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Geochemical aspects of *Meretrix casta* (bivalve) shells of Vellar estuary, southeast coast of India

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The bivalve mollusk, *Meretrix casta* shells are abundant in the Vellar estuary along the East coast of India, they are economically important and used as chief raw material for many lime based industries. Their shells are harvested in large quantities for meat and lime production. The present study focused on understanding the chemical characteristics of *M. casta* shells, collected at eight different locations in the marine zone of Vellar estuary. Slica, alumina, iron, calcium and magnesium were determined by wet analysis method. The concentrations of Cu, Fe, Zn, Cd, Hg and Mg were analysed by inductive coupled plasma - optical emission spectroscopy (ICP-OES). The *M. casta* shells consists of calcium which is up to 54%, silica, aluminum, iron and magnesium constituents are very small. Metal concentrations in the shells were in the following order: Fe>Mg>Zn>Cu. The results of heavy metal concentrations was Fe (1.822 mg/l), Mg (0.420 mg/l), Zn (0.026mg/l) and Cu (0.017 mg/l), the elements Cd and Hg were below detection limit in all the eight locations. The result evidenced that the shells were suitable for industrial applications especially for lime based industries.

Key words: Raw materials, bivalve, *Meretrix casta*, ICP-OES, heavy metals, Vellar estuary.

INTRODUCTION

Meretrix casta (Chemnitz) (Bivalvia: Family Veneridae) occurs in extensive and dense beds all over the East coast of India (Abraham, 1953). It is fairly abundant in Pulicat Lake, Kovalam backwaters, Muthupet swamps, Vellar estuary and Vaigai estuary (Nayar and Mahadevan, 1980). Clam production in Vellar estuary is about 730 t/year (Silas et al., 1982). In Vellar estuary, among the bivalves, *M. casta* and *Tellina* sp. were commonly encountered; the former accounting for 80 to 90% of the total benthic population (Chandran, 1987). *M. casta* is harvested in large quantities from Vellar estuary region for meat and provides a source for proteins, lipids and minerals. Sugesh and Mayavu (2013) studied that *M. casta* are rich in protein and antimicrobial compounds. *M. casta* shells (without animal) are used as a raw material for pulp making, bleaching, pharmaceuticals, leather tanning, shell grit, lime and cement manufacturing industries (Rao, 1969; Alagarswami and Narasimham, 1973; Rasalam

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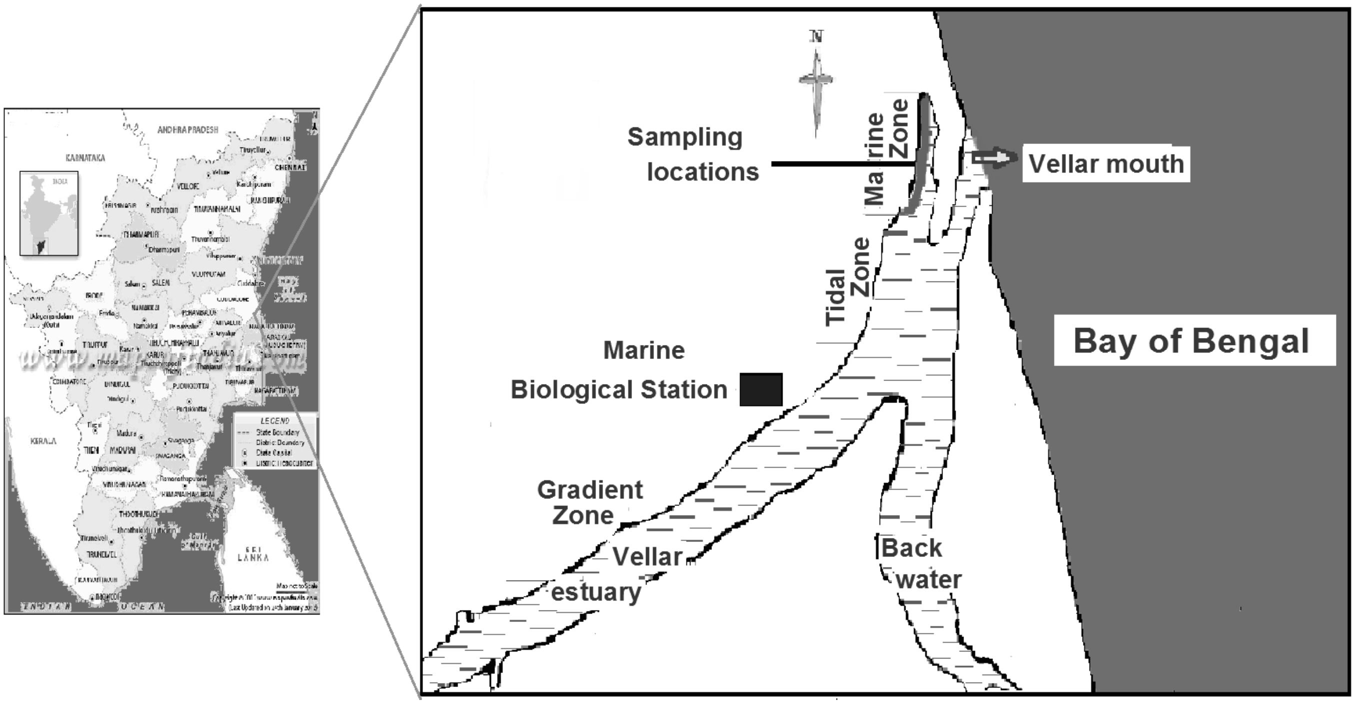

Figure 1. Map showing the study area and sample locality.

and Sebastan, 1976). In agriculture, it is used as pesticide, manure in plantation and poultry-feed. Until recently, shells were burnt merely for mortar and plaster in building work. But, now it is vastly used in paper mills, rayon fibre, calcium carbide, white cement manufacturing and biomaterials for orthopaedic applications (Awang-Hazmi et al., 2007).

In fact, mineral resources are finite and non-renewable resources. Many important minerals are depleting very drastically by mining activities including limestone resource, which is the chief raw material for many lime based industries. In the future, *M. casta* shells will play significant role in sustainable industrial development as well as in countries economic growth, because these are replenishing resources. Fewer studies have been done on economic valuation of bivalves (Boominathan et al., 2008) and the use of *M. casta* shells of east coast of India for preparation of lime (Panda and Misra, 2007). M/S. Travancore Cements Ltd. (TCL), Kerala, India is reportedly the only cement manufacturing industry in the country using lime shell as raw material and mining from Vembanadu backwaters. The white cement made from lime shell is considered to be highly durable and superior in quality, due to absence of magnesium oxide. This product enjoys good reputation in the country and the yearly requirement of lime shell for white cement production by TCL is about 40,000 tonnes (Ravindran et al., 2006). Consequently, the requirement of raw material for lime based industries depends on the lime shell resources in the backwaters/estuaries, river mouths and lagoons along the coastal tract. Geochemical aspects of *M. casta* shells found in the study area in literature are inadequate, particularly with reference to major and trace elemental variations. Comprehensive analysis has shown the chemical composition of shells of this species. To the best to our knowledge, this kind of study may be the first in the study area. Hence, the present study was done to assess the geochemical aspects of the *M. casta* shells from Vellar estuary along the southeast coast of India.

MATERIALS AND METHODS

Study area

The Vellar estuary lies between (latitude 11°17'23" N and longitude 78° 50'24" E), the southeast coast of India, which originates from the Shervarayan hills of Salem District in Tamil Nadu, India. After traversing a distance of about 480 km, it forms an extensive estuarine system at Parangipettai, before it joins with the Bay of Bengal. The Vellar estuary is always open with the Bay of Bengal and it is said to be a "true estuary" as there is no complete closure of the mouth. In terms of salinity characteristics, the estuary is demarcated and divided into four zones based on Rochford (1951) classification of estuarine environment, viz. marine zone, gradient zone, tidal zone and freshwater zone (Ramamoorthi, 1954; Antony Fernando et al., 1983). Geologically, Vellar estuary belongs to quarternary period. The estuarine complex is bestowed with a variety of biotopes such as mangroves and backwaters (Kesavan et al., 2010). The hard clam has a thick, moderately large shell with a brown horny periostracum. A dark greyish band is present at the posterior margin of the shell. The clam reaches a height of 48.7 mm and a width of 38.7 mm in about 18 months. A map of the study area is shown in Figure 1.

Table 1. Microwave parameters for *M. casta* shells digestion.

Maximum power	Power used	Ramp time	Temperature	Holding time
1600 W	100%	15:00 min	200°C	15:00 min

Table 2. Elements symbol detection Wavelength (nm) by ICP-OES.

Cu	Fe	Zn	Cd	Hg	Mg
327.393	238.204	206.200	228.802	253.652	285.213

Table 3. Chemical composition of *M. casta* shells of Vellar estuary.

Location number	SiO_2 (%)	CaO (%)	MgO (%)	Fe_2O_3 (%)	Al_2O_3 (%)	LOI
1	0.10	54.03	1.59	0.08	0.04	44.15
2	0.10	54.04	1.51	0.08	0.04	44.10
3	0.11	54.07	1.53	0.09	0.04	44.14
4	0.10	54.05	1.57	0.08	0.03	44.16
5	0.11	54.06	1.55	0.08	0.04	44.15
6	0.12	54.09	1.52	0.09	0.03	44.10
7	0.11	54.08	1.54	0.09	0.04	44.12
8	0.10	54.20	1.55	0.09	0.03	44.15
Total	0.85	432.68	12.36	0.68	0.29	353.13
Mean	0.11	54.09	1.55	0.09	0.04	44.14

Sample collection

M. casta shells were collected along the marine shoreline (this zone extends up to 0.8 km upstream from the mouth of the river) of Vellar estuary during the month of May, 2012. The shells were collected within eight 1 x 1 m squares in the entire study area. Distance between sample spots was 100 m. In the demarcated area, available *M. casta* shells were collected by hand digging and picking irrespective of size. The shells were then washed with seawater at the point of collection and placed into clean plastic bags and packed separately with sample numbers.

Sample preparation

In the laboratory, the samples were washed thoroughly with clean water and dried. Then, the shells were crushed and pulverized into fine powder with an iron-mortar, agate-mortar and pestle. The well mixed powder samples were tagged separately according to the location numbers for major and trace elemental analysis.

Chemical analysis

Major elemental analysis of *M. casta* was done by wet analysis method and results are shown in compound percentage. The loss on ignition (LOI), silica (SiO_2), iron (Fe_2O_3), alumina (Al_2O_3), calcium (CaO), and magnesium (MgO), were determined. Loss on ignition is about 44.15% which is common in organic shells.

Trace metal concentrations were measured by inductive coupled plasma - optical emission spectroscopy (ICP-OES) using a Perkin Elmer, Optima 5300; 0.5 g of shell powder was taken for analysis and one time aliquots were measured. A total of eight samples were taken for trace metal concentration studies. The samples were digested with 5 ml of concentrated HCl; after digestion, insoluble remains were not found. After the digestion, the solution was transferred and filled into 50 ml with de-ionized water, the clear solution was analyzed. No double correction, bulk analysis was made and organic matrix in the shell was not determined.

The concentrations of Cu, Fe, Zn, Cd, Hg and Mg in the shells of *M. casta* were determined. To analyse trace metal concentration in bivalve shells, the widely used method was used (Lazareth et al., 2003; Gillikin et al., 2006; Uysal et al., 2008; Ravera et al., 2009: Schöne et al., 2010; Voslooa et al., 2012; Yesudhason et al., 2013). The samples were digested with 5 ml of aquaregia in CEM microwave digester using MARSX Press (self-regulating microwave vessel) microwave digester under the following conditions (Table 1), the wavelengths used for determination of elements is shown in Table 2. The values are expressed as mg/l dry sample.

RESULTS

Major elements

The *M. casta* shells are one of the best sources of high grade lime. They are also easy for calcinations. Major analytical results of *M. casta* shells collected in marine zone of Vellar estuary is shown in Table 3.

The average CaO is 54.09% of the total mineral consti-

Table 4. Heavy metal concentration of *M. casta* shells of Vellar estuary (concentrations in mg/l).

Location	Cu	Fe	Zn	Cd	Hg	Mg
1	0.018	1.56	0.03	BDL	BDL	0.369
2	0.012	2.041	0.022	BDL	BDL	0.274
3	BDL	0.947	BDL	BDL	BDL	0.24
4	BDL	1.249	BDL	BDL	BDL	0.268
5	BDL	1.173	BDL	BDL	BDL	0.241
6	BDL	1.308	BDL	BDL	BDL	0.248
7	0.014	3.477	BDL	BDL	BDL	0.911
8	0.023	2.823	BDL	BDL	BDL	0.808
Total	0.067	14.578	0.052	-	-	3.359
Mean	0.017	1.822	0.026	-	-	0.420

*BDL, Below detectable limit.

tution. The average silica content in the shells is about 0.11%. The total iron has been estimated in the form of Fe_2O_3. The Fe_2O_3 content is very small (0.08-0.09%) and the Al_2O_3 compound percentage range between 0.03-0.04% and average is 0.04%.

Heavy metals

The mean heavy metals concentration of *M. casta* shells of Vellar estuary is shown in Table 4.

DISCUSSION

Iron (Fe), Mg, Zn and Cu were the main abundant heavy metals; Cd and Hg were below detectable level (BDL). Fe concentrations (1.822 mg/l) were significantly higher in *M. casta* shells of Vellar estuary as compared to Mg (0.420 mg/l), Zn (0.026 mg/l) and Cu (0.017 mg/l), concentrations of Cd and Hg in the shells of *M. casta* showed below detection limit in all eight locations, indicating that these metals are imprecise in the shells.

Maximum of the Fe concentration is 3.477 mg/l, which is highest concentration in the shells when compared with other heavy metal concentrations. Ramanathan et al. (1999) observed that higher concentration of Fe in the mangrove sediments might be a result of the textural and mineralogical characteristics of the mangrove sediments. In this context, it is important to note that clays and feldspar were the dominant mineral species present in the sand and silt size populations of the sediments. Kesavan et al. (2010) identified the source of Mg concentration in tissue and shells of Vellar estuary. The authors stated that agricultural activities and the release of fresh water from reservoirs which contain high heavy metal concentrations and drains into estuary and mix up with the seawater and also hundreds of boats are available in the study area, which is also an additional source of Mg. Srilatha et al. (2013) found that the Cu concentration in *M. casta* tissue of Vellar estuary were 2.33 mg/l, whereas in the present study, Cu level in shells was 0.017 mg/l, which indicates that Cu concentration is not distributed to shells significantly. Among the eight locations, Zn was reported in only three locations with an average concentration of 0.026 mg/l, Cd and Hg were not reported in all the eight locations. The studied shells heavy metal concentrations are low and they are only in reporting level.

Conclusion

The result revealed that the shells are potential source of lime with low amount of silica, alumina, iron and magnesium. Based on ICP-OES analysis, the concentration of Fe, Mg, Zn and Cu were in least amount and they are only in noticeable levels. The Cd and Hg were below detectable limits. The present study has shown that enough scope for the development of lime based industries in the study area, owing to the availability and quality of *M. casta* shells which are rich in calcium content and poor in Mg content is most suitable for lime making.

Conflict of Interests

The author(s) have not declared any conflict of interests

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