southeast coast of India [78]. It shows that the heavy metal accumulation is increased when compared to the previous study.

CONCLUSION

In conclusion, the study focused on assessing anthropogenic contamination of heavy metals, including Cd, Mn, Pb, Ni, and Cr, in the inter-tidal zone of Vellar estuary during the post-monsoon season, specifically in the specimen *Crassostrea madrasensis*. The researchers also investigated the natural deposition of minerals such as Zn, Ca, Mg, Fe, and Cu. The purification of 50 gallons of water daily by the oysters played a vital role in creating an eco-friendly environment for various organisms in the estuary. The study found that the distribution of heavy metals in both sediments and water samples exhibited similar patterns, with higher accumulation observed in sediment samples compared to water samples. The highest concentrations of metals were recorded in the pre-monsoon period, while the lowest concentrations were observed in the post-monsoon season. This variation was attributed to factors such as organic matter decomposition rates influenced by temperature. Comparisons with previous studies revealed that Cd levels in sediment samples were higher in the present study, emphasizing the non-essential nature of cadmium for animals and humans.

Chromium concentrations were significantly higher in sediment than in water, indicating its accumulation in sediment. The metal concentrations in the Vellar estuary were generally lower than those reported in polluted estuaries, highlighting the non-polluted nature of the Vellar river channel. The bioaccumulation of essential minerals in *Crassostrea madrasensis* showed higher concentrations of magnesium and copper than in previous studies, possibly due to anthropogenic influences. The order of concentration for essential minerals was Ca>Mg>Fe>Zn>Cu. Oysters were identified as good indicators of both essential and toxic metal pollution in marine environments. The study suggested that the order of metal accumulation in the oysters varied with different seasonal periods, influenced by the availability of metals and different uptake and retention mechanisms. The heavy metal accumulation in *Crassostrea madrasensis* was found to be higher than in previous studies, indicating an increasing trend of metal accumulation in the Vellar estuary.

In summary, the research provides valuable insights into the distribution and accumulation of heavy metals and essential minerals in the Vellar estuary, emphasizing the importance of oysters as bio-indicators for environmental monitoring. The findings contribute to our understanding of anthropogenic impacts on estuarine ecosystems and the potential consequences for marine organisms and human communities relying on them as a food source.

ACKNOWLEDGEMENTS

The authors want to thank, The Dean and Director CAS in Marine Biology and authorities of Annamalai University for providing necessary facilities.

CONFLICT OF INTEREST

Authors declare no conflict of interest.

AUTHOR CONTRIBUTION

- A Alex Justin conducted the experiment and analysis and wrote the manuscript. G Ananthan contributed to the data analysis, manuscript revision and guided.
- Sangamesh contributed to the study conception, design, and manuscript revision.
- Beaven and T Mohamed Mushin contributed to sample collection and lab works.

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